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DRIVING TIREDNESS – THE END ENEMY OF THE DRIVER

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Abstract. In modern society, little or no sleep at all has become a habit, almost a good tradition. Fulfilled sleep is one of the key factors of a healthy lifestyle and longevity, along with proper nutrition, physical activity and that one is fighting stress. Driver fatigue reduces the level of traffic safety, having a negative impact on all psychophysical qualities. Fatigue at the wheel, like driving under the influence of alcohol, is a major factor in road accidents and should not be neglected, regardless of the experience of the driver, the car driven or, the road he travels. A moment of inattention at the wheel can turn the driver, passengers or other innocent people into a simple statistics of road accidents. The article describes the signs and causes of fatigue, measures to prevent and restore the driver's work capacity, as well as warning systems introduced by several manufacturers on keeping the car on the lane, monitoring the driver's fatigue etc.

Keywords: *driving fatigue, fatigue, road accidents, traffic accidents, drowsiness,* car safety *systems.*

Rezumat: În societatea modernă, a dormi puțin sau a dormi insuficient a devenit un obicei, aproape o tradiție bună. Somnul împlinit este unul dintre factorii cheie ai unui stil de viață sănătos și longevitate de trai, împreună cu o alimentație adecvată, activitate fizică și luptă cu stresul. Oboseala conducătorului auto reduce nivelul de siguranță a traficului, având un impact negativ asupra tuturor calităților psihofizice. Oboseala la volan, ca și conducerea sub influența alcoolului, este un factor major în producerea accidentelor rutiere și nu trebuie neglijată, indiferent de experiența pe care o are conducătorul auto, de automobilul condus sau de drumul pe care se deplasează. O clipă de neatenție la volan îl poate transforma pe conducător, pe pasageri sau pe alți oameni nevinovați într-o simplă statistică a accidentelor rutiere. În articol sunt descrise semnele și cauzele stării de oboseală, măsurile de prevenire și restabilire a capacității de muncă a conducătorului, precum și sistemele de avertizare introduse de mai mulți constructori privind menținerea automobilului pe banda de circulație, de monitorizare a stării de oboseală a conducătorului etc.

Cuvinte cheie: *oboseala la volan, stare de oboseală, accidente rutiere, accidente de circulație, stare de somnolență, sisteme de siguranță a automobilului.*

1. Introduction

There is no clear definition of the term „*fatigue*". The term defines different meanings: *physical* – the result of hard physical or mental work, *neurobiological* – determined by the rhythm of sleep-wake cycles and *mental/psychological* – lack of energy needed to do something alternatively, demotivating the continuation of an action.

Fatigue also has many direct and indirect causes [1]. It is often directly associated with the period of time in which a person performs certain activities. Fatigue is also due to lack of sleep, which can be chronic or acute. Fatigue or drowsiness can occur without sleep. This type of fatigue is usually related to the daily cycle of sleep, or biorhythm, meaning that within 24 hours, the human body needs sleep several times. It takes place in the prolonged mornings, approximately between midnight and four o'clock in the morning or after 12 hours later, between $14^{\underline{00}}$-$16^{\underline{00}}$.

Among the factors with indirect influence on fatigue can be considered the following: age, physical condition, habit of consuming alcohol, drugs, medications or external factors, such as: temperature, noise, vibration, routine of work. For example, driving alone on a boring road for a long time does not cause fatigue or drowsiness, but can lead to the rapid manifestation of their effects. Fatigue [2, 3] is the natural process of temporary reduction of work capacity, which occurs as a result of human activity. The work capacity of the driver depends on the condition of the central nervous system. As a result of overwork of the brain, disorders occur in the evolution of mental processes, perception, attention, thinking and memory are affected. Moreover, it reduces the acuity of vision, narrows the visual field, worsens stereoscopic vision, confuses the precision of movement coordination, reduces the degree of automatism, intensifies the pulse, increases blood pressure and reaction time, disappears the sensation of speed, apathy and asthenia appear, so that the ability to react quickly to unexpected and unusual changes in traffic situations is lost.

Vision fatigue is directly dependent on the duration of the driver's work. It was found that, after eight hours of uninterrupted work, the driver can visually perceive the road sign not from a distance of 100 m, but only from 80 m [2]. Visual fatigue has a negative effect on the driver's activity. Even experienced drivers, being tired, reduce the radius of visibility; direct the view in front of the vehicle and on the side of the road, which makes it difficult to forecast traffic situations. Only simple skills chiseled to the level of automatism are maintained in a state of fatigue, which gives possibilities to act only in known, standard situations. All these mentioned considerably reduce the reliability of the driver; contribute to the commission of errors and road accidents.

The tired driver involuntarily changes his working position: an improper seat is noticed, that makes it difficult to use the steering wheel, pedals and on-board devices, as well as worsens visibility. The driver with obvious signs of fatigue often loses the accuracy of driving actions, more often than usual he turns the steering wheel from side to side. Fatigue worsens with increasing energy consumption, as a result, serious errors begin to occur.

Signs of characteristic fatigue are noticed at drivers after 4...5 hours of driving, become clearly visible after 6...8 hours of driving, and after 9 hours, strong efforts must be made to drive the vehicle safely [4]. After 9 hours, the risk of a car accident increases. Sad practice shows that more than half of road accidents are caused by tired drivers. The tired driver may not feel tired under the influence of strong psycho-emotional arousal or danger.

The driver, who is beginning to feel tired, may initially drive the vehicle safely, but not for long. Falling asleep or drowsiness usually occurs instantly and unexpectedly, creating a

very dangerous situation on the road. Therefore, you do not have to fight drowsiness, but it is recommended to stop and sleep, or to do some exercise. The most effective way is to get out of the car for a few minutes and relax your muscles.

It is known that the aromas of coffee, lemon, mint and cinnamon remove fatigue, have a beneficial effect on the brain and bring the human body into an active state. Air flavors and lollipops with such flavors are beneficial. It also helps remove drowsiness, music, audio books and conversations with passengers. The open window of the cab allows fresh and cold air to enter, which invigorates the driver.

Every driver should know that driving a tired vehicle is one of the main causes, leading to road accidents from simple bumps to serious and particularly serious ones. Statistics show [2] that drivers who drive a vehicle without breaks for 7...12 hours as a result of drowsiness, are involved in road accidents approximately twice as often, and if the duration of driving exceeds 12 hours, the frequency of driving in road accidents increases 9 times. The driver must rest at least 8 hours before the working day, as drivers who sleep only 6 hours at the end of the working day have less than 2,5 times less attention. Also, according to statistics, 60% of overworked drivers are already asleep at the wheel after 3...4 hours of work.

2. Statistical data on the driver's fatigue

In order to better assess the effects of drowsy driving, some statistical data are presented below [5]:

- if the duration of sleep for 24 hours is less than 6 hours, the risk of drowsiness, which can lead to a car accident, increases 3 times;
- 18 hours of wakefulness in a row leads to a condition comparable to alcohol intoxication;
- $ 12,5 billion – this is the annual loss of *US* money due to road accidents, caused by drowsiness while driving;
- 37% of drivers said that they fell asleep at least once while driving;
- it is estimated that 1550 deaths each year are caused by road accidents caused by drowsy drivers;
- 15% of serious road accidents involving trucks are attributed to driver fatigue;
- 55% of road accidents resulted of fatigue are caused by drivers up to the age of 25.

The mentioned figures refer to the *USA*, but they can also be successfully included in the sad statistics of road accidents in the *Republic of Moldova*.

Driver fatigue leads to a much higher number of road accidents than it previously was believed. The risk group included young people aged 18-20: they often go to bed late at night, but have to wake up early in the morning. In this category of drivers, signs of fatigue are more common during the day than at night.

According to the study conducted by specialists from the *Polytechnic Institute of Transportation in Virginia, USA* [6], the number of road accidents caused by driver fatigue is close to 20% of the total number, so it does not constitute 2-3%, as previously established other studies and surveys on similar topics. The study, called the „*100-car naturalistic study*", was conducted over two years with the participation of the *State Department of Transportation and the US National Road Safety Administration*. The study allowed close monitoring of leaders without direct involvement in their lives.

The study involved 100 car owners from *Virginia* and *Washington*: five cameras were installed on their cars, collision warning systems in the front and rear of the car, several

accelerometers, belt traffic monitoring systems and a network sensor. For the research, the Institute's specialists tried to attract as many drivers up to the age of 25 as possible, as well as motorists whose annual journey is higher than the national average.

With the help of the study, it was possible for the first time to follow the behavior of drivers before the accident. In 20% of all road accidents and in 16% of all situations close to the accident, drivers showed obvious signs of fatigue: closed eyes, „*nibbling*" with the nose, „*disconnection*" of facial muscles, as well as moments of microsleep, when the driver's eyes close slowly, and open immediately.

During the study, experts analyzed 110000 situations in which drivers were involved. Of these, 10500 cases were particularly important, when drivers were involved in a car accident (82 times) or managed to avoid a car accident (761 times), as well as emergencies (8200 times) and other potentially dangerous situations – for example, the driver did not stop at the „*no-stop crossing*" sign (1400 times).

The *European Commission*, together with the *International Road Transport Union* (*IRU*), has conducted a unique scientific study of the causes of road accidents. The aim of this study was to identify the main causes of road accidents with the involvement of trucks. To this end, teams of experts were involved in the study of over 600 road accidents in 7 European countries (*France, Germany, Italy, Hungary, the Netherlands, Slovenia and Spain*) [7].

Of the 624 road accidents investigated in 6% of cases, driver fatigue was the main cause of the road accident. 37% of such road accidents had a fatal end. In 68% of the situations, in which fatigue is the main cause of the road accident, the truck and another vehicle were involved in the accident, and in 29% of the cases, only the truck.

Regarding the time of day, when an accident occurred due to the driver's fatigue, two critical periods of time were identified. Most accidents occurred between $2^{\underline{00}}$ and $3^{\underline{00}}$ at night – the time when the driver's biorhythm is at its lowest point, as well as between $15^{\underline{00}}$ and $16^{\underline{00}}$ – almost at the end of the working day. Almost 90% of all road accidents caused by driver fatigue occurred on highways or roads between localities. In localities, road accidents due to the driver's fatigue are extremely rare.

Most drivers overestimate themselves when it comes to long driving distances, often ignoring fatigue. Many fatal accidents occur a few kilometers from the destination, due to the fact that the driver is confident that he will resist. A study conducted in the *UK* showed that many drivers drive tired, but very few of them resort to measures to protect them from that critical level, which puts them in great danger [8]. The study shows that 70% of drivers prefer to open a window and drive on, while 69% take short breaks to refresh them. 54% of leaders listen to music to stay awake and only 21% stop for a few minutes of sleep, 43% resort to various caffeinated beverages. Of those who stop for refreshment, 39% resort to short walks and only 21% fall asleep for a few minutes.

3. Signs of driver fatigue and circumstances of accelerated fatigue

One of the most important issues regarding road safety is to reduce and avoid driver fatigue. Of great practical importance, it is of concern to many renowned scientists around the world. The more tired the man, the lower his production rates and the higher the probability of serious road accidents.

In such cases, from the point of view of medicine, the events take place according to a certain scheme [9]. About halfway through, the driver feels very tired and begins to fall asleep. Due to the tense pursuit of the road, eye pain occurs, the eyelids become heavy as

lead. Coffee or tea served before departure has no stimulating effect, does not help the sound of the radio or conversations with passengers. The reaction becomes slowed down to the rapid changes of the situation, the pulse rate decreases and for a few fractions of a second a euphoric sleep appears. After the blows, the consciousness clears for a few moments, then drowsiness reappears, but now for a longer period of time. This is the cause of the tragedy. The only way to avoid this tragedy is to stop and fall asleep for a while or give up driving.

Recognition of signs of fatigue is manifested by [3, 10]: difficulties in concentrating attention, keeping eyes open or head up, daydreams and the appearance of random thoughts, the tendency to have hallucinations, especially at night, the sensation of sand in the eyes, and their repeated need to rub, the need to blink more often, and the tears of the eyes, the weakening of coordination between movements, the attenuation of the ability to operate commands, the sensation of weight in hands, feet and eyelids, prolonged and frequent yawning, driving in zigzag and omission of road signs or indicators, anxiety or irritation, etc. Among other manifestations of fatigue: headaches, feeling of lethargy and weakness throughout the body, yawning, unwillingness to communicate with someone.

Although the movements necessary to drive the vehicle are easily performed as a result of accumulated skills and physical effort, without difficulty covered by the driver's energy resources, driving activity, carried out with tension and continuous attention, tires the nervous system of the subject, the fatigue process being accelerated of a number of circumstances. Among these are [3, 9-11] *external causes*: the monotony of some roads and the landscape, the known character of the itinerary, the intense rhythm of the traffic, the driving in the evening and especially at night with intense traffic in the opposite direction way etc.; *causes depending on the vehicle*: uncomfortable or inadequate seats, awkward position while driving, uniform engine noise, rocking motion of the vehicle, heat in the cab, inadequate or incomplete ventilation of the passenger compartment, penetration of harmful gases by technical ventilation or ventilation etc.; *causes that depend on the driver*: the activity submitted before driving, driving under the influence of low alcohol consumption, the influence of drug use contraindicated for driving, prolonged driving time (every fifth car accident occurs after eight hours of driving), psychological state before going on the road, immobility of the driver's position, feeling hungry, excessive smoking while driving, driving with unjustified low speeds, the existence of diseases etc.

All these circumstances often cause sleep, which is why short stops are recommended when leaving the driving position and exercising, proper ventilation of the cabin, having a snack or eating sweets etc., all having an effect disconnecting. Among the signs that precede sleep may be: a pleasant state of lethargy; drowsiness for a short time, during this time the eyes are open and the gaze is fixed forward, but does not perceive anything; the waking state is completely annihilated; the muscles of the hands and feet relax; the trajectory of the vehicle becomes unpredictable, etc. These signs appear in the early hours of the morning or at the end of the program, when the state of fatigue reaches maximum values.

Driving fatigue during driving is manifested by dispersed attention, abnormal reactions to external stimuli, decreased ability to coordinate movements, accuracy and speed of reactions, increased reaction time. The driver who is tired makes an effort to be careful and focused. He notices that he no longer clearly observes the signs, the markings, and he perceives the traffic situations late. To concentrate, the driver consumes the last reserves of physical and mental energy.

Fatigue is a natural process of temporary decrease in work capacity, caused by long or

great effort, but this condition disappears after a good rest, when work capacity is fully restored. Dangerous is the state of over fatigue, over fatigue, i.e. the accumulation of fatigue, which can suddenly manifest itself in a sick state.

Over fatigue is harmful and must be prevented. At the same time, moderate fatigue increases work capacity. If the man is tired at work to the right extent, then he has a good appetite and a good night's sleep. Therefore, it is necessary to know and forecast the functional possibilities, the time of onset of fatigue.

It should be noted that, under road law [12], it is forbidden to drive in an advanced state of fatigue, which affects the driving ability of the vehicle.

At the same time, it is necessary to take into account the experience of driving, keeping in mind that if you have not driven for a long time, then the first trips are accompanied by excessive physical and emotional stress. These emotions are manifested by tightening the steering wheel, following the road carefully and, as a result, static tension, which leads to rapid fatigue. These actions are also characteristic to novice drivers. In parallel with physical tasks, the human information request must be dosed. Lying down all day, doing nothing, for people with strong, mobile nervous system (blood) can be much harder than intense muscle activity. Both monotony and excess of information lead to fatigue. The monotony of the task causes the permanent tension of some and the same centers of the nervous system and this the nervous fatigue develops. The same legitimacies are noticed when poor information request. During the movement on the highway and in the conditions of an information deficit, the situation appears when the driver's eye fulfills one and the same thing – it follows the road. In this case, the same visual centers of the brain are permanently included in the activity and the uniformity of visual perception causes the development of fatigue in the centers of the brain, and the appearance of the inhibition state of some groups of nerve cells causes drowsiness. The lack of information can also be the cause of falling asleep at the wheel.

Fatigue and psychological stress are more pronounced at night, especially if the driver is blinded by car lights, moving in the opposite direction. Roads on which there are trees or poles placed at regular intervals also amplify this aspect. In addition to the feeling of monotony, the driver may enter a state in which sight and hearing are slightly reduced, or at least not as effective as normal. At night, fatigue can turn into a state of drowsiness, this being a very dangerous phase, both for drivers and passengers. This condition can be exacerbated due to situations where uneven surfaces are present on the road. Driving a car at night on a less crowded road, where there are no traffic signs, can also have a negative impact on the driver. A feeling of loneliness may set in, and the driver will be tempted to accelerate to a seemingly safer place. As a result, with acceleration, there is a high risk of losing control of the steering wheel or getting involved in a collision with another vehicle.

It is recommended to drive a car with a companion or to share driving hours with another driver, when it comes to very long roads and especially at night. Of course, the person on the right does not have to sleep, as this is contagious. Autopilot (*Adaptive Cruise Control*) is perhaps the worst choice when the driver is drowsy. It significantly reduces the interaction with the car, thus further accentuating the state of drowsiness.

Roads covered with snow or ice, water or wet can also cause difficulties, as the driver is subject to increased energy consumption. The arrhythmic movements of the wipers, the poor lighting of the headlights can also increase fatigue and reduce the level of attention while driving. The same weakening effect can be produced by billboards of different colors arranged on the side of the road.

4. Measures to prevent and reduce driver fatigue

Fatigue prevention is possible by optimal planning of the race or trip, correct and proportionate staging of the trip, observing time schedules, ensuring the supply of physical and mental energy until the end of the trip, taking breaks to relax, ventilating the passenger compartment of the car, etc. Smoking is not recommended while driving, because polluted air in the cabin accelerates the onset of fatigue, due to the fixation of carbon monoxide on hemoglobin, which reduces the oxygenation capacity of the circulatory system.

In order to reduce fatigue [3, 9, 13], it is recommended to pay attention to the work and rest regime, the duration of the car driving process. Thus, for example, before leaving a long distance, especially if you are going to drive at night, the driver must rest. Several studies have shown that sleeping for about an hour, the body regains its energy level and is rested enough to stay awake all night. The struggle with fatigue and procrastination to save time is not justified, it is much more important for the driver and his passengers to reach their destination healthy and sound.

Immediately before departure, it is recommended to consume 30…50 g of lemon or 1–2 ascorbic acid pills [9]. Pay close attention to medications consumed, some of which can cause severe drowsiness and are not recommended while driving. Even if the driver has eaten well before setting off, he will take a few healthy snacks with him. The fast foods found along the way are convenient and comfortable, but are full of fat, salt and sugar that make you feel tired. Foods that give more energy and provide long-lasting resistance are made up of complex carbohydrates and proteins. Consumption of energy drinks can help in this case, but it is not the safest method. They can increase the level of alertness, but not for long, and then fatigue can occur even more strongly. Sugar-containing drinks are not recommended, as they can also create a greater state of fatigue later, even if for the moment they make us feel good.

During the trip, every 2 hours until noon and 1,5…2 hours after lunch, interruptions of 10…15 min must be made, during which it is recommended to perform the simplest gymnastic exercises, also recommended for passengers. During the warm period of the year, it is recommended to wash your face with cold water. However, when you feel the first signs of drowsiness, you must refresh yourself with fresh air while driving, opening the side window. It works very well if it is hot in the car and cold outside. Cold air gives the body a temporary shock and makes it more alert. The conversation with the passengers also helps, if it does not distract, and in their absence we can open the radio or the tape recorder, but the music must be rhythmic, lively, light and not noisy. It is recommended that the leader himself sing. It is not recommended to listen to radio reports from sports competitions, they distract.

If these easily acceptable measures do not help, then it is necessary to stop the movement, because it is known that the most effective remedy for fatigue is rest. In case of pronounced manifestation of fatigue and drowsiness, a short rest of 30…40 min in the places indicated for this purpose helps to get out of the state of inhibition. Many drivers, fighting fatigue, drink coffee. It really stimulates the body, but for a very short time, after which there is an even more pronounced fatigue.

When the body is about to give in to sleep, on the border with reality you can meet hallucinations (hypnogic). These are practically fragments of dreams, detached from the immediate reality. Under these conditions you can get to what specialists call microsleep. It is a state of sleep, which sets in for a period of 2…10 seconds, often followed by a shock on waking. Then the brain is „*overwhelmed*" by the situation and involuntary reactions occur, such as the sudden steering wheel or brake, which leads to destabilization and loss of control

of the car. During this time, the driver has his eyes open, sees the road, but in a state of blurring of reality. The reflexes are very slowed down, and the driver misses any maneuver to avoid an obstacle.

5. Car safety systems

This state of microsleep, in which the hesitations of maintaining the tread, are the basis of the warning and prevention systems introduced by several car manufacturers. They produce alarm signals, vibrations in the steering wheel and seat, when the driver crosses the lane marking line without signaling. Lane restraint systems could help to avoid many road accidents caused by the driver's fatigue.

The *lane-keeping assistance system* (lane keeping system) helps the driver to keep his or her chosen lane, thus preventing accidents. The system is efficient when driving on highways and national roads, because the quality road marking is drawn on them. There are two types of lane departure assistance systems: passive and active. The passive system warns the driver about the deviation from the chosen traffic lane, the active system, together with the warning, corrects the traffic trajectory.

At different car manufacturers the lane keeping system has its trade name, but all the proposed systems have practically a similar construction [14, 15]:

- *Lane Assist* from *Audi, Volkswagen, Seat* (*figure 1*);
- *Lane Departure Warning System* from *BMW, Citroen, Kia, Ceneral Motors, Opel, Volvo* (*figure 2, a*);
- *Lane Departure Warning* from *Continental Teves AG* (*figure 2, b*);
- *Lane Departure Prevention* from *Infiniti*;
- *Lane Keep Assist System* from *Honda, Fiat*;
- *Lane Keeping Aid* from *Ford*;
- *Lane Keeping Assist* from *Mercedes-Benz*;
- *Lane Keeping Support System* from *Nissan*;
- *Lane Keeping System* from *Continental Teves AG* (*figure 3, a*);
- *Lane Monitoring System* from *Toyota*.

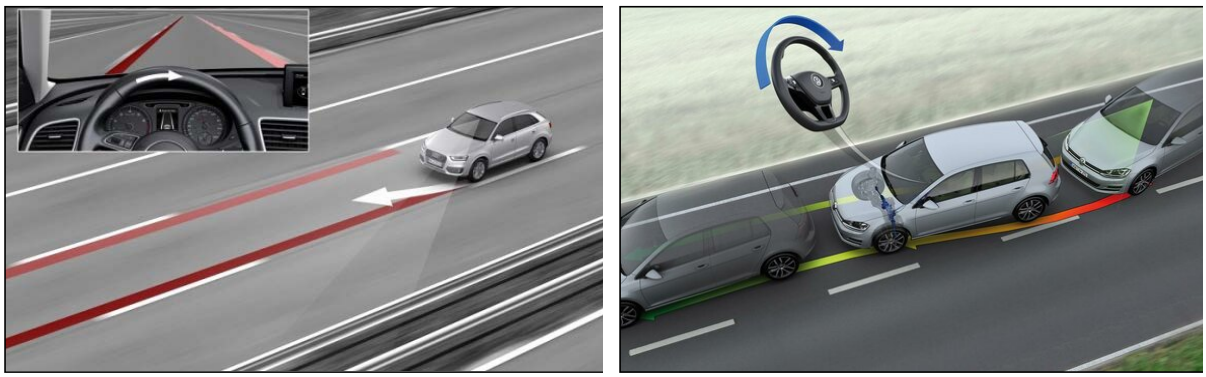
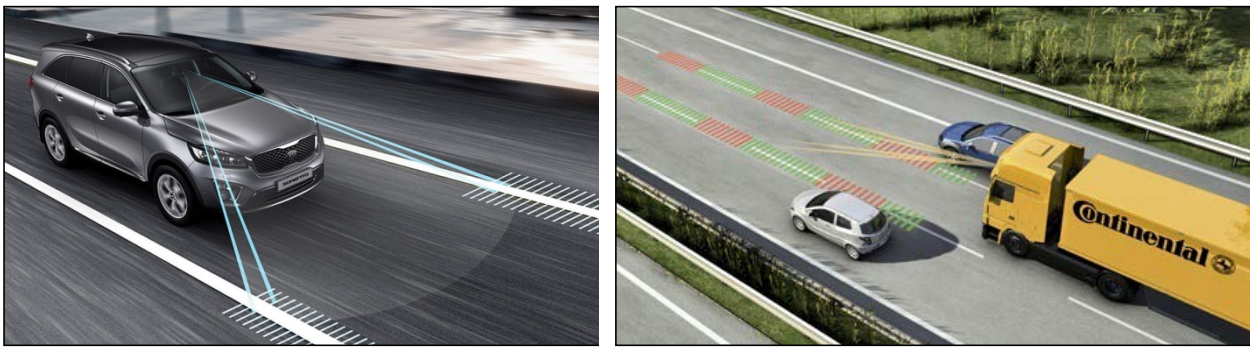


Figure 1. Lane Assist system *LA*.

The Lane Assist system is an electronic system and includes the control button, a video camera, the control unit and the actuators. By means of the control button, the system is activated. System operation information is displayed on the instrument panel as a control lamp. The driver's warning is given by the vibration of the steering wheel or seat, as well as by the visual light and sound signals. The vibrations are generated by a vibrating motor integrated in the steering wheel or seat.



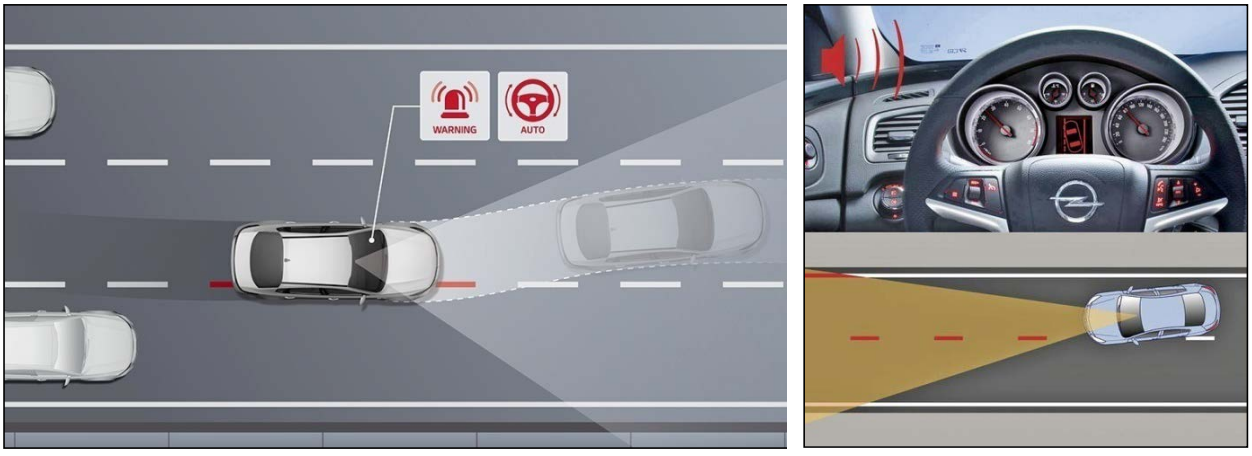
a) b)

Figure 2. Lane Departure Warning systems: a) Lane Departure Warning system *LDWS*; b) Lane Departure Warning *LDW*.

Correction of the travel trajectory is achieved by forced steering of the steering system using an electromechanical amplifier (most systems) or by braking the wheels of a part of the car (*Lane Departure Prevention system*). The control unit operation algorithm determines the position of the lane marking lines, evaluates the quality of the mark recognition, assesses the width of the lane and its curvature and determines the position of the vehicle on the lane. Based on the calculations, a control action is taken on the steering system or the braking system, and if the necessary effect of keeping the car on the lane is not achieved, the driver is warned by the vibration of the steering wheel, seat, audible and light signals.

It should be noted that the value of the torque, applied to the steering mechanism or the braking force on two wheels of a part of the car, is small and can be exceeded by the driver at any time.

When the traffic lane is premeditated, the turn signal must be switched on, otherwise the system opposes the maneuver. In case of unfavorable conditions (lack of one of the lines or the entire road marking, dirty or snow-covered roadway, narrow traffic lane, non-standard marking on the road sections under repair, short-radius curve), the system is deactivated, thus with no help for the driver.



a) b)

Figure 3. Lane Keep systems: a) Lane Keeping system *LKS*; b) *Opel Eye* system.

The *Opel Eye* system (*figure 3, b*) is designed to prevent the car from leaving the lane automatically. The effectiveness of the system on narrow roads with local destination is especially emphasized: it helps to prevent accidents related to the exit on the opposite lane. If this system were installed on all European cars, it would help save 5000 lives and avoid

serious trauma for 20000 people. The doubling of road speed limit signs makes it possible to avoid overtaking it in dangerous areas.

A similar system [15, 16] is also *Alerte de Franchissement Involontaire de Ligne* (warning system for involuntary intersection of road markings), which starts operating at speeds of 80 km/h and determines with the help of transducers the intersection of road markings without connecting turn signal. The system (*figure 4*) prevents the tired or careless driver from vibrating in the seat cushion on one side, which corresponds to the intersecting road marking, so that he can react in time.

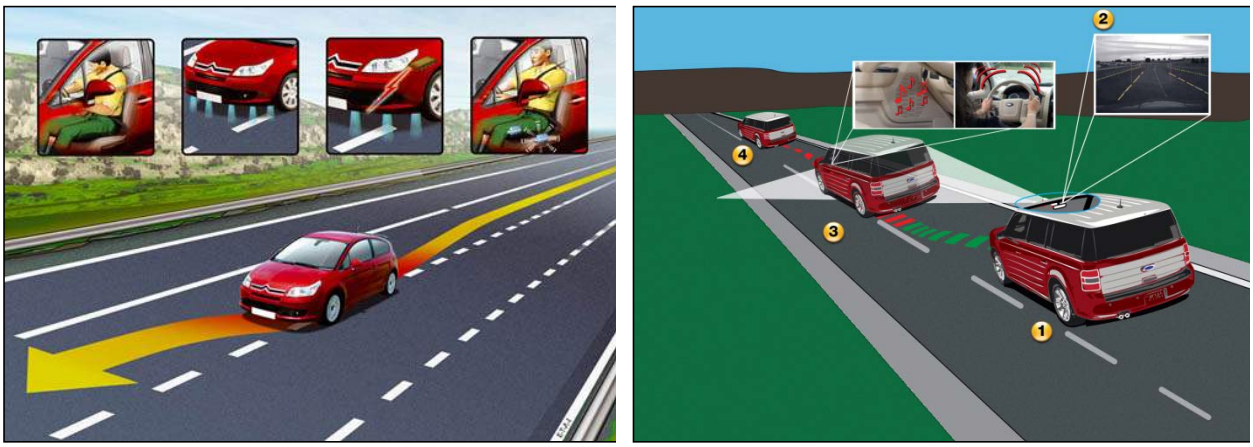


Figure 4. Warning at unintentional intersection of road markings *AFIL*.

Road accident statistics show that the cause of a large number of accidents is the physical condition of the driver. A large number of car manufacturers are actively working on the creation of various driver monitoring systems, designed at least to announce the occurrence of a dangerous condition of the driver and, at most, to intervene in driving and prevent accidents. The work is carried out in several directions, including monitoring fatigue, assessing physical stress, establishing the state of tension of the driver [15, 17].

Volkswagen is installing the emergency system on cars, which is an extension of the lane keeping assistance system. If the driver is unable to drive the car (loses consciousness, falls asleep), the *Emergency Assist* system takes control and stops the car, also warns other road users of a dangerous situation. If the driver does not use the steering system for a certain period of time, the *Emergency Assist* system warns him with visual and audible signals, brakes the car. If there is no reaction from the driver, the system determines that he is not able to drive the car. The lane-keeping assistance system ensures the car's movement within the boundaries of the busy lane, and the adaptive cruising speed system prevents collisions with the car in front. To warn other drivers, the damage signal is triggered, the car starts to move sinusoidally within the lane and finally stops.

Another direction in the development of driver status monitoring systems is the equipment of cars with biometric sensors, with the help of which important health indicators (pulse, respiration rate, skin conductance etc.) can be monitored. These systems are promising and must be installed on mass-produced cars. The closest to solving the problem is *Ford*, which proposes a system for assessing the driver's load (strain), designed to reduce distractions and excessive stress. The physical stress of the driver is estimated by processing several parameters:

- vehicle traffic (*speed, longitudinal and transverse acceleration, speed of rotation*);
- driver actions (*steering wheel rotation angle, accelerator pedal position and brake pedal*);

- road conditions (*traffic density, character of road pavement*);
- biometric indicators (*heart rate, respiratory rate, skin temperature*).

If the load on the driver is large enough, the system takes steps to reduce the tention, including automatically connecting the mobile phone lock function to incoming calls („*do not disturb*" function).

The following biometric sensors are used for the operation of the driver load assessment system:

- piezoelectric sensor in the seat belt for monitoring the respiratory rate;
- conductive conductors on the steering wheel for measuring the pulse;
- infrared sensors on the steering wheel for measuring the temperature of the palms;
- infrared sensor behind the wheel, which monitors the face temperature.

a) b)

Figure 5. Driver Status Monitoring systems:
a) Driver Wellness Monitoring *DWM*; b) Mind Sense systems *MSS*.

The *Jaguar Land Rover* company proposes to monitor the driver's condition with the help of biometric sensors, built into the driver's seat. The *Driver Wellness Monitoring* system (*figure 5, a*) uses breath and pulse rate sensors. If the system identifies serious health problems or excessive driver agitation, measures shall be taken to ensure traffic safety. In case of stress, internal cooling, audio system and air conditioning control are adjusted. In the event of a sudden and serious illness, an emergency call is made and the car stops automatically.

In 2016, *Audi* presented the *FitDriver* project (*figure 6*) under the motto „*My Audi takes care of me*". Vital parameters of the leader, such as pulse and temperature, are monitored using mobile devices (t*raining bracelet or SmartSatch*). These data are supplemented by information on driving style, breathing frequency, weather and road conditions, provided by various car sensors. Taken together, the data obtained allow to determine the current state of the driver, including high fatigue or stress.

Ferrari has patented the technology, which assesses the driver's tention level after changing brain waves. The bioelectrical activity of the brain is measured using wireless sensors, built into the driver's headrest. Depending on the condition of the driver, there is a reduction in the fuel supply of the engine and automatic stabilization of the car.

The *Jaguar Land Rover* is also working in this direction. The *Mind Sense system* (*figure 5, b*) determines when the driver is distracted or falls asleep while driving through brain activity. It has been found that the human brain generates several brain impulses of different frequencies. By constantly measuring the impulses, one can estimate how focused the driver

is (hesitated, drowsy or distracted). The monitoring of brain waves is done with the help of sensors, built into the steering wheel.

Figure 6. The system FitDriver.

If the activity of the brain indicates drowsiness or low concentration of the driver, then the steering wheel or accelerator pedal begins to vibrate, drawing attention to driving. If the driver does not show any reaction, a visual and audible signal is given.

The fatigue monitoring system [15, 17] monitors the driver's physical condition and, if it detects certain deviations, warns the driver about the need to stop and rest. The system suggests a rest pause by means of a warning beep or a signal on the instrument panel „*coffee cup*" (*figure 7, a*). Depending on the method of assessing the driver's fatigue, there are three types of systems. The first are built on the control of the driver's actions, the second – the control of the car's movement, and the third – the control of the driver's eyes. Currently, the driver fatigue monitoring system is implemented on *Mercedes-Benz, Volvo, Lexus* cars.

Since 2011, *Mercedes-Benz* has been installing the *Attention Assist* system on its cars [15, 18], in which the control of the driver's actions is based on many factors: driving style, driving behavior, use of driving organs, character and driving conditions. and so on The control unit processes the input signals and determines:

- driving style (*analysis of speed, longitudinal and transverse acceleration for 30 minutes after starting the movement*);
- driving conditions (*analysis of the time of day, duration of the trip*);
- use of controls (*analysis of the use of brakes, switches under the steering column, buttons on the control panel*);
- the character of the steering wheel rotation (*speed, acceleration analysis*);
- road condition (*lateral acceleration analysis*);
- the character of the car's circulation (*analysis of longitudinal and transverse acceleration*).

As a result of the calculations, the deviations in the driver's actions and the driving trajectory of the car are established. A warning signal about the need for a pause is displayed on the control panel screen and an audible signal sounds. If, after signals, the driver does not stop and continues driving in a state of drowsiness, the system repeats the signals at intervals of 15 min. The system activates at a speed of 80 km/h.

Unlike the *Attention Assist* system, *Volvo's Driver Alert Control* system (*figure 7, b*) only sets the character of the car's movement on the road. The camcorder facing forward fixes the car's position on the lane. Deviation from the established traffic parameters is considered by the system as the beginning of the driver's fatigue. Depending on the driver's condition, the

system performs two levels of warning – „*soft*" and „*hard*". The levels differ according to the intensity and tone of the sound signal. The *Driver Alert Control* system works together with the *Lane Departure Warning* system and is based on its constructive elements. The system activates at a speed of 60 km/h.

Eye control for driver fatigue assessment is introduced by *General Motors*. Based on the existing technique *Seeing Machines* (*figure 7, c*), which used in air, rail, quarry, commercial freight. A special unit controls the degree of opening of the eyes and the direction of the driver's gaze. When recognizing the driver's lack of attention, fatigue or drowsiness, the system warns of the need to stop.

a) b) c)

Figure 7. Driver Fatigue Monitoring systems: a) Attention Assist system *AA*; b) Driver Alert Control system *DAC*; c) Seeing Machines systems *SM*.

The presence of resonant bands in the longitudinal direction is a measure that warns both audibly and sensitively the driver, if the car tends to go off the road or enter the opposite direction of traffic. The positive experience of using resonator tapes in different countries demonstrates the high efficiency of this technology for raising road safety. In the *US*, resonator tapes are used in 85% of countries [19], significantly reducing the number of deaths. On highways in *Japan*, the construction of roadside resonant lanes and the line separating opposite transport flows has reduced the number of collisions with oncoming traffic by up to 55%. In *Finland, Denmark and Sweden*, the use of resonator tapes has also led to a significant reduction in the frequency of accidents and is mandatory for new road construction.

Other safety features related to road infrastructure are sidewalks and off-road parking lots, that limit the consequences of a fatigue accident.

6. Conclusions

1. Based on what is described in the article, it can be concluded that fatigue has a negative effect on car driving skills and road safety, being the cause of many road accidents.
2. The problem of driving a car in an advanced state of fatigue will not lose its relevance as long as each driver will not be aware of the danger to which he is subjected.
3. Traffic fatigue is a problem not only for countries with well-developed road infrastructure or professional drivers, but for all drivers.
4. Driving in an advanced state of fatigue, which affects the driving ability of the vehicle is prohibited in most countries, including the *Republic of Moldova*. But statistics show that this restriction does not reduce the number of road accidents caused by driving fatigue.
5. There are many recommendations on how to reduce fatigue, but the most effective remedy is rest.

Conflicts of Interest: The author declares no conflict of interest.

Bibliography

1. *Accident - fatigue in traffic, causes and effects*. Available online: http://examenauto.md/extramenu/informa%C8%9Bii-utile/accident-%E2%80%93-oboseala-in-trafic,-cauze-si-efecte.html. (accessed 03.01.2022). [in Romanian].
2. Onceanu, V.; Bulgac, A. *Basics of driving behavior and road traffic safety*. Ed. Vite-Jesc, Chişinău, 2008, 237 p. [in Romanian].
3. Goian, V.; Plămădeală, V.; Beiu, I. *Road traffic organization and safety. Normative acts, safety elements and characteristics of road traffic. University course*. Ed. Tehnica-UTM, Chișinău, 2021, vol. 1, 341 p. [in Romanian].
4. *Ustalost` voditelya za rulyom – prichina DTP!* Available online: http://slrgel.ru/news/ustalost-voditelya-za-rulem-prichina-dtp/ (accessed 29.12.2021).
5. *Ustalost` za rulyom namnogo opasnee, chem vy' dumaete*. Available online: https://live-up.co/ustalost-za-rulem-namnogo-opasnee-chem-vy-dumaete/ (accessed 03.01.2022).
6. *Molody'e ustayut opasnee*. Available online: https://www.gazeta.ru/auto/2013/04/16_a_5257705.shtml (accessed 03.01.2022).
7. *Na doroge ustalost` tak zhe opasna, kak i alcogol`*. Available online: https://www.transportnaja-birzha.ru/на-дороге-усталость-так-же-опасна-как-и/ (accessed 03.01.2022).
8. *How to combat fatigue at the wheel*. [online]. Available online: http://www.motorstory.ro/2010/08/cum-sa-combati-oboseala-la-volan/ (accessed 03.01.2022). [in Romanian].
9. Ududovici, D.; Plămădeală, V. *Regulation and road traffic safety. The driver's manual*. Ed. 3rd, revised and completed, Chişinău, 2010, 288 p. [in Romanian].
10. Plămădeală, V. *Road accidents and traffic safety*. Master's thesis, Chisinau, UTM 2006, 159 p. [in Romanian].
11. Avramescu, N.; Cristian, V.; Spînu, V.; Lepădatu, M.; Vrânceanu, N., *Road legislation course for driving schools. Commented and updated*. Ed. Naţional, 1999, 528 p. [in Romanian].
12. Decision no. 357 of 13.05.2009 regarding the approval of the Road Traffic Regulation. In: Official Gazette of the Republic of Moldova, 15.05.2009, no. 92-93, art. 409. Date of entry into force: 15.07.2009. [in Romanian].
13. *How to combat tiredness behind the wheel and stay awake at night*. Available online: https://naturapentrusanatate.com/oboseala-la-volan/ (accessed on 03.01.2022). [in Romanian].
14. Sistemy' sovremennogo avtomobilya**.** Available online: http://systemsauto.ru/active/lane_assist.html (accessed on 05.01.2022).
15. Plămădeală, V.; Goian, V.; Beiu, I. *Road traffic organization and safety. Automobile safety: active, passive, post-crash and ecological. University course*. Ed. Tehnica-UTM, Chișinău 2021, vol. 2, 435 p. [in Romanian].
16. Plămădeală, V. *The danger of talking on the phone while driving. Meridian ingineresc* 2017, 1, pp. 61 – 71. [in Romanian].
17. *Sistema kontrolya sostoyaniya voditelya*. Available online: http://systemsauto.ru/active/monitoring-condition-driver.html (accessed on 05.01.2022).
18. *Sistema kontrolya ustalosti voditelya*. Available online: http://systemsauto.ru/active/drowsiness_detection_system.html (accessed on 05.01.2022).
19. Plămădeală, V.; Plamadeala, A. *The roads of the future. Journal of Engineering Science* 2019, 2, pp. 22 – 35.

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OBJECTIVE APPROACH IN INVESTIGATING IMPLICATION OF ROAD VEHICLE TYRE SAFETY KNOWLEDGE ON COMPLIANCE

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Abstract. Standard effectual directive on tyre safety management operations on its own is nothing without appropriate compliance and application. Deliberate oversight and neglect of safety precautionary measures may result in an accident and eventually be classified as an unforeseen event. This study on safety knowledge and its implication for on-road vehicle tyre safety compliance was conducted among one hundred and thirteen private vehicle owners in Abeokuta, Nigeria. Data collection for this study was done using subjective and physical measurement procedures. The analysis of data obtained showed that sixty-eight participants (60.2%) of the participants had a fair knowledge of road vehicle tyre safety, followed by those that had good knowledge 39 (34.5%). No participant had poor or excellent knowledge. Overall operational tyre safety and compliance with the specifics for tyre standard condition showed that 1 (0.9%) of the assessed vehicles were of very high safe and appropriate compliance status. Forty-three (38.1%) of the assessed vehicles owned and used by the participants were of very low operational tyre safety and practices. This was followed by average safe and appropriate practice 39 (34.5%). Pearson's chi-square test analysis was used to check if there is an association between tyre safety knowledge and safe and appropriate compliance status variables gave $\chi^2 = 1.135$ and $p = 0.769$. This implies that there is no statistically significant association between the two variables.

Keywords: *tyre, safety, knowledge, vehicle, compliance, on-road.*

Rezumat. Directiva standard privind operațiunile de management al siguranței anvelopelor nu valorează nimic fără respectarea și aplicarea corespunzătoare. Supravegherea deliberată și neglijarea măsurilor de precauție de siguranță pot duce la accident și, în cele din urmă, pot fi clasificate ca un eveniment neprevăzut. Acest studiu analizează cunoștințele privind siguranța și implicațiile sale pentru conformitatea anvelopelor vehiculelor rutiere. Studiul a fost realizat în rândul a o sută treisprezece proprietari de vehicule private din Abeokuta, Nigeria. Pentru colectarea datelor s-au folosit proceduri de măsurare subiective și fizice.

Analiza datelor obținute a arătat că șaizeci și opt (60,2%) dintre participanți aveau cunoștințe corecte despre siguranța anvelopelor vehiculelor rutiere, urmați de cei care aveau cunoștințe bune 39 (34,5%). Niciun participant nu avea cunoștințe slabe sau excelente. Siguranța operațională generală a anvelopelor și conformitatea cu specificațiile pentru starea standard a anvelopelor au arătat că 1 (0,9%) dintre vehiculele evaluate avea o stare de conformitate foarte sigură și adecvată. Patruzeci și trei (38,1%) dintre vehiculele evaluate utilizate de participanți au avut o siguranță și practici operaționale foarte scăzute pentru anvelope. Aceasta a fost urmată de o practică medie sigură și adecvată – 39 participanți (34,5%). Testul Pearson a fost utilizată pentru a verifica dacă există o asociere între cunoștințele privind siguranța anvelopelor și variabilele de stare de conformitate sigure și adecvate - $\chi^2 = 1,135$ și $p = 0,769$. S-a constatat, că nu există o asociere semnificativă statistic între cele două variabile.

Cuvinte cheie: *anvelopă, siguranță, cunoștințe, vehicul, conformitate, pe drum.*

1. Introduction

The road accident phenomenon is apparently a complicated and remarkable development due to its diverse resultant effects on lives and property. The associated physical, economic and social problem calls for concern. The frequency and intensity of road traffic crashes are better explained in the witnessed 1.2 million lives it claims yearly and an additional 20 - 50 million non-fatal injury cases [1]. Nigeria alone records 10,050 road accident death cases yearly, with an average of 27 death cases per day [2, 3]. Afolabi and Gbadamosi [4] traced the significance of morbidity and mortality cases from road traffic crashes to population growth flight as well as an increased level of motorization. However, the record of road traffic accidents in the developing countries where vehicles are relatively few is proportionately upsurging but surprising declining in the industrialized nations [5]. From this perspective, Iteke et al. [6] linked the continued amplifying morbidity and mortality cases in road traffic accident records in most developing countries especially in the sub-Saharan Africa region to inconsequential and avoidable causation root factors. That is to say, most road traffic crashes are predictable and perhaps preventable [7].

Road vehicles and their operations play a significant role in road traffic accidents [4]. The features representing road vehicles in road traffic crashes includes defective tyres, faulty braking system, dysfunctional steering system, etc. these factors are directly or indirectly connected to the functions tyres offer in an on-road vehicle which includes acceleration, cornering, braking, and steerability. However, defective operation of any of these systems or components arising from poor maintenance of the vehicle influences the ride comfort and safety [8]. Safe vehicle actions and activities are very crucial in road traffic crashes morbidity and mortality reduction. Vehicle maintenance for safety and ride comfort involves assiduousness management of every component or system involved in vehicle controlling and maneuvering function. This involves compliance with the equipped tire pressure monitoring system specifics for vehicle tyre air pressure, plying speed on different road surfaces whether wet or dry as well as an electronic stability control system [8].

The necessity for accuracy in tyre pressure inflation and wheel alignment is a ride comfort and safety necessity to tyres flexing and heat during wheel rotation [8]. Most assuredly maintenance of appropriate tyre contact patch pattern and effective function in accelerating, steering, braking or cornering is only within its service life and proper inflation. Accordingly, the service life of vehicle tyres should effectively deal with tyre/road interface

interactions at the molecular level as well as the loading and unloading energy absorption of the vehicles [9, 10]. To maintain good tyre road grip, avoid aquaplaning on a wet road, vehicle instability, tyre blowout, and long braking distance, the specifics for tyre condition standard which includes tread depth, tyre age, and inflation pressure must be observed.

Understanding of the accident preventive measures as regards effectual and appropriate tyre safety management operations on its own is nothing without application. Deliberate oversight and neglect of safety precautionary measures may result in an accident and eventually be classified as an unforeseen event [11]. Subjective factors or variables are perchance independent of their actual performance [12]. Azodo and Ismaila [13] observed that awareness depending on its level may or may not translate to appropriate practices. Though subjective procedures for data collection from record raise bias response issues, conscious perception explanations vulnerability and publicly verifiable as a major concern [12, 14, 15]. However, individuals' inner states, potential knowledge and introspective reports about conscious experiences are reliable on the subjects and can only be assessed using a subjective approach [16]. On the other hand, utilizing objective design measures only because of its valid evidence relevant facts, logical implications and viewpoints, and humanitarian purposes in data collection precludes the existence of oblivious perception [17, 18]. That is to say, the adoption of an objective research technique in a study deal with an accepted standard which includes valid evidence relevant facts, logical implications and viewpoints and human purposes of that issue. If relevant valid evidence is denied, an objective approach is impossible. This study, therefore, adopted subjective and objective procedures in investigating the implication of road vehicle tyre safety knowledge on compliance among Nigerians.

2. Materials and Methods

This was a cross-sectional study of safety knowledge and its implication for on-road vehicle tyre safety compliance conducted among private vehicle owners in Abeokuta, Nigeria. Purposive multi-stage random sampling was used in the selection of participants. Subjective and physical measurement approaches were used for data collection in this study. The questionnaire (subjective approach) comprises demographic information (highest educational qualification, occupation and driving experience) whereas the categories of information assessed for knowledge of established operational road traffic safety standards were appropriate size of vehicle tyres, specified tyre inflation pressure, tyres expiry date and roadworthiness tread depth (Table 1). The variables on correct tyre safety rules developed based on the conceptual basis of the study after due consultation with related works of literature and established operational road traffic safety standards were assessed using a self-administered questionnaire. The same formed the guide for the evaluation of operational tyre safety and compliance among the participants. The responses of the participants to the variable were classified as either correct or incorrect. The scaling mean-point of each participant's responses was computed to 100% and presented as 70 – 100 for "Excellence" 60 – 69 for "Very Good", 50 – 59 for "Good", 40 – 49 for "Fair", and 0 – 39 for "Poor" knowledge.

Analysis of the operational tyre safety and compliance with the specifics for tyre standard condition which includes tread depth, tyre age, and inflation pressure was carried out on each participant's vehicle. The physical measurement was conducted before sunrise and also before the owners used the vehicle with regards to the arrangement priory made with the vehicle owners.

Table 1

Applicable road vehicle operational tyre safety standards [19-23]

Road vehicle tyre safety	Road vehicle operational tyre safety specifics
Appropriate tyre inflation pressure	25% below and above the manufacturer's recommended inflation pressure
Inflation pressure specifications guide and size designation recommended by the tyre/vehicle manufacturer.	Driver's door ledge, the fuel tank cover, the manufacturers' car manual or online search using the vehicles model for specified standard inflation pressure.
Shelf life of tyre from date of manufacture (DOM)	Four years
Legal minimum tread depth	1.6 mm
Instructed guide to tyre purchase	Tread depth, DOM and cracks or damage
Factors necessitating change of vehicle tyre	Worn out, expired, bad cut,bulges, punctures, impacts, cracks, and failing often

The scoring scheme associated with systematic observations made through physical measurement was analyzed as appropriate and inappropriate compliance status. This was conducted for the four tyres in each of the assessed vehicles. The level of safe and appropriate practice compliance for each of the assessed vehicles was computed to 100% and evaluated using the scaling range as follows "Very high safe and appropriate practice" = 70 – 100, "High safe and appropriate practice" = 60 – 69, "Average safe and appropriate practice" = 50 – 59, "Low safe and appropriate practice" = 40 – 49 and "Very low safe and appropriate practice" = 0 – 39. The data obtained were subjected to descriptive statistics in the form of frequencies and percentages.

Statistical Package for the Social Sciences (SPSS) software version 16.0 (Chicago, IL, USA) was used for descriptive statistical analysis on the data collected. The measure of the safety knowledge and its implication on operation compliance level regarding the tyre safety was conducted using the Pearson chi-square test at a p-value of 0.05 for significance level.

3. Results and Discussions

The response rate for the one hundred and twenty questionnaires distributed to the private vehicle owners in Abeokuta, Nigeria, was (113/120) 94%. Participants' distribution according to gender showed 60 (53.1%) female and 53 (46.9%) male. The highest educational training among the participants was tertiary education 93 (82.3%) probably owing to the presence of three institutions of higher learning in the study area, Federal College of Education, Oselle, Moshood Abiola Polytechnic, Ojere and Federal University of Agriculture, Abeokuta (Figure 1). The distribution of the participants by occupation showed that most of the participants were civil servants 33 (29.2%), followed by entrepreneurs 22 (19.47%) with the applicants having the minimum number of participants as 4 (3.54%) (Figure 2). Participants' years of present vehicle ownership and driving experience with it are presented in figure 3.

Accidents are a naturally unforeseen event or occurrence that results in death, injury, or property damage but when they happen one can't really say they are unanticipated [24].

However, caution can only be effectively taken and acted upon if appropriate awareness of associated danger is in place [11].

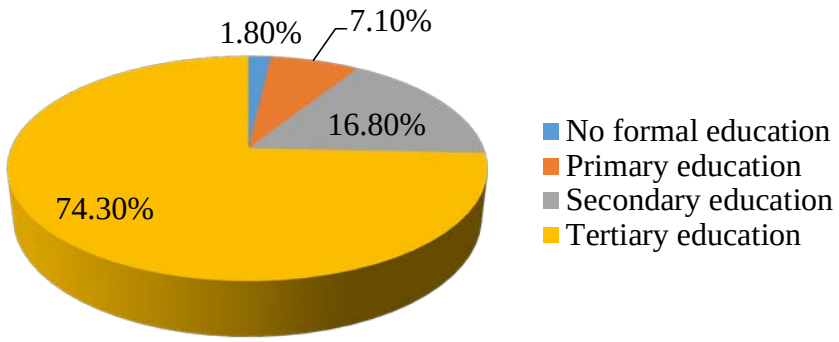

Figure 1. Highest educational training of participants.

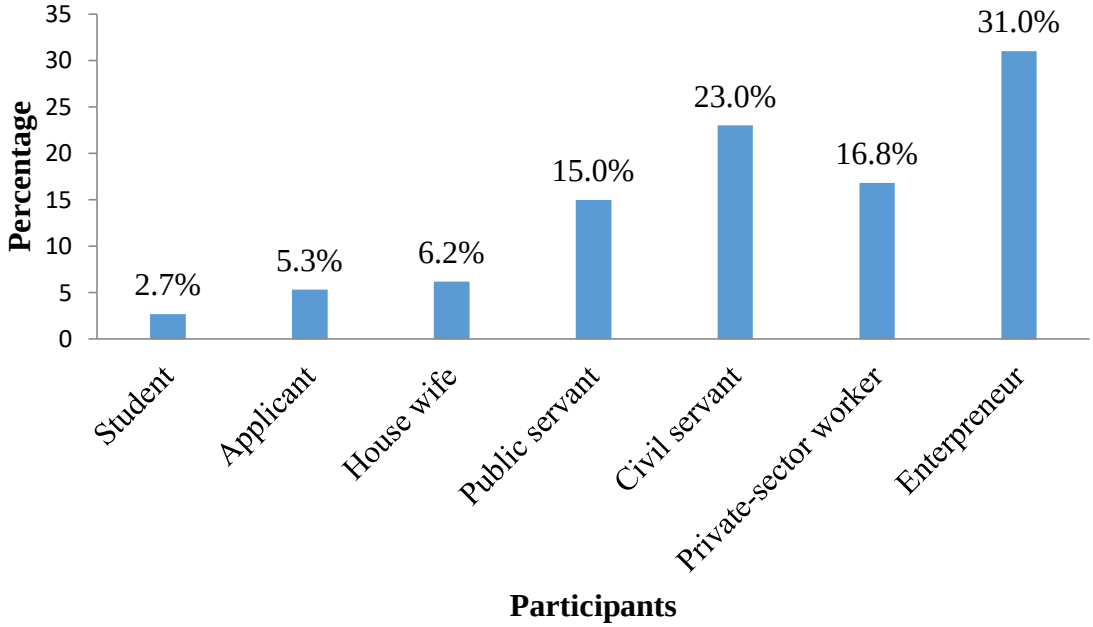

Figure 2. Occupation of participants.

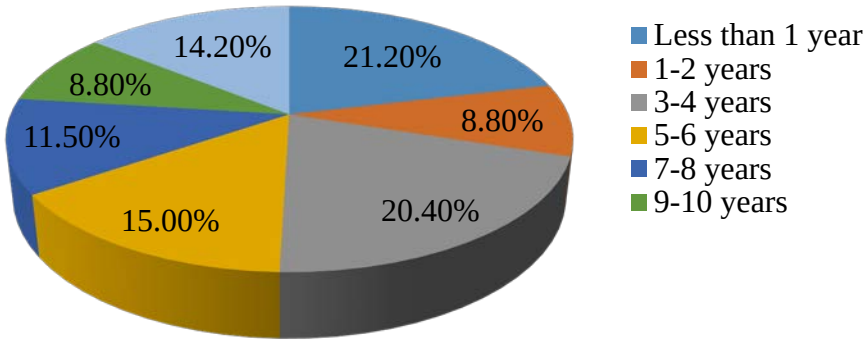

Figure 3. Participants years of driving experience.

Lack of awareness can result in a number of unsafe acts towards tyre safety practices. The safety knowledge and its implication on on-road vehicle tyre safety compliance conducted in this study cut across the lifespan of tyres, tyre pressure, tyre tread wear, and tyre sizes. Table 2 gives the response of the study participants for various levels of knowledge on on-road vehicle tyre safety. Considering that the shelf life of a tyre whether used or not is

four years from the DOM [22]. Sixty-two (54.9%) of the participants had correct knowledge on tyre DOM for expiry date check out of which thirteen (11.5%) of the participants had correct knowledge about the shelf life of tyre from DOM with ninety-three (82.29%) having incorrect knowledge.

Every vehicle has its own tyre inflation pressure specification according to the vehicle manufacturer. It is important to note here that two different models of vehicles may have the same tyre inflation pressure values but this should not be taken for general value. The structural damage scope covered in this study includes tyre inflation pressure (used for under-inflation, over-inflation, and appropriate inflation determination) and tyre wear. Sixty-eight (60.2%) of the participants had correct appropriate tyre inflation pressure knowledge for their vehicle nonetheless the 74 (65.5%) that had correct knowledge of the location where inflation pressure specifications guide for their vehicle by the manufacturers of the vehicles is found (Table 2). Ten (8.85%) of the participants' informed knowledge of appropriate tyre pressure was from the right source (Table 2). Knowledge of the designation location for the recommended tyre size by vehicle manufacturer had 74 (65.5%) correct responses from the participants. The knowledge eight-seven (77.0%) of the participants had about the appropriate size of their vehicle tyre was correct. Fifty-one (45.1%) had correct knowledge instructed guide to tyre purchase whereas on factors necessitating a change of vehicle tyre 74 (65.49%) had correct knowledge (Table 2).

Table 2

Appropriate knowledge on on-road vehicle tyre safety

Assessed variables on knowledge of road vehicle tyre safety	Participants responses for road vehicle operational tyre safety	
	Correct n (%)	Incorrect n (%)
Appropriate tyre inflation pressure for owner's vehicle	68 (60.2)	44 (38.9)
The location where inflation pressure specifications guide for the vehicles manufacturers is found	74 (65.5)	38 (33.6)
Shelf life of tyre from DOM	13 (11.5)	93 (82.29)
Legal minimum road worthiness tread depth	50 (44.2)	63 (55.8)
The designation location for the recommended tyre size by vehicle manufacturer.	74 (65.5)	38 (33.6)
Instructed guide to tyre purchase	51 (45.1)	62 (54.9)
Factors necessitating change of vehicle tyre	74 (65.49)	39 (34.51)
Informed knowledge of correct tyre pressure	10 (8.85)	98 (86.73)
Tyre DOM for expiry date check	62 (54.9)	51 (45.1)
Appropriate size of tyre for owner's vehicle	87 (77.0)	26 (23.0)

Overall safety knowledge of on-road vehicle tyre safety on the various variables assessed in the questionnaire by the participants showed that no participant had poor and excellent knowledge of road vehicle tyre safety. Sixty-eight (60.2%) of the participants had a fair knowledge of on-road vehicle tyre safety, followed by those that had good knowledge 39 (34.5%). Only 6 (5.3%) of the participants had very good knowledge (Table 3).

In a normal and appropriate operation condition, tyres smooth roll and durable functions are imperative for acceleration, cornering, braking, and stability owing to the high-quality composite and expertly-engineered chassis component that is specifically adapted to vehicles to match a variety of different suspension systems and respond accurately for proper traction needed.

Table 3

Overall knowledge road vehicle tyre safety per participant vehicle owner

Levels of road vehicle tyre safety	Frequency (n)	Percentage (%)
Poor knowledge	0	0.0
Fair knowledge	68	60.2
Good knowledge	39	34.5
Very good knowledge	6	5.3
Excellent knowledge	0	0.0
Total	113	100.0

Table-4 shows the analysis of the operational tyre safety and compliance with the specifics of the tyre condition standard which includes tyre size, tread depth, tyre age, and inflation pressure carried out on each participant's vehicle. The assessment was carried out on each of the four tyres; the front right, front left, back right, and back left as well as for the vehicle as a unit. From the standard for tyre roadworthiness in Nigeria [22], tyres have a 4-year validity period from their DOM which means that beyond a four years duration of from its DOM used or not, the such tyre has high accident risk potential, therefore should be avoided. Purchase of new expired tyres is susceptible to road accident risk. The shelf life of tyres in the vehicles showed that only 33 (29.20) of the participant vehicles were road worthy.

Tyre inflation pressure measured when compared with the specification stipulated by the manufacturers either driver's door ledge, the fuel tank cover, the manufacturers' car manual or online search using the model of the vehicle for specified standard inflation pressure with considered accuracy of ±0.05 observed 6 (4.42%) of the participant vehicles had appropriate tyre inflation pressure. In practice, the road contact patch pattern of tyres needs to be maintained through appropriate operational safety standards for it to uphold its shape and perform effectively in load carrying function and stability. In addition, incorrect tyre pressure also increases the potential for hydroplaning (aquaplaning) and much longer stopping distances.

Reithmaier and Salzinger [25] opined that excessive wear of tyres significantly contributes to road traffic accident due to the rolling resistance and friction between the road and tyre. The tyres of the assessed vehicles witnessed a much uneven wear due to inappropriate inflation pressure 33 (29.20%) of the participant vehicles recorded even tyre pressure.

The rolling resistance of tyres mainly depends on how the tread of the tyres touch the road surface. Tread depth is very important in maintaining straight line headway of the loaded tyre, especially at a constant speed. On the basis of hydroplaning potential and stopping distances, it is expected that tyre replacement for safe driving of used vehicle tyre should be at the tread depth of 1.6 mm as the chance of worn out tyre to cause an accident is high especially on the wet road [22, 26]. ROSPA [26] added that increases in stopping distance become significant when the tyre is worn past 3mm. The legal minimum tread depth of 1.6 mm notwithstanding, Hardy and Fenner (2015) reported that tyre tread depth of 3 mm performs 25% better than those at 1.6mm. In this study, the roadworthiness of road vehicle tyres (total compliance of the four tyres) was analyzed on the basis of legal minimum tread depth of 1.6 mm and 3.0 mm for dry and wet road conditions respectively (across 75% of the

tyre). Legal minimum roadworthiness tread depth for wet road conditions analyzed at the depth of 3.0 mm showed that 55 (48.7%) of the assessed vehicles were roadworthy as they had appropriate depth cut. When the legal minimum roadworthiness tread depth for dry road conditions was assessed at the depth of 1.6 mm, it showed that 85 (75.2%) participants' vehicles were of appropriate tread depth.

All the four tyres in a vehicle should be of appropriate sizes, speed rating and construction (radial or cross ply). Of the factors assessed, the same tyre size recommended by the tyre/vehicle manufacturer had the most appropriate safety compliance with a proportion of 105 (92.9%) of the assessed vehicle owned by the participants. This observation is in line with Reithmaier and Salzinger's [25] study.

Table 4

Analysis of the operational tyre safety and compliance with the specifics for tyre condition standard

Assessed variables	Appropriate operational status of tyre from physical measurement data analysis				
	Front right n (%)	**Front left n (%)**	**Back right n (%)**	**Back left n (%)**	**The assessed vehicle n (%)**
Tyre inflation pressure	26 (23.01)	25 (22.12)	25 (22.12)	17 (15.04)	6 (4.42)
Shelf life of tyre	44 (38.9)	46 (40.7)	63 (55.8)	53 (46.9)	33 (29.20)
Even wear of tyre tread	31 (27.4)	33 (29.2)	29 (25.7)	23 (20.4)	13 (11.50)
Legal minimum road worthiness tread depth for wet road condition	89 (78.8)	88 (77.9)	86 (76.1)	78 (69.0)	55 (48.7)
Legal minimum road worthiness tread depth for dry road condition	98 (86.7)	104 (92.0)	101 (89.4)	103 (91.2)	85 (75.2)
The same tyre size recommended by the tyre/vehicle manufacturer.	113 (100)	109 (96.46)	112 (99.12)	111 (98.23)	105 (92.9)

A vehicle is made up of many component parts and systems. A default of any of the component parts and systems, a tyre, for example, may affect the proper functioning of the vehicle. Overall operational tyre safety and compliance with the specifics of the tyre condition standard for each assessed vehicle showed that no assessed vehicle was of very high safe and appropriate compliance status. Forty-three (38.1%) of the assessed vehicles owned and used by the participants' were of very low safe and appropriate operational tyre safety and practices. This was followed by high safe and appropriate practices 39 (34.5%) (Table 5).

Pearson's chi-square test used to analyse data obtained to check if there is an association between tyre safety knowledge and safe and appropriate compliance status variables giving $\chi^2 = 1.135$ and $p = 0.769$ which is greater than 0.05.

This implies that statistically there is no significant association between knowledge of road vehicle tyre safety and operational tyre safety and compliance with the specifics for tyre condition standard among the participants (Table 6).

Table 5

Operational tyre safety and compliance with the specifics for tyre condition standard per assessed vehicle

Levels of safe and appropriate practice compliance	Frequency (n)	Percentage (%)
Very low safe and appropriate practice	43	38.1
Low safe and appropriate practice	30	26.5
Average safe and appropriate practice	39	34.5
High safe and appropriate practice	0	0.0
Very high safe and appropriate practice	1	0.9
Total	113	100.0

Phi and Cramer's used to test the level of association of knowledge of road vehicle tyre safety and operational tyre safety and compliance with the specifics for tyre condition standards showed that the level of association between the two variables was weak (Table 7).

Table 6

Chi-Square tests

	Value	df	Asymp. Sig. (2-sided)
Pearson Chi-Square	1.135[a]	3	0.769
Likelihood Ratio	1.130	3	0.770
Linear-by-Linear Association	0.096	1	0.756
No of Valid Cases	113		

a. 0 cells (0.0%) have expected count less than 5. The minimum expected count is 7.43.

Table 7

The table of symmetric measures

		Value	Approx. Sig.
Nominal by Nominal	Phi	0.100	0.769
	Cramer's V	0.100	0.769
	Contingency Coefficient	0.100	0.769
No of Valid Cases		113	

Conclusions

For a vehicle to serve its intended purpose which is to convey materials, goods, and people safely to their intended destinations, precautionary action must be judiciously observed and implemented. The safety aspect of road transportation and its operation is very important as it is closely related to human lives. This experimental research that assessed the effect of awareness and cautionary information on safe and appropriate tyre safety management operations among private vehicle owners in Abeokuta, metropolis, Nigeria on the established operational road traffic safety standards which includes vehicle tyres sizes, specified tyre inflation pressure, tyres expiry date and roadworthiness tread depth observed

that there was an association between the safety knowledge and its implication on-road vehicle tyre safety but it is not statistically significant. This calls for proactive awareness of tyre safety among vehicle owners.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. WHO, World Health Organization. Road Safety is No Accident: Brochure for World Health day, *Geneva; World Health Organization,* 2004.
2. Ratanavaraha, V.; Suangka, S. Impacts of accident severity factors and loss values of crashes on expressways in Thailand. *IATSS Research* 2014, 37(2), pp. 130-136.
3. Ukwu, J. 7 major causes of road accidents in Nigeria, 2016. https://politics.naij.com/755165-must-read-7-major-causes-road-accidents-nigeria.html
4. Afolabi, O. J.; Gbadamosi, K. T. Road traffic crashes in Nigeria: causes and consequences. *Transport and Logistics*, 2017, 17(42), pp. 40-49.
5. Emenike, G. C.; Ogbole, A. Accidents and the Road Transport Industry in Nigeria. *Journal of the International Centre for Constructive Research (ICCR),* 2008, Corpus ID: 111047477.
6. Iteke, O.; Bakare, M. O.; Agomoh, A. O.; Uwakwe, R.; Onwukwe, J. U. Road traffic accidents and posttraumatic stress disorder in an orthopedic setting in south-eastern Nigeria: a controlled study. *Scandinavian Journal of Trauma, Resuscitation and Emergency Medicine*, 2011, 19(1), pp. 39. Available at http://www.sjtrem.com/content/19/1/39.
7. Atubi, A. O.; Gbadamosi, K.T. Global Positioning and Socio-Economic Impact of Road Traffic Accidents in Nigeria: Matters Arising. *American International Journal of Contemporary Research* 2015, 5(5), pp. 136-146.
8. Azodo, A. P. Survey on road-tyre contact patch pattern and wear related. *Journal of Mechanical Engineering*. 2017, 67(2), pp. 5-12.
   Available at https://www.degruyter.com/downloadpdf/j/scjme.2017.67.issue-2/scjme-2017-0013/scjme-2017-0013.pdf
9. Bharat, M. R.; Sidharth, D. Tyre modelling for rolling resistance. Master's Thesis, Department of Applied Mechanics Division of Vehicle Engineering and Autonomous System, Chalmers University of Technology, Göteborg, Sweden, 2014.
10. Jansen, S. T. H.; Schmeitz, A. J. C.; Maas, S.; Rodarius, C.; Akkermans, L. *Study on some safety-related aspects of tyre use*. Technical report. European Commission Directorate-general for Mobility and Transport, Unit C4, 4/110B-1049 Brussels, Belgium, 2016.
11. Azodo, A. P.; Ogban, P. U.; Okpor, J. Knowledge and awareness implication on e-waste management among Nigerian collegiate. *Journal of Applied Science and Environmental Management* 2017, 21 (6), pp. 1035-1040. Available at https://www.ajol.info/index.php/jasem/article/viewFile/163033/1525 43
12. Szczepanowski, R.; Pessoa, L. Fear perception: Can objective and subjective awareness measures be dissociated? *Journal of Vision* 2007, 7(4), pp. 1-17. http://journalofvision.org/7/4/10/, doi:10.1167/7.4.10.
13. Azodo, A. P.; Ismaila, S. O. Effective solid waste management for environmental quality and sustainability: knowledge and practices among Nigerian households. In: *Proceedings of the 2016 International Conference on SET: A driving force for sustainable development tagged COLENG 2016, Federal University of Agriculture, Abeokuta, 2016*.
14. Eriksen, C. W. Discrimination and learning without awareness: a methodological survey and evaluation. *Psychological review* 1960, 67 (5), pp. 279–300.
15. Bissell, R. E. A Unifying Concept for the "Subjective" and "Objective" Approaches to Understanding the Musical Experience, 1970. Available at http://www.rogerbissell.com/id11a3.html
16. Merikle, P. M.; Smilek, D.; Eastwood, J. D. Perception without awareness: Perspectives from cognitive psychology. *Cognition* 2001, 79 (1-2), pp. 115-134.
17. Bowers, R. M.; Bowers, K. S.; Meichelbaum, D. On being unconsciously influenced and informed. The unconscious reconsidered. Ed. John Wiley & Sons, New York, SUA, 1984, pp. 227–272.
18. Öhman, A. Distinguishing unconscious from conscious emotional processes: methodological considerations and theoretical implications. In Handbook of Cognition and Emotion. Eds Dalgleish T., Power M. (Chichester: Wiley), 1999, pp. 321–352.
19. Kahane, C. J. Lives saved by the Federal Motor Vehicle Safety Standards and other vehicle safety technologies, 1960-2002-Passenger cars and light trucks-with a review of 19 FMVSS and their effectiveness

in reducing fatalities, injuries and crashes (No. HS-809 833), 2004. Available at: https://one.nhtsa.gov/cars/rules/regrev/evaluate/809833.html
20. Dorgan, B. L. Underinflated Tires in the United States. United States Government Accountability Office Washington, DC 20548, 2007. Available at: http://www.gao.gov/new.items/d07246r.pdf
21. Osueke, C. O.; Uguru-Okorie, D. C. The role of tire in car crash, its causes, and prevention. *International Journal of Emerging Technology and Advanced Engineering* 2012, 2(12), pp. 54-57.
22. Sangofadeji, A. O. Human errors and management of road traffic crashes. Alfabright Big Ltd, Ibadan, 2013.
23. Abolghassemi, H. Importance of tyre pressure, 2016. Available at: http://finixx.com/importance-of-tyre-pressure/
24. Azodo, A. P.; Adejuyigbe, S. B. Nigeria engineering students' compliance with workshop safety measures. *International journal of Innovation and Applied Studies* 2013, 3 (2), pp. 425-432. Available at http://www.issr-journals. org/xplore/ ijias/IJIAS/13-091-01.pdf
25. Reithmaier, W.; Salzinger, T. Survey on motor vehicle tyres and related aspects. The European commission enterprise directorate general unit, 2003, pp. 1-173.
26. ROSPA (The Royal Society for the Prevention of Accident), Behind the wheel. The Newsletter for Drivers in Wales. Spring, 2015.

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NEW VAPOR DEPOSITED DIELECTRIC POLYMER THIN FILMS FOR ELECTRONIC APPLICATIONS

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Abstract. Dielectric materials are of great interest in a vast amount of applications ranging from cable insulation to advanced electronic devices. The emerging trend of device miniaturization is creating an increased demand for dielectric thin films that can be produced precisely on the nanometer scale. In addition, special mechanical properties are often required, for example in the field of flexible organic electronics. Polymers are first-choice materials for this purpose. However, it is extremely difficult to produce precise nanoscale thin films, which have a low defect density and are free of e.g. residual solvent, by wet chemistry approaches. Initiated chemical vapor deposition (iCVD) is a solvent-free polymer thin film deposition process which can be used to produce high quality dielectric thin films with nanoscale control and circumvents thus these problems. This work demonstrates the versatility of the iCVD process in the field of electrical applications by some new application examples of iCVD. By adding e.g. a hydrophobic organosiloxane thin film on columnar zinc oxide (ZnO:Fe) gas sensing structures there was a change in the selectivity from ethanol to hydrogen, as well as improved performance at high humidity level. The modified sensors can thus be used in humid ambient, especially for breathing tests, which can lead to the diagnosis of some diseases by cutting edge non-invasive approaches.

Keywords: *Polymers, Initiated Chemical Vapor Deposition, Electronic Materials, Dielectrics, Electrets, Gas Sensors.*

Rezumat. Materialele dielectrice prezintă interes pentru numeroase aplicații, de la izolarea cablurilor până la dispozitive electronice avansate. Tendința emergentă de miniaturizare a dispozitivelor creează o cerere crescută pentru pelicule subțiri dielectrice care pot fi produse exact la scara nanometrică. În plus, sunt adesea necesare proprietăți mecanice speciale, de exemplu în domeniul electronicii organice flexibile. Polimerii sunt materiale de primă alegere în acest scop. Cu toate acestea, este extrem de dificil să se producă filme subțiri precise la scară nanometrică, care au o densitate scăzută a defectelor și sunt lipsite de solvent rezidual, prin abordări ale chimiei umede. Depunerea chimică de vapori inițiată (iCVD) este un proces de formare a peliculei subțiri de polimer fără solvenți care poate fi utilizat pentru a produce pelicule dielectrice de înaltă calitate cu control la scară nanometrică și eludează astfel aceste probleme. Această lucrare demonstrează versatilitatea procesului iCVD în domeniul aplicațiilor electrice prin câteva exemple noi de aplicare a iCVD. Prin adăugarea, spre exemplu, a peliculei subțiri de organosiloxan hidrofob pe structurile de detectare a gazului de oxid de zinc columnar (ZnO:Fe), se atestă o schimbare a selectivității de la etanol la hidrogen, precum și o performanță îmbunătățită la un nivel ridicat de umiditate. Senzorii modificați pot fi astfel utilizați în mediu umed, în special pentru teste de respirație, care pot duce la diagnosticarea unor boli prin abordări non-invazive de ultimă oră.

Cuvinte cheie: *polimeri, depunere chimică inițiată de vapori, materiale electronice, dielectrice, electreți, senzori de gaz*.

1. Introduction

The current advent of polymer thin films enabled by the combination of chemical vapor deposition (CVD) with organic chemistry provides a variety of new pathways in the field of organic electronics and electronic applications. In particular, oxidative chemical vapor deposition (oCVD) and initiated chemical vapor deposition (iCVD) developed by Gleason et al. facilitate the precise deposition of new electronic materials from a few nanometers to several micrometers in film thickness [1]. While in oCVD a step growth reaction allows the preparation of conjugated polymers such as PEDOT or PANI [2], iCVD usually results in insulating films due to the underlying free radical polymerization. In the latter, the polymer backbone is sp3-hybridized and the polymer films can be used as dielectrics. Due to the solvent-free nature of iCVD, the dielectric thin films are of very high quality and have no defects that accelerate e.g dielectric breakdown [3]. Thanks to the CVD-typical growth character, the iCVD process can easily be scaled up and integrated into modern microelectronic process lines. A schematic illustration of the iCVD process is shown in Figure 1(a). The respective monomer (M) and initiator (I) are introduced to the reactor. The reactor is equipped with a heatable filament array, located above a sample stage, which is cooled to room temperature. The monomer molecules adsorb at the substrate stage and once the filaments are heated the initiator molecules are decomposed into free radicals (R). These radicals meet e.g. a vinyl groups of the adsorbed monomer molecules. They start a free radical polymerization, which follows similar kinetics like the well-known kinetics for wet chemistry free radical polymerization [4] in order to produce high quality polymer thin films at the substrate surface.

Figure 1(a) shows schematic design of the iCVD process. It is shown that monomer (M) vapor and initiator (I) vapor are introduced to a hot wire CVD (HWCVD) reactor at the same time. Afterwards, thermally decomposed I results in free radicals (R), which initiate a free radical polymerization with adsorbed M. Figure 1(b) shows possible monomers and initiators

for dielectric thin films. In this work, some application examples of different tailored dielectric iCVD films are shown to demonstrate the versatility of the process in the field of electrical applications.

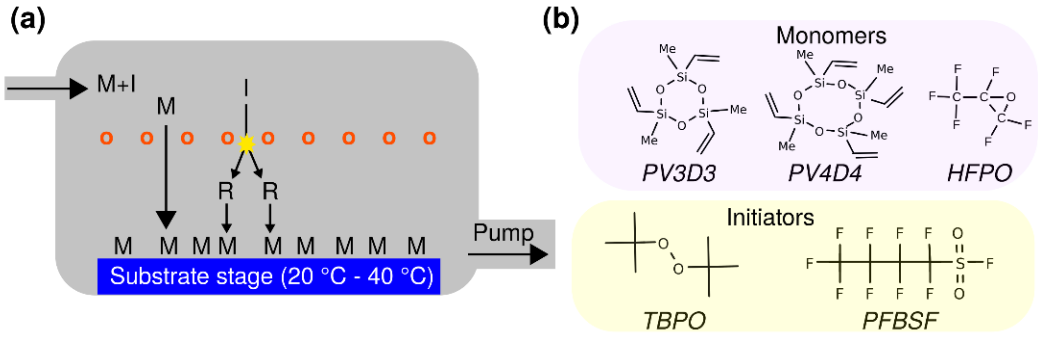

Figure 1. (a) Schematical illustration of the iCVD process. Monomer (M) vapor and Initiator (I) vapor are introduced to a hot wire CVD (HWCVD) reactor. Thermally decomposed I results in free radicals (R), which initiate a free radical polymerization with adsorbed M. (b) Possible monomers and initiators for dielectric thin films.

2. Experimental details

All polymer thin films reported in this study are deposited via iCVD. A home-made ring-inlet iCVD reactor explained in our previous works has been used for this purpose [3, 7, 8]. The hydophobic PV3D3 thin films have been obtained by the combination of the monomer V3D3 with the initiator PFBSF. The electrostatic potential maps have been illustrated using Jmol. The V3D3 and V4D4 molecules have been geometry-optimized employing density functional theory (DFT) at the B3LYP/ccPVDZ level for this purpose. The reported gas sensing structures have been obtained initially by the chemical deposition of solutions (SCS) method, which yields a nanostructured ZnO:Fe film. The film was deposited on a glass substrate (75 mm × 25 mm × 1 mm). The obtained ZnO, ZnO:Fe nanostructured films have been thermal annealed (TA) in furnace for 2 hours at 650 °C in normal ambient. A more detailed description is given in our previous works [5, 6]. An ultra-thin deposition of CuO/Cu_2O with a thickness of 18 nm was grown on the ZnO:Fe film with a custom setup with DC and RF magnetron. After this step a heat treatment was applied to the samples in a furnace at 420 °C for 30 minutes. In the next fabrication step 25 nm of the hydrophobic PV3D3 thin film was deposited on top of the sensors. Finally, Au contacts were sputtered on top of the samples through a meandering mask [9]. For the sensor performance measurements, a computer-controlled Keithley 2400 sourcemeter at 0.2 V applied bias voltage was used. The details on the sensing experiments can be found in our previous works on gas sensing studies [10, 11].

3. Results and Discussion

The application of iCVD thin films as dielectric layer is reported by many authors, especially organocyclosiloxanes, like PV3D3, PV4D4 and fluoropolymers, have demonstrated excellent performance [12-14]. The chemical structure of possible monomers and initiators which yield excellent dielectric properties are presented in Figure 1(b). The polymer films can also be deposited on flexible substrates, as shown in the digital photograph in Figure 2(a), were we use a dielectric iCVD thin film as part of a flexible electronic device. Figure 2(b) shows a schematic representation of trap states, which are positioned between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands of the polymer. Figure 2(c) illustrates calculated electrostatic potential maps of geometry-optimized V3D3 and V4D4.

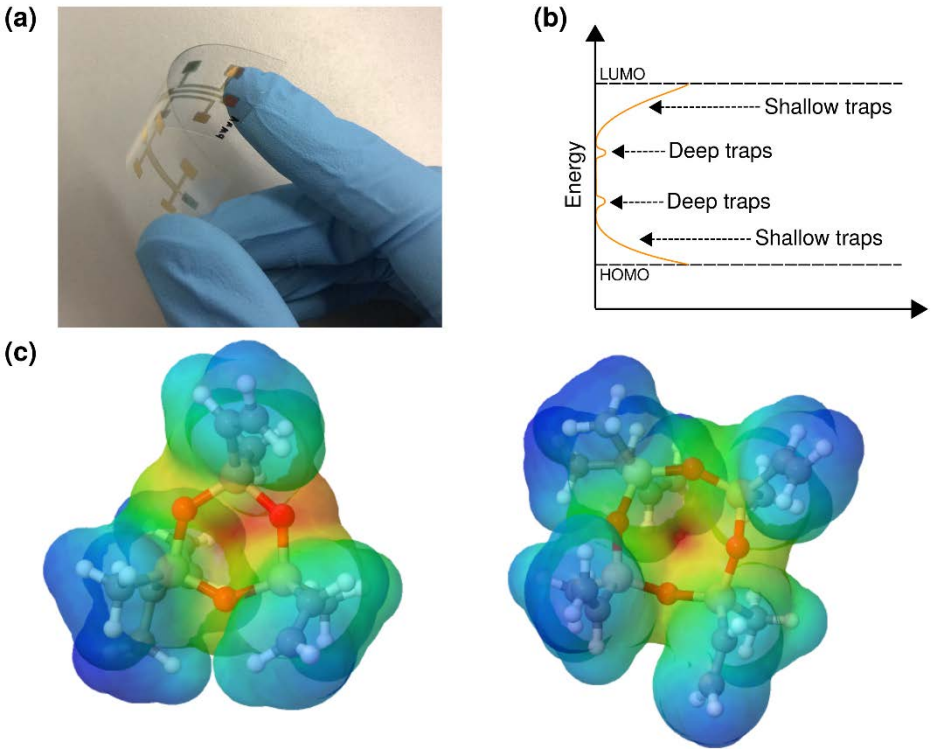

Figure 2. Photograph of the application of an iCVD thin film as part of a flexible electronic device, produced in our lab (a). Schematic illustration of trap states, which are located between the HOMO and LUMO bands of the polymer (b). Calculated electrostatic potential maps of geometry-optimized V3D3 and V4D4 (c).

The iCVD coatings are thus also highly attractive as dielectric thin films for flexible organic electronics. One further argument for using iCVD is the high film quality, because no organic solvents are used during the fabrication of the polymer thin films. Residual solvent and defects can cause e.g. conductive paths and this lowers the dielectric breakdown strength of the material. For dielectric iCVD films the breakdown strength has been found to be extremely high, because of the low defect density and high film quality without residual solvent molecules [3]. Since dielectric iCVD films exhibit such high breakdown strength and film quality, we demonstrated the use of iCVD grown PTFE thin films as electret materials in a previous work [3]. Electrets are dielectric materials with a quasi-permanent surface charge. They can be produced by exposing the dielectric materials e.g. to a corona discharge in order to transfer excess charge to the material. The charge carriers are stored in trap states, which are located in the gap between the HOMO and LUMO of the polymer, as illustrated in Figure 2(b). Typically deep level traps provide enough depth to store the charge carriers over a long period of time. The result is a surface potential which can be applied for many different application fields like portable electret condenser microphones, energy harvesting, air filters or magnetic field sensors [15, 16]. However, the charged film is in a metastable state and at some point the charge will decay. A good electret is thus characterized by the fact that its charge decay is negligible compared to the device lifetime in which it is used. Fluoropolymers like polytetrafluoroethylene (PTFE) typically exhibit the best charge storage properties [3]. The unique adjustability of the functional groups in the iCVD process allows the electrical properties to be specifically tailored. These can also be correlated with theoretical calculations. In Figure 2(c), the calculated electrostatic potential maps of the above-mentioned V3D3 and V4D4 monomers are shown as an example.

In addition to the production of such new tailored polymer thin films for electronic applications by iCVD, it is also possible to functionalize existing electronic devices. As an example, we recently demonstrated the functionalization of metal-oxide gas sensors with an ultra-thin hydrophobic cyclosiloxane-type of polymer [5]. In this previous work we have reported data for $CuO/Cu_2O/ZnO:Fe$ heterostructures, which were as-grown and Rapid Thermal Annealed (RTA) for 60 s at 650°C. After the deposition of the ultra-thin hydrophobic thin film via iCVD using the monomer V3D3 and the hydrophobic initiator PFBSF we were able to tune the selectivity of the gas sensors to hydrogen gas. Furthermore, we were able to operate the sensors at high humidity level, which has been a major problem for metal-oxide gas sensors before. Also, new metal-oxide $CuO/Cu_2O/ZnO:Fe$ heterostructures, which have been thermally annealed (TA) at 650°C for 2h in a furnace in air, can be applied as gas sensors. Scanning electron microscopy (SEM) images of these new structures are shown in Figure 3.

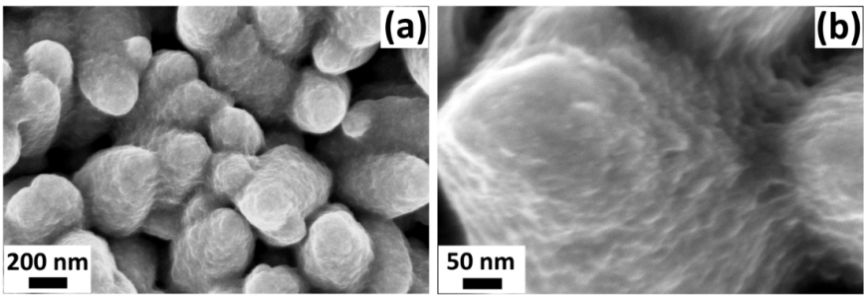

Figure 3. SEM images of $CuO/Cu_2O/ZnO:Fe$ heterostructures after thermal annealing at 650 °C for 2 h at low (a) and high magnifications (b).

From Figure 3 can be concluded that the samples are composed of highly packed columnar-type grains of ZnO:Fe with the CuO/Cu_2O layer on the surface. The structures cover the glass substrate completely. The increasing surface/volume ratio is beneficial for sensor applications.

The gas sensors shown in Figure 3 are coated with 25 nm hydrophobic PV3D3, similar like in our previously reported study [5]. PV3D3 layer was deposited on top of such sensor structure to protect it from the effect of environment and especially from the high relative humidity, which affect the sensor performances seriously. Figure 4 shows the XRD patterns of the samples.

The formation of hetero-junctions is evidenced by the coexistence of the phases of CuO, Cu_2O and ZnO, so that at the values 2θ of 32.45°, 35.3°, 46.15°, 65.4° and 68.05°. The reflections *hkl* were found for the copper oxide CuO (Tenorite) with the Miller planes of (-110), (-111)/(002), (-112), (022) and (113), respectively. These results clearly prove crystal quality and no changes due to iCVD process. Furthermore, the diffractions from the gold layer, Au (111) and Au (220), can be observed, which was deposited on top of the sensor structure as an electrical contact.

Reflections at 2θ of 34.35°, 34.35°, 47.95°, 56.75°, 62.2° and 66.45° with the Miller planes of (002), (102), (110), (103) and (200), respectively, are attributed to zinc oxide ZnO, according to the card (pdf # 36-1451) Zincite syn. In addition, reflections of iron oxide Fe_2O_3 are observed in Figure 4, which indicate the doping of zinc oxide with iron impurities. After thermal treatment Fe_2O_3 is found according to the card (pdf # 89-0599) Hematite syn with Miller indexes (104), (202), (024) and (125) at the 2θ angle of 33.45°, 43.45°, 49.05° and 67.1°, respectively.

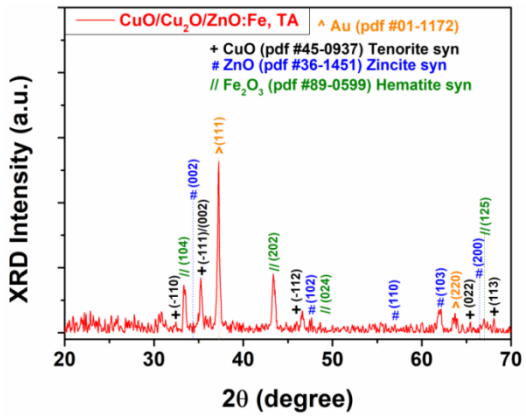

Figure 4. XRD pattern of $CuO/Cu_2O/ZnO$:Fe heterostructures thermally annealed at 650 °C and contacted with Au on top as electrical contacts.

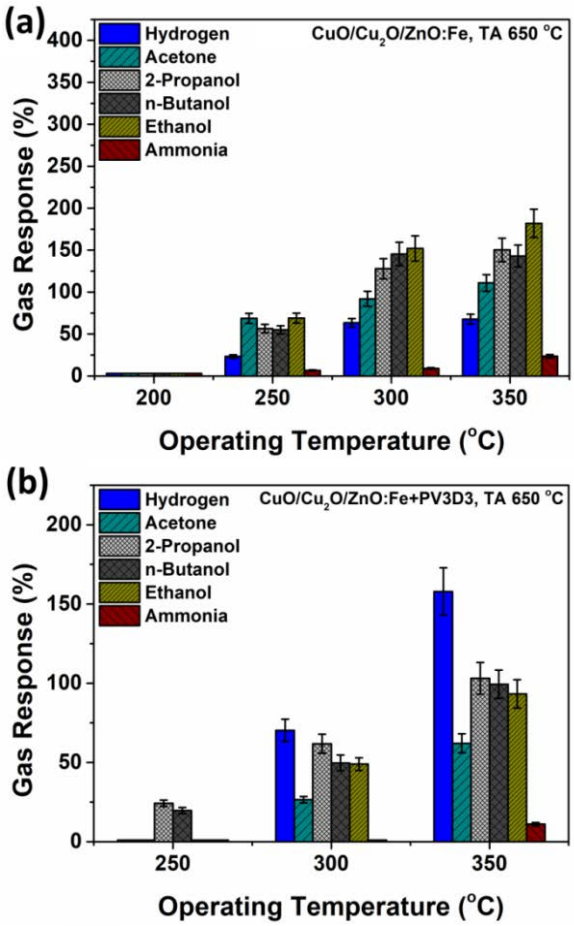

Figure 5. The dependence of the gas response (hydrogen, acetone, 2-propanol, n-butanol, ethanol and ammonia) versus working temperature for (a) uncoated heterostructured samples and for (b) hydrophobic PV3D3 coated samples.

As mentioned above, reflections at 2θ of 37,25 ° and 63,75 ° in Figure 4 are assigned to metallic Au, which originate from the sputtered contacts during device fabrication.

In order to test the final sensor performance with and without the polymer coating we performed gas response measurements with respect to various gas and volatile organic compounds in normal ambient. The results of the measurements of the gas response versus operating temperature are shown in Figure 5.

The sensors have been tested with hydrogen gas, acetone, 2-propanol, n-butanol, ethanol and ammonia vapor at different working temperatures. The results for thermally

annealed CuO/Cu_2O/ZnO:Fe heterostructures without the PV3D3 are shown in Figure 5(a). Results from the sample set of thermally annealed CuO/Cu_2O/ZnO:Fe hetero-structures with additional PV3D3 coating are shown in Figure 5(b) for comparison. Figure 5(a) reveals that the highest gas response can be observed for ethanol vapors. The growth of the hydrophobic PV3D3 on top of the sensor surface shows a shift of the selectivity to hydrogen gas, similar like our observations for the samples from our previous work [5]. The highest response can be obtained at an operating temperature (OPT) of 350 °C with a response value of ~165%. Figure 6(a) illustrates the dynamic response of the uncoated CuO/Cu_2O/ZnO:Fe heterostructures to ethanol vapors in normal ambient. The dynamic response for hydrogen of the PV3D3 coated heterostructures is shown in Figure 6(b), which proves that selectivity was changed from ethanol vapor to hydrogen gas and pulses are reproducible during all experiments.

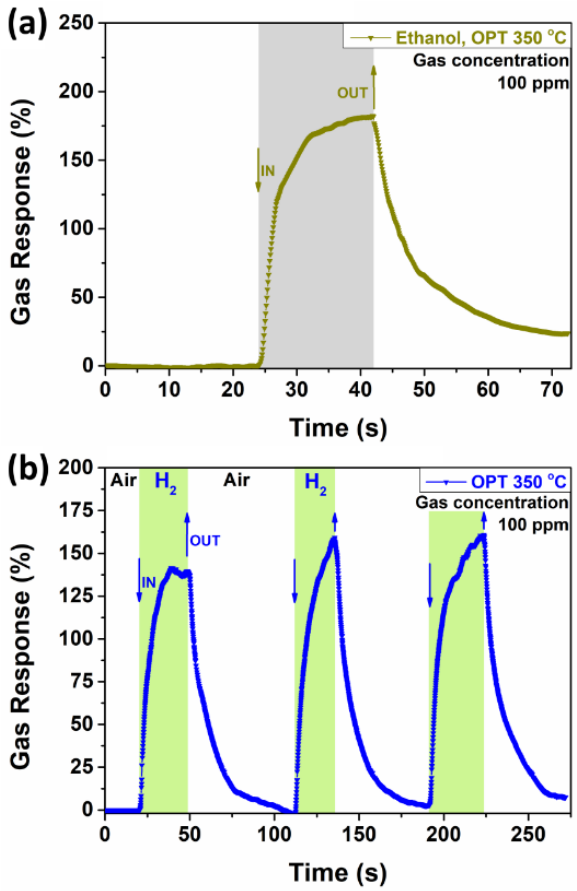

Figure 6. Dynamic response of the CuO/Cu_2O/ZnO:Fe heterostructures thermally annealed at 650 °C for 2 h in air: (a) to ethanol vapors (sample set without PV3D3) and (b) to hydrogen gas (sample set with PV3D3 layer on top of the sensor) at optimal operating temperature of 350 °C measured in normal ambient.

Both measurements have been performed at an OPT of 350 °C and data recorded in normal ambient. The results in Figure 6 demonstrate that uncoated as well as coated heterostructures show quite high response values, when they are exposed to the respective gas. Furthermore, a very good repeatability can be observed in Figure 6(b). The sensors show a complete restoration of the response after each gas pulse.

The current-voltage (I-V) curves of the uncoated as well as coated heterostructures are shown in Figures 7(a) and 7(b), respectively. Figure 7a shows the electrical measurements for an uncoated heterostructure CuO/Cu_2O/ZnO:Fe and Figure 7b shows the measurements for a

PV3D3-coated heterostructure on glass substrates. The measurements have each been performed at different OPT as indicated in the graphs and numbered accordingly. The electrical measurements reveal that the I-V curves for all heterostructures show Ohmic behavior at each of the targeted operating temperatures. This demonstrates that the sensors work correctly even with the additional 25 nm polymer coating on top of the heterostructure. As observed in the measurements above, the selectivity of the covered sensors has shifted towards hydrogen gas due to the additional PV3D3 coating, similar like in our previous study.

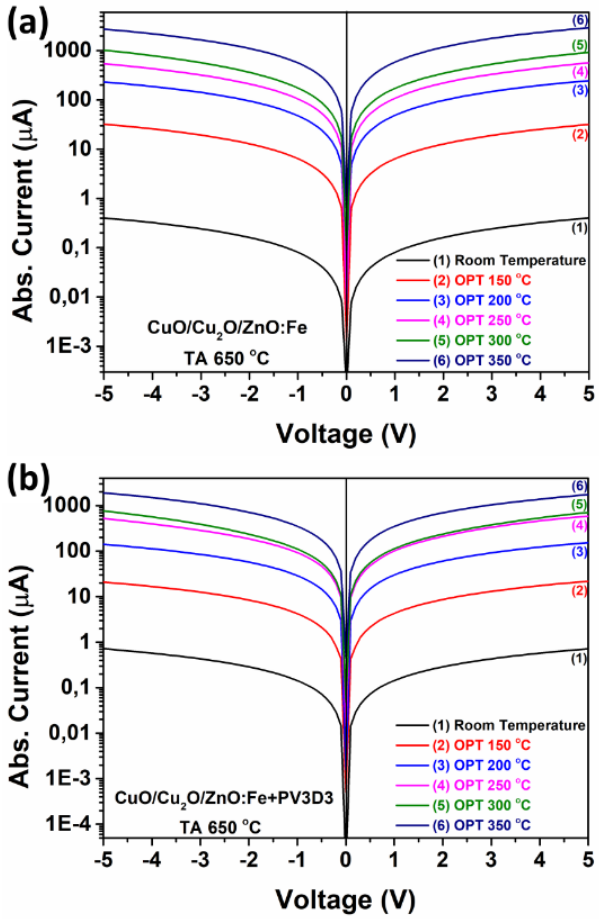

Figure 7. Current-voltage characteristics of the CuO/Cu_2O/ZnO:Fe heterostructures thermally annealed at 650 °C: (a) without PV3D3; and (b) covered with PV3D3 layers.

Dynamic response measurements at different humidity levels have been performed in order to investigate the influence of moisture or value of relative humidity RH on the sensor performance and to identify if it is suitable for breath test, as an example. The obtained results are shown in Figure 8. Figure 8(a) illustrates the dynamic response to ethanol vapor for the uncoated heterostructures. The dynamic response for the PV3D3-coated heterostructures are presented in Figure 8(b) for hydrogen. The gas concentration was in both measurements 100 ppm and the measurements have been performed at 20 % and 65 % relative humidity each. Figure 8(a) shows that the response of the uncoated heterostructure to ethanol vapor decreases drastically by about 88 % at relative humidity of 65 % compared to the response at relative humidity of only 20 %. As expected, this indicates that the gas sensors no longer work reasonably in a high humid environment and can't be used for example in non-invasive breath tests. The dynamic response measurement for the PV3D3-coated heterostructure, which is shown in Figure 8(b), reveals that the response to hydrogen

decreases to about 1/3 of the original response in the high humidity environment. In addition, it is evident that pulses are still repeatable at higher humidity. This clearly proves the effect of the coverage with a PV3D3 thin film to protect the gas sensing samples from moisture. The performed experiments thus show, that the additional hydrophobic PV3D3 coating can also increase the stability of the heterostructure with regard to a high relative humidity, similar like in our previous study. Furthermore, it can also protect the sensing structures from the environment conditions.

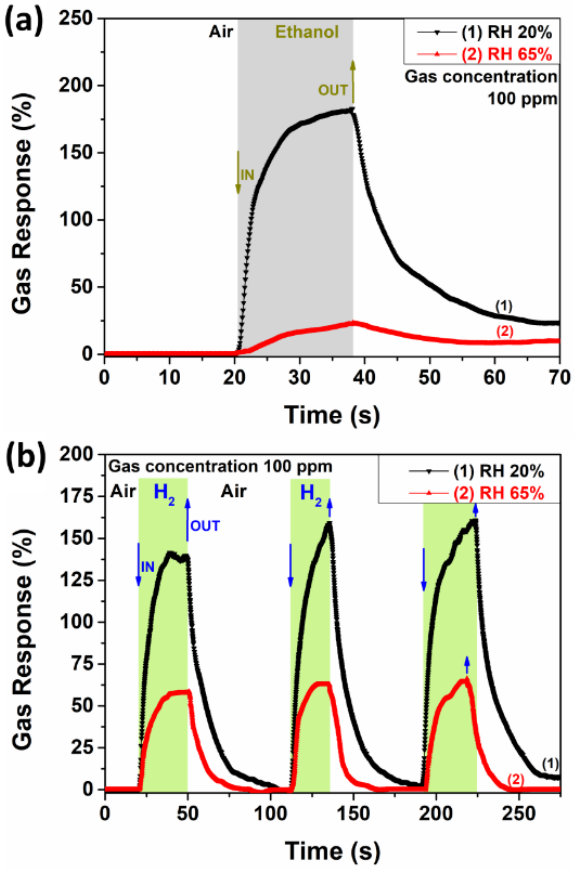

Figure 8. Dynamic response at operating temperature of 350 °C at different concentrations of relative humidity: (a) to ethanol vapors (samples without PV3D3 layer) and (b) to hydrogen gas (samples covered with PV3D3 layer on top).

4. Conclusions

Dielectric thin films deposited by iCVD can be used in a vast amount of electrical and electronic applications. We presented potential applications in organic electronics or as thin film electrets as examples. The individual tunability of the functional groups makes it possible to specifically adjust the electrical properties of the polymer thin films. Furthermore, in addition to creating new polymer thin film materials, existing devices can also be improved. The films can be used e.g. to protect electronic circuits or electronic devices. Following our previous study, we show as a real example, the use of hydrophobic coatings to protect semiconducting oxide-based gas sensors from moisture or high relative humidity. According to the presented results, CuO/Cu_2O/ZnO:Fe heterostructures after thermal treatment at 650 °C for 2 h were successfully obtained in this current work. The structural results were confirmed by XRD data, with a granular morphology of columnar type confirmed by SEM. The heterostructures of CuO/Cu_2O/ZnO:Fe with a thermal annealing regime in the

electrical furnace at 650 °C for 2 h in ambient air are selective for ethanol vapors. After the deposition of a 25 nm hydrophobic PV3D3 thin film on the heterostructure, the selectivity changes from ethanol vapor to hydrogen gas. At the same time, the deposition of the PV3D3 thin film increases the stability at high relative humidity values, namely 65% RH in our experiments. A possible application field for the modified gas sensors in the future are biomedical applications. The sensors can here be applied for e.g. breath tests in non-invasive diagnosis, due to the fact that humidity does not significantly influence the response value to hydrogen gas in a high humid environment.

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Conflicts of Interest. The authors declare no conflict of interest.

References

1. Coclite, A. M.; Howden, R. M.; Borrelli, D. C.; Petruczok, C. D.; Yang, R., Yagüe, J. L.; Ugur, A.; Chen, N.; Lee, S.; Jo,W. J.; Liu, A.; Wang, X.; Gleason, K. K. 25th anniversary article: CVD polymers: A new paradigm for surface modification and device fabrication. *Advanced Materials* 2013*,* 25, pp. 5392-5423.
2. Gharahcheshmeh, M., H.; Gleason, K. K. Device fabrication based on oxidative chemical vapor deposition (oCVD) synthesis of conducting polymers and related conjugated organic materials. *Advanced Materials Interfaces* 2019, 6 (1), pp. 1801564.
3. Schröder, S.; Strunskus, T.; Rehders, S.; Gleason, K. K.; Faupel, F. Tunable Polytetrafluoroethylene Electret Films with Extraordinary Charge Stability Synthesized by Initiated Chemical Vapor Deposition for Organic Electronics Applications. *Scientific Reports* 2019, 9, pp. 2237.
4. Odian, G. Radical chain polymerization. In: John Wiley & Sons, Inc., 4th ed. *Principles of polymerization*. New Jersey: 2004, pp.198-349.
5. Schröder, S.; Ababii, N.; Lupan, O.; Drewes, J.; Magariu, N.; Krüger, H.; Strunskus, T.; Adelung, R.; Hansen, S.; Faupel, F. Sensing Performance of CuO/Cu_2O/ZnO:Fe Heterostructure Coated With Thermally Stable Ultrathin Hydrophobic PV3D3 Polymer Layer for Battery Application. *Materials Today Chemistry* 2022, 23, pp. 100642.
6. Postica, V.; Hölken, I.; Schneider, V.; Kaidas, V.; Polonskyi, O.; Cretu, V.; Tiginyanu, I.; Faupel, F.; Adelung, R.; Lupan, O. Multifunctional device based on ZnO:Fe nanostructured films with enhanced UV and ultra-fast ethanol vapour sensing. *Materials Science in Semiconductor Processing* 2016, 49, pp. 20-33.
7. Schröder, S.; Hinz, A. M.; Strunskus, T.; FaupeL, F. Molecular insight into real-time reaction kinetics of free radical polymerization from the vapor phase by i-situ mass spectrometry. *Journal of Physical Chemistry A* 2021, 125 (7), pp. 1661-1667.
8. Schröder, S.; Polonskyi, O.; Strunskus, T.; Faupel, F. Nanoscale gradient copolymer films via single-step deposition from the vapor phase. *Materials Today* 2020, 37, pp. 35-42.
9. Lupan, O.; Cretu, V.; Postica, V.; Polonskyi, O.; Ababii, N.; Schütt, F.; Kaidas, V.; Faupel, F.; Adelung, R. Non-planar nanoscale p–p heterojunctions formation in $Zn_xCu_{1-X}O_y$ nanocrystals by mixed phases for enhanced sensors. *Sensors and Actuators B: Chemical*. 2016, 230, pp. 832-843.
10. Lupan, O.; Postica, V.; Wolff, N.; Polonskyi, O.; Duppel, V.; Kaidas, V.; Lazari, E.; Ababii, N.; Faupel, F.; Kienle, L.; Adelung, R. Localized synthesis of iron oxide nanowires and fabrication of high performance nanosensors based on a single Fe_2O_3 nanowire. *Small* 2017, 13 (16), pp. 1602868.
11. Lupan, O.; Postica, V.; Cretu, V.; Wolff, N.; Duppel, V.; Kienleand, L.; Adelung, R. Single and networked CuO nanowires for highly sensitive p-type semiconductor gas sensor applications. *Physica Status Solidi - Rapid Research Letters* 2016; 10 (3), pp. 260-266.
12. O'Shaughnessy, W. S.; Edell, D. J.; Gleason, K. K. Initiated chemical vapor deposition of a siloxane coating for insulation of neural probes. *Thin Solid Films* 2009, 517 (12), pp. 3612-3614.

13. Trujillo, N. J.; Wu, Q.; Gleason, K. K. Ultralow dielectric constant tetravinyltetramethylcyclotetrasiloxane films deposited by initiated chemical vapor deposition (iCVD). *Advanced Functional Materials* 2010, 20 (4), pp. 607-616.
14. Lau, K. S.; Caulfield, J. A.; Gleason, K. K. Structure and morphology of fluorocarbon films grown by hot filament chemical vapor deposition. *Chemistry of Materials* 2000, 12 (10), pp. 3032-3037.
15. Hu, F.; Cai, Q.; Liao, F., Shao, M., Lee, S.-T. Recent advancements in nanogenerators for energy harvesting. *Small* 2015, 11, pp. 5611-5628.
16. Minkten, M.; Schweichel, M.; Schröder, S.; Kaps, S.; Carstensen, J.; Mishra, Y. K.; Strunskus, T.; Faupel, F.; Adelung, R. Nanogenerator and piezotronic inspired concepts for energy efficient magnetig field sensors. *Nano Energy* 2019, 56, pp. 420-425.

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GAS SENSITIVE FILMS BASED ON Te-SnO_2 NANOCOMPOSITE ON FLEXIBLE SUBSTRATE

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Abstract. Flexible films based on novel Te-SnO_2 nanocomposites were fabricated for detection of toxic gases at room temperature. The Te-SnO_2 nanocomposites were obtained via solvohermal recrystallization of pure crystalline tellurium in nitric acid in the presence of tin chloride. The energy-dispersive X-ray spectroscopy (EDX) and XRD analyses have shown that the Te-SnO_2 films consists of fluffy structures of tiny agglomerates of the nanodimensional irregular blocks of hexagonal Te and polycrystalline SnO_2. Both current / voltage and transient characteristics of the flexible Te-SnO_2 films were investigated at room temperature in ambiance comprising different toxic gases. The maximum selectivity was revealed toward NO_2, for which in the dynamic range of 0.5 - 5.0 ppm of NO_2, the response and recovery times are about 30 s and 150 s respectively. Analysis of the response kinetics meets the Langmuir theory of adsorption. This study revealed a simple route of fabrication of the printable Te-SnO_2 nanocomposites that can be used in electronics, inclusive for development of flexible and compostable gas sensors, operating at room temperature.

Keywords: *Nanocomposites, Te-SnO_2, Conductometric sensors, NO_2.*

Rezumat. Filme flexibile bazate pe noi nanocompozite Te-SnO_2 au fost fabricate pentru detectarea gazelor toxice la temperatura camerei. Nanocompozitele Te-SnO_2 au fost obținute prin recristalizarea solvotermală a telurului cristalin pur în acid azotic în prezență de clorură de staniu. Spectroscopia cu raze X cu dispersie energetică (EDX) și analizele XRD au arătat că filmele de Te-SnO_2 constau din structuri pufoase de aglomerate mici ale blocurilor neregulate nanodimensionale de Te hexagonal și SnO_2 policristalin. Atât caracteristicile curent/tensiune, cât și tranzitorii ale filmelor flexibile de Te-SnO_2 au fost investigate la temperatura camerei într-o ambianță cuprinzând diferite gaze toxice. Selectivitatea maximă a fost evidențiată față de NO_2, pentru care în intervalul dinamic este de 0,5 - 5,0 ppm de NO_2, timpii de răspuns și de recuperare sunt de aproximativ 30 s și, respectiv, 150 s. Analiza cineticii răspunsului

corespunde teoriei Langmuir a adsorbției. Acest studiu a dezvăluit o cale simplă de fabricare a nanocompozitelor imprimabile Te- SnO_2 care pot fi utilizate în electronică, inclusiv pentru dezvoltarea senzorilor de gaz flexibili și compostabili, care funcționează la temperatura camerei.

Cuvinte cheie: *Nanocompozite, Te-SnO_2, Senzori conductometrici, NO_2.*

1. Introduction

In the last years, printed electronics becomes very attractive due to the ability of using sustainable, compostable and recyclable materials including biobased plastics and paper in the elaboration of different flexible devices, such as photodetectors, light-emitting diodes, transistors, piezo-resistive transducers, circuit boards etc. [1-5]. Many reports are available on development of flexible gas sensors (see extensive reviews [6-7]), based on plastic, polyimide, polypyrrole or polytetrafluoroethylene and paper platforms, using active layers from two-dimensional chalcogenides $SnSe(S)_2$ [8-10], nanostructured spinel ferrite $Zn_{(x)}Fe_{(1-x)2}O_4$ [11], carbon nanotubes graphene [12-15] and others. The flexible gas sensors on paper substrates are of particular interest as they are cheap, ecological and recyclable. Besides, the paper is lighter and exhibits a lower thermal expansion coefficient (2–16 ppm/C) compared to plastic substrates (20–80 ppm/C) [16]. Were reported flexible gas sensors on paper substrates designated to detect hydrogen sulfide [17, 18] ammonia [19-21] and nitrogen dioxide [22, 23]. Hydrogen sulfide gas sensors have been fabricated via printing of polyaniline (PANI)-metal salt ($CuCl_2$) composite on a paper substrate. The resistance of the sensor drops by several orders of magnitude within exposure to H_2S and behaves irreversibly due to gas induced transformation of metal salt into resulting metal sulfide [17]. Ammonia sensors were developed using carbon nanotubes (CNT) and graphite abraded on the fibers of cellulose [19], cellulose –TiO_2 – multiwall carbon nanotube hybrid nanocomposite [20] or multilayered graphene deposited on a filter paper [21]. In all cases the effect of NH_3 consists in reversible increasing of the resistance by gas adsorption, although the sensing parameters are rather different. Thin films based on single walled carbon nanotubes and graphene were also used for the development of flexible nitrogen dioxide gas sensors [21-24]. Single walled CNTs carbon nanotube ink on a cellulosic paper was shown to detect low (~ 0.25 ppm) concentrations of nitrogen dioxide at room temperature [22]. Exposing to NO_2 vapors diminishes the resistance of the sensor. The relative change of resistance nonlinearly decreases with NO_2 concentration increase. No significant change of the baseline was observed but the recovery time is in the range of 7 min. Graphene-based, flexible NO_2 sensors on paper substrates were reported to exhibit a fast (~ 50 s) response once exposed to 200 ppm NO_2 gas, but when the supply of NO_2 is stopped the current drops by ~ 20% at 360 s and slowly decreases thereafter during a long time without reaching the initial value [24]. The overall process of fabrication of such flexible chemical sensors on paper substrates appears to be rather sophisticated. Alongside, in the last decades, the remarkable performances for the NO_2 detection have been achieved via using the thin films based on elemental tellurium and its alloys (extended reviews [25-27]). Although such films exhibit high sensitivity toward nitrogen dioxide at room temperature, their morphology, electrical properties and gas sensing properties strongly depend on fabrication technology, material composition, temperature, geometry and post fabrication treatment [28-30]. The main methods of the fabrication of gas sensitive Te based films implies the thermal vacuum evaporation of either pure polycrystalline Te or its alloys, pulsed laser deposition [31], the rf sputtering [32] or

direct vapor phase process [33] in an argon atmosphere. The films usually were grown onto hard substrates of glass Pyrex, quartz, sintered or porous alumina [34], Si / SiO_2 wafers and others.

In all cases, the growing technology of Te thin films consisted of a number of physical, chemical and electrochemical procedures, including photolithography, electrochemical pickling, thermal vacuum evaporation etc.

The present work is devoted to avoiding the mentioned above complex and costly technology of tellurium based thin films fabrication, maintaining their good gas sensitivity and room temperature operating ability. A simple technology of Te-SnO_2 nanocomposite preparation was developed via thermal dissolution of polycrystalline tellurium powder in nitric acid, followed by Te reduction in the presence of tin chloride. We also demonstrated a facile method of fabrication of thin films based on Te-SnO_2 nanocomposite paste via its painting on standard paper substrates. Being supplied with contacting electrodes these films exhibit sensitivity to toxic and dangerous chemical gasses (NO_2, H_2S, and SO_2) at concentrations of 0.5 – 10 ppm or higher. The highest sensing performance was revealed with respect to nitrogen dioxide within a dynamic range 0.5 – 5.0 ppm with fast, reversible and reproducible response time ~30 s and recovery time ~ 150 s.

2. Materials and Methods

All reagents used in the experiments were of analytical grade and used as received without further purification. HNO_3 (55%) and H_2SO_4 (57 %) were purchased from Centro – Chem but $SnCl_2$ (99.95%) from Brenntag (both Poland). The procedure of the fabrication of Te-SnO_2 nanocomposites can conventionally be divided in four steps:

1) Obtaining the tellurous acid via reaction of the pure Te powder and dilute nitric acid.
2) Obtaining of a solution of the tin chloride $SnCl_2$ via dissolving the $SnCl_2$ salt into diluted sulfuric acid.
3) Obtaining a suspension of Te and SnO_2 via mixing the solutions of tin chloride $SnCl_2$ and tellurous acid.
4) Obtaining of Te-SnO_2 paste via filtering the obtained suspension and washing the filtrate under a vacuum.

In a typical experimental procedure, the tellurium powder (purity 99.999 %) was dissolved via the hydrothermal reaction in diluted nitric acid to form the tellurous acid (H_2TeO_3) accompanied with emission of the gaseous nitric oxides (NO, NO_2).

In parallel the aqua solution of tin chloride ($SnCl_2$) has been prepared via following procedure: 1.6 g of stannous chloride was placed in a container and a solution of 4 g of H_2SO_4 diluted in 150 g of distilled water was added with continuous stirring. As a result, a transparent aqua solution of $SnCl_2$ was obtained, which further has been added to aqua solution of the tellurous acid under a strong stirring. A chemical reaction occurred that resulted in formation of a black colored suspension. The resulting solid product was collected from solution through filtering and repeatedly washing with distilled water. Finally, a viscous paste has been obtained, which then was painted by Doctor Blade coating technique onto a paper substrate forming a large flexible film (Fig.1 a), which after drying at room temperature for 24 h had a thickness of around 35 μm.

Fabricated solid films were cut using scissors for further characterization and gas sensors fabrication. The gas sensor design is schematically shown in Fig. 1b.

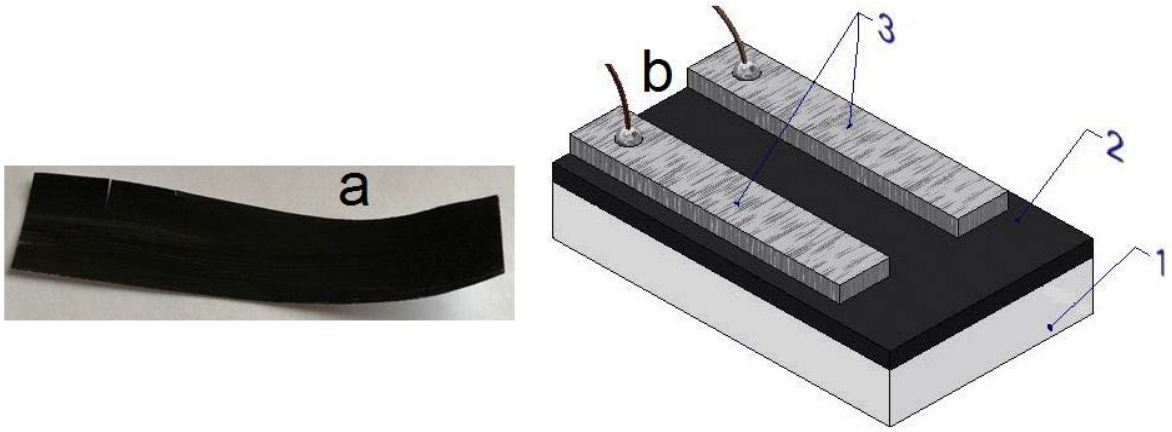


Figure 1. The view of flexible thin film based on Te-SnO_2 nanocomposite on paper substrate (a); schematic of the gas sensor design (b): 1- paper substrate; 2- active sensing Te-SnO_2 layer; 3 - metallic electrodes.

It consists of a paper substrate on which a layer of Te-SnO_2 nanocomposite is printed, above which two (or a series) of metallic (Ag, In, etc.) electrodes in a planar arrangement are deposited or painted. The sensors were encapsulated in sockets, and their contacts were thermally bonded to socket pins by means of copper wires.

Both the surface morphology and thickness of the dried films were investigated with VEGA TESCAN TS 5130 MM scanning electron microscopy (SEM). The film's elemental analysis was performed by the energy-dispersive X-ray spectroscopy (EDX) using INCA Energy 200 EDX equipment coupled with SEM. X-ray diffraction (XRD) was carried out to identify the structural phases in the grown films with a DRONE –YM1 diffractometer using Fe Kα radiations. The scattering angle was between 18 and 80 but the rotation velocity of the scintillation counter was 2 (or / and 4) angle degrees /min.

The description and detailed parameters of the gas sensing testing system, as well as of methodology of the current - voltage (I-U) and current – transient (I-t) characteristics measurement can be found in our recent publication [35]. Gaseous media with different concentration of NO_2 H_2S, NH_3, SO_2, ethanol (C_2H_5OH), acetone ($CH3)_2CO$ and toluene C_7H_8 were obtained by using the calibrated permeation or diffusion tubes (Vici Metronics, USA), which were introduced into the experimental set-up described elsewhere [36, 37].

The sensor sensitivity was defined as the relative resistance variation expressed in percent [35]:

$$S = 100\left(\left|R_a - R_g\right|\right)/R_x \quad (1)$$

where: R_a and R_g are the electrical resistances of the sensor in the air and in the presence of target gas respectively and R_x is the highest from either R_a or R_g.

The response and recovery time were estimated as the times taken to reach or to lose the 90% of steady-state values of the current respectively.

3. Results

3.1 Morphology, elemental composition and structural analysis

Figure 2 shows the typical SEM image of films fabricated in this study. The SEM reveals that Te-SnO_2 films consist of fluffy structures of tiny agglomerates of the nanodimensional irregular blocks of about 100 nm.

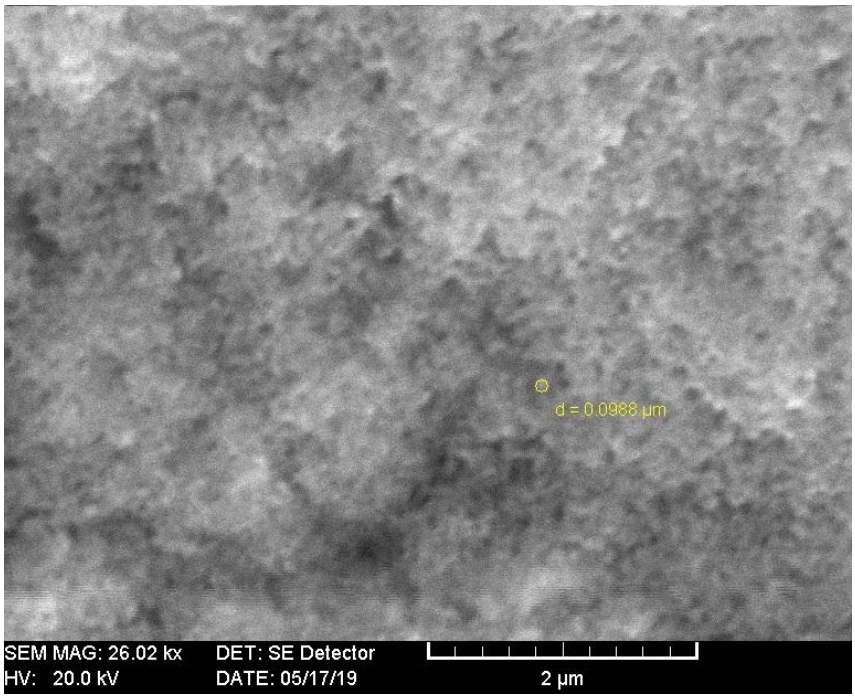
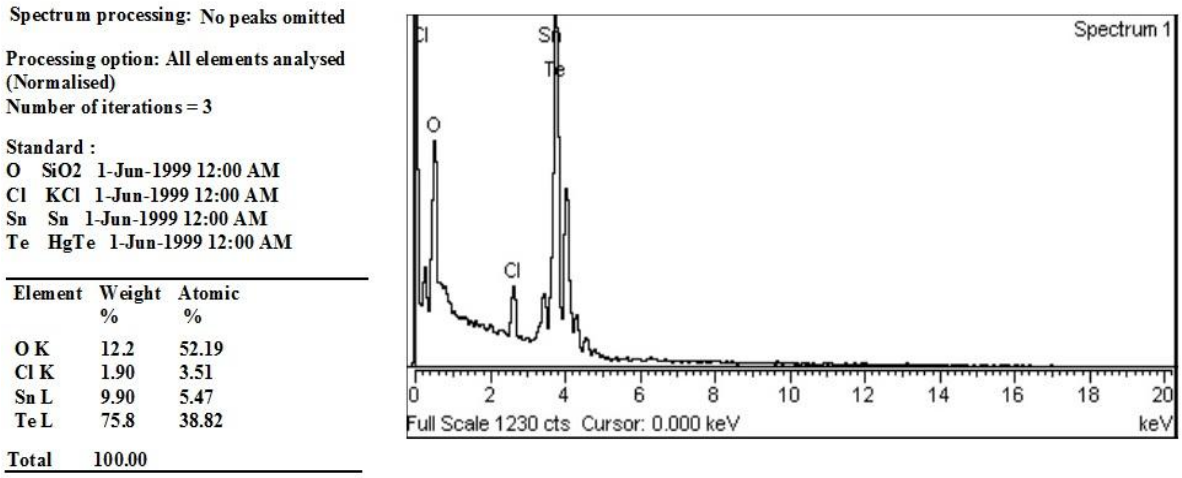


Figure 2. Typical SEM image of Te-SnO_2 based film on paper substrate.

The nanodimensional blocks were identified by energy - dispersive X-ray spectroscopy (EDX) as a composite consisting of several chemical elements. Results of EDX study of the fabricated nanocomposites are depicted in Fig. 3. As can be seen the EDX spectrum revealed the presence of about 39 at. % Te, 52 at. % O, 5.5 at. % Sn and 3.5 at % remnants of Cl.

Compositional and phase state analysis of the fabricated nanocomposite thin films have been examined by XRD, which appeared to be consistent with EDX analysis. Figure 4 displays a typical XRD pattern of the sample obtained via above-described technology along with expected location of the diffraction peaks from standard data for pure Sn [38] and TeO_2 [39] shown by colored dotted lines.



Spectrum processing: No peaks omitted

Processing option: All elements analysed (Normalised)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
Sn Sn 1-Jun-1999 12:00 AM
Te HgTe 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
O K	12.2	52.19
Cl K	1.90	3.51
Sn L	9.90	5.47
Te L	75.8	38.82
Total	100.00	

Figure 3. EDX analysis of Te-SnO_2 based film.

As it is seen, all of the diffraction peaks in this pattern can be readily indexed to the hexagonal phase of tellurium with lattice constants of a = 4.46 Å and c =5.94 Å [40, 41] (JCPDS Card No.: 36-1452), along with polycrystalline tin dioxide, with predominant orientation of the crystals (110) and (002) [42, 43] (JCPDS 41-1445).

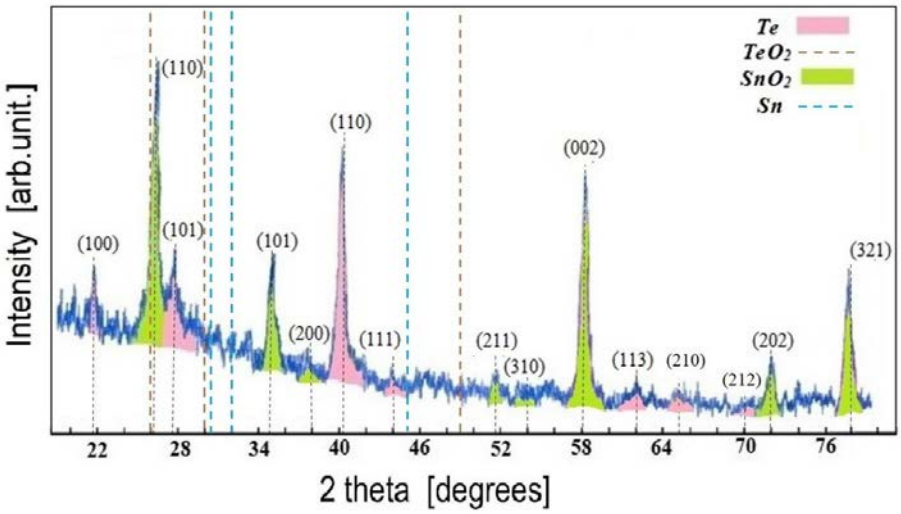


Figure 4. X-ray diffraction pattern of Te-SnO_2 nanocomposite obtained via hydrothermal reaction of tellurium powder, nitric acid and tin chloride.

3.2 Electrical conductivity at interaction with NO_2

3.2.1 Current – voltage characteristics. Effect of bending

Fig. 5 a shows the typical current /voltage characteristic of Ag/Te-SnO_2/Ag functional structures, which was measured at room temperature in ambient air and 1.0 ppm NO_2 gas, respectively. The linearly increased current, independently of the direction of the bias voltage, reflect the absence of depletion regions at the Ag contacts, i.e., they are ohmic in the entire range of applied bias voltage.

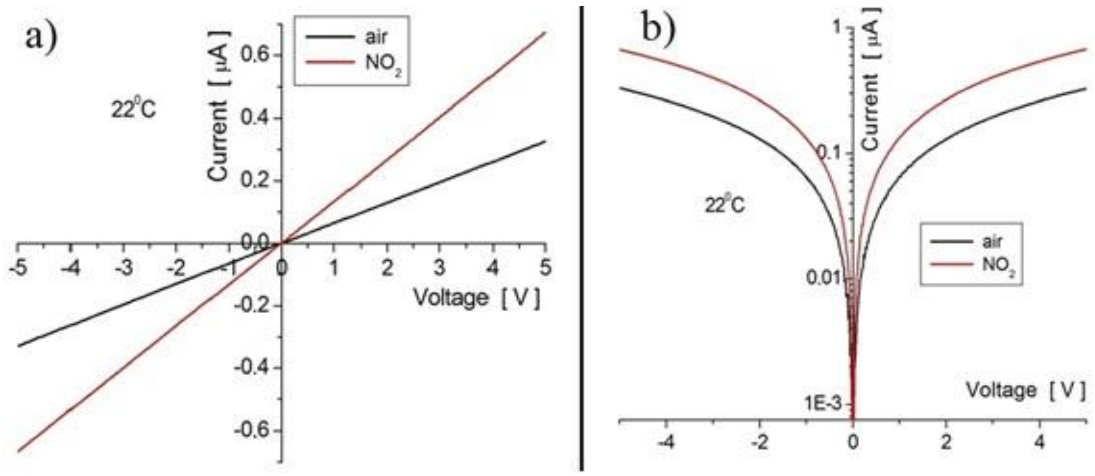


Figure 5. Current / voltage characteristic of Ag / Te-SnO_2 /Ag functional structure in air and in the presence of 1.0 ppm of NO_2 in linear (a) and semi-logarithmic scale (b).

The last is clearly confirmed by representation of I-U characteristic in a semi logarithmic scale (Fig.5 b). The influence of NO_2 gas consists in increasing of the current flow through the specimen, boosting the I-U characteristic slope. To study the effect of bending (stress) on electrical conductivity of Ag / Te-SnO_2 / Ag functional structure, its resistance has successively been measured for many times before and after bending by ~ 90 degrees. Fig. 6 shows the electrical resistance evolution of both straight and bent Ag / Te-SnO_2 / Ag functional structure grown on paper substrate in function of number of bending by ~ 90 degrees.

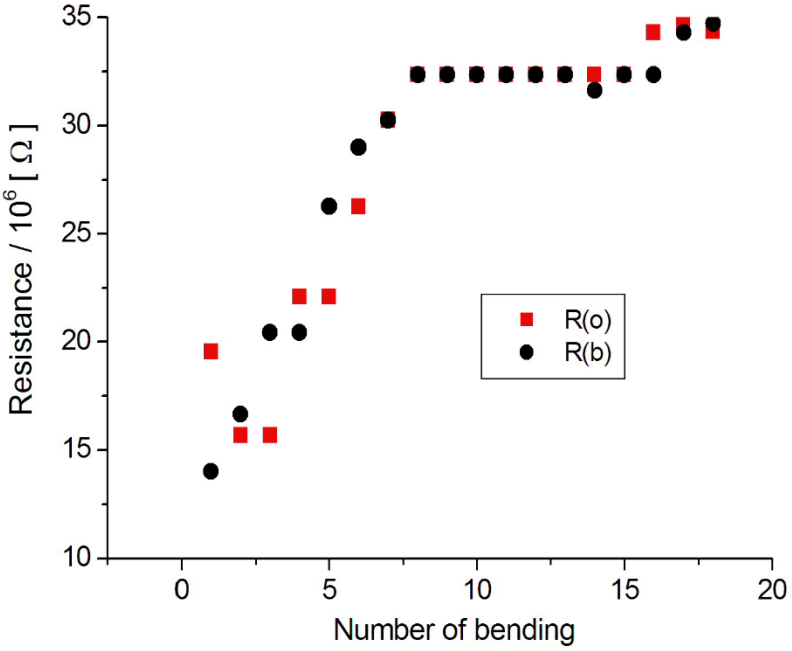


Figure 6. Evolution of electrical resistance of the straight {R(o)} and bent by 90 degrees {R(b)} Ag / Te-SnO_2 /Ag functional structure grown on paper substrate dependent of number of bending.

As can be seen, initially the resistance of both straight and bent devices increases but after approximately one dozen of bends, it tends to saturate. Moreover, for each number of bending the resistance of the straight and bended device does not differ much that confirms its flexibility.

3.2.2 Transient characteristics

Figure 7 shows the dynamic response of a Te – SnO_2 sample towards different concentrations (0.5 - 5.0 ppm) of nitrogen dioxide at room temperature and constant bias voltage, for gas pulses of similar or falling concentration (Fig 7a) as well as at increasing concentration (Fig. 7 b).

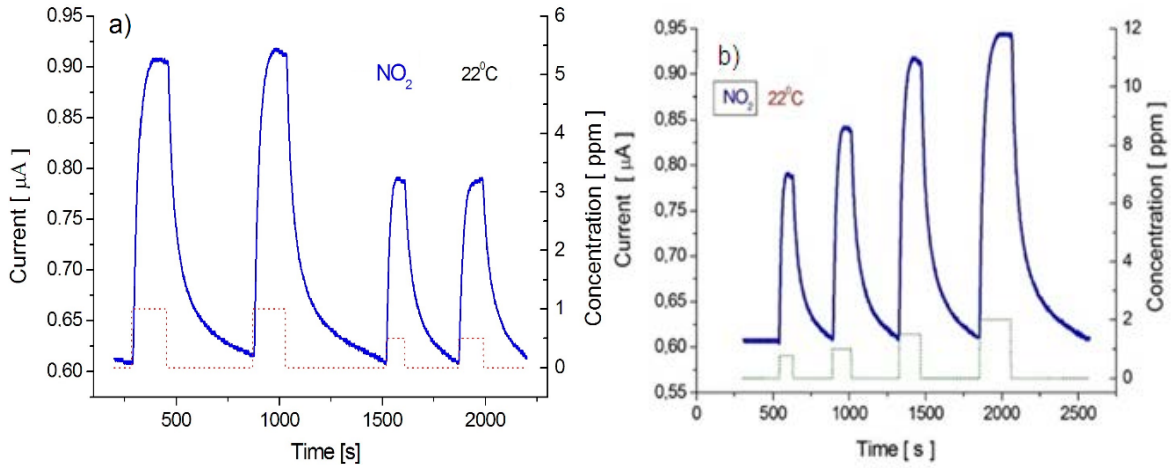


Figure 7. Transient characteristics of gas - induced current by exposure to different concentrations of NO_2 for: a) gas pulses of similar or falling concentration; b) increasing concentration. Dotted lines of the bottom show the schedule of the gas pulses.

It is seen that the sensor shows the reversible and reproducible response following the schedule of the gas application (dotted line on the bottom), without noticeable drift of the baseline. The response time is about 30 s but the recovery time is about 150 s.

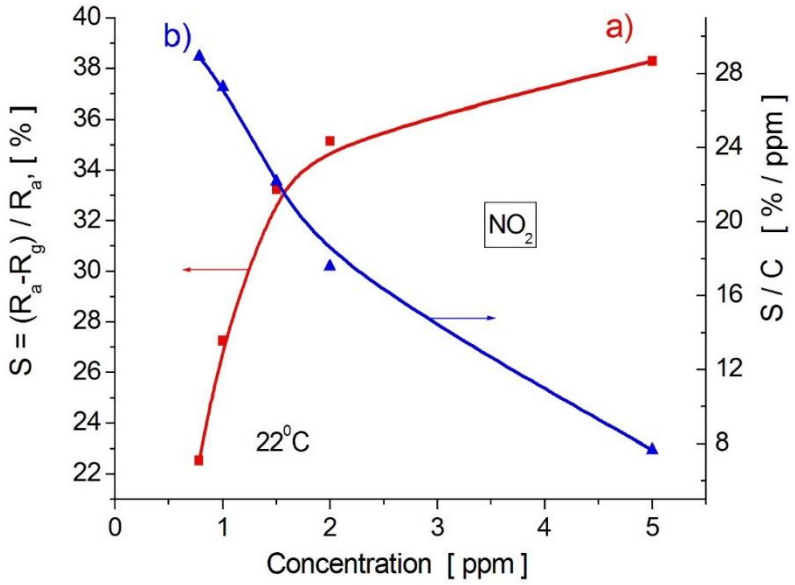


Figure 8. Sensitivity (a) and sensitivity per unit concentration (b) versus NO_2 concentration (calibration curve) at room temperature. C – is gas concentration in ppm.

Fig. 8a shows the calibration curve, that is the relative resistance variation versus gas concentrations. This curve is non-linear: the sensitivity sharply increases but tends to saturate at high NO_2 concentrations**.** As far as the sensitivity per ppm unit is concerned (Fig. 8 b), it oppositely sharply increases at low gas concentrations. Thus, the sensor is able to effectively to detect the low concentrations of NO_2, including the sub ppm range.

3.2.3 Effect of other gases and humidity

The selectivity, i.e. the effect of other gases towards Te – SnO_2 based gas sensitive device has been assessed via direct measurement of the relative variation of the resistance under exposure to H_2S, NH_3, SO_2, ethanol (C_2H_5OH), acetone $(CH_3)_2CO$ and toluene C_7H_8. It was established that ethanol, acetone, toluene and ammonia do not interact with these films as no response signal has been detected. The comparison of sensitivities to the other tested gases can be only qualitative because of very different dynamic ranges. Figure 9 shows the response of Te – SnO_2 based sensor to rectangular pulses of NO_2, H_2S and SO_2. As the ambience usually contains water vapor, we have checked the interfering effect of water vapors with NO_2 sensing at room temperature.

Fig.10 shows the sensor response toward rectangular pulses of humid air with 58% RH (shown by arrows) and 1.0 ppm NO_2 successively applied. The schedule of the NO_2 pulse application is shown by dotted line. It is seen that the effect of both H_2O and NO_2 vapors is to increase the current. Such behavior of the Te –SnO_2 based gas sensitive thin films cordially differs from behavior of the pure Te based ones, in which it was definitely pointed out that the humidification of ambiance diminishes the current flow through the sample [25]. Comparison of Figs. 7 and 10 shows that increasing RH from 20 to 58 % shifts the baseline, but the sensitivity remains nearly the same, around 30% toward 1.0 ppm NO_2.

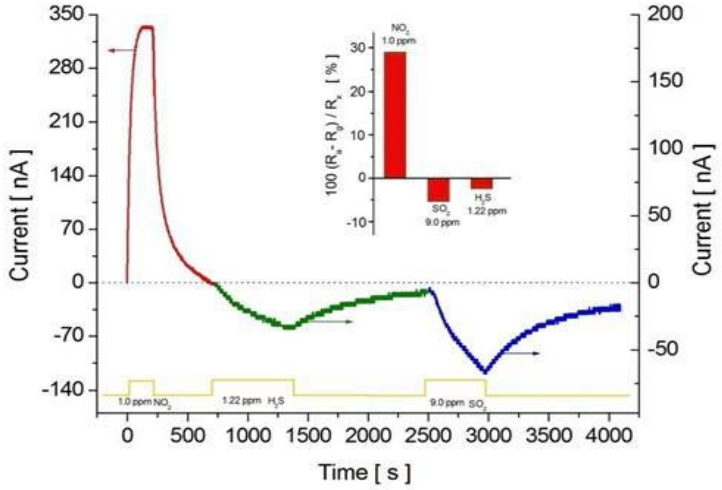


Figure 9. Transient response of a film based on Te – SnO_2 nanocomposite to rectangular pulses of NO_2, H_2S and SO_2 of different concentration and duration, shown by dotted line on the bottom. Inset shows the relative resistance change of sensor under exposure to different gases of indicated concentrations at 22 °C.

Nevertheless, it is evident that the effect of humidity is quite large and requires finding the reason, explanation and ways for its avoidance. This needs additional investigations, which are outside of the present study but are in progress.

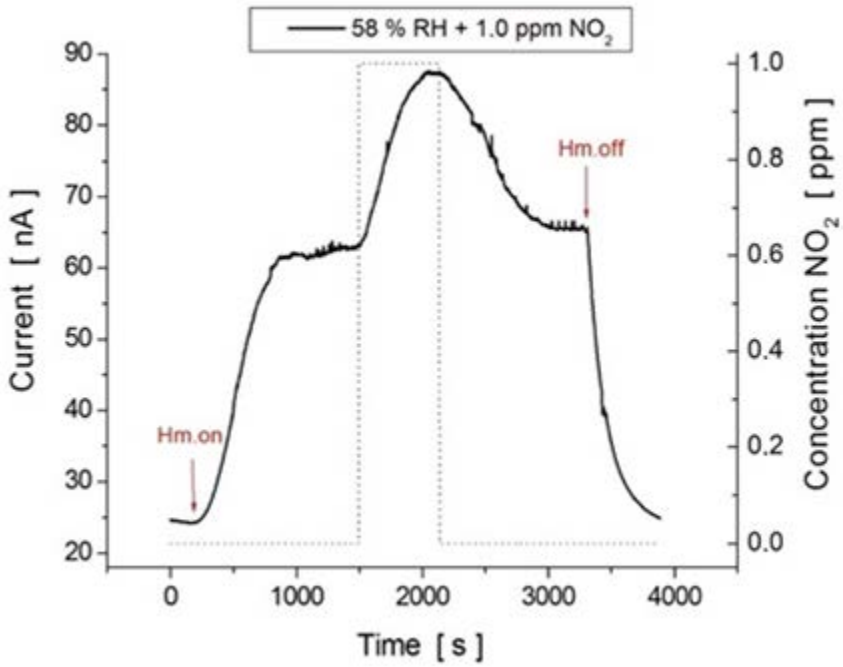


Figure 10. Effect of water vapor on the Te – SnO_2 based film by NO_2 detection at 22 °C.

4. Discussion

The chemical reactions for the synthesis of tellurium-based nanocomposites can be formulated as following: During the hydrothermal reaction, initially, tellurium powder was dissolved in dilute nitric acid to form the tellurous acid (H_2TeO_3) accompanied with emission of the gaseous nitric oxide:

$$Te + 4HNO_3 + H_2O \rightleftharpoons 3H_2TeO_3 + 4NO \quad (2)$$

Alongside, the synthesis of tellurium dioxide occurs via the reactions:

$$2Te + 9HNO_3 \rightleftharpoons Te_2O_3(OH)NO_3 + 8NO_2 + 4H_2O \quad (3)$$

$$Te_2O_3(OH)NO_3 \rightleftharpoons 2TeO_2 + HNO_3 \quad (4)$$

When the aqua solution of $SnCl_2$ has been added to the solution obtained via reactions (2-4) under a continuous stirring, the tin chloride acts as a reducing agent and the followed reaction occurs:

$$H_2TeO_3 + 2SnCl_2 \longrightarrow SnO_2 + SnCl_4 + Te \downarrow + H_2O \quad (5)$$

Thus, the resulting solid products, collected via filtering of black colored resulted suspension followed by multiple washing in distillate water, have to contain pure tellurium, tin oxide and perhaps some leftovers of $SnCl_4$. Meanwhile the XRD analysis of fabricated thin films based on synthesized via above shown reactions black solid paste (Fig.4), has confirmed the presence of hexagonal phase of tellurium alongside with polycrystalline tin dioxide but did not reveal the remainders of $SnCl_4$. Perhaps, the last is due to low amount of $SnCl_4$ in the synthesized nanocomposite that is consistent with EDX analysis. The elemental analysis of fabricated thin films performed via EDX spectroscopy (Fig.3) has identified the presence of only about 3.5 at. % remnants of Cl, alongside with about 39 at. % of the nanostructured Te.

Thus, the compositional and structural analyses of synthetized nanocomposite in conjunction with above shown experimental results related to gas sensing characterization of developed films, provides evidence that the gas sensitivity of films in question is due solely to the tellurium component that change its conductivity proportional to surface coverage [35] given by classical Langmuir's theory of adsorption [44]. The Langmuir's kinetics can be expressed in the form [45]:

$$\frac{d\theta}{dt} = \alpha C(1-\theta) - \beta\theta \quad (6)$$

where ϑ is the surface coverage that is a quantity proportional to surface concentration of adsorbed particles, C is the NO_2 concentration, α and β is the direct and inverse reaction constant respectively. According to this equation, while the surface coverage and the desorption are small, $d\theta/dt \sim (1-\theta)$. In such case, as the gas induced current in Te film is caused by releasing of majority carriers (holes) at chemical adsorption of gaseous (NO_2) species [46], the time derivative of this current, under constant bias voltage, has proportionally to decrease with ΔIincrease.

Fig. 11 shows the response current from data of Fig.7 (b) plotted, as dI/dt, a function of ΔI for several concentrations of the NO_2 applied at 22 ^{0}C. The data in this picture were averaged by 5-point smoothing. It is seen that in principle the response toward NO_2 of Te–SnO_2 based films is consistent with the Langmuir's model of surface coverage. The time derivative of the gas induced current linearly diminishes with change current increase, at that these derivative increases with gas concentration increase and even the slope change of line $dI/dt = f(C)$can be observed.

Finally, it is worth noting that the SnO_2 nanoparticles of nanocomposite in question were not observed to participate in the gas sensing process, that obviously is caused by sensor low operation temperature (~ 22 ˚C). Tin oxide becomes gas (NO_2) sensitive only at operation temperature higher than 200 ˚C [47, 48]. At that, SnO_2 does not disturb the gas sensing properties of Te nanoparticles from nanocomposite but can be the reason for large influence of the humidity.

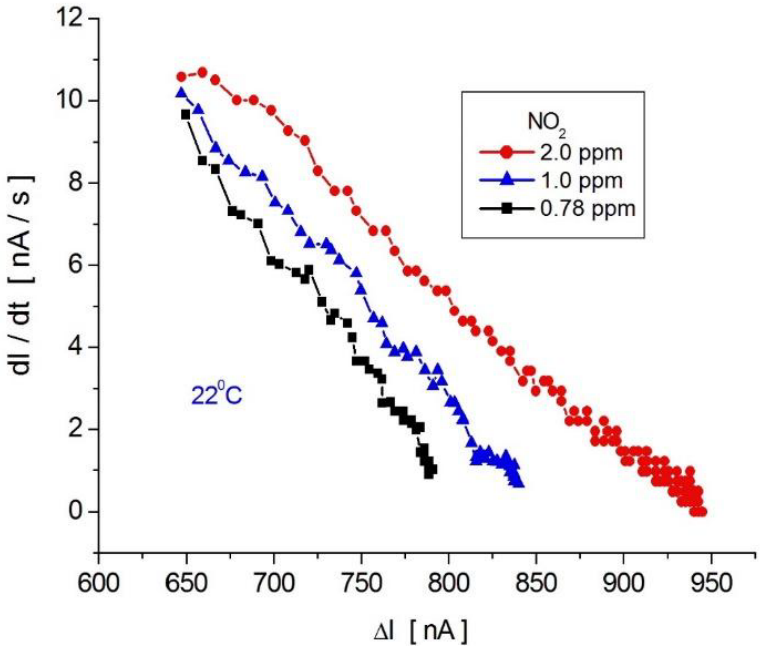


Figure 11. The Langmuir plot of the sensor response toward a rectangular pulse of NO_2 drawn using the data shown in Fig.6 for the Ag / Te - SnO_2 / Ag device.

5. Conclusions

Nano-composites of Te-SnO_2 were synthesized via a simple thermal dissolution of polycrystalline tellurium powder in nitric acid, followed by its chemical reduction in the presence of tin chloride solution. Showed by SEM, EDX and XRD analyses the composites consists of nanoparticles of around 100 nanometers, comprising about 40 at. % Te and 6.0 at. % of tin oxide. The synthesized nanocomposites can be used for fabrication of thin flexible gas sensors via screen printing technology, onto paper sheets. Such sensors exhibit selective and rapid (~30 s) response to nitrogen dioxide and operate at room temperature.

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Conflicts of Interest. The authors declare no conflict of interest.

References

1. Siegel, A. C.; Phillips, S.T.; Dickey, M. D.; Lu, N.; Suo, Z.; Whitesides, G. M. Foldable Printed Circuit Boards on Paper Substrates. *Advanced Functional Materials* 2010, 20, 28–35., https://doi.org/ 10.1002/ adfm.200901363.
2. Kurra, N.; Dutta, D.; Kulkarni, G.U. Field Effect Transistors and RC Filters from Pencil-Trace on Paper. *Physical Chemistry Chemical Physics* 2013; 15 , 8367–8372., https://doi.org/10.1039/C3CP50675D.
3. Zhang, Y.; Ge, L.; Li, M.; Yan, M.; Yu, J.; Song, X.; Cao, B. Flexible Paper-Based ZnO Nanorod Light-Emitting Diodes Induced Multiplexed Photoelectrochemical Immunoassay. *Chem. Commun* 2014; 50, 1417–1419. https://doi.org/10.1039/C3CC48421A.
4. Zheng, Z.; Zhang, T.; Yao, J.; Zhang, Y.; Xu, J.; Yang, G. Flexible, Transparent and Ultra-Broadband Photodetector Based on Large-Area WSe_2 Film for Wearable Devices. *Nanotechnology* 2016; 27, 225501. https://doi.org/10.1088/0957-4484/27/22/225501
5. Tannarana, M.; Solanki, G. K.; Bhakhar, S. A.; Patel, K. D.; Pathak, V. M.; Pataniya, P. M. 2D-$SnSe_2$ Nanosheet Functionalized Piezo-resistive Flexible Sensor for Pressure and Human Breath Monitoring. *ACS Sustainable Chem. Eng.* 2020, 8, 7741−7749. https://doi.org/10.1021/acssuschemeng.0c01827.
6. Alrammouz, R.; Podlecki, J.; Abboud, P.; Sorli, B.; Habchi, R. A review on flexible gas sensors: From materials to devices. *Sensors and Actuators A* 2018; 284, 209-231. https://doi.org/10.1016/j.sna.2018.10.036.

7. Wang, T.; Guo, Y.; Wan, P.; Zhang, H.; Chen, X.; Sun, X. Flexible Transparent Electronic Gas Sensors, *Small-Wiley Online Library* 2016, 12, 28, 3748-3756. https://doi.org/10.1002/smll.201601049.
8. Chen, M.; Li, Z.; Li, W.; Shan, C.; Li, W.; Li, K.; Gu, G.; Feng, Y.; Zhong, G.; Wei, L.; Yang, C. Large-Scale Synthesis of Single-Crystalline Self-Standing $SnSe_2$ Nanoplate Arrays for Wearable Gas Sensors. *Nanotechnology* 2018; 29, 455501. https://doi.org// 10.1088/1361-6528/aade32.
9. Pawar, M.; Kadam, S.; Late, D. J. High-Performance Sensing Behavior Using Electronic Ink of 2D $SnSe_2$ Nanosheets. *Chemistry Select* 2017, 2, 4068–4075. https://doi.org/10.1002/slct.201700261.
10. Pyeon, J. J.; Baek, I-H.; Song, Y. G.; Kim, G. S.; Cho, A-J.; Lee, G-Y.; Han, J. H.; Chung, T-M.; Hwang, C. S.; Kang, C-Y.; Kim, S. K. Highly sensitive flexible NO_2 sensor composed of vertically aligned 2D SnS_2 operating at room temperature. *Journal of Materials Chemistry C* 2020, 34. https://doi.org/10.1039/D0TC02242J
11. Goutham, S.; Sadasivuni, K. K.; Kumarc, D. S.; Rao, K.V. Flexible ultra-sensitive and resistive NO_2 gas sensor based on nanostructured $Zn(x)Fe(1-x)2O_4$, RSC Adv. 2018, 8, 3243–3249. https://doi.org/10.1039/c7ra10478b.
12. Bohao, L.; Liu, X.; Yuan, Z.; Tai, H. A flexible NO_2 gas sensor based on polypyrrole/nitrogen-doped multiwall carbon nanotube operating at room temperature. *Sensors and Actuators B* 2019, 295, 86-92, https://doi.org/10.1016/j.snb.2019.05.065
13. Agarwal, P. B.; Alam, B.; Sharma, D. S.; Sharma, S.; Agarwal, A. Flexible NO_2 gas sensor based on single-walled carbon nanotubes on polytetrafluoroethylene substrates. *Flexible and Printed Electronics* 2018, 3, 035001. https://doi.org/10.1088/2058-8585/aacc8f.
14. Jeong, H. Y.; Lee, D-S.; Choi, H. K.; Lee, D. H.; Kim, J-E.; Lee, J. Y.; Lee, W. J.; Kim, S. O.; Choi, S.-Y. Flexible room-temperature NO_2 gas sensors based on carbon nanotubes/reduced grapheme hybrid films. *Applied Physics Letters* 2010, 96, 213105. https://doi.org/10.1063/1.3432446.
15. Lee, C.; Ahn, J.; Lee, K. B.; Kim, D.; Kim, J. Graphene-based flexible NO_2 chemical sensors. *Thin Solid Films* 2012, 520, 5459-5462. https://doi.org/10.1016/j.tsf.2012.03.095.
16. Alrammouza, R.; Podlecki, J.; Abboud, P.; Sorli, B.; Habchi, R. A review on flexible gas sensors: From materials to devices. *Sensors and Actuators A,* 2018, 284, 209–231. https://doi.org/10.1016/j.sna.2018.10.036
17. Sarfraz, J.; Maattanen, A.; Ihalainen, P.; Keppeler, M.; Linden, M.; Peltonen, J. Printed copper acetate based H_2S sensor on paper substrate. *Sensors and Actuators* B 2012, 173, 868–873. http://dx.doi.org/10.1016/j.snb.2012.08.008
18. Sarfraz, J.; Ihalainen, P.; Määttänen, A.; Peltonen, J.; Lindén, M. Printed hydrogen sulfide gas sensor on paper substrate based on polyaniline composite. *Thin Solid Films* 2013, 534, 621–628. http://dx.doi.org/10.1016/j.tsf.2013.02.055
19. Mirica, K. A.; Weis, J. G.; Schnorr, J. M.; Esser, B.; Swager ,T. M. *Mechanical Drawing of Gas Sensors on Paper*. Angewandte Chemie Int. Edition 2012, 51, 10740–10745. https://doi.org/10.1002/anie.201206069
20. Mun, S.; Chen, Y.; Kim, J.; Cellulose–titanium dioxide–multiwalled carbon nanotube hybrid nanocomposite and its ammonia gas sensing properties at room temperature. *Sensors and Actuators B* 2012, 171– 172, 1186– 1191, http://dx.doi.org/10.1016/j.snb.2012.06.066
21. Ghosh, R.; Singh, A.; Santra, S.; Ray, S. K.; Chandra, A.; Guha, P. K. Highly sensitive large-area multi-layered graphene-based flexible ammonia sensor. *Sensors and Actuators B* 2014, 205, 67–73. http://dx.doi.org/10.1016/j.snb.2014.08.044
22. Ammu, S.; Dua, V.; Agnihotra, S. R.; Surwade, S. P.; Phulgirkar, A.; Patel, S.; Manohar, S. K. Flexible, All-Organic Chemiresistor for Detecting Chemically Aggressive Vapors. *Journal of the American Chemical Society* 2012, 134, 4553–4556. http://dx.doi.org/10.1021/ja300420t |
23. Hassinen, J.; Kauppila, J.; Leiro,J.; Määttänen, A.; Ihalainen, P.; Peltonen, J.; Lukkari, J. Low-cost reduced graphene oxide-based conductometric nitrogen dioxide-sensitive sensor on paper. *Analytical and Bioanalytical Chemistry* 2013, 405, 3611-3617. http://dx.doi.org/10.1007/s00216-013-6805-5.
24. Yang, G.; Lee, C.; Kim, J.; Renb, F.; Pearton, S. J. Flexible graphene-based chemical sensors on paper substrates. *Physical Chemistry Chemical Physics* 2013, 15, 1798. http://dx.doi.org/: 10.1039/c2cp43717a.
25. Tsiulyanu, D. Tellurium thin films in sensor technology. Nanotechnological Basis for Advanced Sensors, Springer 2011, 363-380.
26. Petcov, P.; Tsiulyanu, D.; Kulisch, W.; Popov, C. *Nanoscience Advances in CBRN Agents Detection, Information and Energy Security: An Intoduction*. Springer 2015, 3-13. ISBN: 978-94-017-9697-2
27. He, Z.; Yang, Y.; Liu, J-W.; Yu, S-H. Emerging tellurium nanostructures: controllable synthesis and their applications. *Chemical Society Reviews* 2017, 46, 2732—2753. https://doi.org/10.1039/c7cs00013h.

28. Tsiulyanu, D.; Marian, S.; Miron, V.; Liess, H - D. High sensitive tellurium based NO_2 gas sensor. *Sensors and Actuators B* 2001, 73, 35 – 39. https://doi.org/10.1016/s0925-4005(00)00659-6.
29. Tsiulyanu, D.; Tsiulyanu, A.; Liess, H-D.; Eisele, I. Characterization of tellurium-based films for NO_2 detection. *Thin Solid Films* 2005, 485, 252 -256. https://doi.org/10.1016/j.tsf.2005.03.045.
30. Wüsten, J.; Potje-Kamloth, K. Chalcogenides for thin film NO sensors. *Sensors and Actuators B* 2010, 145, 216–224. https://doi.org/10.1016/j.snb.2009.11.058
31. Popescu, M.; Velea, A.; Sava, F.; Lorinczi, A.; Tomescu, A.; Simion, C.; Matei, E.; Soco, G.; Mihailescu, I. N.; Andonie, A.; Stamatin, I. Structure and properties of silver doped $SnSe_2$ and $Ge_2Sb_2Te_5$ thin films prepared by pulsed laser deposition. *Physica Status Solidi A* 2010, 207, 516–520. https://doi.org/10.1002/pssa.200982900
32. Siciliano, T.; Giulio, M. Di.; Tepore, M.; Filippo, E.; Micocci, G.; Tepore, A. Tellurium sputtered thin films as NO_2 gas sensors. *Sensors and Actuators B* 2008, 135, 250-256. https://doi.org/10.1016/j.snb.2008.08.018.
33. Her, Y.C.; Huang, S.L. Growth mechanism of Te nanotubes by a direct vapor phase process and their room temperature CO and NO_2 sensing properties. *Nanotechnology* 2013, 24, 215603, 9. https://doi.org/10.1088/0957-4484/24/21/215603.
34. Tsiulyanu, D. Gas-sensing features of nanostructured tellurium thin films. *Beilstein J. Nanotechnology* 2020, 11, 1010–1018. https://doi.org/10.3762/bjnano.11.85.
35. Tsiulyanu, D. Conductometric NO_2 gas sensor based on nanolayered amorphous tellurium for room temperature operation. *Sensors and Actuators B* 2022, 352, https://doi.org/10.1016/j.snb.2021.131034
36. Cabala, R.; Meister, V.; Potje-Kamloth, K.; Effect of competitive doping on sensing properties of polypyrrole. *Journal of the Chemical Society, Faraday Transactions* 1997, 9, 131-137. https://doi.org/10.1039/A604780G
37. Tsiulyanu, D.; Ciobanu, M. Impact of adsorbed gases on the transport mechanisms in $Ge_8As_2Te_{13}S_3$ amorphous films. *Glass Physics and Chemistry* 2019, 45, 53–59. https://doi.org/10.1134/S1087659619010140.
38. Hu, R.; Sun, W.; Zeng, M.; Zhu, M. Dispersing SnO_2 nanocrystals in amorphous carbon as a cyclic durable anode material for lithium-ion batteries. *Journal of Energy Chemistry* 2014, 23, 338–345. https://doi.org/10.1016/S2095-4956(14)60156-X.
39. Shen, Y.; Fan, A.; Wei, D.; Gao, S.; Liu, W.; Hana, C.; Cuia, B. A low-temperature n-propanol gas sensor based on TeO_2 nanowires as the sensing layer. *RSC Advances* 2015, 5, 29126–29130. https:// doi.org/10.1039/C5RA00867K.
40. Liang, F.; Qian, H. Synthesis of tellurium nanowires and their transport property. M*aterials Chemistry and Physics* 2009, 113, 523–26.
41. Wang, S.; Wen, H.; Guan, W.; Zhang, L.; Zhang, D.; Huang, S.; Wang, J. Fabricating two-dimensional nanostructured tellurium thin films via pyrolyzing a single-source molecular precursor. *Thin Solid Films* 2010, 518, 4215–20. https://doi.org/10.1016/j.tsf.2009.12.081
42. Bhagwat, A. D.; Sawant, S. S.; Ankamwar, B. G.; Mahajan, C. M. Synthesis of Nanostructured Tin Oxide (SnO_2) Powders and Thin Films Prepared by Sol-Gel Method. *Journal of Nano-and Electronic Physics* 2015, 7, 4, 04037.
43. Li, I.; Chen, C.; Li, J.; Li, S.; Dong, C. Synthesis of tin-glycerate and its conversion into SnO_2 spheres for highly sensitive low-ppm-level acetone detection. *Journal of Materials Science: Materials in Electronics* 2020, 31, 16539–16547. https://doi.org/10.1007/s10854-020-04208-7.
44. Volkenstein, T. *Electronic Processes on Semiconductor Surfaces During Chemosorption.* A Division of Plenum Publishing Corporation, Consultants Bureau, New York, 1987, 427pp.
45. Filippini, D.; Rosch, M.; Aragon, R.; Weimar, U. Field-effect NO_2 sensors with group 1B metal gates. *Sensors Actuators B* 2001, 81, 83–87. https://doi.org/10.1016/S0925-4005(01)00935-2.
46. Tsiulyanu, D.; Ciobanu, M.; Mocreac, O. *Impedance Characterization of Gas Sensitive Chalcogenide Films*. Springer 2017, 317-332, https://doi.org/10.1007/978-94-024-1298-7_31.
47. Gopel, W.; Schierbaum, K.-D.; SnO_2 sensors: current status and future prospects. *Sensors and Actuators B* 1995, 26–27, 1–12. https://doi.org/10.1016/0925-4005(94)01546-T
48. Shi, L.; Hasegawa, Y.; Katsube, T.; Onoue, K.; Nakamura, K.; Highly sensitive NO_2 gas sensor fabricated with RF induction plasma deposition method. *Sensors and Actuators B* 2004, 99, 361-366. https://doi.org/10.1016/j.snb.2003.12.003.

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APPLICATION OF PRIVACY-PRESERVING DATA PUBLISHING IN TERTIARY INSTITUTIONS OF KEBBI STATE USING GENERALIZATION AND SUPPRESSION

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Abstract. The research was conducted in the field of publishing data to preserve confidentiality. Several educational datasets have been used to address privacy and utility. The sample questionnaires served to investigate the level of privacy awareness and enforcement in the records of students in tertiary institutions in Kebbi State, Nigeria. The benchmark datasets were obtained from Kebbi State Polytechnic Dakin-gari. K-anonymity and l-diversity models were used with *k* configurations and suppression limits of 10 and 50% in the ARX 3.9.0 de-anonymization environment. The work evaluates data privacy, quality, and execution time for each k value and suppressions limit. Experimental results demonstrate that the higher the suppression the more balanced exists between privacy and utility. It was observed that suppression of 50% provides less anonymization time irrespective of *k* compared to *k* values in suppression = 10%. This was proved to be due to less time it takes anonymization to be completed Also, from respondents, 92% of students' records were kept permanently in plain and, issued to third parties like that—with no privacy guarantee. This poses privacy threats to datasets.

Keywords: *Arx de-anonymization tool, Dakin-gari, k-anonymity, privacy, quality, utility.*

Rezumat. Cercetarea a fost efectuată în domeniul publicării datelor pentru păstrarea confidențialității. Au fost folosite câteva seturi de date educaționale pentru a aborda confidențialitatea și utilitatea. Chestionarele eșantion au servit pentru a investiga gradul de conștientizare a confidențialității și aplicarea acesteia în dosarele studenților din instituțiile terțiare din statul Kebbi, Nigeria. Seturile de date care au servit drept reper au fost obținute de la Kebbi State Polytechnic Dakin-gari. Modelele de K-anonimitate și l-diversitate au fost utilizate cu configurații *k* și limite de suprimare de 10 și 50% în mediul de de-anonimizare ARX 3.9.0. Lucrarea evaluează confidențialitatea datelor, calitatea și timpul de execuție pentru fiecare valoare k și limită de suprimare. Rezultatele experimentale demonstrează, că o suprimare este mai mare induce echilibru între intimitate și utilitate. S-a observat, că suprimarea de 50% oferă mai puțin timp de anonimizare indiferent de k comparativ cu valorile

k în suprimare = 10%. Acest lucru se datorează faptului că anonimizarea durează mai puțin pentru a fi finalizată. De asemenea, din partea respondenților, 92% din dosarele studenților au fost păstrate în mod permanent neconfidențial, fiind eliberate astfel unor terți, fără garanție de confidențialitate. Acest lucru reprezintă amenințări de confidențialitate a seturilor de date.

Cuvinte cheie: *instrument de dezanonimizare, Arx, Dakin-gari, k-anonimitate, confidențialitate, calitate, utilitate.*

1. Introduction

In Computer Science & Information Technology, privacy could be seen as control over the disclosure of Personally Identifiable Information (PII), or quasi-identifiers (QI). This PII or QI helps in establishing a user profile when combined with a publically available dataset that leads to personality being watched, profiled, and make unwanted revelations that resulted in physical and economic harm. Privacy ought to be guaranteed when sensitive biomedical data is shared for any reason [1], though the most common datasets use are biomedical and demographic data [2]. Notwithstanding, that did not limit other datasets to be used as individuals and industries carry out research from multiple and disparate domains day in and day out where attributes of individual should be protected using industry acceptable techniques. With the current growth of information technologies, various organizations such as hospitals, financial houses, educational institutions are constantly collecting information about individuals and keep it in their databases for future use. These volumes of data increase exponentially [3] as a result of this, privacy becomes the subject of hot debate as it requires models, privacy risks for protecting it as well as providing utility [2]. On this note, this work intends to explore the available resources to apply privacy to student datasets before sharing them with researchers. To protect privacy, recommended data transformation models should be used in the process. Examples of such models are Global recoding, full-*domain generalization* Plus *record suppression* [1], user defines hierarchy is always useful for generalization as it dictates transformation rules that minimize attributes precision in a hierarchical pattern. While full domain generalization makes an attribute generalized on an equal level of associated hierarchy. Refer to figure 1 for generalization hierarchy level 0 of gender and LGA are more specific compared to level 1 and of course level 2 presents the B/Kebbi highest level that cannot be recognized.

As for suppression, the original attribute value is replaced by a symbol such as '*', '#' and so on to detach meaning from it [3].

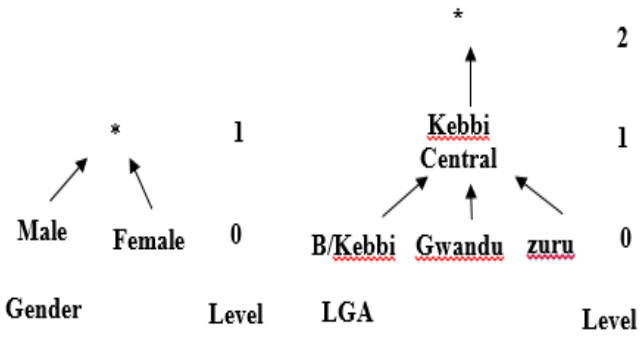

Figure 1. Generalization hierarchy adopted from [4].

1.1. Privacy Models

Privacy models were developed aimed at mitigating the risk of linkage attacks taking quasi identifier (QI) as a target [2], that QI cannot be eliminated from the dataset as they are important and needed for analyses. We formally defined QI as *attributes* A_1…… A_d in table *T* that can be joined with external public data to re-identify individual records such as student matric no., application no., gender, zip code, date of birth, age, etc. K-anonymity is a commonplace model used in preserving QI privacy. For more detail about k-anonymity, refer to [2].

Also, attributes are sensitive if an individual may not want to be linked with it, for example in our case, student registration fee, student department, occupation, salary, and disease in the biomedical domain. To protect sensitive attributes, *l-diversity,* and *t-closeness* as prevalent models are being utilized [5]. Figure 2 below shows the taxonomy of the privacy model.

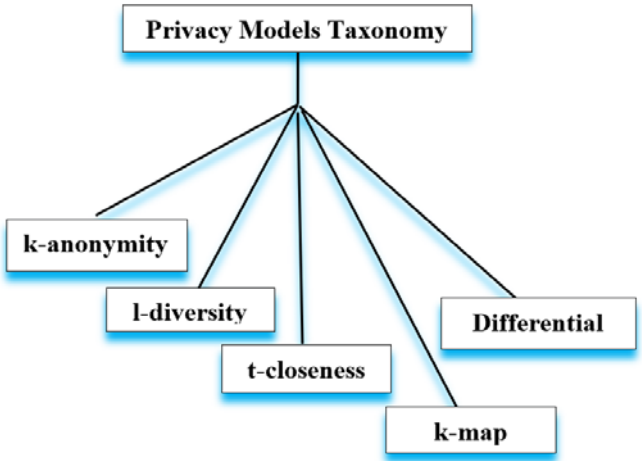

Figure 2. Taxonomy of Privacy Models.

1.2. Contributions

In summary, this work will present the following contributions: 1. Presentation of questionnaire and its response 2. Presentation and analyses of survey results concerning privacy in the educational domain. 3. Application of Student datasets in the field of PPDP using the ARX tool. 4. Extensive evaluation of the anonymized dataset concerning different values and two different suppression limits. And finally, we present the experimental setup used in the work.

1.3. Survey Results

The questionnaire was designed for the survey work to ascertain the level of data privacy, information awareness, and its application in all tertiary institutions in Kebbi State. Each institution was administered 30 questionnaires with the targeted respondents of Level Coordinators, Management and information Units, Bursary and Registry among others, and below are the name of the institutions:

1. Waziri Umaru Federal Polytechnic Birnin Kebbi **(WUFP)**,
2. Kebbi State Polytechnic Dakingari **(K/S Pol. Dakingari),**
3. Collage of Education Argungu **(COE Argungu)**,
4. Health Technology Jega **(Health Tech.Jega)**,
5. Aleiro University of Science and Technology **(AUST)**,
6. Federal University Birnin Kebbi **(FUBK)**.

The table below provides samples of questionnaires administered and the associated responses per each institution.

Table 1

Sample of questionnaire responses

Question	WUFP l	K/S Pol. Dakingari	COE. Argungu	Health Tech. Jega	AUST	FUBK
What is the total number of students in your institution?	Above 5000-(66.66%)	1000-2000-(66.66%)	4000-5000-(46.66%)	Above 5000-(63.66%)	Above 5000-(60.66%)	Above 5000-(60.66%)
Does your institution keep student records?	Yes – (80%)	Yes – (100%)	Yes – (100%)	Yes – (73.33%)	Yes – (100%)	Yes – (100%)
How long does your institution keep the student's record?	Forever-(68.96%)	Forever-(73.33%)	Forever-(90%)	Forever-(20%)	Forever-(100%)	Forever-(100%)
Which of the student's details do you consider sensitive?	Account No.-(36.66%)	Account No.-(93.33%)	Account No.-(50%)	Account No.-(50%)	Account No.-(20%)	Account No.-(20%)
Does your institution use a computing platform in keeping student records?	Yes.-(100%)	Yes.-(86.66%)	Yes.-(86.66%)	Yes.-(86.66%)	Yes.-(93.33%)	Yes.-(100%)
Does the student's record keep in plain text?	Yes.-(56.66%)	Yes.-(60%)	Yes.-(56.66%)	Yes.-(76.66%)	Yes.-(80%)	Yes.-(80%)
How simple it is to identify individual records?	Very Simple.-(63.33%)	Very Simple.-(66.66%)	Very Simple.-(53.33%)	Very Simple.-(66.66%)	Very Simple.-(96.66%)	Very Simple.-(96.66%)
Does your institution give out student data to a third party?	Yes.-(23.33%)	Yes.-(66.66%)	Yes.-(56.66%)	Yes.-(56.66%)	Yes.-(26.66%)	Yes.-(26.66%)
Are you aware of information privacy and data protection law?	Yes.-(46.66%)	Yes.-(86.66%)	Yes.-(36.66%)	Yes.-(53.33%)	Yes.-(80%)	Yes.-(80%)
Does the institution prevent students' data from any attack?	No.-(100%)	No.-(100%)	No.-(100%)	No.-(100%)	No.-(100%)	No.-(100%)

From Table 1 above, the results provided are consolidated for the whole six (6) higher institutions of learning in the state. We chose to use a one-sided response as it is the majority and provides insight into what the research wants. The most interesting things to note from the table are: (1). 92.22% of the student records were collected for the entire institution only, and 75.38% were kept for eternity. Though 92% of the record were stored in computing platforms used by various institutions, 68.33% of the total record were kept as plain text-(as is collected). This shows the extent of privacy threats faced by the record. (3). Also as indicated in the table above, 73.88% of all student records in the entire school are prone to internal attack due to the simplicity of identifying individual records with less effort. For these, we can attest to the fact that the entire records for the whole institutions of Kebbi state are being faced with privacy threats as figures shown in table 1 due to the absence of any privacy protection techniques applied to the information. Even though respondents claimed to be aware of information privacy and data protection law.

2. Methodology

In this section, we will present the methodology used in the conduct of this work such as the experiment framework, the dataset used, the Experiment setup, the toolbox used, and the results in discussion. Figure 3 below is the entire work activity diagram.

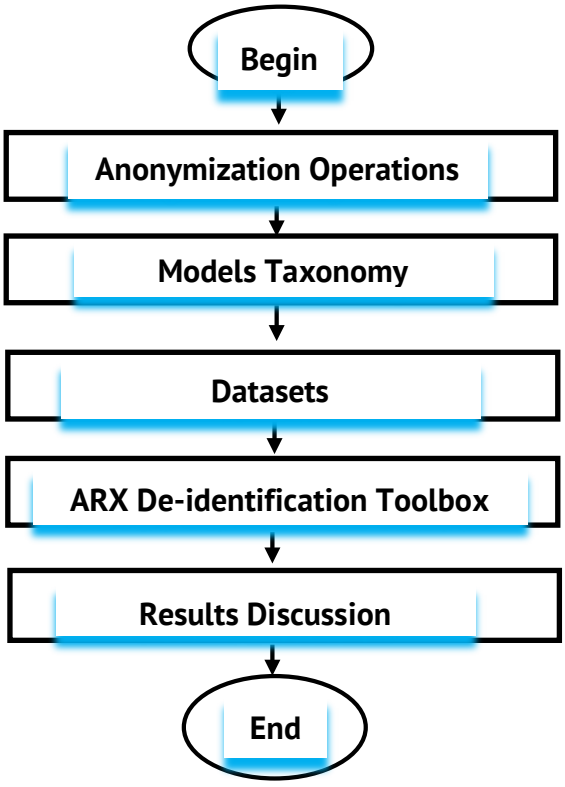

Figure 3. Activity Diagram.

Anonymization operations and taxonomy tree has been explained in the previous section above.

2.1. Experiment Framework

Figure 4 below shows the framework for experimenting. The first process involved in the framework is *New Project* where a user must provide the name of the newly created project before the ARX environment becomes enabled. *Importing data* is a process also where ARX

user brings in .csv datasets for the anonymization process and will only be enabled if a project is created. The *configuration* enables the user to create and edit rules, define privacy guarantees, parameterize the coding model and configure utility measures. While *anonymizing* is a process of performing data transformation. Filtering, analyzing the solution space, and organizing transformations are done through *Explore results*. The user keeps doing this process until the anonymized data suits his needs. If the final results are acceptable then, *Analyze Results* process is used where the main analysis takes place to compare and analyze the input and output such as attribute analysis, equivalence class analysis, performing local recoding, and final results summary. Lastly, the final results are stored for further use and analysis.

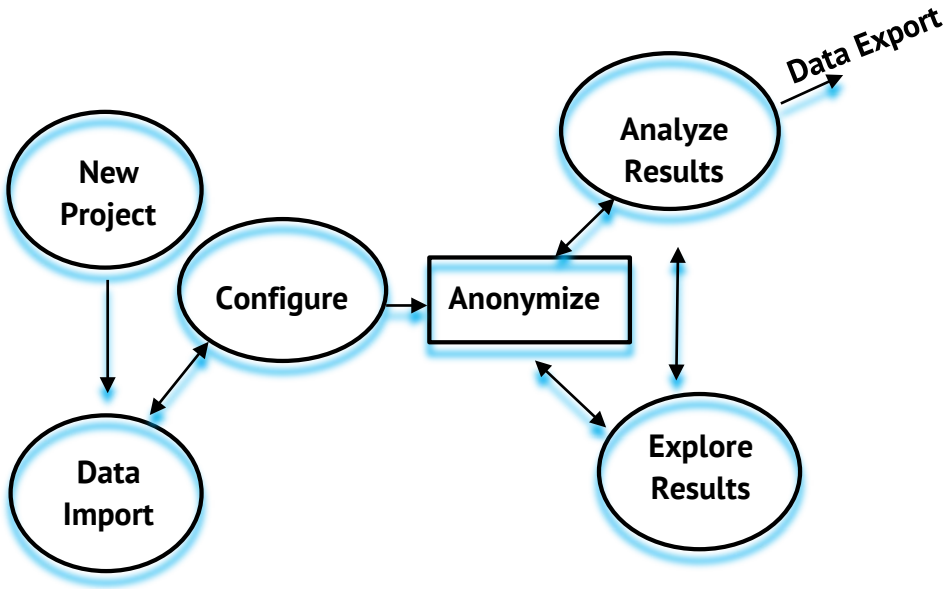

Figure 4. Experiment Framework.

2.2. Dataset

To the best of our knowledge, no dataset benchmark is set for the educational domain and since the ARX anonymization toolbox works with any dataset we chose to use a dataset collected from one of the institutes of higher learning in Kebbi State, Nigeria, known as Polytechnic Dakingari. Initially, the dataset contained 260 records which after data cleanup became 180 records only. Tables 2 and 3 show the overview of the datasets.

Table 2

Overview of the datasets

Dataset	Quasi-Identifier	Records	Highest Transformation	Size (KB)
Student	8	180	1,223,040	2

Table 3

Overview of the attributes in the datasets

Dataset	Quasi-Identifier (height of Hierarchy)	SA (Distinct Values)
Student	Sex (2), Matric Number (13), invoice (11), Application number (9), State (7), local govt. (12), session (1), status (1)	Department (23)

2.3. Experimental Settings

In this work, the experiments were conducted on a laptop computer running 64-bit Windows 8 (6.2, Build 9200) with AMD E-300 APU with Radeon (TM) processor at 1.3GHZ clock speed with 4 GB RAM. As for the five models, this work uses the ARX anonymization toolbox, to be explained next. Moreover, all the five models and the metrics are implemented in the toolbox. The research did not perform any pre-computation in the toolbox that can give an advantage to some models over others.

2.4. Parameter Value

Parameter values of k used in the experiment were recommended as the best configurations in[5]. As for parameter *L* values also cannot exceed the distinct values of SA for a good result, refer to [5] and [2], thus, this research takes care of that. Our work use recursive (c, l) diversity, where *c* stands to be constant and *l* "well represented" sensitive value. Table 4 below summarizes the configurations used in the experiments carried out.

Table 4

Experimental Configurations

Experiment	Parameter Settings	Datasets (Size)
Varied Parameter values Suppression limit = 10%	[k-value = 3, c =4, l=3 k-value = 5, c =4, l=3 k-value =7, c =4, l=3 k-value = 9, c =4, l=3 k-value = 11, c =4, l=3]	Student (180)
Varied Parameter values Suppression limit =50%	[k-value = 3, c =4, l=3 k-value = 5, c =4, l=3 k-value =7, c =4, l=3 k-value = 9, c =4, l=3 k-value = 11, c =4, l=3]	

2.5. ARX Anonymization Toolbox

ARX - Powerful Anonymization Toolbox is a comprehensive open-source software for anonymizing sensitive personal data. It supports full-domain generalization, record suppression, local recoding, and microaggregation [6]. It was developed within three years by five computer scientists in Germany, refer [7]. For ARX graphical interface refer to [2].

3. Results and Discussion

In this section, the results obtained during the experiments using the configuration and student dataset above are going to be analyzed and explained about certain quality metrics such as Granularity, Non-uniform entropy, and Discernibility. Also, some transformations and anonymization time per run will be presented. The best score is the one with the lowest score [8].

***Granularity*.** This model collects and presents the granularity of the output dataset. From the first set of four bars in figure 5 we can see how this model displays two different sets of results as the suppression limit is 10%. As *k* = 3 and 5, almost 90% of the output dataset cannot be identified due to a high level of anonymization. This indicates that when this data is shared for research purposes, it will provide little utility and hardly achieve

research purposes due to high privacy. Similarly, as the *k* value increased from 3 to 5, the same results were obtained with no effect. On the other hand, when the *k* value moved to 7, 9, and 11, we can observe the slightest increase from 91.11% to 95% all through. This no doubt affects the attribute quality more and made it unworkable by researchers, though privacy became higher than 3 and 5. But, the effect of the *k* value became constant as observed.

In figure 6 below displays results as suppression limit = 50%, indicating attributes level details are clearer than when suppression was 10%. All the returned results indicate 61% down. That proves that privacy and quality were balanced.

***Non-uniform entropy*.** This model measures information loss based on common information in a dataset that measures the amount of information that can be obtained about the original values of variables in the input dataset by observing the values of variables in the output dataset. However, the metric makes this quantification for an individual attribute in the dataset. In the second four bars of figure 5 below, as suppression limit = 10%, we can also see that as the *k* value keep increasing from 3 through 7, information loss for the datasets keeps decreasing, though, with different values of 16.58%, 8.88% and 6.03 % respectively. However, 6.03% remains constant from *k* = 7 through 11. Meaning that the datasets cannot be de-anonymized more than *k* = 7 and, these values provides minimum loss.

On the other hand, figure 6 presents results as a suppression limit = 50%. It is evident that as *k* = 3 and 5, distortion was not much compared to the same values as suppression = 10%. When *k* = 9, loss of information is almost the same as its counterpart in 10% above. On the other hand, in the 10% limit, *k* = 7 and 11 outperformed their counterparts in the 50% limit.

***Discernibility*.** This measures how identical a record is to others within each equivalence class by assigning an additional penalty to it equal to the size of the equivalence class it belongs. For detail refer to [9]. As indicated in the third group of bars in figure 5 as suppression = 10%, the best scores are when *k* = 7, 9, and 11 which showed the highest identicality of the records in the output dataset. And that indicates higher privacy than quality. But in figure 6 where suppression = 50%, we can also observe the third group of bars with different scores all less than in figure 5. This indicates not much additional penalty as there are fewer equivalence classes.

***Anonymization Time*.** This quantifies the time taken to complete transformation per run and, it measures in seconds. From the last group of four bars in figure 5, we can observe that as the suppression limit is 10%, the last time was when *k=9*, followed by *k=5*. That should not be unconnected with search space until a global optimum solution was returned. And in these two values, the time to return was small. We can also see that as *k=11*, anonymization time was the longest, because of the time taken to return the global optimum.

In figure 6, when the suppression limit was 50 % we can deduce that *k=3* returned the least anonymization time compared to its counterpart in suppression limit 0f 10 %. This happened because the privacy has been relaxed the more and returning to global optimum will not take much time. Also, the rest of the *k* values here outperformed their counterparts above with the increase of values even though they maintain consistent values among themselves. That could be understood that as the suppression limit is relaxed to 50, the increase of *k* values has little or no effect on anonymization time unlike when suppression is tight to 10% which showed different timing due to stricter privacy and suppression.

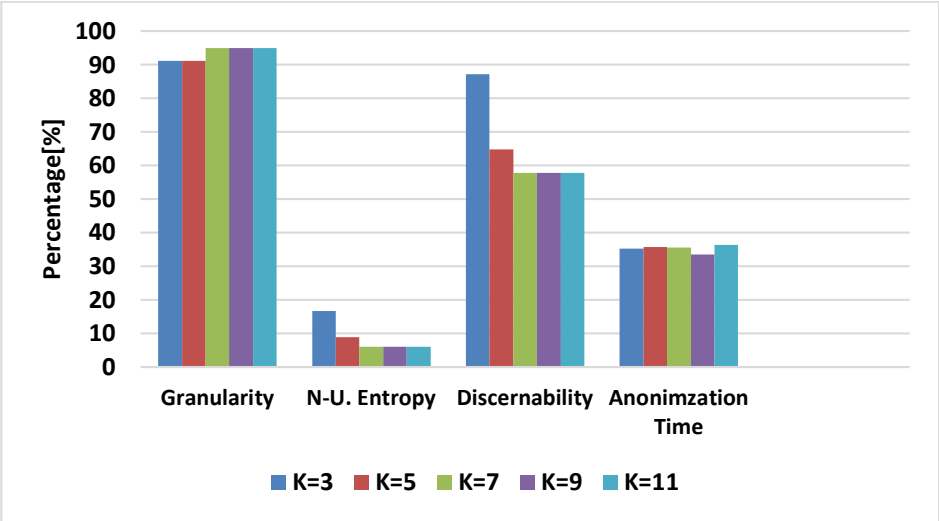

Figure 5. Suppression limit of 10%.

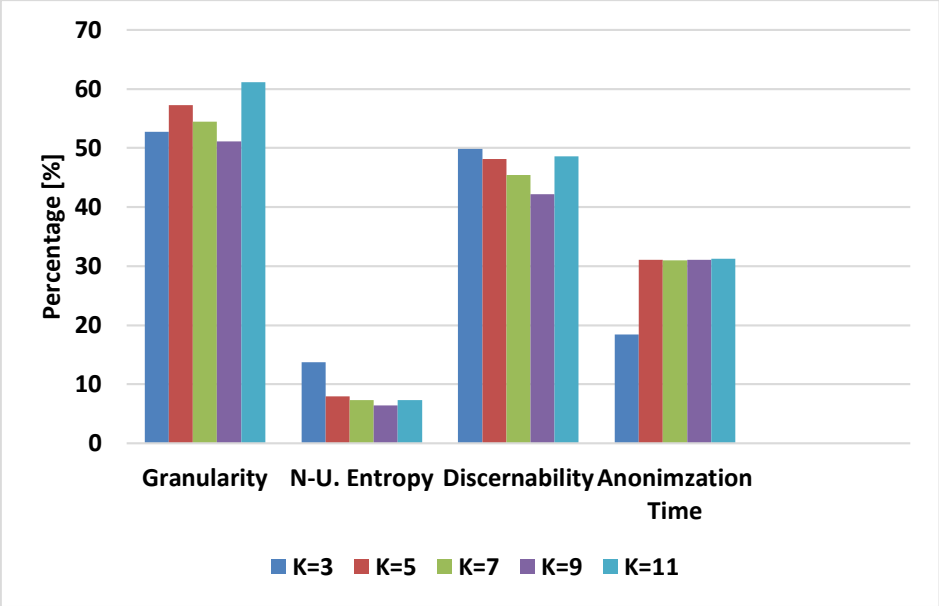

Figure 6. Suppression limit of 50%.

In [10] three privacy models were compared based on information loss metrics. The experiment was conducted using three datasets of which the largest among them contains 16, 422 tuples. In their work, it was concluded that t-closeness has better utility compared to k-anonymity and l-diversity. Yadav compared only two models and the dataset was unknown [11]. Execution time was measured, and it was concluded that *k*-anonymity outperformed l-diversity. In the work of [8], five privacy models were compared out of which one of them-slicing is the anonymization technique and not the privacy model [12]. Furthermore, only one benchmark dataset was used in the work but with a larger size (640,000 records). It was reported that k-anonymity outperformed the rest in terms of execution time. On the other hand, slicing was the worst performer. Prasser et al. present a comprehensive theoretical review of the three most prominent privacy models in big data. The advantages and limitations of these models were stated therein. Though, their proposed solutions can only work where there is only one sensitive attribute in the dataset.

In a model proposed by [13] that data utility can be increased and maintain significant privacy based on the outlier equivalence class. *K*-anonymity and l-diversity were used but,

with the single configuration of 5 and 2 respectively. In their work, two datasets were used with a suppression limit of 100%. However, their work was conducted using ARX 3.5.1 environment. Also [14], proposed a model based on superclass substitution for utility improvement on k-anonymity. Their model proved better quality than the other two. Furthermore, a student admission dataset was used. In a similar research effort by [15], four privacy models were used made in a single framework-ARX. The beauty of this work is that various parameter values were used to ascertain the correctness and validity of the result. Though the metric used during the analysis was also four, the dataset is non-educational, and the factor of study is information loss as parameter values changes. The authors in [16] used adult dataset from UCI machine learning repository which was partitioned into five groups from 40000 to 640000 records. On each set of group, five different privacy models were run against execution time and data utility. Though from their work non-of the model outperformed others from all angles.

Based on this literature, we can confirm that none of the work mentioned above has categorically used a dataset from the educational domain, and none used the quality model of *Granularity, Non-uniform Entropy,* and *Discernibility*. Also, none of them used this set of configurations in the ARX environment based on suppression limits of 10 and 50% respectively.

4. Conclusions

In this research, it could be concluded that the higher the suppression limit the more balance exists between privacy and utility. Also, it was observed that the suppression limit of 50% provides less anonymization time in respective *k* values compared to *k* values in suppression = 10%. This was proved to be due to less time it takes anonymization to search and return a globally optimum solution. Conclusively, we can say that the suppression limit of 10% does not provide a balance between privacy and quality. However, the work observed that 92% of the students, records faced privacy threats as there was no privacy policy implemented on data at rest or during sharing with a third party in all Kebbi State educational institutions. Additionally, none of the respondents has a clear view of what privacy is all about. We note also that all the respondents misunderstood data privacy with data confidentiality. Therefore, there is a need for stakeholders in all the institutions to educate data holders about privacy and privacy-enhancing technologies.

Conflict of interest. The authors declare no conflict of interest.

References

1. Prasser, F.; Kohlmayer, F.; Kuhn, K.A. Efficient and effective pruning strategies for health data de-identification. *BMC Medical Informatics and Decision Making* 2016, pp. 1 - 14.
2. Kohlmayer, F.; Prasser, F.; Kuhn, K.A.; Spengler, B.E. Lightning: Utility-Driven Anonymization of High-Dimensional Data. *Transactions on data privacy* 2016, 9, pp. 161 - 185.
3. Narula, D.; Kumar, P.; Upadhayaya, S. Performance Evaluation of K-Anonymization Algorithms for Generalized Information Loss. *IJCTA* 2016, pp. 227 - 235.
4. Shehu, A.; Salihu, A.; Sani, A. Application of Privacy-Preserving Data Publishing on Students' Data in Tertiary Institutions of Kebbi State Using K-Anonymity. *International Journal of Innovative Science and Research Technology* 2022, 7, pp. 1083 - 1091.
5. Kohlmayer, F.; Prasser, F.; Kuhn, K.A. The cost of quality : Implementing Generalization and Suppression for Anonymizing Biomedical Data With Minimal Information Loss. *Journal of Biomedical Informatics* 2015, 58, pp. 37 - 48.

6. Prasser, F.; Kohlmayer, F.; Kuhn, K. A Benchmark of Globally-Optimal Anonymization Methods for Biomedical Data. In Proceedings of the IEEE 27th International Symposium on Computer-Based Medical Systems, New York, USA, May., 2014, pp. 66 - 71.
7. Kohlmayer, F.; Prasser, F.; Kuhn, K.A.; Spengler, E.B. A Tool for Optimizing De-Identified Health Data for Use in Statistical Classification. In Proceedings of the IEEE 30th International Symposium on Computer-Based Medical Systems, Thessaloniki, Greece, June, 2017, pp. 169 - 174.
8. Kohlmayer, F.; Prasser, F.; Kuhn, K.A. The Importance of Context: Risk-based De-identification of Biomedical Data. *Methods of Information in Medicine* 2016, 55, pp. 347 - 355.
9. Jain, P.; Gyanchandani, M.; Khare, N. Big Data Privacy: A Technological Perspective and Review. *Journal of Big Data* 2016, 3, pp. 1 - 25.
10. Emam, A. Data Privacy on E-health Care Yystem. *International Journal of Engineering, Business and Enterprise Application* 2013, 3, pp. 89 - 99.
11. Yadav, D. Secure Techniques of Data Anonymization for Privacy Preservation. *International Journal of Advanced research in Computer Science* 2017, 8, pp. 1693 - 1695.
12. Kohlmayer, F.; Prasser, F.; Kuhn, K.A. A Flexible Approach to Distributed Data Anonymization. *journal of Biomedical informatics* 2014, 50, pp. 62 - 76.
13. Yilmaz, V.; Murat, A. A New Approach to Utility-Based Privacy Preserving in Data Publishing. In Proceedings of the 2017 IEEE International Conference on Computer and Information Technology (CIT), 2017, pp. 204 - 209.
14. Ravindra, T.; Maheshwari, P.; Binod, K. A Comparative Study of Data Suppression Technique for Privacy of Individuals. *International Journal of Current Trends in Engineering & Technology* 2018, 4, pp. 230 - 241.
15. Moein, A.M.; Taha, S.R.; Noman, M.; Hadi, H. The risk-utility tradeoff for data privacy models. In Proceedings of the 8th IFIP International Conference on New Technologies, Mobility and Security (NTMS), 2016, pp. 1 - 5
16. Antony, P.J.; Selvadoss, T.A. Comparison and Analysis of Anonymization Techniques for Preserving Privacy in Big Data. *Advances in Computational Sciences and Technology* 2017, 10, pp. 973 - 984.

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INTEREST BASED ADAPTIVE BILLBOARD CONTENT MANAGEMENT

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Abstract. The street advertising has undergone some significant changes in recent years: traditional billboards are gradually being replaced by electronic display devices (LED screens) that are able to change in real-time the broadcast advertising, thus allows the dynamic content management. This paper aims to develop an adaptive advertising strategy based on the preferences of the people in front of the screen. Each of them has a special application installed on their personal smartphone through which they can configure their interests regarding the broadcast advertising. These interest profiles are then collected by billboards which, based on them, select the most appropriate type of ad to run at that time. The proposed method focus on transformation of a simple display equipment into an intelligent one, capable of adapting the broadcast content to the requirements of the nearby audience and aims to maximize the efficiency of the billboard operation and at the same time bring maximum satisfaction to the target audience. The performance of the method was evaluated using agent based computer simulation.

Keywords: *adaptive content management, digital advertising screens, street advertising.*

Rezumat. Publicitatea stradală a suferit câteva schimbări semnificative în ultimii ani: panourile tradiționale sunt înlocuite treptat cu dispozitive electronice de afișare (ecrane LED) care sunt capabile să modifice în timp real publicitatea difuzată, permițând astfel gestionarea dinamică a conținutului. Această lucrare își propune să dezvolte o strategie de publicitate adaptativă bazată pe preferințele oamenilor din fața ecranului. Fiecare dintre ei are instalată pe smartphone-ul personal o aplicație specială prin care își pot configura interesele cu privire la publicitatea difuzată. Aceste profiluri de interes sunt apoi colectate de panouri publicitare care, pe baza lor, selectează cel mai potrivit tip de anunț pentru a rula în acel moment. Metoda propusă se concentrează pe transformarea unui echipament simplu de afișare într-unul inteligent, capabil să adapteze conținutul difuzat la cerințele publicului din apropiere și are ca scop maximizarea eficienței operațiunii panoului publicitar și, în același timp, să aducă satisfacție maximă țintei public. Performanța metodei a fost evaluată folosind simularea computerizată bazată pe agenți.

Cuvinte cheie: *management adaptiv al conținutului, ecrane de publicitate digitală, publicitate stradală.*

1. Introduction

Street or outdoor advertising, called more recently out of home (OOH) advertising is one of the oldest and simplest methods of promoting products and services. Street advertising is usually represented by billboards designed to display information about products, manufacturers, sellers, services, locations, etc. [1]. They are managed by specialized companies which display that information for a certain period of time. The advertising companies are interested in implementation of new display strategies in order to reach as wide audience as possible and to increase in this way their profits.

In the Republic of Moldova, OOH accounts for approximately 20% of the advertising market volume. The street advertising market in Moldova offers more than 10 formats (billboard, big-board, city-light, LED screens, cubes, clocks, panels, banners, light-boxes at public transport stations, etc.). Also, the street advertising market in the Republic of Moldova has more than 10 operators with a total of over 6000 different advertising billboards.

Advantages of the street advertising:

- More than 70% of people spend most of their time outside their homes.
- Street advertising is the best cost-effective advertising method.
- It has a high visual impact on the people compared to other advertising sources: print media, online press, shops, telephone.
- Continuous display of the message 24/24 hours for all nearby pedestrians and all cars in traffic in the area with the possibility to reach busy, active, and moving people. Statistics show that we spend an average of 1.3 hours per day on the street.
- It is free and doesn't require specific technical means to access it.
- It reaches a lot of nearness people without requiring significant investments.

A more detailed analysis of this topic can be found in [1, 2].

The main disadvantages of the traditional street advertising are the inability to select the target audience and the extremely low volume of disseminated information (laconic text of up to 2-3 sentences, some images, etc.) without the possibility to provide details [3].

Among the factors influencing the efficiency of the billboard are its location, the quality of the content presentation, and, last but not least, the coherence between the broadcasted content and the existing at that time audience near the billboard. As the everyday audience is very heterogeneous, it is practically impossible for traditional billboards to adapt the broadcasted content to present people. More recently, one of the most important factors for increasing efficiency is the use of digital display equipment, its impact on the audience being about 2.5 times higher compared to traditional display. These equipments have marked a new era in the development of the street advertising known as Digital Out Of Home advertising (DOOH) and which offer great possibilities compared to the classic methods. The DOOH was stormy developed in recent years [4, 5].

A lot of new approaches for advertising management based on DOOH technologies have been proposed aiming to improve the effectiveness and to touch better the targeted audience [6-9]

This article proposes an innovative person-centric adaptive method (according to classification proposed in [10]) of organizing street advertising which, been based on modern technological displaying equipment and smart technologies, is able to collect the information about the composition of the people in front of the billboard and adapts in real time the broadcasted content to the interest of as many as possible people.

2. Description of the proposed method

In this article we will analyze the operation of a billboard with digital display (LED screen, plasma screen, projector, etc.) on which are displayed advertising information that is perceived by pedestrians passing in front of the billboard (Figure 1).

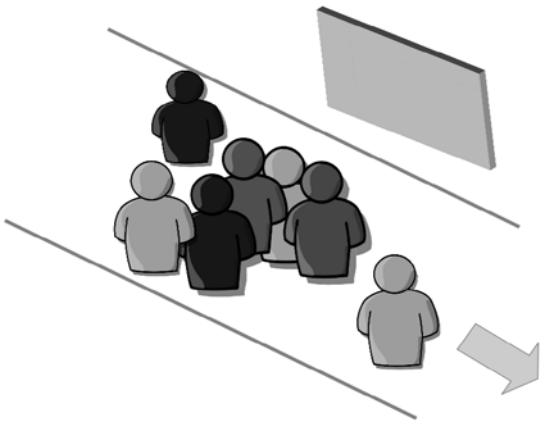

Figure 1. Traditional billboard.

The efficiency of this approach is relatively low for the simple reason that the same information is disseminated for a long time (weeks or even months) and the public passing on the street tends to be largely the same (people leaving and returning home from service, those walking through the street near the house, etc.). The proportion of these people can be considerable, reaching in some cases 80-90%. Which means that the informative value of the display decreases day after day, hence the low efficiency of this approach. It depends largely on the location of the billboard and can be quite high in places where the public varies a lot every day (near stations, markets, shopping malls, etc.).

Equipping the billboard with a digital display screen greatly reduces these problems because the information displayed can be changed more often, thus maintaining pedestrians' interest in it. The advertising company can run advertising for several products for the same duration, which leads to a considerable increase if the revenue.

The proposed method aims to increase the efficiency of the billboard by adapting in real time the strategy of the content dissemination to the surrounding public. Assuming that the most part of pedestrians have a smartphone capable to connect to WiFi wireless network (IEEE 802.11), this equipment can be used, in addition to all, as a source of information about the preferences of its owner. In order to define his preferences, the user will be asked to install on his phone a mobile application available in the store (Google Play for Android operating system and iTunes for Apple products). That proposal should be attractive in order to interest the user to accept it (a smart marketing solution is required here). It could also include other useful services (eg weather forecast display, exchange rate, etc.). When installing the application, a questionnaire will be launched. By answering the asked questions (checking the answers in a proposed list) the user will create his profile that will specify his preferences and interests. This mobile profile that doesn't contain any personal information (name, phone number, address, email, etc.) may be broadcasted on-demand if requested by another application on the network or may be continuously broadcasted by the application in order to discover certain services in the proximity network (for example, to search in the network some people with similar preferences). It is very important to establish the structure of the questionnaire, which should be neither too voluminous with the risk of boring the user

when completing it, nor too short to avoid an incomplete and uninformative profile. In order to simplify the structure of the questionnaire, users' preferences will be divided into categories (e.g. sports products, mobile phones, women's clothing, footwear, household appliances, etc.). The user profile will be specified through a list of selected categories in the questionnaire. It will start with the most favorite categories followed by others arranged in descending order according to the degree of the preference. It may also be proposed to set the weights for each category in the list. The definition of the content and of the optimal structure of the questionnaire requires a more rigorous analysis and will not be discussed further in this article. The simplest strategy for running advertising is to use a circular algorithm (Round Robin type) displaying the advertising one by one for a certain duration for each of the categories on the server. The same policy can be applied to products that fall into the same category. This method is a traditional one and ensures an equal display time for each product in the long run. It is not adaptive and does not take into account the audience composition next to the billboard. Its only advantage is the simplicity and the fairness of the display resources sharing between the promoted products.

One way to improve the efficiency of this system would be to adapt the broadcasted content to the preferences of the audience near the billboard. For this purpose, it is proposed to equip the advertising screen with a WiFi access point that will be open (unsecured) and that will support the connection without security key of any equipment in the radio sensitivity area with a radius that can reach up to 100 meters. Given the omnidirectional nature of radio coverage for traditional access points, the billboard should be installed at the side of the road so that pedestrians pass only in front of it and not have the rear access. Another solution would be to use a directed broadcast access point (which transmits and receives radio waves only in a certain direction or which uses shielding elements to limit emissions/receptions in/from unwanted directions). The panel will also contain a server with some installed applications for ensuring the logic of the system work, including a video streaming server and the information to be broadcasted. The advertised content may be modified in real time through the network. The information about the promoted products is classified in the same categories that were specified in the questionnaire. When it is decided to launch the display of a certain category, a product in this category will be selected according to a predefined algorithm and that information will be displayed on the screen.

When the pedestrian enter into the radio sensitivity area near the panel he will automatically connect to the access point and the server will receive his profile. The appearance of the pedestrian will be counted by entering his profile in a list and by increment a variable that corresponds to the number of present users in front of the billboard. From this moment the server will start monitoring the presence of the respective equipment in the sensitivity area, this being possible because its IP address is known being assigned to it by the DHCP server on the access point. Presence monitoring is done by transmitting through the network at regular intervals of short messages (pings) to which the mobile equipment will respond confirming its presence. From the moment when no confirmations are received from the respective mobile phone, it is removed from the list and the presence variable is decremented. The proposed system is shown in Figure 2. Pedestrians move in the billboard direction, reach the sensitivity area and then leave it continuing their way.

Given that we have N categories of advertising, we expect to have near the panel up to N groups of pedestrians, each of which will correspond to one of the categories defined above.

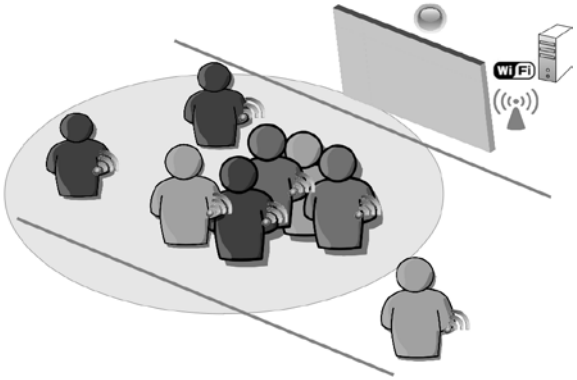

Figure 2. Billboard with adaptive content management.

The groups are monitored separately to know in real time the number of pedestrians in each of them. The application that manages the advertising display performs the following functions: receives user profiles with their preferences and interests, continuously monitors their presence, counts the audience in the area of radio sensitivity, makes decisions about real-time content be displayed on the advertising screen, etc. For simplicity, we'll assume that the ad delivery time for all products in all categories is the same (for example, 30 seconds). That means the information displayed on the screen must change every 30 seconds regardless of the evolution of other factors.

The decision on the content been broadcasted in the next time interval is based on the data collected in the previous interval. Advertising will be broadcasted for the category that has the largest presence in front of the panel and at the same time information will be collected about the composition of the audience that will be used in the next time slot.

3. Effectiveness estimating of the method

The methods of advertising effectiveness estimation are very different: from conducting a survey on its quality [11] to assessing its impact on the sales volume of the advertised products [12]. In this article we will use a specific evaluation method based on results obtained by simulation, that would show us the efficiency of our method in relation to other methods. We aimed to use an agent-oriented approach for simulation [13] and to implement our model using a specialized software: GAMA platform [14,15], a modeling and simulation development environment for building spatially explicit agent-based simulations. This approach makes possible to describe each agent and its spatial movement through its attributes and behavior. In this case, each pedestrian and the ads screen are represented by specific agents that interact with each other, thus realizing the logic of the system operation.

We have to define some technical parameters of the analyzed system before the simulation. We will simplify the initial model described in the previous chapter by reducing the number of advised product categories to 4 assuming that a user can request only one category (the simplest case). Consequently, we will have only 4 groups of pedestrians who will move in both directions in front of the billboard. The sensitivity area will be a square with the size 50x50 meters, the speed of pedestrians will be from 0.5 m/s (slow pedestrians) to 1.5 m/s (fast pedestrians). The pedestrian speed and his moving direction will be chosen randomly. Pedestrian arrivals are independent, there are 4 types of pedestrians (one for each category). Pedestrians can move in any direction, they are counted at the entrance on the sensitivity area and at the exit of this area.

In Figure 2 the product categories are coded by color: we have pedestrians belonging to each of the 4 categories (so 4 different colors or gray degrees in our case) and the screen

can also broadcast 4 categories of advertising that correspond to those colors (the color of the light on the screen in Figure 2 corresponds to the color of the broadcast category at a certain time). We will set the duration of a time slot equal to 30 seconds (it corresponds to the duration of the advertisement for a product belonging to one of the categories), and the simulation time in the example analyzed below is 700 minutes. The simulation environment and the respective process are shown in Figure 3: pedestrians cross the sensitivity area of the billboard moving in arbitrary directions. The system monitors and counts these movements and establishes the category of advertising currently broadcasted taking into account the largest group (the color of the square that corresponds to the ads screen in Figure 3).

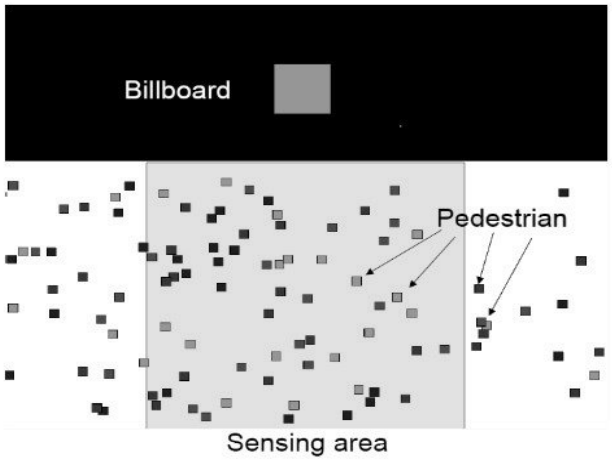

Figure 3. Simulation environment and the system simulation (pedestrian movement, dynamic content changing) in GAMA platform.

In Figure 4 are shown the evolution of the groups and the state of the screen: at the top is the number of pedestrians in the 4 groups (4 different colors), and at the bottom are presented the timers for each time slot, their color indicates the category advertising displayed on the screen in that time slot.

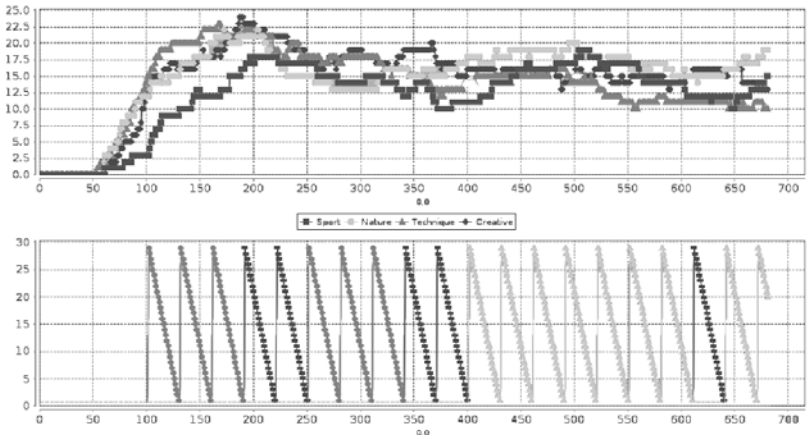

Figure 4. The evolution of the groups and of the screen status over the time.

During the simulation for each pedestrian we will calculate the satisfaction index defined by the ratio between the display time of his favorite advertisement and the total duration of his presence in the sensitivity area in front of the screen. The range of variation of this index: [0,1]. The average of these values will be used to estimate the overall system performance index: the overall average satisfaction. The index allows us to compare different system configurations: the larger it is, the more efficient is the system.

Following the long-term similar simulation of the system described above and the one with circular screen allocation, it turned out that the first one is on average 15-20 percent more efficient than the Round Robin system.

4. Conclusions

The main purpose of the article is to propose a solution that would allow an adaptive management of the content broadcast through billboards based on digital display equipment using information collected in real time about the preferences and the interests of the people in front of the screen. The obtained results are encouraging, they demonstrate the feasibility of the proposed method and its adaptability in real time. The new proposed performance index allows the comparison of results for different configurations of the analyzed system.
In the future, a more detailed and realistic simulation of the proposed method is foreseen: several product categories and profiles with multiple weighted preferences, more complex pedestrian flows with grouped arrivals, studying the possibility of integrating the method at the level of billboard network.

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Conflicts of Interest. The authors declare no conflict of interest.

References

1. Arens, W.F.; Weigold, M.F.; Arens, C. *Contemporary advertising*. McGraw-Hill Higher Education, 16th edition, 2021, 734 p.
2. Roux, A. T.; Van Der Waldt, D. L. R. Out-of-home advertising media: theoretical and industry perspectives. *Communitas* 2014, 19, pp. 95-115
3. Taylor, C.; Franke, G.; Bang, H. Use and Effectiveness of Billboards: Perspectives from Selective-Perception Theory and Retail-Gravity Models. *Journal of Advertising* 2006, 35(4), pp. 21-34.
4. Stalder, U. Digital out-of-home media: means and effects of digital media in public space. *Pervasive Advertising*. Springer, London, 2011. pp. 31-56.
5. Lee, H.; Cho, C. Digital advertising: present and future prospects. *International Journal of Advertising* 2020, 39(3), pp. 332-341.
6. Lasinger, P.; Bauer, C. Situationalization, the new road to adaptive digital-out-of-home advertising. In: *Proceedings of IADIS International Conference e-Society* 2013, pp. 162-169.
7. Fang-Zhou, J.; Kanchana, T.; Mahbub, H.; Yusheng, J.; Aruna, S. Efficient Content Distribution in DOOH Advertising Networks Exploiting Urban Geo-Social Connectivity. In *Proceedings of the 26th International Conference on World Wide Web Companion*. International World Wide Web Conferences Steering Committee, Geneva, CHE, 2017, pp. 1363–1370.
8. Lai, J.; Cheng, T.; Lansley, G. Improved targeted outdoor advertising based on geotagged social media data. *Annals of GIS* 2017, 23(4), pp. 237-250.
9. José, R.; Soares, A. M. *Towards new advertising models for situated displays* [on-line]. 2010, pp. 1-10, [accesat 10.05.2022]. Disponibil: https://repositorium.sdum.uminho.pt/handle/1822/18875
10. Bauer, C.; Lasinger, P. Adaptation strategies to increase advertisement effectiveness in digital media. *Management Review Quarterly* 2014, 64(2), pp. 101-124.
11. Mehta, A. Advertising Attitudes and Advertising Effectiveness. *Journal of advertising research* 2000, 40(3), pp. 67-72.
12. Mukesh B.; Donthu N. Sales Response to Outdoor Advertising. *Journal of advertising research* 1999, 39(4), pp. 7-17.
13. Ioretti, G. Agent-based simulation models in organization science. *Organizational research methods* 2013, 16(2), pp. 227-242.
14. Drogoul, A.; Amouroux E.; Caillou P.; Gaudou B; Grignard A.; Marilleau N.; Taillandier P.; Vavasseur M.; Duc-An V.; Zucker J-D. GAMA: A Spatially Explicit, Multi-level, Agent-Based Modeling and Simulation Platform. In: *International Conference on Practical Applications of Agents and Multi-Agent Systems*. Springer, Berlin, Heidelberg, 2013. pp. 271-274.
15. *GAMA platform* [on-line]. [accesat 20/11/2021], Disponibil: https://gama-platform.github.io/.

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SMART CITY SERVICES BASED ON SPATIAL-TEMPORAL LOGIC

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Abstract. The development and research of Smart City Service Systems is a very important area for the future of mankind. The urbanization process imposes new criteria for qualitative and quantitative assessment of population well-being, which will involve processing a very large volume of information, organizing the data exchange and processing. This paper proposes a Multi-Agent Smart City Services system based on Spatial-Temporal logic. In order to optimize the criteria for the qualitative and quantitative evaluation of services, the set of agents is divided into: the subset of agents that deliver services and the subset of service consumers agents. The system diagram, the synthesis of the agents, the operators of temporal and spatial logic was elaborated. The relationship between the subset of service delivery agents and the subset of agents of service consumers is determined by game theory models.

Keywords: *Spatial - Temporal Logics, Distributed Computing, Multi-Agent Systems, Swarm Intelligence, Collective Decision Making, Game Theory, Knowledge Bases.*

Rezumat. Dezvoltarea și cercetarea sistemelor Smart City Service prezintă un domeniu foarte important pentru viitorul omenirii. Procesul de urbanizare impune noi criterii de evaluare calitativă și cantitativă a bunăstării populației, care va implica procesarea unui volum foarte mare de informații, organizarea schimbului de date și procesarea acestora. În lucrarea de față se propune un sistem Multi-Agent Smart City Services bazat pe logica Spațial-Temporală. Pentru optimizarea criteriilor de evaluare calitativă și cantitativă a serviciilor, mulțimea de agenți este divizată în: sub-mulțimea de agenți care livrează servicii și sub-mulțimea de agenți consumatori de servicii. A fost elaborat diagrama sistemului, sinteza agenților, operatorii de logică temporală și spațială. Relațiile dintre sub-mulțimea de agenți care livrează servicii și sub-mulțimea de agenți consumatori de servicii este determinată de modele din teoria jocurilor.

Cuvinte chee: *Logica Spațial-Temporală, Calcul Distribuit, Sisteme Multi-Agent, Inteligența Roiului, Luarea Deciziilor Colective, Teoria Jocurilor, Baze de Cunoștințe.*

1. Introduction

The smart city can be defined as a set of services offered by a distributed computing system that explores large volumes of data and applies communication technologies in order to improve the quality of life of its citizens. The target objectives of the services offered by the smart city are oriented towards the application of knowledge bases and databases, at the same time being based on information provided by its citizens online. The paper [1] proposes a Smart City Service System that is implemented as an ontology-oriented system, which ensures decision-making based on reasoning and inference, and provides objective information characteristic of the situation in the city.

Designing a smart city is a long and complex process because it involves human, financial, technical and technological essential resources. In order to meet the requirements of the Smart City Service System, a holistic approach on the management process is necessary [2, 3], where service is the basic concept, or rather the element of interaction between the actors involved in the decision-making process (citizens, administration, enterprises, organizations, etc.).

The smart city system, in order to provide the most relevant information, requires the application of decision-making models' knowledge based or cognitive. A cognitive system has a complex structure that has the ability to self-develop by accumulating new information and knowledge in the process of evolution in space and time [4, 5].

Since the Smart City Service System has a spatially distributed structure, it is obvious that models based on architectures of distributed computing, parallel or cloud are applied for data processing [6-8]. At the same time, it can be mentioned that the same performance features are offered by Multi-Agent systems [9, 10] and collective / collaborative systems for decision-making [11], based on Artificial Intelligence methods and models [12, 13].

The smart city being a dynamic system that evolves in space and time requires a special approach to apply decisional models based on spatial-temporal logic in which geographical position and time to play a decisive role in decision making. In parallel with the definition of spatial-temporal logic, also appears the notion of event that takes place in space and time. Temporal logic also plays a very important role in agency theory, a field of science where the integration between philosophy, computer science and game theory takes place which provides paradigms for researching Multi-Agent systems that make decisions and gain new knowledge in real time [14]. The problem of combining and the relationship between spatial logic and temporal logic is analyzed in paper [15] which addresses how computational complexity and the expressive power of component logic are related to the complexity and expressiveness of spatial-temporal logic.

This paper proposes a method of applying spatial-temporal logic for the development of Smart City Service Systems. The system represents a distributed computing architecture consisting of a set of Agents working together aiming to solve a common problem. The set of agents is divided into two subsets: the first is the subset of Agents that deliver services, the second subset are the agents that request services. These two subsets are always in the process of concurrency the balance between which is regulated by the Nash Equilibrium [16].

2. Synthesis of the Diagram for Smart City Service System

Nature-based computing provides a designer with the most efficient methods and models for developing complex systems, especially Smart City Service systems, which can be considered as multi-dimensional and dynamic systems in space and time. Therefore, solving

the problem of finding the optimal solution in the definition space requires the involvement of essential resources for processing a very large volume of data coming from a lot of heterogeneous sensors or stored on distributed systems. Reducing the complexity of these systems can be achieved by applying computational models based on intelligence agents and evolutionary algorithms [17-19] with distributed or concurrent data processing.

The Spatial-Temporal Diagram of the Smart City Service System is shown in Figure 1, where: SDA - Service Delivery Agent; SCA - Service Consumer Agent; GPS - Global Positioning System; $G5$- Fifth-Generation Technology Standard for Mobile Communications.

Let be in the activity space $S \subset (R^K \cup X \cup Y \cup Z \cup T)$ the Multi-Agent decisional distributed system is defined:

$$A^S = \{SDA,\ SCA,\ GPS,\ G5\}, \tag{1}$$

where: K are the total set of services and parameters defined for the Smart City activity; X, Y, Z are the spatial coordinates of the agent; T is the time coordinate; $SDA = \{SDA_n, n = \overline{1,N}\}$ is the set of Agents that deliver services; $SCA = \{SCA_m, m = \overline{1,M}\}$ is the set of mobile or stationary agents of services consumers; GPS is global positioning system that provides information for the spatial positioning of agents; $G5$ is the communication system that ensures the transfer of data between the set of agents and the temporal synchronization.

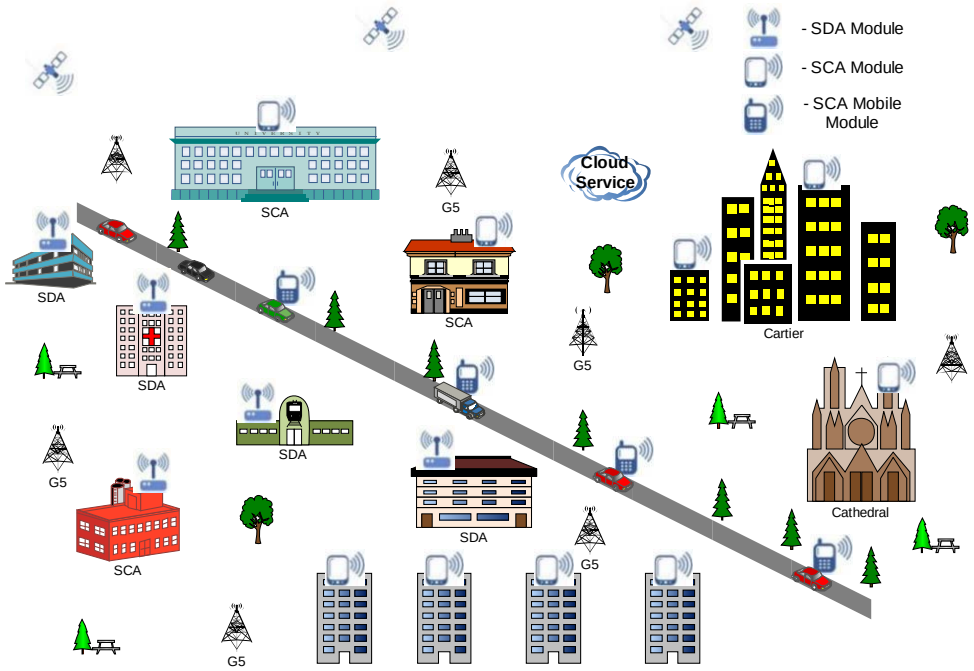

Figure 1. Spatial-Temporal Diagram of the Smart City Service System.

3. Agent Synthesis

The Smart City Service System includes two types of Agents: SDA - Service Delivery Agents and - Service Consumer Agents.

3.1. Service Delivery Agent Synthesis

The functional model [22,24] of the Service Delivery Agent is defined by the expression (2):

$$A_{SDA} = \{k_{Sv[T]},\ KB[T],\ SD: (Ev[T], TLP[T], SLP[T], Sv[T])\}, \tag{2}$$

where: $k_{Sv[T]}$ - the request coefficient for the services offered by *SDA* for *SCA*; $KB[T]$ - the knowledge [20,23] base available to the *SDA* agent at the time T; SD - data processing logic applied by the *SDA* agent; $Ev[T]$ - the set of events used by the *SDA* agent for data processing for the purpose of delivering quality services to *SCA* agents; $TLP[T]$ - temporal logic operators used for data processing; $SLP[T]$ - spatial logic operators used for data processing; $Sv[T]$ - the multitude of services offered by the *SDA* agent at the time T.

3.2. Service Consumer Agent Synthesis

The functional model of the Service Consumer Agent is defined by the expression (3):

$$A_{SCA} = \{k_{SQ[T]}, KB[T],\ SC: (Sv[T], TLP[T], SLP[T], SQ[T])\}, \tag{3}$$

where: $k_{SQ[T]}$ - the quality coefficient of the services used by *SCA* provided by *SDA*; $KB[T]$ - the knowledge [20,23] base available to the *SCA* agent at the time T; SC - data processing logic applied by the *SCA* agent; $Sv[T]$ - the set of services provided by *SDA* agents used by the *SCA* agent for data processing; $TLP[T]$ - temporal logic operators used by the *SCA* agent for data processing; $SLP[T]$ - spatial logic operators used by the *SCA* agent for data processing; $SQ[T]$ - the result of the evaluation of the quality of the services used by the *SCA* agent.

4. Temporal Logics Operators

Temporal logic operators [21] present mathematical models for events processing $Ev[T]$. The model and basic components of an operator are specified in the expression (4):

$$O(\tau): \{Op_1(\tau),\ Op_2(\tau), \ldots,\ Op_I(\tau)\}, \tag{4}$$

where: $Op_i(\tau)$, $i = \overline{1,I}$ is the set of operands involved in the operator $O(\tau)$.

The operand model is defined by the expression (5):

$$Op_i(\tau) = \{Ev_i[T],\ p_i(t)\},\ i = \overline{1,I}, \tag{5}$$

where: $p_i(t)$ is the coefficient of decisional influence of the event $Ev_i[T]$ within the operand $Op_i(\tau)$.

For the evaluation of the coefficients $p_i(t)$ three models of temporal evolution are defined: events in the past, events in the present and events in the future.

The mathematical model for calculating the coefficients of decisional influence for past events $p_i^t(t)$ is performed based on the formula (6):

$$p_i^t(t) = Ev_i[T]/(k + t^2/\beta),\ t = \overline{T, +\infty}. \tag{6}$$

The mathematical model for calculating the coefficients of decisional influence for present events $p_i^p(t)$ is performed based on the formula (7):

$$p_i^p(t) = Ev_i[T]/(k + t^2/\beta),\ t = \overline{-\infty, +\infty}. \tag{7}$$

The mathematical model for calculating the coefficients of decisional influence for future events $p_i^v(t)$ is performed based on the formula (8):

$$p_i^v(t) = Ev_i[T]/(k + t^2/\beta),\ t = \overline{-\infty, T}. \tag{8}$$

In formulas (6), (7) and (8) are mentioned: $Ev_i[T]$ the event underlying that operand; k is the coefficient of credibility; t is the time interval in which the coefficient of decisional influence is evaluated; β is the coefficient of decision stability.

The list of temporal logical operators is defined according to the functionality of the Smart City System. The following are some examples of temporal logic operators present in the most Smart City Systems:

1) $O(\vee^{\tau}) = \max\{Op_1(\tau),\ Op_2(\tau), \ldots,\ Op_I(\tau)\}$;
2) $O(\wedge^{\tau}) = \min\{Op_1(\tau),\ Op_2(\tau), \ldots,\ Op_I(\tau)\}$;
3) $O(\cup^{\tau}) = \cup\ \{Op_1(\tau),\ Op_2(\tau), \ldots,\ Op_I(\tau)\}$;
4) $O(\cap^{\tau}) = \cap\ \{Op_1(\tau),\ Op_2(\tau), \ldots,\ Op_I(\tau)\}$;

5. Spatial Logics Operators

Spatial logic operators present mathematical models for event processing $Ev[s]$, where $s \subset (X \cup Y \cup Z)$. The model and basic components of an operator are specified in the expression (9):

$$O(s): \{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s)\}, \quad (9)$$

where: $Op_j(s)$, $j = \overline{1,J}$ is the set of operands involved in the operator $O(s)$ and $s = \sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}$.

The operand model is defined by the expression (10):

$$Op_j(s) = \{Ev_j[s],\ p_j(s)\},\ j = \overline{1,J}, \quad (10)$$

where: $p_j(s)$ is the coefficient of decisional influence of the event $Ev_j[s]$ within the operand $Op_j(s)$.

For the evaluation of the coefficients $p_j(s)$ the formula is applied (11):

$$p_j(s) = 1/(k + s^2),\ s \in S, \quad (11)$$

where: k is the credibility coefficient of the event $Ev_j[s]$.

The following is a list of the most common space logic operators in the Smart City System:

1) $O(\vee^{s}) = \max\{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s)\}$;
2) $O(\wedge^{s}) = \min\{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s)\}$;
3) $O(\cup^{s}) = \cup\ \{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s)\}$;
4) $O(\cap^{s}) = \cap\ \{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s)\}$;

For the functional extension of the list of operators is possible a combination of temporal logic operands and spatial logic operands. The list of spatial-temporal logical operators is presented below:

1) $O(\vee^{st}) = \max\{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s),\ Op_1(t),\ Op_2(t), \ldots,\ Op_I(t)\}$;
2) $O(\wedge^{st}) = \min\{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s),\ Op_1(t),\ Op_2(t), \ldots,\ Op_I(t)\}$;
2) $O(\cup^{st}) = \cup\ \{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s),\ Op_1(t),\ Op_2(t), \ldots,\ Op_I(t)\}$;
2) $O(\cap^{st}) = \cap\ \{Op_1(s),\ Op_2(s), \ldots,\ Op_J(s),\ Op_1(t),\ Op_2(t), \ldots,\ Op_I(t)\}$;

The list of operators for data processing based on spatial-temporal logic can be extended in relation to the complexity of the developed Smart City System.

6. Economic Model of the Smart City Service System

The economic model of the Smart City Service System can be interpreted as a model of economic relations defined by game theory (Nash equilibrium) [16, 24, 25], in which two sets of agents are involved: *SDA* and *SCA*.

The profit P obtained by the set of *SDA* agents as a result of providing services for the set of *SCA* agents is calculated in relation to $k_{Sv[T]}$ and $k_{SQ[T]}$ from the expression (12):

$$P = \rho\left(k_{Sv[T]},\, k_{SQ[T]}\right), \tag{12}$$

where ρ is the calculation function.

The target objectives of the set of *SDA* agents are defined by the expression (13):

$$k_{Sv[T]} = \max_{s \in S}\left(v\left(k_{SQ[T]}, Sv[T], s, t\right)\right), \tag{13}$$

where v is the calculation function.

Whereas the target objectives of the set of *SCA* agents are defined by the expression (14):

$$k_{SQ[T]} = \max_{s \in S}\left(v\left(k_{Sv[T]}, SQ[T], s, t\right)\right), \tag{14}$$

where v is the calculation function.

Expressions (13) and (14) determine that the set of *SDA* agents will strive to provide with as many services as possible for the set of *SCA* agents, but the set of *SCA* agents will look for the solution to use the highest quality services offered by the set of *SDA* agents.

7. Conclusions

The research led in this paper is part of the development of distributed computing systems for Smart City Services. The functional logic of the system is based on spatial-temporal logic models in which the decision-making capacity of an event depends on its spatial position and its evolution over time.

The synthesis of the diagram for the Smart City Service System was performed. The decision-making functionality of the system is based on the presence of two subset of agents: Service Delivery Agents and Service Consumer Agents. Mathematical models of agents have been developed that include qualitative and quantitative parameters of decisional influence.

The functional logic of the Smart City Service system is based on the application of a set of temporal, spatial or spatial-temporal logic operators. An operator includes a lot of operands for which mathematical models of spatial-temporal evolution have been developed. An operand characterizes an event.

The economic model of the system is presented as a relationship between the subset of agents that provide as many services as possible and the subset of agents that consume high quality services.

There are planned researches in the development of the system at the level of hardware and software architecture for the future.

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References

1. D'Aniello, G.; Gaeta, M.; Orciuoli, F.; Sansonneti, G.; Sorgente, F. Knowledge-Based Smart City Service System. *Electronics* 2020, 9, pp. 965.
2. Hidayat, T.; Suhardi, N.; Kurniawan, B. Smart city service system engineering based on microservices architecture: Case study: Government of Tangerang city. In *Proceedings of the 2017 International Conference on ICT For Smart Society (ICISS),* Tangerang, Indonesia, 18–19 September 2017, pp. 1–7.

3. Polese, F.; Botti, A.; Monda, A.; Grimaldi, M.: Smart City as a Service System: A Framework to Improve Smart Service Management. *J. Serv. Sci. Manag.* 2019, 12, pp. 1–16.
4. Gomila, A.; Muller, V.C. Challenges for Artificial Cognitive Systems. *Journal of Computer Science* 2012, 13, pp. 453-469.
5. Langus, A.; Nespot, M. Cognitive Systems Struggling for Word Order. *Cognitive Psychology* 2010, 60, pp. 291-318.
6. Hwang, K.; Fox, G.C.; Dongarra, J.J. *Distributed and Cloud Computing*. Ed. Elsevier, 2012, 670p.
7. Talekar, B.; Chaudhari, S.; Shinde, V. Distributed Computing Challenges. *IOSR Journal of Computer Engineering* 2014, 16 (2), pp. 28-31.
8. Ahire, K.N. Distributed Computing – Future and Applications. *International Research Journal of Engineering and Technology* 2017, 4(10), pp. 2005-2007.
9. Byrski, A.; Drezewski, R.; Siwik, L.; Kisiel-Dorohinski, M. Evolutionary Multi-Agent Systems. *The Knowledge Engineering Review* 2015, 30(2), pp. 171-186. 2015.
10. Rocha, J. *Multi-Agent Systems*. Ed. InTechOpen, 2017, 218 p.
11. Chen, L.; Huepe, C.; Gross, T. Adaptive Network Models of Collective Decision Making in Swarming Systems. *Phys. Rev. E* 2016, 94, 022415.
12. Ertel, W. *Introduction to Artificial Intelligence*. Ed. Springer, 2011, 317p.
13. Poole, D.L.; Mackworth, A.K. *Artificial Intelligence: Foundations of Computational Agents*. Ed. Cambridge University Press, 2010, 662p.
14. Van Benthem, J.; Pacuit, E. Temporal Logics of Agency. *Journal of Logic, Language and Information* 2010, 19(4), pp. 389-393.
15. Kontchakov, R.; Kurucz, A.; Wolter, F.; Zakharyaschev, M. Spatial Logic + Temporal Logic. Capter 1. *Handbook of Spatial Logics,* 2007, 73p.
16. Ababii, V.; Sudacevschi, V.; Munteanu, S.; Bordian, D.; Calugari, D.; Nistiriuc, A.; Dilevschi, S. Multi-Agent Cognitive System for Optimal Solution Search. In *The International Conference on Development and Application Systems (DAS-2018)*, 14th Edition, May 24-26, 2018, Suceava, Romania, pp. 53-56.
17. Eiben, A.E.; Smith, J.E. *Introduction to Evolutionary Computing*. Second Edition, Springer, 2015, 287p.
18. Coello, C.A.; Lamont, G.B.; Van Valdhuizen, D.A. *Evolutionary Algorithms for Solving Multi-Objective Problem*. Second Edition, Springer, 2007, 800 p.
19. Mashwani, WK.; Salhi, A.; Asif, M.; Sulaima, M.; Khanum, R.A.; Algarni, A. Evolutioary Algorithms Based on Decomposition and Indicator Factions: State-of-the-art Survey. *International Journal of Advanced Computer Science and Applications* 2016, 7(2), pp. 583-593.
20. Munteanu, S.; Sudacevschi, V.; Ababii, V.; Braniste, R.; Turcan, A.; Leashcenco, V. Cognitive Distributed Computing System for Intelligent Agriculture. *International Journal of Progressive Sciences and Technologies* 2021, 24(2), pp. 334-342.
21. Ababii, V.; Sudacevschi, V.; Munteanu, S.; Alexei, V.; Melnic, R.; Turcan, A.; Struna, V. Cognitive Distributed Computing System Based on Temporal Logic. In *Proceedings of Workshop on Intelligent Information Systems WIIS-2021*, October 14-15, 2021, Chisinau, Republic of Moldova, pp. 16-25.
22. Munteanu, S.; Sudacevschi, V.; Ababii, V.; Borozan, O.; Ababii, C.; Lasco, V. Multi-Agent Decision Making System based on Membrane Computing. In *The 11th IEEE International Conference on Intelligent Data Acquisition and Advanced Computing Systems: Technology and Applications*. 22-25 September 2021, Cracow, Poland, 2021, 2, Vol. 2. pp. 851-854.
23. Ababii, V.; Sudacevschi, V.; Munteanu, S.; Borozan, O.; Nistiriuc, A.; Lasco; V. IoT based on Membrane Computing Models. In *Proceedings of the 13th International Conference on Electromechanically and Energy Systems (SIELMEN-2021); 7-8 October; 2021*, Chisinau, Republic of Moldova, 2021, pp. 010-014.
24. Ababii; V.; Sudacevschi; V.; Braniste; R.; Nistiriuc; A.; Munteanu; S.; Borozan; O. Multi-Robot System Based on Swarm Intelligence for Optimal Solution Search. In *The International Congress on Human-Computer Interaction; Optimization and Robotic Applications; HORA-2020*, June 26-28; 2020; Ankara; Turkey, 2020, pp. 269-273.
25. Suleiman; R. Economic Harmony—A Rational Theory of Fairness and Cooperation in Strategic Interactions. *Games* 2022, 13 (34), 21p.

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A NOVEL CLASSIFICATION WITH DEEP CONVOLUTIONAL NEURAL NETWORKS ON PULMONARY NODULE

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Abstract. Medical images are an important part of a patient's health record, and they need data manipulation, processing, and handling by computers. As a result, medical data is a type of bigdata, and its analysis has become complex. Because manual disease diagnosis takes longer and produces less accurate results, it may result in incorrect treatment. Three DCNN architectures have been exploited and evaluated for tumor detection and classification. The sample image for the experimentation is chosen from Lung Image Database Consortium (LIDC) with Image Database Resource Initiative (IDRI) and Kaggle dataset which consists of normal and abnormal image. The experimental results of proposed DCNN classifier achieved best accuracy than the GoogleNet, AlexNet, Artificial neural network and support vector machine.

Keywords: *Lung cancer, DCNN, LIDC and GoogleNet, AlexNet.*

Rezumat. Imaginile medicale sunt o parte importantă a dosarului de sănătate al pacientului și necesită manipularea, procesarea și manipularea datelor de către computere. Drept urmare, datele medicale sunt un tip de *bigdata*, iar analiza lor a devenit complexă. Deoarece diagnosticarea manuală a bolii durează mult și produce rezultate mai puțin precise, aceasta poate duce la un tratament incorect. Trei arhitecturi DCNN au fost exploatate și evaluate pentru detectarea și clasificarea tumorilor. Imaginea eșantion pentru experimentare este aleasă din *Lung Image Database Consortium* (LIDC) cu *Image Database Resource Initiative* (IDRI) și setul de date Kaggle care constă dintr-o imagine normală și anormală. Rezultatele experimentale ale clasificatorului DCNN propus au obținut mai bună acuratețe decât GoogleNet, AlexNet, rețeaua neuronală artificială și mașina de suport vector.

Cuvinte cheie*: cancer pulmonar, DCNN, LIDC și GoogleNet, AlexNet.*

1. Introduction

The Lung tumor detection and classification is one of the most difficult tasks in medical image processing due to the wide variation in tumor density, size, and location, as well as the low contrast of the scanned image. Because it directly affects human mortality,

the accuracy of such a classification system should be high. When the volume of input is large, the existing classifier performs poorly. As a result, there is a need to develop an algorithm that provides greater accuracy in lung tumor detection and classification.
Tumors' unpredictable appearance makes detecting their presence, as well as determining shape and size, difficult tasks in medical image analysis. Medical images are prone to contrast and luminance issues, resulting in very low image quality and degraded image features. As a result, it is critical to develop an algorithm that combines image enhancement and segmentation to solve the segmentation problem.

2. Survey of the work

SVM classifier for predicting lung tumors. Image denoising was performed using variation-based denoising, followed by optimal thresholding and morphological-based segmentation. SVM classifier was used to classify lung tumors. Pixels within the very dense body and chest wall structures have a different density distribution than low-density pixels [1]. The region of interest is a lung nodule, and a labelling algorithm is used to extract the region. Correlation, homogeneity, energy, contrast, and area were extracted as texture and region features.

A hyper plane represents the largest separation or margin between the two classes in an SVM linear classifier used for tumor classification. When tested on a large image database, this classification algorithm performs less well [2].

Eigengene extraction via Independent Component Analysis (ICA) is one method for tumor classification feature extraction. A novel approach for tumor classification based on eigengene and SVM-based Classifier Committee Learning (CCL) algorithm. The algorithm must still investigate the design of an effective approach for optimal results [3].

SVM classifier for classifying cancer stages. Image features are extracted after preprocessing. Then, for classifying medical images, the support vector machine algorithm is used. When the input data became large, processing time was required, and it was suspected to be notoriously redundant [4].

By applying the kernel trick to maximum margin hyper planes, a nonlinear classifier was created. Kernel functions of various types were used, including polynomial, quadratic, and Multi-Layer Perceptron (MLP). SVM produces better classification results [5-7]. They combine generalization control with a method for dealing with the curse of dimensionality. The kernel mapping provides a unifying framework for the majority of the model architectures that are commonly used. When the number of images used in the testing process increases, the accuracy of image enhancement must improve [8-10].

A two-stage CAD system for automatically detecting and classifying MRI brain tumors. The system classified brain tumor images as normal or abnormal. The abnormal MRI is then used to determine whether the tumor is benign or malignant [11-14]. K-means clustering is used for image segmentation, DWT is used for feature extraction, and PCA is used for feature reduction. The feature reduction method is used after feature extraction to select the relevant features. Classification was used to determine whether an image was normal or abnormal [6]. This system was tested for brain image classification, which had not previously been done for the other modalities. ANN is used to create a system for detecting and classifying brain cancer. The main issue in detecting the edge of a tumor is that the tumor appears very dark on the image. Histogram equalization was used to solve this problem [15-16]. Segmentation is the process of dividing an image into its constituent parts or objects.

Deep learning architecture for classifying medical images of anatomy objects in a modified CNN architecture with different convolutional and pooling layers used for feature learning in the modified CNN architecture [7]. The outcomes were compared to existing architectures such as LeNet, AlexNet, and GoogLeNet. a pulmonary CT image classification using a hybrid 3D-DCNN architecture. This CNN architecture was implemented with various layers, and the results were compared to 3D-AlexNet and 3D-GoogleNet.

3. Layout of Proposed Work

DCNN architecture 2 is made up of thirteen layers: seven convolutional layers, four pooling layers, a fully connected layer, and a SoftMax classifier. All convolutional layers have a filter size of 5 5 and pooling layers have a filter size of 2 2. In convolutional layers, the number of filters on feature maps is 64, 96, 128, 192, and 256, respectively. Similarly, DCNN architecture 3 has seven convolutional layers, four pooling layers, two fully connected layers, and a SoftMax classifier. In the first convolutional layer, 64 filters with 5 5 filter size are applied to 256 256 patch size input images. By applying 2 2 filters, the max pooling layer reduces the output size of the previous convolutional layer. The first pooling layer's output image size is 126126; this image is passed to the second and third convolutional layers, which apply 98 and 128 filters to the image, respectively. Following that, max pooling is used, resulting in an output image size of 5959. Initially, DCNN architecture 1 was implemented with a small number of layers, yielding good results up to a thousand images. Accuracy decreases as the number of images in the dataset grows. As a result, two additional DCNN architectures are implemented in this work that shows in Figure 1.

To improve accuracy, the number of convolutional and pooling layers is increased in this architecture compared to architecture 1. Approximately ten thousand images were tested with these classifiers and yielded better results. Similarly, the fourth and fifth convolutional layers with 128 and 192 filters are applied to the down sampled images with the third max pooling layer, yielding a 2525 feature map. The model progresses through the remaining layers until it reaches fully connected layers, where all neurons are connected to all neurons of the previous layer.

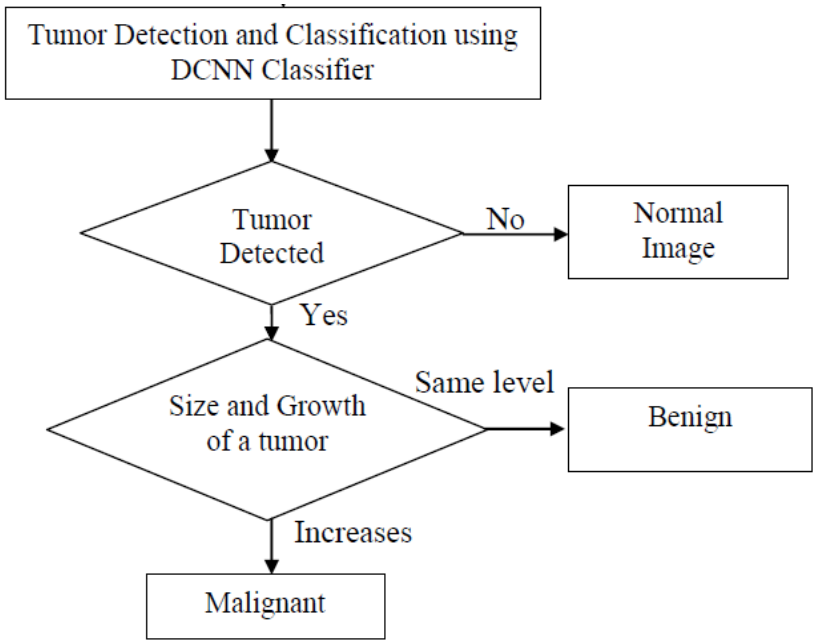

Figure 1. Proposed system flow.

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DCNN consists of two important layers:

1. Input layer
2. Classification layer

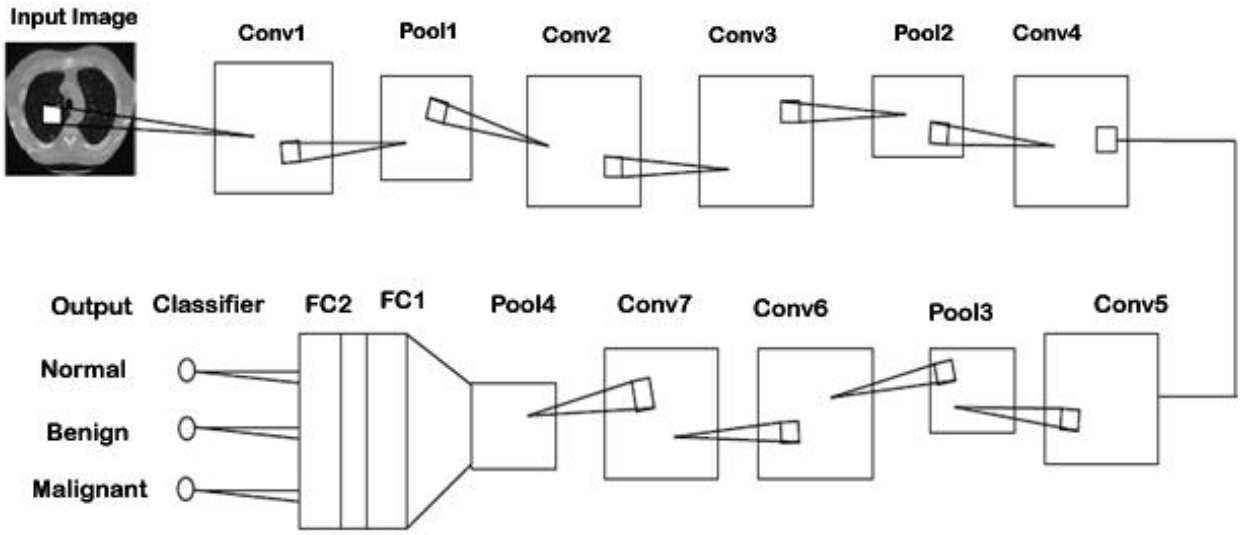

Figure 2. Proposed DCNN Architecture 3.

Finally, the SoftMax classifier is used to determine whether the images are normal, benign, or malignant. The accuracy of the second architecture is higher than that of the first. In addition, one fully connected layer with the same layer descriptions and hyperparameters is included in architecture 3 shows in Figure 2.

4. Results and Discussion

From the result, 85.02% accuracy rate obtained in the proposed architecture 3 which is higher than other two architectures. The second-best accuracy rate is 84.34% and the next better accuracy rate achieved by 83.53% of the proposed architecture 2. By considering of all three architectures, the architecture 3 used a greater number of convolutional and fully connected layers it leads to extract more features and resulted in received higher accuracy rate. Graphical representation of accuracy comparison is presented in the Figure 3.

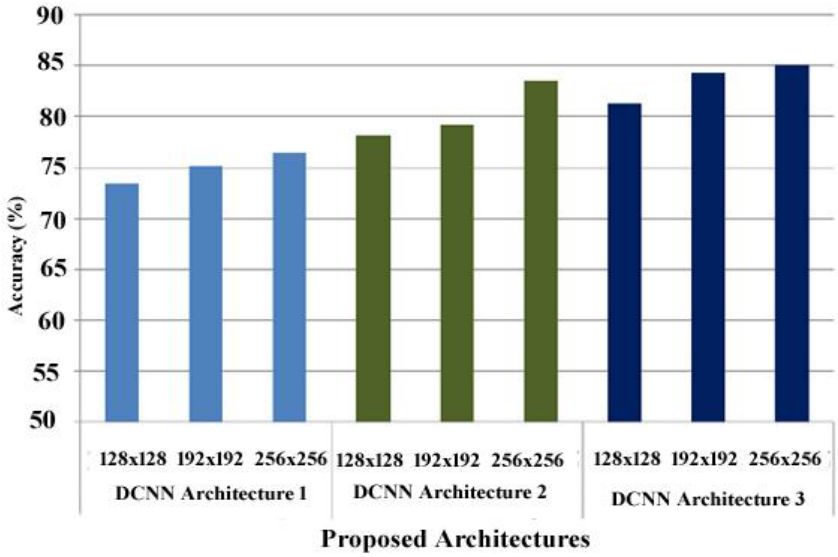

Figure 3. Accuracy of three proposed DCNN Architectures.

Precision is calculated for all three architectures using 9696, 128 128, 192192, and 256 256 patches, in that order. The results show that architecture 1 had a higher true positive prediction rate in 128 128 patches, but this rate gradually decreased as patch size increased. The architecture 2 received better results in 128 128 and 256 256 patches, but the true positive rate gradually increased in architecture 3, which also produced better results when compared to the other two architectures, as shown in Figure 4.

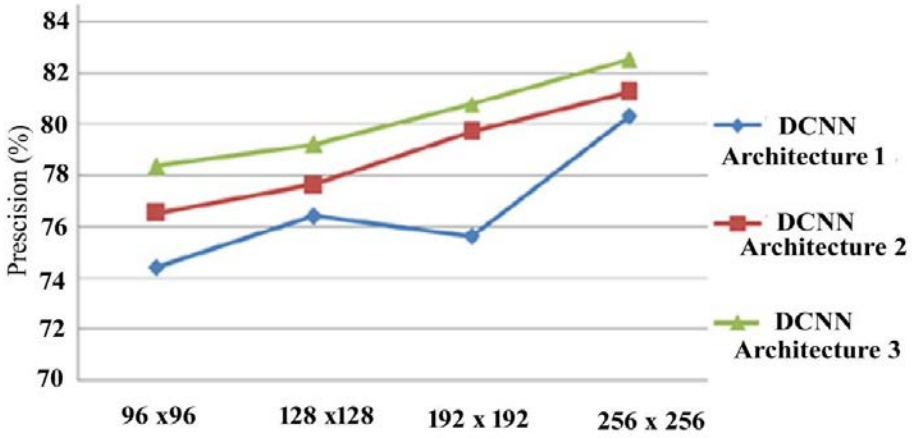

Figure 4. Precision Comparison for proposed architectures.

The results show that the GoogleNet achieved higher precision of 82.43%, recall of 83.55% and Specificity of 84.77% compared to AlexNet architecture, but the proposed architecture is obtained higher precision, recall and specificity than the GoogleNet architecture shown in Figure 5.

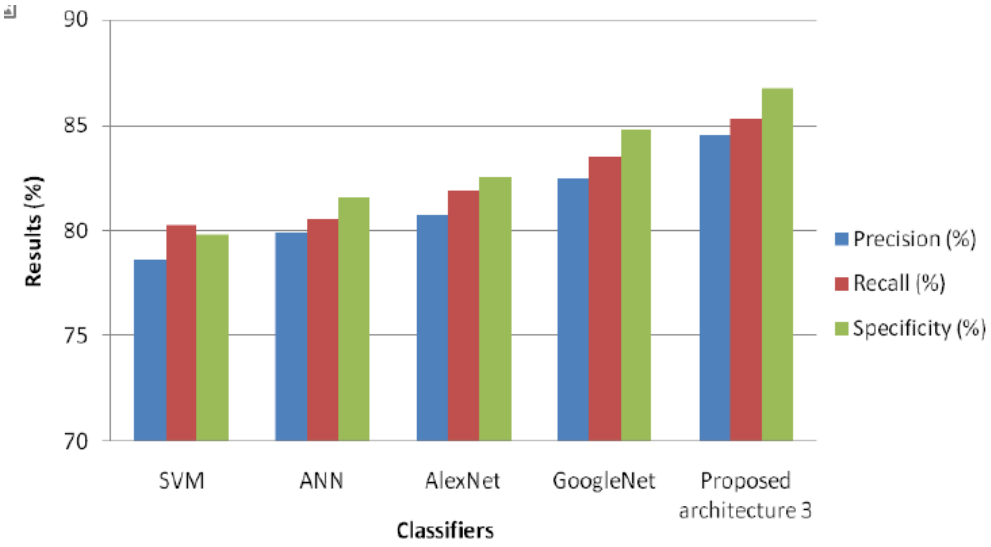

Figure 5. Performance of proposed DCNN architecture with existing algorithm.

5. Conclusions

Deep learning-based algorithms are currently emerging in the field of medical image classification. Deep learning-based DCNN architectures for CT lung image detection and classification were presented in this section. The layers of deep learning architecture were discussed in detail, along with the proposed three types of DCNN architectures. This section describes the hyperparameters used in the proposed architectures, as well as the input and output feature sizes. The proposed DCNN architectures take a CT lung image as input and

classify it as normal, benign, or malignant. The experimental results show that the proposed architecture 3 outperforms other existing architectures in terms of accuracy, precision, recall, and specificity for CT lung image classification. In the future, the proposed HPSO algorithm can be tweaked to produce higher accuracy with a shorter execution time. HPSO parameters such as the number of iterations and particles can be optimized to produce better image quality

Conflicts of Interest. The authors declare no conflict of interest.

References

1. Krizhevsky, A.; Sutskever, I.; Hinton, G.E. Imagenet classification with deep convolutional neural networks. *Advances in neural information processing systems* 2012, 25, 9 p.
2. Jain, M.; Tomar, P.S. Review of image classification methods and techniques. *International Journal of Engineering Research and Technology* 2013, 2 (8), pp. 852-858.
3. Mehena, J.; Adhikary, M.C. Brain Tumor Segmentation and Extraction of MR Images Based on Improved Watershed Transform. *IOSR Journal of Computer Engineering* 2015, 17(1), pp. 1-5.
4. Lingayat, N.S.; Tarambale, M.R. A Computer Based Feature Extraction of Lung Nodule in Chest X-Ray Image. *International Journal of Bioscience, Biochemistry and Bioinformatics* 2013, 3(6), pp. 624.
5. Sangamithraa, P.B.; Govindaraju, S. Lung tumour detection and classification using EK-Mean clustering. In *International Conference on Wireless Communications, Signal Processing and Networking (WiSPNET)* 2016 Mar 23, 2016, pp. 2201-2206.
6. Makaju, S.; Prasad, P.W.; Alsadoon, A.; Singh, A.K.; Elchouemi, A. Lung cancer detection using CT scan images. *Procedia Computer Science*, 2018, 125, pp. 107-114.
7. Cao, W.; Li, J.; Liu, J.; Zhang, P. Two improved segmentation algorithms for whole cardiac CT sequence images. In 9th International Congress on Image and Signal Processing, BioMedical Engineering and Informatics (CISP-BMEI) 2016 Oct 15, pp. 346-351.
8. Peschl, H.; Han, D.; Van Ooijen, P.; Oudkerk, M.; Dorrius, M.; Rook, M.; Vliegenthart, R.; Heusse, C. P.; Batora, N.; Kauczor, H.; Da Silva, C.; Von Stackelberg, O.; Rubtsov, R.; Wielputz, M.; Ather, S.; Tsakok, M.; Arteta, C.; Pickup, L.; Hussain, S.; Gleeson, F. Lung Cancer Prediction Using Deep Learning Software: Validation on Independent Multi-Centre Data. *Journal of Thoracic Oncology* 2018, 13(10), S428.
9. Baldwin, D.R.; Gustafson, J.; Pickup, L.; Arteta, C.; Novotny, P.; Declerck, J.; Kadir, T.; Figueiras, C.; Sterba, A.; Exell, A.; Potesil, V.; Holland, P.; Spence, H.; Clubley, A.; O'Dowd, E.; Clark, M.; Ashford-Turner, V.; Callister, M.E.; Gleeson, F.V. External validation of a convolutional neural network artificial intelligence tool to predict malignancy in pulmonary nodules. *Thorax*. 2020, 75(4), pp. 306-312.
10. Ardila, D.; Kiraly, A.P.; Bharadwaj, S.; Choi, B.; Reicher, J.J.; Peng, L.; Tse ,D.; Etemadi, M.; Ye, W.; Corrado, G.; Naidich, D.P.; Shetty, S. End-to-end lung cancer screening with three-dimensional deep learning on low-dose chest computed tomography. *Nat Med*. 2019, 25(6), pp. 954-961.
11. Coudray, N.; Ocampo, P.S.; Sakellaropoulos, T.; Narula, N.; Snuderl, M.; Fenyö, D.; Tsirigos, A. Classification and mutation prediction from non–small cell lung cancer histopathology images using deep learning. *Nature medicine* 2018, 24(10), pp. 1559-1567.
12. Bhatia, S.; Sinha, Y.; Goel, L. Lung cancer detection: a deep learning approach. In *Soft Computing for Problem Solving*. Ed. Springer, Singapore, 2019, pp. 699-705.
13. Abdullah, D. M.; Ahmed, N. S. A review of most recent lung cancer detection techniques using machine learning. *International Journal of Science and Business* 2021, 5(3), pp. 159-173.
14. Chen, C. L.; Chen, C. C.; Yu, W. H.; Chen, S. H.; Chang, Y. C.; Hsu, T. I.; Chen, C. Y. An annotation-free whole-slide training approach to pathological classification of lung cancer types using deep learning. *Nature communications* 2021, 12(1), pp. 1-13.
15. Tian, P.; He, B.; Mu, W.; Liu, K.; Liu, L.; Zeng, H.; Li, W. Assessing PD-L1 expression in non-small cell lung cancer and predicting responses to immune checkpoint inhibitors using deep learning on computed tomography images. *Theranostics* 2021, 11(5), pp. 2098.
16. Al-Yasriy, H. F.; Muayed, A. H. The IQ-OTHNCCD lung cancer dataset. *Mendeley Data* 2020, 1.

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NANOTECHNOLOGY: REFLECTIONS ON HEALTH BENEFITS AND RISKS

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Abstract. There is a constant increase in the demand for engineers who can transform nanotechnology from a scientific result into a commercial solution. However, new technologies often caused conflicts between those who want to exploit them as soon as possible and those who are waiting to receive absolute proof of safety. Certain types of nanoparticles are well studied and recommended for use in medicine, biology, chemistry, cosmetology, etc. Some nanoparticles are proven to be extremely toxic, with drastically different properties from the same volume compounds. The risks associated with using nanotechnologies and products containing nanoparticles cannot be minimized in the absence of regulations, which would allow adequate control to protect the environment and the population's health. Companies are also extremely careful in investing in this field as long as there is no transparent regulation, as the ultimate goal is to protect the surrounding environment and society. In this paper, we present an overview of the benefits of nanotechnology in areas that affect human health, as well as the risks that may arise from the early use or ill-will of nanotechnologies.

Keywords: *nanotechnology, applications, biomedical engineering, impact, risk, regulation.*

Rezumat. Există o creștere constantă a cererii pentru ingineri care pot transforma nanotehnologiile din rezultate științifice în soluții comerciale. Dar tehnologiile noi totdeauna au generat conflicte între cei care doresc să le exploateze cât mai repede posibil și cei ce sunt în expectativă să primească dovezi absolute de siguranța lor. Anumite tipuri de nanoparticule sunt bine studiate și utilizate sau recomandate pentru utilizare în medicină, biologie, chimie, cosmetologie. Multe nanoparticule se dovedesc a fi extrem de toxice, cu proprietăți radical deosebite de aceiași compuși în starea de volum mai mare. Riscurile legate de utilizarea nanotehnologiilor si a produselor care conțin nanoparticule nu pot fi minimizate în lipsa unor reglementări ce ar permite un control pentru a proteja sănătatea populației și mediului. Companiile sunt extrem de precaute în a investi în domeniul nanotehnologiilor atât timp cât nu există reglementări transparente deoarece este vorba de protecția oamenilor și mediului care-l înconjoară. Prezenta lucrare este o trecere succintă în revistă a beneficiilor nanotehnologiei în domeniile ce influențează sănătatea omului, precum și a riscurilor ce pot apărea din utilizarea precoce sau din rea-voință a nanotehnologiilor.

Cuvinte cheie: *nanotehnologie, aplicații, inginerie biomedicală, impact, risc, reglementare.*

1. Introduction

Nanoscience is the convergence of physics, materials science, and biology, which deals with handling materials on an atomic and molecular scale. Nanotechnology and nanoengineering represent the ability and process to measure, manipulate, assemble, control, and manufacture nanoscale matter. This science is relatively new and consists of known processes, as well as new unknown processes. Therefore, it is not surprising that there is no clear public perception of this topic: on the one hand there is the fear of the unknown as a potential source of danger, and on the other hand is the potential for good. The ability to deal with the matter at the atomic or molecular level allows for a deeper understanding of physical phenomena and control over the functionality of new devices.

In the paper [1] there is a mention, that time ago M.C. Roco predicted the following four stages in the development of nanotechnology products:

- passive nanostructures, passive properties of nanomaterials, including nanotubes and nanolayers, which provide more opportunities to renew products in everyday life;
- active nanostructures, which can change their state during use in a predictable way;
- nanosystems - nanorobotics, nanobiotechnologies, information nanotechnologies;
- molecular nanosystems are the most advanced by the intelligent design of devices at the molecular, atomic, and quantum effects level.

Nanotechnology, nanoengineering, and their microscopic universe are the globalization product with large investments for research and development around the world, already representing a huge industry. The global nanotechnology market was estimated at $1.76 billion in 2020, increasing to $100 billion in 2030. Nanomaterials offer a wide range of functionalities due to their physical and chemical properties manifested in their new state. These offer new methods in diagnosis, therapy, and in healthcare monitoring, with opportunities to solve unanswered medical problems. The applications of nanotechnology in energy, agricultural, food, consumer products, transport, logistics, and environmental sectors are also growing rapidly. The fastest growing domains are expected to be health, nanoelectronics, energy, aerospace, and defense. The USA, Brazil and Germany are expected to lead the nanotechnology industry in 2024, with a significant presence in the top countries such as Japan, China, South Korea and India.

Regarding the rapid development of nanotechnologies, we note that in 2019, over 40% of scientific publications on nanoscience came from China, followed by the USA and India. When it comes to patents, in 2019 the US had the most active market in the world for nanotechnology innovations (8900 patents filed), followed by the EU, China and South Korea.

From the dynamics of the infiltration of nanotechnologies in practically all the fields that influence our life, it is paramount that the regulations are aligned with the evolutions. The safety assessment of nanomaterials is an important process and we expect this to be safe by design. For these reasons, researchers, innovative engineers and regulators are best placed in developing guidelines for toxicological assessments and analytical methods to implement new definitions and various regulatory requirements.

2. Diversity of nanotechnology application in the vital area

To understand the impact of nanotechnology on human health, we analyze a predictable roadmap for nanotechnology (Figure 1). We note the usefulness of both phases, both the initial manufacturing process (obtaining new material, measurements and characterizations, attempts at technology transfer in various fields) and the final process of

developing the architecture of nanodevices and possible applications (operating theories, modeling, formation of functional biochemical systems, new approaches).

The prospects for nanoscience, nanoengineering and nanotechnology are promising to the society and at the same time these achievements can be recognized as potential threats to humans in the lack of knowledge.

There are virtually no areas of activity that are not influenced by advances in nanotechnology and nanoengineering.

And all of them have an impact on human health, including those in the telecommunications, chemical, textile, automotive, etc. industries [2-8]. In our analysis we will refer exclusively to those areas (Figure 2), which we consider having a major impact on human health.

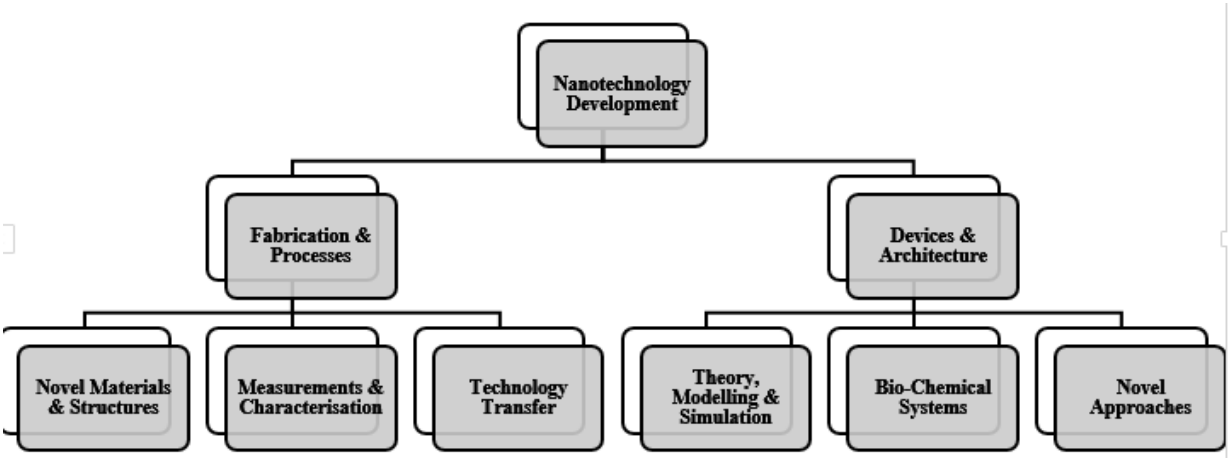

Figure 1. Predictable phases of nanotechnology development.

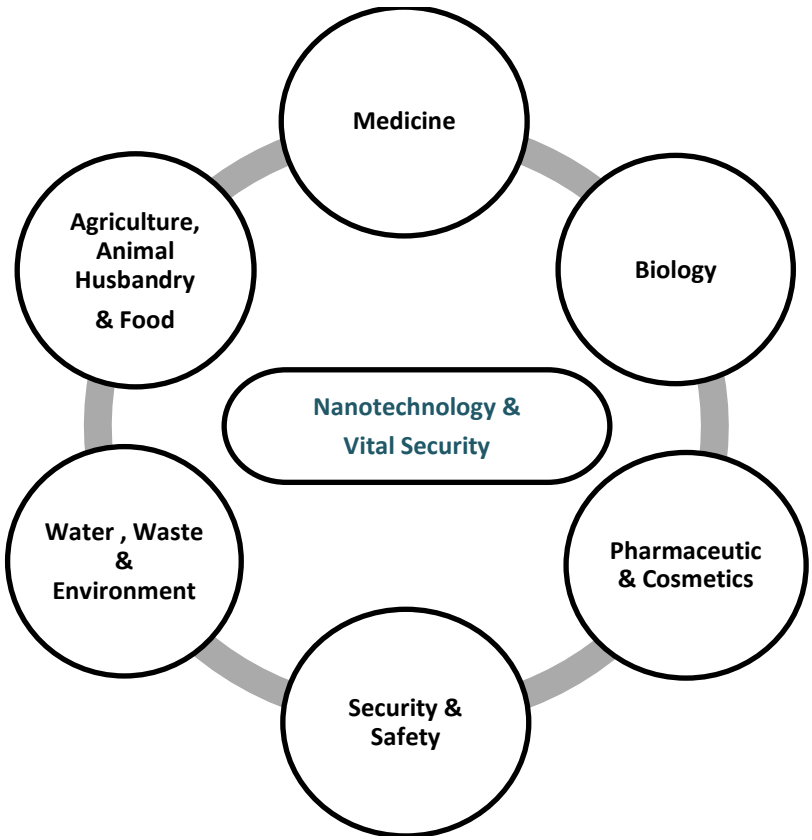

Figure 2. Nanotechnologies and vital security.

3. Nanotechnology and the environment

Nanoparticles (NPs) have been recommended as extremely useful for the protection and cleaning of the environment [8, 9]. There are applications of selective membranes that can filter contaminants or even salt from water, or nanostructured traps to remove pollutants from industrial effluents. Monitoring and characterization of the environment are performed using nanosensors, and nanostructured intelligent sensory systems (Figure 3). Nanomaterials contribute to significant reductions in the consumption of materials and energy, while the sources of pollution are maintained, and the need for industry maintenance determines increased opportunities for recycling [9]. Therefore, there is a potential to reduce environmental pollutants.

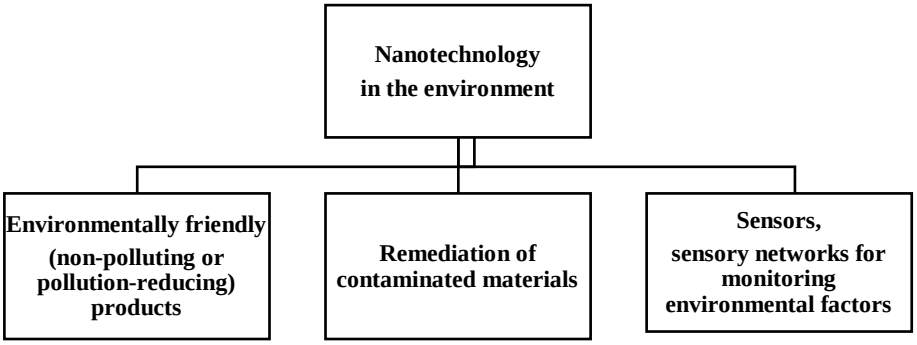

Figure 3. Nanotechnology in the environment.

However, we also identify the negative side due to reasons such as insufficient regulation, drastic growth of the nanotechnology industry, and the use of NPs in various fields that reside through the uncontrolled release of NPs into the environment. For these reasons, the assessment of the risk of NPs in the environment must be performed in terms of their mobility, reactivity, ecotoxicity and persistence. In the absence of rigorous control, nanoengineering applications increase the concentration of nanopollutants in groundwater and soil, which are the most common routes of exposure for environmental risk assessment.

Due to the high ratio of surface to mass NP, the distribution of the contaminant in the solid/water environment will be dictated by the absorption at the natural NP surface, the aggregation of the NP, or the co-precipitation at NP formation. The interaction of contaminants with NP is complex depending on the physicochemical characteristics such as size, chemical composition, morphology, porosity, state of aggregation/disaggregation, surface reactivity, surface loads, and surface passivation. In addition, environmental characteristics such as pH, temperature and light intensity affect the toxicities of some nanostructures. The same nanomaterial, but with different geometry: diameter, length, crystal structure and different surface modification, will have different toxicities.

The environmental pollution with nanoproducts represents a major problem with unpredictable consequences. Although many nanoproducts are considered harmless (e.g. nanoelectronics), their tiny size being scattered volens-nolens in the environment can cause serious consequences, which we do not know yet. Let's take a simple example, a drug in the form of nanopowder or nanodrage, useful for a person, but out of hand, or thrown away at the expiration of the easy time will pollute the atmosphere and cause unpredictable consequences for a healthy person. As a new source of pollution, nanotechnologies need to be given additional attention through appropriate regulations, following various research on ecological toxicity.

4. Nanotechnology, agriculture, and animal husbandry

The focus on sustainable agriculture argues for the implementation of the ecosystem method, in which abiotic-biotic living beings are in harmony with coordinated stability of food chains and their energy balances. Nanotechnology is one of the most effective solutions in achieving this goal by using nano- fertilizers, nanopesticides, nanoherbicides, etc. [13]. Water treated with nanotechnologies used for seed softening, irrigation, dilution of agrochemicals and fertilizer treatment positively influences the rate and condition of seed germination, seedling quality and crop yield and quality.

Plant genetic engineering leads to personalized benefits, such as increased crop yields currently achieved through the scientific application of NP chemicals. Nanotechnology is widely used in various ways (Figure 4) to improve agricultural production. Nanopesticides and nano-fertilizers have been shown to have little, or no toxicity due to much smaller and strictly dosed calculated amounts, while improving the effects [13, 19]. The control efficiency of biopesticides on a nanoscale is one to three times higher than that of regular pesticides when the dose was the same, reducing the cost by half.

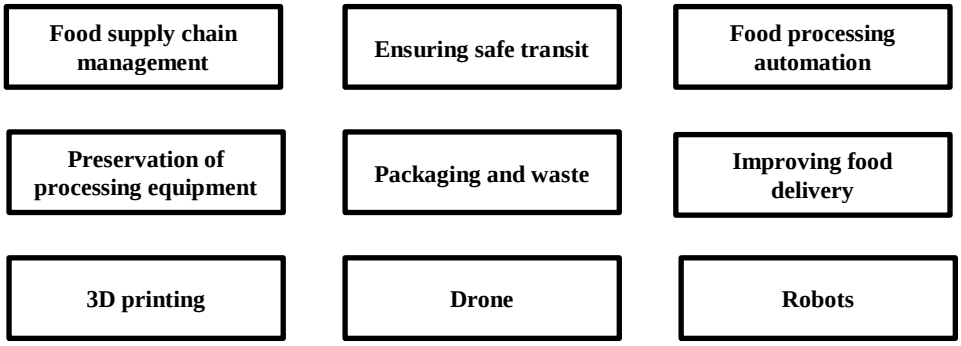

Figure 4. Nanotechnology in the food industry.

Nanofungicides and nanoinsecticides have considerable potential that was not yet been sufficiently explored in agriculture and nanotechnology-based delivery systems. Nanotechnologies have the increased ability to inhibit or kill various types of microbes and are useful in the environmental disinfecting. Also, NPs are useful for monitoring microelements in soil and plants, detecting soil toxins, detecting, and diagnosing crop diseases. The sensitivity of nanodevices can be used for the rapid, economical, and efficient detection of phytopathogens, thus reducing the chance of large-scale destruction of crops.

Nanotechnology is used in animal husbandry to improve the diagnosis, treatment, delivery of medicines, food preservation, reproduction, monitoring, and improvement of animal health, as well as for higher quality production [10, 14]. Nanobiocides are recommended to be effective in disinfection, disinsection, and rodent control procedures that contribute to sustainable and ecological agriculture.

5. Nanotechnologies in civil security

There is practically no civilian or military field in which nanotechnologies don't have applications. As research is the mainstay of identifying new applications of nanotechnology, it has become a key research priority since the EU's Sixth Framework Program for RTD (FP6, 2002-2006) containing projects targeting security applications. The applications of nanotechnology for civil security in FP6 covered four areas: detection, protection, identification, and assessment of societal consequences.

Direct or indirect detection (including imaging, sensory/sensory networks) of radiation, pathogens, and chemicals refers to the detection of viruses, bacteria, DNA, RNA, proteins, and nucleotides to prevent acts of bioterrorism, chemicals, industrial harmful gases, ionizing radiation, but also to other harmful electromagnetic waves, etc. [15-19, 45].

Detection devices for civil security were progressively influenced by the advances in nanotechnologies and we classify them arbitrarily into three categories:

- X-ray imaging, IR detection, and the emerging field of imaging at THz wavelengths;
- direct or indirect detection sensors of biological and chemical agents. We assign nanotubes and nanowires to direct detection sensors and electrical and electromechanical, colorimetric, quantum dots to sensors with indirect detection. Biological barcodes, consoles for the detection of biomolecules, and microorganisms we also assign to this category;
- polyfunctional smart miniature sensor networks (smart dust).

Referring to *protection devices* we note improved nanomaterials with new physical properties and functionalities, including higher strength and durability, built-in sensory capabilities and active materials.

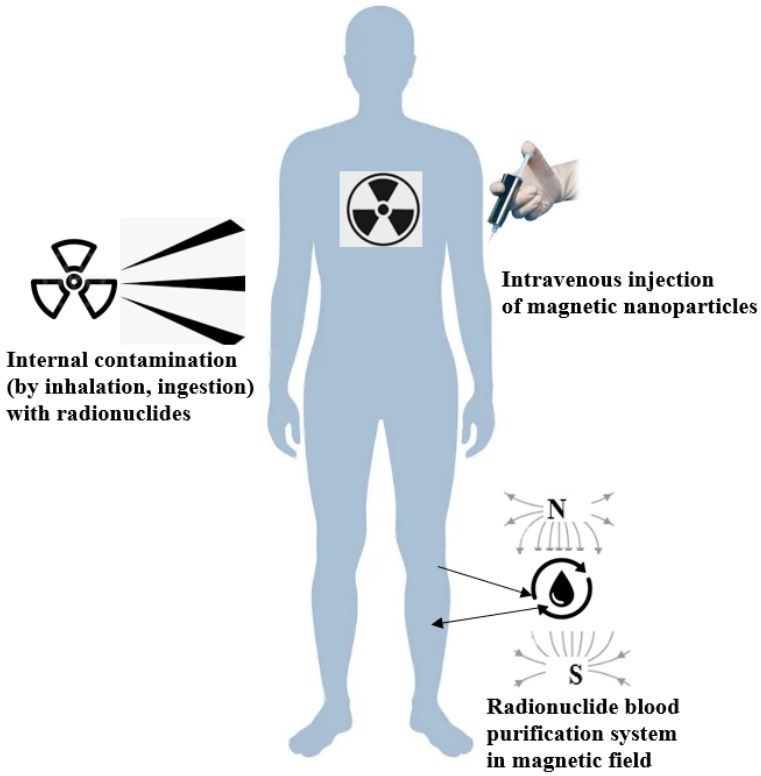

Figure 5. Example of blood purification of radionuclides with intelligent NP (adaptation from [45]).

In terms of civil security applications, nanodevice protection devices mainly benefit from the following functional materials:

- the advanced physical-mechanical, thermal, chemical resistance and low specific weight for flexible anti-ballistic textiles; reactive nanoparticle armor; shock absorber nanotubes; nanofibers, clothing and nano-coatings for biological products or chemical decontamination; switchable fabrics or materials to improve thermal control and fire protection etc.;

- smart, containing integrated nanosensors, reactive elements, intelligent materials for diffusion control and active transport of mass or electric charge control; smart NPs that recognize, capture, incorporate, eliminate, or destroy certain toxins or radionuclides. For example, at intravenous injection, biodegradable nanospheres circulate through the bloodstream, where surface proteins bind to targeted radionuclides. Nanospheres with identified and captured toxins are removed from the bloodstream through a small inserted into an artery shunt. The magnetic field applied to the shunt (Figure 5) immobilizes the Fe-based particles with radionuclides allowing the direction of the cleaned blood in the blood flow [45];
- shielding or absorption of electromagnetic interference in electromagnetic radiation fields, depending on wavelengths.

Nanotechnology is effective in the national security field by introducing smart weapons and nanosensors. But this also represents a major disadvantage of nanotechnology. Increasing the functionality or capability of weapons, such as miniaturization, can also constitute a threat. If this technology falls into the hands of terrorists or malicious actors, then we should be prepared for it as well, or we need adequate countermeasures and products that would protect people and the environment.

6. Nanotechnology and biomedicine

Interestingly, the colloidal solutions of iron sucrose NP were already in clinical use in 1949, 10 years before Feynman's (1960) call for the world of nano state. We can now confirm the realization of the idea of another scientist - Paul Ehrlich, who in his work on the concept of targeted therapy, stated the need for a "Zauberkugel" (magic bullet) - so a drug that would be specific and intended exclusively for the target without affecting normal host cells.

If we refer to the diversity of nano states of inorganic materials currently used in medicine (Figure 6), they all show some therapeutic, diagnostic, or delivery properties and markers [11-12, 15-20]. For example, antibody-functionalized nanostructured surfaces are used to detect specific proteins or cells resulting from the increased interaction surface and adhesion that give increased sensitivity in detection and NPs serve as markers for detecting biomolecules, pathogens, and MRI contrast agents.

Medical diagnosis with nanopores requires small volumes of evidence for counting and distinguishing a complex mixture of a variety of biological molecules by accessible electronic measurements. The simplicity, speed, and versatility of nanopore analyzes are promising for molecular diagnosis.

Quantum dots are another group of nano states, with a unique potential for clinical use, especially in diagnosis. The ability of quantum fluorescence points in different spectral regions would be useful for marking and imaging cells, cell structures, or biological pathogens, as well as observing processes in dynamics, which take place in cells, tissues, and the body as a whole.

Dozens of metal oxides in the form of NP are currently used in therapy (Figure 7), which shows, depending on the oxide, neuroprotective properties, antioxidants, antibacterial, antimicrobial, anticancer, drug carriers, etc. The most significant advances in nanotechnology in biomedicine are observed in cancer therapy, offering innovative solutions to overcome the limitations of chemotherapy and radiotherapy, through the targeted delivery of drugs, proteins, and polynucleotides. NPs based on micelles, liposomes, and polymers with "capture molecules" attached [11], along with single-walled nanotubes, are used as carriers of drugs for target delivery.

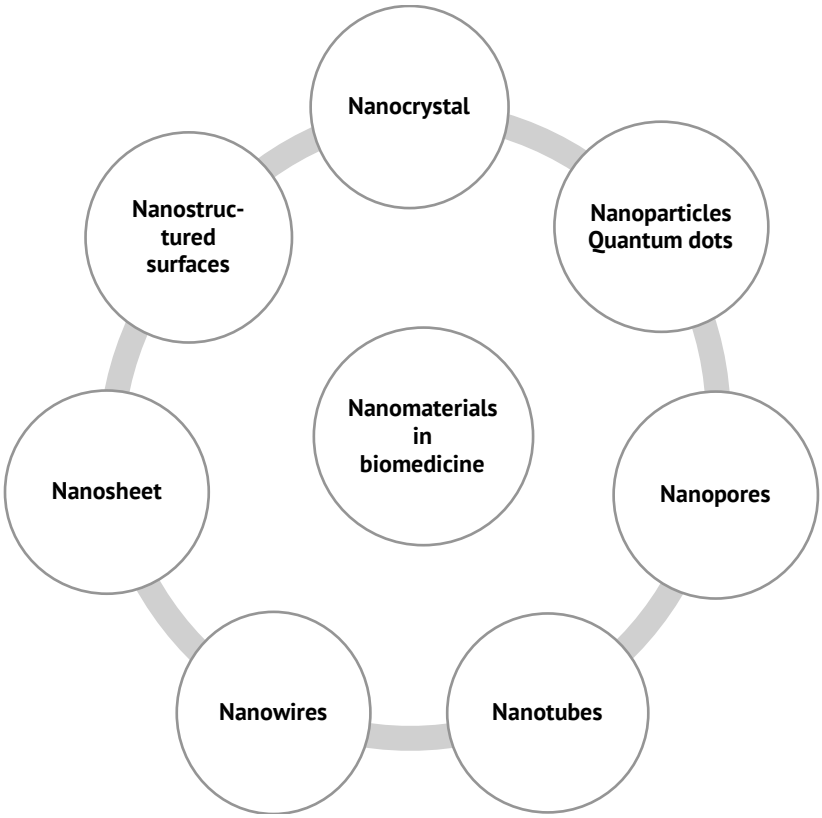

Figure 6. The diversity of nanostates used in biomedicine.

The unique form of NPs allows them to enter selectively through biological barriers by delivering drugs to the target in the minimum quantities necessary to obtain and maintain the therapeutic effect, thus reducing the possible toxicity of drug preparations. This is especially important in the case of very toxic and short-lived chemo- and radiotherapeutic agents [21-25].

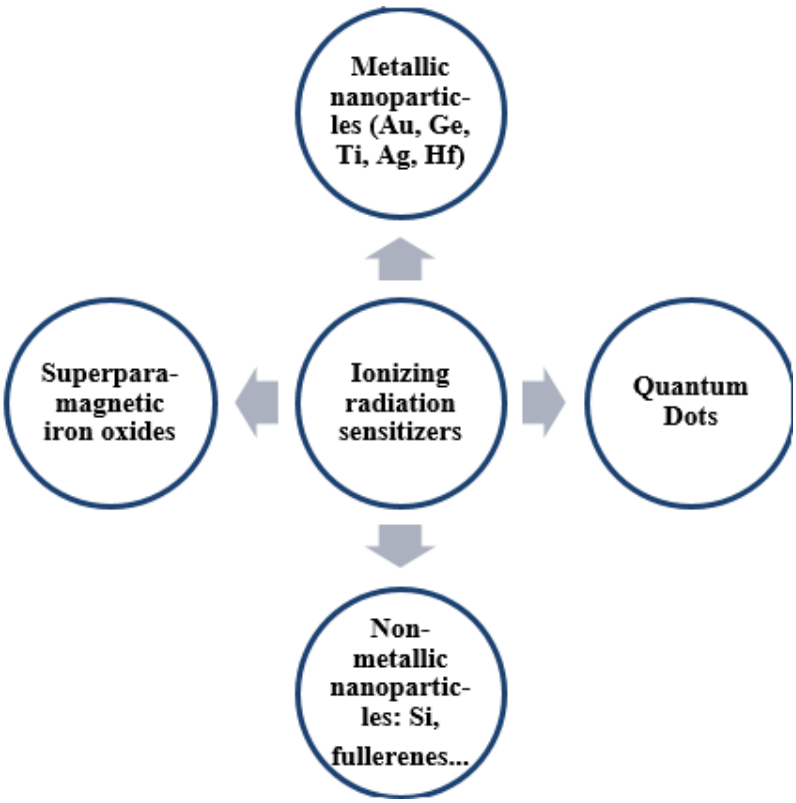

Figure 7. Nanoparticles types as sensitizers for medical purposes.

Another broad area of use of NPs in biomedicine is the design of biosensors for monitoring physiological parameters, as well as the detection of specific DNA fragments and regions or the identification of bacterial cells, etc. Thus, nanowires and Graphene oxide (GO-nS) are recommended to identify cellular interactions *in vivo* [26].

The potential of nanopores in the detection of direct sequencing of individual DNA molecules can provide useful information about an individual's genetic structure and determine the increased risk for certain diseases such as cancer. This nanopore-based detection sensor has potential for application in agriculture, security, defense, and evolving biology, where genomic information is useful.

Carbon nanotubes are being intensively investigated from the perspective of applications in therapy, especially in the treatment of cancer, but also for the development of new diagnostic agents and nanosensors. Carbon nanotubes can also be used for the targeted administration of drugs for the generation of new bone tissue.

The use of drugs in the form of nanocrystals facilitates absorption by the body. Nanocrystals are also used as markers of areas of interest in biomedicine for further studies, such as by immunofluorescence microscopy.

A report on the beneficial effects of NPs in thermoradio (immune) therapy, targeted delivery of pharmaceuticals, contrast agents, local amplification of the exposure dose [27-29], and the summary spectrum of the exposed benefits are represented in Figures 7 & 8.

Furthermore, NPs containing Ag in addition to antimicrobial and cytostatic effects useful in medicine serve as preservatives in the cosmetics industry.

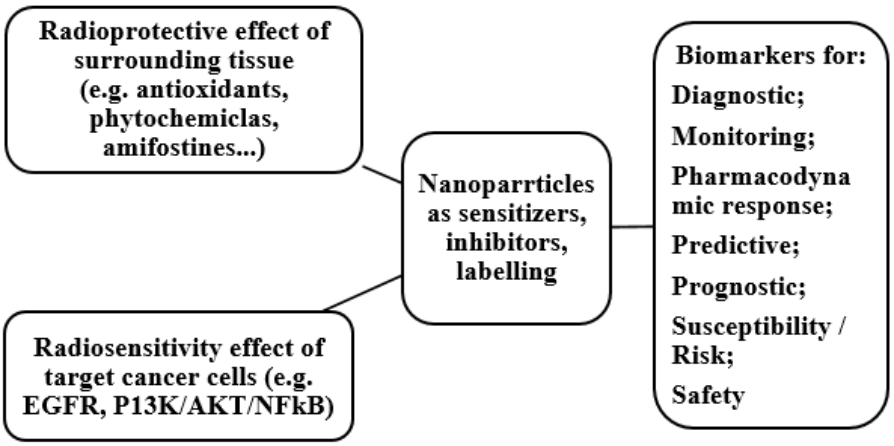

Figure 8. Nanoparticles as sensitizers, radioprotectors, or labelling of ionizing radiation for the treatment, diagnosis, and monitoring of cancer and other diseases (adaptation from [28]).

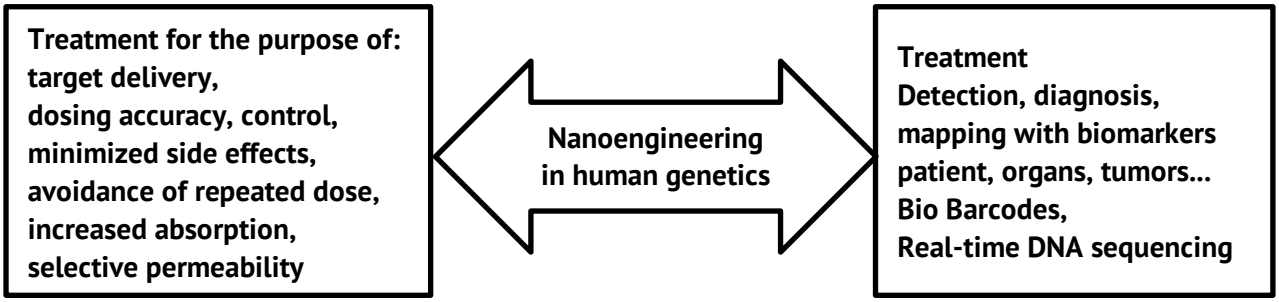

Figure 9. The usefulness of nanotechnologies in human genetics.

When we talk about the interrelationship between nanotechnology and biomedicine, let's not forget about the achievements [30-33] in the field of human genetic engineering (Figure 9). Without going into details, Figure 8 shows the benefits of nanotechnologies in treatment and diagnosis.

7. The nanotechnologies specifics risk

Various applications of nanotechnology expose people to potential dangers, such as potential toxicity. Uncontrolled exposure to NPs occurs through various pathways in the body: inhalation, ingestion, skin penetration, and intravenous injection [34, 35]. NPs reaching the extracellular fluid are conjugated with biomolecules present in the environment, which allows them to be internalized in cells by penetration directly or indirectly through known mechanisms, e.g. via phagocytosis, endocytosis or pinocytosis.

As a concern, we note with sufficient reasoning, that the skepticism of the usefulness of nanotechnologies is based on the lack of knowledge about their toxicity to humans and the environment. It is already established that we are not entitled to deduce the toxicity of a nanomaterial guided exclusively by its toxicity in macro form, as it is being a complex function of many parameters. Because of this, some are convinced that NPs are so risky that they require stopping research and applications in everyday life.

However, the precautionary principle cannot be used to stop nano-state research. We need to find a stable balance between the further development of nanotechnology and the need for research to identify potential dangers for establishing a scientifically susceptible database for risk assessment, with subsequent justified risk management procedures.

The small size of various shapes NPs gives a high penetration of epithelial and endothelial barriers in the lymph and bloodstream. This ensures the transport of NPs to all organs and tissues, including intercellular transport by transcytosis or simple diffusion across the cell membrane with adverse results in the penetration of cells by nanoparticles [36-39], such as physical damage to the membrane, structural changes in cytoskeleton components, disruption of transcription and oxidative DNA damage, mitochondrial damage, lysosome function disturbance, generation of reactive oxygen species, impaired membrane protein function and synthesis of inflammatory factors and mediators.

The penetration of NP into the bloodstream opens up to the possible penetration of the blood-brain barrier with consequences that are difficult to underestimate. Experiments that model NP toxicity on the body have shown that NP can cause thrombosis, inflammation of the upper and lower respiratory tract, neurodegenerative disorders, strokes, myocardial infarction, etc. What is certain is that NP, thanks to its size, can penetrate not only organs, tissues and cells, but also penetrate the cellular organs themselves (mitochondria and nuclei) which can drastically alert cellular metabolism and cause DNA damage, mutations and cell death.

We underline that public concerns about the increased toxicity of nanoparticles have a legitimate experimental basis for many years (silicosis, asbestosis, "black lung" disease, or anthracnosis) if we refer to their interaction with cells and tissues. Some scientific studies show the ability of the human body to clean itself of non-specific nanoparticles in the body, others - reiterate a tragic end of their action on the body through irreparable consequences or diseases. The ignorance of the interaction of the human body with the whole spectrum of nanoparticles does not allow us to say for sure about a total success story of nanotechnologies, and nanostructures, especially in biomedicine.

New technologies have always caused conflicts between those who want to exploit them as soon as possible and those who expect to receive reliable evidence. A particular concern of many is the likelihood that nanotechnology will spiral out of control to the detriment of humanity. These concerns relate to some advances in the ability of nanorobots to self-replicate and self-direct.

8. Risks associated with nanotechnology

Given the wide range of applications of the nanotechnologies mentioned above and the variety of industrial sectors affected, it is certain that the risks associated with nanotechnologies will be complex. The focus on the type of risks to be considered depends on the perspective of the particular entity involved in nanotechnologies. Suffice it to name just a few of these potential risks:

- political and economic,
- military (proliferation of WMD),
- societal impact,
- proliferation of bio-chemo-terrorism,
- environmental (uncontrolled release of NPs into the environment,
- nanoparticle harm risks/work hazards,
- risks of final ignorance of the interaction of the NPs with the biological environment or with other NPs,
- futuristic risks such as the nanotechnology of Homo sapiens, and the risk of the existence of Homo sapiens caused by the self-replication of nanomachines.

As with any new technology, risks can arise that we do not even intuit yet, which confirms the need for continuous and dynamic risk analysis. We risk saying that virtually all the safety issues addressed about nanotechnologies are related to the "free" uncontrolled nano state and less to the built-in, "fixed or immobilized" states of the already designed NPs. Of course, there are exceptions when products or materials with embedded NPs are thrown away, burned or destroyed in an uncontrolled manner by humans, thus causing risks that can be easily avoided.

From the risks outlined above, we draw attention to occupational hazards caused by the potential harm of nanoparticles. As shown in Figure 10, several conditions can be expected for potentially hazardous exposure of workers employed in nanotechnology research and innovation.

Nanotechnology activities	Examples of work tasks	Potentially hazardous exposures conditions	Potentially exposed workers
Innovation reseurch activities	Sinthesizing & producing of NMs. Testing measurements involves toxicological & environmental impacts in *in vitro* & *in vivo* experiments	Handling nanopowders pouring & mixing nano-liquid suspensions; Cleaning spills or waste. Maintaining equipment	Reseurchers, engineers, technicians. Maintenance and waste handling personnel

Figure 10. Potentially hazardous exposure conditions for research and innovation workers (inspired from [6]).

Nanomaterials can present significant, often unknown, hazards to researchers, engineers, laboratory technicians, and support staff. In this regard, an analysis of the risk and impact of the life cycle of nanomaterials undergoing research on workers' health is needed.

Although during evolution the human body has developed a tolerance to most elements and molecules in their natural form of existence (dust, microparticles) with which it comes into contact, it has no natural immunity to new substances, new forms of existence (e.g. nano state) to identifying them as toxic, causing a reaction of the body's intolerance.

As mentioned, NP toxicity can be dictated by many factors (Figure 11) [34-38]. Moreover, NP size and surface area play an important role, largely determining the unique mechanism of NP interaction with living systems.

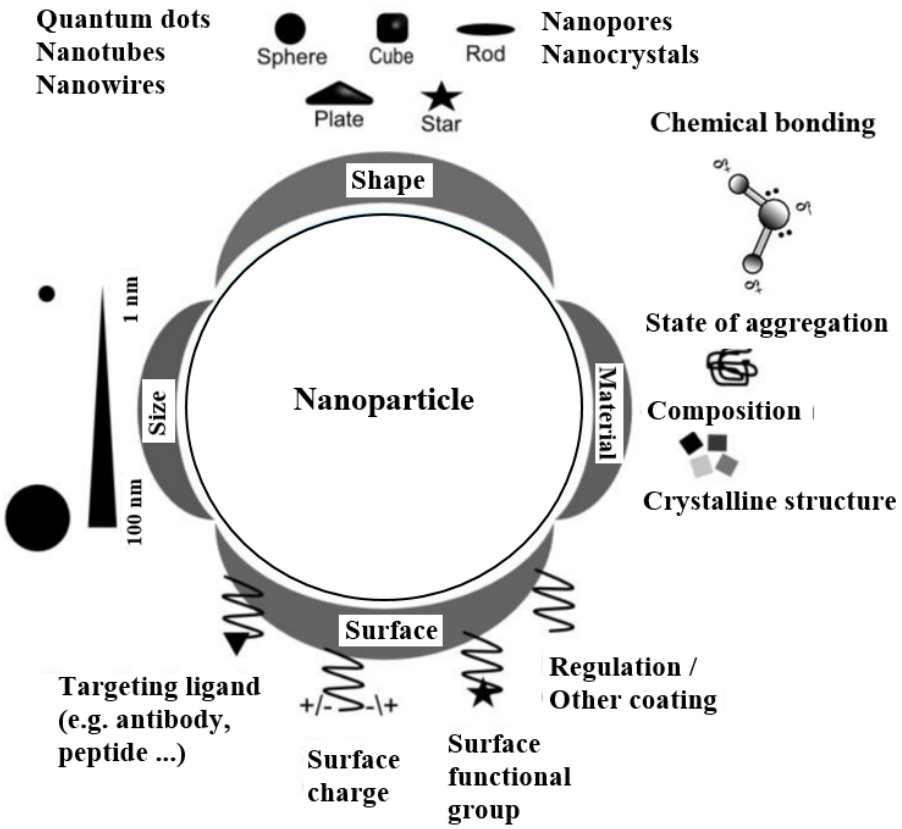

Figure 11. Determinants of nanoparticle toxicity (adaptation from [26]).

NPs are characterized by a very large specific surface area, which determines their high reaction capacity and catalytic activity. Dimensions from 1 to 100 nm are comparable to the size of protein cells (2–10 nm), the diameter of the DNA helix (2 nm), and the thickness of cell membranes (10 nm), which allows them to easily penetrate cells and organs [26]. For example, it is shown that gold NPs less than 6 nm penetrate easily into the cell nucleus, while the largest (10-16 nm) penetrate only through the cell membrane and are found only in the cytoplasm. This suggests that NPs of a few nanometers may be more toxic than NPs of 10 nm or more that cannot penetrate the nucleus. The toxicity dependence of gold NPs depends on their size in the range of 0.8 to 15 nm. It has been identified that 15 nm NP is 60 times less toxic than 1.4 nm NP for fibroblasts, epithelial cells, macrophages and melanoma cells. It is noteworthy that the 1.4 nm nanoparticles cause cell necrosis, while the 1.2 nm nanoparticles predominantly cause apoptosis. These data show us not only that NPs can penetrate the nucleus, but also that the correspondence of the geometric size of NPs (1.4 nm) with that of

the major DNA groove allows them to interact effectively with the backbone of DNA. Sugar-phosphate loaded with negative sac and blocks the transcription.

The results of several studies show that carbon nanotubes, similar in shape to asbestos fibers, cause mesothelioma in the lungs. Also, inhaled carbon NP can weaken the immune system by affecting the T-cells responsible for its organization. On the other hand, it is shown that the harmfulness of nanocarbon is dictated by its durability, so its shape, the more durable it is, the more the behavior resembles asbestos particles.

The convergence of nanotechnology, synthetic biology and chemistry allows the creation of new agents and increases the resilience and lethality of existing ones. There is already talk of the possibility of editing various bacterial DNAs to create complex organisms and new chemicals.

New horizons of chemical-biological nano-generation delivery methods can create diagnostic and treatment impediments, reducing the body's immunity and causing ineffective diagnostic and treatment methods. As an example, carbon nanotubes can be used to supply only the lethal parts of the anthrax virus - without the imprinted protein that is recognized by the immune system.

9. Social impact and regulation

Exposure to nanomaterials is versatile and is achieved through production, transportation, storage, dissemination, use, and final disposal. Nanoparticles may not be recyclable or environmentally friendly, and when they lose control of their existence throughout their life, they could form a new category of non-ecological toxins and create a new threat to health, including through the environment. For these reasons, risk-based regulation of nanotechnologies is needed. Bowman and Hodge propose a model [40] that would argue for a complex regulation for nanotechnology (Figure 12).

This model takes into account product safety, civil society awareness, ethical and social issues, health, intellectual property rights, the international legal framework, including the environment. The soft and tough legal framework refers to various aspects of the consequences of nanotechnology and is applied in various fields: innovation research (through Codes of Professional Ethics) and, health, industry, pharmaceuticals, chemical industry, textile, automotive, etc.

We note that the governance system required for nanotechnologies does not differ substantially from the approach applied to other important environmental and public health issues. However, we mention that nanotechnologies come with specific challenges such as:

- the profound interdisciplinary character not previously encountered;
- high speed of development and enormous impact on industries and social benefits;
- low and delayed public awareness of nanotechnologies;
- the nature of the risks [41] created by some nanotechnologies;
- ethical, legal and social issues associated with some of the nanotechnologies.

The specific challenges and risks associated with some nanomaterials have posed questions to regulators, politicians, and researchers about the coverage of nanotechnologies and nanomaterials within the existing regulatory framework. To fill this regulatory gap, for example, the Commission of the European Communities has adopted a so-called *incremental approach* that recommends adapting existing legislation to the regulation of nanotechnologies and amending them.

This approach has led to some changes in European regulations and directives.

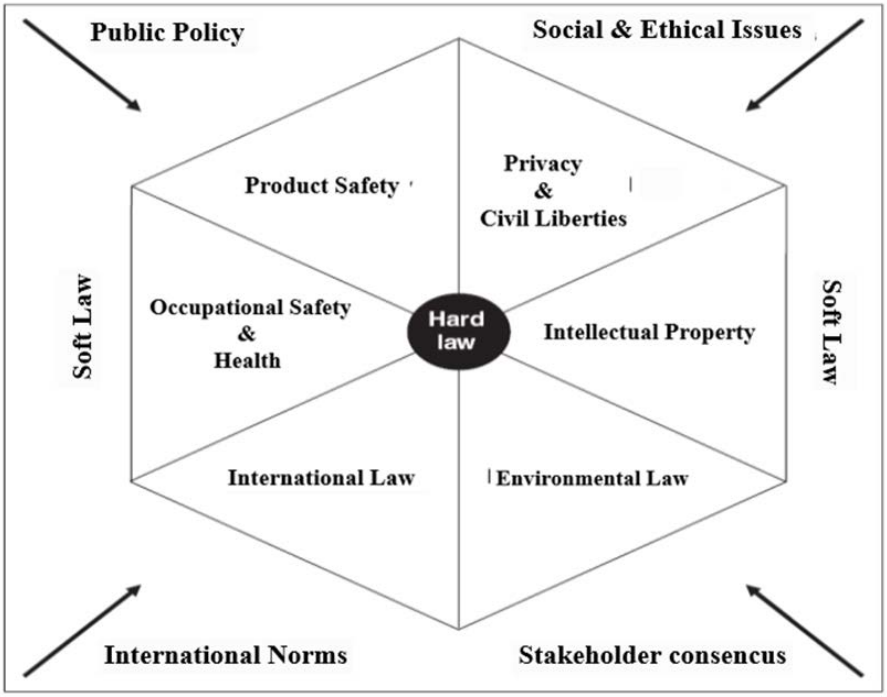

Figure 12. Bowman & Hodge nanotechnology regulatory model [40].

Thus, nanomaterials in the chemical, cosmetics, food, medical devices, plastic packaging for food, waste, and waste management are somehow indirectly regulated [42-44]. However, regulation by the incremental approach of the existing legal framework is characterized by several deficiencies.

10. Conclusions

Certainly, nanoelectronics is perhaps the most harmless nanotechnology with minimal adverse impact on human health. Exceptions may be due to non-compliance with the vital security in the technological process of obtaining as well as the uncontrolled discharge of technological waste into the environment.

Nanotechnologies in biomedicine represent dual-use technologies, which are characterized by both positive and negative impact from the current final ignorance of the mechanisms of interaction of nanoparticles with the biological environment.

The perspective of nanoparticles in medicine is primarily related to immunotherapy for diagnosis and clinical therapy depending on the type of nanoparticles. Immunotherapy combined with the targeted delivery of nanomedicines, characterized by high efficiency due to penetration, specific retention, and expected and predictable actions (destroying tumor cells) is under development for the treatment of various types of untreated diseases.

Nanoparticles have been shown to enter the human system in three ways: inhalation, ingestion, and penetration of the skin. Thus, it becomes extremely important to know the interaction of nanoparticles with cells, organisms, the biological environment, biomolecules, and other biosystems, but also the interaction with other nanoparticles parts of biosystems. These will determine the biocompatibility, toxicity and efficacy of nanoparticles in biological environments. This will ultimately allow the identification and design of non-toxic and beneficial nanomaterials in biomedicine.

Partially, in branches of the industry where nanotechnologies are used, nanoparticles are already regulated. Although nanotechnologies were not regulated by law in the recent past, their future in some areas must be largely determined by new regulations.

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References

1. Jain, N.; Gupta, V. Impact factor of Nanotechnology on Society. *IJERT* 2013, 02 (12), pp. 1982-1986.
2. Eight of The Most Important Applications of Nanotechnology in Biology and Medicine. *The Scientific World*, October 15, 2019. Available online: https://www.scientificworldinfo.com/2019/10/applications-of-nanotechnology-in-biology-and-medicine.html (accessed on 10 August 2022).
3. Applications of Nanotechnology in Electronics and Communication Engineering. *The Scientific World*, January 12, 2020. Available online: https://www.scientificworldinfo.com/2020/01/nanotechnology-in-electronics-and-communication.html (accessed on 11 August 2022).
4. Ahmed, E.S.A.; Sohal, H.S. Nanotechnology in Communication Engineering: Issues, Applications, and Future Possibilities. *WSN* 2017, 66, pp. 134-148.
5. Opportunities and risks of Nanotechnologies. Report in co-operation with the OECD International Futures Program. Ed. Dr. Christoph Lauterwasser, Allianz Center for Technology, 2019.
6. Iavicoli, I.; Leso, V.; Ricciardi, W.; Hodson, L.L.; Hoover, M.D. Opportunities and challenges of nanotechnology in the green economy. Environmental Health. 2014, 13:78, pp. 2-11.
7. Strajtova, L.; Zubal, L.; Komarkova, J.; Munzarova, M.; Kubesova, B. The New Possibilities of Nanomaterial Usage in Medicine. In: NANOCON 2011. Brno, Czech Republic, 21-23 09.2011.
8. Sun, H. Grand Challenges in Environmental Nanotechnology. *Front. Nanotechnology* 2019, 1, article 2.
9. Taran, M.; Safaei, M.; Karimi, N.; Almasi, A. Benefits and Application of Nanotechnology in Environmental Science: an Overview. *Biointerfeace Research in Applied Chemistry* 2021, 11 (1), pp. 7860-7870.
10. Singh, R. Applications of Nanotechnology in Animal Husbandry. March 6, 2021. Available online: https://www.pashudhanpraharee.com/applications-of-nanotechnology-in-animal-husbandry/ (accessed on 10 August 2022).
11. Nikalje, A.P.G. Nanotechnology and its Applications in Medicine. *Med chem* 2015, 5(2). pp. 80-89.
12. Filipe, J.A. Nanotechnology and Medicine Improvement. *IJAR*, 2015, 7 (2), pp. 33-37.
13. Huang, S.; Wan, L.; Liu, L.; et al. Nanotechnology in agriculture, livestock, and aquaculture in China. A review. *Agron. Sustain. Dev*. 2015, 35, pp. 369–400.
14. Hill, E.K; Li, J. Current and future prospects for nanotechnology in animal production. *J Animal Science and Biotechnology*. 2017, 8, pp. 1-13.
15. Kang, J.; Tahir, A.; Wang, H.; Chang, J. Applications of nanotechnology in virus detection, tracking, and infection mechanisms. *WIREs* 2021, 13 (4), e1700.
16. Cheng, X.; Chen, G.; Rodriguez, W.R. Micro- and nanotechnology for viral detection. *Anal Bioanal Chem*. 2009, 393 (2), pp. 487-501.
17. Hernando, P.J.; Dedola, S.; Marín, M.J.; Field, R.A. Recent Developments in the Use of Glyconanoparticles and Related Quantum Dots for the Detection of Lectins, Viruses, Bacteria and Cancer Cells. *Frontiers in Chemistry* 2021, 9, article 668509, pp. 1-8.
18. Chandrasekaran, A.R.; Punnoose, J.A.; Zhou, L.; Dey, P.; Dey, B.K; Halvorsen, K. DNA nanotechnology approaches for microRNA detection and diagnosis. *Nucleic Acids Res*. 2019, 47 (20), pp. 10489-10505.
19. Chaudhary, V.; Jangra, S.; Yadav, N.R. Nanotechnology based approaches for detection and delivery of microRNA in healthcare and crop protection. *J Nanobiotechnology*, 2018, 16, pp. 40.
20. Xiaopei, H.; Yuting, Z.; Tingting, D.; Jiang, L.; Zhao Hang, Z. Multifunctional Gold Nanoparticles: A Novel Nanomaterial for Various Medical Applications and Biological Activities. *Frontiers in Bioengineering and Biotechnology* 2020, 8, article 990. pp. 1-20.

21. Tumkur, P.P.; Gunasekaran, N.K.; Lamani, B.R.; Bayon N.; N.; Prabhakaran K.; Hall J.C.; Ramesh G.T. Cerium Oxide Nanoparticles: Synthesis and Characterization for Biosafe Applications. *Nanomanufacturing* 2021, 1, pp. 176–189.
22. Marill, J.; Anesary, N.M.; Zhang P. et al. Hafnium oxide nanoparticles: toward an in vitro predictive biological effect? *Radiation Oncology* 2014, 9(150), pp. 1-11.
23. Dukhinova, M.S.; Prilepskii, A.Y.; Shtil, A.A.; Vinogradov, V.V. Metal Oxide Nanoparticles in Therapeutic Regulation of Macrophage Functions. *Nanomaterials* 2019, 9, pp. 1631.
24. Montaser, H.; Kruger, C.A.; Abrahamse, H. Inorganic Nanoparticles Applied for Active Targeted Photodynamic Therapy of Breast Cancer. *Pharmaceutics* 2021, 13(3), pp. 296.
25. Ivask, A.; Juganson, K.; Bondarenko, O.; Mortimer, M.; Aruoja, V.; Kasemets, K.; Blinova, I.; Heinlaan, M.; Slaveykova, V.; Kahru, A. Mechanisms of toxic action of Ag, ZnO and CuO nanoparticles to selected ecotoxicological test organisms and mammalian cells in vitro: A comparative review. *Nanotoxicology* 2014, 8(1), pp. 57-71.
26. Auría-Soro, C.; Nesma, T.; Juanes -Velasco, P; Landeira-Viñuela, A.; Fidalgo-Gomez, H.; Acebes-Fernandez, V.; Gongora, R.; Almendral Parra, M.J.; Manzano-Roman, R.; Fuentes M. Interactions of Nanoparticles and Biosystems: Microenvironment of Nanoparticles and Biomolecules in Nanomedicine. *Nanomaterials* 2019, 9, pp. 1365.
27. Chatterjee, D.K.; Wolfe, T.; Lee, J.H.; Brown A.P.; Singh P.K.; Bhattarai S.R.; Diagaradjane P.; Krishnan S. Convergence of nanotechnology with radiation therapy- insights and implications for clinical translation. *Transl. Cancer Res*. 2013, 2 (4), pp. 256-268.
28. Kwatra, D.; Venugopal, A; Anant, S. Nanoparticles in radiation therapy: a summary of various approaches to enhance radiosensitization in cancer. *Transl. Cancer Res*. 2013, 2(4), pp. 330-342.
29. Pellico, J.; Peter, J. Gawne, P.J.; de Rosales, R.T.M. Radiolabeling of nanomaterials for medical imaging and therapy. *Chem. Shock. Rev*. 2021, 50, pp. 3355.
30. Jindal, A.; Sarkar, S.; Alam, A. Nanomaterials-Mediated Immunomodulation for Cancer Therapeutics. *Front Chem*. 2021, 9, pp. 629635.
31. Mirón-Barroso S.; Domènech, E.B.; Trigueros, S. Nanotechnology-Based Strategies to Overcome Current Barriers in Gene Delivery. *Int. J. Mol. Sci*. 2021, 22 (16), pp. 8537.
32. Ponce Del Castillo, A.M. Nanos in the human body - Medical perspectives and ethical concerns, 2009, HesaMag # 01, pp. 36-40. Available online: https://www.researchgate.net/publication/301299187_Nanos_in_the_human_body_-_Medical_perspectives_and_ethical_concerns (accessed on 11 August 2022).
33. Huo, S.; Jin, S.; Ma, X.; Xue, X.; Yang, K.; Kumar, A.; Wang, P.C.; Zhang, J.; Hu, Z.; Liang, X-J. Ultrasmall gold nanoparticles as carriers for nucleus-based gene therapy due to size-dependent nuclear entry. ACS nano, 2014, 8, 6, 5852-62.
34. Rhazouani, A.; Gamrani, H.; El Achaby, M.; Aziz, K.; Gebrati, L.; Uddin, M.S.; Aziz, A. Synthesis and Toxicity of Graphene Oxide Nanoparticles: A Literature Review of In Vitro and In Vivo Studies. *Biomed. Res. Int*. 2021, 5518999.
35. Ou, L.; Song, B.; Liang, H.; Liu, J.; Feng, X.; Deng, B.; Sun, T.; Shao, L. Toxicity of graphene-family nanoparticles: a general review of the origins and mechanisms. *Part Fiber Toxicol*. 2016, pp. 1-24.
36. Lee, Y.J; Ahn, E.Y; Park, Y. Shape-dependent cytotoxicity and cellular uptake of gold nanoparticles synthesized using green tea extract. *Nanoscale Res. Lett*. 2019, 14 (129), pp. 1-14.
37. Sukhanova, A.; Bozrova, S.; Sokolov, P.; Berestovoy, M.; Karaulov, A.; Nabiev, I. Dependence of Nanoparticle Toxicity on Their Physical and Chemical Properties. Nanoscale Research Letters, *SpringerOpen*, 2018, pp.1-21.
38. Adewale, O.B.; Davids, H.; Cairncross, L.; Roux, S. Toxicological Behavior of Gold Nanoparticles on Various Models: Influence of Physicochemical Properties and Other Factors. *International Journal of Toxicology* 2019, 38 (5), pp. 357-384.
39. Lai, W.; Hu, Z.; Fang, Q. The Concerns on Biosafety of Nanomaterials. *JSM Nanotechnol Nanomed* 2013, 1 (2), pp. 1009.

40. Bowman, D.M.; Hodge, G.A. Nanotechnology: mapping the wild regulatory frontier. *Futures* 2006, 38, pp. 1060-1073.
41. Marchant, G.E.; Sylvester, D.J.; Abbott, K.W. Risk Management Principles for Nanotechnology, *Nanoethics*, 2008, 2 (1), pp. 43-60.
42. Hansen, S.F.; Baun, A. European Regulation Affecting Nanomaterials - Review of Limitations and Future Recommendations. *Dose-Response* 2012, 10(3), Article 9.
43. Ponce Del Castillo, A.M. The EU approach to regulating nanotechnology. Working Paper 2010.05. European trade union institute. Available online: https://www.etui.org/sites/default/files/Nano-working-paper.pdf (accessed on 14 August 2022).
44. Rauscher, H.; Rasmussen, K.; Sokull-Klüttgen, B. Regulatory Aspects of Nanomaterials in the EU. *Chemie Ingenieur Technik* 2017, 89 (3), pp. 224-231.
45. Tenth Nanoforum Report. Nanotechnology and Civil Security. June 2007, Ed. Mark Morrison. pp. 64 Available online: https://www.nanowerk.com/nanotechnology/reports/reportpdf/report72.pdf (accessed on 14 August 2022).

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PHOTOVOLTAICS SOLUTIONS AND ENERGY COMMUNITIES IN A CLEAN ENERGY ROADMAP

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Abstract. The present paper deals with solutions regarding the development of the Energy Strategy toward 2050 for a clean and sustainable future. At the national level conceptual elements are needed to draw a roadmap for the energy transition in the Republic of Moldova. The paper presents the renewable energy potential of the country with focus on photovoltaic energy production. A specific PV deployment solution is also analysed, namely the floating PV, while use cases for using this solution for serving energy communities in the rural area has been also proposed. The solutions can be considered steps that will foreshadow the national energy long-term strategy in the energy sector. An efficient transition to decarbonised energy systems requires the search for innovative solutions to increase the penetration of renewable energy sources, for changing the future energy system by promoting and evaluating innovative perspectives.

Keywords: *energy transition, roadmap, energy strategy, renewable energy sources, floating PVs, energy community.*

Rezumat. Articolul prezintă soluții privind dezvoltarea strategiei energetice a Republicii Moldova până în anul 2050, în vederea unui viitor energetic curat și sustenabil. Sunt necesare în acest sens elemente conceptuale care să traseze o foaie de parcurs pentru tranziția energetică în Republica Moldova. Articolul prezintă potențialul de energie regenerabilă a țării cu focalizare pe producția de energie bazată pe centrale fotovoltaice. Se analizează de asemenea o soluție particulară de implementare a acestora, respectiv centralele fotovoltaice plutitoare, fiind totodată propuse studii de caz care să deservească comunități energetice din zona rurală. Soluțiile pot fi considerate exemple de urmat în cadrul strategiei pe termen lung a sectorului energetic. O tranziție eficientă către diminuarea conținutului de carbon a sistemelor de energie necesită găsirea de soluții inovatoare care să crească prezența surselor de energie regenerabilă, pentru a schimba sistemul energetic al viitorului prin promovarea și evaluarea unor perspective inovative.

Cuvinte cheie: *tranziție energetică, foaie de parcurs, strategie energetică, surse de energie regenerabilă, centrale fotovoltaice plutitoare, comunități energetice.*

1. Introduction

After 2010 the supply of energy from renewable sources in the Republic of Moldova increased slowly, as first steps in learning and applying the new trend which has been pushed more strongly in countries such as Germany and some USA states, for example in California. Consequently, the energy from renewable sources in the primary energy supply increased by 27.2% in 2019 compared to 2010 and represents 22.5% of the primary energy of the country [1]. To be noted that according to [1], 67.5% of CO_2 emissions in Republic of Moldova are allocated to energy sector in 2019, as a reduction form 70% in 2010, which suggests that energy sector is a priority for reaching high decarbonisation goals.

With a gradual decarbonisation process, the Republic of Moldova can contribute not only to the global efforts to mitigate climate change, but also to improving the health and the quality of life of its citizens. More efficient use of cheap and abundant renewable energy sources, with the help of digital technologies, will transform cities, transport, industry and agriculture, reducing greenhouse gas emissions and improving air quality. Thus, decarbonisation is not just an abstract goal of the European Union or the United Nations, but a policy with immediate and tangible benefits for all. And the decisive factors that will generate these benefits will be the digitization and electrification of the usable potential.

In this context, the opportunities of the Republic of Moldova (RM) in the energy sector are considered in the long-term development. It is especially worth to mention that the electricity will have to become a strategic tool for the future of transport, air conditioning and household needs, but the promotion of smart grids will be proved to be the best way to make this to be possible. Decarbonisation and air quality are also on the list of priorities and ensuring an adequate access to the energy for the most vulnerable members of the society continues to be a subject of the maxim importance.

2. PVs as a priority and high potential in the future RES mix

In the study which has been extensively presented in [2], it has been shown that a small part of the agricultural area of the Republic of Moldova is needed to provide 30% or even 50% of the annual volume of electricity used in the country. Even so, recent studies show that such areas can be found in the form of uncultivated land, but the areas where agricultural activities take place have as well a very high potential, through the application of the technologies that are particularly promising, namely agricultural activity combined with photovoltaics.

In this respect, pilot projects in several parts of the world show that there are synergies between agriculture and the production of renewable energy sources (RES) with photovoltaics (PV), which may, in fact, change the perception that PV is in competition with agriculture.

The amount of photovoltaic power plants capacity in the Republic of Moldova can be determined in a simplified way based on the calculations performed in [2]. The average yearly energy produced for one kW of installed PV in the Republic of Moldova has been calculated in [2] by using 11 geographical points with inputs from [3] and gave 1,182 kWh / year for 1 kW of PV installations (also referred as 1 kWp, where p denotes maximum power of the photovoltaic panels in defined conditions). A revisited and more refined calculation based on more geographical points (20 points, organised in four zones: North, Middle, South and left Dniester, as per administrative organisation from [4]) gives a value of 1,191 kWh / year / kW (Table 1), which is very near to the initial estimation (only 0.7% difference in the more complex calculation).

Table 1

Average yearly energy produced by 1 kWp PV in based on 20 geographical points [3]

No	Location	County	Zone	Latitude (°)	Longitude (°)	Yearly energy (kWh/year)	Y2Y variation (kWh)
1	Edineț	Edineț	North	48.169	27.298	1,130.78	57.66
2	Briceni	Edineț		48.354	27.065	1,141.13	42.08
3	Soroca	Soroca		48.146	28.282	1,144.24	57.76
4	Costesti	Rișcani		47.866	27.235	1,174.87	40.84
5	Bălți	Bălți		47.781	27.909	1,148.16	55.43
6	Șoldănești	Șoldănești	Middle	47.812	28.776	1,179.57	51.34
7	Telenesti	Telenesti		47.512	28.354	1,182.75	46.95
8	Orhei	Orhei		47.396	28.831	1,174.61	51.81
9	Ungheni	Ungheni		47.220	27.815	1,174.53	54.02
10	Chișinău	Chișinău		47.039	28.858	1,193.99	58.97
11	Hîncești	Lăpușna	South	46.843	28.596	1,186.33	52.10
12	Leova	Leova		46.486	28.243	1,228.96	47.39
13	Căușei	Tighina		46.661	29.413	1,194.83	56.03
14	Cahul	Cahul		45.929	28.196	1,235.68	37.53
15	Palanca	Stefan Vodă		46.407	30.078	1,263.10	58.52
16	Comrat	Găgăuzia		46.315	28.661	1,213.68	49.74
17	Vulcănești	Vulcănești		45.679	28.457	1,267.61	50.59
18	Rîbnița	Nistru	Left Dniester	47.769	29.060	1,172.62	53.01
19	Dubăsari	Nistru		47.272	29.212	1,200.64	52.52
20	Tiraspol	Nistru		46.866	29.634	1,207.17	60.54
	Average energy over a year [kWh/year/kW installed]					**1,190.76**	51.74

The places considered for the refined average energy production with PVs are presented in Figure 1, while the average specific energy in each zone is also presented (based on administrative organisation from [4]), showing a slight improvement of solar energy in the south region compared with the north part (only 4% more in South). It shows that there are appropriate conditions for PV installations everywhere across RM, everywhere from North to South.

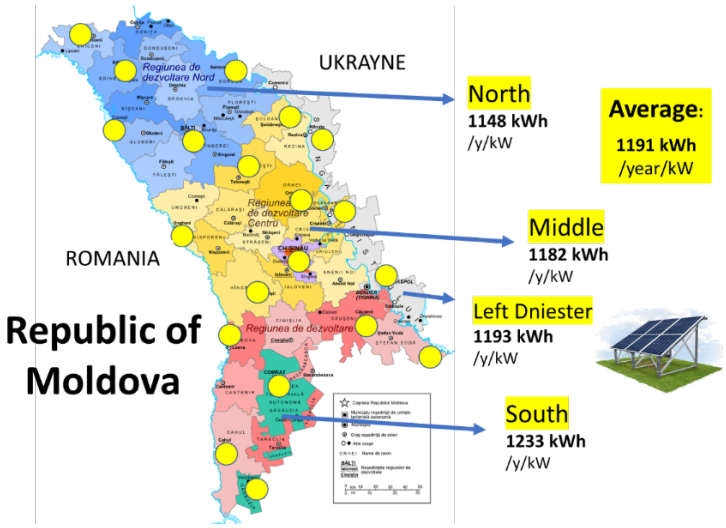

Figure 1. Places in the Republic of Moldova used to calculate the annual average energy with PV power plants.

Based on the method described in [2], the energy coverage with PVs of yearly country consumption is shown in Figure 2, which uses as inputs the following data:

a) the average value of yearly-based specific PV production in RM (1,191 kWh/year/kW) from Table 1.
b) The yearly consumption of RM, based on data from year 2020, which was 5940 GWh (based on processed data obtained from [5]).

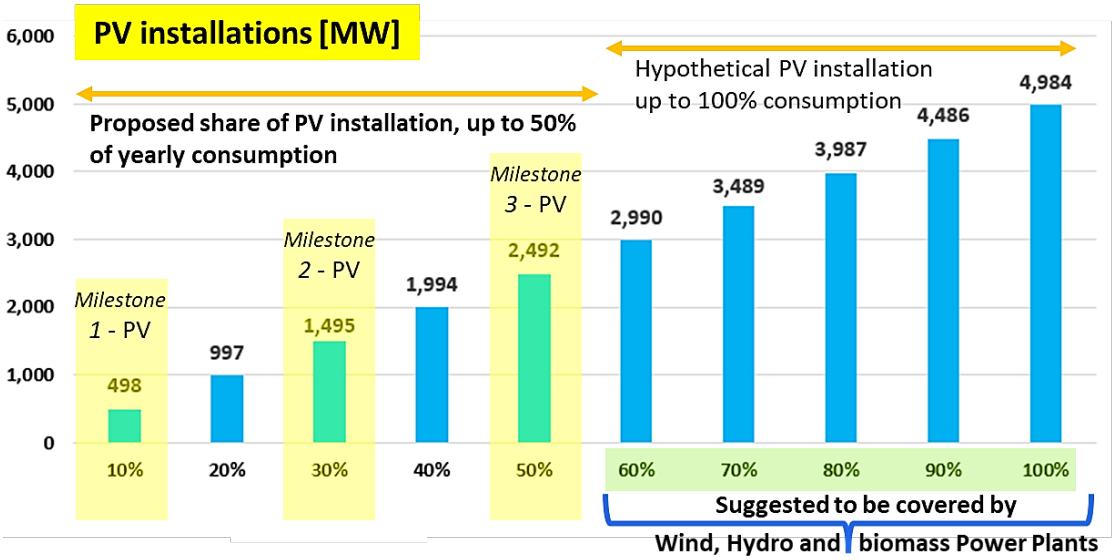

Figure 2. The need of PV power for various levels coverage of the consumption on yearly basis in Republic of Moldova and suggested share with wind, hydro and biomass.

It is observed that for 100% of required consumption the country, the needed capacity for PV installations is 4.98 GW, while for covering 50% are needed only 2.49 GW.

Wind power plants have the potential to contribute essentially to the second half of the RES energy production (as suggested in Figure 2). This is already treated in other works. For instance, in [6] are shown the areas of the Republic of Moldova with wind potential, while the paper deals extensively with their integration into the national energy system of the Republic of Moldova.

3. Impact on land use in the scenario of high PV share in the future RES mix

In order to assess if the land needed for PVs if up to 50% of RM yearly consumption is obtained from PV production, it is needed to estimate the specific area for a power unit of PVs.

Figure 3 shows the relevant geometry of PV rows for deducting the surface needed for 1 kW of PV panels.

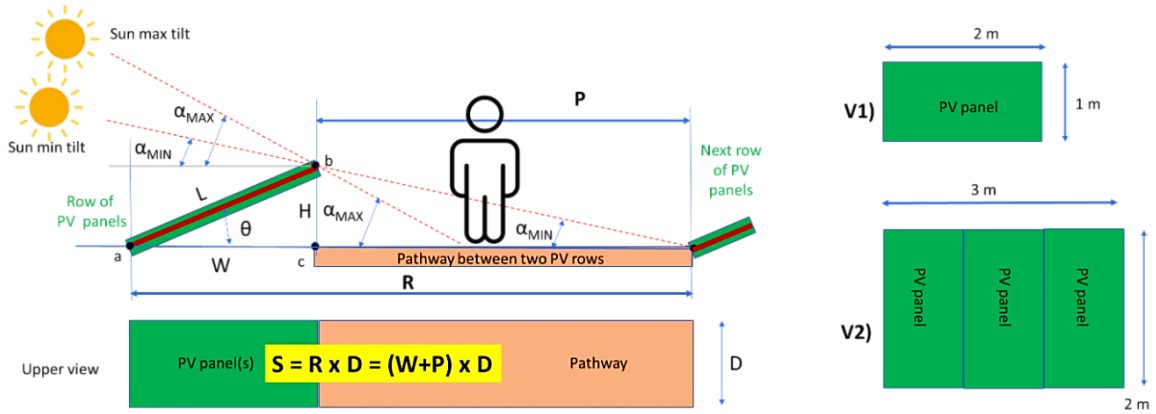

Figure 3. PV rows geometry for land-based deployment of Photovoltaic Power Plants.

The ideal tilt angle θ of the PVs - for a maximum energy obtained over a year, is around 35° for RM, similar for different points, as has been calculated with [3].

The calculation of the power density is based on geometry from Figure 3 (left side) by applying the following formulas:

$$S = R * D = (W + P) * D = (L\cos\theta + H/\tan\alpha_{MIN}) * D \quad (1)$$

$$= (L\cos\theta + L\sin\theta\,/\tan\alpha_{MIN}) * D \quad (2)$$

$$S_{1kW} = S/P_{PV\_panel} \quad (3)$$

For $\theta = 35^{0}$ (best tilt angle for highest energy over a year) and for $\alpha_{MIN} = 12^{0}$ (as a lowest sun angle during winter without shadow) we analyse two types of PV installations:

- Rows of one PV panel of 1000 x 2000 mm (D_{PV} x L_{PV}), having P_{PV} = 420 Wp/panel (conservative value, higher values may exist) and mounted with D_{PV} side on the ground (the small side), as per the design V1 in Figure 5 (lower right side). The length L is therefore equal to L_{PV} = 2 m, while the depth in the row is equal to D_{PV} = 1 m. The power of the row is P_{ROW} = P_{PV} = 420 Wp, as it is only one panel in the considered D_{PV} depth.
- Rows of 3 x PV panels of the same dimension of 1000 x 2000 mm (D_{PV} x L_{PV}), having the same output P_{PV} = 420 Wp / panel and mounted with L_{PV} side on the ground (the large side), as per the design V2 in Figure 5 (upper right side). The length L is therefore equal to 3 x D_{PV} = 3 m while the depth in the row is equal to D_{PV} = L_{PV} = 2 m. The power of the row is P_{ROW} = 3 x P_{PV} = 3 x 420 =1260 Wp.

The total needed surface for one row can be deducted as being:

$$S_{V1} = (2\cos 35^{0} + 2\sin 35^{0}\,/\tan 12^{0}) * 1 = 7.03\ m^{2} \quad (4)$$

$$S_{V2} = (2\cos 35^{0} + 3\sin 35^{0}\,/\tan 12^{0}) * 2 = 21.11\ m^{2} \quad (5)$$

$$S_{1kW\_V1} = 7.03\ /\ 0.420 = 16.7\ m^{2}/kWp \quad (6)$$

$$S_{1kW\_V2} = 21.11\ /\ 1.260 = 16.7\ m^{2}/kWp \quad (7)$$

In both situations it is needed the same land area, which shows that they are equivalent in terms of density. Therefore, both design geometries as used, as per Figure 4 real implementation examples (V1 on the left, as from [7] and V2 on the right, as shown at [8]).

Figure 4. Real PV implementation of design V1 (left) and V2 (right) geometry.

The 16.7 m^2/kWp has been calculated at the most difficult situation in winter, when the sun has a min to max tilt angle which are very low (lowest is expected for 21st of December).

According to [9], in Chisinau area, during the day of 21st of December 2022, we have $\alpha \geq \alpha_{MIN} = 12^{0}$ in the time period between 9h:34m and 14h:32m, which means that there is

no shadow for approximate 5 hours. From the same site, it can be deducted that $\alpha \geq \alpha_{MIN} = 10^0$ for 5 hours and 40 minutes (13.3% longer period), so the needed land for 1 kW PV is also calculated for 10º.

For $\alpha_{MIN} = 10^0$ the minimum needed land is:

$$S_{V1\_10grd} = (2\cos 35^0 + 2\sin 35^0 / \tan 10^0) * 1 = 8.15\ m^2 \quad (8)$$

$$S_{1kW\_V1} = 8.15 / 0.420 = 19.4\ m^2/kWp \quad (9)$$

The calculations show that in usual PV power plants, around 20 m^2 can be considered for each 1 kW installed, based on the ideal tilt angle of the PV (around 35º for Moldova) and eventually by adding some areas for access roads and other power plant necessities.

With this value $S_{Specific} = 20m^2/kWp$, a total power of 2.49 GW in PVs will need only:

$$S_{50\%} = P_{PV_{50}\%} * S_{Specific} = 2.49 * 10^6 * 20 = 49.8 * 10^6\ m^2 = 49.8\ km^2$$

Higher densities of PV panels (needing e.g. 12 m^2/kWp PV) can be obtained for instance if $\alpha_{MIN} = 15^0$ and $\theta = 25°$ (lower tilt angle, which brings lower PV specific energy per year).

The need for 4.98 GW in CEF installations (100% coverage of yearly consumption in RM) uses under 0.8% of the country's agricultural land (based on method used in [2]) to cover the entire volume on an annual basis, is consistent with similar results for other countries [10,11]. One conclusion of Greenpeace is that, at the moment, only political will is needed to achieve such a goal [12]. A World Wildlife Fund study shows that in Germany, 2% of the country's land area is enough to produce all the energy used annually from renewable sources alone [13]. The potential for electricity supply from RES alone is also highlighted in [14], showing that 1% of the EU's surface area can supply the entire usable EU electricity needs.

Moreover, a new field of sustainable development can be addressed, that of the harmonious interweaving of agriculture with CEF, i.e. an "agro-photovoltaic" development at the country level [15]. Such a concept is extremely conducive to a country like the Republic of Moldova, characterized by important activities related to the use of agricultural land, which can approach new values of their potential to support a society that can keep traditional activities in a sustainable and competitive way. In [15] are listed explicitly also floating PVs and their potential is analysed in more depth in the next section.

4. Floating PV solutions for Republic of Moldova

A new field of interest in deploying photovoltaics power plants is the promotion of floating PVs. There are several reasons why they may become attractive:

a) such installations do not occupy land usable for ordinary human activities (agriculture, urban areas, etc.).

b) floating PVs ensures a higher conversion yield during the summer, because the PV panels, whose efficiency decreases with increasing temperature, are better cooled by the surface of water on which they float;

c) often such water surfaces (e.g. lakes) are located near urban or suburban areas, for which it can provide energy in an area close to the place where it can be used.

This section will assess the level of installed power which can be reached with PVs when using floating PV technology. In this respect, Figures 5 [9], 6, 7 and 8 present the potential of some of these lakes in the Republic of Moldova. The lake areas have been obtained by using the “Distance” tool of [16].

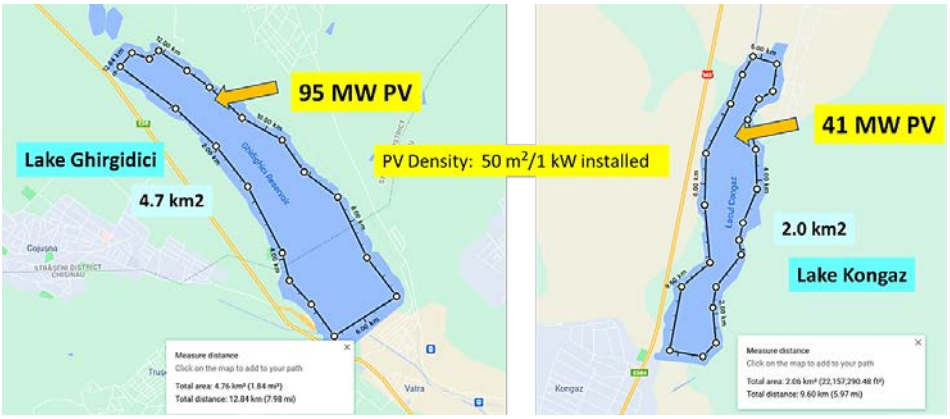

Figure 5. The potential of photovoltaic capacity for two lakes in the Republic of Moldova: Ghidighici and Kongaz, in the conditions of a low density of photovoltaic panels: 50 m^2/kW installed.

Figure 6 particularly looks in the potential of some lakes placed nearby Prut River, which can be considered as reservoirs of water related to this river.

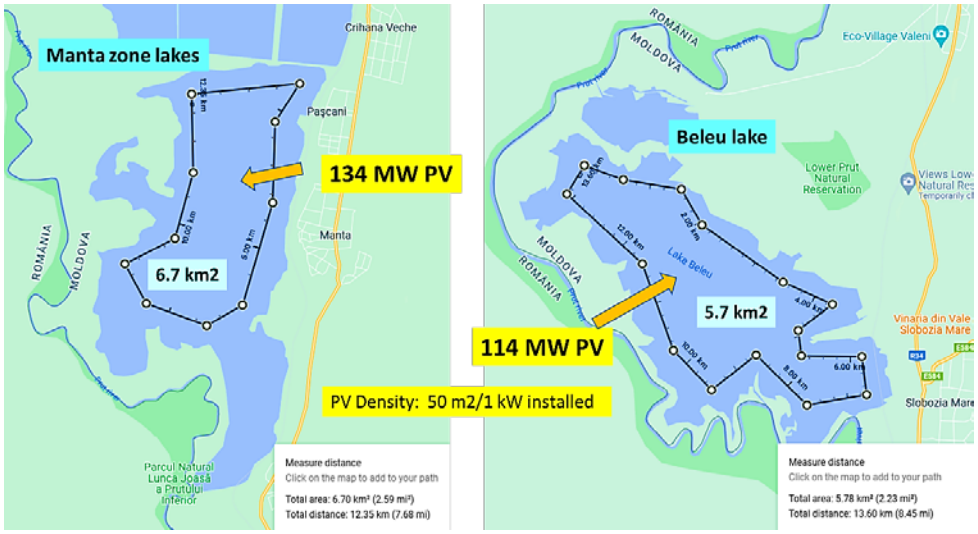

Figure 6. The potential of photovoltaic capacity for two lakes in the Republic of Moldova: Manta and Beleu zones.

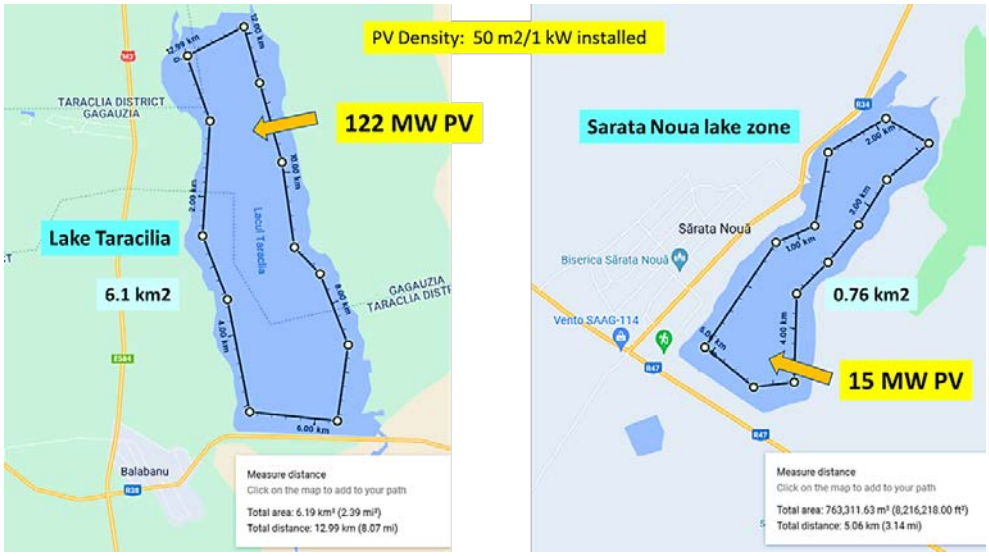

Figure 7. The potential of photovoltaic capacity for two lakes in the Republic of Moldova: Taracilia and Sarata Noua zone.

In Figure 8 it is analysed also the potential of using a hydro-power-plant lake (Costești, on the right side) with dual use: reservoir for the hydro-plant and lake for floating PVs. Such combination has been also discussed for other lakes around the world [17].

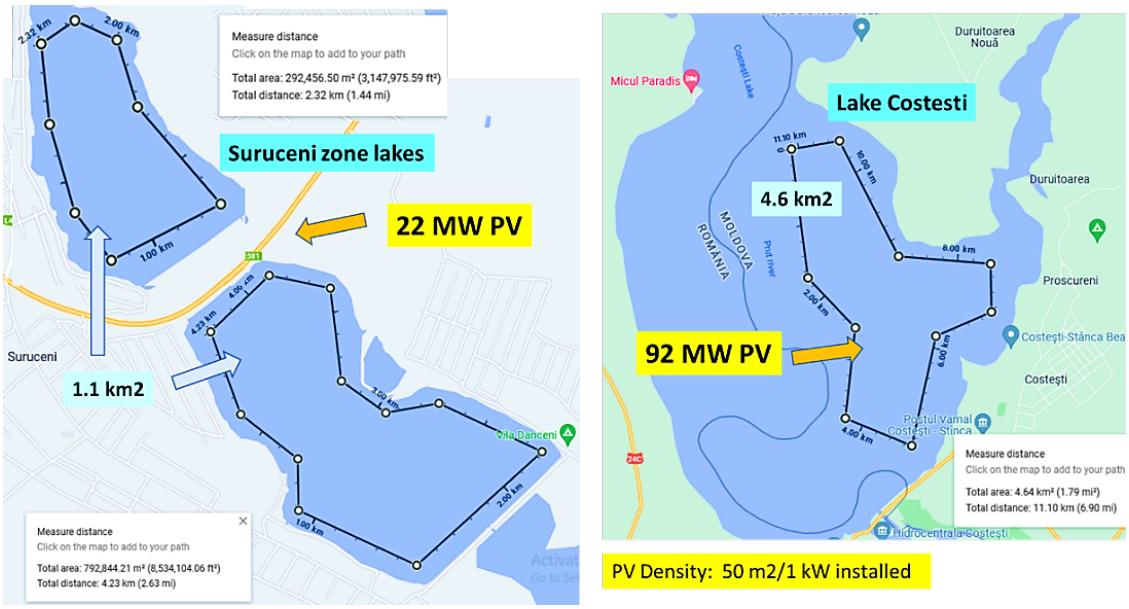

Figure 8. The potential of photovoltaic capacity for two lakes in the Republic of Moldova: Suruceni and Costești zone.

For the floating PV it is considered a lower density, to allow other lake-based activities, meaning that the area needed for 1 kW of PV is chosen to be studied in two cases:

- 50 m^2/kW (low density), which is 2.5 to 3 times lower than for usual ground-based implementations.
- 80 m^2/kW (even lower density), which is 4 times lower than for usual ground based implementations.

A brief overview of representative figures related to these locations is presented in the Table 2, while choosing the low-density PV implementation.

Table 2

Power and yearly energy potential for the selected lakes of RM for low density of 80 m^2/kW in PVs

	Lake denomination	Area (km^2)	PV power potential (MW)	Estimated yearly energy (GWh)
			Density V1: 50 m^2/kW	
1	Ghirghidici	4.7	94	111
2	Kongaz	2.0	40	47
3	Manta	6.7	134	158
4	Beleu	5.7	114	135
5	Taracilia	6.1	122	144
6	Sarata Noua	0.76	15	18
7	Suruceni	1.1	22	26
8	Costesti	4.6	92	109
	Total	**31.7**	**633**	**748**
	RM consumption coverage			**10.7%**

Table 3 presents the potential of the same lakes by considering an even lower density (80 m²/kW) of the PV panels on the lake surface.

It can be seen that the potential of such lakes is not negligible, they also have the advantage of being close to the cities (e.g. in the case of lakes nearby Chisinau and Kongaz). Other lakes exist also in other zones of the Republic of Moldova, however even these locations can bring high contribution of PV based RES:

- 6.7% of yearly consumption in the case of lower PV density of 80 m² / kW installed, respectively
- 10.7% of yearly consumption in the case of low PV density of 50 m² / kW installed.

Table 3

PV Power and yearly energy potential for the selected lakes of RM for lower density of 80 m² / kW

	Lake denomination	Area (km²)	PV power potential (MW)	Estimated yearly energy (GWh)
			Density V2: 80 m²/kW	
1	Ghirghidici	4.7	**59**	69
2	Kongaz	2.0	**25**	30
3	Manta	6.7	**84**	99
4	Beleu	5.7	**71**	84
5	Taracilia	6.1	**76**	90
6	Sarata Noua	0.76	**10**	11
7	Suruceni	1.1	**14**	16
8	Costesti	4.6	**58**	68
	Total	**31.7**	**396**	**468**
	RM consumption coverage			**6.7%**

To be noted that usual density in fields dedicated to PV panels installations is around 20 m²/kW. The lower densities proposed for the floating PVs placed on lakes allow the placement of the panels at least in two ways:

- With larger access lanes between PV lines allowing other activities such as fishery in between the PV lines.
- With clusters if classic density PVs (e.g. with 20 m²/kW), other activities may be fully developed in between the clusters.

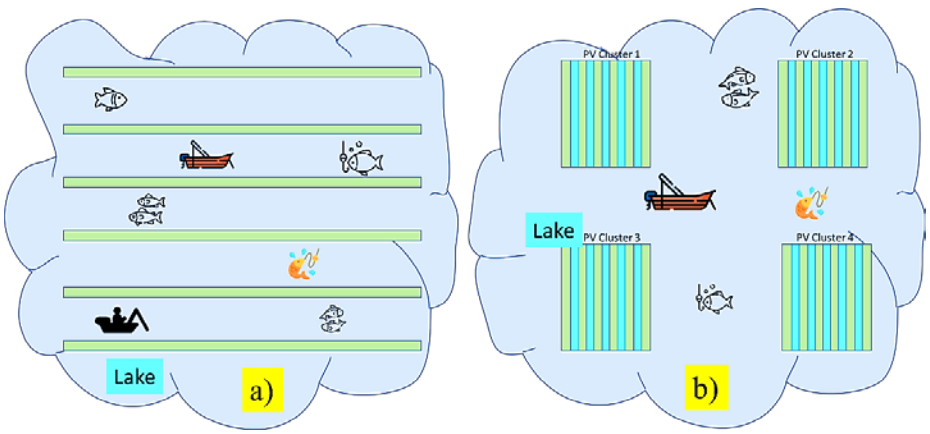

Figure 9. PV panels setups: a) Large access lanes between PVs; b) Clusters of PVs.

Moreover, placing 1 kWp of PVs on 50 or 80 m^2, creates a spatiality which practically avoids shadowing between tow PV rows nearly the whole day even in worst situations in December.

5. Rural energy communities sustained by local RES production. Examples involving floating PV solutions

A particularly important added value of encouraging energy production at the local level is the possibility to grow energy communities around these energy sources. The following advantages ca be considered:

- local production at traditional users, who thus become active users (prosumers); this type of distributed production is generally achieved through PV mounted on roofs, especially in rural areas and in urban neighbourhoods that predominantly have own houses. The power installed on these roofs, with PVs mounted usually towards south, is usually in the field of 3 to 10 kW;

- local production for the active medium size users, which refers to state institutions such as schools, hospitals and other public buildings, to industrial buildings and for commercial use. The PV power of these installations can be from 50 to hundreds of kW. If the parking lots of the shopping complexes are added, using special carports, the total power can reach the MW range;

- a third important category represents the energy community. Frequently the users of a community do not have a functional space to invest each individually in a RES installation, but are willing to organize themselves in energy "cooperatives", which may be in collaboration with the mayor's office or other public or private entity from their area. This aspect of the energy community will be developed further using two cases of small floating-PV applications.

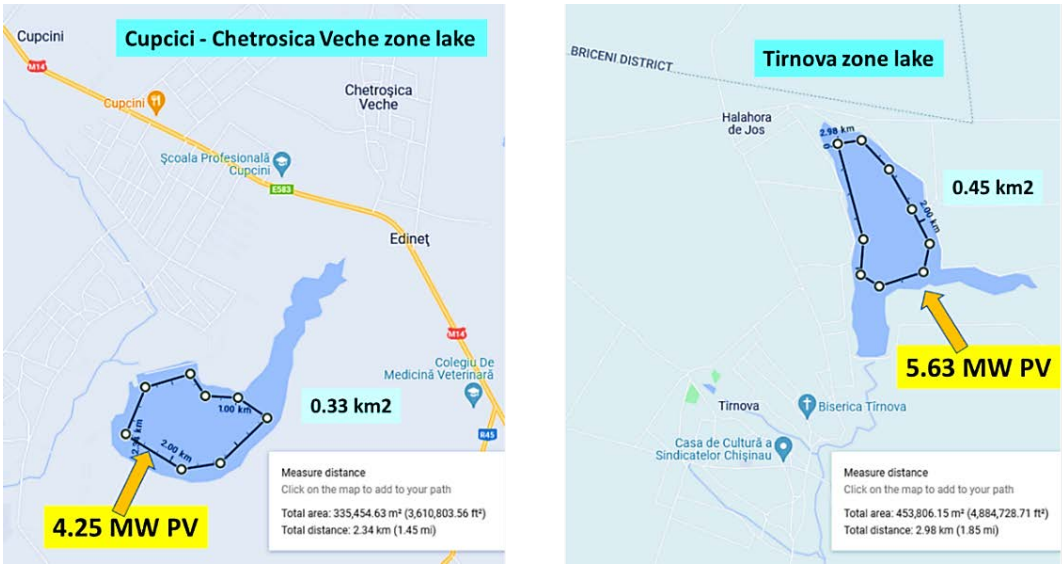

Figure 10. The potential of photovoltaic capacity for two small lakes and a potential formation of energy communities.

In can be seen that the small power between 4 to 6 MW in floating PVs can supply nearby communities, as ca be seen in Figure 11, in areas of 1 up to 7 km radius, while Table 4 estimates installed power in floating PVs and the annual energy for 1191 kWh / kW chosen in section 1.

Figure 11. Energy communities' formation: a) small community with km range radius; b) larger community, with up to 7 km radius.

Table 4

PV Power and yearly energy potential for the selected lakes of RM for lower density of 80 m²/kW of floating PVs

	Lake denomination	Area (km²)	PV power potential (MW)	Estimated yearly energy (GWh)
			Density V2: 80 m²/kW	
1	Cupcici-Chetrosica Veche	0.34	4.25	5.06
2	Tirnova	0.45	5.62	6.70

In order to be a sustainable energy community, the energy from the floating PVs need to cover an important part of the yearly consumption of the energy community. Table 5 presents an estimated yearly production of the PVs (column 6) which is compared with the community production over the year (column 5).

The population of the two energy communities is based on [18] and [19]. As shown also in Figure 11, the energy communities have the following structure:

- Cupcici community: with 7190 inhabitants in Cupcici and 817 inhabitants in Chetroșica Veche; the total number of inhabitants of the small energy community (km range radius) is 8007
- Tîrnova community: with the following number of inhabitants: 2050 in Tirnovam 3108 in Trinca, 3265 in Gordinesti and 1921 in Hlinaia; the total number of inhabitants of the larger energy community (up to 7 km radius) is 10344.

Table 5

Energy community KPIs

Energy community	Population	Houses	Energy/ month (kWh)	E_cons / year (MWh) community	E_prod PV / year (MWh)	Procent of consumption
Cupcici	8007	2669	200	6405.6	5060	79.0%
Tirnova	10344	3448	200	8275.2	6700	81.0%

To be noted that the number of houses has been estimated as being an average of one for each 3 inhabitants, rule which provides the numbers from column 3. In order to estimate the yearly consumption of the community, a simplified approach is to base these values on an average monthly consumption per house. The study considers a value of 200 kWh/month/household, while households may consume between a lower energy of around average 100 kWh and a higher energy of around 300 kWh/month.

Table 5 shows that the yearly consumption is covered in a share of around 80% for both communities. The assessment suggests that most of the energy is therefore produced locally and that only a small share of around 20% is needed to be purchased from the public network. This result shows the potential of such approach, respectively to produce locally, on a non-agricultural surface (on a lake belonging to the community area), close to entire yearly need of the community.

This situation allows also to implement aspects of resilience such as:

- *Resilience of energy*, meaning that short to medium time periods without supply of energy from main grid can be surpassed by off-grid local supply
- *Resilience of local businesses*, as most of the energy is supplied based on already known tariffs deducted from the feasibility study of the local energy investment, which is not influenced by external factors after the objective is operational.

For the energy resilience it is needed that the PV production is also accompanied by electrical storage. The need for storage at country level has been already studied in [20] For local PV production, a usual level of 1 to 2 kWh of energy storage is used already in some applications for shaving the peak power of 1 kW of PV.

This storage resource allows also a certain resilience (e.g. 1 to two hours or more) if the main grid fails to supply energy to the community, depending on the adaptation of consumption to lower values during the power outage.

A priority can be given in this situation only to the most important loads, e.g.: refrigerators (for keeping food in good conditions), telecommunication means (modems, routers, switches etc.), low-consumption computers such as laptops or tablets, LED-based light etc.

For the resilience of the local business, it is targeted finally a sustainable development of the community, which is less influenced by volatile prices due to external factors, such as political or proxi-wars situations. This type of resilience is in many cases neglected, despite the fact that the impact of external factors may be dramatic in some cases.

While the coverage of up to 80% of the consumption over a year looks quite promising, two additional factors may be also considered:

- Shifting of classic ICE - based cars to electromobility.
- Heating with electricity

The paper is analysing only the first factor.

6. Impact of electrical vehicles

The ongoing revolution in switching to electrical vehicles plays a key role in its effect of the energy field. Due to a growing market and a smaller effect of business-as-usual inertia and the monopolies associated with maintaining this situation, electromobility is the main driver of the innovation through batteries, power electronics, artificial intelligence and associated ITC components, having a beneficial effect in the energy field, much more related to natural and historical monopolies and the fear of changes.

Let's consider that each household has also a light vehicle and that in 2030 we may have 20% of these cars shifted to EV technology and 50% in year 2040. We consider a scenario with the following inputs:

a) an EV is driven 10000 km/year, with half of it expected to be covered by local charging.
b) the average consumption of a light EV is around 15 kWh / 100 km

It means that an EV will need 5000 km supported by local energy production, which means 15 x 50 = 750 kWh / year / EV.

With the data already used in tables 3 and 4, the table 6 shows that additional consumption energy needed for the 20% and 50% EV fleet. Table 5 shows the impact of EV charging in the community, compared with the community PV production over a year (energies shown in MWh).

Table 6

Energy community KPIs related to electrical vehicles introduction

Energy community	Vehicles	EVs-2030	EVs-2040	Energy for EVs 2030	Energy for EVs 2040	Percentage in 2030 of PV prod.	Percentage in 2040 of PV prod.
Cupcici	2669	534	1335	400.5	1001.25	7.97%	19.93%
Tirnova	3448	690	1724	517.5	1293	7.78%	19.45%

The table shows that around 8% in 2030 and 20% in 2040 of the energy community production with floating PVs is needed for covering EV charging due to the rapid expansion of EVs in the studied energy communities. This means that for the households consumption presented in table 5 it remains only around 60% of local production for the time horizon of 2040. This situation suggests that the floating PV solution need to be complemented with additional local sources, such as agri-photovoltaics. By considering also electric heating, the energy produced locally can be doubled, with a 50% share in floating PVs on the local lake, while the remaining can be mounted on ground.

The assessment shows however that a local sufficiency is a tangible target and that each solution need to be treated case by case.

7. Roadmap to 2050 in the Republic of Moldova

In continuation it is presented a roadmap to 2050 in the Republic of Moldova, based on what has been proposed in [15], with essential elements that can be the basis of the national policies.

1) It will be facilitated the development of renewable electricity sources distributed in all regions of the country where there is high consumption in the neighbourhood (cities, industry, etc.). These must be especially based on photovoltaic and wind-based power plants, in a proportion that corresponds to the environmental conditions of the Republic of Moldova, following in-depth, multi-criteria studies. A contribution of at least 50% to the solar proved to be possible [5]. The paper particularly develops specific solutions for floating PVs and their potential to help local energy communities. A suitable solar-wind combination requires further study. It will also be analyzed whether there is still hydropower potential that can be attracted in the energy mix.

2) It will be supported the increase the flexibility of the electrical power system, especially through important projects, such has the construction of at least one Pumped Hydro Plant (PHP, with favourite locations being on Dniester river), combined with Battery Energy Storage Systems (BESS), these one being projected to hold the biggest amount of the necessary [12].

3) It will be taking into consideration flexibility measures which will reduce the dependence on technological services system provided by neighbouring countries (especially Ukraine).

4) It will be electrified in stages the household heating, through various methods (direct heating through Joule effect, heating with increased efficiency – by using heat pumps, use of existing thermal power plants combined with heating, adapted for green H_2 și CH_4 etc.), all these being accompanied by the methods to increase the efficiency of heat consumption through retrofitting (modernization) at the heating installations level and at the buildings level.

5) It will be electrified in stages the small vehicles park and then the one with trucks and busses and it will be promoted EVs with V2G; this process will be accompanied by ITC charging coordination solutions (solutions equivalent to demand response) and the promotion of EVs with V2G facilities, whose potential to provide flexibility through the use of energy in batteries, is extremely high.

6) The introduction of renewable energy sources will be accompanied as much as possible by agro-photovoltaic solutions which will bring synergistic benefits to both areas, including accelerated electrification of agriculture; where feasible, floating CEFs on lakes close to large consumers will also be encouraged.

7) It will be encouraged the digitalisation of the energy activity, including through smart metering, energy and flexibility services markets, SCADA systems and promotion of initiatives which contain Smart Grid functionalities.

8) It will be encouraged the creation of resilient energy communities which will reduce their risk according to the defects in the public network, of large price fluctuations in the energy field compared to extreme climatic situations. These communities will also be formed in the perspective of building future smart cities, in which resilience and sustainability play key roles. In the same context, small RES producers will be encouraged to become active users.

9) It will be encouraged the realisation of pilots for the emerging technologies, such as Power-to-Gas, respectively obtaining and transporting green hydrogen, inclusively in mixture with methane gas; this field is to be developed cautiously by 2030, waiting for the gradual maturation of technologies at the international level.

10) It will be encouraged new business models, such as Power Purchase Agreements (PPAs) - which guarantee low prices over known periods of time (helping predictably and sustainably other activities of the society), but also appropriate approaches for new technologies, such as financial models Storage as a Service or RES + local storage coupling models, as unitary solutions.

11) It will be encouraged the high-level education and scientific research to support new energy revolution with qualified staff and appropriate solutions, in its ambitious path towards carbon neutrality.

12) Energy policies should be achieved such that they stimulate in an efficient manner these objectives, through lawmakers, government and regulation agency in the energy field.

8. Conclusions

In conclusion, the country's future in the energy field looks pretty good in the long term perspective. However, in order to ensure that this potential is exploited, the Republic of Moldova must take courageous decisions to attract investments. There is a fierce global competition between countries in the world to attract capital, especially between developing and emerging countries. The Republic of Moldova can be a good participant in this race, if it presents a solid business plan in the medium and long term development.

The paper presents the potential pf PV-based energy production at national level, with clear figures for different participations in the total RES, while suggesting a contribution of up to 50% of total yearly consumption, to be complemented by wind, hydro and biomass-based RES production. A connection between the power needed to be installed and the necessary land are is also addressed, while the calculation of needed area for 1 kWp is presented in detail. Moreover, the potential of floating PVs is assessed for various lakes in RM and is proven to be of interest in the future. Finally, the local production with floating PVs has been combined with two local communities needs, by proposing a model for energy communities, more resilient to power outages and to unpredictable energy prices from external sources.

The paper makes also a brief presentation of a roadmap of energy developments till 2050 in the Republic of Moldova. These transformations will happen if the energy strategy planned for decades, state policies and regulations will be put into practice based on specific projects to be carried out in the energy sector, in order to prepare for the inevitable energy transition. The Republic of Moldova will face a lot of challenges in the energy sector in the next ten years, but it is still a process that can be prepared and successfully implemented.

Conflicts of Interest. The authors declare no conflict of interest.

References

1. Towards a green transformation of the Republic of Moldova. Analysis of the situation from 2021. National report based on the OECD set of green growth indicators. EU4Environment. Funded by the EU. 2021. p. 89. Available online: https://euneighbourseast.eu/wp-content/uploads/2022/02/report-green-growth-indicators-republic-moldova-2021-rom.pdf (accessed on 30 June 2022).
2. Efremov, C.; Arion, V.; Sănduleac, M. Short Term Daily Storage Need Assessment for a Large PV Deployment Scenario - Preliminary Case Study for Republic of Moldova. In: 10th International Conference on Energy and Envinonment: proc. IEEE CIEM 14-15 Oct. 2021, Bucharest, Romania, 2021, pp. 1-5. Available online: http://repository.utm.md/handle/5014/18632.
3. Joint Research Centre. Available online: https://re.jrc.ec.europa.eu/pvg_tools/en/tools.html (accessed on 15 May 2021).
4. Administrative map of Moldova. Available online: https://commons.wikimedia.org/wiki/File:Moldova_harta_administrativa.png (accessed on 05 April 2022).
5. Moldelectrica. Technical and operational information regarding the power system operation. Available online: https://moldelectrica.md/ro/activity/operative_info, accessed 10.07.2022 (accessed on 23 June 2022).
6. Gropa, V. Estimation of the impact of Wind Power Plants on the Electrical Power System of Republic of Moldova. Doctoral Thesis, Technical University of Moldova, Republic of Moldova, 2017.
7. https://www.saurenergy.com/solar-energy-news/bhel-bags-order-for-50-mw-solar-pv-power-plant-in-madhya-pradesh-on-epc-basis (accessed on 20 July 2022).
8. https://balkangreenenergynews.com/hydropower-plant-operator-to-install-10-mw-solar-power-plant-in-bih/ (accessed on 30 March 2022).
9. Suncalc online calculator Available online: https://www.suncalc.org/#/47.072,28.7897,9/2022.12.21/14:32/1/3 (accessed on 11 June 2022).
10. How we can use solar energy to unleash an economic boom and protect the climate. Available on: https://www.ise.fraunhofer.de/de/presse-und-medien/presseinformationen/2021/wie-wir-mit-

sonnenenergie-einen-wirtschaftsboom-entfesseln-und-das-klima-schuetzen.html (accessed on 26 July 2022).
11. Germany needs up to 446 GW of solar PV to achieve 100% renewables, Available on: https://renewablesnow.com/news/germany-needs-up-to-446-gw-of-solar-pv-to-achieve-100-renewables-750437/ (accessed on 18 May 2022).
12. Germany needs 446 GW of PV for 100% renewables scenario. Available on: https://www.pv-magazine.com/2021/08/12/germany-needs-446-gw-of-pv-for-100-renewables-scenario/ (accessed on 07 January 2022).
13. WWF says 2% of Germany's surface is enough for 100% renewables. Available on: https://www.pv-magazine.com/2018/10/17/wwf-says-2-of-germanys-surface-is-enough-for-100-renewables/ (accessed on 15 December 2021).
14. Converting just 1% of land to renewable energy production can provide EU's electricity consumption, Available on: https://ec.europa.eu/jrc/en/news/converting-just-1-land-renewable-energy-production-can-provide-eus-electricity-consumption (accessed on 24 July 2022).
15. Efremov, C. Contributions to increase the flexibility of the energy system in order to integrate renewable energy sources. Doctoral Thesis, Technical University of Moldova, Republic of Moldova, 2022.
16. http://maps.google.com (accessed on 15 July 2022).
17. https://www.hydropower-dams.com/wp-content/uploads/FPV_report.pdf (accessed on 10 July 2022).
18. https://statistica.gov.md (accessed on 13 July 2022).
19. https://localitati.casata.md (accessed on 14 July 2022).
20. Efremov, C.; Leu, V.; Sănduleac, M. Increasing System Flexibility Through a Combination Of Pumped-Hydro and Battery-Storage Systems. Preliminary Case Study for Republic of Moldova". 2021 International Conference on Electromechanical and Energy Systems (SIELMEN), 2021, pp. 237-242, doi: 10.1109/SIELMEN53755.2021.9600386. Available on: https://ieeexplore.ieee.org/document/9600386 (accessed on 15 December 2021).

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RHEOLOGICAL CHARACTERIZATION OF INDUSTRIAL WASTE MODIFIED BITUMEN

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Abstract. The aim of this research is to evaluate the rheological properties of industrial waste modified bitumen. The varying proportion of polypropylene ranging from 0% to 20% of the weight of bitumen at 5% interval with 60/70 penetration grade was used. The asphalt binder modification was prepared by using high-speed mixer at temperature from 150 °C to 190 °C. The conventional test like softening point, penetration, ductility, flash and fire point test were carried out to assess the physical characteristics of polypropylene modified and unmodified bitumen, thereafter dynamic shear rheometer and rotational viscosity test were conducted to determine the rheological properties of bitumen. The result indicated that polypropylene has ability to improve the conventional properties of bitumen by increased penetration and ductility, decrease softening point and flash and fire point. Polypropylene modified bitumen provides better resistance against permanent deformation due to their increase in complex modulus and rotational viscosity and decrease in phase angle. It can be concluded that polypropylene modified bitumen could improve the level of performance and service life of the road.

Keywords: *industrial waste, modified bitumen, performance, polypropylene, rheology.*

Rezumat. Scopul acestei cercetări este de a evalua proprietățile reologice ale deșeurilor industriale de bitum modificat. A fost utilizată proporția variată de polipropilenă, variind de la 0% la 20% din greutatea bitumului la interval de 5% cu grad de penetrare 60/70. Modificarea liantului asfaltic a fost preparată utilizând un malaxor de mare viteză la o temperatură de la 150 °C la 190 °C. Testele convenționale cum ar fi punctul de înmuiere, penetrarea, ductilitatea, punctul de aprindere și punctul de foc au fost efectuate pentru a evalua caracteristicile fizice ale bitumului modificat și nemodificat cu polipropilenă, apoi au fost efectuate reometrul de forfecare dinamică și testul de vâscozitate rotațională pentru a determina proprietățile reologice ale bitumului. Rezultatul a indicat că polipropilena are capacitatea de a îmbunătăți proprietățile convenționale ale bitumului prin creșterea

pătrunderii și ductilității, scăderea punctului de înmuiere și a punctului de aprindere și de foc. Bitumul modificat cu polipropilenă oferă o rezistență mai bună împotriva deformării permanente datorită creșterii modulului complex și a vâscozității de rotație și scăderii unghiului de fază. Se poate concluziona că bitumul modificat cu polipropilenă ar putea îmbunătăți nivelul de performanță și durata de viață a drumului.

Cuvinte cheie: *deșeuri industriale, bitum modificat, performanță, polipropilenă, reologie*.

1. Introduction

The asphalt binders are considered as one of necessary materials of construction in flexible pavement, and the performance of flexible pavement is related to asphalt binders. Asphalt pavement with its superior quality has become one of necessary pavement type demanded in Nigeria. It is achievable to increase the service life of asphalt pavement and decrease the maintenance activities by using modifies. The bitumen characteristics can be enhanced using modifies and the toughness of asphalt concrete mixture at high temperature can be reduced which will help in lay down and compaction during constructions.

Waste plastic have been enormously utilized in different area of their significant benefit in term of durability, availability, light and cost effectiveness [1]. The worldwide production of waste plastic attained 368 million metric tons in year 2019 [2], and Nigeria is one of largest producers, accounting for 25%. The diffused use of waste plastic contributes outstanding comfort to everyday life and improves social and economic development. However, large quantity of waste plastic consumed has caused stresses on our environment. Presently, various nations have different waste management strategies for plastic waste. Landfill and incineration have been adopted as a simple way of disposing waste in United State of America, China and other countries. United Stated of America received 27 million tons of plastic by municipal solid waste (MSW) stream in landfill [2]. Landfill has been the natural plastic disposal method that demanded high land resource which also becomes problem facing plastic waste disposal in different countries [2]. The environmental threat created by chemical leaching from plastic into soils and waters could many decades which are disadvantage of using landfill method of disposal of waste plastic. But then, incineration is method of reducing mass and volume of waste in which air pollution results from the high temperature process in the incinerator producing dioxin, CO_2 and other toxic emission [3]. The heavy metals such as lead (Pb) and Cadmium (Cd) released from waste plastic during incineration process is dangerous to the human health [4]. Additionally, micro plastic gotten from degradation of plastic waste created intensive worry for waste management sector, as micro plastic were able to find their way through filtration system and become hard to take way [5]. Accordingly, plastic pollution is one most urgent environmental threat to the modern world [6].

Asphalt binder plays an essential role in pavement performance because it demonstrates the viscoelastic characteristics under pavement operative condition [7]. In other to enhance the reliability of flexible pavement to satisfy the traffic, climatic and other requirements, the use of modified binder rather than unmodified binder has been commended approach [8].

It is established facts that polymer can improve flexible pavement performance in term of high temperature stability [9]. High costs of construction combined with environmental problem created by plastic waste have promoted the utilization of plastic waste in flexible pavement.

Many researchers have investigated the suitable application of utilizing waste plastic in asphalt binder, environmental concern, modified morphology, the properties of waste plastic modified binder and modified mechanism [10]. The utilization of packaging waste polymer and organic montmorillonite was researched by [11] studied and they concluded that waste polymer content resulted increased in viscosity and decrease in penetration while organic montmorillonite decrease the viscosity and improved cracking resistance. The use PET as partial replacement for fine aggregate and result indicated the highest resistance to permanent deformation was recorded at 20 % PET was studied by [12]. The polymer modified asphalt depend on test temperature, asphalt source and polymer type in a study concluded by [13]. They further concluded that polypylene-maleic anhydride and oxidized PE required lower compaction and temperature. A crumb rubber (CR) modified decreased susceptibility to cracking at low temperature and increased the toughness of asphalt concrete in investigation carried out by [14]. The use of rubber tire (scrapped) as a replacement to bitumen was studied by [15] and concluded that scrap rubber modified asphalt binder increased softening point and had 55% elastic recovery which is higher than 35% of unmodified. The utilization of low density polyethylene (carry bag waste) in asphalt concrete was studied by [16], they obtained 10% waste content by weight of bitumen as optimum content and concluded that low density polyethylene improved resistance to fatigue, provide better blending between asphalt binder and aggregate and as well decreased the permanent deformation. Another studied on polymer waste aggregate (PCA) modified blended using polypropylene by [17] reported reduction in water absorption and decrease abrasion of aggregate in asphalt concrete.

Present curiosity in recycling waste plastic indicate substantive gain of utilizing it as a sustainable polymer in enhancing bituminous characteristics, achieving environmental stability and advancing economic-industrial growth. Several type of industrial waste such as modifier were tried globally to improve the rheological characterization of bitumen, such as nano-materials [18], waste plastic [19], crumb rubbers [20] and geopolymers [21]. Waste plastic based polypropylene could be used to enhance the rheological characteristics of bitumen. Polypropylene modified bitumen for road construction can improve the permanent deformation and thermal cracking resistance at high and lower temperature. These possible enhancements can improve the pavement life [22].

The main commonly utilized polymer worldwide includes 75% elastomeric modified binder, 15% plastometric and remaining 10% belongs to either rubber or other modification. The elastomers often use to increase the bitumen at low and high temperature. Nevertheless plastomers are well known efficient additive that can increase high service temperature [23]. Polypropylene belongs to plastomers family which provides rigidity to the bitumen and decrease the deformation under load and effect is more profound when the concentration of polypropylene is high by weight of the base bitumen. Different researchers have examined the possibility of using modifiers in polymer form on the bitumen and asphalt concrete mixture characteristics. The result of these research indicated that modifying using polymers could alter bitumen properties by increasing viscosity [24], increasing softening point [25], improving the performance of grade [26] and decreasing the penetration [27].

Polypropylene is one of the most effective polymer modifiers which are generated from polymer industry. It is semi-crystalline material with excellent chemical resistance, wears resistance, good fatigue and has wide range of properties. Polypropylene is a simple structure that has a long chain of carbon atom with hydrogen atoms attached to each carbon atom. It provides good resistance to organic solvent with low moisture absorption rates.

Polypropylene is commonly use in sweet wrapping, straws, textile, furniture and automobile industrial. These qualities have made polypropylene efficient enough to be used as modifier of bitumen.

2. Materials and Method

2.1. Materials

The bitumen utilized in the present research is 60/70 penetration grade bitumen obtained from K.K Hassan Construction Company in Akure, Nigeria. As shown (Plate 1 and 2) local waste plastic in form of polypropylene were collected at dumping site, washed and grounded to 0.5 to 0.05 mm to be utilized as efficient polypropylene modifier in 60/70 bitumen penetration grade.

Figure 1. Dumping site of waste plastics.

Figure 2. Grounded waste plastic.

2.2 Sample preparation

Samples were prepared using melt blending method. The 200 mg of bitumen was filled inside steel bowel and pre-heated in oven at 130 °C. The grounded polypropylene was replaced at varying proportion of 5%, 10%, 15% and 20% by weight of bitumen. The modified bitumen was thoroughly blended at mixing temperature of 185 °C. Mixing was continued for 45 minute to produce homogenous mixtures. Empirical tests such as softening point, penetration, ductility, flash and fire point were carried out on the samples and thereafter dynamic shear rheometer and rotational viscosity test were conducted to determine the rheological properties of modified bitumen.

2.3 Test Method

The physical test performed on the bitumen and modified bitumen to determine its suitability was flash and fire point test [28], softening point [29], viscosity test [30], ductility test [31] and penetration test [32]. The rheological test conducted in the bitumen and modified bitumen were dynamic shear rheometer test [33] at temperature of 60, 70, 80 and 90 °C and rotational viscosity tests [34] at 135 and 165 °C.

3. Results and Discussion

3.1 Conventional test result of modified and unmodified bitumen mixture

The experimental results of conventional physical properties of modified bitumen with varying percentages of polypropylene are indicated in Figure 3, 4, 5 and 6. It is showed that penetration values continued to decrease as percentage of polypropylene increased as

indicate in Figure 3. They decreased resulted to hardness of modified bitumen because polypropylene has higher molecular weight thereby increase viscosity of the bitumen [35].

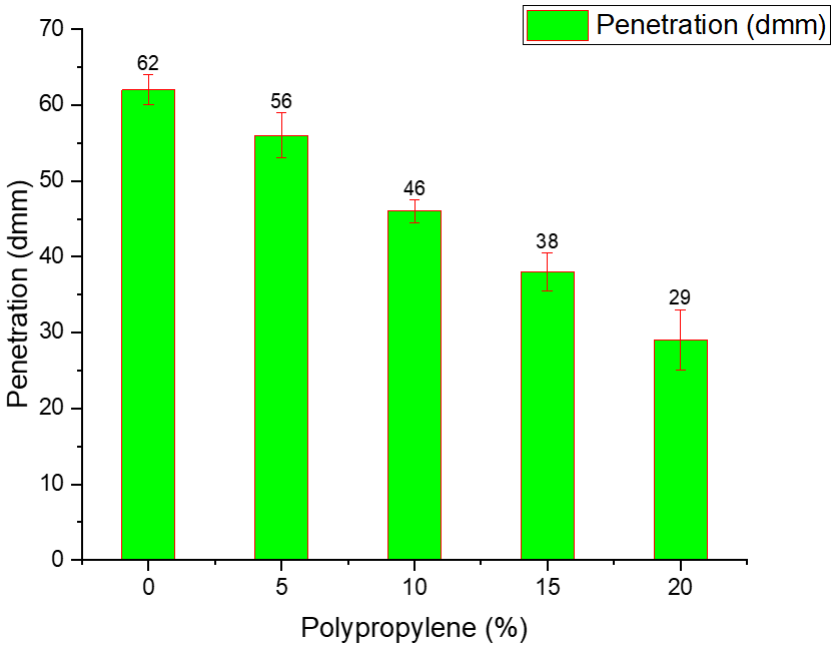

Figure 3. Penetration of Polypropylene.

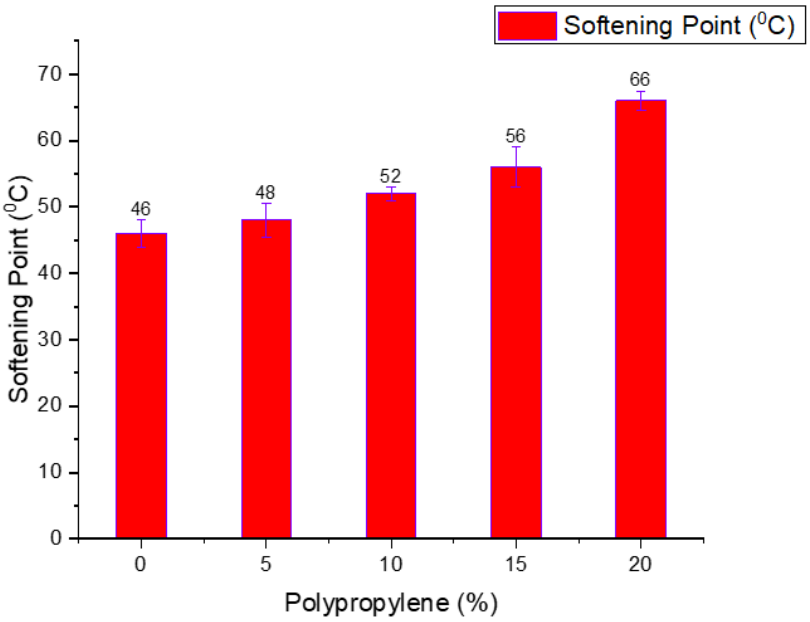

Figure 4. Softening Point of Polypropylene.

Softening point result increased as percentage of polypropylene increased as shown in Figure 4, the result clearly indicated that addition of polypropylene to bitumen increased softening point values. This could be as result of bitumen resistance to the essence of temperature and this shall decrease asphalt pavement to soften in hot weather, thus polypropylene modified bitumen will be less affected to temperature changes [35]. Flash and fire point increased continuously as various proportion of polypropylene increases as indicated in Figure 5. This can be attributed to the different in temperature of the polypropylene and bitumen blended together at increase in temperature. This also showed

that addition of polypropylene content into asphalt mixture will like to decrease fire hazard in asphalt pavement [36].

The result of ductility obtained showed that ductility trend to decrease continuously as proportion of polypropylene increases as shown in Figure 6. As the polypropylene modified bitumen get harder and stiffer, it could resist anti-cracking performance of asphalt concrete at low temperature [37].

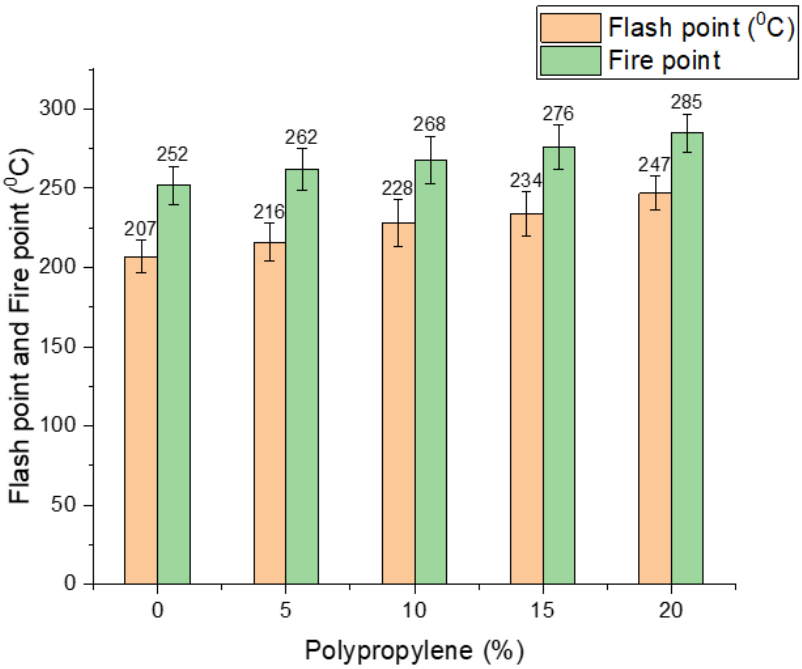

Figure 5. Flash and Fire Point of Polypropylene.

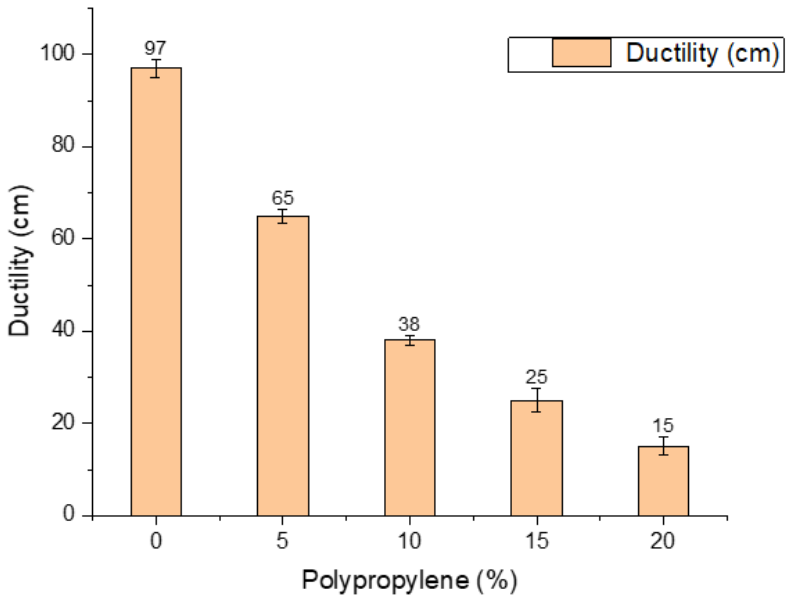

Figure 6. Ductility of Polypropylene.

3.2 Rheological result of modified and unmodified bitumen

The viscoelastic behavior of asphalt binders was characterized at temperature of 60°C, 70°C, 80 °C, and 90 °C using dynamic shear rheometer (DSR). The test results are shown in Figures 7 and 8 which illustrate the complex modulus and phase angle respectively against

different temperature in the binder. The values of complex modulus obtained at 0% (385.9 kPa, 392.5 kPa, 419.8 kPa, 425.7 kPa, 452.9 kPa); 5% (369.5 kPa, 388 kPa, 418 kPa, 421 kPa, 441.8 kPa); 10% (396 kPa, 407.7 kPa, 411.5 kPa, 431.2 kPa, 435.8 kPa); 15% (379.6 kPa, 385 kPa, 379.6 kPa, 401.5 kPa, 415 kPa), 20% (344 kPa, 368 kPa, 385.3 kPa, 400.5 kPa, 408 kPa) and the values of phase angle at 0% (89.2 δ, 86.5 δ, 82 δ, 78.2 δ, 75 δ); 5%(80 δ, 79.5 δ, 77.8 δ, 75 δ, 72.5 δ); 10%(82.5 δ, 77.6 δ, 71.9 δ, 73 δ, 70 δ) δ, 15%(82 δ, 80 δ, 78.6 δ, 77 δ, 60.4 δ); 20% (70.1 δ, 65.2 δ, 60 δ, 58 δ, 52.6 δ). From the result, it can observe that, all samples indicated decrease in phase angle and increase in complex modulus values as the temperature increases. These could be as result of higher shear blending of polypropylene modified bitumen mixture and its synergistic process, which might resist changes in polypropylene asphalt binder particle size and arrangement. The engineering properties of modified was enhanced as seen Figure 7 and 8.

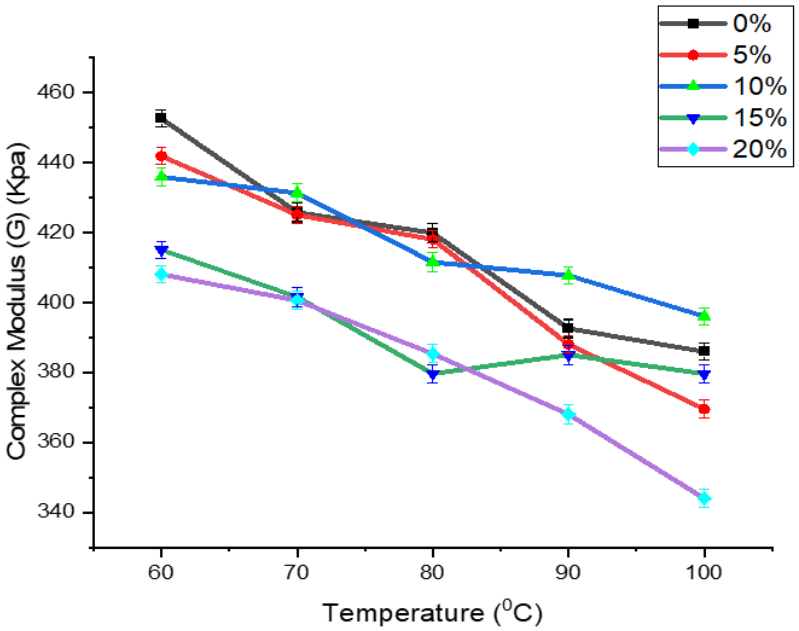

Figure 7. Complex Modulus of Polypropylene.

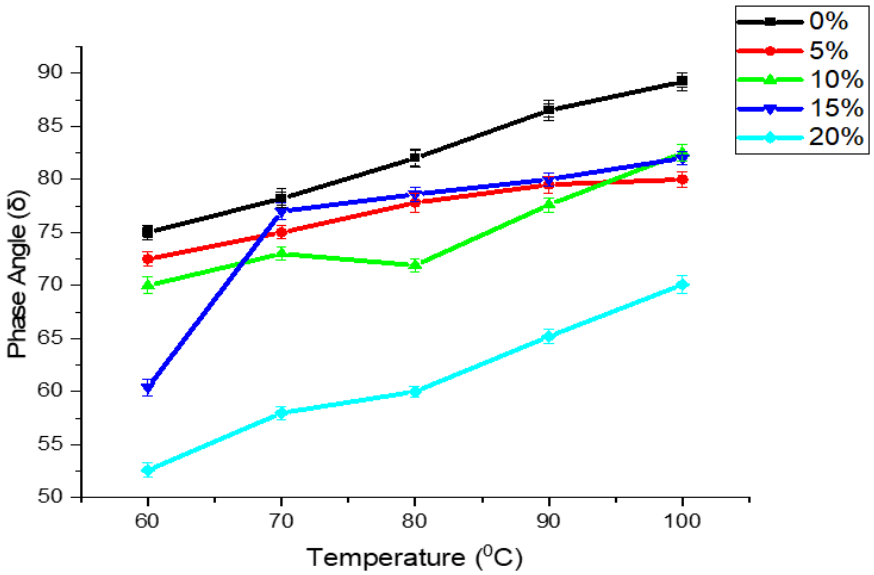

Figure 8. Phase Angle of Polypropylene.

The increase in elasticity is because of the position arrangement of molecule and bonding system with each other which made it more elastic and tough and therefore more resistant to rutting and permanent deformation [38]. Moreover when temperature to the existence to each other increased, it will have higher improvement. The lower phase angle δ means that asphalt concrete mixture is more elastic than viscous and will recover to its original condition without break up [39]. Also, at high temperatures, the lower phase angle is desirable since this will decrease permanent deformation. The addition of Polypropylene had a significant effect on the rotational viscosity of the asphalt as shown in Figure 9. By increasing the Polypropylene content, the rotational viscosity of the asphalt increased rapidly. According to the laboratory test results, Polypropylene contents at 135 °C have high rotational viscosity values while Polypropylene content at 165 °C has low rotational viscosity values because polypropylene decrease molecular weight due to higher temperature was applied [40].

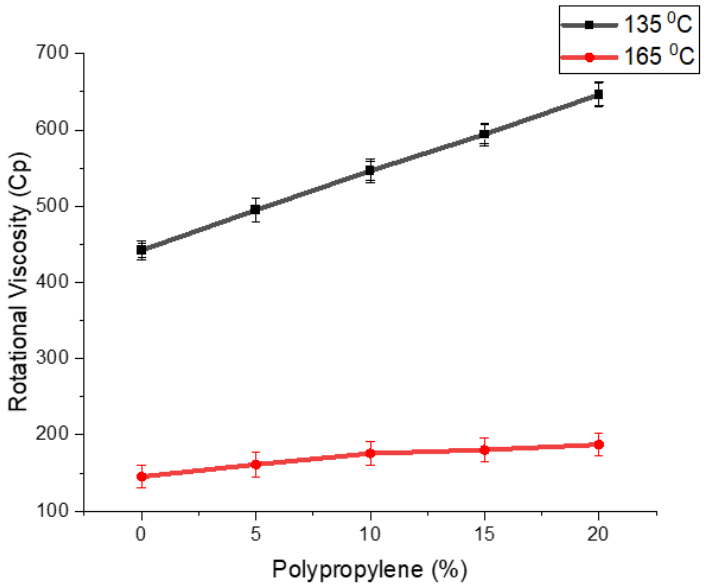

Figure 9. Rotational Viscosity of Polypropylene.

4. Conclusions

The modification of bitumen using polypropylene improves conventional and rheological properties of the modified bitumen produced. Based on the experimental results, the asphalt binder containing polypropylene resulted decrease in penetration, increase in softening point, decrease in ductility and increase in flash and fire point. These results demonstrated that polypropylene modified bitumen improve resistance against permanent deformation and also more advantage when compared to unmodified bitumen used in pavement industry. The rheological property of bitumen was highly affected by addition of polypropylene as indicated by result of dynamic shear rheometer and rotational viscosity. This indicated that polypropylene used as a modifier showed better performance in term of enhancing the rutting deformation and decrease the bitumen susceptibility to crack and deformation at higher temperature.

Conflicts of Interest. The authors declare no conflict of interest.

References

1. Hopewell, J.; Dwrak, R.; Kosior, E. Plastics recycling: challenges and opportunities. *Journal of Philosophical Transaction of Biological Science* 2009, 364 (1526), pp. 2115–2126.
2. Plastic Europe, Avaliable online:https//www.plasticeurope.org/en/resource/market-data (accessed on 20th July, 2021).
3. Wang, X.; Zhang, Y.; Huang, B.; Chen, Z.; Zhong M., Wang, W.; Liu, X.; Fan, Y.N; Hu W. Atompheric phthalate pollution in plastic agricultural green house in Shaanxi Province, Chan. *Journal of Environmental Pollute* 2021, 269, 116096.
4. Brasileriro, L.; Moreno-Navarro, F., Tauste-Martinez ,R.; Matos, J.; Rubio- Gamez, M. Reclaimed polymer as asphalt binder modifier for more sustainable roads. *Journal of Sustainability* 2019, 11(3), pp. 646.
5. Ding, Y; Zou, X.; Wang, C.; Fang, Z.; Fan, Q.; Chan, H. the abundance and characterization of atmospheric microplastic disposition in the northwestern South China Sea in the fall. *Journal of Atom Environment* 2021, 253, pp. 118389.
6. Wang, M.H; He, Y.; Sen, B. Research and Management of plastic pollution in coastal environments of China. *Journal of Environmental Pollution* 2019, 248(5), pp. 898-905.
7. Chan, S.; Che, T.; Mohoseni, A.; Heiden, P.A.; You, Z. Preliminary study of modified asphalt binders with thermoplastic: the rheology properties and inter facial adhesion between thermoplastic and asphalt binder. *Journal of Construction and Building Materials* 2021, 301, pp. 124373.
8. Ragab, A.A.; Fara, R.K.; Kandil, U.F.; El-Shafie, M.; Saleh, A.M.M.; El-Kafarwy, A.F. Thermo-mechanical properties improvement of asphalt binder by using methymethracrylate/ ethylene glocol dimethacrylate. *Egypt Journal of Petroleum* 2016, 25, pp. 379-407.
9. Kalantar, Z.N.; Karim, M.R; Mahrez, A. A review of using waste and virgin polymer in pavement. *Journal of Construction and Building Material* 2012, 33(3), pp. 55-62.
10. Mashaan, N.; Chegenizade, A.; Nikraz H. Laboratory properties of waste PET plastic-modified asphalt mixes recycling. *Journal of Recycling* 2021, 6(3), pp. 49.
11. Fang, C.; Yu, R.; Li, Y.; Zhang, M.; Hu, J.; Zhang, M. Preparation and characterization of asphalt modifying agent with waste packaging polyethylene and organic montmorillonite. *Journal of Polymer Testing* 2013, 32, pp. 973-960.
12. Nobinur R.M.D.; Ahmeduzzaman M.; Sobhan M.A.; Ahmed T.U. Performance evaluation of waste polyethylene and PVC on hot asphalt mixtures. *American Journal of Civil Engineering and Architectures*, 2013, 1, pp. 97-102.
13. Xiao, F.; Amirkhanian, S.; Wang, H.; Hao, P. Rheological property investigations for polymer and polyphosphoric acid modified asphalt binders at high temperature. *Journal of Construction and Building Materials* 2014, 64, pp. 316-323.
14. Cong, P.; Xun, P.; Xing, M.; Chan, S. Investigation of asphalt binder containing various crumbs rubber and asphalts. *Journal of Construction and Building Materials* 2013, 40, pp. 632-641.
15. De-Almeida, J.A.F.; Battistelle, R.A.; Bezena, B.S. Use of scrap tire rubber in place of SBS in modified asphalt as an environmentally correct alternative for Brazil. *Journal of Cleaner Production* 2012, 33, pp. 236-238.
16. Musa, E.I.A.; Haron, H.E.F. Effect of LDPE carries bags on the asphalt mixture. *International Journal of Engineering Research and Science and Technology* 2014, 3, pp. 86-93.
17. Chavan, A.J. Use of plastic waste in flexible pavements. *International Journal of Application or Innovation In Engineering and Management* 2013, 2, pp. 540-552.
18. Saltan, M; Terzi, S; Karahancer, S. Examination of hot mix asphalt and binder performance modified with nano silica. *Journal of Construction and Building Material* 2017, 156, pp. 976-984.
19. Anwar, M; Shah, S; Alhazmi, H. Recycling and utilization of polymers for road construction project. *An Application of Circular Economy Concept of Polymer* 2021, 13, pp. 1330.
20. Gowdzik, B; Matynia, T; Blazejowski, K, the use of de-vulcanized recycled rubber in the modification of road bitumen. *Journal of Material Science* 2020, 13, pp. 4864.
21. Milad, A.; Ali, A.S.B; Babalghaith, A.M; Memon, Z.A; Mashaan, N.S; Arafa, S. Utilization of waste-based geo polymers in asphalt pavement modification and construction. *A Review of Sustainability* 2021, 13, pp. 333.
22. Modarres, A. Investigating the toughness and fatigue behavior of conventional and SBS modified asphalt mixes. *Journal of Construction and Building Material* 2013, 47, pp. 218-222.
23. Ameri, M; Mansourian, A; Sheikhmotevali, A.H. Laboratory evaluation of ethylene vinyl acetate modified bitumen and mixtures based upon performance related parameters. *Journal of Construction and Building Material* 2013, 40, pp. 438-447.

24. Babalghaith, V.O; Rek, V.; Makkovic, K.J. Rheological property and stability of ethylene vinyl acetate polymer modified bitumen. *Journal of Polymer Engineering Science* 2013, 53, pp. 2276-2283.
25. Milad, A.A; Ali, A.S.B; Yusoff, N.I.M. A review of the utilization of recycle waste material as an alternative modifier in asphalt mixture. *Journal of Civil Engineering* 2020, 6, pp. 421-460.
26. Yan, K; You, L. Wang, D, High Temperature performance of polymer modified asphalt mixes. *Journal of Preliminary Evaluation of the Usefulness of Standard Technical Index in Polymer Modified Asphalt* 2019, 11, 1404.
27. Mansourian, A; Goahri, A.R. Khosrowshahi, F. Kn. Performance evaluation of asphalt binder modified with EVA/HDPE/ nanochay based on linear and non-linear viscoelastic behavior. *Journal of Construction and Building Materials* 2019, 208, pp. 554-563
28. ASTM Standard test method for flash and fire point by Cleveland open cup tester. *American Society of Testing and Materials International West Conshohocken* 2016.
29. ASTM Standard test method for softening point of bitumen (ring and ball Apparatus). *American Society of Testing and Materials international West Conshohocken* 2014.
30. ASTM standard test method for viscosity of bitumen material. *American Society of Testing and Materials International West Conshohocken* 2010.
31. ASTM Standard test method for ductility of asphalt materials. *American Society of Testing and Materials International West Conshohocken* 2017.
32. ASTM Standard test method for penetration of bituminous material. *American Society of Testing and Materials International West Conshohocken* 2013
33. ASTM standard test method for determining the rheological properties of asphalt binder using a dynamic shear rheometer. *American Society of Testing and Materials International West Conshohocken* 2015.
34. ASTM standard test method for determining rotational viscosity in the bitumen. *American Society of Testing and Materials International West Conshohocken* 2015.
35. Kalantar, Z.N; Karim, M.R; Aziz, M.A. Effect of waste plastic bottle on properties of asphalt. *Proceeding of Eastern Asia Society for Transportation studies* 2011, 11, pp.1-10.
36. Gupta, Y; Shailendra, P; Tiwari J.K. Utilization of plastic waste in construction of bituminous road. *NBM and CW*, pp. 92.
37. Oyedepo, O.J; Oluwajana, S.D. Evaluation of properties of bitumen modified with waste tyre. *Nigeria Journal of Technology* 2014, 33, pp 119-124.
38. Amir, S; Kareem M.M; Al-Baiati, M.N. Improved asphalt binder using recycled polyethylene terephthalate polymer. *Material Science Engineering* 2019, 571, pp. 82-92.
39. Ghuzlan, K.A; Al-Khatab, G.G; Qasm, Y. Rheological Properties of Polypropylene modified asphalt binder, *Athens Journal of Technology and Engineering* 2014, pp. 1-14.
40. Aflaki, S; Tabatabaee, N. Proposal for Modification of Iranian Bitumen to meet the climate requirement of Iran, *Journal of Construction and Building Material* 2008, 2, pp. 1-10.

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PHYSICOCHEMICAL CHARACTERIZATION OF ASMARA BREWERY EFFLUENTS

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Abstract. Brewing industry is water intensive and consequently generates huge volumes of wastes. Bottle washing and brewing operations recognized as the major effluent sources of Asmara Brewery Corporation Share Company (ABCSC), Eritrea. Effluents of bottle cleaning and brewing sections and their mix of 2:1 characterized on weekly basis for the resemblance of national and international effluent standards. DO levels of wastes detected as low as 2.14 mg/L, which does not support any life and eventually poses severe environmental issues. TSS, COD and BOD_5 levels have exceeded EU and EPA effluents standards. COD and BOD_5 concentrations estimated were higher than other reported breweries and beyond the benchmarks of Brewer's Association, USA. Brewery wastewater has a mean COD of 83240 mg/L and BOD_5 of 11066 mg/L and highly contaminated than bottle cleaning and mixed effluents. Therefore, in order to reuse voluminous wastewater and to curb excessive COD levels, effluents from ABCSC require special attention prior to their discharge into the public sewer line.

Keywords: *Industrial wastewater, characterization, breweries, environmental pollution, chemical oxygen demand, biological oxygen demand.*

Rezumat. Industria berii este consumatoare de apă și, în consecință, generează volume uriașe de deșeuri. Spălarea sticlelor și operațiunile de fabricare a berii sunt recunoscute ca surse majore de efluent ale Asmara Brewery Corporation Share Company (ABCSC), Eritreea. Efluenții secțiilor de curățare a sticlelor și de preparare a berii și amestecul lor de 2:1 sunt caracterizați săptămânal privitor la corespunderea lor standardelor naționale și internaționale pentru efluenți. Nivelurile de DO ale deșeurilor detectate variază până la 2,14 mg/L, ceea ce nu susține nicio formă de viață și în cele din urmă ridică probleme grave de mediu. Nivelurile TSS, COD și BOD_5 au depășit standardele UE și EPA privind efluenții. Concentrațiile de COD și BOD_5 estimate au fost mai mari decât pentru alte fabrici de bere raportate și dincolo de criteriile de referință ale Asociației Berarii, SUA. Apa uzată a fabricii de bere are un COD mediu de 83240 mg/L și BOD_5 de 11066 mg/L și sunt contaminate la curățarea sticlelor și

amestecarea efluenților. Prin urmare, pentru a reutiliza volumele mari de ape uzate și pentru a reduce nivelurile excesive de COD, efluenții din ABCSC necesită o atenție deosebită înainte de deversarea lor în canalizarea publică.

Cuvinte cheie: *Ape uzate industriale, caracterizare, fabrici de bere, poluare a mediului, necesar chimic de oxigen, necesar biologic de oxigen.*

1. Introduction

Water usage has been increasing globally by 1% every year since 1980's and is expected to accelerate at similar rate in future due to continuous growth of population and socio-economic development activities [1]. Prudent utilization of fresh water resources accompanied with promising protection of natural ecosystems is one of the most prominent issues of today's world. Plenty of research has been done or in progress emphasizing optimization of fresh water consumption in domestic, agricultural and industrial applications. Furthermore, there have also been reported the utilization of wastewater with innovative treatment technologies which, at the same time reduces environmental pollution significantly. Different types of chemicals discharged into the aquatic systems through industrial activities pose risk to human health and environment. Some of them are persistent, toxic and partly biodegradable; hence, they do not easily removed in conventional wastewater treatment plants and need a special attention to develop an eco-efficient method for the treatment of a specific pollutant [2].

The brewing industry is water intensive and consequently produces huge volumes of wastewater despite of the beer is fifth most consuming alcoholic beverage in the world and brewing is a multibillion-dollar industry that creates jobs, generates taxes, supports agriculture and attracts tourism [3, 4]. Beer brewing also characterized by the use of high-quality fresh water due to public perception about the deterioration in quality of beer [3, 5]. It was mentioned in several reports that for every 1 L of beer production, approximately 6 to 10 L of water is used [3, 6, 7]. Water in any brewery used typically for brewing, cleaning and cooling processes [7]. Usually, wastewater is pre-treated within the brewery before being discharged into the waterway or municipal sewer system [3]. However, most of them dispose their effluents without adequate characterization, quantification and pre-treatment due to economic and technological constraints, which may have adverse effects on the municipal treatment plant by reducing the efficiency of waste treatment plant and overloading the system [6]. In recent years, a considerable number of environmental issues includes water and soil pollution problems such as eutrophication of rivers and dams [6], inhibition of seed germination, reduction of soil alkalinity and damage of agricultural crops have been reported due to high inorganic and organic matters from industrial effluents [2].

The quantity and characteristics of brewery wastewater can differ significantly from time to time and location to location as it depends on several different processes that occur within a brewery such as malting, mashing, wort processing, fermentation, filtration, bottle cleaning and packaging. [3, 7]. Commonly, the effluents of the brewery are characterized by high organic load and high acidic content [3, 6, 7]. It consists of soluble sugar, soluble starch, carbohydrates, ethanol, volatile fatty acid, suspended solids, yeast etc. [7]. However, the major component of brewery effluents is organic material, as evidenced by high chemical oxygen demand (COD) and biological oxygen demand (BOD) [3, 8]. Both of these parameters (i.e. COD and BOD) are imperative diagnostic parameters for determining the quality of water in natural waterways and waste streams [3, 9].

Case Studied

Asmara Brewery Corporation Share Company (ABCSC) originally known as "MELOTTI BREWERY" established in 1939 and currently it is the only brewery in Eritrea, located in the southern region of Asmara city in central region of the country. The plant's water consumption rates fluctuates from 8.12 to 19.80 L with an average value of 10.76 L for every 1 L of beer produced against 3.5 L, an average water use by the international best practices. Due to the poor design of water supply infrastructure with lack of awareness of water management policies, the water usage rates are very high in the plant [10]. The total average daily available process water is about 870 m^3/day, which is slightly less than the planned water demand of 882.38 m^3/day on average, regardless of the status of water quality and water use and management. Hence, ABCSC system manufacturing operations are vulnerable to the scarcity of process water and it is essential to adopt the best practices of water use minimization, and it is mandate to develop wastewater reuse and recycle technologies as early as possible. Because of voluminous water usage, brewery industry discharges large volumes of highly polluting effluents the year [11]. Noted that effluents from individual process steps are variable. For example, bottle-washing results in a large wastewater volume, but it contains only a minor part of the total organics discharged from the brewery processes. On the other hand, effluents from fermentation and filtering are high in organics/biochemical oxygen demand (BOD), but generally low in volume, accounting for about 3% of the total wastewater volume but 97% of the BOD [11]. Therefore, the present study mainly intensive on identification of major manufacturing operations of the plant that generates higher volumes of wastewater and assessment of effluent compositions to facilitate necessary data for further development of appropriate treatment methods for wastewater recycling. In addition, this may serve as database for the industry and local authority as well to assess the degree of compliance by the industries to the legislative guidelines for effluent disposal.

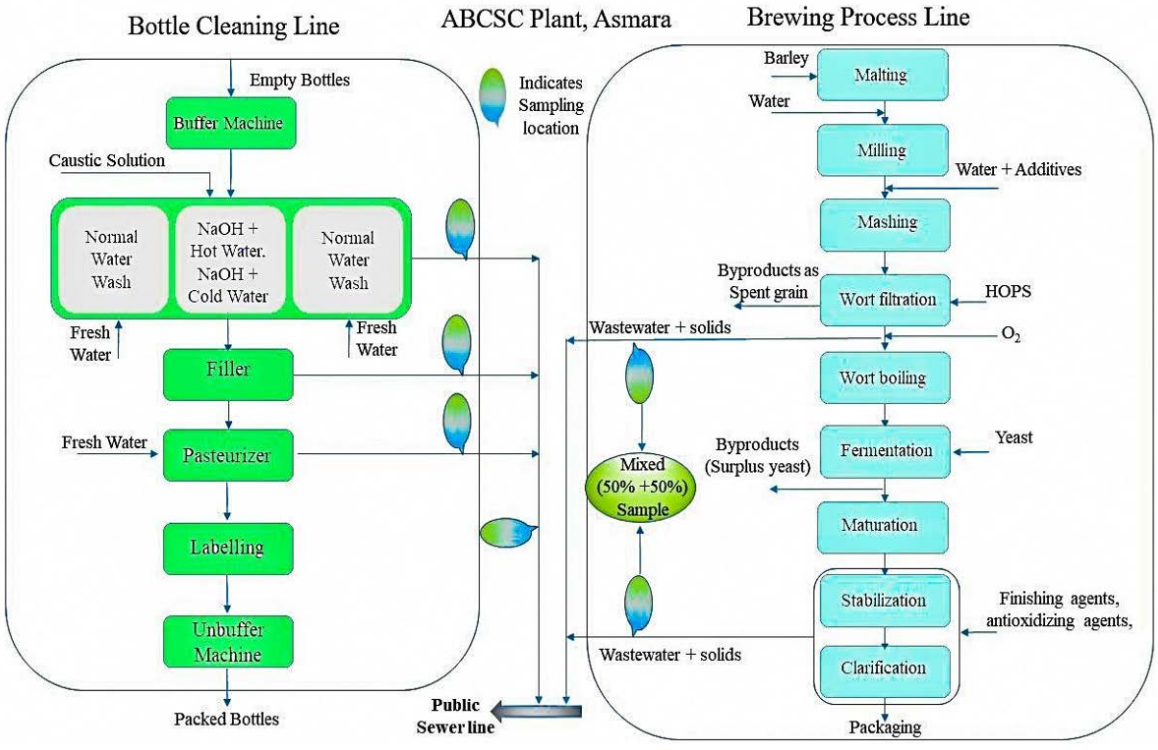

Figure 1. Bottle cleaning and brewing process lines of ABCSC with specified sampling location.

2. Materials and Methods

2.1. Wastewater Sample Collection

Effluent water samples collected from the pre-screened independent sewer exit points of bottle cleaning and brewing sections, two major wastewater-generating units of Asmara Brewery Corporation Share Company (ABCSC) for every week during April and May months, 2021. Samples also collected for one time from Washer, filler and pasteurizer units of bottle cleaning section.

2.2. Characterization of wastewater

Wastewater samples analyzed for physicochemical parameters such as pH, temperature, total alkalinity, salinity, electric conductivity (EC), turbidity, total suspended solids (TSS), Dissolved Oxygen (DO). They were also tested to know the presence of cations such as Sodium (Na^+), Potassium (K^+), Manganese (Mn^{2+}), Total Iron (Fe) and Chromium (Cr^{6+}). Anions such as Sulphate (SO_4^{2-}), Chlorine (Cl), Nitrate (NO_3^-), Nitrite (NO_2^-), Phosphate (PO_4^{3-}),) were also measured. Chemical contaminants were determined by quantifying Chemical Oxygen Demand (COD) and Biological Oxygen Demand for five days (BOD_5).

2.3. Conventional and Instrumental Testing Methods

Salinity, Electric Conductivity (EC) and Temperature measured by using calibrated electrode (WTW Multi 197i, USA). Although pH does not have direct impact, usually it act as an indicator of the process stability and it was read by using a pH meter (HANNA instruments, UK), while the conductivity display the presence of total dissolved solids (TDS) and palatability of water [12]. The dissolved oxygen (DO) content of water determines the activation of biological processes, measured by using a DO meter in mg/L. Total alkalinity, Chloride, total hardness and $CaCO_3$ were measured using digital titration procedures followed by the laboratory of Ministry of Water, Land and Environment of Eritrea.

To measure total alkalinity, 25 mL of a sample titrated with 0.02N H_2SO_4 in presence of Bromcresol Green – methyl red pillow powder (BCG) reagent has turned the solution from green color to pink. Turbidity describes the cloudiness of water caused by suspended particles, chemical precipitates, organic particles and organisms. Turbidity typically expressed as nephelometric turbidity units (NTU) and measured by using Eutech TN-100 instrument made by Thermoscientific, UK. The BOD_5 measurement accomplished using the respirometric method for five days (WAGTECH, FTC 90 system, UK). The COD concentration in the wastewater determined by close refluxing according to the standard method 5220D. Block heater (Stuart, SBH 200D, UK) was first used to digest the samples at 150°C for 2 h in COD vials containing the digestion solution (0–15,000 mg COD/L, acquired from HACH, Germany). Then, COD concentration quantified using a discrete auto-analyzer (HACH, Germany).

Spectrophotometer applied to know the presence of various chemicals in the sample of wastewater tested. System was calibrated at corresponding wavelengths to measure nitrogen in nitrites and nitrates, manganese, iron, sulfates, phosphates and chromium as shown in Table 1. After calibrating the equipment, a bottle of 25ml filled by the sample and appropriate reagent was added and mixed for specified reaction time and measured corresponding absorbance on spectrophotometer. Nitrate and nitrite ions not found from the spectrophotometer reading directly. Instead, nitrogen in nitrates and nitrites found from the spectrophotometer reading, later Nitrates and Nitrites are calculated as:

$$NO_3^- = N - NO_3^- \times 4.429$$
$$NO_2^- = N - NO_2^- \times 3.286$$

The amount of sodium and potassium present in the wastewater sample measured using the flame photometer shown in fig 2B. The function of this instrument is similar to spectrophotometer except that it uses flame rather than light. Initiation step takes some time once it turned on, then system calibrated prior to read the values for actual samples. After that, by taking the sample in a small measuring cup and inserting aspiration tube in to the cup of the sample, and supplied into the flame photometer to read its absorbance.

Table 1

Characterization methodology using spectrophotometry

Test	Code	Wave length (nm)	Reagent	Mixing method	Reaction time (min)
Manganese(Mn^{+2})	295	525	Buffer, citrate type Sodium Periodate	Invert to mix Invert to mix	2
Total Iron (Fe)	265	510	FerroVer	Swirl to mix	3
Sulfates (SO_4^{2-})	680	450	SulfaVer 4	Swirl vigorously to mix	5
Nitrates (N-NO_3^-)	355	500	NitraVer 5	1min vigorous shake	5
Nitrites (N-NO_2^-)	371	507	NitriVer 3	Swirl to mix	15
Phosphates (PO_4^{3-})	490	890	PhosVer 3	30sec vigorous shake	2
Chromium (Cr^{+6})	90	540	ChromaVer 3	Swirl to mix	5

2.4. Statistical Analysis

Compositions of bottling line wastewater and mixed streams of 2:1 of bottling and brewery lines wastewater samples are analyzed and the results are verified with analysis of variance (ANOVA) study using Microsoft Excel®, 2016 software.

Figure 2. a) Spectrophotometer b) Flame Photometer.

The variance and mean values of characterized parameters are determined for the comparison with the reported values for other breweries and other industrial effluents from the literature and also with national and international industrial effluent standards.

3. Results and Discussion

According to the informants of ABCSC, approximately 8.455 L of wastewater discharges per every L of beer produced and it is mainly comprised of two major process lines i.e., bottle cleaning (BC) line and brewing line. Despite of the water consumed in BC line discharged totally into the sewer a basis for the wastewater treatment set by assuming that BC line alone contribute 2/3rd of the total wastewater generated from the ABCSC plant and the remaining by the brewing line. To identify the qualitative nature of the BC wastewater, samples tested once from each cleaning equipment for physicochemical characteristics as given in Table 2. Wastewater from filler and pasteurizer units have low pH values whereas in washer shown significantly higher values and which resulted a further higher value of the BC line sample collected from a single exit point source just before it discharges into public sewer line. Filler and pasteurizer wastes have shown greater variation from washer operations. Higher COD values recorded for filler and pasteurizer discharges.

Table 2

Physicochemical Properties of Wastewater from Bottle Cleaning Operations in ABCSC

Parameter	Point Sources Wastewater from Bottle Cleaning Section					
	Filler	**Pasteurizer**	**Washer 1**	**Washer 2**	**Washer 3**	**Bottle Cleaning**
Temperature (^oC)	17.3	17.4	16.9	16.3	17.7	19
pH	5.72	5.91	11	10.81	11.04	12.36
EC (µs/cm)	499	566	1696	1350	1290	3840
Turbidity (NTU)	5.85	83.8	94.5	382	1400	112
Salinity (mg/L)	0	0	0.7	0.5	0.4	3.5
Sodium Na^+(mg/L)	37.5	38.4	269	209.7	210	526.5
Potassium K^+ (mg/L)	16.1	14.5	3	17.1	3	12.2
DO (mg/L)	2.43	0.67	5.66	5.85	5.87	3.28
COD (mg/L)	4700	1350	30	42	90	4800
BOD_5 (mg/L)	1926.7	806.7	8.9	10	11.1	2310

Note: DO-dissolved oxygen; COD-chemical oxygen demand; BOD_5 - biological oxygen demand for five days.

Brewing line has two major discharge streams from wort filtration and clarification units, hence samples of mixed (50 % of wort filtration waste and 50 % of clarification wastewater) stream have considered as brewery wastewater. Samples were collected for five consecutive weeks, from the both BC line (BCWW) and brewery lines (BRWW) and mixed wastewater (MWW) samples of 2/3rd of BC line discharge and 1/3rd of brewery line discharge were also prepared. Weekly samples characterized for physicochemical parameters and their analysis revealed that they possess greater diversity in COD values and the samples collected during first two weeks have recorded with higher COD values as shown in Figure 3, whereas BRWW samples have shown higher BOD_5 than BCWW and MWW samples in Figure 4.

BOD_5/COD values were higher for BRWW samples; a value of 0.547 was observed as greater than any other sample and recorded by 4th sample of BRWW as in Figure 5.

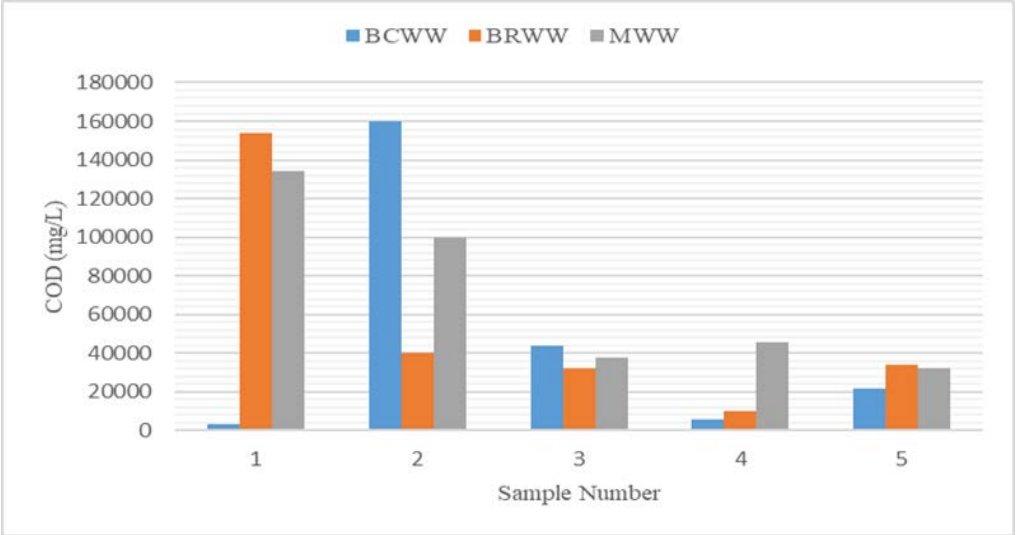

Figure 3. Weekly estimated chemical oxygen demands of Asmara brewery waste samples.

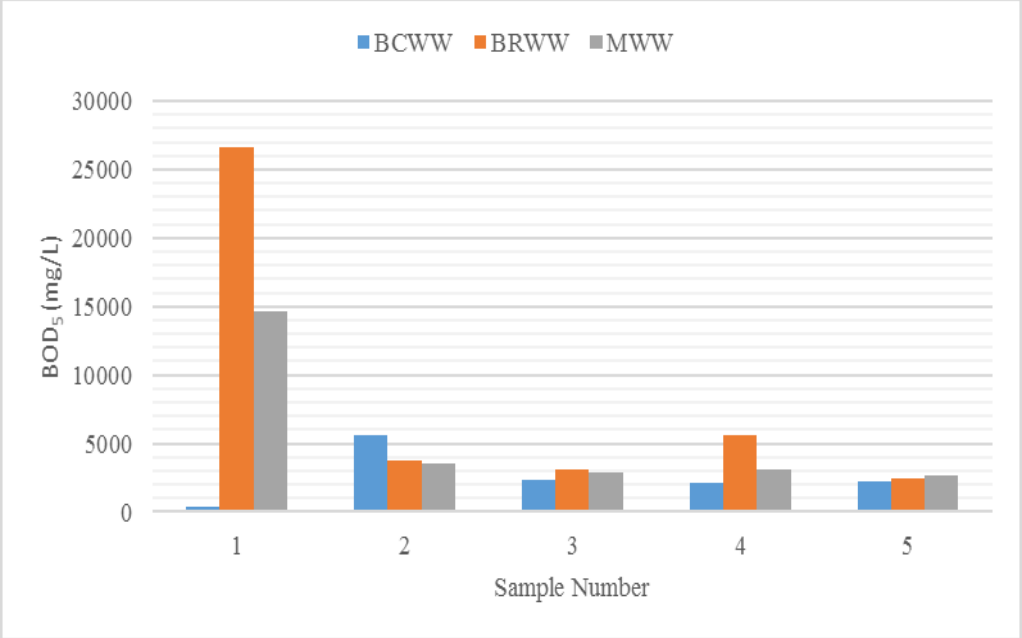

Figure 4. Weekly estimated biological oxygen demands of Asmara Brewery waste samples.

Although pH usually has no direct impact on environment, it is one of the most important operational water quality parameters and plays key role in controlling minimization of corrosion of water carrying systems. pH values of all the samples studied hold relatively higher pH values except for the samples collected during 2nd week. Bottle washer consumes chemicals such as caustic soda, it caused for higher pH values of BCWW samples.

However, lower- pH (approximately pH -7 or less) water is more likely to be corrosive. BRWW samples shown lower pH values than BCWW and MWW samples and a pH of 2.62 was noted in the sample collected during 1st week as the lower than any other samples as shown in Figure 5(a).

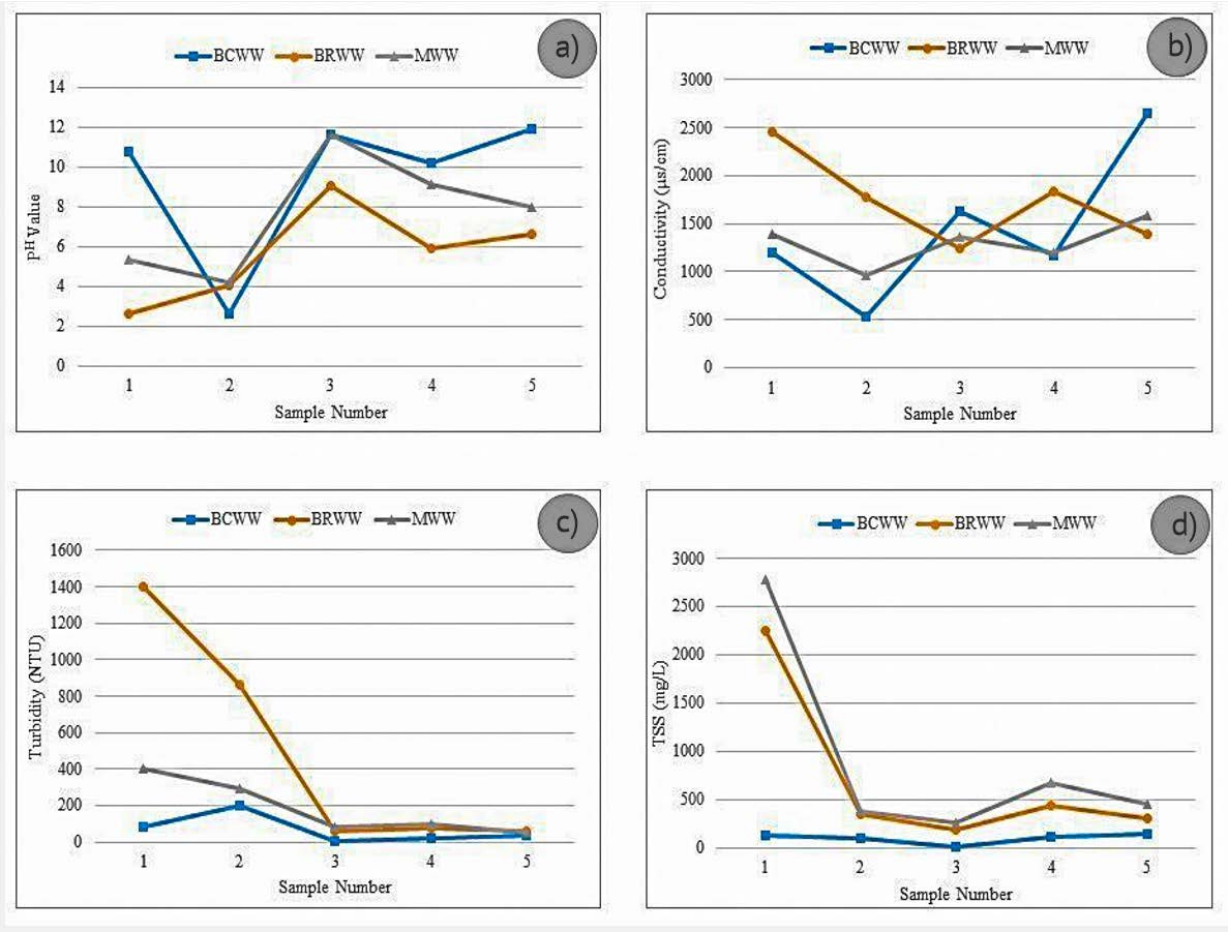

Figure 5. Weekly estimated pH (a), electric conductivity (b), turbidity (c) and total suspended solids (d) values of Asmara Brewery effluents.

Dissolved oxygen (DO) levels in the water indicate the potential existence of aquatic life. Nevertheless, a value of DO less than 4.5 mg/L can't support any life in water [13]. Figure 6 depicts that BRWW samples has lower DO levels than any other samples and it was also seen a lowest value of 0.39 mg/L for BRWW sample collected during 2nd week of our study. Thus, BRWW and MWW samples doesn't support any aquatic life but BCWW has comparatively higher DO levels, yet they are far lower than 9.5 mg/L above which a healthy life could be identified in water bodies [13].

The palatability of water is determined with the presence of total dissolved solids (TDS) which can be estimated through electric conductivity. Higher levels of TDS, greater than about 1000 mg/L may objectionable to handle, owing excessive scaling in pipes, heaters, boilers and household appliances [12]. Higher conductivity has seen for BRWW samples collected during 1st week and also for the BCWW samples collected in 5th week. MWW samples have shown less deviation among the conductivity values measured as described by the Figure 5(b). Turbidity describes the cloudiness of water, increasing turbidity reduces the clarity of water to transmitted light. Brewery wastewater samples have recorded with higher turbidity values than BCWW and MWW whilst BCWW has lower turbidity than both MWW and BRWW for all the samples. Turbidity also indicate the presence of physical, chemical and biological contaminants. Presence of total suspended solids (TSS) indicate the direct measure pollutants in the wastewater, and higher TSS values were noticed in the first week samples of MWW and BRWW. MWW samples have shown higher TSS levels than any other samples

collected in every week as shown in Figure 5(d) whereas BCWW samples were observed with lower TSS values.

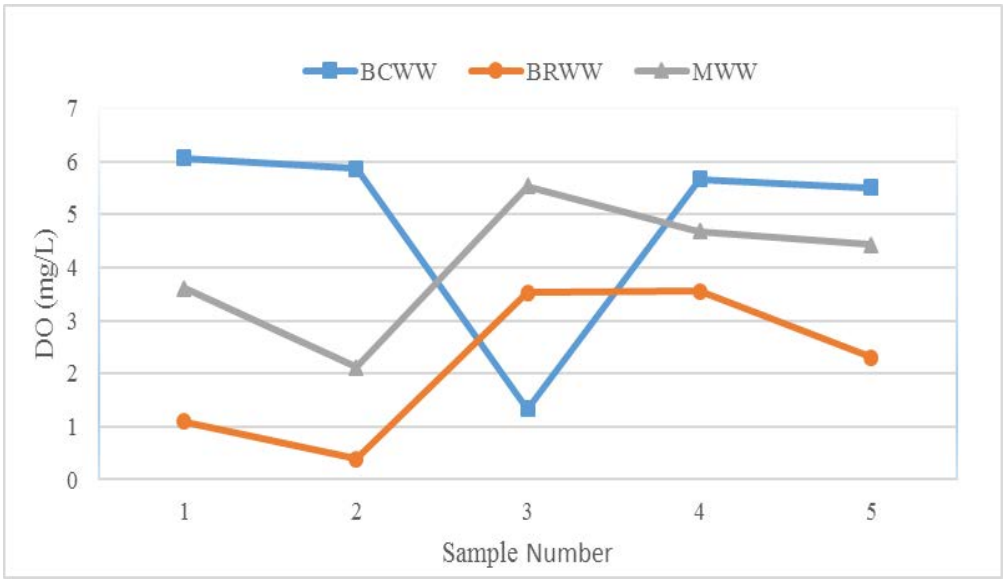

Figure 6. Weekly estimated dissolved oxygen levels of Asmara Brewery discharges.

Table 3

ANOVA Study of ABCSC Brewery and Bottle Cleaning and Mixed wastewater characteristics

Parameters	Bottle cleaning wastewater		Brewery Wastewater		Mixed Wastewater	
	Range	Mean	Range	Mean	Range	Mean
Temperature (°C)	19-34.4	28.36	26.3-34.4	29.6	24-31.2	27.94
pH	2.62-12.36	9.41	2.62-9.03	5.6	4.22-11.59	7.8
EC (µs/cm)	538-3840	1432.6	1244-2450	1740.2	968-1578	1297.2
Turbidity (NTU)	5.03-112	83.366	58.9-1400	599.8	51.3-400	218.3
Salinity (mg/L)	0-3.5	1.01	0.4-1.1	0.7	0.3-0.6	0.46
Sodium Na^+ (mg/L)	29.8-526.5	246	26.7-199.4	108	39.5-185	122.27
Potassium K^+ (mg/L)	2.1-184.8	52.12	6.7-64.5	24.8	6.3-41.1	17.77
DO (mg/L)	1.33-6.06	3.84	0.39-3.55	2.14	2.12-5.53	3.98
COD (mg/L)	3500-160000	43560	10200-154000	83240	32000-134000	70000
BOD_5 (mg/L)	357-5633	3594	3133-26667	11066	2856-14667	6641
COD/BOD_5	2.57-28.41	13.9	1.83-14.08	8.51	9.17-27.9	15.44
Total hardness	40-400	166.67	400-900	709.33	68-392	273.33

Note: EC - electric conductivity; DO - dissolved oxygen; COD - chemical oxygen demand; BOD_5 - biological oxygen demand for five days; NTU - nephelometric turbidity units.

A single factor analysis of variance (ANOVA) study was performed to determine the mean and variance values of all characteristic parameters and the results are listed in Table 3. COD and BOD_5 values were deviated highly for BCWW, BRWW and MWW samples. The highest mean of COD has seen as 83240 mg/L for BRWW samples with a range of 10200-154000mg/L. Although BCWW samples have shown less mean value, a significant range of COD, 3500-160000 mg/L was noted. The mean COD values of all BRWW, BCWW and MWW samples were too far from the benchmarks of Brewers Association, USA (Table 4). The variations in the COD concentrations for each week could be as a result of variation in the activities and housekeeping practices of the brewery plant, which could cause serious environmental impact and closure of the production plant by the municipal authority, if not checked.

Table 4

Comparison of brewery wastewater with Eritrean Effluent standards and Effluent benchmarks of BA

Parameter	Bottle Cleaning line Effluent Composition	Brewing line Effluent Composition	Mixed (2:1) Effluent Composition	Industrial Effluent standards entering Public Sewers in Eritrea [15]	Brewers Association (USA) Benchmarks for Effluent [14]
Temperature (^oC)	28.36	29.6	27.94	< 43	NA
pH	9.41	5.6	7.8	6-10	3-12
TDS	1228.67	1166	869	< 3000	< 3000
TSS	98.2	606.8	203	< 600	200-1500
Sulphate (mg/L)	50.5	236.75	95	< 1500	NA
Fe (mg/L)	0.714	1.466	0.896	< 25	NA
Mn (mg/L)	2.03	7.13	3.325	< 25	NA
COD (mg/L)	43560	83240	70000	NA	1800-5500
BOD_5 (mg/L)	3594	11066	6641	NA	600-5000
COD/BOD_5	12.12	7.522	10.54	NA	NA

Note: TDS - total dissolved solids; TSS - total suspended solids; COD - chemical oxygen demand; BOD_5 - biological oxygen demand for five days.

Physicochemical characteristics of BCWW, BRWW and MWW were analyzed to compare with industrial effluent quality standards that permit into public sewers of Eritrea as shown in Table 4. Mean values of Temperature, pH, TDS, TSS, Sulphate, Iron, Manganese were observed as within permissible limits of national industrial effluent standards, Eritrea. Average concentration of pH, TDS and TSS were also notified as within the limits of effluent benchmarks set by the Brewer's Association, USA. BOD5 is an indicator of organic loading in the effluent streams, brewery operations have showed 4 times greater BOD_5 than bottle washer line. Mix of $1/3^{rd}$ of brewery effluent with $2/3^{rd}$ of BCWW, has doubled the levels of BOD_5. Brewery discharges also shown doubled COD loadings than bottle cleaning wastes. BOD_5 & COD levels of wastewater from bottle cleaning line were comparatively lower and BOD_5 concentration was also dwell within the limitations of Brewer's Association, benchmarks. In all other cases, COD and BOD_5 levels were very much higher than usual

brewery effluents which indicates greater chemical and biological contamination of ABCSC effluents. As COD/BOD_5 is 12.12 for BCWW, it has loaded with high levels of chemical contaminants than BRWW and MWW, whereas COD/BOD_5 is 7.522 for BRWW, it contains higher organic loadings.

Table 5

Comparison of ABCSC wastewater characteristics with other reported parameters in the literature

Parameter	This work	Gemeda et al. [16]	Akunan et al. [17]	Enitan et al. [18]	Brito et al. [19]	Driessen & Vereijken, [20]
Temperature (°C)	24-31.2	20.9	ND	27.9	30-35	18-40
pH	4.22-11.59	6.55	5-11	6.0	6.5-7.9	4.5-12
EC (µS/cm)	968-1578	5425	ND	1516	ND	ND
TSS (mg/L)	154-520	140.15	ND	1826.74	ND	200-1000
TN (mg/L)	0.004-14.7	166.5	20-600	13.29	12-31	25-80
TP (mg/L)	0-19.45	11.55	4-103	23.71	9-15	10-50
Total COD (mg/L)	32000-134000	210.9	1800-50000	5341	800-3500	2000-6000
BOD_5 (mg/L)	2700-14667	209	2700-38,000	3215.27	520-2300	1200-3600

Note: EC - electric conductivity; TSS - total suspended solids; TN - total nitrogen; TP - total phosphorous; COD - chemical oxygen demand; BOD_5 - biological oxygen demand for five days.

Quality of ABCSC mixed wastewater (MWW) composition was comparable with other reported parameters in the literature as in Table 5.

Table 6

Comparison of brewery wastewater with other industrial and municipal wastewater

Parameter	Brewery	Dairy (Milk-cheese) plants	Tannery	Textile Mills	Municipal
pH	4.22-11.59	5.2-11.3	8-11	4.5-10.1	6-8
Salinity (g/L)	0.3-0.6	0.5	6-40	0.5-0.9	<0.5
TSS (mg/L)	154-520	350-1082	2070-4320	20-210	100-350
TN (mg/L)	0.004-14.7	14-450	250-1000	14-72	20-85
TP (mg/L)	0-19.45	37-78	4-107	1-18	4-15
Total COD (mg/L)	32000-134000	189-20000	3500-13500	1900-100000	250-1000
BOD_5 (mg/L)	2700-14667	709-10000	1000-7200	700-1650	110-400
Reference	This Work	Bielefeldt, 2017 [21]	Bielefeldt, 2017 [21]	Bielefeldt, 2017 [21]	Bielefeldt, 2017[21]

Note: TSS - total suspended solids, TN - total nitrogen; TP - total phosphorous; COD - chemical oxygen demand; BOD_5 - biological oxygen demand for five days.

The range of pH was similar with Driessen and Vereijken study in 2003 [20]. Enitan et al. [18] has reported a conductivity of 1516 μS/cm, which dwell in the range of this study. TSS concentrations of this report are moderate when it compared with Enitan et al. [18], F.T. Gemeda et al. [16], and Akunan et al. [17], have reported higher range of total nitrogen (TN) values, but this study is comparable with Enitan et al. [18], and Brito et al. [19]. Total Phosphates (TP) are comparable with all the reports with slight deviation. COD concentrations are too higher than any other reported values, which indicate the presence of high levels of chemical contaminants in ABCSC wastewater. BOD_5 levels also higher than all reported values except Akunan et al. However, these quantitative comparisons made a clear conclusion that all the characteristics are case specific and have greater diversity in their values.

The study also considered brewery industry to compare with other relevant process industries in Eritrea concerning their effluent compositions. Dairy, tannery, textile mills and domestic wastewater were comparable with brewery effluents as shown in Table 6. Chemical loadings of ABCSC effluents are competitive with effluents of textile mills. BOD_5 concentrations are approximately in the rage of dairy wastes, pH values are as high as dairy and tannery wastes and nutrients such as nitrogen and phosphorous are typically in the rage of textile wastes. Noted that most of the parameters of brewery industry wastes are different from municipal wastewater. Brewery wastes cannot be treated usually with municipal wastewater treatment plant, as they require special attention.

Table 7

Assessment of ABCSC effluent quality with EU and EPA effluents standards

Parameter	Bottle Cleaning line Effluent Composition	Brewing line Effluent Composition	Mixed (2:1) Effluent Composition	EU, Effluent Limits [22]	EPA, Effluent Standards [23]
TSS	98.2	606.8	203	35	50
COD (mg/L)	43560	83240	70000	125	150
BOD_5 (mg/L)	3594	11066	6641	25	50
COD/BOD_5	12.12	7.522	10.54	5.0	3.0

Note: TSS - total suspended solids; COD - chemical oxygen demand; BOD_5 - biological oxygen demand for five days.

TSS, COD and BOD_5 levels of ABCSC discharges are beyond international limits such as EU discharge limits EPA, USA effluents standards as shown in table 7. Suspended solid are more in brewery effluent than bottle cleaning wastewater, and it is 17 times and 12 times of EU and EPA standards. COD concentration of mixed effluent is 560 and 467 times of EU and EPA effluents limits respectively, which indirectly warns the company to take immediate action to control such higher chemical contaminants in the effluents. In other words, organic loadings of mixed effluent exceed 256 and 133 times the permitted values of EU and EPA. COD/ BOD_5 estimated as twice the EU limit and thrice the EPA regulated value that specifies more presence of chemicals than organics.

4. Conclusions

According to the informants of ABCSC, approximately 8.455 L of wastewater discharges per every L of beer produced and it is mainly comprised of two major process lines i.e., bottle cleaning (BC) line and brewing line. Thus, samples of bottle cleaning and brewery effluents were collected weekly and their physicochemical characteristics were analyzed. Mean values of dissolved oxygen (DO) of all wastewater samples were found lower than 4.5 mg/L. Thus, it indicates no life in such effluents and subsequently causes for severe environmental issues. The results of this study showed that COD and BOD_5 concentrations of wastewater from ABCSC are higher than other brewery industries reported in the literature and they are also beyond the benchmarks set by Brewer's Association, USA. TSS, COD and BOD_5 levels have exceeded the international standards such as EU and EPA effluents standards, which indicate an immediate action by the company to prevent the cost of penalties. Therefore, there is a need to treat the brewery wastewater in order to protect the environment and to reduce the use of fresh water sources.

The levels of pH, TSS, COD and BOD_5 of brewery effluents are beyond the ranges of municipal waste water, hence they can't be treated together. Instead, brewery wastewater might be treated separately with a special attention to remove higher COD levels. As the characteristics of bottling and brewery effluents are distinct, treatment technologies can be developed based on their significant variation in characteristics. As COD/BOD_5 is 12.12 for BCWW, it contains high levels of chemical contaminants than BRWW and MWW, whereas COD/BOD_5 is 7.522 for BRWW, it has higher organic loadings. Characteristics of mixed wastewater were determined to develop a suitable pretreatment plant for the potential reuse of water through an existing RO plant in ABCSC.

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Conflicts of Interest. The authors declare no conflict of interest.

References

1. Ramesh Babu, A.; Samsom, K.; Samuel, M. Experimental studies on Step Response of Water Level Control System with P, PI and PID Control Mechanisms. *IRJET* 2020, 10(7), pp. 1504-1509.
2. Akbarzadeh, R.; Adeniran, J.A.; Lototskyy, M.; Asadi, A. Simultaneous brewery wastewater treatment and hydrogen generation via hydrolysis using Mg waste scraps. *JCP*, 2020, 20, pp. S0959-6526. https://doi.org/10.1016/j.jclepro.2020.123198
3. Simate, G.S. Water treatment and reuse in breweries. *Brewing Microbiology* 2015, pp. 425-456.
4. Richey, D. California craft brewing industry: An economic impact study. California Craft Brewers Association, 2012. Available online: http://www.californiacraftbeer.com/wp-content/ uploads/2012/10/Economic-Impact-Study-FINAL.pdf. (accessed on 12, Aug 2021)
5. Janhom, T.; Wattanachira, S.; Pavasant, P. Characterisation of brewery wastewater with spectrofluorometry analysis. *JEM*, 2009, 90, pp. 1184–1190.
6. Abimbola, M.E.; Feroz, M.S.; Josiah, A.; Faizal, B. Assessment of Brewery effluent Composition from a Beer Producing industry in Kwazulu-Natal, South Africa. *FEB* 2014, 3(23), pp. 693-701.
7. Kothiyal, M.; Semwal, G.N. Performance Evaluation of Brewery Biological Wastewater Treatment Plant. *MOJ Eco Environ Sci.* 2018, 3(1), pp. 00058.

8. Brewers of Europe. Guidance note for establishing BAT in the brewing industry. Brussels: Brewers of Europe, 2002. Available online: http://www.brewersofeurope.org/docs/ publications/ guidance.pdf. (accessed on 25, February 2022)
9. Mantech. PeCOD application note1. Mantech Inc, Ontario, 2011. Available online: http://www.titralo.hu/WEBSET_DOWNLOADS/613/PeCOD-Wastewater%20Industry.pdf. (accessed on 15, February 2022).
10. Water and Environment Department Committee (WAEDC) Report, Evaluation and Upgrading of process water for system manufacturing operations in Asmara Breweries Corporation Share Company (ABCSC) 2014. Available with ABCSC, Asmara and accessed with permission during our project tenure, 2021.
11. Simate, G.S.; Cluett, J.; Iyuke, S.E.; Musapatika, E.T.; Ndlovu, S.; Walubita, L.F.; Alvarez, A.E. The treatment of brewery wastewater for reuse: State of the art. *Desalination* 2011, 273, pp. 235-247. doi:10.1016/j.desal.2011.02.035.
12. Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva: World Health Organization; 2017. Licence: CC BY-NC-SA 3.0 IGO. ISBN 978-92-4-154995-0.
13. Report on Dissolved Oxygen, Available online: https://www.enr.gov.nt.ca/sites/enr/files/dissolved_oxygen.pdf, (accesses on 10, April 2021).
14. Wastewater Management Guidance Manual, Brewers Association, USA. Available online: www.brewersassociation.org. (accessed on 15, April 2021).
15. Industrial Effluent standards entering Public Sewers in Eritrea. Available with Analytical lab, Ministry of Water, Land and Environment (MoWLE), Asmara, Eritrea. Accessed with permission in the month of May 2021.
16. Gemeda, F.T.; Guta, D.D.; Wakjira, F.S.; Gebresenbet, G. Physicochemical characterization of effluents from industries in Sabata town of Ethiopia. *Heliyon*, 2020, 6 (8), e04624.
17. Akunna, J.C. Anaerobic treatment of brewery wastes. *Brewing Microbiology* 2015, pp. 407-424.
18. Enitan, A.M.; Swalaha, F.M.; Bux, F. Assessment of Brewery Effluent Composition from a Beer Producing Industry in Kwazulu-Natal, South Africa. *FEB* 2014, 23.
19. Brito, A.G. Brewery and Winery Wastewater Treatment: Some Focal Points of Design and Operation. Utilization of By-Products and Treatment of Waste in the Food Industry. Springer, Boston, MA. 2007. https://doi.org/10.1007/978-0-387-35766-9_7.
20. Driessen, W., Vereijken, T. Recent developments in biological treatment of brewery effluent, The Institute and Guild of Brewing Convention, Livingstone, Zambia, March 2-7, 2003.
21. Beilefeldt, A.R. Water Treatment, Industrial. Reference module in Life Sciences, 2017. doi:10.1016/B978-0-12-809633-8.13124-3
22. Council Directive. Concerning urban Wastewater treatment, Official Journal of European Communities, No. l 135/40, 1991.
23. EPA Effluent Standards, Revised by EPA Order Huan-Shu-Shui-Tzu No. 1030005842, January 22, 2014.

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RECENT ADVANCES IN SMART KITCHEN AUTOMATION TECHNOLOGIES: PRINCIPLES, APPROACHES, AND CHALLENGES

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Abstract. The Internet of Things (IoT) is a growing network of physical devices that are connected to various types of sensors and can share data with the aid of internet connectivity. Safety is an important consideration when designing a house, town, smart kitchen, etc., and it continues to play an important role in today's world. In general, the kitchen is regarded as one of the most crucial tasks in our everyday lives, making it imperative to equip this vital element of human life with smart devices to avoid commonplace incidents such as gas leaks, intense particles in the environment, or fire outbursts. Gas leaks in the kitchen can be dangerous and deadly, resulting in fires if they go unchecked. For smart kitchens, various systems have been built to combat gas leaks and fire outbreaks. However, despite their high precision, these systems each have their own set of flaws that have severely restricted their implementations. The state-of-the-art in gas leakage, fire, and smoke detection in a smart kitchen is discussed in this paper. Different methods of gas leakage and fire detection are also addressed, along with their strengths and weaknesses, as well as products available in the market today.

Keywords: *Internet of things (IoT), smart kitchen, gas leakage, smoke, safety systems.*

Rezumat. Internetul lucrurilor (IoT) este o rețea în creștere de dispozitive fizice care sunt conectate la diferite tipuri de senzori și pot partaja date cu ajutorul conexiunii la internet. Siguranța este un aspect important atunci când proiectați o casă, un oraș, o bucătărie inteligentă etc. și continuă să joace un rol important în lumea de astăzi. În general, bucătăria este considerată una dintre cele mai cruciale sarcini din viața noastră de zi cu zi, ceea ce face imperativ să echipam acest element vital al vieții umane cu dispozitive inteligente pentru a evita incidentele obișnuite, cum ar fi scurgerile de gaz, particulele intense în mediu sau incendiul. izbucniri. Scurgerile de gaz în bucătărie pot fi periculoase și chiar mortale, ducând la incendii dacă nu sunt controlate. Pentru bucătăriile inteligente, au fost construite diverse sisteme pentru combaterea scurgerilor de gaze și a focarelor de incendiu. Cu toate acestea,

în ciuda preciziei lor ridicate, aceste sisteme au fiecare propriul set de defecte, care le-au restricționat sever implementările. Echipamente de ultimă generație în detectarea scurgerilor de gaze, a incendiilor și a fumului într-o bucătărie inteligentă sunt discutate în această lucrare. De asemenea, sunt abordate diferite moduri de scurgere de gaze și de detectare a incendiilor, împreună cu punctele forte și punctele slabe ale acestora, precum și produsele disponibile pe piață astăzi.

Cuvinte cheie: *Internetul lucrurilor (IoT), bucătărie inteligentă, scurgeri de gaz, fum, sisteme de siguranță.*

1. Introduction

Cooking is often performed in the kitchen and is considered one of the most important activities in our daily lives and is one of the most important tasks that people do [1]. The use of the gas cylinder, which is popular in most smart kitchens, is rapidly growing, but it is also extremely dangerous because it can trigger fires. This work is motivated by the dangers posed by gas leakage, CO contamination, and fire outbreaks in humans and their resources. Gas leaks in the home are normally caused by equipment that has been improperly installed, operated, or damaged [2]. Gas leakage, lit cigarettes, short circuits, and overheating mobile phones have all been identified as common causes of fire outbreaks at home. While high temperatures in the frying pan, vegetable oil, and old oil in a deep fryer are all common sources of smoke in the kitchen, etc. [3]. Since natural gas is odourless, it cannot be detected by smell alone. As a result, a chemical (Mercaptan) is applied to give it a distinct odour to warn people in the event of a leak [4]. Some people, on the other hand, have a very weak sense of smell, which has contributed to the development of gas detection systems. Fire detection systems are designed to detect fires in their early stages (which includes all types of fires), giving people precious minutes to flee to safety, saving lives, and reducing property damage, as well as taking decisive measures to stop the fire from spreading [5]. Figure 1 shows a typical smart kitchen with smart lights, a smart food heater (microwave), intrusion detectors, a smart electric cooker, a smart kitchen seat, smart cooling appliances, and so on. Smart systems, smart meters, smart appliances, smart power outlets, and sensing devices are installed in the smart kitchen to encourage the development of intelligent solutions for the everyday life of people [6].

Figure 1. A Typical Smart Kitchen [6].

Various studies on gas, smoke, and fire detection have been carried out; however, this paper aims to explore the state-of-the-art achievement in gas leakage, fire, and smoke detection technologies in smart kitchen automation, as well as the research gap and open issues that need to be addressed in the field of smart kitchen automation technologies. The rest of the paper is organized as follows: an overview of gas leakage, fire, and smoke detection system in a smart kitchen is presented and discusses gas leakage and detection system in a smart kitchen. Also, their strength and weakness are discussed. A smoke and smoke detection system in a smart kitchen is presented, and the fire and fire detection system in a smart kitchen is discussed as well. Lastly, related works in gas, fire, and smoke detection systems in a smart kitchen; open issues and challenges in gas leakage, smoke, and fire detection in a smart kitchen; and the conclusion of the research work.

2. Overview of Gas Leakage, Fire, and Smoke Detection Systems in A Smart Kitchen

Protection systems are also referred to as fire, smoke, and gas detection systems. System safety is a branch of systems engineering those aids in the management of program risk. To improve protection, engineers and managers use engineering and management concepts, requirements, and techniques. The goal of a safety system is to improve safety by detecting and removing or managing safety risks by designs and/or procedures that are focused on appropriate system safety priorities [7]. When designing any detection device, there are a variety of existing systems and techniques to consider, some of which are discussed in this paper.

3. Gas Leakage and Detection System in a Smart Kitchen

As poisonous gases and vapours build up to unhealthy levels, or when the air is depleted of oxygen, it can be highly dangerous to people, buildings, and equipment [8]. The safety and health of a family, machinery, and property must be entrusted to perfectly working sensors. This is because human sensory organs are often unable to detect airborne threats, and even when they do, they do so too late.

As a result, hazards must be detected in real-time and consistently, because false alarms trigger production downtime. As a result, the sensor is the most crucial part of a gas detection device.

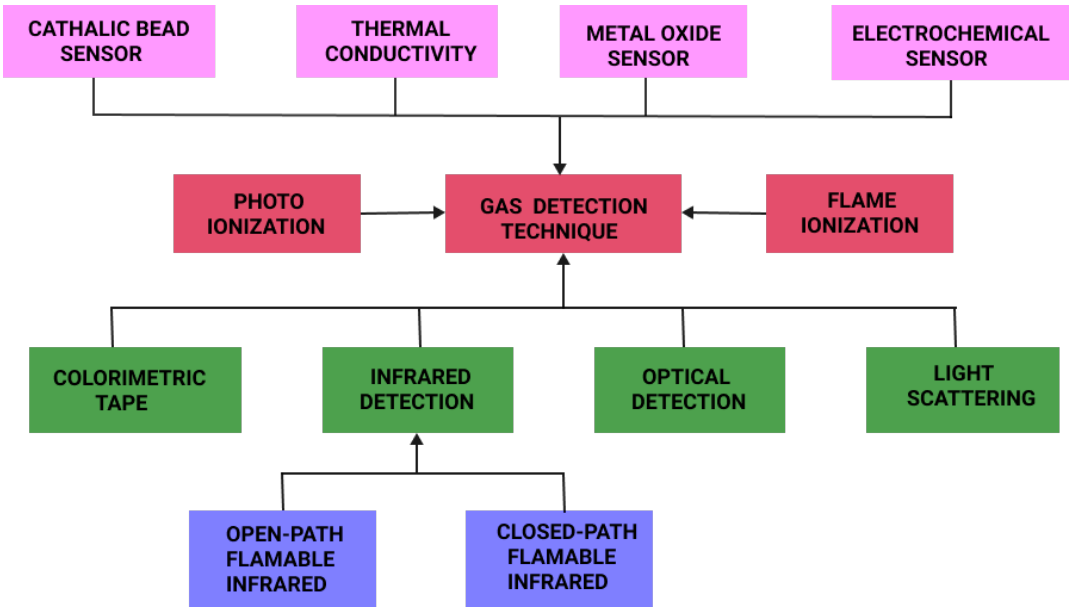

Figure 2. Various Gas Leakage Detection Techniques.

It converts the measured variable into an electrical signal using chemical or physical processes, depending on the type of sensor. The accuracy with which dangerous substances suspended in the air can be detected is largely determined by the sensors used to detect them. As a result, both the gas detector and the sensor must be perfectly balanced [9]. Catalytic Bead Sensor, Thermal Conductivity, Infrared Gas Detection, Electrochemical sensor, Metal oxide sensors, Colorimetric tape, Optical Gas Detection, Open-path Flammable Infrared Gas Detection, Open-path Toxic Infrared Gas Detection, Photo Ionization, Flame Ionization, and light scattering are some of the techniques used to design gas detectors. Figure 2. depicts the most often used techniques for detecting gas leaks.

3.1. Catalytic Bead Sensors

A heated catalytic bead (usually platinum or palladium) burns at a lower temperature than combustible gas concentrations (a concept identical to that of a catalytic converter in a car). The thread in the bead heats up as the gases burn. The resistance of the wire increases as the temperature rises. This temperature rise is compared to a non-catalytic reference bead using a Wheatstone bridge to provide a reading of the fuel gas [10].

3.2. Thermal Conductivity

Heat is transported at various rates by different gases. As a result, in the air, the heated wire can lose heat at a different rate than in gases like helium. This distinction can be used in the development of a gas detector. Since low-level heat loss is difficult to detect accurately, this approach is typically used only when the percentage of gas volume is detected. The detection of the volume percent of combustible gas, helium, and carbon dioxide is one of the most common applications [10].

3.3. Colorimeter Sensors

If any chemicals are exposed to other chemicals during a chemical reaction, they will change color. This idea is used to construct a "spot" that can then be seen or sensed electronically. This approach is used in low-tech detector tubes as well as detection systems developed specifically for the semiconductor gas detection industry (arsine, phosphine, etc.) [10].

3.4. Metal Oxide Sensors

Some metal oxides (such as tin) have semiconducting properties that make them ideal for gas detection. Fuel gases and hydrogen sulfide are popular applications, but the device can also detect a wide range of other chemicals. The electrical resistance of these semiconductors decreases when they are exposed to certain gases. The decrease in gas concentration can then be measured and related. These sensors are often used in hostile environments because they are robust and long-lasting [10].

3.5. Electrochemical Sensors

To oxidize or reduce a chemical, electrochemical sensors use two or more electrodes in an electrolyte. It is possible to make sensors for a variety of gases by changing the electrode materials and electrolytes. For the detection of oxygen and poisonous gases, electrochemical sensors are widely used. They are not usually used for organic compounds [10].

3.6. Infrared Detection

The use of infrared light to detect combustible hydrocarbon gas is known as infrared gas detection. A source of infrared light, an optical filter to select the correct wavelength, and

an optical infrared receiver make up the detector. Hydrocarbon molecules in the gas absorb some of the infrared energy as it passes through the vacuum between the source and receiver. As a measure of the amount of hydrocarbon gas present, the receiver detects a decrease in receiving energy. The output signal of an Infrared Gas Detector is also compensated for the effects of temperature, humidity, and the presence of moisture or dirt on the optical filters by using two wavelengths of infrared radiation, one active wavelength for gas absorption and the other as a reference wavelength to compensate the output signal of the Infrared Gas Detection device for the effects of temperature, humidity, and the presence of moisture or dirt on the optical filters. Open-path detection and close-path (point) detection are two classifications of infrared gas detection systems [11]:

I. Close-path infrared gas detection (Point devices) measure the amount of gas present at a fixed location.
II. Open path detectors consist of separate transmitters and receivers that detect the presence of gas up to 200 meters away. To give the best level of safety, a combination of open-path and point detectors can be used in most circumstances.

3.7. Flame Ionization

A flame ionization detector (FID) is a scientific device that detects analytes in gas streams. In gas chromatography, it is commonly used as a detector. This is a mass-sensitive instrument since it measures ions per unit of time. Standalone FIDs can be used in stationary or portable instruments for applications such as landfill gas monitoring, fugitive pollution monitoring, and internal combustion engine emissions measurement [11].

3.8. Photo Ionization

The Photo Ionization Detector (PID) is a vapour and gas detector that can detect a wide range of organic compounds. When an atom or molecule absorbs enough light to allow an electron to leave and become a positive ion, this is known as photoionization. An ultraviolet lamp releases photons that are absorbed by the compound in an ionization chamber, and this is how the PID works.

Electrodes collect the ions (atoms or molecules that have gained or lost electrons and thus have a net positive or negative charge) generated during this process. The analyte concentration is determined by the current produced. This method is considered non-destructive since only a small fraction of the analyte's molecules is ionized, allowing it to be used in combination with another detector to validate analytical findings. PIDs are also available in a variety of lamp configurations and compact hand-held versions. Results are almost instantaneous [11].

3.9. Optical Detection

Safety Scan specializes in using optical gas imaging to detect hydrocarbon gas leakage using infrared thermal imaging. Real-time thermal images of gas leakage are provided by highly specialized infrared cameras. Optical emission detection is a relatively new technology that has been developed to identify fugitive gas emissions quickly, accurately, and safely. This technology allows the user to "see" hydrocarbon gas emissions that would otherwise be invisible.

Thermal imaging aids in the precise detection of the leak's source, which is critical for repair efforts. This provides a safer, more effective environment for a variety of industrial applications, enabling engineers to pinpoint the leak's source and size in real-time [11].

3.10. Light Scattering

A detector used in high-performance liquid chromatography (HPLC), ultra-high-performance liquid chromatography (UHPLC), purification liquid chromatography such as flash or preparative chromatography, countercurrent or centrifugal partition chromatography, and Supercritical Fluid chromatography is an evaporative light scattering detector (ELSD) (SFC). It is widely employed for the study of substances that do not easily absorb UV light, such as sugars, antivirals, antibiotics, fatty acids, lipids, oils, phospholipids, polymers, surfactants, terpenoids, and triglycerides, where UV detection may be a limitation. The charged aerosol detector (CAD) is similar to ELSDs, and both come within the destructive detector family. Both compounds that are less volatile than the mobile phase, i.e., nonvolatile and semi-volatile compounds, can be detected using an evaporative light scattering detector (ELSD) [12]. However, these techniques have their strengths and constraints as summarized in table 1.

Table 1

Summary of gas detection techniques, strengths, and weaknesses

S/N	Technique	Mode of Operation	Strengths	Weaknesses
1.	Catalytic Bead sensor	Makes use of elements (beads) with catalytic sensors where resistance-change is directly related to the gas concentration in the surroundings and is displayed in a meter.	Relatively inexpensive, rugged, and has a long shelf-life.	They are non-specific and the beads are susceptible to poisoning compounds.
2.	Thermal conductivity	Makes use of varying temperatures and the difference in transport rate with air as reference.	Simple to design and have a long shelf-life.	They have limited application & cannot detect low concentrations
3.	Colourimeter	Makes use of the difference in the chemical reaction of various gases when exposed to other chemicals.	Low cost and detects varieties of gases. It can also detect low-level concentrations	Has limited shelf life with a low level of accuracy. Also, the "paper tape" used is costly to purchase
4.	Metal Oxide sensor	Makes use of semiconductors. Takes full advantage of the properties of some metal oxides to detect a change in their electrical resistance.	They are rugged, durable, and resistant to many sensor poisons.	They are non-specific and tend to give false alarms. Also, they have less reliability.

Continuation Table 1

5.	Electrochemical sensor	Makes use of electrochemical sensors and electrodes to oxidize or reduce a chemical to create sensors for various gases.	They are portable, durable, and have low power consumption.	The electrolyte is prone to leakage. They have a limited shelf-life and consume more power.
6.	Infrared detection	The detector consists of a source of infrared light, an optical filter to select the proper wavelength, and an optical infrared receiver.		
7.	Flame Ionization	The FID works by detecting ions that are produced during the burning of organic molecules in a hydrogen flame. The number of organic species in the sample gas stream determines how many of these ions are produced.	It is relatively inexpensive to acquire and operate and has low maintenance requirements with rugged construction.	Inorganic compounds and some highly oxygenated or functionalized species are not detectable.
8.	Photo Ionization	When compounds reach the detector, they are assaulted by high-energy UV photons and are ionized when they absorb the UV light, causing electrons to be ejected and positively charged ions to form.	It has a wide range of applications due to its linearity; it also has low maintenance requirements.	It is not suitable for the detection of semi-volatile compounds and does not identify the type of volatile compounds present.
9.	Optical Detection	Uses as well as an optical sensor Lightray are converted into an electrical signal by an optical sensor. This is comparable to the function of a photoresistor.	It has high sensitivity, reliability, and a wide dynamic range. It is also chemically inert and is suitable for remote sensing.	It is subject to environmental disturbance and is relatively pricey. It's also vulnerable to bodily harm.
10.	Light Scattering	It is widely employed for the analysis of chemicals where UV detection is a limitation, such as when the compounds do not absorb UV radiation efficiently.	Good for nonvolatile solutes and are low molecular weight polymer.	It has the potential for a high false alarm rate and must be cleaned daily.

Most of the time, these detectors are set to detect no more than two separate gases. When gas is detected, most gas detectors sound a warning buzzer, while others send an SMS to subscribers. Only a select few make provisions to prevent further gas leakage [2]. While these systems have flaws, their implementation and installation have so far resulted in the saving of lives (both plants and animals) and properties.

4. Smoke Detection System in A Smart Kitchen

A smoke detector is a system that detects smoke as a warning sign of a fire. As part of a fire alarm system, commercial security systems send a signal to a fire alarm control panel, while household smoke detectors, also known as smoke alarms, typically emit a local audible or visual alarm from the detector itself [13]. Smoke detectors can detect smoke either optically (photoelectric) or physically (ionization); they can use either or both methods [14]. Smoking can be detected and therefore discouraged in places where smoking is prohibited using sensitive alarms. In large commercial, manufacturing, and residential buildings, smoke alarms are typically operated by a central fire alarm device that is powered by the building's power with a battery backup [15]. Domestic smoke detectors vary in size from individual battery-powered devices to multiple interconnected mains-powered units with battery backup; with these interconnected units, if one detects smoke, they all go off, even if the power is out in the building. In homes with functioning smoke detectors, the chance of dying in a house fire is cut in half [13]. Ionization and photoelectric (optical) techniques are the two main techniques used in smoke detection, as previously described. Figure 4 shows the various smoke techniques in use. The mode of operation, strength, and constraints of these techniques are summarized in table 2.

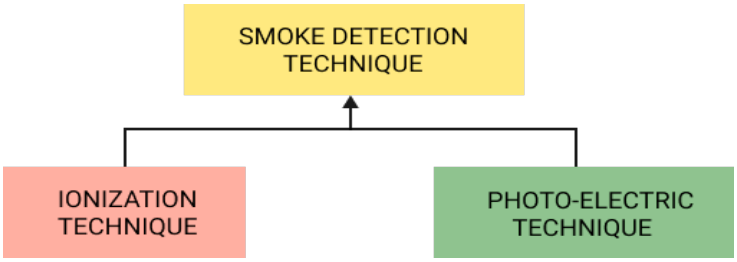

Figure 4. Diagrammatical Representation of Smoke Techniques.

4.1. Ionization Technique

Tiny amounts of radioactive material are present in ionization smoke detectors. Radiation travels through the ionization chamber, which is an air-filled space between two electrodes that allows a slight constant current to flow through them. Any smoke that enters space absorbs alpha particles, reducing ionization and disrupting the current, setting off an alarm. This form of alarm works best in the event of a fast-moving fire. Optical detectors are less sensitive to the stage of fire than ionization detectors [16].

4.2. Photoelectric (Optical) Technique

A light source, a collimated light beam device, and a photoelectric sensor are used in photoelectric smoke detectors. When smoke approaches the optical chamber and travels along the direction of the light beam, the smoke particles disperse a portion of the light, pointing it towards the sensor and triggering the detector. Slow smouldering fires respond better to this sort of warning. Optical detectors are particularly susceptible to fires that are already in the early stages of combustion [16].

Table 2

Comparisons between smoke detection techniques

	A light source, a collimated light beam device, and a photoelectric sensor are used in smoke detectors.	It works well for detecting fires that are swift and blazing. Thanks to its widespread availability, it is still the most common method of smoke prevention.	It is slow in detecting fires with slow properties.
	Makes use of a small amount of radioactive material and electrodes.	Works best in detecting fires characterized by their low properties. Also, a reduced number of false alarms triggered by cooking steam.	Not reliable when checking for fires with high properties.

Using a hybrid solution (ionization and photoelectric) when designing a smoke detector has proved to be more effective. Regardless of the type of detector technique used, the proper positioning and management of the instrument must be taken into account for optimum efficiency.

5. Fire and Fire Detection System in a Smart Kitchen

Fire is one of the most destructive occurrences that can occur; it happens every minute of the day anywhere on the planet. Although fire is always our ally, it may often be our greatest enemy when it is unregulated and left to spread within a structure. Of course, fire is explosive, and smoke from a fire causes a poisonous, hazardous environment [17]. Every year, early warning and containment of fire will save thousands of lives, thousands of deaths, and millions of dollars in property damage. Smoke alarms and warning sensors have been integrated to form life-safety mechanisms in the field of fire detection [5]. An automatic fire alarm system's goal is to detect a fire, warn the control panel and appropriate authority, and advise the occupants to take action.

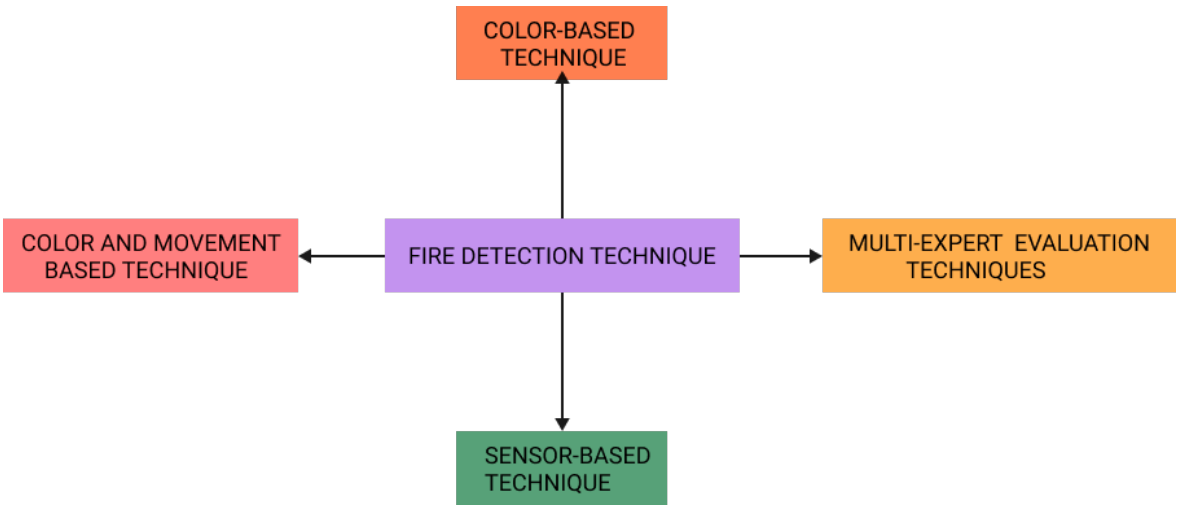

Figure 6. Various Fire Detection Techniques.

A flame detector that uses a sensor to detect and respond to the presence of a flame or fire is used to detect and respond to the presence of a flame or fire. Sound an alarm, shutting off a fuel line (such as a propane or natural gas line), and turning on a fire control device are all possible responses to a perceived blaze, depending on the installation [18]. Figure 6 shows the various techniques for fire detection currently in use.

5.1. Color-Based Fire Detection

The colour of fire pixels is compared to the colour of candidate pixels in colour-based detection. This is achieved on the basis that the fire pixels would be reddish-yellow in colour. The methods that employ these features are based on the premise that flames are created by common materials such as wood, plastic, paper, and other materials. Such that the colour components in RGB (Red, Green, and Blue), YUV (Luminance, Chrominance), or some other colour space will accurately characterize the colour to recognize the existence of flames [15].

5.2. Sensor-Based Fire-Detection Method

Fire detection is critical in a variety of settings, including mines and other industrial settings. As a result, having an alert device capable of detecting fire and sounding an alarm is critical. Sensor-based fire detection methods use sensors to track fire. In general, the use of sensors yields high efficiency in all types of detection processes. The sensors detect features such as fire, light, and other factors to make a decision [15].

5.3. Color and Movement-Based Evaluation

Colour-based assessment will aid in the identification of fire pixels, but it will be less effective in densely populated environments. This is because these pixels are selected solely based on their colour. Some aspects go well with the colour of the flames. It would be more precise if we combine the function of movement with colour-based assessment. This is founded on the fact that the fire pixels would be in a constant state of motion. As a result, it would analyze each frame by comparing it to its previous and subsequent frames. As a result, fire detection will be a little more precise [15].

5.4. Multi-Expert Evaluation

Multi-Expert Evaluation will combine the opinions of many experts and conclude. In the current scenario, it tests each of the characteristics of fire, such as colour, movement, and form, as experts and uses them to detect fire. Because of the special colour of flames, colour is one of the most significant features used. Other elements, such as movement and shape, may be added to increase efficiency. The flame's movement is assessed based on the fact that it is constantly moving in nature, and its form is taken into account since the flame's shape varies every minute seconds. As a result, if we take adjacent pictures, the flame pixels' values will rapidly change. Multi-Expert Systems usually make use of this property [15].

6. Review of Related Works in Gas, Smoke and Fire Detection in a Smart Kitchen Automation System

Several analyses of gas, smoke, and fire detection methods have been published previously, either as academic articles or scientific studies. These efforts have shown to be beneficial in reducing the risk of dangerous effects. This section presents each of these research works, as well as their contributions, achievements, and shortcomings.

Research in [19] created a gas leakage detector for protection and protection using an LPG gas sensor attached to an IoT using an ESP module. The primary controller was an

Arduino. The project's final output was used to detect gas leakage from cylinders and also to alert the consumer through IoT software. It had three major issues, including energy efficiency, localization, and routing; however, the proposed solution is less expensive than currently existing detectors. Research in [20] used the Internet of Things to build a device that eliminates risks in kitchens (IoT). Multiple sensors, a control unit, an alarm buzzer, and a GSM module made up this device. To control a gas leak, this mechanism automatically shuts off (closes) the valve. This machine often controls the cylinder's gas level, and when the device's weight falls below the "fixed point," it immediately schedules the cylinder for a refill from the gas agency. This proposed architecture has a wide range of applications that have proved to be effective and reliable. Research by Adekitan et al. in [21] presented a design that used a pragmatic protection strategy to track and evacuate gas leaks before they fire. A control unit, a buzzer bell, a GSM module, and an actuator are all included. This configuration had the advantage of automatically shutting off the gas supply solenoid valve and evacuating the gas by turning on the evacuator fans. However, since untreated gas leakage will cause actual fire outbreaks, there is no actual countermeasure for an actual fire outbreak. Research by Sharma et al. [17] devised a new approach for detecting fire at an early stage to reduce risk. A control unit (Arduino UNO), an MQ-5 gas sensor to detect a gas leak, a GSM module for mobile communications, a buzzer for warnings, an exhaust fan, batteries, LEDs, and other components are included in the device. The system had safety features such as turning on the exhaust fan to remove gas from the environment. However, it had no provisions for dealing with real fires or explosions caused by the use of expired gas cylinders.

Research by in [16] proposed a multi-sensor solution for a fire warning system prototype. MQ-5 gas sensor, Grove temperature sensor, Grove light sensor, Arduino microcontroller, GSM module, and GPS shield is included. In the event of fire detection and outbreak, the device is configured to transmit alerts to registered contacts. Although it is restricted to residential buildings, this device can identify and distinguish between hazardous and non-harmful smoke. Research in [22] in their paper, suggests a framework that uses the Internet of Things (IoT) to connect multiple physical objects that are embedded with electronics, sensors, and software that can capture data from the environment and transfer it over the internet. This device can be used for a variety of purposes, including defense, agriculture, and more. This system necessitates the deployment of a vast number of sensor clusters for greater reliability. Research in [23] proposed an intelligent smoke detector device the machine used the Random Forest Algorithm to detect smoke, ZigBee Transmission Technology to create a wireless network, E-charts for data analysis, and a smoke detector module to capture environmental data. Temperature, humidity, pressure, and dust sensors are among the sensors employed. The machine makes use of a low-power optimization scheme, but there is no safeguard measure put in place. Research in [24], describes the use of an LPG gas sensor to detect a leak and generate the results in audio and visual formats, as well as alerting humans via SMS (SMS). The sensors used have excellent sensitivity and a fast response time, but no countermeasures are provided for the observed leakage.

Research in [25] with the aid of an Arduino, creates a device that can detect a variety of dangerous gases. This work alters the currently available structures, which are mostly found in commercial settings but can also be used in homes and at work. The LCD detects and displays poisonous gases such as butane (also known as LPG), methane, and carbon monoxide. The percentage concentration of these would be shown on the LCD, but it has a slow reaction time and does not have countermeasures against the detected gas. [26], the

design of a gas leakage safety device is the subject of this paper. LPG is highly flammable and can cause a fire even if it is far away from the source of the leak. Most fire accidents are caused because of a poor-quality rubber tube or when the regulator is not turned off. The supply of gas from the regulator to the burner is on even after the regulator is switched off. If the knob is switched on by accident, gas leaks will occur.

The detection, monitoring, and control system for LPG leakage is the subject of the research. The stove knob is operated automatically by a relay DC motor. Along with safety features, the mechanism has the added benefit of automatically rebooking the cylinder when the gas level falls below the cylinder's usual weight. GSM connectivity, on the other hand, is disabled. While [27], their work focuses on the Internet of Things (IoT) connectivity of every sensor to create a smart home. Temperature sensors can also monitor high and low temperatures, allowing the system to identify the temperature and alert the user. The created android application would allow the user to turn on and off the lights manually. This provides a significant benefit to the IoT-based smart home system. [28], also, with the assistance of an Arduino Nano microcontroller, a gas sensor, and an XBee, a gas leakage detection device was suggested. The sensor node can detect a minute concentration of gas based on the voltage output of a sensor and will also capture gas leakage data, allowing the sensor node to be pinpointed to a particular location. A GSM module served as a link between the microcontroller and the mobile phone unit. It has a wide range of applications, such as in petrochemical plants and agricultural factories, but it does not provide any safeguards against detected gases and has a longer response time.

Research in [29], the concept and implementation of an SMS-based Industrial/Homes Gas Leakage Monitoring and Detection Alarm System were presented in this article. The device is designed to deter gas leaks from causing damage or deaths. Hardware and software were designed, developed, configured, and incorporated into the system. When a gas leak is detected, the time it takes for the customer to receive an SMS from the system control unit is often reviewed and tested for accuracy to ensure timely transmission of the system's early warning alert, but it does not have any countermeasure against the detected gas. Research in [30], in his job, developed and introduced a framework to meet the gas leakage health and safety requirements. The suggested device is tested, and the findings are checked, by generating an early warning signal in less extreme conditions and activating a high-pitched alert during LPG leakage to protect consumers. Even though the device is noisy due to the lack of a mechanism to switch off the warning buzzer and no precautionary precautions against detection, the average system cost is smaller and the reaction time is faster. Research in [31], when the concentration value of toxic gases such as carbon monoxide reaches the usual value, the paper developed a system that positions gas sensors in the leak points, which detects the concentration value of toxic gases such as carbon monoxide and imitates to the mobile unit. The signal is sent to the PIC microcontroller, which uses the ZigBee communication module to inform the mobile computer. This architecture has a quick response time, but it is more realistic for large-scale petrochemical applications, so it is limited to petrochemical industries for optimum efficiency. Research by Saeed et al. in [32], A GSM-based gas detector system for propane and butane gases was built in this work, and a GSM module was used to relay messages to the consumer in the event of a leak. The device, on the other hand, has no safeguards against actual detection. In the work of Saeed, [33], using multiple sensors, a wireless sensor network was developed and tested for early fire detection of a house fire. To stop false alarms, GSM was used. Low-cost sensor nodes,

temperature, light, and smoke data are spread out around the forest in this device to gather information, which is then fed into ANN models and transformed into knowledge. There is a significant time delay that could endanger human life and property; however, the results produced are correct.

Research by Kusampudi et al. in [34] Using Fuzzy Logic strategies, proposed a device architecture for fire-fighting robots that sense the fire and enter the target area without touching any obstacles, avoiding damage to lives and property. Many ultrasonic sensors installed on the robot sensed the turn angle between the robot head and the target, the distance of obstacles around the robot (front, left, and right, including other mobile robots), and were used as feedback fuzzy members in another contribution. The aim of developing fire-fighting robots is for them to enter a fire area zone without colliding with any obstacles to avoid causing harm in an unfamiliar environment. Despite its high reliability and performance, the net device cost is not cost-effective; therefore, it could be out of reach on average. Research by Sarwar et al. in [35] with the help of Artificial Intelligence Technology Fuzzy Logic, created a simple way to detect fire using multiple sensors instead of a single sensor. In a human way of thought, the built framework was easier to use and was closely similar to the actual model idea. It needs an accurate dataset for optimum efficiency, which could be difficult to obtain, and it has no mode of communication (i.e., GSM module), but it is extremely reliable. Research by Sowah et al. in [36] describes a device for detecting fire in vehicles using an Arduino microcontroller and Fuzzy Logic Artificial Intelligence Technology to prevent any harm to the vehicle caused by fire. When a fire is observed, temperature sensors, flame sensors, and smoke sensors are used. When a fire is detected, a sound detector is activated, and carbon dioxide is sent to the site, causing both environmental and noise emissions. A system is installed and tested in a medium-sized physical vehicle, with a 2 kg cylinder fixed behind the passenger's back seats. Research by Çelik et al. [37] proposed a model for detecting fire and smoke without the use of any sensors in their work, which is focused on image processing. The framework is set up in such a way that colour data and motion analysis are integrated using the derived model. Environmental contamination may cause this system to fail, resulting in inaccurate readings. This method, on the other hand, has improved accuracy. In the intelligent house, Suli et al. [38] built an automatic fire alarm and fire control linkage system. The machine intelligently predicts fire, monitors gas, and has an automated fire alarm and linkage feature, however, there are no countermeasures in place to prevent real leaks and fire outbreaks. Finally, Slavkovikj et al. in [39] Social networking networks are being used to spot fires in the current architecture. According to the author, as the number of social networks and services grows, so does the volume of knowledge that is shared on the internet. The author suggested a web design for wildfire social sensors (WSS). As a result, social media can provide a human-centric sensor network for the early identification of disasters such as fire; however, the optimum efficiency of this architecture is solely dependent on the network's stability.

7. Open Issues and Challenges in Gas Leakages, Smoke, and Fire Detection in A Smart Kitchen Automation System

The critical findings made during the analysis are taken into account. To build an effective detection system in a smart kitchen, precise knowledge of the application is often needed. The reviewed papers contain material that can be used as a foundation upon which a study can begin. It's also important to note that none of these devices can be trusted if their

reactions to external factors including gas, smoke, and fire aren't tested regularly. Available systems in today's market face problems such as most conventional home systems are automatic, so they cannot change and respond to the consumers' actual working environmental conditions. Also, according to the poll, certain devices have a high likelihood of causing a false alarm because they are vulnerable to noise and minor variations in the environment's sounds. While these devices sense a fire until it spreads, there is little control or precautionary measures in place, making property loss almost unavoidable. Also, in some designs, multiple sensors were used to increase accuracy, however, it requires large numbers of "clusters" of sensors to be deployed which will inevitably increase overall system cost and deployment cost.

8. Conclusions

This review paper serves as a basic guide to help researchers choose the right technology for gas leakage, smoke, and fire detection in a smart kitchen. A comprehensive survey of several smart kitchen automation systems was performed in this research. Also included is a description of what has been done in this area to date, as well as the research gap and open issues that need to be addressed in this research area. A wide range of gas leakage, fire, and smoke detection systems in a smart kitchen was studied and classified into three main categories: gas leakage detection, smoke detection, and fire detection in a smart kitchen. Finally, the research gaps and unsolved challenges in gas leak detection, fire detection, and smoke detection in a smart kitchen were reviewed. We found that the majority of existing systems are not dynamic, and as a result, they are unable to adapt and react to the user's present operating environment. Furthermore, because some of the systems are sensitive to noise and tiny changes in the environment, they have a high likelihood of generating a false alert.

Conflicts of Interest. The authors declare no conflict of interest.

References

1. Atsushi, H.; Mori, N.; Funatomi, T.; Yamakata, Y.; Kakusho, K.; Minoh, M. Smart kitchen: A user centric cooking support system. In *Proceedings of 12th International Conference on Information Processing and Management of Uncertainty for Knowledge-Based Systems (IPMU 2008)*, Malaga, Spain, June 22-27, 2008, 8, pp. 848-854.
2. Simon, A.; Erameh, K.; Iruansi U. Design and development of kitchen gas leakage detection and automatic gas shut off system. *Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS)* 2014, 5(3), pp. 222-228.
3. Diaa, S. A. M.; Abd-ELfattah, M.; Ali M. A. Design of an Internet of Things (IoT) network system for Kitchen food waste management. *International Journal of Computer Science and Network Security (*IJCSNS) 2018, 18(5), pp. 130-138.
4. Ejaz, A. F.; Gurusamy, P.; Kumar, G.; Mahavignesh S. LPG Detection Using GSM Module. *International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering (JAREEIE)* 2016, 5(1), pp. 12-15.
5. Lars, B.; Frantzich, H. Fire alarm in a public building: How do people evaluate information and choose an evacuation exit? *Fire and Materials Journal* 1999, 23(6), pp. 311-315.
6. Andi, A.; Dani, A. W. Design of small smart home system based on Arduino. In *Proceeding of Electrical Power, Electronics, Communicatons, Control and Informatics Seminar (EECCIS 2014)*, Malang, Indonesia, August 27-29, 2014, pp. 121-125.
7. Kontogiannis, T.; Leva, M.; Balfe, N. Total safety management: principles, processes and methods. *Safety science Journal* 2017, 100, pp. 128-142.
8. Poorva, K.; Duggal, P.; Pawar, A.; Bhalerao, M. R. Smart Gas Booking & LPG Leakage Detection System. *International Journal of Advance Research and Innovative Ideas in Education* 2019, 5(3), pp. 825-830.
9. Sunil, P.; Waqar, A. GSM Based Gas Leakage Detection & Prevention System for Disabled and Handicapped. *International Journal of System Modeling and Simulation* 2016, 1(1), pp. 7-10.

10. Kleven, B. A. *Summary of Gas Detection.* 1st edition, Tucson: Arisona, USA, 2007, pp. 1-12.
11. Skoog, D. A.; Holler, F. J.; Crouch, S. R. *Principles of instrumental analysis*. 7th Edition, Sunder College Publisher: New York, USA, 2017; pp. 9-15. Available online: https://www.amazon.com/ Principles-Instrumental-Analysis-Douglas-Skoog/dp/1305577213.
12. Douville, V.; Lodi, A.; Miller, J.; Nicolas, A.; Clarot, I.; Prilleux, B.; Megoulas, N.; Koupparis, M. Evaporative light scattering detection (ELSD): a tool for improved quality control of drug substances. *Pharmeuropa scientific notes* 2006, 1, pp. 9-15.
13. Alsaadi, A. Smart smoke and fire detection with wireless and global system for mobile technology. Master Degree Thesis, California State University, Long Beach, January 2016.
14. Alan, W. Smoke alarm detection, broadcast notifications and social implications. Master Degree Thesis, University of Otago, New Zealand, November, 2010.
15. Saylee, G.; Birla, S.; Pandey, S.; Dargad, R.; Pandita, R. Smoke and fire detection. *International Journal of Advanced Research in Computer and Communication Engineering* 2013, 2(6), pp. 2420-2424.
16. Obanda, Z. S. Multi-sensor fire detection system using an Arduino Uno microcontroller. Master Degree Thesis, Strathmore University, Kenya, June, 2017.
17. Sharma, S.; Singh, D.; Rathore, S. S.; Bansal, P. Fire detection system with GSM using arduino. *Imperial Journal of Interdisciplinary Research* 2017, 3(4), pp. 2243-2245.
18. Sivaranjani, S.; Gowdhami, D.; Karthikkannan, P. An appraisal on gas leakage detection and controlling system in smart home using IoT. *Emerging Technologies in Networking and Security (ETNS)* 2016, 7(9), pp. 608-615.
19. Naren, V.; Indrajith, P.; Prabhu, R.; Ganesh, C. Intelligent Gas Leakage Detection System with IoT Using ESP 8266 Module. *International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering 2018,* 7(12), pp.4157-4161.
20. Anandhakrishnan, S.; Nair, D.; Rakesh, K.; Sampath, K.; Nair, G. S. IOT based smart gas monitoring system. *IOSR Journal of Electrical and Electronics Engineering (IOSR-JEEE)* 2017, pp. 82-87.
21. Adekitan, A. I.; Matthews, V. O.; Olasunkanmi, O. A microcontroller based gas leakage detection and evacuation system. *Materials Science and Engineering* 2018, 413(1), pp 1-7.
22. Shinde, R.; Pardeshi, R.; Vishwakarma, A.; Barhate, N. Need for wireless fire detection systems using IOT. *International Research Journal of Engineering and Technology (IRJET)* 2017, 4(1), pp. 1078-1081.
23. Wu Q., Cao J., Zhou C., Huang J., Li Z., Cheng S. M. and Pan G. Intelligent smoke alarm system with wireless sensor network using ZigBee. *Wireless Communications and Mobile Computing Journal* 2018, 2018 (3), pp. 1-11.
24. Selvapriya, C.; Sathya, P. S.; Abdulrahim, M.; Aarthi K. LPG leakage monitoring and multilevel alerting system. *International Journal of Engineering Sciences & Research Technology* 2013, 2(11), pp. 3287-3290.
25. Katole , K.; Bagade , V.; Bangade , B.; Soni , A. ; Kamde , H. Hazardous Gas Detection using ARDUINO. *International Journal of Science Technology & Engineering* 2016, 2 (10), pp. 534-538.
26. Soundarya, T.; Anchitaalagammai, J.; Priya, G. D.; Kumar, S. K. C-leakage: Cylinder LPG Gas leakage Detection for home safety. *IOSR Journal of Electronics and Communication (IOSR-JECE)* 2014, 9(1), pp. 53-58.
27. Mehta, H.; Jadhav, K.; Mishra A.; Deshmukh, A. IOT based home automation system using arduino board. *International Research Journal of Engineering and Technology (IRJET)* 2017, 4(1), pp. 1541-1544.
28. Mujawar, T.; Bachuwar, V.; Kasbe, M.; Shaligram A.; Deshmukh, L. Development of wireless sensor network system for LPG gas leakage detection system. *International Journal of Scientific & Engineering Research* 2015, 6(4), pp. 558-563.
29. Georgewill, O. M.; Ezeofor, C. J. Design and Implementation of SMS-Based Industrial/Homes Gas Leakage Monitoring & Detection Alarm System. *International Journal of Engineering Trends and Technology (IJETT)* 2016, 35(9), pp. 410-416.
30. Gupta, A. Economical and optimal gas leakage detection and alert system. *International Journal of Scientific and Research Publications* 2017, 7(11), pp. 260-263.
31. Ganesh, D.; Bala, A. Improvement on gas leakage detection and location system based on wireless sensor network. *International Journal of Engineering Development and Research* 2015, 3(2), pp. 407-411.
32. Shrivastava, A.; Prabhaker, R.; Kumar, R.; Verma, R. GSM based gas leakage detection system. *International Journal of Technical Research and Applications* 2013, 1(2), pp. 42-45.
33. Saeed , F.; Paul , A.; Rehman , A.; Hong , W. H. ; Seo H. IoT-based intelligent modeling of smart home environment for fire prevention and safety. *Journal of Sensor and Actuator Networks* 2018, 7(11), pp. 1-16.
34. Kusampudi, N.; Sanjeev, J. Navigation of autonomous fire-fighting robots using fuzzy logic technique. *International Journal of Engineering Science Innovation and Technology* 2015, 4, pp. 138-147.

35. Sarwar, B.; Bajwa, I. S.; Jamil, N.; Ramzan, S.; Sarwar, N. An intelligent fire warning application using IoT and an adaptive neuro-fuzzy inference system. *Sensors* 2019, 19 (3150), pp. 1-18.
36. Sowah, R.; Ampadu, K. O.; Ofoli, A.; Koumadi, K.; Mills, G. A.; Nortey J. Design and implementation of a fire detection and control system for automobiles using fuzzy logic. In Proceeding of *IEEE industry applications society annual meeting*, Portland, Oregon, USA, October 2-6, 2016, pp. 1-8.
37. Çelik, T.; Özkaramanlı, H.; Demirel H. Fire and smoke detection without sensors: Image processing based approach. In *15th European Signal Processing Conference (EUSIPCO-07)*, Poznan, Poland, September 3-7, 2007, pp. 1794-1798.
38. Suli, W.; Ganlai, L. Automatic fire alarm and fire control linkage system in intelligent buildings. *International Conference on Future Information Technology and Management Engineering (FITME 2010)*, Changzhou, China, October 9-10, 2010, 1, pp. 321-323.
39. Slavkovikj, V.; Verstockt, S.;Van Hoecke, S.; Van de Walle, R. Review of wildfire detection using social media. *Fire Safety Journal* 2014, 68, pp. 109-118.

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EVALUATION OF GLUTEN CONTAMINATION IN GLUTEN-FREE PRODUCTS IN THE REPUBLIC OF MOLDOVA

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Abstract. Celiac disease (CD) is an autoimmune condition, triggered by gluten ingestion, which affects the small intestine, destroying the villi. It is considered that in recent years CD has undergone a real "metamorphosis" due to the constant increase in diagnosed cases. The only treatment available for BC is to stick to a gluten-free diet throughout your life. Adherence to a GFD requires strict elimination of gluten-containing products, as patients with CD are very sensitive to the toxic effect of gluten. The purpose of the research is to evaluate whether the products marketed on the territory of the Republic of Moldova, labeled as gluten-free products, are safe for people with celiac disease, from the perspective of their gluten content. The identification of gluten in GF products sold in supermarkets in the capital was done using the GlutenToxPro gluten detection kit for food, beverages, and work surfaces (AOAC-RI). Research has shown that both gluten-free products imported with the Crossed Grain logo and those just labeled gluten-free (both imported and local), pose no risk to people with gluten-related disorders: the gluten content of all samples was up to 20 ppm. Local, non-packaged GF products (developed and made available to consumers by the supermarkets concerned) pose an increased risk of contamination.

Keywords: *celiac disease, certified products, Crossed Grain logo, food safety, food labeling, gluten free.*

Rezumat. Boala celiacă (BC) este o afecțiune autoimună, declanșată de ingestia la gluten, care afectează intestinul subțire, cu distrugerea vilozităților. Se consideră că în ultimii ani BC a suferit o adevărată „metamorfoză” din cauza creșterii constante a cazurilor diagnosticate. Singurul tratament disponibil pentru BC este aderarea pe tot parcursul vieții la o dietă fără gluten. Aderarea la un GFD impune eliminarea strictă a produselor care conțin gluten, deoarece pacienții cu BC sunt foarte sensibili la efectul toxic al glutenului. Scopul cercetării constă a evalua dacă produsele comercializate pe teritoriul Republicii Moldova, etichetate ca produse fără gluten, sunt sigure pentru persoanele cu maladia celiacă, din perspectiva conținutului de gluten în ele. Identificarea glutenului în produsele GF comercializate în supermarketurile din capitală s-a realizat cu ajutorul kitului de detecție a glutenului pentru alimente, băuturi și suprafețe de lucru GlutenToxPro (AOAC-RI). Cercetările au arătat că atât produsele fără gluten importate cu sigla Crossed Grain, cât și cele doar etichetate fără gluten

(atât de import cât și locale), nu prezintă niciun risc pentru persoanele cu tulburări legate de gluten: conținutul de gluten din toate probele a fost de până la 20 ppm. Produsele GF locale, neambalate (elaborate și puse la dispoziția consumatorilor de către supermarketurile în cauză) reprezintă risc sporit de contaminare.

Cuvinte cheie: *etichetarea alimentelor, fără gluten, maladia celiacă, produse certificate, siguranța alimentelor, sigla spicul tăiat.*

1. Introduction

Celiac disease (CD) is an autoimmune condition, triggered by gluten ingestion, which affects the small intestine, destroying the villi. It is considered that in recent years CD has undergone a real "metamorphosis", largely due to the constant increase in diagnosed cases [1,2]. Some theories suggest that this is due not only to the high availability of screening tests, but also to globalization, including the consumption of large amounts of gluten (up to 20 g / day), which has led to the increased prevalence and incidence of MC [3]. It is estimated that over 70% of people with celiac disease remain undiagnosed, which means that they become chronic patients who experience a decrease in quality of life associated with various gluten-related health problems that occur over time [4,5].

The incidence of MC in the world is about 1%. People with MC may experience a wide variety of gastrointestinal and malabsorption symptoms or extra-intestinal symptoms. The only treatment available for celiac disease is to stick to a gluten-free diet throughout your life. Adherence to a GFD refers to the strict elimination of gluten-containing products [6,7]. Gluten is made up of protein fractions, which are found mostly in the endosperm of grains, such as wheat, barley, rye, and foods that are derived from grains (e.g., semolina, durum, spelled, triticale, kamut, and malt) [8–11].

Gliadin, a glycoprotein, alcohol-soluble fraction of gluten, is thought to be responsible for the immune reaction to gluten consumption. In general, gliadin contains both toxic and immunogenic peptides.

- Toxic peptides can affect tissues, causing damage to the intestinal mucosa, justifying the activity of T-helper lymphocytes, by activating an innate immune reaction [12].
- Immunogenic peptides can activate the acquired immune response by specifically stimulating HLA-DQ2/DQ8 T lymphocytes and B lymphocytes [13].

Due to the chemical complexity, the digestibility of gliadins is quite low. Fragments obtained from the partial digestion of proline and glutamine cause inflammation and destruction of intestinal epithelial cells. According to the electrophoretic mobility of prolamins, 4 fractions were identified: α-, β-, γ- and ω.

The α-gliadin fraction, with 266 amino acids, is considered to be the most toxic, containing the most active epitopes for the immune system [14, 15].

In people with CD, the sequence 31-34 (A-gliadin) has no immunological activity against T-helper lymphocytes and is transported across the mucosa of celiac patients in double amounts compared to healthy individuals (Figure 1).

The main protein fractions are prolamins and glutelins and are responsible for the development of symptoms in celiac disease [2].

According to European legislation and Codex Alimentarius, a food can only be labeled “gluten free” if it contains less than 20 ppm gluten (20 mg /kg) in the final product [12–14].

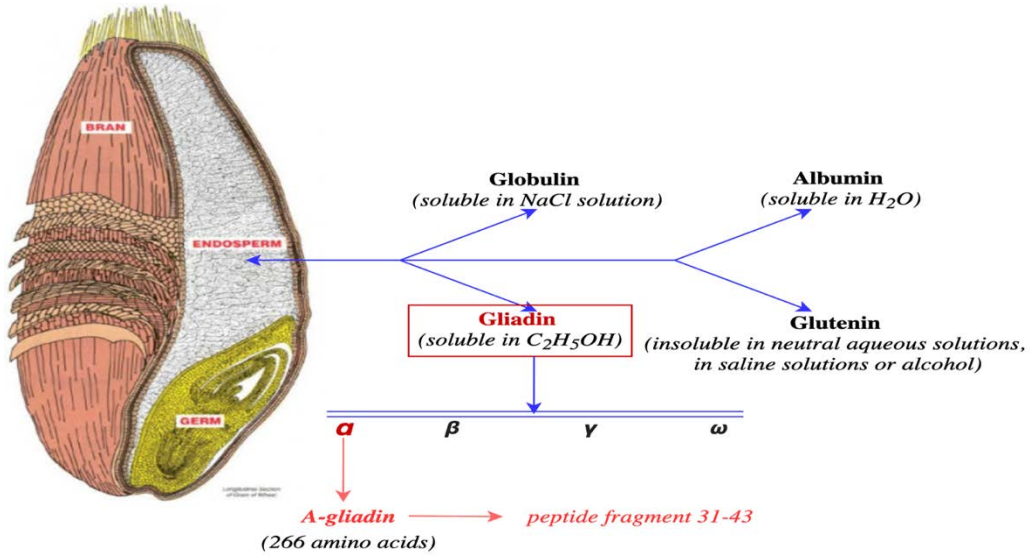

Figure 1. Protein fractions of cereals and subfractions of gliadin.

Also, a food labeled "very low gluten" may be labeled as such if it contains less than 100 ppm gluten (100 mg/kg) in the final product [12,14,15]. There are studies that have shown that prolonged ingestion of even traces of gluten (10–50 mg/day) can affect the integrity of the intestinal mucosa, an increased number of IELs being the first marker of mucosal damage [16].

The most significant long-term risk factor is inadequate adherence to a gluten-free diet [5,6,17]. A strict gluten-free diet normalizes the levels of antibodies associated with celiac disease and, respectively, the recovery of the affected tissues takes place, which can often take several months [4,12,17]. Carefully performed and monitored by a specialist, the GF diet will positively influence the health of the patient with gluten-related disorders [2].

2. The market for gluten-free products

The size of the global gluten-free market has been estimated at $ 5.9 billion in 2021 and is expected to expand at an annual growth rate (CAGR) of 9.8% from 2022 to 2030 (Figure 2).

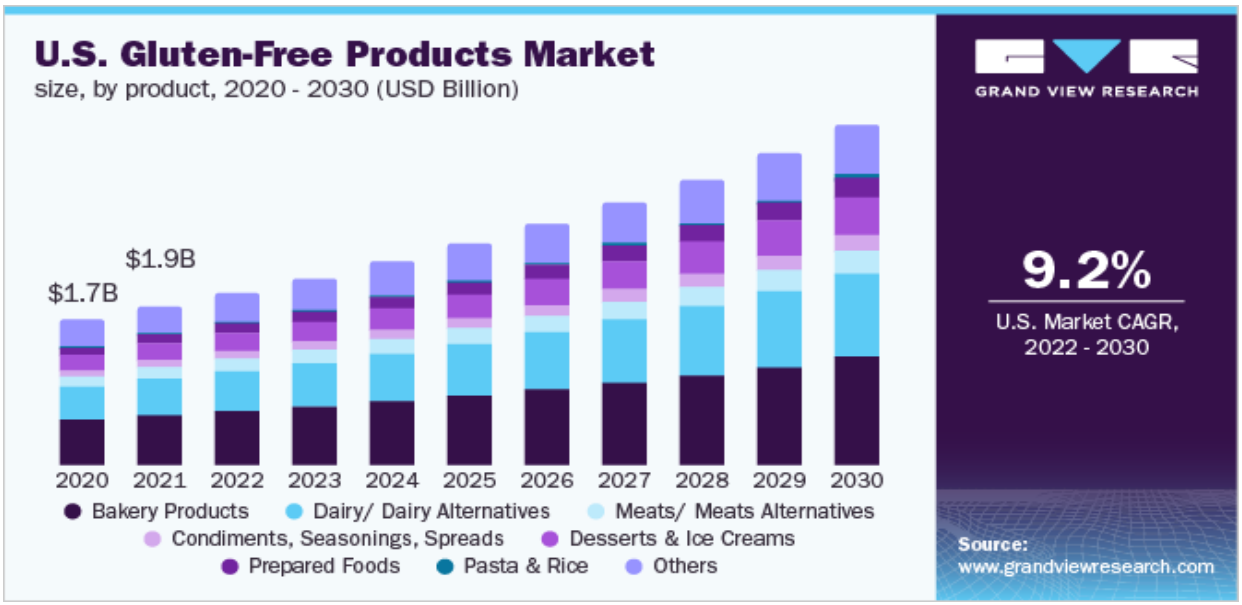

Figure 2. The global market for gluten-free products [18].

The bakery market accounted for the largest share of revenue of almost 29.0% in 2021 and is expected to maintain its dominance over the forecast period. The growing prevalence of gluten-related disorders stimulates the demand for gluten-free products. The COVID-19 pandemic has also exponentially affected the use of gluten-free products due to growing concerns about health and well-being among consumers. Inspired by those who encourage gluten-free diets for better health, many consumers have joined the diet of people for whom gluten-free consumption is a mandatory medical necessity [18,19]. Studies in the field have shown that the rate of adherence to a GFD varies from 44 to 90% in patients with MC. Most often the adherence to a GF diet is restricted by the high cost of these products, compared to the classic products.

A review of the cost of gluten-free products in the United States found that the total cost of gluten-free products is 183% higher than their wheat-based counterparts. Gluten-free biscuits have been found to be 270% more expensive than those made with gluten-containing flours. Commodities such as bread and pasta were also significantly more expensive - by 229% and 227%, respectively. In a survey conducted by GIG in 2021, 78% of respondents - followers of a gluten-free diet said that the cost of gluten-free foods was the biggest challenge they faced. 38% said access to gluten-free foods in general is a challenge [20].

The food safety of people following a GF diet is disturbed by other factors such as: limited availability of gluten-free products, insufficient labeling, risk of cross-contamination, lack of certification policies for GF products, etc. [6,17,21–24]. Patients with CD are very sensitive to the toxic effects of gluten.

The purpose of the research is to evaluate whether the products marketed in the territory of the Republic of Moldova, labeled as gluten-free products, are safe for people with celiac disease, from the perspective of their gluten content.

3. Materials and methods

During the month of May, this year, the supermarkets and small (corner) stores in the capital were visited to identify if they have GF products and to evaluate their assortment. List of supermarkets and subsidiaries under investigation:

1. Nr. 1.
4. Fourchette.
5. Linella.
6. Metro.
7. Kaufland.

A total of 13 supermarkets and 23 small (corner) stores were visited. GF products were purchased to assess whether they were contaminated with gluten, as well as the degree of contamination.

3.1. Materials

The gluten-free products (48 products) purchased were classified into 3 categories:

- Imported products, labeled *gluten free*.
- Imported products, labeled *gluten-free*, with the logo of the *Crossed grain*.
- Gluten-free local products (non-certified) - 17 products.

GlutenToxPro Kit (AOAC-RI).

3.2. Methods

In order to achieve this goal, imported and domestic GF packaged products were purchased from the supermarkets in the capital. A total of 45 products were purchased: bread, pasta, flour and flour mixes, pastries. Products were tested for gluten using the GlutenToxPro Kit (AOAC-RI) (Gluten Detection Kit for Food, Beverage, and Workspaces) [25].

GlutenToxPro is an immuno-chromatographic test used to detect gluten in foods with different levels of processing. The test is used in routine gluten monitoring and to ensure that products are HACCP compliant and properly labeled. Tests also allow decisions and corrective action to be taken quickly if there is a risk of contamination along the production chain. The kit contains the G12 antibody that specifically recognizes the 33-mer peptide of the α-gliadin protein that induces celiac disease [26], (Figure 3). This recognition sequence is repeated three times within the gliadin 33-mer peptide. The G12 antibody recognizes immunotoxic prolamins from wheat, barley, rye and also from some varieties of oat [27]. The G12 antibody is also capable of reacting to other epitopes that are found in other toxic prolamins [27,28].

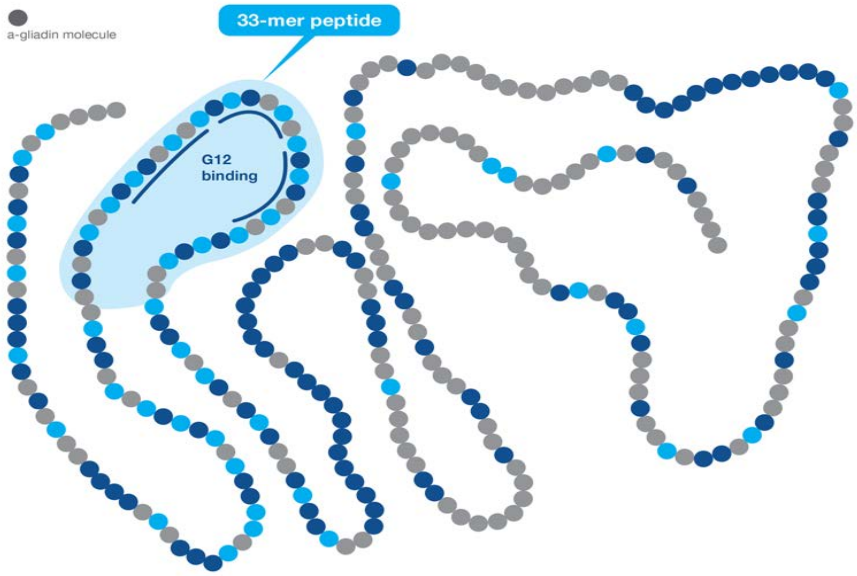

Figure 3. The 33-mer peptide and G12 antibody binding.

The principle of the method. The method consists in the reaction of immunotoxic peptides, like peptide 33 in the sample, with colored conjugates, previously fixed on the stick. That complex has capillary spread on the test strip. In the case of a positive result, a red line appears in the test area of the strip. The result is negative if the red line is missing.

If the test has been performed correctly, a blue line (the control line) will appear on the test strip, regardless of whether or not there is gluten in the tested sample. The detection threshold is conditioned by the number of drops (1, 2, 4 or 10 drops) added to the blue cap dilution bottle (Table 1).

Table 1

Interpretation of results

		Detection threshold			
		10 drops	4 drops	2 drops	1 drop
Test result	Positive	>5 ppm	> 10 ppm	> 20 ppm	> 40 ppm
	negative	< 5 ppm	< 10 ppm	< 20 ppm	< 40 ppm

Warning and limitations. The efficiency of gluten extraction depends on the type of test samples and in such cases, involves conditions of maximum sensitivity (for a detection limit of at least 10 ppm, 10 drops of extract are required in the dilution bottle with a blue cap).

This product category includes:

• Food with ingredients (up to 70%) containing polyphenols or tannins in high concentrations (coffee, black tea, chocolate, wine, berries, legumes, etc.).

• Foods rich in antioxidants (vitamin A, E and C).

• Heat-treated foods with temperatures above 180 °C.

The gluten content could be underestimated in samples subjected to intense hydrolysis processes (beer, sourdough, syrups) [33].

The tests were performed in May 2022, at the Technical University of Moldova, Department of Food and Nutrition.

4. Results and Discussion

Complete avoidance of gluten in the diet is difficult to maintain. A "pervasive" nutrient, gluten can contaminate gluten-free items along the production chain, from the field to the grinding, storage, and manufacturing stages [16]. Most supermarkets had a (common) section for special purpose products (diabetic products, vegan products, organic products, gluten-free products, etc.). Of the 13 supermarkets, only eight had a higher availability of gluten-free foods during that period. Probably because of the Covid 19 pandemic [29], but also of the war in Ukraine, the range of GF products was quite limited. Small (corner) stores did not have gluten-free products.

A total of 48 GF foods were analyzed. The selected products included different brands of bakery and pastry products, flours and mixes of flour and pasta: 13 imported products, labeled GF; 18 imported products, with the *Crossed Grain* logo; 15 local packaged products and 2 local products for use current (unpackaged). The results of the research are presented in Table 2.

Table 2

Level of gluten contamination in the products examined

Tested product category (GF)	Number of products	Gluten content (GC)		
		> 20 ppm	> 10 ppm	< 10 ppm
Imported products, labeled GF	n = 13	-	1 (8%)	12 (92%)
Imported products with the Crossed grain logo	n = 18	-	-	18 (100%)
Packaged local products	n = 15	-	5 (33%)	10 (67%)
Unpackaged local (current) products	n = 2	2 (100%)		

The European License System (ELS) is the standard by which gluten-free products are certified. It refers to those products that carry the Crossed Grain logo on the packaging [13]. The products, which had the Crossed Grain on their packaging, have confirmed their safety and integrity, and continue to be seen as the most effective means of communicating to consumers that these products are safe for people with MC [12,15,30]. All 18 products tested, with the Crossed Grain logo on the package, contained less than 10 ppm gluten.

Another 13 imported products, which had the label gluten free but did not have the Crossed Grain logo, confirmed their safety for consumers with disorders related to gluten consumption: in 12 of them the gluten content was below 10 ppm and only in one product, the gluten content was between 10 ppm and 20 ppm. What characterizes these products as gluten-free products.

The packaged local products under test were products that were naturally gluten-free. Namely cereal derivatives (sorghum flour, corn, legumes, from different producers). It should be noted that the list of local products, labeled gluten-free, contained: flour, semolina and sorghum groats, corn flakes, corn flour, chickpea flour, bean flour, potato flour and flour mixes. The list did not include any products such as bread, biscuits, pasta, snacks, etc. The results showed that even local products, labeled as gluten-free products, do not pose risks for people with disorders related to gluten consumption: in 10 of the 15 local products tested, the gluten content was below 10 ppm, and in 5, between 10 ppm and 20 ppm.

Only one chain of supermarkets in Chisinau offered consumers gluten-free products for current consumption, namely bread made from legumes and pseudocereals. These products were developed in the bakery sections of the supermarkets involved. Those products had the list of ingredients listed on the label and were marketed as gluten-free products. In both products, the gluten content exceeded 20 ppm, which constitutes a risk for the safety of people with celiac disease.

Research has shown that both gluten-free products imported with the Crossed Grain logo and those just labeled gluten-free pose no risk to people with gluten-related disorders: the gluten content of all samples was up to 20 ppm.

Local products labeled gluten-free, according to the results obtained, are just as safe. We just have to keep in mind that when we refer to local GF products, we usually refer to grains, legumes and their derivatives. In the Republic of Moldova, gluten-free products such as: bread, pasta, croissants, pizza, puff pastry, etc. are not currently produced.

5. Conclusions

- Gluten-free products are an example of reverse functional foods, in which gluten is eliminated and not included, like other constituents. These are currently an area in full swing.
- According to the results obtained, GF products with the Crossed grain logo as well as those certified GF continue to be seen as the most effective means of communicating to consumers about their safety for people with MC.
- The assortment of gluten-free foods in the Republic of Moldova is extremely low, and this makes the food security of these categories of people vulnerable. However, research results have shown that local products (cereals, legumes, and their derivatives, etc.) labeled as gluten-free products do not pose risks for coeliacs.
- Unpackaged local GF products (developed and made available to consumers by the supermarkets concerned) pose an increased risk of contamination.
- The lack of certification policies for this product category reduces confidence in the safety of local GF products.
- Food education, informatization of the population, especially those in the food industry, with reference to gluten sources, workplace hygiene, sources, and consequences of cross-contamination with gluten, would contribute to a better

safety of these products and increase nutritional security of people with disorders related to gluten consumption in the Republic of Moldova.

- Launching a systematic gluten-free food sampling program would help to quickly identify risky products, ensure the safety of available products, and ultimately improve the long-term well-being of people with CD or other gluten-related disorders.

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References

1. Volta, U.; Ubaldi, E. *Celiac disease in general medicine*. Ed. Pacini.; Publisher: Ospedaletto (Pisa), Italy, 2010; 64 p.
2. Dolinšek, J.; Dolinšek, J.; Rižnik, P.; Krencnik, T.; Klemenak, M.; Kocuvan Mijatov, M., A.; Ornik, S.; Jurše, M.; Vidmar, M.; Korponay-Szabo, I.; Palcevski, G.; Milinovic, M.; Dovnik, I.; Gyimesi Gallisz, J.; Szitanyi, P; Floriankova, M.; Krajnc, K.; Popp, A.; Man, O.; Carnohorski, I.; Mišak, Z.; Piskernik, M.; Maria Luisa Mearin, M., L.; Wessels, M.; Dragutinovic, N.; Pavkov, V.; Christina Hauer, A.; Markovic, M. *Life with celiac disease*. Ed. Pika Advertising; Publisher: INSMC Alessandrescu-Rusescu, România, 2021; 76 p. Available online: https://www.interreg-danube.eu/uploads/media/approved_project_output/0001/48/9d1dbf5e30a5329690faefee43147bd67750ea6a.pdf (accessed on 02.04.2022).
3. Caio, G.; Volta, U.; Sapone, A.; Leffler, D.A.; De Giorgio, R.; Catassi, C.; Fasano, A. Celiac Disease: A Comprehensive Current Review. *BMC Med* 2019, 17, pp. 142, doi:10.1186/s12916-019-1380-z.
4. Arranz, E.; Fernandez-Banares, F.; Rossell, C. M.; Rodrigo, L.; Pena, A. S. *Advances in the Understanding of Gluten Related Pathology and the Evolution of Gluten-Free Foods*. Ed. OmniaScience: Barcelona, Spain, 2015; 714 p.
5. Demirkesen, I.; Ozkaya, B. Recent Strategies for Tackling the Problems in Gluten-Free Diet and Products. *Critical Reviews in Food Science and Nutrition* 2022, 62, pp. 571–597, doi:10.1080/10408398.2020.1823814.
6. Al-sunaid, F.F.; Al-homidi, M.M.; Al-qahtani, R.M.; Al-ashwal, R.A.; Mudhish, G.A.; Hanbazaza, M.A.; Al-zaben, A.S. The Influence of a Gluten-Free Diet on Health-Related Quality of Life in Individuals with Celiac Disease. *BMC Gastroenterol* 2021, 21, pp. 330, doi:10.1186/s12876-021-01908-0.
7. Sapone, A.; Bai, J.C.; Ciacci, C.; Dolinsek, J.; Green, P.H.; Hadjivassiliou, M.; Kaukinen, K.; Rostami, K.; Sanders, D.S.; Schumann, M. Spectrum of Gluten-Related Disorders: Consensus on New Nomenclature and Classification. *BMC Med* 2012, 10, pp. 13, doi:10.1186/1741-7015-10-13.
8. Taraghikhah, N.; Ashtari, S.; Asri, N.; Shahbazkhani, B.; Al-Dulaimi, D.; Rostami-Nejad, M.; Rezaei-Tavirani, M.; Razzaghi, M.R.; Zali, M.R. An Updated Overview of Spectrum of Gluten-Related Disorders: Clinical and Diagnostic Aspects. *BMC Gastroenterol* 2020, 20, pp. 258, doi:10.1186/s12876-020-01390-0.
9. Siminiuc, R.; Coșciug, L.; Popescu, L.; Bulgaru, V. The effect of dehulling and thermal treatment on the protein fractions in soryz (Sorghum oryzoidum) grains. *The Annals of the University Dunarea de Jos of Galati* 2012, 36, pp. 97–103.
10. Siminiuc, R.; Țurcanu, D. Certain Aspects of Nutritional Security of People with Gluten-Related Disorders. *FNS* 2020, 11, pp. 1012–1031, doi:10.4236/fns.2020.1111072.
11. Wieser, H.; Segura, V.; Ruiz-Carnicer, Á.; Sousa, C.; Comino, I. Food Safety and Cross-Contamination of Gluten-Free Products: A Narrative Review. *Nutrients* 2021, 13, pp. 2244, doi:10.3390/nu13072244.
12. FAO. Codex Alimentarius Standard for Foods for Special Dietary Use for Persons Intolerant to Gluten 2008. Available online:https://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FStandards%252FCXS%2B118-1979%252FCXS_118e_2015.pdf (accessed on 02. 04.2022).

13. Crossed grain trademark product certification 2019. Available online: file:///Users/rada/Downloads/crossed-grain-tm-european-companies-2019%20(1).pdf (accessed on 05.04.2022).
14. Food and Drug Administration, HHS Food Labeling; Gluten-Free Labeling of Fermented or Hydolyzed Foods 2020. Available online: https://www.fda.gov/about-fda/economic-impact-analyses-fda-regulations/food-labeling-gluten-free-labeling-fermented-or-hydrolyzed-foods-regulatory-impact-analysis-final (accessed on 12.04.2022).
15. European Union Law Regulation (EU) No 1169/2011 of the European Parliament and of the Council of 25 October 2011 on the Provision of Food Information to Consumers 2011. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R1169&from=EN (accessed on 15.04.2022).
16. Verma, A.; Gatti, S.; Galeazzi, T.; Monachesi, C.; Padella, L.; Baldo, G.; Annibali, R.; Lionetti, E.; Catassi, C. Gluten Contamination in Naturally or Labeled Gluten-Free Products Marketed in Italy. *Nutrients* 2017, 9, pp. 115, doi:10.3390/nu9020115.
17. La Vieille, S.; Dubois, S.; Hayward, S.; Koerner, T. Estimated Levels of Gluten Incidentally Present in a Canadian Gluten-Free Diet. *Nutrients* 2014, 6, pp. 881–896, doi:10.3390/nu6020881.
18. Gluten-Free Products Market Size Report, 2022-2030. Available online: https://www.grandviewresearch.com/industry-analysis/gluten-free-products-market (accessed on 05.04.2022).
19. Gluten-free Products Market by Type (Bakery products, Snacks & RTE products, Condiments & dressings, Pizzas & pastas), Distribution channel (Conventional stores, Specialty stores and Drugstores & Pharmacies), Form & Region - Global Forecast to 2025. Available online: https://www.marketsandmarkets.com/Market-Reports/gluten-free-products-market-738.html (accessed on 02.09.2022).
20. GIG Gluten Intolerance Group. Food Insecurity in the Gluten-Free Community 2022. Available online: https://gluten.org/2021/12/14/food-insecurity-in-the-gluten-free-community/ (accessed on 02.09.2022).
21. Lee, H.J.; Anderson, Z.; Ryu, D. Gluten Contamination in Foods Labeled as "Gluten Free" in the United States. *Journal of Food Protection* 2014, 77, pp. 1830–1833, doi:10.4315/0362-028X.JFP-14-149.
22. Siminiuc, R.; Coșciug, L. Effect of Dehulling and Hydrothermal Treatment on the Amino Acid Content of Soriz (<I>Sorghum Oryzoidum</I>). *FNS* 2021, 12, pp. 1232–1242, doi:10.4236/fns.2021.1212090.
23. Falcomer, A.L.; Luchine, B.A.; Gadelha, H.R.; Szelmenczi, J.R.; Nakano, E.Y.; Farage, P.; Zandonadi, R.P. Worldwide Public Policies for Celiac Disease: Are Patients Well Assisted? *Int J Public Health* 2020, 65, pp. 937–945, doi:10.1007/s00038-020-01451-x.
24. Bradauskiene, V.; Vaiciulyte-Funk, L.; Shah, B.; Cernauskas, D.; Tita, M. Recent Advances in Biotechnological Methods for Wheat Gluten Immunotoxicity Abolishment – a Review. *Pol. J. Food Nutr. Sci.* 2021, pp. 5–20, doi:10.31883/pjfns/132853.
25. AOAC, Performance Tested Researh Institute. License number 061502 Gluten detection kit for foods, drinks and working surfaces, KIT3000 (KT-5660). Available online: https://www.hygiena.com/wp-content/uploads/2020/10/INS3000_GlutenToxPro_Manual-Rev-C.pdf (accessed on 02. 09.2022).
26. Morón, B.; Bethune, M.T.; Comino, I.; Manyani, H.; Ferragud, M.; López, M.C.; Cebolla, Á.; Khosla, C.; Sousa, C. Toward the Assessment of Food Toxicity for Celiac Patients: Characterization of Monoclonal Antibodies to a Main Immunogenic Gluten Peptide. *PLoS ONE* 2008, 3, e2294, doi:10.1371/journal.pone.0002294.
27. Morón, B.; Cebolla, Á.; Manyani, H.; Álvarez-Maqueda, M.; Megías, M.; Thomas, M. del C.; López, M.C.; Sousa, C. Sensitive Detection of Cereal Fractions That Are Toxic to Celiac Disease Patients by Using Monoclonal Antibodies to a Main Immunogenic Wheat Peptide. *The American Journal of Clinical Nutrition* 2008, 87, pp. 405–414, doi:10.1093/ajcn/87.2.405.
28. Real, A.; Comino, I.; de Lorenzo, L.; Merchán, F.; Gil-Humanes, J.; Giménez, M.J.; López-Casado, M.Á.; Ma Isabel Torres; Cebolla, Á.; Sousa, C.; et al. Molecular and Immunological Characterization of Gluten Proteins Isolated from Oat Cultivars That Differ in Toxicity for Celiac Disease. *PLoS ONE* 2012, 7, e48365, doi:10.1371/journal.pone.0048365.
29. Siminiuc, R.; Turcanu, D. The impact of the pandemic on the agri-food system. *JSS* 2020, 3 (3), pp. 85-94, doi:10.5281/zenodo.3971973.
30. Al-Toma, A.; Volta, U.; Auricchio, R.; Castillejo, G.; Sanders, D.S.; Cellier, C.; Mulder, C.J.; Lundin, K.E.A. European Society for the Study of Coeliac Disease (ESsCD) Guideline for Coeliac Disease and Other Gluten-related Disorders. *United European Gastroenterol. J.* 2019, 7, 583–613, doi:10.1177/2050640619844125.

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EFFECT OF BIOACTIVE ADDITIVES ON BIOMASS FERMENTATION FROM AGRO-INDUSTRIAL SECTOR

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Abstract. Wastes from the agro-industrial sector, due to their toxic effects with regard to plants and living organisms, cannot be dumped in the soil. However, they can serve as renewable source of value-added products, following the specific digestive treatment. This research was focused on studies of vinasse fermentation processes in the presence of bioactive substances introduced directly into the digested biomass. The results obtained testify that the substances of natural origin used as additives, demonstrate the pronounced effects on alcoholic fermentation of vinasse under the mesophilic conditions. The comparative assessment of different additives action in the studied processes have demonstrated that the dihydroxyfumaric acid caused the emission of 266 cm^3 CO_2 in 76 hours, aescinum – 251 cm^3 in 55 hours, tomatin – 233 cm^3 during 78 hours, sclareol – 232 cm^3 during 55 hours, vanillin – 229 cm^3 during 69 hours, whereas catechin – 180 cm^3 during 61 hours of fermentation, until the fermentation process was completed. Thus, the study of the effects of bioactive substances with possible antioxidant properties on biomass from winemaking sector with identification of these processes mechanisms can be a perspective direction, suggesting the new ways of wastes valorisation.

Keywords: *Agro-industrial wastes, vinasse, fermentation, bioactive additives.*

Rezumat. Deșeurile din sectorul agroindustrial, datorită efectelor toxice asupra plantelor și organismelor vii, nu pot fi aruncate în sol, dar pot servi drept sursă regenerabilă de produse cu valoare adăugată. Prezenta cercetare s-a axat pe studiul procesului de fermentare a vinasei în prezența substanțelor bioactive, introduse în biomasa digerată. Rezultatele obținute mărturisesc că substanțele de origine naturală utilizate ca aditivi demonstrează efectele pronunțate asupra fermentației alcoolice a vinasei în condiții mezofile. Evaluarea comparativă a acțiunii aditivilor a demonstrat că acidul dihidroxifumaric a determinat emisia de 266 cm^3 CO_2 în 76 ore, aescinum – 251 cm^3 în 55 ore, tomatin – 233 cm^3 în 78 ore, sclareol – 232 cm^3 în 55 ore, vanilină – 229 cm^3 timp de 69 de ore, în timp ce catechina – 180 cm^3

pe parcursul a 61 de ore de fermentație, până la finalizarea procesului de fermentație. Astfel, studiul efectelor substanțelor bioactive cu posibile proprietăți antioxidante asupra biomasei din sectorul vitivinicol cu identificarea mecanismelor acestor procese poate fi o direcție de perspectivă, sugerând noi modalități de valorificare a deșeurilor.

Cuvinte cheie: *Deșeuri agroindustriale, vinasă, fermentație, aditivi bioactivi*.

1. Introduction

The problem of wastes management from agro-industrial sector, to prevent the environmental pollution with toxic components and at the same time, to obtain the series of value-added products, is an important issue requiring a smart and complex approach. The wastes treatment technology is should be selected on the base of the initial wastes nature, composition and amounts, which, on their turn, are functions on the main production cycle, raw materials, process technology and conditions applied.

Specifically, in the agricultural regions having the wine, spirit, beer and juice-producing industries, the specific types of liquid wastes are generated in the state of continued digestion, which implies the strict prevention of their discharges/dumping directly into the landfills, natural water bodies or other environmental compartments as they can destroy the chemical composition of soil, violate the natural balance of microorganisms, plants, and other living organisms. Existing methods of the solid organic wastes management involve their application in agriculture, burning (although the rather costly process associated with air emissions), anaerobic digestion, composting, etc. The liquid wastes from agro-industrial sector can be treated by sedimentation, decanting in stabilization ponds, anaerobic fermentation, etc.

To produce ethanol from carbohydrate-containing raw materials, the fermentation process is applied commercially [1]. Alcohol is obtained by fermentation of the sugars present in the different raw materials, which are metabolized by microorganisms belonging to the genera *Saccharomyces, Zymomonas, Kluyveromyces,* and *Zygosaccharomyces* [2]. The structural carbohydrates in biomass componence are broken down into the sugars using enzymes. Subsequently, the sugars released are transformed by microorganisms into the alcohols, hydrocarbons or some organic acids during the fermentation process under the atmospheric pressure and temperature 25-70^{o}C. Intermediate sugars can be also utilized to obtain certain useful chemicals [3].

Currently, the operation of the most of processing industries in agriculture, including those dealing with the grain processing into the alcohol, remain unsafe for the environment [4, 5]. Meanwhile, closed ecologically safe production cycles will make it possible to resolve fundamental issues such as rational use of natural raw resources, environmental protection and improving the quality of final product [6]. The alcohol industry affects first of all the water resources, then air and soil.

Specific consumption of fresh water makes 195-325 m^3/t alcohol (10-17 L water/ 1 L alcohol produced), depending on the raw material type and processing technology, namely, recycled water supply [7, 8]. Such high amounts of water used trigger the high volumes of liquid wastes thus formed [9, 10]. The admixtures contained in the waste waters contain mineral and organic substances of vegetable origin. Such wastes are poorly filtrated, quickly rotting, releasing unpleasant odors.

Therefore, the indicator of technology efficiency is important, as it determines the degree of transformation of the initial raw material. Amount of substrate that can be

transformed in ethanol by microbiological synthesis, depends first of all on the type of raw material and selected production technology [11]. Basically, from 5 to 60% of substrate, in average 32-36%, depending on its type and ethanol production method, are transformed into the production wastes [12]. Thus, conversion degree of glucose in ethanol makes 95-100%, fructose – 95-100%, xylose – 60-90%, sucrose – 94-100%, hemicellulose – 40-81%, cellulose – 90-100%. The wastes generated from the alcohol production include yeasts, vinasse, carbon dioxide, ester-formaldehyde fraction, fuel oils (0.94 kg/t grain). Distilled grain residue is the main solid waste which contains carbohydrates, proteins, lipids and some microbial metabolites, which is used as feed, fertilizer or culture substrate for edible mushrooms [13].

Among these residues, the main type is alcohol vinasse (or post-distillery vinasse), which is the biomass separated in the distillation process and represents a liquid with suspended particles, acid pH and high contents in organic matter.

On average, the vinasse production makes about 10-15 L vinasse/L ethanol [14]. Vinasse represents a liquid solution containing the suspended particles, with acid pH The liquid wastes from food industries have high amounts of organic matter, and, as a consequence, rather high contents of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and suspended solids (SS) values: wastes from alcohol production from grain have on average 130-160 g O_2/L BOD, 200-220 g O_2/L COD, 340-360 g/L SS and pH= 6.5-8.8, whereas the liquid wastes from sugar industry (sugar beet) have around 2370 g O_2/L BOD, 7540 g O_2/L COD, 21320 g/L SS and pH=8.0 [15].

In some cases, vinasse can be discharged to sewerage system, reaching the wastewater treatment plant, thus significantly impairing its operation. Vinasse discharges into the environment as a rule, case serious environmental problems. As an alternative, it could be used as a liquid food additive for cattle or poultry [16-18], biogas production [19-21] or for fertilization of agricultural fields [22-24]. But the direct suing of vinasse for animals is not always safe or rational, and cannot resolve the issue of its complete utilization. Some standardized methods have been developed to evaluate generation of byproducts and residues in alcohol production cycle, including the entire supply chain, and minimize negative impacts from crop establishment to consumption of fuel ethanol [25-27].

High water contents in the organic wastes with high fermentable sugar contents and wet biomass implies their obligatory treatment or recovery which is however rather costly [28]. Therefore, the development of useful valorization of this waste to obtain the other value-added products is a perspective approach.

To break down the waste biomass into sugars that can be further converted into the gas or liquid biofuels, or other useful products, the biochemical conversion by microorganisms and enzymes is often used [29-31], although the other approaches such as coagulation and oxidation have been also proposed [32]. Generally, biochemical digestion is rather slow process that requires some time for biomass transformation into the products. Among these technologies, anaerobic digestion and fermentation are most popular processes, resulting in producing the biogas which mainly contains biomethane, carbon dioxide, and in a smaller amounts biohydrogen, hydrogen sulfide [33-35]. During the anaerobic digestion, bacteria are applied to hydrolyze carbohydrates into the sugars that are digestible by other, methanogenic bacteria, which in their turn, produce biogas from the digestible components of biomass. In dependence on the biochemical digestion conditions, biogas with high contents in methane [36-38] or hydrogen [39, 40] may be produced under the oxygen-free

conditions, or under the elevated pressure [41, 42], or using the other approaches such as adding of bioactive compounds accelerating the biochemical digestion and making it possible to obtain much higher amounts of biomethane of biohydrogen per shorter time [43-45]. Biogas can be burnt to produce the heat, or can be converted to energy, or both energy and heat, using the cogeneration devices [46, 47].

However, not only the biofuels but also a series of value-added products such as sugar alcohols (xylitol) can be obtained by using the combined technologies such as chemical or biochemical process combined with the thermochemical method [48, 49].

Production of alcoholic and non-alcoholic beverages generates the wastes and by products that may be recovered, thus allowing not only to reduce their disposal costs and minimize the environmental pollution, but also to develop the new useful products, in addition to the traditional uses of such wastes as animal feed or soil fertilizers. Dumping in the environment of such residues can provoke the problems such as rotting, higher soil acidity, phytotoxicity, methane gas production, etc. [50].

Wine-and juice production is a large source of wastes in agriculture [51]. Grape marc is generated in the grapes processing in rather large amounts in Moldova [52]. Bioactive compounds are among the potential value-added products than can be extracted from the organic wastes. They could be isolated and structurally investigated, and subsequently used for the development of innovative products [53, 54]. Thus, the grape marc along with the other solid and liquid wine-production residues is used for feeding the cattle and poultry in agricultural sector, although having a low nutrition value [55, 56], and is also applied as fertilizer in agricultural fields [57]. But, according to the previous studies, the grape marc is a prospective raw material for obtaining of series of bioactive substances, specifically, fatty acids, pectins, phenols, etc. to be further used in the food production, supplements, medical products, cosmetics, colorants [58-61].

According to numerous works, polyphenols and other components contained in the grapes, wine or juice have beneficial effects on human health, such as inhibiting the development of certain cancer cells acting as free radical scavengers [62], antihyperglycemic, cardioprotective, anti-hyperlipidemic, etc. effects [63, 64]. Apart from the phenolic compounds, grape marc also contains significant amount of such potentially useful substances, some of them having the pronounced antioxidant activity as catechin, epicatechin, hydroxytyrosol, tyrosol, cyaniding glycosides, a series of acids like gallic, caffeic, procatechinic, syrignic, vanillic, *o*-coumaric, *p*-coumaric [65]. A solid-liquid extraction method [66, 67], hydrothermal treatment [68] and other approaches have been applied to extract the bioactive components from grape pomace, considering the fluctuating composition of its solid fraction for further using in food production. As waste biomass from agro-industrial sector can serve as a raw material for not only the energy production, but also for food and animal feed production, as a source of bioactive and other substances with useful properties for industry, its conversion efficiency needs to be improved. For this reason, current research is focused on increasing the product yields, improving the biochemical conversion technologies, increasing the conversion degree of biomass, improving the entire biochemical conversion system. Biochemical digestion of waste biomass using the microorganisms has an important advantage that no high temperatures are needed. In addition, the wet biomass of organic wastes has high water contents, making it necessary to apply the effluent treatment.

Our studies are focused on investigation of an original approach in enhancing the conversion rate and conversion degree of organic wastes biomass, using the small amounts

of biologically active substances introduced into the fermented mixture, to accelerate the process rate and obtain the valuable products and, at the same time, to prevent the discharges of harmful mixtures into the environment. It was of special interest to study the effect of various additives of natural vegetal origin, introduced into the digested mixture and un type of biomass used.

2. Materials and Methods

The overall scope of the work was to elaborate processes of liquid wastes treatment from the agri-food sector, with obtaining the value-added products and avoid discharges into environment of toxic substances which may provoke unfavorable effects on soil, water, air and living organisms.

The following instruments and equipment were used for the research: thermostat PURA, digital pH-meter PH-3CU, refractometer Brix, titration equipment, bench-scale biochemical reactor. The studies of the effect of biologically active substances (BAS) on the digestion process have been performed using the vinasse resulted from the grains distillation at the" Garma Grup" company (Hâncești, Republic of Moldova). Also, the other types of wastes biomass have been taken for the research, such as wastes biomass from corn distillation.
Bench-scale technological experiments have been performed using the laboratory set-up in which the nutrition mixture and various types of bioactive additives have been introduced. The nutrition mixture has been prepared using 30 mL fresh grape juice with 10 % fermentation yeast 10^{10} CFU/g), 20 mL inversed sugar (42 %), 150 mL vinasse and 2 mL of BAS (3 g/L).

The biomass mixed with the nutrition mixture was left for alcohol fermentation under the mesophilic conditions (20-32°C). The digestion process was followed by the volume of emitted gas (CO_2) which replaced NaOH, determined by standard method (titration with phenolphthalein). Composition and characteristics of initial vinasse used to study the fermentation process in the presence of bioactive additives, is shown on Table 1 and 2.

Table 1

Composition of initial vinasse* [69, 70]

	Component	*Corn vinasse*	*Grain vinasse*	*Barley vinasse*	*Rye vinasse*
1.	Dry matter, %	8.5	4.2	26.0	8.0
2.	Proteins (% of dry matter)	25.5	34.8	31.3	42.4
3.	Lipids (% of dry matter)	11.7	2.2	10.2	3.5
4.	Fibers (% of dry matter)	10.6	3.4	13.7	5.9
5.	Ash (% of dry matter)	4.7	8.6	2.1	3.5

* P≥0,95

Table 2

Physico-chemical indices of media study mediums

	Indicator	*Vinasse*	*Grape juice*
1.	Sugar content, g/L	26.27 ± 0.91	124. 4 ± 1.6
2.	pH	3.91 ± 0.07	3.77± 0.12
3.	Titratable acidity, g/L sulfuric acid	3.417± 0.241	2.74± 0.322
4.	Contents in amine nitrogen, mg/L	492.2± 0.63	140.8± 1.2

3. Results

Digestion process was studied with introduction of biologically active substances of natural origin into the fermented biomass, which included the waste biomass and nutrition mixture. As can be seen from Figure 1, additives of aecium and betuline suppress the CO_2 emission, whereas using of tomatine ensures higher amount of gas evolved, or more intensive fermentation process, as compared to the witness test.

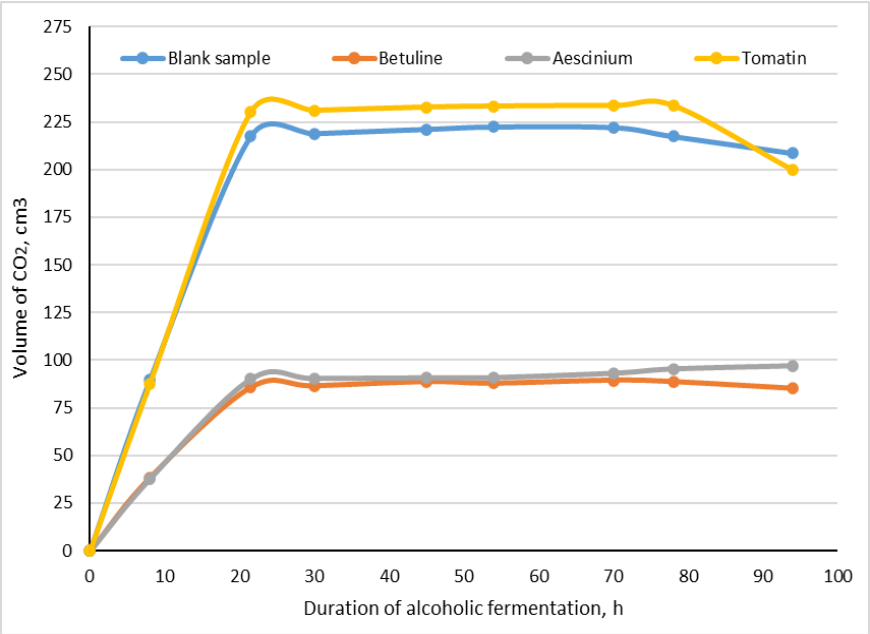

Figure. 1. Kinetics of carbon dioxide (CO_2) emission during the vinasse alcoholic fermentation in the presence of 0,006 g additives /L.

Practical experiences have shown that introduction of sclareol accelerates the biomass digestion, whereas addition of aescinum suppresses this process (Figure 2). Unlike these two bioactive substances, sclareol at the first stages of digestion significantly suppresses the CO_2 emission, and after 30 hours of fermentation, it makes this process somewhat more intensive as compared to the witness test.

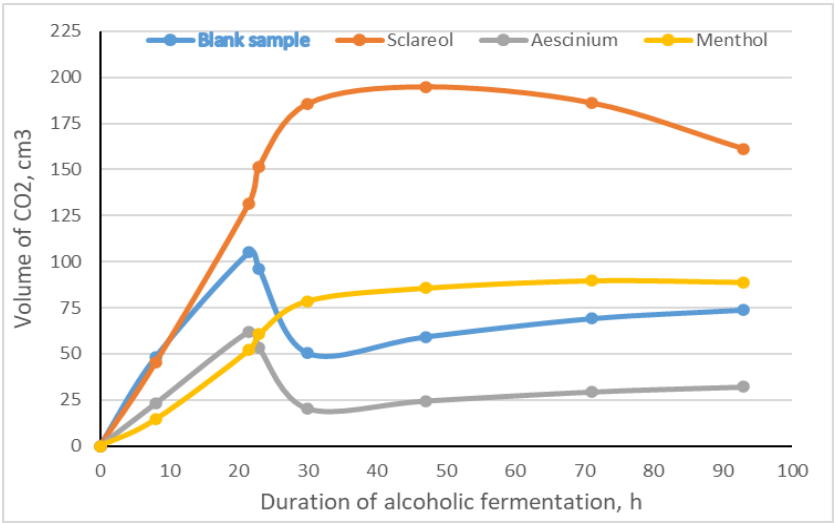

Figure. 2. Kinetics of the vinasse fermentation in the presence of additives of aescinum, menthol and sclareol of 0.006 g /L biomass.

At the same time, introduction into the alcohol fermentation of sclareol and menthol in different amounts (0.003-0.012 g/L biomass) have shown that the amount of additive introduced has no significant effect on the fermentation rate, although the higher amounts (0.012 g/L) of both additives did not demonstrate higher efficiency; on the opposite, the fermentation rate was lower as compared to first 3 addition (Figure 3). As compared to menthol, sclareol provokes more intensive fermentation at a much lower concentration.

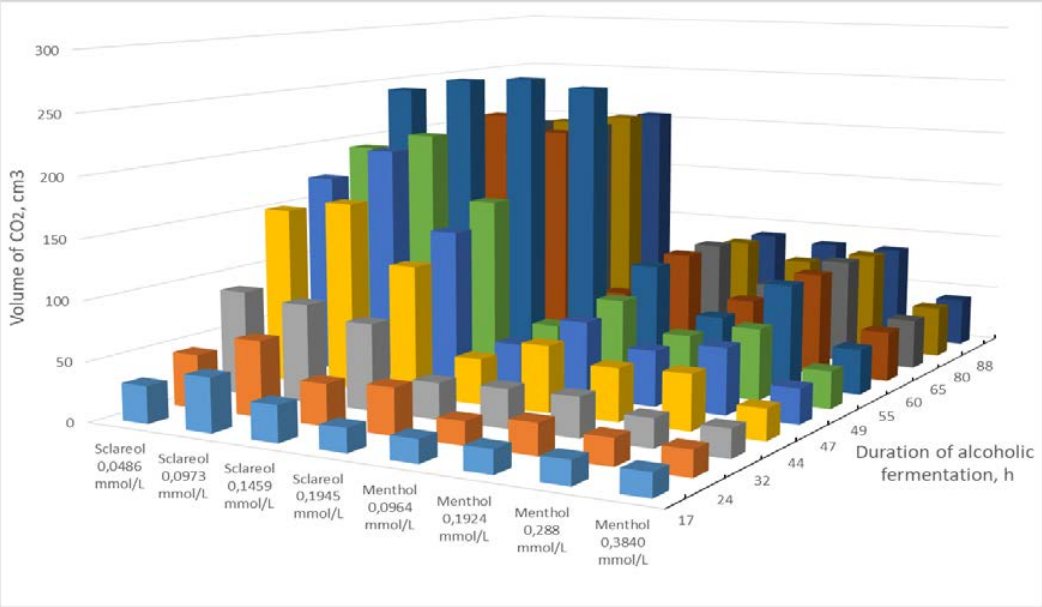

Figure. 3. Kinetics of the vinasse fermentation in the presence of sclareol and menthol additions.

In the presence of dihydroxyfumaric acid the vinasse fermentation proceeds somewhat more easily as compared to witness test, being approximately similar in case of introduction of additive in various concentrations (0.1013 ÷ 0.4052·10^{-6} mol/L), although with the lesser amount of addition 0.1013·10^{-6} mol/L the fermentation was accelerated significantly (Figure 4).

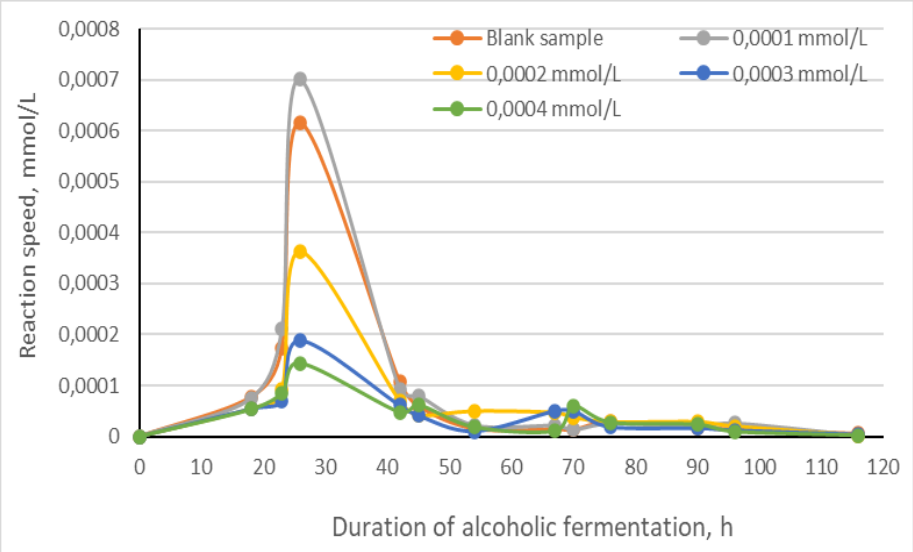

Figure. 4. Reaction rate dynamics of the vinasse alcoholic fermentation in the presence of dihydroxy fumaric acid addiction.

In case of vanillin introduction into the fermented mixture, likewise, the fermentation process was suppressed in case of introduction of higher amount of additive (0.19 ÷ 0.39 $\cdot 10^{-3}$ mol/L), whereas the insignificant acceleration of carbon dioxide emission, as compared to the witness test, was observed in case of the using of 0.098 mmol/L amount of vanillin addition (Figure 5).

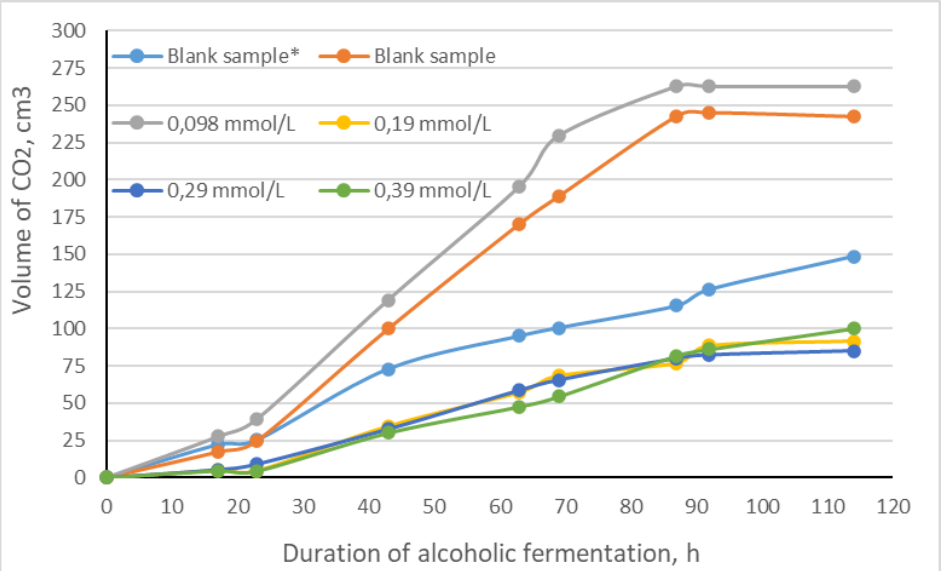

Figure. 5. Kinetics of the vinasse fermentation in the presence of vanillin additive.

Different amounts of catechin introduced in biomass have shown a difference in carbon dioxide gas emission: smaller amounts of additive provoked the lower efficiency of fermentation, and the higher concentration made the process more intensive as compared to witness test (Figure 6).

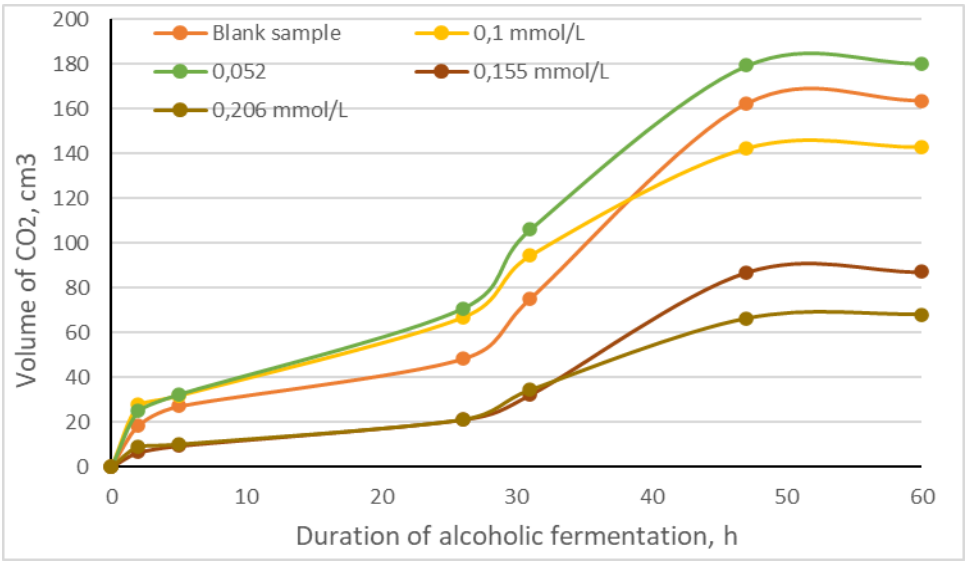

Figure. 6. Kinetics of the vinasse fermentation in the presence of catechin additive.

The results obtained demonstrate that the substances of natural origin with bioactive / antioxidant properties show the pronounced effects on the alcohol fermentation of vinasse under the mesophilic conditions. The most efficient concentrations of studied additives are summarized on Table 3.

Table 3

Comparative efficiency of different types of additives of bioactive substances in the vinasse fermentation process at concentration of 0,003 g/L biomass.

Nr. crt.	Bioactive substance used as an additive to the fermented biomass	Total volume of CO_2 emitted gas, cm^3	Fermentation time, h
1.	Dihydroxy fumaric acid	266.00	76
2.	Aescinum	251.01	55
3.	Tomatin	233.46	78
4.	Sclareol	232.50	55
5.	Vanillin	229.00	69
6.	Catechin	180.00	61
7.	Betuline	250.00	80
8.	Menthol	200.00	70

The results demonstrate that introduction of higher compounds of additives into the fermented biomass is not rational, as generally does not accelerate the fermentation process. It can be suggested that the ability of studied additives to accelerate the fermentation of liquid wastes from agro-industrial sector are connected with their molecular structure and antioxidant, antihypoxant, antimutagen, etc. properties.

4. Conclusions

The study of the influence of additives of biologically active substances on waste biomass fermentation from agro-industrial sector, along with the revealing of these processes' mechanisms can open a new perspective research direction in this area. This would allow not only to manage the fermentation processes, accelerating or suppressing them for the specific scopes, but also to obtain a series of value-added products under the more favorable conditions, as well as to prevent the discharges of harmful wastes into the environment. It was found that in case of tomatin application, higher amounts of emitted gas were observed, whereas in case of menthol, dihydroxyfumaric acid, sclareol, vanillin the rate of the gas emission was lower. At the same time, it became obvious that introduction of 2-4 times higher amounts of additives in many cases makes no sense as it does not provoke further acceleration of alcoholic fermentation process.

Products of alcohol fermentation can have the added value in agriculture and adjacent fields. Thus, carbon dioxide emitted during the biomass digestion can be used, for instance, in the microalgae cultivation basins, which in their turn, could serve as a valuable feed for poultry/cattle in zootechnical sector, while the water separated from solid fraction can be used for technical scopes at the industries (cleaning machines and apparatuses, cleaning and washing up the production halls and territory, etc.), or watering the plants in the city parks, flower beds, etc. The solid fraction after the fermentation, with the condition of its controlled composition, can be used as fertilizer for technical crops.

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References

1. Bušić, A.; Marđetko, N.; Kundas, S.; Morzak, G.; Belskaya, H. Bioethanol Production from Renewable Raw Materials and Its Separation and Purification: A Review. *Food Technol Biotechnol.* 2018, 56(3), pp. 289–311.
2. Moreno-Arribas, M.V.; Polo, M.C. Winemaking biochemistry and microbiology: current knowledge and future trends. *Crit. Rev. Food Sci. Nutr.* 2005, 45, pp. 265–286.
3. Binder, J.; Raines, R.T. Fermentable sugars by chemical hydrolysis of biomass. *Proceedings of the National Academy of Sciences of the USA (PNAS*) 2010, 107(10), pp. 4516-4521.
4. Christofoletti, C.A.; Escher, J.P.; Correia, J.E.; Marinho, J.F.U.; Fontanetti, C.S. Sugarcane vinasse: environmental implications of its use. *Waste Manag.* 2013, 33, pp. 2752–2761.
5. Grossi-Botelho, R.; Tornisielo, V.L.; Alves de Olinda, R.; Maranho, L.A.; Machado-Neto, L. Acute toxicity of sugarcane vinasse to aquatic organisms before and after pH adjustment. *Toxicol Environ Chem. 2012,* 94, pp. 2035–2045.
6. Hidalgo, D.; Martin-Marroquin, J.M.; Corona, F. A multi-waste management concept as a basis towards a circular economy model. *Renewable and Sustainable Energy Reviews* 2019, 111, pp. 481-489.
7. Wu, M.; Mintz, M.; Wang, M.; Arora, S. Water Consumption in the Production of Ethanol and Petroleum Gasoline. *Environmental management* 2009, 44, pp. 981-97.
8. Liu, H.; Ren, L.; Zhuo, H.; Fu, S. Water Footprint and Water Pinch Analysis in Ethanol Industrial Production for Water Management. *Water 2019,* 11, pp. 518.
9. Mikucka, W.; Zielińska, M. Distillery Stillage: Characteristics, Treatment, and Valorization. *Appl Biochem Biotechnol.* 2020, 192, pp. 770–793.
10. Gerbens-Leenes, W.; Hoekstra, A.Y. The water footprint of sweeteners and bio-ethanol. *Environ. Int.* 2012, 40, pp. 202–211.
11. Matkovsky, P.E.; Yarullin, R.S.; Startseva, G.P.; Sedov, I. Bioethanol: technologies of its production from renewable raw materials and application areas. *Alternative power engineering and ecology* 2010, 6(86), pp. 95 (in Russian).
12. Pilarski, K.; Pilarska, A.A.; Boniecki, P.; Niedbała, G.; Witaszek, K.; Piekutowska, M.; Idzior-Haufa, M.; Wawrzyniak, A. Degree of Biomass Conversion in the Integrated Production of Bioethanol and Biogas. *Energies* 2021, 14, pp. 7763.
13. Wang, T.; Wang, S.; Zhong, X.; S, Zh.-Y.; Huang, Y.-L.; Tan, L.; Tang, Y.-Q.; Kida, K. (2017). Converting digested residue eluted from dry anaerobic digestion of distilled grain waste into value-added fertilizer by aerobic composting. *Journal of Cleaner Production* 2017, 166, pp. 530-536.
14. Ferraresi-de Arraujo, J.G.; Nino-Castillo, I.N. Vinasse: current concept, challenges and opportunities for the sustainability. *ECORFAN-Journal-Republic of Nicaragua* 2021, 7(13), pp. 1-9.
15. Araujo, G.; Oliveira, S. Energy and environmental analysis of vinasse processing using internal circulation biodigesters and concentrators for different production ranges of ethanol and its potential impact on Brazil. *Environment, Development and Sustainability: A Multidisciplinary Approach to the Theory and Practice of Sustainable Development* 2021, 23(3), pp. 3130-3163.
16. López-Campos, O.; Bodas, R.; Prieto, N.; Frutos, P.; André s, S.; Girá ldez, F. Vinasse added to the concentrate for fattening lambs: Intake, animal performance, and carcass and meat characteristics. *Journal of animal science* 2010, 89, pp. 1153-1162.
17. Stemme, K.; Gerdes, B.; Harms, A.; Kamphues, J. Beet-vinasse (condensed molasses solubles) as an ingredient in diets for cattle and pigs - Nutritive value and limitations. *Journal of animal physiology and animal nutrition* 2005, 89, pp. 179-183.
18. De Oliveira, M.C.; da Silva, D.M.; de Almeida Faleiros, C. Effect of including liquid vinasse in the diet of rabbits on growth performance. *Revista Braziliera de Zootecnia* 2013, 42 (4), pp. 259-263.
19. Van Lier, J.B.; Tilche, A.; Ahring, B.K.; Macaria, H.; Moletta, R.; Dohanyos, M.; Hulstoff Pol L.W.; Lens, P.; Versaete, W. New perspectives in Anaerobic Digestion. *Water Science and Technology*, 2001, 43(1), pp. 1-18.
20. Cruz-Salomón, A.; Ríos-Valdovinos, E.; Pola, F.; Meza Gordillo, R.; Lagunas Rivera, S.; Ruíz-Valdiviezo, V. Anaerobic treatment of agro-industrial wastewaters for COD removal in expanded granular sludge bed bioreactor. *Biofuel Research Journal* 2017, 16, pp. 715-720.
21. Parsaee, M.; Kiani, M.K.D.; Karimi, K. A review of biogas production from sugarcane vinasse. *Biomass Bioenergy* 2019, 122, pp. 117–125.

22. Arsanoglu, H.; Tumen, F. Potassium struvite (slow release fertilizer) and activated carbon production: Resource recovery from vinasse and grape marc organic waste using thermal processing. *Process Safety and Environmental Protection* 2021, 147, pp. 1077-1087.
23. Tejada, M., Gonzalez, J.L. Effects of two beet vinasse forms on soil physical properties and soil loss. *Chain* 2006, 68, pp. 41–50.
24. Moran-Salazar, R.G.; Sanchez-Lizarraga, A.L.; Rodriguez-Campos, J.; Davila-Vazquez, G.; Marino-Marmolejo, E.N.; Dendooven, L. Utilization of vinasses as soil amendment: consequences and perspectives. *Springerplus* 2016, 5, pp. 1007.
25. Miret, C.; Chazara, P.; Montastruc, L.; Negny, S.; Domenech, S. Design of bioethanol green supply chain: Comparison between first and second generation biomass concerning economic, environmental and social criteria. *Computers & Chemical Engineering* 2015, 85, pp.16-35.
26. Mikulski, D.; Kłosowski, G. Integration of First- and Second-generation Bioethanol Production from Beet molasses and Distillery Stillage After Dilute Sulfuric Acid Pretreatment. *BioEnergy Research*. 2022, 15 (6), pp. 454-465.
27. Gallejones, P.; Pardo, G.; Aizpurua, A.; Del Prado, A. Life cycle assessment of first-generation biofuels using a nitrogen crop model. *The Science of the total environment* 2014, 505C, pp. 1191-1201.
28. España-Gamboa, E.; Mijangos-Cortes, J.; Barahona-Perez, L.; Dominguez-Maldonado, J.; Hernández-Zarate, G.; Alzate-Gaviri, L. Vinasse: characterization and treatments. *Waste Manag Res.* 2011, 29, pp. 1235–1250.
29. Choeisai, P.; Jitkam, N.; Silapanoraset, K.; Yubolsai, C.; Yoochatchava, W.; Yamaguchi, T.; Onodera, T.; Syutsubo, K. Sugarcane molasses-based bio-ethanol wastewater treatment by two-phase multi-staged up-flow anaerobic sludge blanket (UASB) combination with up-flow UASB and down-flow hanging sponge. *Water Sci Technol.* 2014, 69, pp. 1174–1180.
30. Ferreira, L.F.; Aguiar, M.; Pompeu, G.; Messias, T.; Monteiro, R.T. Selection of vinasse degrading microorganisms. *World Journal of Microbiology and Biotechnology* 2010, 26, pp. 1613-1621.
31. Ordaz-Diaz, L.A.; Bailon-Salas, A.M. Molecular identification of microbial communities in the methane production from vinasse: A review. *BioResources* 2020, 15(2), pp. 4528-4552.
32. Guerreiro, L.F.; Rodrigues, C.S.; Duda, R.M.; de Oliveira R.A.; Boaventura, R.A.; Madeira, L.M. (2016). Treatment of sugarcane vinasse by combination of coagulation/flocculation and Fenton's oxidation. *J Environ Manage.* 2016, 181, pp. 237–248.
33. Moraes, B.S.; Junqueira, T.L.; Pavanello, L.G.; Cavaletti, O.; Mantelatto, P.E.; Bonomi, A. Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? *App Energy* 2014, 113, pp. 825–835.
34. Adekunle, K.; Okolie, J. A Review of Biochemical Process of Anaerobic Digestion. *Advances in Bioscience and Biotechnology* 2015, 6, pp. 205-212.
35. Deublein, D.; Steinhauser, A. *Biogas from Waste and renewable Resources: An Introduction*. Wiley-VCH, Weinheim, 2008, pp. 89-290.
36. Asam, Z.U.Z.; Poulsen, T.G.; Nzami, A-S.; Raxique, R.; Kiely, G. and Murphy, J.D. How Can We Improve Biomethane Production Per Unit of Feedstock in Biogas Plant. *Applied Energy*, 2011, 88, pp. 2013-2018.
37. Nevers, L.; Ribeiro, R.; Oliveira, R. and Alves, M.M. (2006). Enhancement of Methane Production from Barley Waste. *Biomass and Bioenergy* 2006, 30, pp. 599-560.
38. Gunaseelan, V.N. Anaerobic Digestion of Biomass for Methane Production: A Review. *Biomass and Bioenergy* 1997, 13, pp. 83-144.
39. Kamaraj, M.; Ramachandran, K.K; Aravind, J. Biohydrogen production from waste materials: benefits and challenges. *International J. Environ. Sci. Technol. 2020,* 17, pp. 559–576.
40. Karapinar, K.I.; Kargi, F. (2006). Bio-hydrogen Production from Waste Materials. *Enzyme and Microbial Technology* 2006, 38, pp. 569-582.
41. Siciliano, A.; Limonti, C.; Curcio, C.M. Performance Evaluation of Pressurized Anaerobic Digestion (PDA) of Raw Compost Leachate. *Fermentation* 2022, 8(1), pp. 15.
42. Lindeboom, R.E.F.; Fermoso, F.G.; Weijma, J.; Zaqt, K.; van Lier, J.B. Autogenerative high pressure digestion: anaerobic digestion and biogas upgrading in a single step reactor system. *Water Sci Technol.* 2011, 64(3), pp. 647-653.
43. Covaliov, V. Improving the Biogas Production Systems. *Academos*, 2015, 4 (39), pp. 38-44.
44. Duca, Gh.; Covaliov, V; Covaliova, O. *Intensive biochemical processes of wastewater treatment with high caloricity biogas production*. In: Emerging Developments and Environmental Impacts of Ecological Chemistry. Chapter 13. IGI Global Publ. House, USA, 2020, pp. 291-306.

45. Covaliov, V.; Senicovscaia, I.; Nenno, V.; Bobeica, V.; Covaliova, O. Effects of Amaranths' Seeds on Dehydrogenase Activity and Gases Emission in Methanogenic Bioreactors. *Studia Universitatis Moldaviae. Real and Natural Sciences Ser*. 2015, 1(81), p.230-235.
46. Dalpaz, R.; Konrad, O.; Cândido da Silva Cyrne, C.; Panis Barzotto, H.; Hasan, C.; Guerini Filho, M. Using biogas for energy cogeneration: An analysis of electric and thermal energy generation from agro-industrial waste. *Sustainable Energy Technologies and Assessments* 2020, 40, p. 100774.
47. Lobato, L.C.S.; Chernicharo, C.A.L.; Pujatti, F.J.P.; Martins, O.M.; Melo, G.C.B.; Recio,A.A.R. Use of biogas for cogeneration of heat and electricity for local application: performance evaluation of an engine power generator and a sludge thermal dryer. *Water Sci. Technol.* 2013, 67(1), pp. 159-167.
48. Arcaño, Y. D.; García, O. D.; Mandelli, D.; Carvalho, W. A., and Pontes, L. A. Xylitol: A review on the progress and challenges of its production by chemical route. Catal. Today 2020, 344, pp. 2–14.
49. Audemar, M.; Ramdani, W.; Junhui, T.; Raluca Ifrim, A.; Ungureanu, A.; Jérôme, F. Selective hydrogenation of xylose to xylitol over Co/SiO2 catalysts. *ChemCatChem.* 2020, 12, pp. 1973-1978.
50. Velásquez-Riaño, M.; Meneses-Sánchez, J.S.; Carvajal Arias, C.E. Evaluation of acute toxicity of vinasse by means of *Daphnia magna* and *Aliivibrio fischeri*: a comparative study. *Interdiscip Toxicol*. 2019, 2(3), pp. 143-148.
51. Devesa-Rey, R.X.; Vecino, J.L.; Varela-Alende, M.T.; Barral, J.M.; Cruz, A.B. Moldes. Valorization of winery waste vs. the costs of not recycling. *Waste management* 2011, 31 (11), pp. 2327-2335.
52. Musteata, G.; Balanuta, A.; Restica, A.; Filimon, R.V.; Baetu, M.M.; Patras, A. Capitalization of secondary wine products – an opportunity for the wine sector of Republic of Moldova and Romania. *Journal of Social Sciences* 2021, 6(2), pp. 117-127.
53. Ghendov-Mosanu, A.; Cojocari, D.; Balan, G.; Patras, A.; Lung, I.; Soran, M.-L.; Opris, O.; Cristea, E.; Sturza, R. Chemometric Optimization of Biologically Active Compounds Extraction from Grape Marc: Composition and Antimicrobial Activity. *Molecules* 2022, 27(5), p. 1610.
54. Ferri, M.; Vannini, M. ; Ehrnell, M.; Eliasson, L.; Xanthakis, E.; Monari, S.; Tassoni, A. (2020). From winery waste to bioactive compounds and new polymeric biocomposites: A contribution to the circular economy concept. *Journal of advanced research* 2020, 24, pp. 1-11.
55. Yu, J.; Ahmedna, M. Functional components of grape pomace: Their composition, biological properties and potential applications. *Int. J. Food Sci. Technol.* 2013, 48, 221–237.
56. Moate, P.J.; Williams S.R.O.; Torok, V.A.; Hannah, M.C.; Ribaux, B.E.; Tavendale, M.H.; Eckard, R.J.; Jacobs, J.L.; Auldist, M.J.; Wales, W.J. Grape marc reduces methane emissions when fed to dairy cows. *Journal of Dairy Science* 2014, 97(8), 5073-5087.
57. Bustamante, M.A.; Moral, R.; Paredes, C.; Pérez-Espinosa, A.; Moreno-Caselles, J.; Pérez-Murcia, M.D. Agrochemical characterisation of the solid by-products and residues from the winery and distillery industry. *Waste Manag. 2008, 8*, pp. 372–380.
58. Teixeira, A.; Baenas, N.; Dominguez-Perles, R.; Barros, A.; Rosa, E.; Moreno, D.; Garcia-Viguera, C. Natural bioactive compounds from winery by-products as health promoters: A review. *Int. J. Mol. Sci.* 2014, 15, pp. 15638–15678.
59. Spinei, M.; Oroian, M. The Potential of Grape Pomace Varieties as a Dietary Source of Pectic Substances. *Foods* 2021, 10(4), p. 867.
60. Brazinha, C.; Cadima, M.; Crespo, J.G. Optimization of extraction of bioactive compounds from different types of grape pomace produced at wineries and distilleries. *J. Food Sci.* 2014, 79, pp. E1142–E1149.
61. Rondeau, P.; Gambier, F.; Jolibert, F.; Brosse, N. Compositions and chemical variability of grape pomaces from French vineyard. *Industrial Crops and Products.* 2013, 43, pp. 251-254.
62. Nerantzis, E.; Tataridis, P. Integrated enology utilization of winery by-products into high added value products. *E-J. Sci. Technol.* 2006, 1, pp. 79–89.
63. Arvanitoyannis, I.S.; Ladas, D.; Mavromatis, A. (2006). Potential uses and applications of treated wine waste: a review. *International Journal of Food Science & Technology.* 2006, 41 (5), pp. 475-487.
64. Chakka, A.K.; Babu, A.S. Bioactive Compounds of Winery by-products: Extraction Techniques and their Potential Health Benefits. *Applied Food Research.* 2022, 2(1), p. 100058.
65. Negro, C.; Tommasi, L.; Miceli, A. Phenolic compounds and antioxidant activity from red grape marc extracts. *Bioresour. Technol.* 2003, 87, pp. 41–44.
66. Pinelo, M.; Ruiz Rodrıguez, A.; Sineiro, J.; Señoráns, F.; Reglero, G.; Núñez, M. Supercritical fluid and solid-liquid extraction of phenolic antioxidants from grape pomace: A comparative study. *European Food Research and Technology*. 2007, 226(1), pp. 199-205.

67. Azmir, J.; Zaidul, I.S.M.; Rahman, M.M.; Sharif, K.M.;Mohamed, A.; Sahena, F.; Omar, A.K.M. Techniques for extraction of bioactive compounds from plant materials: A review. *Journal of food engineering* 2013, 117 (4), pp. 426-436.
68. Bassani, A.; Alberici, N.; Fiorentini, C.; Giuberti, G.; Dordoni, R.; Spigno, G. Hydrothermal treatment of grape skins for sugars, antioxidants and soluble fibers production. *Chemical Engineering*, 2020, p. 79.
69. Scull, I.; Savón, L.; Gutiérrez, O.; Valiño, E.; Orta, I.; Mora, P.O.; Orta, H.; Ramos, Y.; Molineda, A.; Coto, G.; Noda, A. Physico-chemical composition of concentrated vinasse for their assessment in animal diets. Cuban *Journal of Agricultural Science*. 2012, 46(4), p. 385.
70. de Godoi, L.A.G.; Camiloti, P.R.; Bernardes, A.N. Seasonal variation of the organic and inorganic composition of sugarcane vinasse: main implications for its environmental uses. *Environ Sci Pollut Res*. 2019, 26, pp. 29267–29282.

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SPECTRAL AND CHROMATOGRAPHIC CHARACTERISATION OF THE YELLOW FOOD DYE FROM SAFFLOWER

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Abstract. Recently, an increasingly trend of public concern for the food safety is observed. Use of additives in food industry growing steadily. Present study deals with separation and identification of compounds from Yellow Food Dye from Safflower (YFDS). Spectral and chromatographic characteristics of YFDS were obtained and discussed. Dry powders and solutions of YFDS were examined using Thin Layer Chromatography (TLC), UV-Vis spectroscopy and reversed-phase HPLC. TLC was carried out in three systems I (HCl 0.1 M), II (aqua 50%, ethanol 45%, citric acid 5%) and III (water, butan-1-ol, acetic acid). Spectral determinations in the range of 200 to 600 nm were carried out at various pH values. HPLC method was carried out by the gradient elution technique. Chromatographic method showed that it is impossible to separate and to identify the components of the YFDS by paper chromatography. UV-Vis Spectra demonstrated that the most successful interval for the practical use of YFDS is in the pH range of pH = 4...5, since in this range the coloration activity of dyes is maximal. HPLC method demonstrated that YFDS-compounds corresponds to the composition of dry Safflower petals, which confirms its high biological activity. Powdered yellow pigment from Safflower petals is containing natural chalcones and can be successfully used in the dairy producing.

Keywords: *Anhydrosafflower Yellow B, Chalcones, Hydroxisafflower Yellow A, Izosafflomin C, Precarthamine, Safflomin C.*

Rezumat. Actualmente se observă o creștere din ce în ce mai mare a îngrijorării consumatorilor față de siguranța alimentelor consumate. Utilizarea aditivilor în industria alimentară este în continuă creștere. Studiile în acest domeniu demonstrează, că apar noi aspecte ale toxicității coloranților sintetici. În studiul de față, s-a efectuat separarea și identificarea compușilor din amestecul de compuși a colorantului galben alimentar din șofrănel (YFDS). Au fost testate caracteristicile spectrale și cromatografice ale YFDS. Pulberile uscate și soluțiile de YFDS au fost studiate, utilizând cromatografia în strat subțire (TLC), spectroscopia UV-Vis și HPLC cu fază inversă. TLC a fost efectuat în trei sisteme I (HCI 0,1 M), II (aqua 50%, etanol 45%, acid citric 5%) și III (apă, butan-1-ol, acid acetic). Determinările spectrale s-au efectuat în intervalul de la 200 la 600 nm la diferite valori a pH-ului. Metoda HPLC a fost efectuată prin tehnica de eluare cu gradient. Metoda cromatografică

a arătat că este imposibil de separat și de identificat componentele YFDS prin cromatografie pe hârtie. Spectroscopia UV-Vis a demonstrat că intervalul cel mai de succes pentru utilizarea practică a YFDS este în intervalul de pH de la 4 la 5, deoarece în acest interval activitatea de colorare a coloranților este maximă. Metoda HPLC a demonstrat că compușii YFDS corespund compoziției petalelor uscate de șofrănel, ceea ce confirmă activitatea sa biologică ridicată. Pigmentul galben sub formă de pulbere din petalele de șofrănel conține chalconi naturali și poate fi utilizat cu succes în fabricarea produselor lactate.

Cuvinte cheie: *Anhidrosafflora Galben B, Chalcone, Hydroxisaflomină Galben A, Izosaflomină C, Precartamină, Safflomină C.*

1. Introduction

Consumers striving for naturalness choose a food product not only in appearance, but also in composition, rightly considering this factor to be extremely important. The existing demand for partial or complete abandonment of synthetic dyes in food products is expressed by a decrease in the growth rate of the production of synthetic dyes, and an increase in the production of natural ones [1]. At the same time, existing natural sources of food colors are already actively exploited, and they are clearly insufficient. Therefore, in order to effectively replace of the synthetic dyes with natural ones, it is necessary to found new and suitable sources of the latter.

The perspective plant which can be used as a source of food colours is Safflower (*Carthamus tinctorius* L.) [2]. Safflower seeds are an important sourse for extracting oil in Asia, North and Central America [3]. Safflower florets are widely used in cosmetics, modern and popular medicine [4]. By Safflower petals extraction it can be obtained dyes of two colors: yellow and red [5]. According to the chimical structure, the dyes represent different chalcones [6].

There are many reasons, which causes confusions in the taxonomy of the sources of raw materials and/or of the compounds, obtained from these sources. Safflower (*Carthamus tinctorius L., Asteraceae*) is often confused in Internet, also in traditional printed scientific sources, with consonant Saffron (*Crocus sativus L., Iridaceae*) [7]. Due to this confusion, Carthamin is considered a dye, extracted from Saffron. But Saffron does not include red dimeric chalcone Carthamin in composition: red compounds of Saffron are anthocyanins [8]. Instead of correct "Safflower Yellow", a mistakeous name "Carthamin Yellow" is used in some research papers [9], but in commerce and Internet especially. So, "Carthamin Yellow" is not a compound, instead of the correct name, which is not Carthamin (red) but this a yellow dye derived from Safflower. The Yellow Precarthamin is the biochemical precursor of Red Carthamin. Precartamin is enzymatically converted to Red Carthamin both in vivo and in vitro [10]. In the strong acid environment, red Carthamin isomerizes to yellow Izocarthamin [11]. Main goal of this paper is to stable the physico-chemical properties of powered yellow colour from Safflower petals, growned in Republic of Moldova, in order to its utilisation in food industry.

2. Materials and Methods

Safflower petals. Safflower was grown in the experimental fields of the Institute of Genetics and Plant Protection, Chisinau, Moldova. The petals were collected manually. The green sepals and light gray (almost white) seeds were carefully separated from the petals.

Purified petals were dryed in the dark to an absolute humidity of no more than 5% and were stored in an airtight container.

Solvents. Food grade ethanol 96% (v/v) ("Kvint" distillery, Moldova), freshly prepared bidistillate, acetic acid purum ("Severodonetsk Azot Association", Ukraine) and HPLC-grade acetonitrile, n-butanol and methanol ("Merck KGaA", Germany) were used for spectrophotometric and chromatographic analysis.

Separation of the Yellow Food Dye from Safflower (YFDS). Dried safflower petals were treated with a sodium carbonate solution with a hydromodule of 1:10 at a temperature of 18…20°C. The resulting mixture was pressed in four steps to give a yellow extract. This solution was centrifuged for 10 minutes at 6000 rpm. Yellow liquid solution, which remained after the carthamine was removed [12], was purified with activated carbon and cellulose 1 gram per liter for 10 minutes. After filtration, solution was evaporated in a rotary evaporator at 60-75°C, with speed of 150-210 rpm, under pressure 60-100 mbar. In obtained dark-brown viscous solution were added 3 volumes of ethyl alcohol and intensely mixed to obtain very viscous mass, which was dried in vacuum at 65-80 °C and 80-100 mbar. The dry mass of YFDS constituting 40 % of dry petal mass.

Thin Layer Chromatography (TLC). Chromatograms were obtained in vertical camera on 24×3cm sheets of Whatman Chromatographic Paper, by ascension technique. Three chromatographic systems with different polarity were used as liquid mobile phases: System I – acidic medium (HCl 0.10 mol/L); System II – (50% distilled water, 45% ethanol, 5% citric acid); System III – (4 parts distilled water, 5 parts butan-1-ol, 1 part acetic acid).

UV-Vis spectra. Standard solution of YFDS was prepared by dissolving of 0.2 g of powder in 200mL distilled water (Solution P1). For farther directly spectroscopic measurements, Solution P1 was diluted 5.0 times and adjusted to different pH value by adding crystals of sodium carbonate and citric acid. Distilled water was used as a reference sample. Spectra of Safflower extracts were recorded at Hach-Lange "DR 5000" spectrophotometer in the range of 200...600 nm, step of 1 nm, using quartz cell with l = 10mm.

Photodiode Array (PDA) coupled HPLC. Shimadzu "Provinience-i LC-2030C 3D-Plus", with integrated Photodiode Array Detector (PDA), on reversed-phase C_{18} column "Phenomenex" (4.6x150mm, particle size 4µm, pores 80nm), gradient elution technique by two mobile phases: Water, containing 0.1% (v) Acetic Acid (Phase A) and Acetonitrile containing 0.1% (v) Acetic Acid (Phase B) were used. Default flow: Phase B 5% at the constant rate of 0.8 mL/min. Constant oven and detection cell temperatures of 30 °C. Elution gradient program: 0...2 min – Phase B 5% (default flow); 2...18 min – Phase B from 5% to 40%; 18...20 min – Phase B from 40% to 90%; 20...24 min – Phase B 90%; 24...25 min - Phase B from 90% to 5%; 25-40 min – Phase B 5% (default flow). Data acquisitions and interpretations were performed using Shimadzu LabSolutions software.

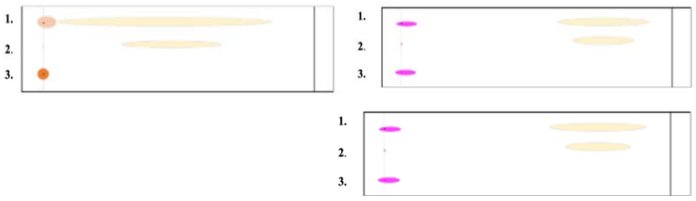
3. Results and Discussion

3.1. TLC of red and yellow Safflower dyes

Investigations of the chromatography conditions of the Yellow Food Dye from Safflower (YFDS) and Cartamine dyes were performed using three chromatography systems, Table 1. Most acid System I (HCl 0.1 mol/L) confirms the instability of the Carthamin in the environment with pH = 1.00 [11]. Chromatographic systems II and III demonstrated the effective separation of Carthamine from yellow dyes. At the same time, we failed to separate the components of yellow dyes by paper chromatography.

Table 1

Thin Layer Chromatography of the Safflower Pigments

System	I	II	III, superior layer
Composition	HCl 0.1 mol·L^{-1}	Aqua, 50% (v) Ethanol, 45% (v) Citric Acid, 5% (m)	Water, 4 parts (v) Butan-1-ol, 5 parts (v) Acetic Acid, 1 part (v)
View			
Rf (Yellow)	0.51 ± 0.05	0.71 ± 0.05	0.35 ± 0.05
Rf (Crt)	0.00	0.03 ± 0.02	0.03± 0.02

*Spotted consecutively: 1 - Safflower extract; 2 - YFDS; 3 - Carthamin

Thus, to obtain a bright yellow (and not orange) YFDS, it is necessary to treat the extract with a suspension of microcrystalline cellulose.

3.2. UV-Vis Spectroscopy and pH-sensitivity of YFDS

Prepared samples of solutions with different pH values were spectrophotometrically, and two diagrams were built from the obtained spectra. The spectra were processed using the Excel program.

The UV-Vis spectra of the yellow dye in Safflower were analysed as a function of pH (Figure 1). Almost all curves have the same shape with maximum wavelengths between 392 nm and 412 nm and the presence of the left shoulder. The spectra, obtained at acidic (5.10) and basic (10.95) pH values show an obvious deviation. The maximum absorption of the yellow pigment solutions takes place in an acid medium (2.12) with a peak wavelength of 405 nm. From the analysis of the spectra of the liquid yellow dye at different pH, it follows that a change in pH causes a shift in the absorption maxima of the dyes. This is clearly seen in the graphs λmax = f (pH). The most successful interval for the practical use of dyes is the pH range = 4...5, since in this range the absorption of dyes is maximum and color of the solutions is bright yellow.

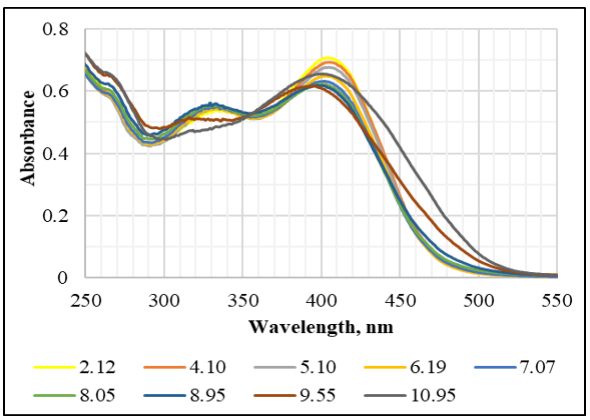


Figure 1. Spectra of YFDS, pH function.

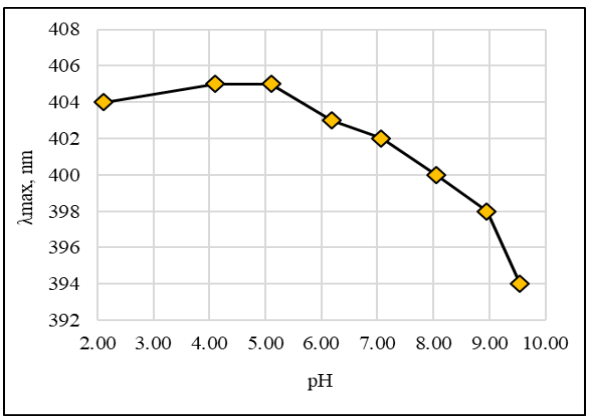


Figure 2. YFDS absorbtion maximum, pH function.

Thus, despite the removal of the Cartamine, highly sensitive to pH, YFDS does not completely lose sensitivity to the pH value. At the same time, minor changes in the position of the absorption maximum, 394-405 nm (Figure 2), cannot significantly affect color perception, which means that YFDS can be successfully used over a wide pH range.

3.3. HPLC profile of Safflower petals extract and YFDS

HPLC profile of Safflower petals and YFDS were analysed using the same method. The HPLC results (Figure 3) show the five separate peaks were at the retention times of 18.861, 19.589, 20.844, 22.273, 24.398 in YFDS extract, what corresponded to the peaks and retention time in petals extract. The peaks show the clear separation of yellow compounds and identification of Safflomin C, Izosafflomin C, HSYA, AHSYB and Precarthamin. This fact that the composition of the YFDS, obtained from Safflower petals correspond the composition of the petals, known for its biological activity [13], suggests that the YFDS can be used as a natural food yellow colorant, which can be successfully in the production of dairy products [14-16].

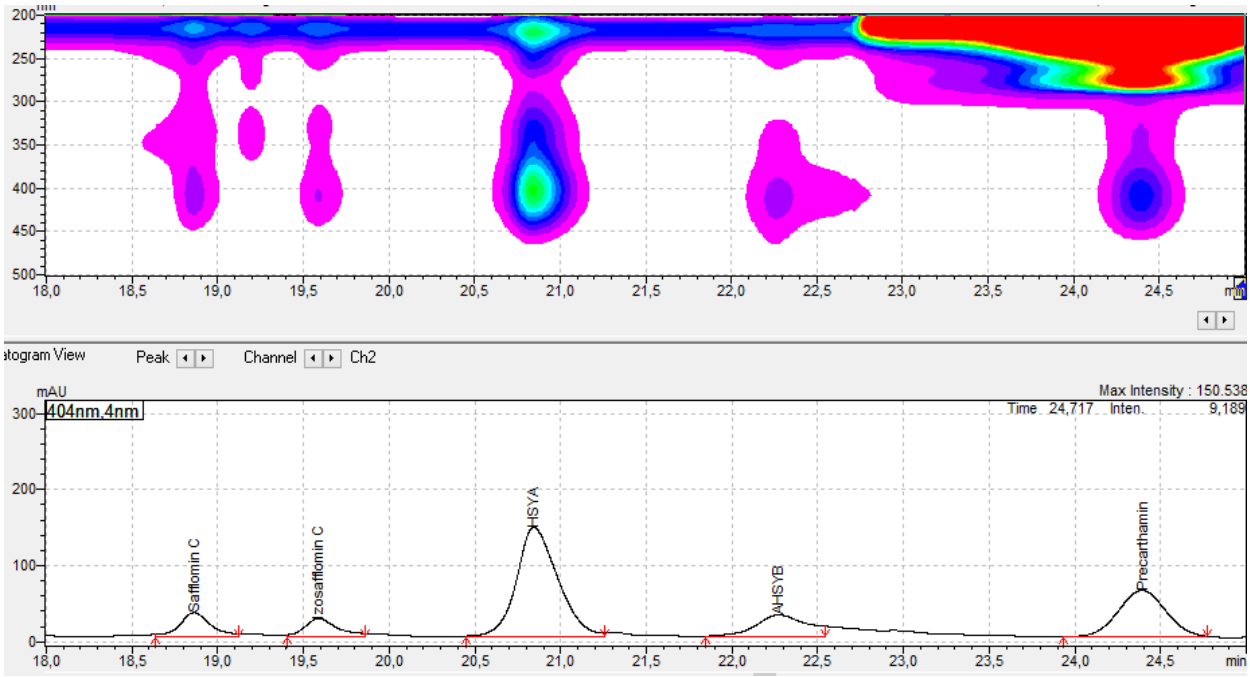


Figure 3. Multichromatogram UV-Vis = f (Time), and ordinary chromatogram at 404nm.

Table 2

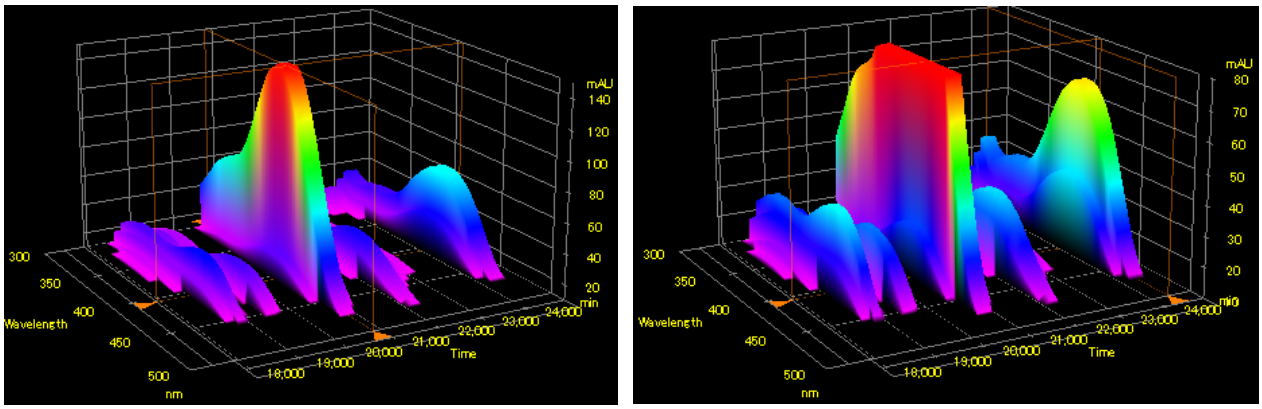
Chromatographic data for yellow compounds from Safflower petals and YFDS

Peak No.	R_T (min)	Area	Area (%)	λ_{max} (nm)	Identification
		Safflower Petals Extract			
1	18.62	263361	2.3	218, 332, 406	Safflomin C
2	19.40	241525	2.2	216, 315, 404	Izosafflomin C
3	20.63	8997460	80.1	223, 335sh, 402	HSYA
4	22.32	628858	5.6	219, 335sh, 410	AHSYB
5	24.67	1098554	9.8	335sh, 407	Precarthamin

Continuation Table 2

Yellow Food Dye from Safflower					
1	18.86	394512	8.1	215, 332, 408	Safflomin C
2	19.59	313120	6.4	216, 327, 408	Izosafflomin C
3	20.84	2410258	49.5	220, 335sh, 402	HSYA
4	22.27	594323	12.2	218, 335sh, 412	AHSYB
5	24.39	1159907	23.8	335sh, 408	Precarthamin

The UV-Vis spectra clearly seen that the mixture of dyes is yellow in colour (Figure 1), however, the presence of which yellow components in the mixture are most present, is impossible to identify using spectroscopy method. Thanks to 3D chromatogram, it was possible to establish that the largest amount of yellow colour in YFDS is accounted for by HSYA (R_T = 20.84, Figure 4a). Precarthamin (R_T = 24.39), AHSYB, Safflomin C and Isosafflomin C also give yellow colour, in correspondingly decreasing order (Figure 4b).



a) b)

Figure 4. YFDS 3D-chromatogram: a) at 140 mAU resolution; b) at 80 mAU resolution.

4. Conclusions

Five yellow dyes of the chalcone class with a similar chromophore structure were confirmed in the Safflower petals extract and in the powdered pigment which was obtained at the concentration of this extract.

Essential condition to obtain bright yelloe colour, is the absence of traces of red carthamine, which is will achive by treatment of Safflower extract with cellulose.

The separation of yellow substances into individual components is not advisable, since they have similar UV-Vis absorption spectra, and hence the colour. Therefore, there is no need to separate the yellow powder into individual components for its further use in the food industry**.**

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Conflicts of Interest. The authors declare no conflict of interest.

References

1. Global Food Coloring Market: Intensive Growth in the Natural Segment. [online]. [accesat 10.05.2022]. Available:

https://www.giord.ru/news/novosti_otrasli/mirovoy_rynok_pishchevykh_krasiteley_intensivnyy_rost_naturalnogo_segmenta/ - [in Russian].
2. Jadhav, B.; Joshi, A. Extraction and quantitative estimation of bio active component (yellow and red carthamin) from dried safflower petals. *Indian Journal of Science and Technology*, 2015, 8, pp. 1-5. http://dx.doi.org/10.17485/ijst/2015/v8i16/42380
3. Mateaș, I. M.; Tabără, A.; Albai, A.; Niță S. The degree of branching in safflower (Carthamus tinctorius L.) a few lines under the influence of sowing. *Journal of Agricultural Science*, 2014, 46, pp. 26-28.
4. Fatahi, N.; Carapetian, J. Comparing stability of carthamin and safflower yellow pigments at pH, temperature and light, from Safflower (Carthamus tinctorius L.) florets. *Journal of Biological Sciences*, 2009, 4, pp. 250-253.
5. Fatahi, N.; Carapetian J.; Heidari R. Spectrophotometric measurement of valuable pigments from petals of safflower (Carthamus tinctorius L.) and their identification by TLC method. *Journal of Biological Scinces*, 2008, 3, pp. 761-763.
6. Hye – Ryeon, Y.; Young – Sook, P. Isolation of two quinochalcones from carthamus tictorius. *Applied Biological Chemistry*, 2008, 51, pp. 169 – 171.
7. Koshi, Saito; Masatoshi, Katsukura. On manganese-induced reddening of florets from dyer's saffron capitula. *Food Chemistry*, 1992, 44, pp. 349-355. https://doi.org/10.1016/0308-8146(92)90267-6
8. Khazaei, K.M.; Jafari, S.M.; Ghorbani, M.; A. Hemmati Kakhki, A.H.; Sarfarazi, M. Optimization of Anthocyanin Extraction from Saffron Petals with Response Surface Methodology. *Food Analytical Methods*, 2016, 9, pp. DOI: 10.1007/s12161-015-0375-4
9. Wan, L.; Chen, J.; Li, L.; Xiong, W.; Zhou, L. Protective effects of Carthamus tinctorius injection on isoprenaline-induced myocardial injury in rats. *Pharmaceutical Biology*, 2011, 49, pp. 1205. https://doi.org/10.3109/13880209.2011.576348
10. Cho, M.H.; Paik, Y.S.; Hahn, T.R. Enzymatic Conversion of Precarthamin to Carthamin by a Purified Enzyme from the Yellow Petals of Safflower. *Journal Of Agriculture And Food Chemistry*, 2000, 48, pp. 3917. https://doi.org/10.1021/jf9911038
11. Baerle, A.; Savcenco, A.; Tatarov, P.; Fetea, F.; Ivanova, R.; Radu, O. Stability limits of a red carthamin – cellulose complex as a potential food colourant. *Food & Function*, 2021, 12, pp. 8037 – 8043. DOI: 10.1039/d1fo01376a.
12. Savcenco, A.; Baerle, A.; Tatarov, P.; Ivanova, R. Process for producing dyes from Safflower petals. *Patent of Moldova*, MD-1453, issued 31.03.2021.
13. Xinbing, W.; Huiqing, L.; Xia, S.; Fengua, F.; Xiumei, Z.; Jin, W.; Jie, A.; Hua, D. Hydroxysafflor yellow A protects rat brains against ischemia-reperfusion injury by antioxidant action. *Neuroscience Letters*, 2005, 386, pp. 58-62. https://doi.org/10.1016/j.neulet.2005.05.069
14. Machewad, G.; Ghatge, P.; Chappalwar, V.; Jadhav, B.; Chappalwar, A. Studies on extraction of safflower pigments and utilization in ice cream. *Journal Of Food Proccesing & Technology*, 2012, 3, 3p. DOI: 10.4172/2157-7110.1000172
15. Popescu, L.; Ghendov-Moșanu, A.; Baerle, A.; Savcenco, A.; Tatarov, P. Color stability of yogurt with natural yellow food dye from safflower (Carthamus tinctorius L.). *Journal Of Engineering Science*, 2022, 29, pp. 142 - 150. https://doi.org/10.52326/jes.utm.2022.29(1).13
16. Popescu, L.; Savcenco, A.; Baerle, A.; Tatarov, P.; Ghendov-Moșanu, A.; Sturza, R.; Patraș, A. Process for producing yogurt. *Patent of Moldova*, MD-1625, issued 30.06.2022

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