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INNOVATIONS – SUSTAINABILITY – MODERNITY – OPENNESS

WATER

edited by
Iwona Skoczko
Dorota Anna Krawczyk
Ewa Szatyłowicz

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Iwona Skoczko
Dorota Anna Krawczyk
Ewa Szatyłowicz

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Faculty of Civil and Environmental Engineering
Bialystok University of Technology
45E, Wiejska Street
15-351 Bialystok
www.wb.pb.edu.pl

Association of Sanitary Engineers
and Technicians in Bialystok
2, M. C. Skłodowskiej Street
15-950 Bialystok
www.pzits.bialystok.pl

Contents

Eliza Hawrylik

Bialystok University of Technology
Faculty of Civil and Environmental Engineering
Department of Chemistry, Biology and Biotechnology
e-mail: e.hawrylik@doktoranci.pb.edu.pl

THE USE OF ULTRASOUNDS IN IMPROVING THE SANITARY QUALITY OF SEWAGE SLUDGE

keywords: ultrasounds, sanitary quality, sewage sludge, sonification

Abstract:

The aim of this article is to study the effect of low frequency ultrasound on the disintegration of microorganisms present in mixed sewage sludge. Initial and excessive sewage sludge are used for examinations coming from the Bialystok Sewage Treatment Plant. They are exposed to ultrasound at 20 and 40 kHz, in varying sonfication times and in the case of variable operation of the ultrasonic cleaner (continuous and pulsating work). Research shows that ultrasound is demonstrating the effective action with the tested microorganisms. The 30-minute interaction of ultrasounds at 20 kHz on the bacteria present in sewage sludge results in a significant decrease in the number of these microorganisms. The obtained results, therefore, indicate the possibility of using this method to disintegrate microorganisms in municipal wastewater treatment plants.

Introduction

The problem of rendering microorganisms harmless is a very important aspect from a microbiological point of view. The inactivation of microorganisms is based on two main methods: disinfection and sterilization. The difference between these methods consists on total destroying microorganisms in case of the sterilization, however disinfection only is reducing their number.

The pioneer of introducing and developing the first methods of destroying microorganisms is Ludwik Pasteur, considered to be one of the fathers of microbiology. His research has contributed to the further development and introduction of new methods. Removal of microorganisms found in water, sewage and sewage sludge is a significant problem of the 21st century.

Sewage sludge is an inherent product resulting from the wastewater treatment process. Until now, no effortless wastewater treatment processes have been developed, or solutions allowing for the elimination of sewage sludge from the environment. Paradoxically, the amount of sediments increases with the development of more and more effective methods of chemical and biological wastewater treatment. Sewage sludge do not exceed the 3% of the volume of sewers, however, it contains more than 50% of raw sewage pollutants [6].

Figure 1. presents changes in the amount of the sewage sludge arising in Poland over the last decade (2008-2017).

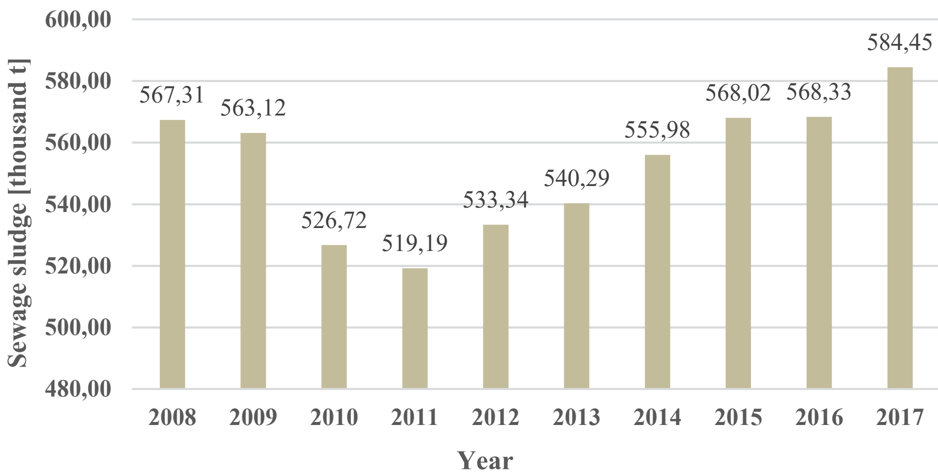

Fig. 1. Changes in the volume of generated sewage sludge (in thousands of tonnes) in Poland over the last decade (2008-2017)

Source: [16].

According to the data included in the chart, it can be noted that the amount of sewage sludge arising throughout the country is constantly increasing. This is caused by the intensification of the wastewater treatment process, and hence by the increase in the number of newly constructed wastewater treatment plants and translates directly into the problem of managing sewage sludge characterized by different chemical and sanitary properties.

Sanitary properties of sewage sludge are recognized to a lesser degree than their chemical properties. The research on sewage sludge in terms of sanitary properties was initiated by the National Institute of Hygiene and was based mainly on parasitological infections.

Sewage sludge is undoubtedly an environment conducive to the development of microorganisms. They are the place of existence of microflora and microfauna, which includes: bacteria, fungi, viruses, protozoa and parasitic worms.

The most frequent group of microbiological sewage sludge pollutants are bacteria, and the most frequently marked are: *Escherichia coli, Salmonella sp., Shigiella sp., Pseudomonas aeruginosa, Bacillus anthriacis, Clostridium perfingens, Vibro cholerae* (in tropical countries), *Listeria monocytogenes, Proteus vulgaris, Streptococcus faecialis* [2, 10].The highest importance is attached to the occurrence of *Salmonella*, which is the basic indicator of the quality of sewage sludge. The lack of these tips in the sediments makes it possible to use them for fertilizing or recultivating farmland. According to Nowak [10]these bacteria are responsible for 87% of cases of bacterial etiology [10].

Sanitary properties of sewage sludge are variable and depend on many external factors, i.e. sanitary conditions, health of people, amount and type of sewage and technologies used for their treatment. The degree of danger caused by sediments formed at various stages of wastewater treatment is diversified. The most dangerous from a sanitary point of view are screenings, which are subjected to the process of hygienization. Although sewage sludge treatment methods are commonly used, they do not guarantee a product that is safe in terms of sanitation[2].

In the field of legal regulations concerning the quality of sewage sludge, the only document in force in Poland is the Regulation of the Minister of the Environment of 6 February 2015 on municipal sewage sludge (Journal of Laws of 2015, item 257).Criteria put by the regulation are focusing mainly on chemical properties and only take a small amount of sanitary properties into account. From the sanitary point of view, the regulation only requires determining whether sewage sludge is present in pathogenic bacteria of the genus *Salmonella* and eggs of intestinal parasites belonging to *Ascaris sp., Trichuris sp., Toxocara sp.*

Hygiene of sewage sludge is the process of reducing or completely eliminating pathogenic organisms. Sludge sanitizing can occur in the different degree, in various processes of the processing of deposits or in the allocated process. Every process of the alteration of sewage sludge influences the reduction in the number of microorganisms [11].

Table 1. shows the influence of selected processes of sewage sludge treatment on reducing the number of pathogenic organisms.

Tab. 1. Influence of selected sewage sludge treatment processes on reducing the number of pathogenic organisms (log reduction*)

Process	Bacteria	Viruses	Protozoans and nematodes
Anaerobicstabilization	0,5 - 4,0	0,5 - 2,0	0,5
Oxygenstabilization	0,5 - 4,0	0,5 - 2,0	0,5
Composting	2,0 - 4,0	0,5 - 4,0	2,0 - 4,0
Drying	0,5 - 4,0	0,5 - 4,0	0,5 - 4,0
Stabilization with lime	0,5 - 4,0	4,0	0,5

*Reducing the size of pathogenic organisms by the 1-log individual is equivalent to reducing them numerous by the 90%

Source: [1, 8].

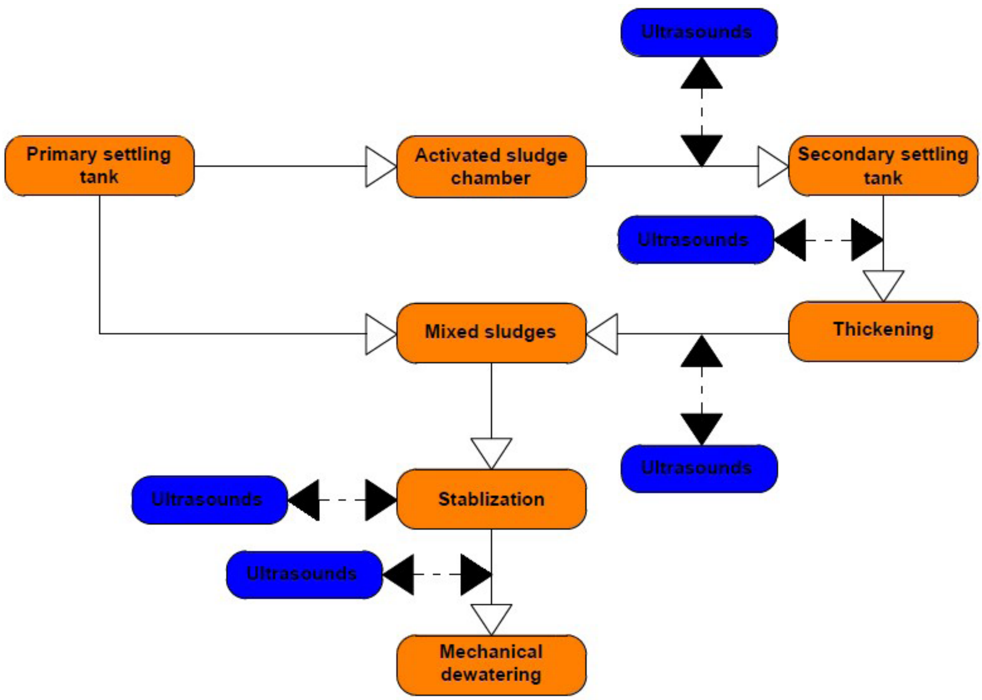

Fig. 2. Variants of the application of the ultrasonic disintegration process of wastewater and sludge

Source: [18].

Ultrasounds used for many years in medical diagnostics, air purification and defectoscopy have also begun to be used in environmental engineering. The main groups of application of ultrasound in environmental engineering are: water treatment (to improve the process of particle separation and bacterial inactivation), wastewater treatment processes (for the degradation of pollutants and improvement of biodegradation) and sludge processing (improvement of sedimentation, stabilization and sediment conditioning) [13, 14, 15]. Fig. 2. presents variants of the application of the ultrasonic disintegration process of sewage and sediments.

In recent years, interest in low frequency ultrasound has been growing. Research works conducted in many international research centers focus primarily on: conditioning of sediments with ultrasounds, increasing the availability of the ChZT soluble fraction, or the impact of the sludge disintegration process on increasing biogas production during fermentation. There are few publications on biological issues, although ultrasounds successfully destroy microorganisms (especially filamentous bacteria) [3].

In connection with the above, studies on the influence of low frequency ultrasound transitions (20 and 40 kHz) on the disintegration of microorganisms present in mixed sludge have been carried out.

Methodology of laboratory tests

The study of the influence of low frequency ultrasounds on the survival of microorganisms present in sewage sludge was carried out at the turn of January and February 2019 in the laboratory of the Department of Chemistry, Biology and Biotechnology of the Faculty of Civil and Environmental Engineering at Białystok University of Technology. The subject of the analysis was a mixed sewage sludge, which is a mixture of excess sludge and sludge from the primary settling tank in the ratio 40:60, which came from Białystok Sewage Treatment Plant, which is the largest facility of this type in north-eastern Poland. Białystok Treatment Plant treats municipal and industrial sewage. During the year, the treatment plant receives about 15 500 000 m^3 of municipal sewage and 204 000 m^3 of industrial sewage. Wastewater treatment processes are based on the conventional method of activated sludge and are divided into technological nodes: mechanical and biological [17].

Ultrasonic washers from Polsonic company with frequency of ultrasounds 20 and 40 kHz were used for ultrasonic disintegration.

The aim of the experiments was to determine the effect of low-frequency ultrasounds (20 and 40 kHz) on the survival of microorganisms present in mixed sludge.

The sewage sludge, after transporting from the place of collection to the microbiological laboratory, was immediately analyzed. Eachtime, 2 dm^3 of mixed sewage sludge was placed in the Polsonic ultrasonic washer with a frequency of 20 kHz ultrasound generation (attempts were performer at the constant and pulsating mode) and 40 kHz and they surrendered sonification for 30 minutes.

The volume of the sample resulted from the device that produced the ultrasound used in the study. Prior to the sonication, the number of bacteria in the reference sample (not subjected to ultrasounds) was determined.

For this purpose, 1 cm^3 of sediment was collected along with the bacteria and were prepared serial dilutions in the range from 10^{-1} to 10^{-6}, moving the charged volume to the tubes containing 9 cm^3 of physiological saline. Subsequently, the tested sediment sample was sonicated. After 5, 10, 15, 20, 25, 30 minutes, 1 cm^3 of the mixture was removed and then were performer dilutions identical to those used for the reference test. In the further stage of the research was performed the culture of the collected samples on enriched agar.

To determine the number of bacteria, the plates were placed in an incubator at 37°C and incubated for 24 hours. After incubation was counted the number of colony forming units (cfu) grown on the plates. Only these tiles, on which it grew were being taken into consideration from 10 to 150 colonies were considered. On the basis of the obtained results, average values of cfu/cm^3 were calculated.

In the experiments conducted, the number of bacteria in the reference sample as well as in the samples subjected to sonication was calculated based on the formula:

$$N = \frac{A}{R} \tag{1}$$

where:
N – number of bacteria in 1 cm^3,
A – numer of cfu grown on the plate,
R – dilution of the sample used for in oculation on a given plate.

Research results and discussion

Table 2. shows changes in the number of microorganisms present in mixed sewage sludge treated with ultrasounds at 20 and 40 kHz, while in Figure 3. Presented the percent changes in the number of bacteria depend on the time of sonication.

Tab. 2. Number of microorganisms in mixed sewage sludge treated with ultrasound

Time of sonication [min]	20 kHz – continuous operation	20 kHz – pulsating work	40 kHz
0	$2{,}8*10^6$	$5{,}5*10^5$	$4{,}2*10^5$
5	$2{,}7*10^6$	$3{,}9*10^5$	$3{,}9*10^5$
10	$1{,}5*10^6$	$3{,}8*10^5$	$3{,}8*10^5$
15	$1{,}2*10^6$	$2{,}8*10^5$	$2{,}9*10^5$

Time of sonication [min]	20 kHz – continuous operation	20 kHz – pulsating work	40 kHz
20	$6{,}7*10^5$	$2{,}5*10^5$	$2{,}7*10^5$
25	$3{,}8*10^5$	$2{,}0*10^5$	$1{,}9*10^5$
30	$2{,}1*10^5$	$0{,}1*10^5$	$1{,}8*10^5$

Source: Ownstudy.

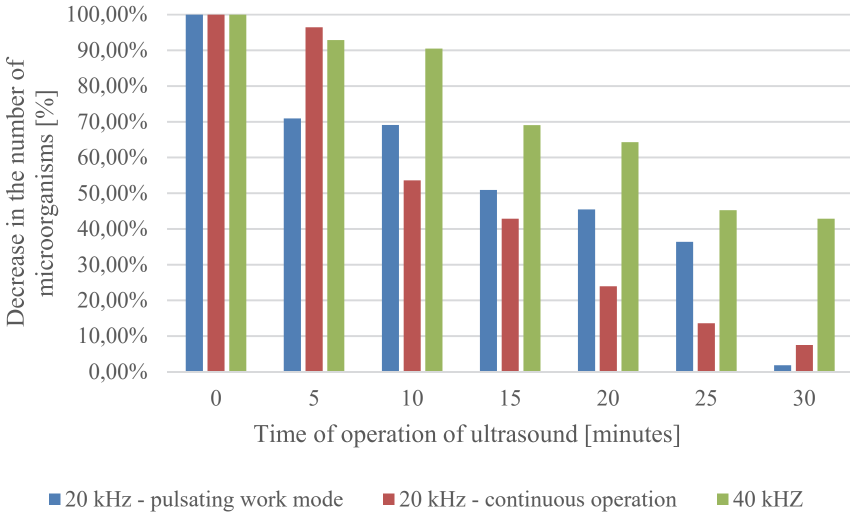

Fig 3. Percentage changes in the number of microorganisms present in mixed sludge subjected to ultrasound

Source: Ownstudy.

On the basis of the obtained test results, a clear reduction in the total number of microorganisms present in the mixed sewage sludge was found.

Already after 5 minutes of ultrasound sonication at the frequency of 20 kHz in the pulsatory mode of operation, a decrease in the number of bacteria was recorded by 29.09%, with a slight increase in temperature - about 1ºC. With time, the number of bacteria gradually decreased. At the 15th minute of sonication, the number of investigated microorganisms decreased by half (49.09%), and as a result of 30-minute operation of ultrasound was only 1.82% compared to the reference sample, which indicates about 100 % percentage of ultrasound effectiveness at 20 kHz frequency with pulsating mode of operation. The biggest decrease (by 34.55%) was recorded between 25 and 30 minutes of ultrasound. The temperature range during the measurements was lowreaching 25ºC, with the initial value of 21ºC.

Operation of ultrasounds with a frequency of 20 kHz, however, with a continuous mode of operation of the device, caused similar effects as in the pulsed operation of the ultrasonic cleaner. After 15 minutes of the process, there was a decrease in the number of microorganisms by 57.14%, and after 30 minutes it was 92.50%. During the whole process, the temperature increased by 11ºC (17-28ºC).

The work of the ultrasonic cleaner on the frequency of generating waves at the level of 40 kHz did not cause such a clear inhibition of the growth of microorganisms present in the mixed sewage sludge. After 5 minutes of the sonication process, there was a decrease of 7.14%, after 15 minutes - 30.95%, and after 30 minutes the number of bacteria decreased by 57.14% compared to the reference sample. The temperature during the proces increased by 13ºC, to a maximum of 27ºC.

General rise in temperature increase during all tested variants of the sonication process was small, therefore it is concluded that the temperature achieved in the experiment performed did not have a major impact on the microbial destruction process.

The research on the ultrasonic disintegration of microorganisms of those present in sewage sludge was also performed by other authors.

Butarewicz [3] examined the effect of ultrasounds at 40 kHz on the number of mesophilic microorganisms present in mixed sludge. The results obtained by him indicate a significant reduction in the total number of bacteria during the first 10 minutes of the disintegration process (decrease by 93.73%). In the long term, the decrease in the number of microorganisms was small, despite the additional processs upport increasing temperature of the mixed sludge (from 21 to 47 ºC) [3].

Nowak [9] analyzed changes in the number of mesophilic bacteria in the fermented sewage sludge indicating a reduction in the number of microorganisms by over 98% in comparison to the control sample with the participation of ultrasounds at 22 kHz for 30 minutes.

Comparable to the above mentioned references, the level of reduction was achieved in the conducted experiment, however, by the action of ultrasounds at 20 kHz, in the absence of a temperature factor.

Butarewicz [3] also checked the effect of low frequency ultrasounds on selected species of indicator bacteria present in sewage sludge. It achieved a nearly 100% decrease in the number of *E. coli, Enterococcus faecalis, Salmonella enteritidis* and *Bacillus subtilis* during 10 minutes of ultrasoundat 20 kHz, however, in eachcase a significant increase in temperature during the proces played a big role [3].

Hawrylik et al. [8] indicated a reduction in the number of *Enterococcus faecalis* bacteria at the level close to 100% as a result of a 10-minute interaction of ultrasounds at 40 kHz and proved a decrease in the number of *Escherichia coli* bacteria at 99.99% in mixed sediment under ultrasound treatmentat 20 kHz for a period of 10 minutes.

The literaturę also indicates that ultrasonic disintegration affects changes in the number of filamentous bacteria found in active sewage sludge, what proved by Butarewicz et al. [5]. These reports were confirmed by Hawrylik [7], which additionally pointed to the operation of low frequency ultrasound in relation to changes in foam structure coming from the aeration chamber of the municipal sewage treatment plant.

Issues of the disintegration of microorganisms present in sewage sludge is becoming more and more widely recognized by literature, and the presented results show the effectiveness of low frequency ultrasounds for the destruction of microorganisms present in hydrated sewage sludge.

Conclusions

1. Based on conducted research an effective action of low frequency ultrasound has been demonstrated in relation to the disintegration of microorganisms present in mixed sewage sludge.
2. The influence of ultrasounds at the frequency of 20 kHz caused almost 100% drop in the number of bacteria in the mixed sludge after 30 minutes of the sonication process, both in the pulsating and permanent mode of operation of the device.
3. Ultrasound at a frequency of 40 kHz resulted in a reduction in the number of microorganisms at a level close to 60%, after a 30-minute exposure time.
4. Better results, in terms of reducing the number of microorganisms contained in sewage sludge, give ultrasounds of frequency of 20 kHz.
5. Low-frequency ultrasound should find wider application in municipal wastewater treatment plants.

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Weronika Skoczko[1)] Klaudia Jarocka[2)], Piotr Kraśnicki[2)], Angelika Kisiel[2)], Karolina Baczewska[2)], Anna Zambrzycka[2)], Izabela Skowrońska[2)], Marta Zagórska[2)], Ewa Szatyłowicz[2)], Iwona Skoczko[2)]

[1)] University of Gdansk
Faculty of Faculty of Law and Administration

[2)] Bialystok University of Technology
Faculty of Civil and Environmental Engineering
Department of Chemistry, Biology and Biotechnology

Corresponding author: i.skoczko@pb.edu.pl

CARBON DIOXIDE EMISSIONS IN POLAND AND EUROPE

keywords: CO_2 emission, global warming, climate change

Abstract:

More and more people are hearing about the fight against droughts that cause infertility and lead to forest and field fires. The talk of global warming is getting louder and louder. The climate is warming at an alarming rate, and rising temperatures are not good for people, animals or plants. There are many more effects of global warming, and the the root cause may be identified without any problem.

The inconspicuous gas that accompanies us in many everyday activities, such as breathing, has been a threat and annihilation for many years. This problem, although it has not existed for today, is ever more acute and alarming than it was years ago. Carbon dioxide – for that is what we are talking about – is responsible for climate change and the greenhouse effect.

Global warming is a problem for the whole world, and therefore also for Europe, where Poland occupies a significant and disgraceful place in terms of CO_2 emissions into the atmosphere. We are still far from being among the leaders of global growth – China and India, or the leaders of Europe such as Russia and Germany, but this does not change the fact that the steps taken to reduce CO_2 are insufficient and further changes are very much needed [2].

Emissions per capita in the European Union are on average 7 tonnes per year. In Poland, this average is significantly exceeded, as it amounts to as much as 8.6 tons per person [1]. Moreover, last year's CO_2 emissions of our country were by 7.1 million tons higher than in 2017 [2]. So why, despite all efforts, is the problem still growing?

Unfortunately, the largest producer of carbon dioxide is the human being. And it is not about the mentioned earlier breathing - human activity plays a significant role here. The biggest CO_2 emission is, of course, the energy sector, which has been feeding the atmosphere with unfavourable greenhouse gases (GHG), mainly CO_2, practically since the beginning of power plants construction. The extraction of oil, gas or coal also has an impact on the spreading of CO_2. Replacing hard coal or lignite with renewable sources or nuclear energy could partially solve the global problem. Partly, because energy is not everything - economic sectors such as transport and industry remain. Moreover, it is only a drop in the ocean, because there are more causes and their number is constantly growing year by year.

CO_2 emissions in the world increased by 2% in 2018. For comparison, this is the same as the annual average over the last 50 years [2]. Although it would seem that, knowing the causes and effects of this battle, we can quickly prevent its further spread, the problem is much more widespread and its publicity is necessary.

Carbon dioxide emission

The emission of carbon dioxide to the atmosphere is caused by human activity and contributes to increasing the intensity of the greenhouse effect. The reason for this is the fact that this gas remains in the atmosphere until it is absorbed by e.g. plants [6]. The national inventory covers the following gases and greenhouse gas groups: carbon dioxide (CO_2), methane (CH4), nitrous oxide (N2O), HFC (hydrofluorocarbons), PFC (perfluorocarbons), sulphur hexafluoride (SF6), nitrogen trifluoride (NF3), which are reported in five categories (Figure 1):

1. Energy,
2. Industrial processes and product usage
3. Agriculture,
4. Land use, forestry and their changes,
5. Waste.

Coal travels in the so-called "carbon footprint" and moves in the so-called "carbon cycle" between the biosphere, atmosphere, rocks, waters and sediments. Natural emissions are compensated by natural absorptions, therefore the total amount of carbon in the cycle should not change in short time scales [7].

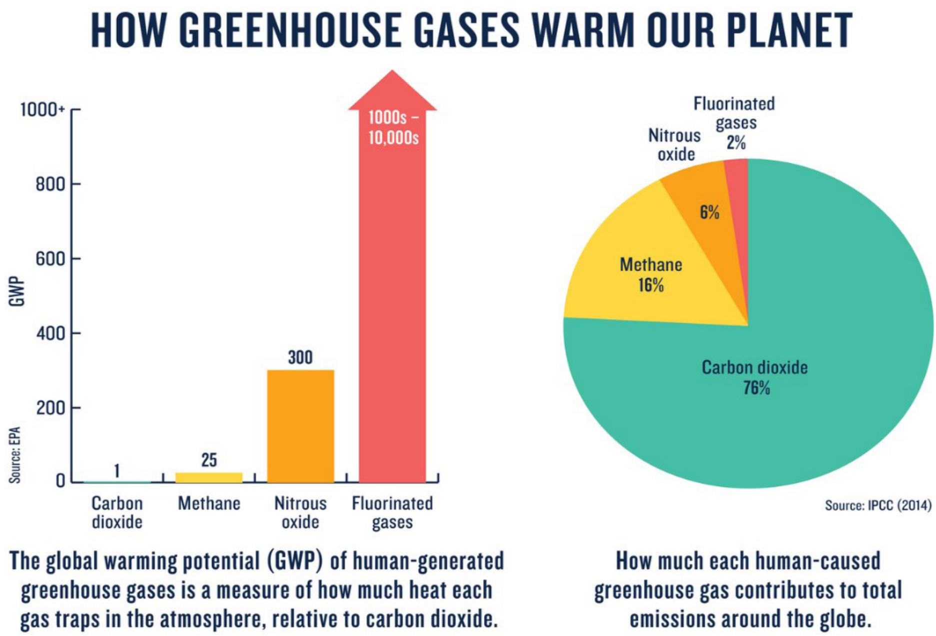

Fig. 1. Greenhouse gasses global view [31]

The Figure 2 shows the total greenhouse gas impact in particular sectors of the economy, such as agriculture, energy, transport, industry, fuel extraction, construction, as well as biomass combustion and waste disposal. It also presents the breakdown of emissions into sectors for the three main greenhouse gases – carbon dioxide, methane and nitric oxide. By far the largest percentage of the greenhouse effect is caused by carbon dioxide in the atmosphere, which is produced by burning coal and hydrocarbons such as natural gas and oil. It is more than 72%. The main source of emissions is mainly energy, which accounts for almost 30% compared to other sectors. Processes from combustion of fuels create so-called point sources of emission. Industry, like transport, accounts for about 20%. On the other hand, construction, deforestation and biomass combustion account for a slightly lower percentage of revenues, although they are equally important [3].

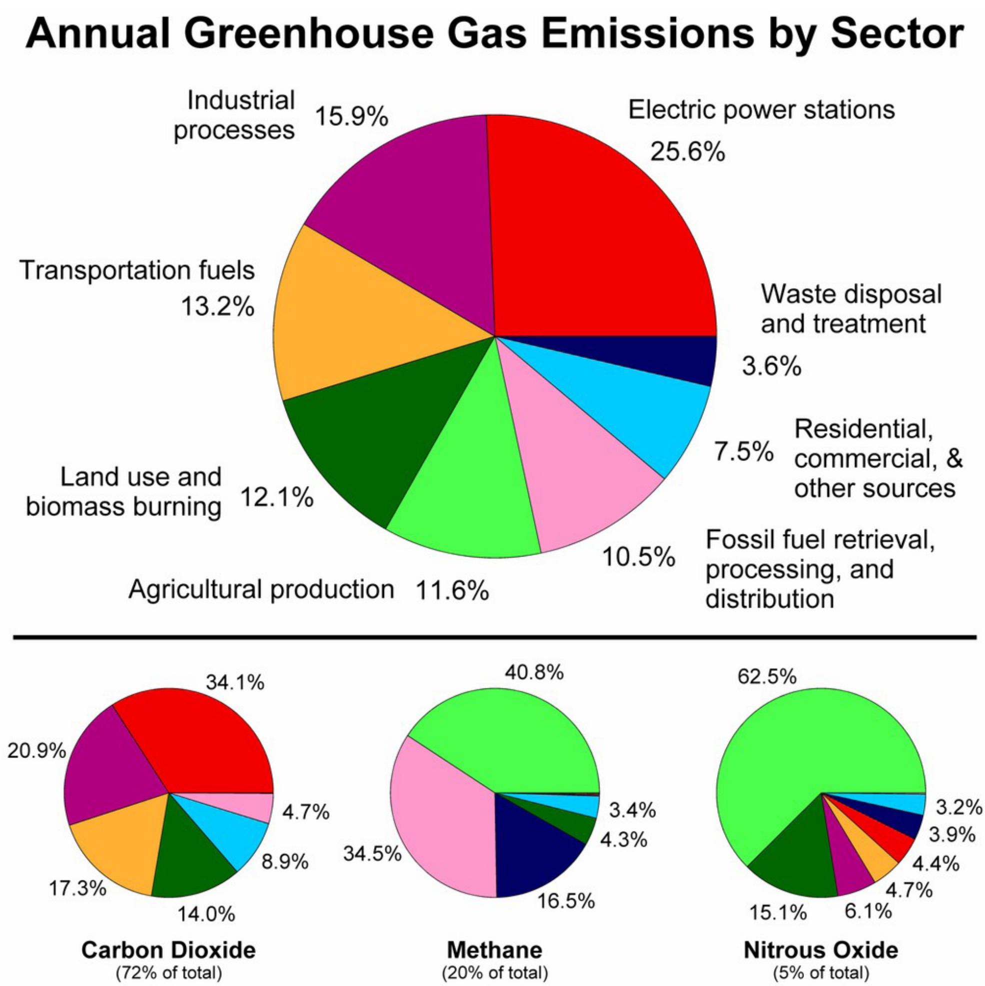

Fig. 2. Annual global GHG human emissions by sectors [9].

By far the most important source of CO2 emissions is the burning of fossil fuels in power plants. Almost all the carbon dioxide emitted by humans comes from this process. Moreover, it contributes to the generation of additional amounts of carbon, which are introduced into its natural cycle, thus causing excess CO_2 [9].

Road transport also has a huge impact on CO2 emissions. The steadily increasing number of cars influences the significant emission of greenhouse gases. The average CO2 emission per 1 km covered by a passenger car is approximately 16 grams, by an off-road vehicle even 0.5 kg. In addition, a further 20% of energy consumption and carbon dioxide emissions should be added to transporting the oil to the refinery and processing it. Road transport is responsible for about 65% of the pollutants emitted into the atmosphere in the European Union. As many as

7 trees are needed to neutralize the emissions generated by one car within a year. In addition, car exhaust fumes are much more harmful to human health than pollution from industry. The reason for this is the fact that they spread in high concentrations at low altitudes and in the immediate vicinity of people [10].

Another important source of carbon dioxide emission to the atmosphere is deforestation. Significant amounts of CO2 are emitted by burning wood or other types of biomass. However, the cycle will remain in balance if new trees grow on the site of the burnt forests. They will absorb as much carbon dioxide as it is released during combustion. However, continuous deforestation leads to a disruption of the carbon cycle, which can significantly increase the greenhouse effect. Deforestation, i.e. the removal of forests in order to obtain a tree for heating or to convert wooded land into agricultural land without planting new trees. Regardless of whether the felled trees will be burned or decayed spontaneously, it will cause the release of carbon dioxide.

If no new trees are planted, it will not be possible to assimilate the released carbon, which will also increase the amount of CO_2 in the atmosphere [7].

CO_2 emissions are a major contributor to global warming and contribute around 80 per cent of all greenhouse gas emissions in the EU. They are influenced by climatic conditions, economic growth, population, transport and industrial activities [3].

CO_2 emission in Poland

In 2005, the value of GDP per capita in Poland amounted to 13894 USD, and this was “bought” by emission of 8.53 t of CO_2 per capita. A statistical inhabitant of Poland emits about 30% more CO_2 than an average inhabitant of another country of similar wealth.

There are two main causes of the high CO_2 emissions in Poland. The first is the high share of coal in the primary fuel balance, particularly in electricity production.

The production of 1 kWh of electricity from different types of primary energy results in the following CO_2 emissions (Figure 3):

– hydropower and other renewable energy sources 0 kg,
– nuclear energy 0-0,03 kg,
– energy from natural gas 0,4-0,45 kg,
– energy from crude oil 0,72-0,76 kg,
– energy from hard coal 0,9-1,02 kg,
– energy from lignite 1,02-1,30 kg.

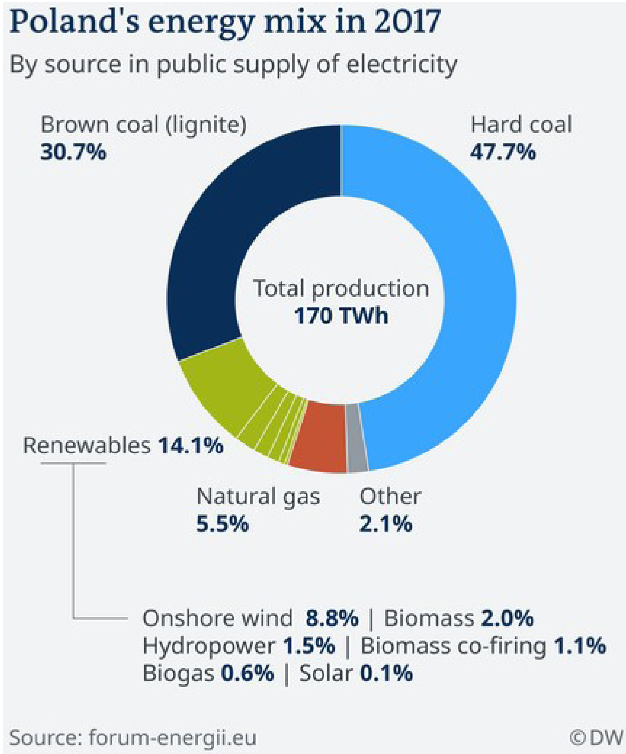

Fig. 3. Power sources in Poland [32]

The second reason is the excessive energy intensity of the economy. Primary energy consumption in Poland in relation to GDP is 50% higher than the average in 25 EU countries [4].

For years, “28” has been pursuing a policy aimed at reducing emissions through, among other things, the introduction of paid permits, thanks to which companies can release CO_2 into the atmosphere. Such an additional cost motivates them to switch to low-emission technologies and even to move away from coal-fired power generation [5].

Over a decade ago, the Polish energy sector relied 90 per cent on coal (the rest was gas and renewable sources), so now the coal is responsible for 78 per cent, while the vast majority of the remaining 22 per cent are Renewable Energy Sources (RES) [3].

Since the beginning of the transformation, the energy sector in Poland has already reduced its CO_2 emissions by 1/3. At present, the industry is on the threshold of radical diversification of energy sources. The recently presented draft of the Polish Energy Policy assumes, among others, full use of the potential of wind energy in the Baltic Sea - said Witold de Chevilly, Director of the Office of the Polish Electricity Committee in Brussels [5].

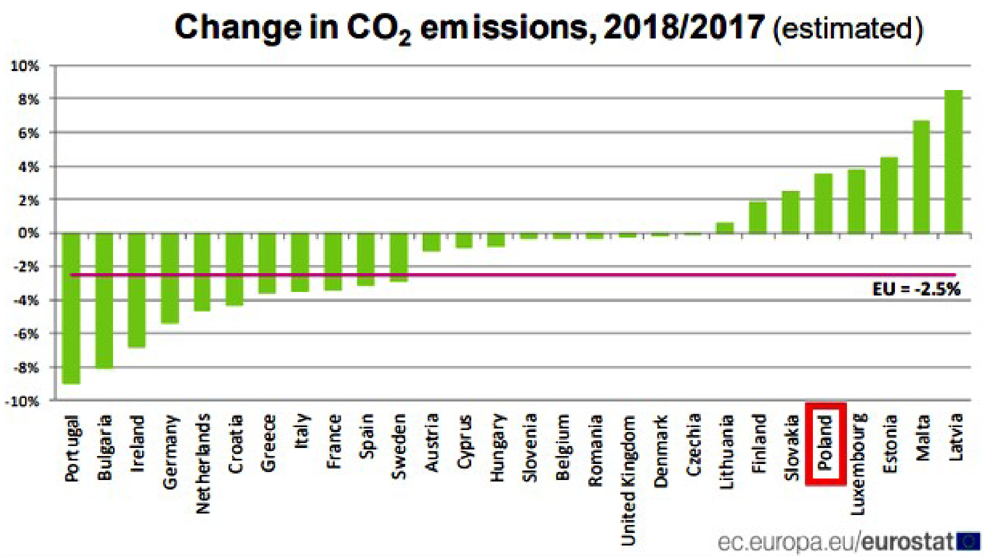

Fig. 4. CO_2 emission change in 2018 [28]

Fig. 5. CO_2 emission change in Poland in 2018 [28]

Germany is responsible for the largest share of CO_2 emissions in the whole EU (22.5%) (Figure 4). The second place was taken by Great Britain with the result of 11.4%, and the third by Poland. Our country releases to the atmosphere 10.3% of total carbon dioxide emissions in the EU. At the same time, our neighbour from across the Oder River reduces the level of CO_2 emissions and Poland increases it (Figure 5).

CO_2 emission in Europe

Nowadays, a negative impact of human activity on the environment is observed. One of the most serious environmental problems is climate change [21]. This is influenced by the production of greenhouse gases, mainly CO_2. Its emissions are supplied to the environment mainly from fossil fuel flue gases, industrial activities and transport [22]. It is important that the concentrations of greenhouse gases in the atmosphere stabilize at a level that would prevent dangerous anthropogenic phenomena of interference with the climate system [21]. One of the ways of limiting the introduction of CO_2 is the use of renewable energy sources or nuclear energy, afforestation and implementation of carbon sequestration in geological structures [22].

The diagram shows the greenhouse gas emissions in the EU-28 from different sectors. Energy is responsible for 78% of greenhouse gas emissions, including 1/3 from transport, agriculture for 10.1%, industry and product use for 8.7% and waste management for 3.7% [23]. Greenhouse gas emissions in the European Union by sector is shown in Figure 6:

According to Eurostat data presented in Figure 4, in 2018 carbon dioxide emissions fell by 2.5%. The biggest falls were recorded in Portugal (-9%), Bulgaria (-8.1%) and Ireland (-6.8%). Germany, which is one of the biggest European issuers, recorded a fall of -5.4%. However, eight EU countries recorded an increase in CO_2 emissions. The largest increases were recorded in Latvia (8.5%), Malta (6.7%), Estonia (4.5%), Luxembourg (3.7%) and Poland (3.5%) [23]. CO_2 emissions per capita in the European Union are on average 7 tons per year [27].

The countries emitting the most CO_2 according to Eurostat are Estonia, United Kingdom, Germany and Poland (Figure 7).

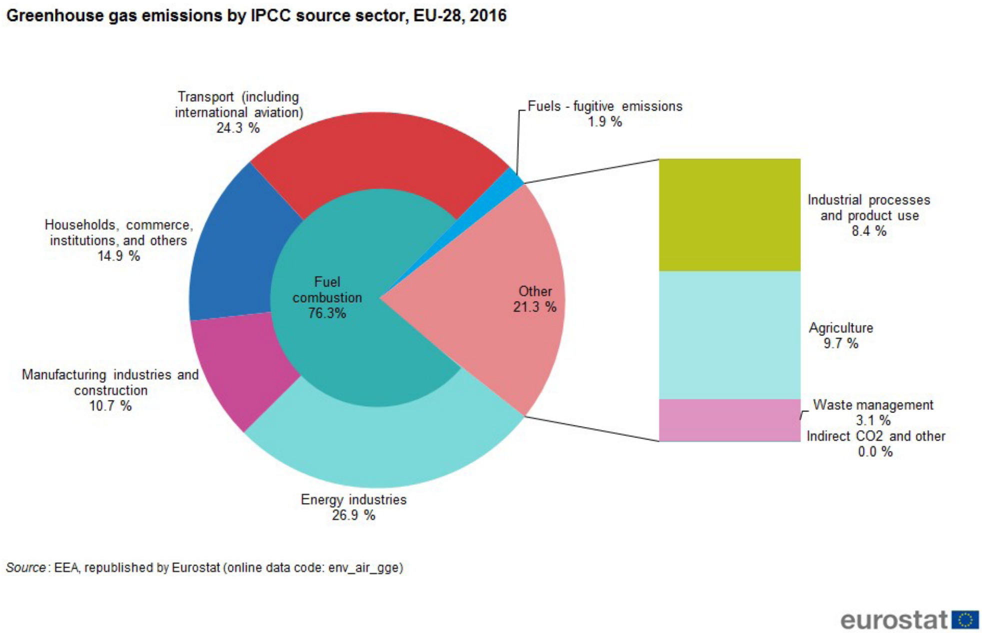

Fig. 6. Greenhouse gas emissions in the European Union by sector [23]

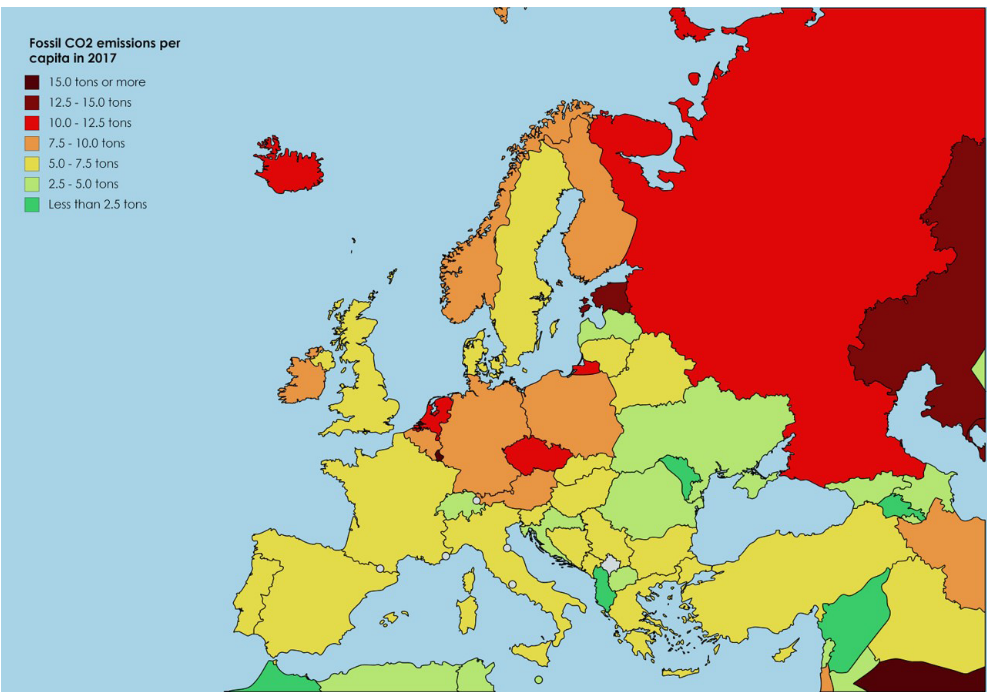

Fig. 7. Emission comparison in Europe [24]

The European Union emits 10% CO_2 in global emissions. This is relatively little, but it gives the EU the third place in the world. In 2018, a slight decrease of -0.7% was forecast (forecasts ranged from -2.6 to 1.3%). This is well below the -2% annual decrease over the decade until 2014 [27].According to the first estimates of Eurostat, in 2018, carbon dioxide (CO_2) emissions from burning fossil fuels in the European Union significantly decreased. In comparison with the previous year, the atmosphere received 2.5% less CO_2 [3].

Effects of CO_2 emissions

Based on the information provided by the World Meteorological Organization WMO, the concentration of carbon dioxide in the atmosphere increased rapidly [11]. Carbon dioxide is the basic gas responsible for climate change and the greenhouse effect [12]. Its excessive emission causes global warming, rising sea level, melting glaciers and weather anomalies, i.e. strong cyclones, tornadoes, powerful downpours [13]. If the emission of this gas is to continue at the present level, it may lead to a mass extinction of animals and people [14].

The Earth, heated by solar rays, emits infrared radiation, while greenhouse gases absorb it. As a result, they increase their temperature and also radiate infrared, partly towards the Earth. As carbon dioxide and other greenhouse gases in the air increase, the atmosphere absorbs and emits radiation more and more intensively. It is precisely due to the increase of its amount in the atmosphere that the average temperature of the planet's climate will be 2-3 degrees higher in the middle of the 21st century [15]. Figure 8 shows the scenarios of climate change.

If mankind decides to burn all fossil fuels, it is likely that by 2300 the temperature will increase by 8°C. However, if emissions in the second half of the 21st century fall below zero as a result of active and large-scale activities aimed at removing CO_2 from the atmosphere, then the optimistic plan will be implemented [16].

The oceans absorb more than one million tonnes of carbon dioxide per hour in order to slow down the rate of increase in the concentration of this gas in the atmosphere. The result of this process is an increase in the acidity of the oceans [16]. It consists in the absorption of carbon dioxide by the ocean water, which dissolves easily in them, and then the formation of acid, which lowers the pH of the surface waters of the oceans [17]. Currently, the acidity level of water is 8.1 pH, which means that the acidity of water has increased by as much as 30% since the Industrial Revolution [16]. As a result, ocean waters will see a reduction in nutrients, a reduction in the amount of light in the water, and a change in the way sound propagates. Furthermore, it will have serious consequences for the organisms building up the outer limestone skeletons and shells. Many species will not survive these changes [16,17]. There is also an increasing epidemiological threat associated with higher water temperature in the sea and lakes, which favours bacteria and cyanobacteria [20].

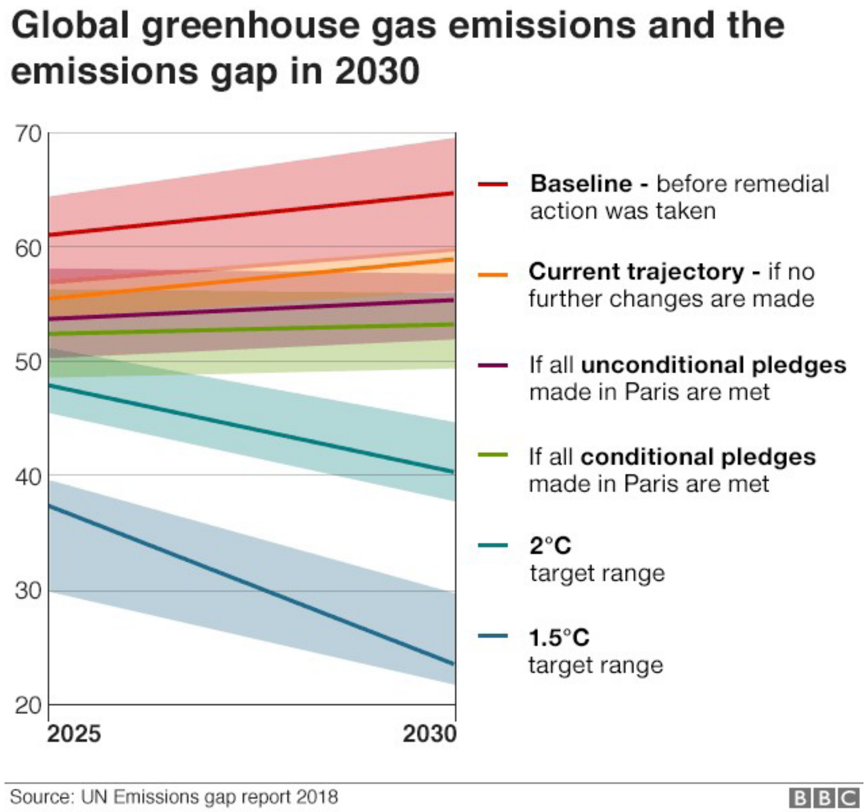

Fig. 8. CO_2 emissions scenarios [7]

According to a report prepared by the World Wildlife Federation (WWF), further CO_2 emissions at the current level are very harmful to fauna and flora. For half of the species to die out, an average temperature increase of 1.5°C [14] is sufficient. Forecasts show that further warming of the Earth's climate, related to CO_2 emissions from energy, industry, agriculture and transport, will threaten the existence of valuable ecosystems, such as coral reefs and rainforests [18]. An increase in the average temperature of 3.2°C on Earth will result in the rapid extinction of about 60% of plant species and 50% of animal species in the Amazon basin. In the case of 4.5°C it will be as much as 70% of reptiles and plants and 60% of mammals and birds [14].

According to the calculations of the Ministry of Agriculture and Rural Development, last year's drought affected 130,000 farms and destroyed 3.5 million hectares of crops, generating losses of over PLN 3.6 billion. Estimates of the Central Statistical Office concerning the harvest of basic cereals indicate a 14% decrease as compared to 2017. The effects of drought will be felt by all inhabitants of Poland - the prices of many foodstuffs will rise, and compensation for farmers will be paid by the State Treasury, i.e. all of us. Droughts in our region will occur more and more often and will be more and more burdensome [19].

Higher temperatures all year round are preferable for insects, e.g. species of mosquitoes carrying exotic diseases. The more the global temperature increases as a result of anthropogenic CO_2 emissions, the better the living and reproduction conditions for insects in Europe will be. This means that the risk of contracting dangerous diseases will increase in an ever-increasing area of our continent. Forecasts show, for example, that in the middle of the century Poland will be within the range of the dengue vector mosquito species [20].

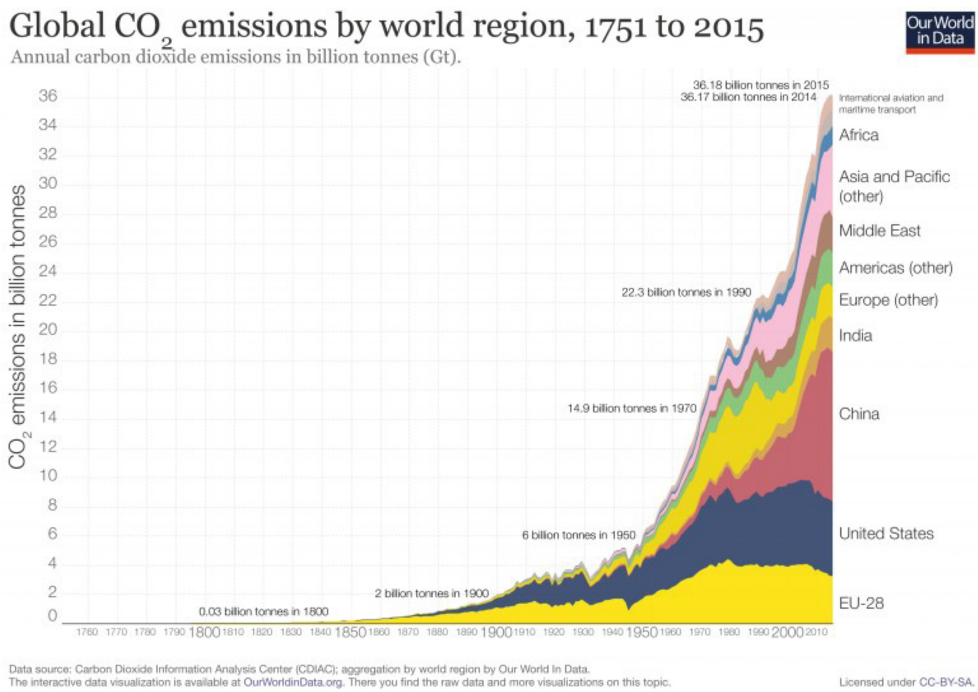

Fig. 9. Global CO2 in 2017 [27]

In 2018, the European Union decided to adopt a regulation that will enable it to meet its commitments to reduce greenhouse gas emissions by 40% by 2030 compared to 1990 levels. It is estimated that once the legislation is fully implemented, emissions could be reduced by around 45% by 2030 due to EU action in the field of renewable energy and energy efficiency. Member States will need to define policies and measures to further reduce emissions to meet their commitments [25].

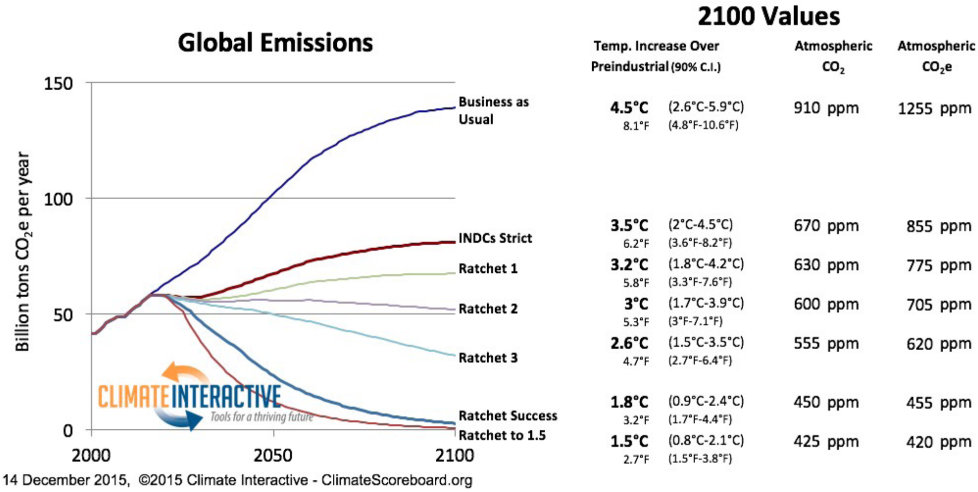

Fig. 10. GHG emissions forecast to 2100 [25]

A key element of EU climate change policy is the EU Emissions Trading Scheme (EU ETS). It is an essential tool to reduce greenhouse gas emissions. It is the world's largest carbon market. The system operates in 31 countries (28 EU countries) as well as Iceland, Norway and Liechtenstein. Thanks to it, emissions from more than 11,000 power plants, industrial plants and airlines are reduced [26].

Summary

Over the next decades and hundreds of years, humanity is threatened by an unprecedented ecological catastrophe, causing irreversible loss of many species of plants and animals and directly endangering human life and health. One of the main causes is the emission of man-made greenhouse gases, which cause global warming. The current level of CO_2 emissions in Poland and around the world clearly indicates the need to reduce emissions in the shortest possible time.

In order to reduce CO_2 emissions, Poland must radically change its energy structure based on burning fossil fuels. The draft of the Ministry of Energy from 2018 "Energy Policy of the State until 2040" assumes that achieving 21% RES in the final gross energy consumption in 2030. The sources to be developed are mainly: solar energy (photovoltaic), energy from biomass and biogas, wind energy (mainly at sea). The commencement of investments in offshore wind farms is conditional on the completion of works on strengthening the transmission grid in the northern part of the country, so that it is possible to carry out power inside the country. It is expected that the first offshore wind farm will be included in the power balance after 2025. The Polish coastline offers the possibility of implementing further offshore installations.

Development of low-emission heat sources and increased use of system heating. Significant reduction in the use of solid fuels in individual farms by 2030. Poland currently does not have a nuclear power plant. The development of nuclear power is planned. The commissioning of the first unit (with a capacity of about 1-1.5 GW) of the first nuclear power plant is scheduled for 2033. This is a distant prospect caused by the lack of technology and personnel, which is associated with the time consuming investments and requires constant and high financial outlays [29]. The development of RES will significantly reduce the reduction of CO_2, but under Polish conditions it is impossible to completely replace energy from coal with RES. Only nuclear power generation can fully replace coal-fired power generation, while reducing the vast majority of Poland's CO_2 emissions. However, the process of diversification of energy sources and abandonment of coal will take several decades. It should be noted at this point that comparing Poland with Western countries is inappropriate. Our energy sector is based on coal, because coal is, and was, the cheapest source of energy for us. In the 20th century, our country was torn by two world wars, communism and numerous economic problems lasting to this day and had few opportunities for diversification of energy sources. At that moment, western countries were developing renewable energy sources and nuclear energy. For example, France had in 2011 58 nuclear reactors and 75% – 78% of energy demand was covered by nuclear energy [30].

Polish CO_2 emissions are only 1% of global emissions, which means that only decisive actions and cooperation of the largest powers and global corporations can improve the situation. However, the Climate Agreements are repeatedly disregarded. The number of people in the world, together with their energy and consumption needs, is constantly growing. Increases in emissions are not regulated by afforestation; on the contrary, global deforestation is progressing. A drop in emissions is urgently needed, but the example of Poland shows that this is a long-term process. All these factors do not inspire optimism. Reducing CO_2 and other greenhouse gas emissions is one of the biggest challenges for humanity in the 21st century.

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Levani Mamatsashvli[1)], Jacek Dawidowicz[2)]

[1)] Georgian Technical University
Faculty of Civil Engineering
Department of Water Supply, Sewerage systems, Heat-Air-Supply
and Ventilation nad Engineering Equipment of Buildings
rectoroffice@gtu.ge

[2)] Bialystok University of Technology
Faculty of Civil and Environmental Engineering
j.dawidowicz@pb.edu.pl

WATER SUPPLY AND SEWAGE DISPOSAL SYSTEMS

keywords: water supply, sewage disposal systems

Abstract:

If the waste is not treated properly these things can happen. You would be filled with sewage around you in no time, at the rate our population is growing this can be super short. Your ground water sources would be affected as you pour untreated sewage into rivers and sea. They seep into the underground polluting your drinking and bathing water. Communicable diseases will be on the high as rivers would be running with sewage. The most important of them all, you could save the good water that is mixed with sewage and use it to grow trees or if you treat it really well you can drink it. Segregation of sludge (solid waste present in sewage) is a very good way to generate methane - it can be burnt for energy. Though not very efficient at the moment it definitely is a good source of energy. It's time we started treating every drop of sewage in our cities to prevent nationwide dialysis.

Introduction

In rural communities across the world, many people face issues around having insufficient or unsafe water supplies, poor access to improved sanitation facilities, and low agricultural yields due to lack of water and fertilizer. In villages of my country Georgia, these issues are particularly prevalent, due to poverty and lack of education of the population, political upheaval, remote locations of villages and challenging topography. For these reason, Georgia is selected for the research into issues relating water and sewage with the aim to find solutions and eliminate the problems. My country has a good source of water. Sewage systems use water to carry waste away in pipes. They can improve community health, especially in crowded urban areas. But to prevent health problems, sewage must be treated to make the water safe to return into waterways and for reuse. In Georgia, especially in villages and areas surrounded cities are problems of sewage disposal systems, people chose to build their own sewers.)

Basics of the water supply

Water supply systems get water from a variety of locations after appropriate treatment, including groundwater, surface water (lakes and rivers), and the sea through desalination. The water treatment steps include, in most cases, purification, disinfection through chlorination and sometimes fluoridation. Treated water then either flows by gravity or is pumped to reservoirs (the main destination of reservoirs is to regulate, store treated water for firefight. When in the inhabited area is less water consumption than water supply in reservoirs excess water is stored in reservoirs, unless in peak hour when water consumption is more than water supply in reservoirs, at this time stored water is supplied in a water supply network.) which can be elevated such as water towers or on the ground (difference between water towers or reservoirs is that when geodesic benchmark of the inhabited area is higher than reservoirs benchmark, at this case water tower is needed. Height of water tower must be deference between benchmark of inhabited area and benchmark of reservoirs. Water pipeline network must supply any type of inhabitant with required water quantity and quality. Pressure in water pipeline can be high pressure or low pressure. The buildings which are higher than piezometric line and needs higher pressure in this case such buildings must have their own amplifier which will serve only one building or maybe several buildings.

Water supply systems depend on topography, on water user (which can be people who needs water for domestic purposes, or for irrigation and the enterprises that use water for technological purposes) and on technical-economical liability. In a populated place water supply network can be united, when drinking, irrigation, firefight and production water supply is carried out by one system. Separated, when we have two independent water supply system. One of them serves drinking water and other one serves for enterprises. In this case water for firefight and irrigation often is held on drinking water. Semi-detached is called system, when we have independent from each other drinking and production water system, which have water supply source and headgear systems.

Water supply network also can be classification by destination, by size of pressure and by water supply source.

Making project in city conditions is very difficult. To relieve water user and existing communications takes time, but every company which provide town or settled area withdifferent communications must have database, for example: program such as ArcGIS is helpful for pre-project research. With this program you already know exact communications location and it is helpful for making decision to locate new pipes. Also programs such as Zulu, Epanet, Sewer hydro and Sewergems helps to account hydraulic. Programs can also analysis an existing network. Water supply systems main goal is to provide settled area with drinking water in 24-hour mode.

Basics of the sewerage systems

The sewage can be disposed of without treatment or after suitable treatment finally, the sewage is disposed of either in natural water courses or on land.The disposal of sewage by discharging it into watercourses such as streams, rivers or large body of water such as a lake, sea is called dilution. These methods of disposal are only possible when the natural water in required quantity is available near the town. While discharging the sewage in this way care should be taken that the sewage may not pollute the natural water and render it unfit for any other purpose such as bathing, drinking, fish culture, rough industrial use and irrigation When the sewage is evenly spread on the surface of land methods is called land treatment. the water of sewage percolates in the ground and the organic suspended solids remain at the surface of the ground the organic suspended solids are partly acted upon by the bacteria are partly oxidized by exposure to atmospheric action of heat light and air.

A sewerage system is a system that contains pipes of several lengths and diameters which are very important to convey the wastewater, including domestic, residential, industrial and commercial treatment services. Sewerage system plays a critical role in that it supports public health and environmental protection. Normally, the wastewater flow in the sewerage system is directly related to human usage for all kind of activities. The typical sewerage system is based on gravity. It means that the water flows under gravity force. 80 % of water supply is returned as waste water. Once water is used, wastewater is typically discharged in a sewer system and treated in a sewage treatment plant before being discharged into a river, lake or the sea or reused for landscaping, irrigation or industrial use (see also sanitation). Sewage treatment to a city is as important as kidneys to a human being.

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Ketevan Gordeziani[1)], Maria Walery[2)]

[1)] Georgian Technical University
Faculty of Civil Engineering
Department of Water Supply, Canalization, Heating and Air Conditioning System and Plumbing Installation
k.gordeziani@gmail.com

[2)] Bialystok University of Technology
Faculty of Civil and Environmental Engineering
m.walery@pb.edu.pl

WATER SUPPLY SYSTEMS OF GEORGIA

keywords: water supply systems

Abstract:

Georgia has abundant water resources. Among the total water resources of 63 billion m^3/year (long-term average) only 1.6 billion m3/year or about 2% are being abstracted. About two thirds of the abstracted water is used for irrigated agriculture, and the other third for municipal and industrial uses. Despite the abundance of water resources, the Eastern part of Georgia is relatively dry and is regularly affected by droughts. The country's major river, the Kura River, rises in Turkey and receives half of its flow from snowmelt and glaciers. The river, which flows from Georgia to Azerbaijan, is increasingly polluted downstream of Tbilisi.

Access to water supply and sanitation in Georgia is high. The definition of improved sanitation includes pit latrines with slabs, while it excludes pit latrines without slabs. It is often difficult for surveyors conducting general household surveys to get reliable responses to the question that refers to the exact type of latrine in a house, so that the above access numbers should be treated with some caution.

Fig. 1. Map of Georgia)

Source: https://www.visitgeorgia.ge/about-georgia/map-of-georgia/.

Introduction

Water supply and sanitation in Georgia is characterized by achievements and challenges. Among the achievements is the improvement of water services in the capital Tbilisi where the water supply is now continuous and of good quality, major improvements in the country's second-largest city Batumi on the Black Sea where the country's first modern wastewater treatment plant now is under operation, as well as a general increase in access to drinking water in the entire country).

Infrastructure

Tbilisi obtains most of its drinking water from the basin of the Aragvi River north of the city. Groundwater (60% of the total) is pumped from well fields, while surface water (40%) is mostly obtained from the reservoir of the Zhinvali Dam 42 km from the city. The water is treated in two plants: the Samgori plant built in the 1950s and the Grmagele plant, located at the Zhinvali Dam, built in the 1980s. The length of the water distribution network in Tbilisi is 3,600 km. About 35% of the main network is made of iron pipes and 65% of steel pipes. Polyethylene pipes have been installed only recently. There are 84 reservoirs and 169 pumps. The sewer network consists of 1,600 km of pipes made of ceramic, reinforced concrete, cast iron, asbestos cement and polyethylene. The wastewater is transferred by trunk sewer with a length of 72 km to the Gardabani waste water treatment plant commissioned in 1979 with a capacity of 1 million m^3/day. The biological treatment at the plant is not in operation due to its high energy consumption and the associated high cost. The untreated wastewater is discharged into the Kura River.

Water problems

The main problems with water are shortages of water, shortages of clean water and waterborne diseases. Around 80 percent of all deaths from illness in the developing world are caused by lack of access to safe water. More than 5 million people die each year from water-related diseases such as severe diarrhea, hepatitis A and dysentery.

An estimated 900 million to 1.1 billion people worldwide lack clean drinking water and 2.4 billion lack basic sanitation, and demand for water is currently increasing at a rate faster than population growth. Over the past 70 years, while the world's population has tripled demand for water has increased six fold. The United Nations estimates that in 2025 that 5 billion of the world's 8 billion people will live in areas where water is scarce and many of these people will have difficulty attaining enough water to meet their basic needs.

Growing populations, expanding agriculture, industrialization and high living standards have all boosted demand for water while drought, overuse and pollution have all decreased supplies. To make up for the shortfall water is often taken from lakes, rivers and wetlands, causing serious environmental damage. According to a 2018 United Nations report, "Across the globe, groundwater is being depleted by the demands of megacities and agriculture, while fertilizer runoff and pollution are threatening water quality and public health."

Every week it seems there are alarming predictions related to water: disease, starvation, crop disasters, famines, war. One of the major challenge in many developing countries is to provide decent drinking water and sanitation to sprawling shanty towns and areas occupied by the urban poor in the cities. In rural area at least the poor can dig wells and take care of the sanitation in their fields.

Water disputes

Scientists and government officials predict that in the coming decades water, not oil, will become the most important resource and the one that holds the greatest potential for conflict. Disputes between countries over water could escalate into war. There has been some discussion of setting up peacekeeping forces to deal with water disputes.

The United Nations has yet to develop a scheme on how to divide the water of major rivers between countries that share it. This applies to the Nile, the Danube, the Euphrates River and others. The greatest potential for conflict involves countries with mountains that are sources of rivers sometimes build dams that prevent water from reaching neighboring countries, which are not comfortable with the fact that source country has the power to cut off or greatly reduce their water supply.

There are political problems and potentials for war if two countries extract water from the same aquifer. None of the numerous treaties on water use cover underground water. There are also conflicts within countries as to who will get water: primarily between industries, cities and farms. Environmental refugees from places with water shortages flock to the rich countries.

Wasted water and PET bottles

Water is wasted because of bad drainage, water pipes that leak, evaporation from reservoirs and canals, poor irrigation and industrial practices, and lack of wastewater and drinking water treatment.

Bottled water is also a problem: not so much because it wastes water but because it wastes energy and money. Even in the developing world, people are becoming increasingly dependent on bottled water from private companies rather than developing public water systems. In some cases the poor spend a large percentage of their income on water from private source for water that should come virtually free from the tap. In some cases residents of slums in pay four times for water what Americans pay.

PET (polyethylene terephthalate) bottles make up about 0.25 percent of total worldwide oil consumption. One bottle is made of 24 grams of ethylene and paraxylene, both chemicals derived from crude oil. The biggest waste of energy is not the oil used to make the bottles as much as it is the energy costs of moving all this water great distances when water that is just as good is available for 1/10,000th the price from the tap. Many bottles end up as litter.

Polluted water

People often bathe, wash their clothes and swim in disgusting water. They often drink water of dubious quality obtained from ponds and streams used by animals.

Agriculture-related water pollution comes from fertilizer, pesticides, herbicides, animal waste, salts from evaporated irrigation water, and silt from deforestation that wash into streams, rivers, lakes, ponds and the sea. Agricultural runoff is sometimes so severe it creates “dead zones” in coastal water zones.

Industry-related water pollution comes from toxic chemicals and heavy metals from manufacturing and mining. Power plant emissions create acid rain which contaminates surface water.

Much of the pollution in rural areas is caused by untreated sewage resulting from a lack of toilets and sewers; salts, fertilizers and pesticides from irrigated land that contaminates flowing water and groundwater supplies; and salt water entering overused aquifers. Places with sewers often have no waste-water treatment facilities and sewage is dumped directly into water supplies from which people draw their water.

The air and water around the cities is polluted but the rural areas are so vast pollution nationwide is not a big problem.

Solutions to water problems

One of the goals of planners is took keep water cheap enough so that the poor can get what they need but have water prices high enough so that people do waste it. In many places water is subsidized, and the cheap prices encourage people to waste it. The obvious solution here is to end subsidies so that water is wasted.

Reusing and recycling water is a solution. It is estimated that some cities can meet a fifth of their water needs by recycling water. Worldwide, two thirds of urban water does even get treated. Systems that treat and reuse wastewater are often the least costly and most efficient way to clean water but they have difficulty overcoming the aversion that many people have to drinking water derived from sewage.

Ultraviolet radiation is a popular means of disinfecting water but is less effective when the water contains sediments and sludge. In places where water is collected from dirty ponds and lakes, people have learned to clean the water by folding clean cloths several times, placing them over a jug, and pouring water through it. The cloth filters many kinds of disease-causing organisms.

Summary

Georgia has abundant water resources. Among the total water resources of 63 billion m3/year (long-term average) only 1.6 billion m3/year or about 2% are being abstracted. About two thirds of the abstracted water is used for irrigated agriculture, and the other third for municipal and industrial uses. Despite the abundance of water resources, the Eastern part of Georgia is relatively dry and is regularly affected by droughts. The country's major river, the Kura River, rises in Turkey and receives half of its flow from snowmelt and glaciers. The river, which flows from Georgia to Azerbaijan, is increasingly polluted downstream of Tbilisi.

To solve a multi-objective optimization problem, it is necessary to convert the problem into a single objective optimization problem, by using adjustments, such as a weighted sum of objectives. The objectives of the company are as follows: rehabilitation and construction of water infrastructure; maintenance and improvement of water quality; eradication of water losses; modernization of parking lot and base for special machinery; perfecting the charging and recovery processes; complete metering of company customers; creation of economic and technical rationale; introduction of accurate system of human resources management; rendering the activities of Company compliant with environment protection norms; energy-efficiency; enhancement of financial situation, and improvement of financial management system.

Access to water supply and sanitation in Georgia is high. Based on household surveys and census results, the Joint Monitoring Programme for Water Supply and Sanitation estimates that access to an improved water source was universal in 2015. Access to improved sanitation stood at 86% (95% in urban areas, 76% in rural areas). According to these estimates based on census and household survey data access to water improved from 96% in 1990 to 100% in 2010, while access to sanitation declined from 98% in 1990 to 86% in 2015. The decline in access to sanitation was most marked in rural areas, where it declined from 96% estimated during a survey in 1996 to 79% estimated through a survey in 2013. The definition of improved sanitation includes pit latrines with slabs, while it excludes pit latrines without slabs. It is often difficult for surveyors conducting general household surveys to get reliable responses to the question that refers to the exact type of latrine in a house, so that the above access numbers should be treated with some caution.

At the same time, the global water cycle is intensifying due to climate change, with wetter regions generally becoming wetter and drier regions becoming even drier. Other global changes (e.g., urbanisation, de-forestation, intensification of agriculture) add to these challenges.

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Zdenka Kovacova[1), Stefan Demcak[2), Magdalena Balintova[3)

[1) Technical University of Kosice
Faculty of Civil Engineering
Institute of Environmental Engineering

[2) Technical University of Kosice
Faculty of Civil Engineering
Institute of Environmental Engineering

[3) Technical University of Kosice
Faculty of Civil Engineering
Institute of Environmental Engineering

Correspondence address:
Vysokoskolska 4, 042 00 Kosice, Slovakia
e-mail: zdenka.kovacova.2@tuke.sk

REMOVAL OF COPPER, ZINC AND IRON FROM WATER SOLUTIONS BY ADSORPTION ON SPRUCE SAWDUST

keywords: adsorption, model solutions, spruce sawdust, heavy metals

JEL: Q25, Q52.

Abstract:

The water pollution by toxic elements is one of the major problems threatening human health as well as the environmental quality. Sorption technique is considered as a cost effective methods that are able to effectively remove heavy metals. During past few years researches have been giving their interest to using low-cost adsorbents like bark, lignin, chitosan peat moss and sawdust.

This paper deals with the study of copper, zinc and iron adsorption by spruce sawdust obtained as by-product from locally used wood. Raw spruce sawdust was used to heavy metal ions removal from the model solutions with concentration of appropriate ion 10 mg/L during 24 hour's or 5, 10, 15, 30, 45, 60, 120 min, respectively. Fourier transform infrared spectroscopy was applied to determine func-

tional groups of sawdust. Sorption efficiency was higher than 67% in short-time experiments and higher than 75% in one day experiments for all tested cations.

Introduction

The significant pollution of air, soil, and water is a result of people's efforts to improve their lives. The industrial activities together with technology development lead to a release of large quantities of contaminants to the water. Among a wide range of pollutants contained in wastewater, metals are one of the most toxic substances. They do not biodegrade and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings which means – negative effect on whole environment. Inorganic pollutants most ordinary presented in wastewaters are copper, nickel, zinc, lead; iron, chromium and cadmium. These heavy metals were intensively investigated from the point of view of persistence and toxicity (Abdel-Raouf, 2016; Larous, 2012; Gogoi, 2018; Simón, 2019).

Copper can be found in high concentration because it is usually used in many industrial sectors like metal finishing, electroplating, plastics and etching. It is recognized to be one of the heavy metals most wide spread heavy metal contaminants in the environment. Water contaminated with copper must be treated before discharging to the environment because of its toxic properties even at low doses. High concentrations of copper can cause serious toxicological concerns because it can be affected the brain, skin, liver and pancreas. This can lead to nausea, vomiting, headache, diarrhea, respiratory difficulties, liver and kidney failure (Al-Saydeh, 2017; Ageena, 2010; Larous, 2012).

Zinc is widely used in electroplating, galvanized pipes, iron, alloy and brass production and paper production. At trace amounts, zinc is an essential nutrient for certain biochemical and physiological functions of the organism. At concentrations beyond the permissible level (2.00 mg/L), zinc can lead to a malfunction of various systems in the human body and it can cause nausea, vomiting, epigastric pain, lethargy, fatigue, a short-term illness called „metallic smoke fever" and restlessness. Zinc is also poisonous to plants at high concentrations and can be damaging in soils because of its high mobility (Simón, 2019; Udomkitthaweewat, 2019).

Contamination of water with iron can either be geogenic or via industrial effluents and domestic waste. Iron is essential for human, its deficiency may lead to anaemia and loss of well-beingits but vice versa its presence above a certain level may cause harm severe health problems in human beings such as vomiting, liver cancer, diabetes, cirrhosis of liver, heart diseases and infertility etc. The presence of higher concentrations of iron corrodes water pipe lines, changes colour, taste, odour of water and leaving stains on clothes (Al-Shahrani, 2013; Kumar, 2017).

From all these reasons, the proper treatment of the wastewaters before to its discharge to the environment is needed.

There are several methods of removing heavy metals from wastewaters for example:

- precipitation which is simple process and is based on the fact that some metal salts are insoluble in water,
- ion – exchange method uses ions on a matrix to exchange with metal ions in the water solutions,
- reverse osmosis utilize a high pressure to filter out the metal ions trough a membrane (Simón, 2019; Ageena, 2010).

From the reason to increase of use eco-friendly and economical materials, interests of researchers about searching of new adsorbents that can be used for this purpose have been increased. The adsorption process (figure 1) has been considered as one of the most efficient methods with many advantages including low cost, more flexibilities, high efficiency, good selectivity, simplicity of design, ease of operation, insensitivity to toxic pollutants, high quality purified product and recyclability with various materials (Elkady, 2017; Balintova, 2016; Demcak, 2019).

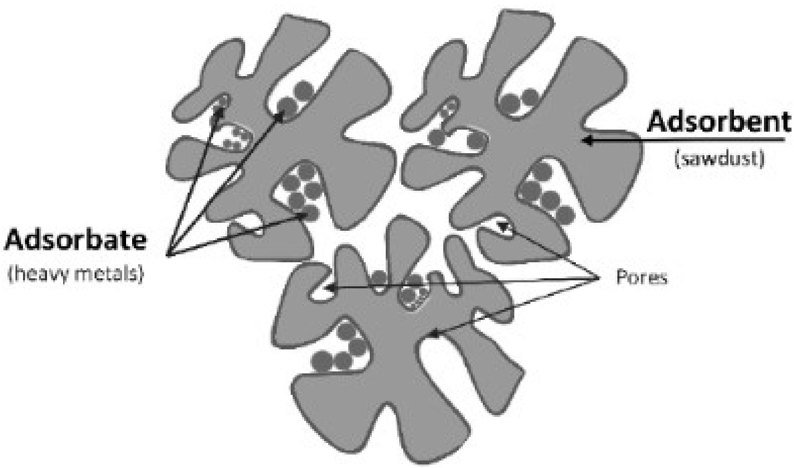

Fig. 1. Realization of adsorption process using sawdust as adsorbent
Source: Ouafi, 2017, p. 117.

In recent years, extensive research has been made for the purpose of identifying new and economically priced sorbents for the removal of different heavy metal ions. The low cost adsorbents including aquatic plants, waste tea leaves, bark, peat moss, lignin and sawdust have also been reported that as efficient and potential materials. Sawdust is one of the most appealing timber industry by-products that is available in large quantities, is cheap and easily regenerated after use (Memon, 2008; Thapak, 2015; Ince, 2017; El-Saied, 2017).

The aim of this research was to investigate application of spruce wooden sawdust for Cu(II), Zn(II), and Fe(II) removal from aquatic solutions. Copper, zinc, and iron are the general metals found in much nitrogen rich wastewaters (Zhang, 2019), from these reason were selected as model ions to removal from aquatic solutions. The spruce wooden sawdust was also characterized by FTIR method in order to determine the changes caused by adsorption/ion – exchange process.

Research methods

The spruce sawdust (particle size less than 2 mm) from local resources has been used directly without any pre-treatment, as a sorbent for the removal of selected heavy metals ions from aqueous solution. Wooden sawdust was analysed by FTIR on Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). A total of 24 scans were carried out in the range of 4,000–400 cm^{-1}.

Dry spruce sawdust (1 g) was mixed with 100 mL of aquatic solutions. The water solutions with concentration 10 mg/L of Cu(II), Zn(II) and Fe(II) were prepared by dissolution of calculated amount of $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$ and $FeSO_4.7H_2O$ in deionised water.

The first experiment was focused interaction between sorbent and sorbate during 24 hours. The sawdust was initially mixed with the model solution and left at room temperature (20 ± 1°C) for the duration of the experiment.

The next attempt was kinetic study, the contact time between sorbent and sorbate was 5, 10, 15, 30, 45, 60 and 120 min, respectively. During this time spruce sawdust was intensively mixed in the model solution at room temperature (20 ± 1°C).

After the experiments, the concentration of heavy metals in the filtrates was determined by colorimetric method (Colorimeter DR890, Hach Lange, Germany) with appropriate reagent. Changes of pH were measured by pH meter (Mettler Toledo FG2, Schwerzenbach, Switzerland). The percentage efficiency was calculated by following equations:

$$\eta = \frac{(c_0 - c_e)}{c_0} \cdot 100 , \quad (1)$$

where:

η – sorption efficiency (%),

c_o – the initial concentration of appropriate ions (mg/L),

c_e – equilibrium concentration of ions (mg/L).

Results of the research

Infrared sprectra

Metal adsorption capacity is influenced strongly by the surface structures of C–O and C–OH functional groups which are present in organic materials (Ricordel, 2001). FTIR method was used to determine active sites existing in the surface structure of sawdust (El-Saied, 2017). IR spectrum of spruce sawdust is shown in figure 2. The main components of sawdust are lignin, cellulose and hemicelluloses. A broad band in the region of 3336 cm^{-1} represented presence of hydroxyl groups (−OH), the valence vibration related to aromatic C−H is shown on the spectrum at the 2883 cm^{-1}. The aromatic functions of lignin are characterized by infra-red absorption bands, which is characteristic of the C=C vibrations of the aromatic skeleton of lignin at the 1648 cm^{-1} region. Another bands of lignin (carbonyls (C=O), alcohols and ethers) were observed at 1508, 1451, and at 1316 cm^{-1}. Wavenumbers at 1422, 1367, 1316, 1260, 1026 and 895 cm^{-1} belong to cellulose. The functional groups of aromatics were noticed at 895 cm^{-1} (Salamat, 2018; Schwanninger, 2004).

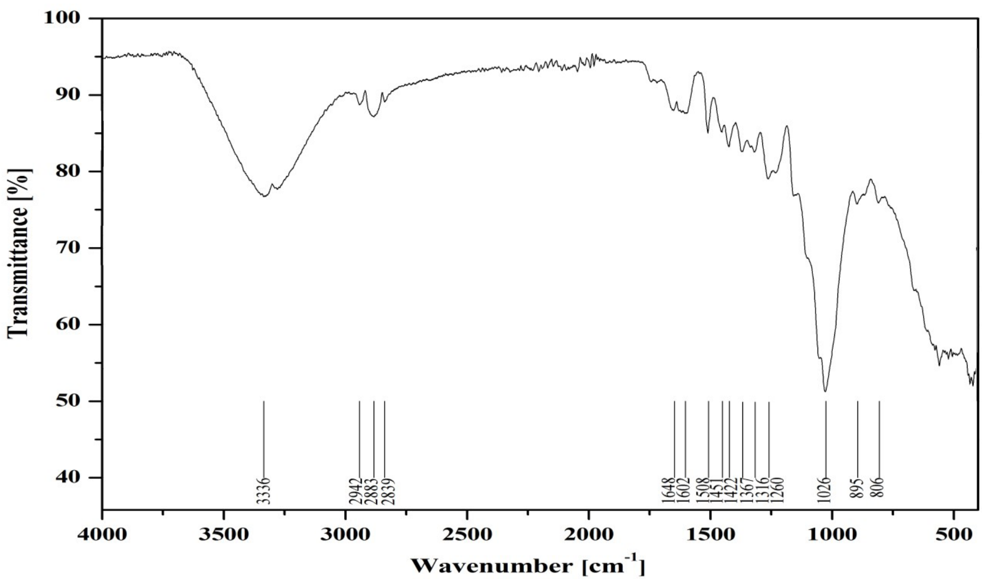

Fig. 2. Infrared spectra of spruce wooden sawdust

Source: author's own work.

Sorption experiments – 24 hour's results

Results of 24 hour's experiments with initial concentration of cooper, zinc and iron ions 10 mg/L are shown in table 1. In all situations was the sorption efficiency more than 75%. The best removal efficiency was observed in case of copper ions (more than 85%). The pH of the aqueous solution is an important controlling parameter in the adsorption process and thus the effect of pH has been studied (Balintova, 2011). Initial pH of the solutions was influenced only by the sort of the used chemicals , so adsorption process were performed in the different pH ranges. In all cases pH was decreasing in comparation to the initial value. The decrease of pH values could be caused by the competition for adsorption between metal ions and H^+ (Demcak, 2019).

Table 1. Results of 24 hour's experiments

Heavy metal ion	Input value		Output value		Sorption efficiency (%)
	c_o (mg/L)	pH	c_e (mg/L)	pH	
Cu(II)	10.00	6.3	1.48	5.3	85.2
Zn(II)	10.00	6.2	1.92	5.4	80.8
Fe(II)	10.00	5.9	2.49	5.2	75.1

Source: author's own work.

Sorption experiments – short-time results

Results of short-time experiments of copper removal from aquatic solutions are in figure 3. Larous et al. (2005) revealed that the copper adsorption on sawdust is depend e.g. on the solution pH, the temperature, the agitation speed, the initial concentration, the contacting time, the liquid to solid ratio, and the ionic strength. A significant increase in sorption was observed at the time 10 min, when efficiency achieved more than 80%, the rest of the time is characterized by slowly changes in removal efficiency a can be evaluated as relatively constant. The highest efficiency of Cu(II) (≈ 90%) was reached after 60 min. %. Changes of pH, due to ion exchange between metal ions in model solutions and functional groups of spruce wood sawdust are the major mechanism of retention of copper by sawdust.

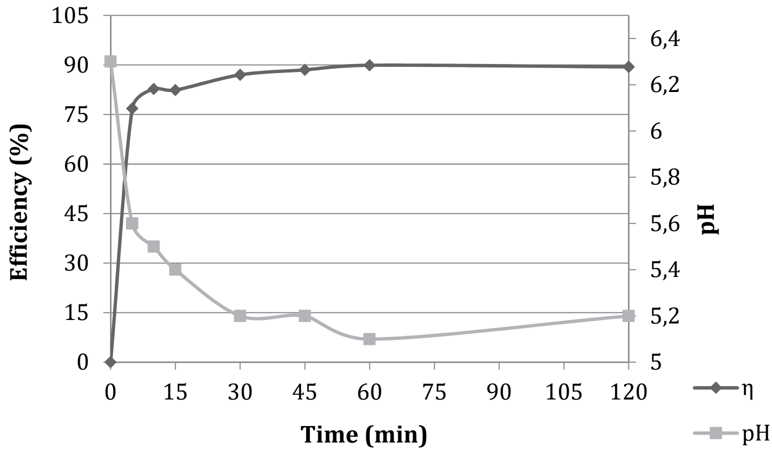

Fig. 3. Dependence of sorption efficiency η and changes of pH on time during experiment on copper removal from aquatic solutions

Source: author's own work.

In figure 4 are presented the results of zinc removal during the experiment (from 5 to 120 min). In all experiments was the removal efficiency hight than 73 %. The result indicates that zinc removal decrease pH of the solutions in the range from 6.2 to 5.7. The maximum efficiency removal of Zn(II) was about 82% at pH 5.7. Pragati et al. (2015) used the ground sawdust to zinc removal from aquatic solutions. They investiged that the maximum removal of zinc iones (at pH 5, during 120 min of contact time, and adsorbent dose 0.5g/100 mL) is about 90%.

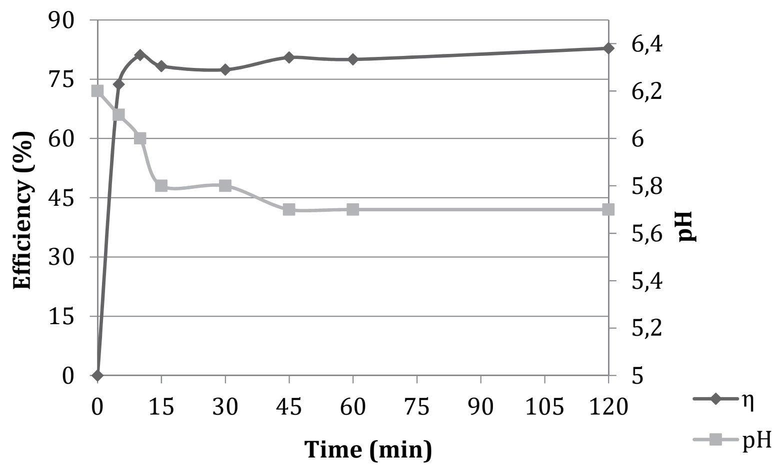

Fig. 4. Dependence of sorption efficiency η and changes of pH on time during experiment on zinc removal from aquatic solutions

Source: author's own work.

The results of iron removal in short-time indicated the removal efficiency higher than 67% (5 min), the heighest was during 45 min about 76% (figure 5). The value of pH was decreasing from 6,3 to 5,3 due to ion exchange. Senin et al. (2006) investiged the the maximum adsorption efficiency by sawdust was found to be 71.7% which corelated with the results of the experiment.

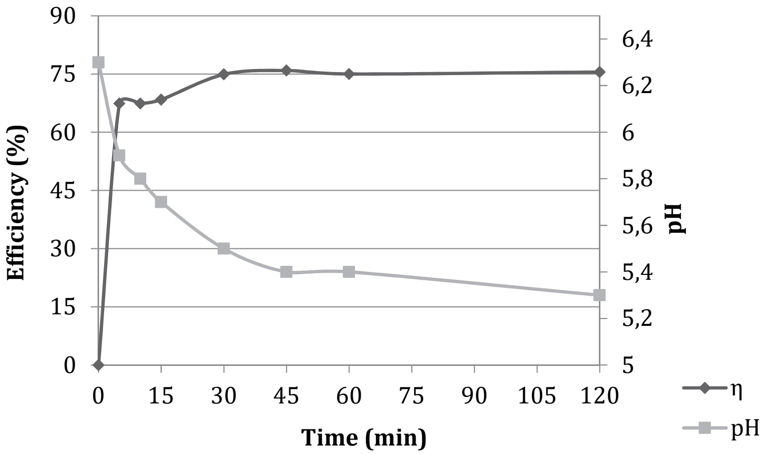

Figure 5. Dependence of sorption efficiency η and changes of pH on time during experiment on iron removal from aquatic solutions

Source: author's own work.

Conclusions

The current international tendency to obtain higher environmental standards favours the usage of cheap and health harmless systems for treatment of effluents. Adsorption is one of the most effective techniques for removal of pollutants from aqueous media. Inexpensive, readily available materials like wood sawdust can be used as sorbent for purification of wastewaters.

The Fourier-transform infrared spectroscopy of the spruce sawdust confirmed the presence of the functional groups that they are able to bind heavy metals ions.

In 24 hour's experiments was the highest removal efficiency in case of copper more than 85% and the lowest efficiency was in iron ions removal more than 75%.

In all experiments was Cu(II), Zn(II) and Fe(II) removal more that 67%. In case of copper, zinc and iron was the equilibrium concentration of ions highest in 60 min (1.01 mg/L) for Cu(II), 120 min (1.72 mg/L) for Yn(II) and 45 min (2.41 mg/L) for Fe(II). Changes of values pH showed the processes of adsorption and ion exchange for all experiments shown pH decreasing tendency.

The sorption experiments showed a potential of the wood spruce sawdust, especially to remove heavy metals ions from water solutions. The results from experiments also provide promising perspectives for the utilization of sawdust for reducing metal pollution.

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The contribution of the authors

Zdenka Kovacova – 40%
Stefan Demcak – 30%
Magdalena Balintova – 30%

Stefan Demcak and Magdalena Balintova conceived and planned the experiments. Zdenka Kovacova and Stefan Demcak carried out the experiments and contributed to the final version of the manuscript. Magdalena Balintova supervised the paper.

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Andrzej Bąk[1)], Violetta Kozik[1)],
Aleksandra Świetlicka[1)], Agnieszka Środa[1)],
Krzysztof Barbusiński[2)], Natalia Howaniec[3)], Adam Smoliński[3)]

[1)] University of Silesia
Department of Chemistry
Szkolna 9, 40-007 Katowice, Poland
andrzej.bak@us.edu.pl; violetta.kozik@us.edu.pl; aswietlicka@us.edu.pl; agsroda@us.edu.pl

[2)] Silesian University of Technology
Konarskiego 18, 44-100 Gliwice, Poland
krzysztof.barbusinski@polsl.pl

[3)] Central Mining Institute
Plac Gwarków 1, 40-007 Katowice, Poland
nhowaniec@gig.eu; asmolinski@gig.eu

Correspondence authors: andrzej.bak@us.edu.pl; aswietlicka@us.edu.pl

ELECTROCHEMICAL CORROSION MONITORING IN LOW CONDUCTIVE FLUID: PILOT-SCALE STUDY ON SULFOLANE CORROSION POTENTIAL

keywords: corrosion, sulfolane, aprotic solvent, carbon steel

Abstract:

Solvents are a group of chemical compounds that are widespread in the organic chemistry. Taking into account the chemical nature, solvents are divided into the protic and aprotic ones. An attractive alternative to commonly used industrial extractive liquids is an anthropogenic, organosulfur medium – sulfolane. Sulfolane is a five-membered heterocyclic sulfur-organic compound from the group of sulfones ($ArSO_2$), which contains an apolar hydrocarbon backbone and a polar functional group. It is a selective solvent in the liquid-liquid and liquid-vapour extraction processes used for the removal of close-boiling alkanes from cycloalkanes or for the separation of compounds with different degree of saturation and polarity in the extractive rectification of arenes from non-aromatic

saturated hydrocarbon mixtures. In the standard conditions sulfolane is not an aggressive solvent for steel, but at higher temperature (170-180ºC) and oxygen availability, it may be decomposed and subsequently some corrosive (by-)products can be formed. The primary purpose of the presented pilot-case study was to verify the applicability of the industrial, multi-electrochemical technique for reliable detection of the corrosion processes in the low conductive fluids.

Introduction

A worldwide rise of atmospheric pollution due to the expansion of industrial/agricultural areas and urban settlements is a peculiar 'landmark' of the modern civilization. The global ecosystem is confronted with volatile organic compounds (VOCs) as well as inorganic odorous compounds (VICs) that pose hazards to health of human beings and plants vegetation forming a significant part of indoors/outdoors pollution [1]. Pollutants emitted from liquids originate from anthropogenic activity and/or the biogenic emissions of reactive hydrocarbon derivatives formed in the result of the natural transformations. The odor-producing mixtures of sulfur-based pollutants compose a relevant group of contaminants with increasingly detrimental impact on human health in the long-term exposure [2]. The individual sulfur derivatives exert some irritant and toxic effects being classified as a potential mutagenic and carcinogenic risk factors. In fact, a wide range of environmental contaminants was rationally designed and engineered for industrially-specific targets. On the other hand, impurities such as hydrogen sulfide (H_2S) or carbon dioxide (CO_2) are constantly present in the natural gases, the removal of which, is a part of 'sour' gas refinement process. In particular, the process of dispatching the acidic gases, composed of H_2S/CO_2 ¬mixture, to 'soften' the natural/industrial (off)gases is called gas treatment [3]. The increasing public awareness of necessity for environmental protection is the main driving force for the increasingly stringent regulations governing release of hazardous pollutants and reduced sulfur compounds (RSCs) as well. Hence, the environmental legislations are constantly pushing industry for developing/optimizing of the cost-effective 'green' manufacturing technologies that impose less burden on the ecosystem [4]. In consequence, the removal of sulfur-containing compounds (e.g. H_2S, COS, mercaptans, organic sulfides) from unprocessed natural gases can be conducted in the liquid-liquid extraction process, where industrial solvents are applied in a 'closed' loop, recovered and regenerated on-site [5]. Regarding this context, the questions about the 'green' solvents and manufacturing procedures for the liquid-liquid extraction are pretty important. In fact, a range of solvents can be employed in the extraction process used in oil refining including (di/tri/tetra)ethylene glycol (D/T/TT/EG), diglycol amine (DGA), n-methyl pyrolidone (NMP), dimethylsulphoxide (DMSO), dimethylformamide (DMF), morpholine and carbonate derivatives. An attractive alternative to commonly used industrial extractive liquids is sulfolane ($C_4H_8SO_2$), an anthropogenic organosulfur medium that is widely distributed in the industry due to its physicochemical properties. Although the spelling 'sulfolane' may be astonishing for British English users, this name has been widely accepted as the generic name for hydrogenated sulfones of butadiene [6]. On the other hand, sulfolane is also known under a variety of synonyms/numbers including thiolane 1,1-dioxane (IUPAC), 2,3,4,5-tetrahydrothiophene-1,1-dioxide (systematic), thiocyclopentane-1,1-dioxide, (cyclo) tetramethylene sulphone, dihydrobutadiene sulphone, sulphoxaline, 126-33-0 (CAS) or 204-783-1 (EINECS), respectively [7]. Formally, sulfolane belongs to a group of cyclic sulfone, containing a four-membered carbon ring and sulfonyl functional group (R_2SO_2) with a sulfur atom double-bonded to two oxygen atoms as shown in Figure 1.

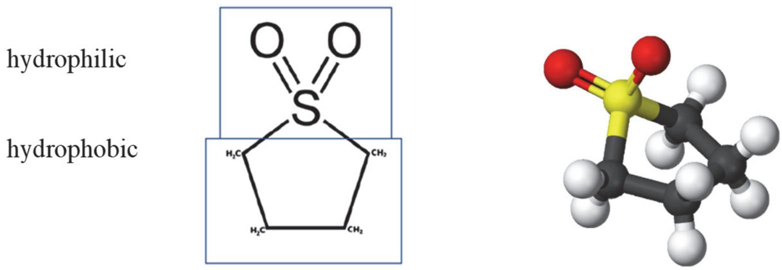


Fig. 1. Structure of sulfolane with (a) hydrophilic and hydrophobic parts and (b) 3D geometry.

Source: [Own study].

As a matter of fact, sulfolane was the first time described in the chemical literature in 1916; however the study for commercial application of sulfolane were initiated in the early 1940s [8]. Due to its satisfactory selectivity, low boiling temperature and its capacity for dissolving large quantities of aromatics sulfolane is the preferred solvent in the liquid-liquid and liquid-vapour extraction processes for the separation of compounds with various degree of saturation and polarity in the extractive rectification of BTX (benzene, toluene, xylene) mixture from the non-aromatic saturated hydrocarbons [9]. The unique combination of physical and chemical properties (inertness and stability) makes it possible to apply sulfolane not only as a 'sour gas sweetener', but also as a biomedical reagent (g.e., sulfolane-induced hypothermia) [10].

It begs the question of whether sulfolane is an appealing liquid to the scientific community? In fact, we found some highly interesting regularity while exploring the commercially available Reaxys database [11]. Oddly enough, a visible tendency of waxing and waning interest in sulfolane during the space of the last fifty years is observed in Figure 2 as indicated the analysis carried out on the data stored in the Reaxys database. Basically, 1644 hits were identified with the word 'sulfolane' in the title or abstract of the paper published in the range of the last fifty years (from 1969 to 2018) – most of them describe sulfolane physicochemical properties (approximately 43%).

It is natural to ask the question what actually induced a growing interests in sulfolane that fades after some years? Not surprisingly, the waves of interests correlate quite well with the general trends observed on the commercial market of oil production as indicated in Figure 2.

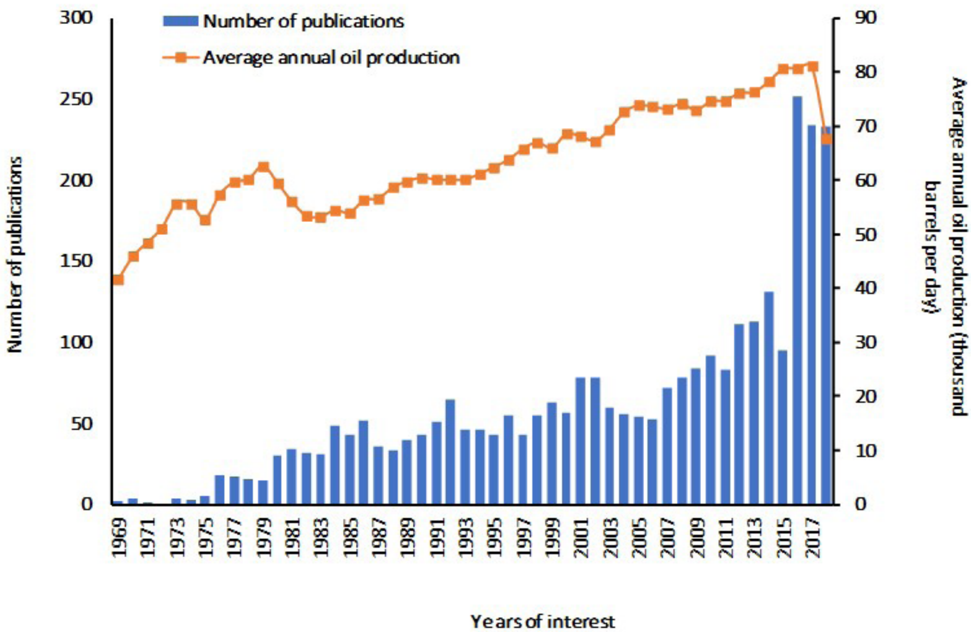
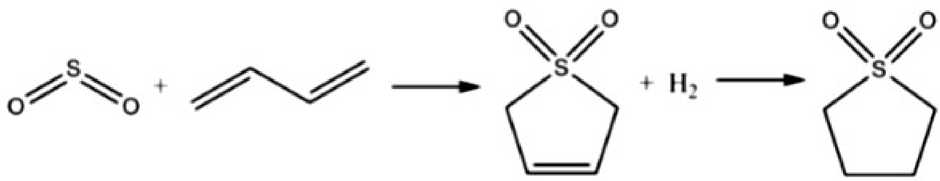


Fig. 2. Trends in the average annual crude oil production and interests in sulfolane during the space of last fifty years. Plot of the number of papers, where sulfolane was searched in paper title or abstract and average annual oil production (thousand barrels/day) based on Reaxys and EIA data [11,12].

Source: [Own study].

Basically, the constant growth in the annual oil production is observed throughout the last five decades that is directly related with the increased global oil consumption. It generally means that some 'magic extractors' are urgently needed in the petrol-related industry for the dearomatization of petroleum fractions and (pre)treatment of natural gases, respectively. In other words, the indicated 'wavy' trends in the sulfolane-related scientific activity is an illustration of the partial correlations with the annual oil production. It is noticeable that even some 'plateau' in the number of published papers superimpose with the periods of the relative annual oil production as observed between 1984 and 1987 or at the beginning of new millennium as well. It is obvious that economic aspects of the aromatic extraction in the refining processes used in the oil industry put pressure on the scientific community.

Originally, the process of sulfolane synthesis was composed of three basic stages involving the hydrogenation of 3-sulfolene (**c**) obtained as a product of sulfur dioxide (**a**) and butadiene (**b**) reaction as illustrated in Scheme 1.



Sch. 1. Industrial process of sulfolane synthesis.
Source: [Own study].

Regarding the environmental constraints the introduction of the eco-friendly catalytic protocols was promoted in the contemporary methods for sulfolane preparation with the operational simplicity, rapid reaction rates and effective formation of the easily handled reagents, respectively [13]. Recyclable pollution-free catalysts reused in the mild reaction conditions with halogen-free solvents and 'green' oxidants are attractive alternative for the large scale industrial sulfolane production estimated at 18,000 – 36,000 tons per year [14]. Theoretically, large-scale industrial usage of sulfolane is disposal/leakage-free due to its on-site recovery and regeneration; however in practise some unpredicted/accidental spills as well as leaks from extraction units in refineries or gas plants were reported worldwide resulting in the soil and groundwater contamination, therefore the environmental fate of the compound is being extensively studied [15]. In this context naturally appears the question about the major reasons of the accidental leaks and spills of sulfolane. Is it important to monitor the sulfolane-induced corrosion of the industrial systems since pure sulfolane under standard operating conditions is considered to be a stable compound and non-aggressive to steel? Unfortunately, the answer to question is positive, because sulfolane-containing systems, if contaminated by traces of oxygen and at typical process conditions (170-180ºC), may lead to sulfolane decomposition and formation of corrosive (by-)products with generation of SO_2 and formation of corrosive H_2SO_3 according to the following equation:

$$C4H8O2S + O2 + H2O \Rightarrow H2SO3 + C3H7CO2H \qquad (1)$$

Hence, the corrosion of steel can be quite rapid, causing severe damage to industrial installations, therefore sulfolane should be stored under a nitrogen blanket and out of contact with oxygen and strong oxidizing agents such as chlorates, nitrates and peroxides, that can result in its decompositions. Moreover, the presence of impurities such as oxygen and/or chlorides or water can accelerate sulfolane 'breakdown' process as well. In fact, some general correlations between oxygen/chloride and water concentrations are described, where sulfolane degradation and production of acidic corrodents lead to enhanced sulfolane corrosivity [16,17]. For instance, oxygen-degraded sulfolane is characterised by a lower pH with lower extractive power, a higher acid number and a darker color compared to pure sulfolane as depicted in Figure 3.

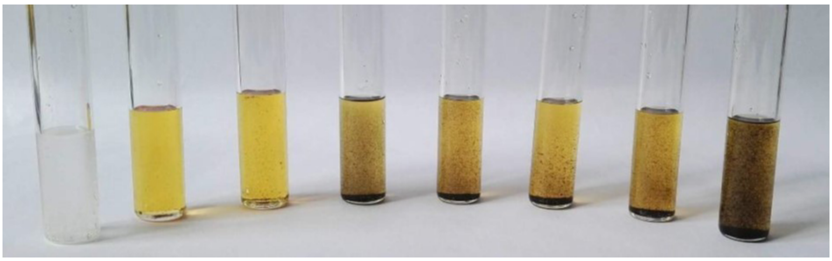


Fig. 3. Samples of sulfolane, from the left: pure sulfolane, sulfolane after the experiment at 95 °C, sulfolane with water 2%, 3%, 4%, 5%, 6%, 6% with oxygen and 6% with chlorides.

Source: [Own study].

It should be emphasised that there is 'a gap on the path from data to knowledge' in the detailed and quantitative assessment of the individual impurities on the sulfolane-induced corrosion of carbon and alloyed steels.

The main purpose of the previous and current pilot-case studies was to verify the applicability of the industrial, multi-electrochemical technology for reliable detection of corrosion processes in the fluids with low conductivity. Several aspects of the corrosion measurement were taken into account, including the influence of process parameters (temperature as well as the impact of impurities, e.g. water, oxygen and chlorides) on the corrosion of carbon steel in the pure sulfolane. In our studies we used the SmartCet® by Honeywell whose operation is based on Low Frequency Impedance (LFI), Harmonic Distortion Analysis (HDA) and Electrochemical Noise (ECN). The industrial, wired transmitter, model CET5500 was used conjugated with the HART (Highway Addressable Remote Transducer) system. The set of the flat coupon electrodes made of AISI 1010 carbon steel was used (dimensions: 89 × 20 × 2 mm) in the study. Moreover, a dedicated testing vessel was designed and constructed. The electrodes were supported on a special, grooved glass frame to ensure their stability during the experiment and to maintain contact with the solvent. Several aspects of the corrosion measurement of general and localized corrosion modes were scrutinized extensively. The incipient attempts to quantify impact of process parameters (temperature) and impurities (e.g. water, oxygen and chlorides) on carbon steel corrosion in the pure sulfolane provided meaningful data [18]. Moreover, the oxygen ingress to the pure sulfolane showed minimal impact on the corrosion rates but engendered enhanced localized corrosion activity. As we observed, chlorides enhanced both general and localized corrosion, respectively. The obtained findings for carbon steel demonstrate the applicability of multi-technique electrochemical monitoring systems for rapid and accurate detection of sulfolane corrosion [17,18].

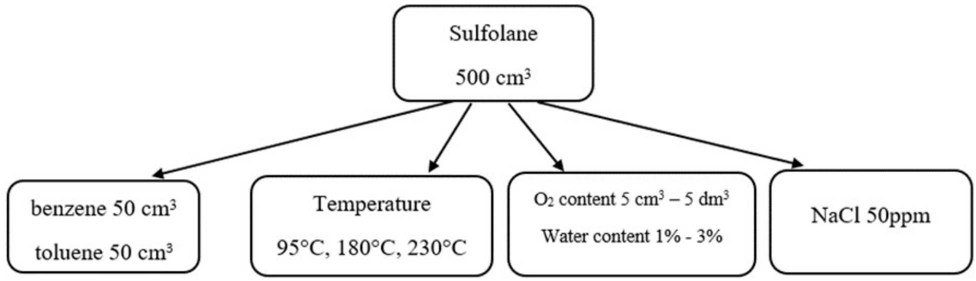
Materials and Methods

Pure sulfolane is not considered to be a substance causing or accelerating corrosion and destruction of steel. The corrosion of steel associated with the use of sulfolane is the result of the by-products of the decomposition of sulfolane. The main reason for this type of corrosion is the presence of impurities at individual extraction stages of the sulfolane usage, which accelerate decomposition processes. In particular, oxygen or chlorides in contact with sulfolane cause its degradation. Sulfolan is thermally stable up to about 220 °C when it begins to break down into sulfur dioxide and a polymeric material. Oxygen is present in the extraction by air penetrating into the vacuum processes or by the air dissolved in the hydrocarbon feed. Direct reaction of sulfolane with oxygen creates sulfuric and organic acids as well as aldehydes and ketones. Sulfolane degraded by oxygen has a lower pH, a higher acid number and a darker color than pure sulfolane (Figure 3). In addition, under oxygenating conditions, it tends to reduce the efficiency of aromatic compound extraction in the aromatic extraction process [19].

The main purpose of the described pilot-scale study conducted on carbon steel AISI1010 was preliminary analysis of selected factors that could potentially affect the low-conductivity corrosion rate. Monitoring of specific parameters allows to determine trends, similarities and differences between general and local corrosion mechanisms. Laboratory tests regarding the impact of process parameters (temperature) and pollutants (oxygen and chloride) on the corrosion of the carbon steel in pure sulfolane provided important data and clues that may find the practical application in the large-scale industrial processes. For the purpose of the proposed investigations a dedicated testing vessel was designed and constructed as well. Electrodes were supported on a special, grooved glass frame to ensure their stability during the experiment and maintain contact with the solvent. Electrodes were separated by additional glass spacers. Electrodes were immersed in a round bottom, thick-walled reactor vessel of 500 cm^3 capacity, made of heat-resistant glass. The test vessel was also equipped with mercury thermometer and a reflux condenser with a moisture adsorber filled with $CaCl_2$. The overall corrosion-test setup is shown in Figure 4. To limit the contact of liquid with air, special silicone-type grease was used on all glass connections. For additional protection against the air ingress, each experiment was conducted under inert gas (99.995% Argon) blanket. The test vessel was placed in a heating bowl and heated to the appropriate temperature. During experiment (c.a. 96h) sulfolane solution was continuously stirred (c.a. 1000 rmp, 1 cm magnetic stirrer) to simulate flowing conditions.

Fig. 4. The laboratory-scale setup for sulfolane corrosivity evaluation.
Source: [Own study].

All measurement results were recorded using the industrial electrochemical monitoring system – SmartCET, which uses low frequency impedance (LFI), harmonic distortion analysis (HDA) and electrochemical noise (ECN). Each parameter, e.g. general corrosion rate, local corrosion potential (Pitting factor), current Stern-Geary coefficient – B value and Corrosion Mechanism Index (CMI) were measured and recorded at 60 second intervals using the appropriate data recording system. The brief description of measured parameters is given in Table 1. The experiment time was set to 96 hours on the non-standard electrodes made of carbon steel AISI1010. A series of corrosion test were carried out, maintaining the process temperature in the range of 95ºC, 180-190ºC and 230-240ºC with the pure sulfolane [17,18]. During the experiments with the addition of oxygen, an air was introduced under the surface of the sulfolane solution in the appropriate quantities within 3 days. The influence of chlorides (50 ppm) on the steel corrosion was examined as well. The detailed description of each of the conducted experiments is beyond the scope of this paper; therefore we focused on the introduction of the selected water case study.



Sch. 2. Experimental design diagram.
Source: [Own study].

Tab. 1. Description of recorded corrosion parameters

Parameter	Definition
General corrosion rate (PV)	Measurement of the real part of the Low Frequency Impedance (LFI) of the working electrode. SmartCET uses Linear Polarization Resistance (LPR) technique to calculate the General Corrosion Rate, that is usually the prime variable of interest, because it reflects the overall rate of metallic corrosion. Corrosion may be directly related to operational parameters, e.g., temperatures, flow, chemical composition.
Pitting Factor (PF)	Ratio of the depth of the deepest pit (point or small area, that takes the form of cavities) resulting from corrosion divided by the average penetration as calculated from weight loss. It is a measure of the overall stability of the corrosion process obtained from a measurement of the intrinsic current noise of the working electrode and comparing this measurement to the general corrosion obtained from the LPR measurement.
Dynamic B value	Corrosion constant also known as the 'Stern-Geary constant'. It is an essential part of the corrosion rate calculation being directly proportional to the corrosion rate value. It represents a correction factor constant determined by the mechanism/kinetics of the corrosion process. In a dynamic process the B value is not constant. The knowledge of the B value enables to refine the LPR-generated corrosion rate estimatimation, since the uncertainty regarding the standard (default) B value is removed. The B value is directly related to the mechanistic properties of the component anodic and cathodic corrosion processes.
Corrosion mechanism indicator (CMI)	The CMI is a qualitative indicator of a surface film presence. If there is no film and only corrosion is present, the CMI will have an intermediate value. Inorganic scale, or thick passive oxide films with little or no conductivity, will show a low CMI value.

Source: [20].

Results and Discussion

All experiments were monitored using the Honeywell CET5500 Corrosion Transmitter at selected intervals (60 seconds) and recorded using a computer system for 96 hours. To visualize and interpret the results obtained from the experiments, two software scripts were implemented in the MATLAB environment for downloading and analyzing data from a text file, where a data binning (or bucketing) as a data pre-processing was used to show more accurately the trends of measured values – the average value was calculated from each interval. The implemented software scripts and operational configuration of the laboratory-scale aparature were applied to monitor the water content (1%, 2% and 3%) and corrosion parameters such as general corrosion rate (PV – primary variable) expressed in mils per year (mpy), localized corrosion potential (dimensionless Pitting Factor), actual Stern-Geary coefficient – B value (mV) and a capacitance-related Corrosion Mechanism Indicator (dimensionless CMI). It should be emphasised that pure sulfolane used for experiments contained less than 0.2% vol. of water; however it was interesting to analyse the impact of water content on the corrosion processes on the carbon steel (AISI1010). Under the extreme of some measurements (temperature >230°C), it is obvious that the water would evaporate when the temperature exceeds 100 ºC, therefore we decided to conduct our experiment at a temperature not exceeding 95 ºC.

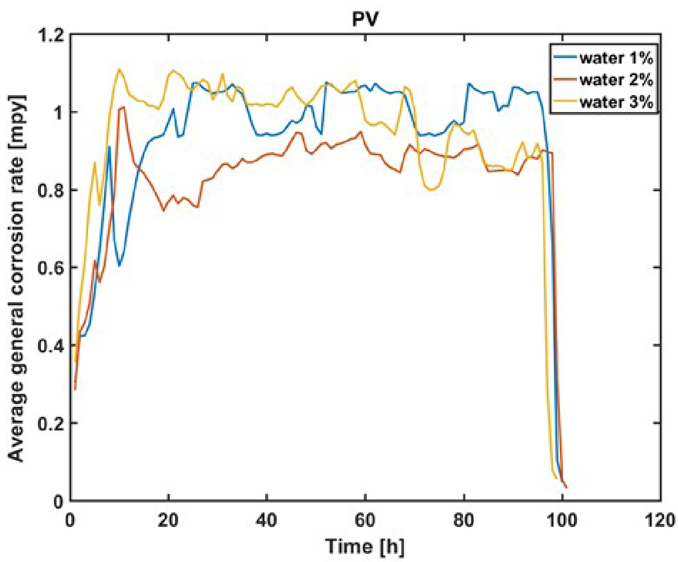


Fig. 5. General corrosion rate measured in sulfolane solutions with the addition of 1%, 2% and 3% vol. water at 95°C.

Source: [Own study].

Surprisingly, the general corrosion rate does not increase with the amount of water in sulfolane solution; however some general trends were easily observed. It is evident that, in the first 15 hours of each experiment the average PV parameter is increased and subsequently stabilized with the fluctuations in the range of approximately 0.2mpy as illustrated in Figure 5. We confirmed some general correlations between water concentration and sulfolane corrosivity that were reported in the literature, where water above concentration 3% accelerate sulfolane degradation and production of acidic corrodents [16,17].

For all experiments with water-contained sulfolane the localized corrosion potential, expressed by Pitting Factor, was at very low level (<<0.1) indicating domination of general corrosion mechanism as depicted in Figure 6.

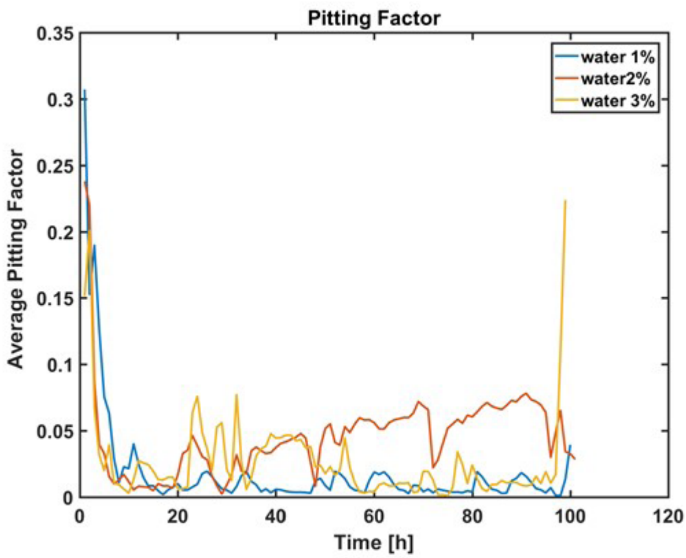


Fig. 6. Localized corrosion potential measured in sulfolane solutions with the addition of 1%, 2% and 3% vol. water at 95°C.

Source: [Own study].

The B value (see Figure 7) is quite stable during the experiment irrespective of water content; however the presence of water at concentration of about 1%vol, at 95ºC, generated the lowest level of corrosion. After the initial fluctuations the CMI parameter for the experiments with water addition did not exceed 50 units (see Figure 8), which means that no surface layer was formed during the measurement.

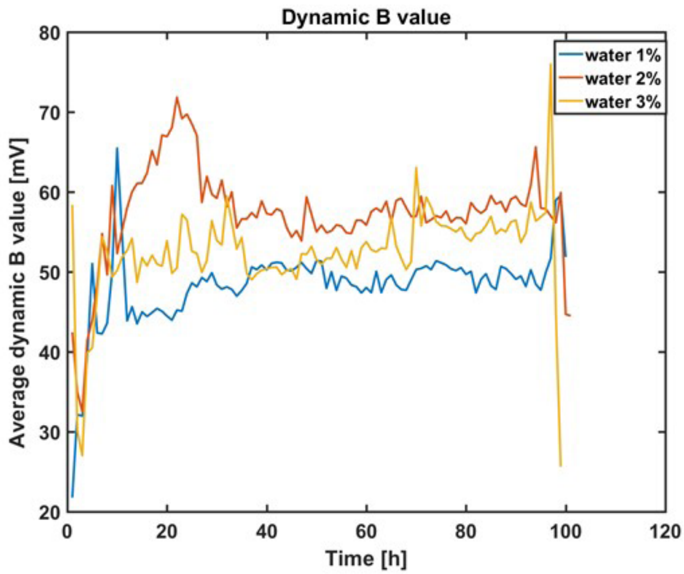


Fig. 7. Dynamic B value measured in sulfolane solutions with the addition of 1%, 2% and 3% vol. water at 95°C.

Source: [Own study].

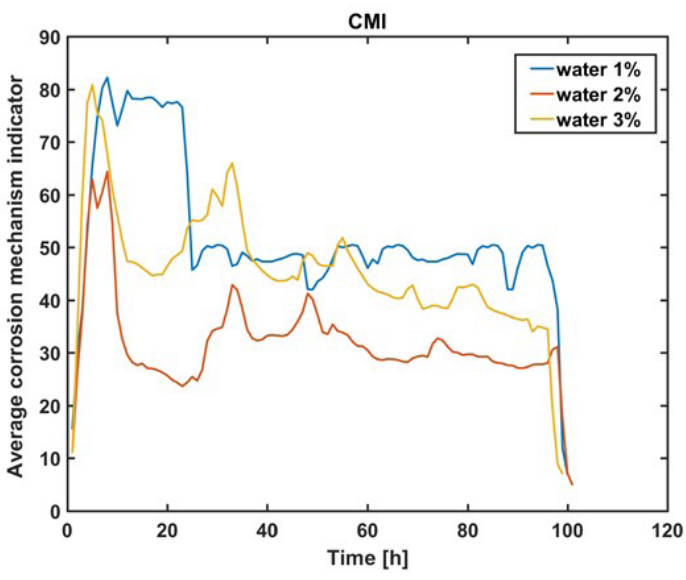


Fig. 8. Corrosion mechanism indicator measured in sulfolane solutions with the addition of 1%, 2% and 3% vol. water at 95°C.

Source: [Own study].

An interesting observation was made regarding sulfolane color during the experiments in sulfolane-water system. The more water in the solution the more black sediment was observed as illustrated in Figure 3. It seems a bit surprising since all experiments were performed at about 95ºC, that is far below sulfolane decomposition temperature (200-230ºC). Apparently, presence of water accelerates decomposition reactions, even at relatively low temperatures, causing more suspended solids, but also increasing the corrosion level.

Conclusions

A relevant subgroup of water and soil contaminants is composed of the sulfur-based derivatives and their metabolites, sometimes called as 'old devils of green chemistry' due to their detrimental impact on human health following long-term exposure. In over-polluted world contemporary chemistry plays a key role in the design of the sustainable, atom-economical and operationally simple procedures to produce eco-friendly (by-)products; however some industrially-engineered solvents are invariably regarded as environmentally unfavorable. On the other hand, the demand for environmental protection is the major driving force for the imposition of the increasingly stringent regulations governing the emission of hazardous pollutants and reduced sulfur compounds. The growing public awareness of necessity for reducing the burden of ecosystem is constantly pushing industry to develop and/or optimize the manufacturing technologies. In fact, the eradication of sulfur-based compounds can be performed in the liquid-liquid extraction process, therefore 'green' solvents and cost-effective large-scale procedures are highly desirable. An attractive alternative to commonly used industrial extractive liquids is sulfolane – a versatile dipolar aprotic solvent. Due to its 'unique' physicochemical properties as well as the potential of sulfolane to cause equipment corrosion and subsequent spills it can be both regarded as 'magic extractor' or 'bad actor' [18]. The primary objective of the presented case study was to verify applicability of industrial, multi-electrochemical technique for reliable detection of corrosion in low conductive process fluids. Several aspects of corrosion measurement of general and localized corrosion modes were investigated using the dedicated testing vessel that was designed and constructed. A number of experiments to evaluate the impact of different process parameters on the corrosion behavior of AISI 1010 carbon steel in sulfolane were carried out. In summary, a noticeable impact of water (even at low temperature) on sulfolane corrosivity was observed, where the increase of water concentration accelerates sulfolane degradation as indicated by elevated corrosion rate and increase of suspended dark deposits. It should be highlighted that the described case study should be enhanced including a wider range of solution conditions and the corresponding electrode surface analysis, respectively.

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Bartosz Stanisław Bednarz

Warsaw University of Technology
Faculty of Building Services, Hydro and Environmental Engineering
Division of Hydraulic Engineering and Hydraulics
bbednarz.wis@gmail.com

NUMERICAL VERIFICATION OF THE THICKNESS OF GRP PANELS FOR MODERNIZATION OF LARGE-DIAMETER SEWAGE COLLECTORS WITH NON-CIRCULAR CROSS-SECTIONS

keywords: GRP, relining, pipelines, numerical modeling, FEM, trenchless methods

The article was made at the Department of Hydraulic Engineering and Hydraulics under the scientific supervision of Prof. Paweł Popielski PhD. Eng.

Abstract:

Today, development of cities and metropolises creates new challenges related to providing residents with appropriate living conditions. More and more intensive expansion and modernization of water supply system and sewage networks, water treatment stations and sewage treatment plants is needed. It also involves the renovation of existing networks which, due to their long operating time and outdated technology, require the necessary repairs. Trenchless methods are increasingly used for this purpose. There are many new technologies for modernizing existing networks. One of them replaces existing infrastructure by creating a new object or as others e.g. Relining – regenerating pipelines or collectors by new self-supporting elements, preserving the existing structure. One of the methods is based on regeneration using GRP panels.

The aim of the article is to compare the efficiency of dimensioning and selection of the appropriate The GRP panels wall thickness for non-circular sections using analytical methods and numerical methods taking into account the collector-soil interaction.

The analysis of GRP wall thickness selection was carried out on the example of a hypothetical collector model with a non-circular cross-section. To analyze the aforementioned issue, the finite element method (FEM) was used.

Introduction

Intensive expansion and modernization i.a. water supply and sewage networks, water treatment stations and sewage treatment plants in times of rapid development of cities and metropolises are needed. It also concern the renovation of existing networks that require the necessary repairs due to the long service life.

Existing collectors subjected to modernization were formerly built as rigid objects. Objects of this type, placed in soil, practically do not deform under the influence of loads acting on them, and the lack of deformation of the cross-section causes that there are large concentrations of stresses in the cross-section, especially at low compaction of soil in the side zones of a construction excavation. [1],[2]

Nowadays, the collectors are made mainly of flexible materials, which thanks to their elasticity interact with the surrounding soil during loads transfer. The distribution of stresses in such objects is characterized by high homogeneity in relation to rigid objects. [1],[2]

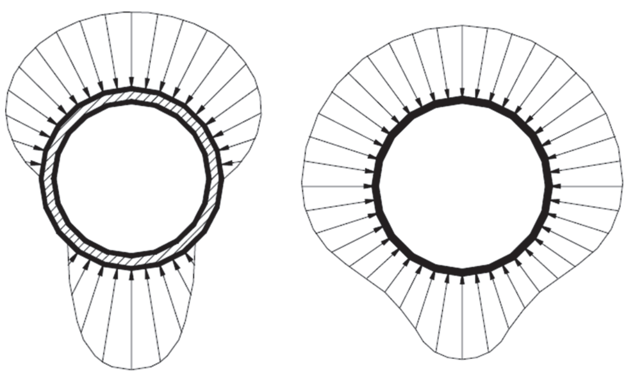

Fig. 1. Load distribution for rigid pipe (left) and for flexible pipe (right)
Source: [1].

The main advantages of collectors made of materials flexible is: [1]
- low weight in relation to rigid pipes (stoneware, cast iron, concrete),
- high ring stiffness at low wall thickness,
- the possibility of producing pipes with large lengths,
- long period of expected exploitation,
- resistance to degradation and reduction of strength and hydraulic properties,
- high abrasion resistance of the collector’s active surface,

- low operating costs,

Building of collectors from flexible materials also has disadvantages, i.a.: [1]

- lack of experience in using pipes confirmed by real measurements and observations,
- instability of strength parameters over time,
- susceptibility to deformation under load,
- difficulty in determining the collector-soil cooperation,

Therefore, it is important to include in the calculations the collector-soil interaction. The appropriate amount of information regarding the parameters of the soil and the collector is also important, because with a poor recognition of the soil center and the complicated collector cross-section, calculations may be diffcult and their results may be unreliable.

Many new technologies are created to modernize existing networks from the methods of replacing existing infrastructure with new pipelines to methods so-called *relining* – the process of pipeline/collector regeneration using new self-supporting elements, preserving the existing structure.

One of the methods of renovating collectors using the relining method is based on regeneration using thin-walled GRP panels (Glass Reinforced Plastic). This technology consists in inserting or pulling a new pipe into the repaired pipeline. The space between the panels and the channel is filled with the injection mass which works well in the case of various materials from which the channel is built, such as brick, clinker, stoneware, concrete and plastics. [3]

Fig. 2. The GRP panel during transport (left) and during assembly in the existing collector (right)

Source: [4].

The GRP panels are elements of the collector made of polyester resins reinforced with fiberglass. Due to the multilayer structure, they are called composite pipes.

The following technologies can be distinguished in the production of GRP panels:

- *centrifugal casting*, where the wall of the pipeline is built from the outer layer in a rotating casting mold. After placing all the ingredients in the mold, the speed of rotation of the mold increases. Thanks to the centrifugal acceleration, which can reach up to 75 G, the individual layers of the tube join in a compact composite with no lacks between the layers. At the final stage of production, the pipeline go through a thermal curing process. Rotation of the casting mold during the production process ensures that the pipeline is maintained circular shape and uniform wall thickness along its entire length. [5] This technology only allows the production of circular pipelines.
- *helical fi lament winding*, where pipelines are made on special forms by winding mats of glass fibers and roving fabrics (sheets composed of one or more two-directional fiber layers), or by spraying fibers glass saturated with polyester or vinyl ester resins. [4] The local reinforcement is mainly in the form of: mats, roving fabrics, unidirectional tapes and three-dimensional fabrics. [6] With this technology, it is possible to obtain any shape of pipelines with variable wall thickness in cross-section. [7]

Numerical calculations

The thickness verification calculations for GRP panels were made on the example of a hypothetical concrete collector model with a non-circular cross-section of dimensions 3.0x2.5m (with technological shelves of 0.5m height, on both sides, reducing the flow of sewage for low levels). The calculations took into account the collector-soil interaction, in order to reflect the actual working conditions of the structure. [8] The collector was placed at a depth of 8.65 m below the terrain in a homogeneous soil with the properties of fine sand, whose parameters were determined based on experiences. Table 1 shows the properties of the soil. For the soil, a plastic-elastic model was used with the Coulomb-Mohr plasticity condition as *continuum* elements.

For the GRP panels, *3D Shell* elements with the parameters given in Table 1 were used. The existing collector has been modeled using dedicated *continuum for structures*. Between the *3D Shell* and the *continuum* elements the contact zone (*interface*) was used.

Tab. 1. Variants of the application of the ultrasonic disintegration process of wastewater and sludge

No.	Type of material	E [GPa]	ν [-]	γ [kN/m3]	k [m/d]	ϕ [°]	c [kPa]
1	Concrete	200	0,20	25,00	-	-	-
2	Soil (fine sand)	45	0,30	17,50	1	30	0
3	GRP panel	800	0,30	17,50	-	-	-

Source: [9].

The calculations were made for the 1st and 3rd technical condition of the collector according to the ATV guidelines, where the 1st technical condition describes the existing collector capable of carrying loads together with the GRP panel and the injection between them. The 3rd technical condition describes the lack of load carrying capacity by the collector and injection, causing full transfer of loads to the GRP panel. [10]

Two types of cross-section shapes of GRP panels were considered. One of them (cross-section A) is determined by minimizing local stresses in which sharp edges are replaced with circular arcs. However, this results in a significant reduction in the area of the existing cross-section of the concrete collector. To fill the space between the existing collector and the GRP panel, a large amount of injections is needed, constituting 19% of the existing collector cross-sectional area. In cross-section B1, sharp edges have been preserved, so it maps the geometry of the existing collector cross-section and reduces the collector's active surface to a small extent. The cross-sections are shown in Figure 3. For all computational cases, a groundwater table was assumed at a depth of -5.0 m below terrain level (0.45 m above the collector).

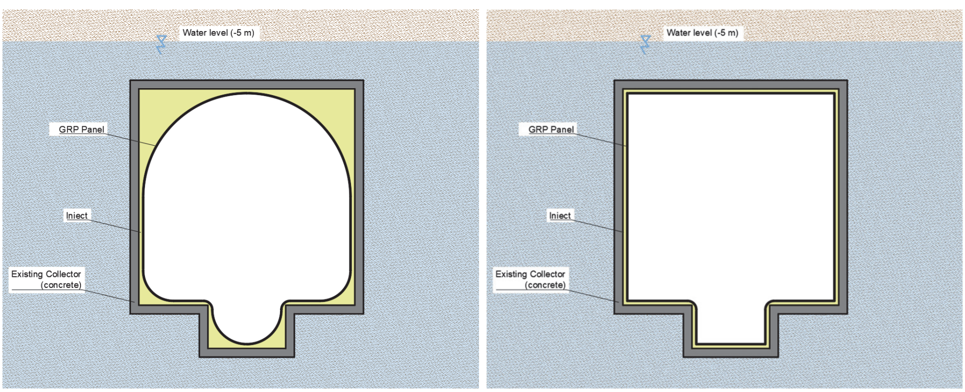

Fig. 3. The GRP panel during transport (left) and during assembly in the existing collector (right)

The wall thickness of the GRP panel was widened (Fig. 4) to reduce the concentration of circumferential stresses in cross-section B. The cross-section is referred to as B2.

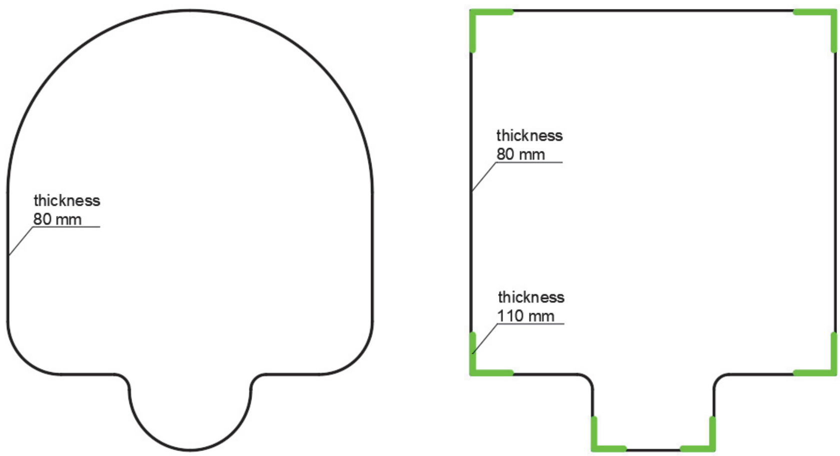

Fig. 4. Diagram of c-s A and c-s B2 (with thickening of sharp edges)

The difference in cross-sectional area reduction between the existing collector and the GRP panels is: 19% for the c-s A and 8% for the c-s B (the difference between c-s A and B is 11%). The difference in the use of injections between the A and B cross-sections is 58%.

The calculations were made for the 1st and 3rd technical condition of the collector [10] in the four stages shown in Fig. 5, where:

Stage 1 – initial state of stress of the substrate,
Stage 2 – construction of an existing collector,
Stage 3a – inserting the GRP panel with A cross-section and injection filling,
Stage 3b – inserting the GRP panel with B cross-section and injection filling,
Stage 4 – weakening of strength parameters of concrete and injection to soil parameters.

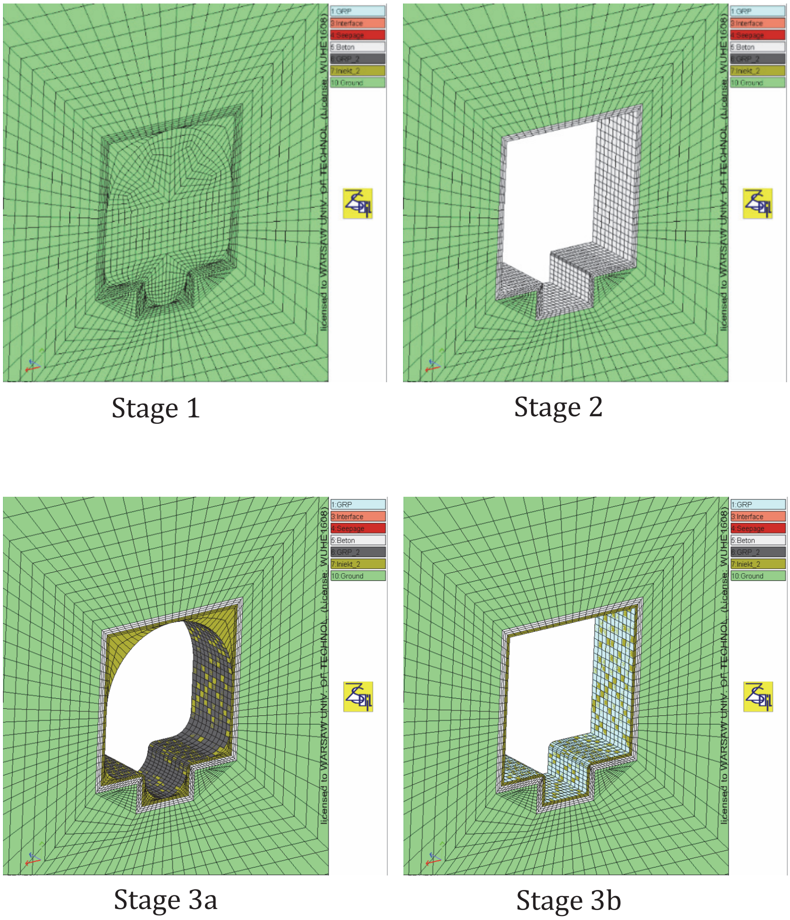

Fig. 5. Graphically illustrates the steps used in the calculation model

Analysis of 1st technical condition

The 1st technical condition describes situations where the existing collector is in a condition requiring repair for exploitation, but is capable of carrying loads.

For the assumed wall thickness value of 20mm, the circumferential stresses in the existing collector casing are very small. It can be noticed, however, that the change in thickness at the edges of the sharp section B causes a significant reduction in stress. The results are summarized in Figure 6 and Table 2. The displacement results were less than 1mm for all cross-sections.

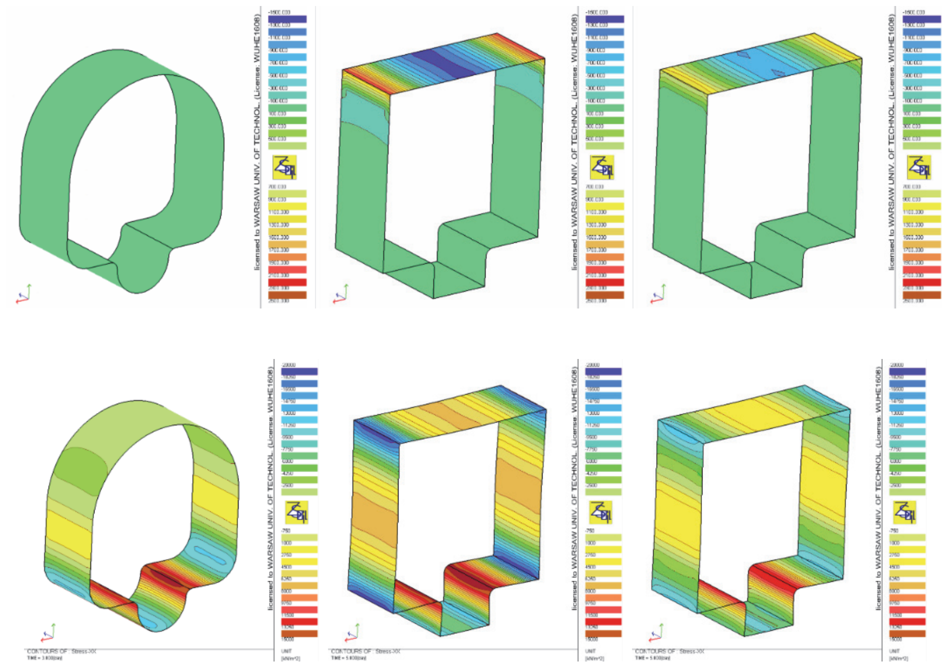

Fig. 6. The circumferential stresses for the cross-sections (in sequence) A (20mm), B1 (20mm) and B2 with variable wall thickness (20 / 30mm).

Numerical analysis allows to determine local stress concentration places, which gives the opportunity to choose places requiring reinforcement. In Fig. 6 it can be noticed that there is no stress concentration at the bottom of the panel section, so there is no need to change the thickness of the corners in this part.

Tab 2. The results of circumferential stresses in GRP panels for the 1st technical condition

Section name	Circumferential tensile stresses	Circumferential compressive stresses
	MPa	MPa
A	0.1	-0.1
B1	2.1	-1.3
B2	1.3	-0.9

Analysis of 3rd technical condition

The 3rd technical condition describes situations where an existing collector is in a condition requiring repair and is not able to carry loads. The GRP panel must therefore transfer the total load from the soil. For reasons of durability and maximum permissible displacement, the minimum thickness of the GRP panel capable of transferring loads from the soil has been chosen with the value of 80mm.

With the assumed soil conditions and the selected minimum wall thickness of the GRP panel, the circumferential compressive stresses in cross-section A were 11.8 MPa. For cross-section B1, circumferential compressive stresses having a value of 19.7MPa occurred (higher by 67% than values in c-s A). By expanding the thickness of the panel by 30mm in places as in Fig.7. we managed to reduce stress values to 12.7 MPa. It also influenced the reduction of circumferential tension stresses to the value of 13.1 MPa, (smaller by 20% in relation to the Circumferential tensile stresses in c-s A). The results are presented in Table 3.

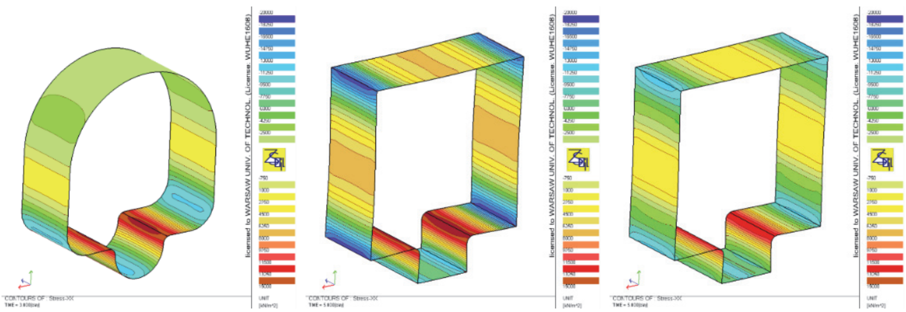

Fig.7. The circumferential stresses for the cross-section (in sequence) A (80mm), B1 (80mm) and B2 with variable wall thickness (80 / 110mm).

Tab. 3. Results of circumferential stresses in GRP panels for 3rd technical condition.

Section name	Circumferential tensile stresses	Change of value (ref. A)	Circumferential compressive stresses	Change of value (ref. A)
	MPa	%	MPa	%
A	16.1	-	-11.8	-
B1	16.7	3.7	-19.7	67,0
B2	13.1	-18.6	-12.7	7,6

The displacement values for the GRP panel are relatively large for the cross-sections B1 and B2 compared to the cross-section A, but are within the limits of permissible displacements. [10] For a panel with a B2 cross-section, a significant reduction of displacements in relation to the B1 c-s is visible. The displacement values for all cross-sections are shown in Table 4.

Tab. 4. Results of displacements in GRP panels for 3rd technical condition.

Section name	Horizontal displacement	Change of value (ref. A)	Vertical displacement	Change of value (ref. A)
	mm	%	mm	%
A	6	-	6	-
B1	28	366	21	350
B2	18	200	15	150

Summary

The use of GRP panels enables effective modernization of large-diameter sewage collectors by improving the load-bearing capacity of the existing collector structure.

The use of a local increase in wall thickness saves the use of glass fiber material, reducing the overall thickness of the panel wall, and allows you to save the amount of injection between the existing collector and the GRP panel.

Numerical analysis allows to determine places of stress concentration, which allows optimization of the location of the wall thickness widening in the GRP panel cross-section. This can means that numerical calculations are superior to calculations using analytical methods.

Displacements in the GRP panel with sharp edges come out much larger than in the panel with rounded edges. However, considering that the limit values of 6% of the vertical change in collector replacement diameter for the 3rd technical condition [10] have not been exceeded, It can be concluded that the GRP panels with a larger cross-sectional area (B) is more advantageous than the cross-section A in terms of the work surface.

The modeled sharp edges in the GRP panel in fact have the minimum radius of curvature resulting from the production technology. In this calculation, this aspect is omitted, but in practice it will have a positive effect in the form of additional stresses reduction.

When designing the wall thickness of GRP Panels, it is necessary to consider the economic factor that can determine whether the cost savings on injection translates into the cost of manufacturing panels of variable thickness. The transport issues should also be considered, where sharp-edged panels are more susceptible to damage.

It is recommended monitoring during repairs and subsequent exploitation of the modernized collector using GRP panels. This will allow for verification of numerical calculation and optimization them in the future.

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Weronika Rogowska

Bialystok University of Technology
Faculty of Civil and Environmental Engineering
45E Wiejska St., 15-351 Bialystok
rogowska_weronika@wp.pl

MAIN SOURCES OF MICROPLASTICS POLLUTANTS IN THE WATER ENVIRONMENT

keywords: microplastics, microplastics sources, wastewater treatment, litters, water ecosystem

Abstract:

Plastics are synthetic or modified natural polymers which contain additives that alter their properties. Plastics are wide-spread materials in everyday life and industry, because of lightness, durability, resistance to chemical agents and inexpensive production [2]. Huge quantities of wastes, which are proceed from plastics, are provided to the natural environment, in particular to water ecosystems [8]. Plastics can get in on environment as micro-sized products or generated by full-sized plastic products fragmentation; in this process microplastics are generated. Due to properties such as littleness, durability and widespread of potential sources, microplastics are able to pose a threat to the water environment [6]. Microplastics take part in diverse processes, such as migration, accumulation and adsorption, which procure their ability to integrate into natural processes in the ecosystem [40].

The paper has a general character. The purpose of the publication is to present sources and distribution of microplastic in water ecosystems and an analysis of microplastic pollutants' influence on environment.

Introduction

Presence of wastes is undeniably related to human activity and constitutes one of its indicators. In the modern 'era of plastics' – Anthropocene – plastics found tons of applications in the industry and daily life. However, cause of their durability, unsustainable usage and difficulty with domesticating of plastics wastes, they are accumulated in the environment [38]. Global production of plastics in 2016 hit over 320 million tones. Simultaneously, it is calculated that 5 to 13 million tonnes of wastes are located in oceans every year [35]. Plastics represent main component of pollution in rivers and other aquatic ecosystems. Products of their degradation also negatively affect on soil environment. The influence of full-sized plastic wastes – macroplastics as aquatic ecosystems pollutant is investigated for many years because of aesthetic considerations, which have specific importance of tourist industry. In addition, macroplastics pose a threat to many industry branches, for instance shipping or fishing [7]. Moreover, crucial danger is connected with influence on animals. Water fowl is often tangled in plastic elements. It is possible that birds consume plastic debris, which may yield wounds, inflammations, ulceration digestive system and even starvation of many individuals [37]. On the other hand a problem of occurrence small plastics debris in oceans first time was already pointed out in the seventies by Carpenter and Smith (1972) [7] but this concern is again differentiated; currently researches in the matter of wastes emerging from plastics are carried out and take so-called microplastics on a board. Microplastics particles widely exist in diverse ecosystems [20]. The problem connected with occurrence of microplastics in environment considers toxic substances in composition and an ability to accumulate heavy metals from surrounding environment [39]. It is established that much of organic pollutants are accumulated on surface plastic particles and inside them [25]. What is more, plastic debris takes part in interactions with organisms which settle freshwater and marine ecosystems by plugging into food webs. Thereby microplastics are widely detected in bodies of aquatic organisms [34].

The purpose of paper is instigating the topic of microplastics, sources of plastic debris in environment and behaviors in aquatic ecosystems.

Plastics and microplastics

The term 'plastics' is used to describe subcategory of large material class, which are polymers. Polymers are long-chained molecules, so they are marked high average molecular weight. Polymers can consist of interconnected identical subunits (homopolymers) or subunits which are diverse and associated each other (copolymers). Materials which became softened during heating and differentiated by ductility are called plastics. These include both original plastic elements as well as the resins mixed with numerous additives to enhance the performance of the material. The most common additives are fillers, plasticizers, dyes, stabilizers and processing aids. Except thermoplastic materials, to plastics should be included heat-hardening materials, which cannot be plasticized by heating [18]. Plastics has many applications because of durability. Low manufacturing cost, lightness and ability to treat products from oxygen and moisture contribute to use plastics as packing and displace materials such as glass, metal and paper [1].

Microplastics are not homogeneous group of substances. They may differ from each other polymeric constitution, size, and shape and may contain additives or be in lack of them. All of these features have an impact on proceedings small plastic debris in environment [19]. Usually there are named two types of microplastics. The distinction base is a fact if plastics were produced in small size all along or tiny particles flaw as a result of large elements fragmentation. The division let isolate sources of microplastics in environment to some extent.

Primary microplastics are produced in size smaller than 5 mm [9]. They have many applications, including manufacturing plastics goods – plastics pellets are melted and molded into proper products [18]. Moreover, plastic pellets are utilized to forming cosmetics and hygiene products to face, hands etc. [1]. On the other hand, primary microplastics have the deployment as a matter of scrubbers used to remove rust and coloring from engines and hulls. Pellets are used repeatedly, up to taper of force and sizes decrease. As a result of this process microplastics often are contaminated by heavy metals, for example cadmium, chromium and lead [7].

Secondary microplastics come into being as a result of disintegration large plastic elements. The proceedings may take place on the landmass, as well as in aquatic ecosystems. In the environment, due to physical, chemical and biological processes, small plastic debris are formed [7]. Creation of this type of plastic debris may ensue before the leak to the environment [10], for instance during usage of products such as artificial textiles, tires or dyers [18]. Secondary microplastics have an ability to stay in freshwater ecosystem for days and it does not depend if reservoir is natural, modified or structured by humans [10].

Microplastics sources in environment

The knowledge about plastics presence and influence in freshwater and terrestrial ecosystems is definitely lower than the awareness on the subject of debris in the marine environment. Tiny size and low microplastics density are conductive to migration on long distance, in particular due to ocean current. The presence of microplastics stated on every continent shoreline [10]. It determined that total amount of pelagic particles of microplastics in east Asian seas is larger by whole order of magnitude than in other world oceans [16]. Microplastic particles were detected in many rivers, including the Rhine [23], Thames [15], Nile, Niger and Congo River [17]; seas: Mediterranean Sea and Sea of Cortez [13] and lakes: Lake Victoria, Tanganyika, Lake Chad [17]. Sediments of Gdańsk Bay are also contaminated [45]. Presence of microplastics was noted in organisms which live in the Baltic Sea – 23% cods and herrings from the Baltic Sea and the North Sea had plastic elements in stomachs. These plastic debris had a diameter larger than 100 μm [21]. According to the International Union for Conservation of Nature (IUNC), sources of microplastics include: synthetic textiles, tires, layers of marine vehicles and personal care products [3].

It is necessary to get better to know sources, from where plastic debris penetrates to the environment and mechanism how it works to prevent problem of microplastics. There are many potential sources but wealth of them hinders to fix accurate plastic pellets background. Plastic wastes, thrashed deliberately or inadvertently, may be launched to marine ecosystems directly or mediately by rivers, low tides or wind [31]. Published research indicate that occurrence of microplastics in aquatic ecosystems is connected with areas, where industrial activity is elevated, for example urbanized sites or harbors [30]. In certain cases there is the possibility to connect microplastics appearance with specific industry sector but it is necessary to allow for diverse constitution. It procures a difficulty with determinate their origins [18]. Secondary microplastics are produced during fragmentation large plastic elements, what make additional trickiness with assigning particular source. Sewage treatment plants are different source of plastic debris in aquatic ecosystems [4].

Sewage treatment plants

There is observed the correlation among microplastics quantity and population density but connection between population density and diameter of plastic elements is not clearly notified. By reason of this hypothesis quality of sewage treatment has an important meaning in microplastics distribution. Larger impurities are removed in sewage treatment plants, but cleaning devices are not adapted to retain so small-sized particles. Despite the bulk of sewage are not carried to the environment, former places of discharge to surface waters contained approximately 250% much more microplastics than referenced places in 2011 [4].

Sewage treatment plants remove pollutants due to diverse physical, biological and chemical processes. In the stream of sewage quantity of microplastics reaches 10^4 to 10^5 particles/m^3 and incomplete removals yield an emission to ecosystems [11]. The most of wastewater treatment facilities in industrial countries have developed primary as well as secondary phases of cleaning but in sewage treatment plants which work rightly majority of plastic debris is removed in initial stages [5]. The most important phases of cleaning, guided removal microplastics, are disposure of greases and sands. Wastewater treatment facilities may be successful in combating plastic particles from municipal wastes but tiny amounts of microplastics released per liter may cause significant quantities these type impurities in environment. It is a result of huge volume swage which are treated [27]. In some countries sludge cake is used to fertilize farmlands, as a result plastic debris migrate to soil and consequently, by surface runoff, to aquatic environment [42]. According to research conducted in Great Britain, samples, which were collected from sewage sediment landfill places on coast of six continents, contained one microplastics particle per liter on average. Major part of these particles comes from synthetic textile fibers from the drain of the washing machine [4].

Synthetic textile materials

There are some evidences, that one of the most important sources of microplastics are synthetic fibers from clothing. In fact, colored elements stand main type of microplastics and it may mean that municipal waste is crucial source of plastic debris in environment, because of colored products application is more probably in daily consumption than in fishing nets or lines. Plastics play a key role in maintenance of human comfort in the modern world and dyeing is common way to improve market attractiveness of plastic goods [41]. A quantitative research, which determined microplastics concentration in 18 places in the world, demonstrated that one single clothing element has an ability to release more than 1900 microplastic fibers per washing. Ensuing microfibers migrate to the marine environment due to cleaned sewage discharge into surface waters [25]. Secondary microplastics produced as fibers from synthetic textiles (mainly made out of polyester, acrylic and polyamide) washing are able to reach quantities higher than 100 fibers per liter of sewage [10]. Marine habitant situated in proximity to sewage disposal places contain proportions of polyester and acrylic microplastic fibers reminiscent ratio of these materials, deployed in synthetic clothing production [25]. It is affirmed that microplastic fibers from textiles have a capability of persisting in whole food chain, from zooplankton to large animals such as whales [3].

Cosmetics and personal care products

Microplastics are used to manufacturing cosmetics to substitute natural desquamative components, for example pumice, walnut husks or apricots stone. They are present in many products, including skin care products, soaps, toothpastes, shampoos, suntan creams, facial and body scrubs etc. Approximately, 93% of ‘micro balls’ applied in cosmetics are made out of polyethylene, although they may consist of polypropylene, polymethacrylate or nylon [29]. Single desquamative cleaning product may contain until 360 000 micro-pellets. Microplastics contained in personal care products after applications migrate through drainage, but cause of small size, part of them come in aquatic ecosystems [12]. It is considered that microplastics in sewage treatment plants come not only from cosmetics and personal care products but also from many others plastics such as fragments of larger objects. It is impossible to track precisely the origin of pellets because of the same polymers have diverse applications. For example, polyethylene is widely applied such as cosmetics component but also polyethylene is the most popular type of plastics produced in the world so these elements may descent as well as from personal care products and millions other sources [22]. As of today, sale of cosmetic products which contains microplastic pellets is prohibited in the USA, Canada, Australia and in some European nations. More countries probably launch similar bans but focusing on personal care products only will not eliminate every culprit of microplastics penetration in aquatic ecosystems. Even if using plastics in cosmetics production will be banned, this type of impurities will still penetrate to environment [44].

Fishing

Recreational and commercial fishing, water carriage and marine industry are sources of plastics, which have an ability to penetrate to marine environment, causing a threat for fauna and flora, as well as macroplastics and secondary microplastics after long-standing degradation. Microplastics are produced as a result of discarding on shore materials, which were carried by longshore and ocean currents [33]. For instance, ships repair works in dry docks may pose a source of polyurethane, nylon, polystyrene and polyester pellets. Moreover, worn and eroded monofilament lines, fishing nets and rope made form polypropylene are also responsible for presence of plastics in aquatic ecosystems [28].

Plastics products industry

During manufacturing products from plastics, fine resin pellets are pick up on as feedstock. Many of plants, where plastic raw material is used, are located nearby water reservoirs, what render a threat those materials, as a result of leak, during transport or inappropriate application can easily migrate to aquatic ecosystems. According to one of water research in Sweden, typical concentration of microplastics hovered inside 150-2400 plastic pellets/m3, whereas in harbor placed in the neighborhood of plastics production facility totaled 102 000 plastic pellets/m^3 [7].

Because of health considerations, an important meaning has also appearance of microplastics in drinking water. One of research demonstrated presence of small plastic elements in 93% of bottled water, derived from 11 different brands; there were computed 325 plastic pellets per liter on average. In comparison to tap water, water from plastic bottles contained twice as much microplastics. Some of impurities probably come from process of bottling and packing water [24].

Microplastics fate in aquatic environment

Distribution of plastic debris in aquatic ecosystems depends on type and localization of source and subsequent physical, chemical and biological processes, which guide their properties [18].

When the microplastic particles gain entry environment, their chemical structure is disintegrated and as the result of this process average molecular weight of polymers is decreased. Because of the fact, that the plastics mechanical integrity rest on average molecular weight, processes of degradation weaken a structure of material quintessentially. Macroscopic as well as microscopic elements can be degraded subsequently and in the sequel organic carbon is transformed to carbon dioxide and launched to marine biomass. The type of degradation is classed by factors, which bring the process. Types of degradation include:

- biodegradation – connected with activity of living organisms, mostly microorganisms
- photodegradation – influenced by light, usually the sunlight, on the outside
- degradation caused by thermooxidation – slow degradation influence by oxidation processes in mild temperature
- hydrolysis – the type of disintegration by water; there is no environmental degradation mechanism [1].

In the lump, plastics are characterized by long environmental lifetime. In large part of polymers, complete conversion degradation products to carbon dioxide, water and inorganic particles is extremely slow and mainly succeed as a result of UV-B radiation, derived from sunlight. Once initiated degradation may flow in thermooxidative process for some past time, without one more exposition on radiation, if there is fulfilled the requirement of oxygen approach. Research proves that other types of degradation are slower by an order of magnitude. Because of small sunlight availability and low temperature, the rate of plastics disintegration in marine ecosystems is significantly slower than on the land environment [40].

The most of plastics, for example polyethylene and polypropylene, may be transported in the marine ecosystems by sea and ocean currents. The currents pertain to perpetual, directed movement of water mass due to factors such as Coriolis effect, wind, differences in temperatures, salinity and the Moon gravitation [40]. Microplastics are susceptible to so-called biofouling, that is microorganisms, algae etc. accumulation on the particle surface and it rings that plastic debris reach the density similar to density of seawater and come into water column such as floating neutrally or slow-sinking particles, which lead to sedimentation [40]. On the ground of probable slow sedimentation of microplastic debris, on their dissipation may influence floating water circulation on various depth. It is verify that microplastics sedimentation amount to 10-150 meters per day. It indicates that plastic debris get to the seabed from surface approximately one month to up to one year. Sinking particle is able to float 1 do 35 kilometer in a lever, from the begin point [18]. Microplastic debris are accumulated in subtropical oceanic whirlpools as a result of concentration of convergent sea currents and in the 'not-opened' seas, such as Mediterranean Sea, where surface water is retained for a long time because of narrow circulation of water in the north Atlantic [18].

Plastics have an ability to absorb impurities on the surface. Some of contaminations observed in microplastics including polychlorinated diphenyls (PCB), polycyclic aromatic hydrocarbons (WWA), petroleum hydrocarbons, chloroorganic pesticides, polybrominated diphenyl ethers, alkylphenols and bisphenol A (BPA) [25]. Comparison of PCB and DEE concentrations in debris from seawater suggest high level of accumulation (apparent absorption coefficient within limits 105-106), what let to name plastics as transport medium and source of organic toxic chemical substances in the mare environment [26]. On the other hand, there is low knowing about metal absorption mechanisms. There was monitored the increase of metal absorption such as argentum, cobalt, nickel, lead and zinc to plastics with crescive pH. The influential role in this process plays presence of biofilm, which boost a charge, porosity and hydrophilicity of material [40]. It is assumed that connection between heavy metals and plastics has an important role in impurities exporting into digestive system many of organisms. As a result of this process, ensue bioaccumulation or releasing metals to water in more penetrable biological forms [14]. The shape can also plays a role in toxicity of ingested microplastics; long-shaped debris are reputed as more toxic than spherical ones [43]. Many of marine species organisms consume debris, confound it with the kill. Microplastics absorption though the digestive system may cause injuries and digestion containment but it may bring toxic results because of assimilation chemicals located on debris surface [36]. Moreover, small elements of plastics cause physical pounding, which lead to cell necrosis, infections and tissues wrenching in digestive system [33]. The entwining by plastic wastes and ingesting of them is noted in the dozens of thousands single individuals and at least 558 species, including all known species of sea turtles, 66% of whole species marine mammals and half of spices marine fowl. In some species, intake of microplastics is noted in over than 80% examined population [32].

Summary

This paper is a brief review in microplastics sources in aquatic ecosystems. Current state of knowledge to the subject of high order effects of microplastics presence in the environment is relatively thin. All things considered, plastic pellets quantities in the environment may depends on per capita consumption of consumer plastics, population demographics, and the capability of infrastructure to manage with plastic wastes. Plastic debris concentrations may evolve in time because of changes in population density and urbanization, development in sewage treatment technologies, wastes policy [38]. Better understanding of microplastic sources and mechanisms of migration into environment will help to introduce new techniques in plastic wastes removal. On the other hand, we cannot focus on plastics debris disposal but make a move in prevention. Efforts should include a well-balanced consumption of plastic goods, education, reuse and designs for recycling, plastic waste management. It is assumed that plastic debris may influence not only on single organisms but also they are have an ability to modify population structure, thereby impact on ecosystem dynamics [43]. Prospective accumulation of microplastics in the food chain, especially in fish and shellfish may have an influence on food safety and thereby on humans' health [18]. That renders problem of microplastics especially important and force to search new materials that could displace plastic and technologies, which safe the environment from still unknown consequences.

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Paweł Puzowski, Iwona Skoczko

Bialystok University of Tchnology
Faculty of Civil and Environmental Engineering
Wiejska 45 E, 15-351 Białystok
pawel.puzowski@wp.pl, i.skoczko@pb.edu.pl

WATER TREATMENT ASSESSMENT IN CHOSEN TOWN IN PODLASKIE VOIVODESHIP

keywords: water treatment, iron, manganese, filtration

Abstract:

The goal of the research was to assess the pollution level of water in the real water treatment station in Pelele in the municipality of Punsk. The station needed to be rebuild because the equipment in operation there have not been changed for years. As part of the research efforts, a new water purification system was designed. The technology of the station is based on a two-stage water treatment system. Water picked up directly from the intake (raw water) as well as purified water at the old and new stations were analyzed. Then the results obtained from water tests before and after modernization of the station were compared. There were such parameters analyzed as: color, turbidity, pH, iron (Fe), Manganese (Mn). Conducted research and received results of pollution parameters have proved that raw water as well as treated water have revealed level of Fe and Mn. Their concentrations have proved that water even in new station is not useful for human consumption just after modernization process.

Introduction

The definition of water quality is a set of features determining its suitability for specific purposes. From a chemical point of view, water occurring in nature is a solution of inorganic and organic substances appearing on the Earth (Skoczko 2019, Chełmicki 2001). The substances in the water are of natural or anthropogenic origin. They are dissolved or suspended in water, colloidal, sedimentary or flotating materials. Water quality is determined by comparing the parameters and required pollution indicators of the evaluated water with relevant regulations or standards. The aim is to define the conditions under which a water type can or cannot be used for a variety of human needs, including, for example, drinking water [www.wios.bialystok.pl]. Almost every type of water on Earth, if properly prepared, can be used in the production of drinking water. Most often, surface water resources of fresh (rivers, lakes, springs) or salt water (seas) are used for preparation and production of water for both economic and municipal purposes (Dowigałło2002, Skoczko et al 2016). The type of water intake depends on the geographical location. In areas dry and poor in surface water or with a significant surface run-off preventing adequate water retention, for industrial purposes and as a source of drinking water, groundwater is used. Groundwater is characterised by the Water Law Act of 20 July 2017. (Journal of Laws of 2017, item 1566, 2180, 2018, item 650, 710, 1479). It is located at various depths below the surface of the ground.

Underground water in Poland is one of the basic sources of water supply used both for household and industrial purposes and in industrial production. It is caused by the geographical location of Poland in areas of poor in water and high surface outflow. Poland is one of the poorest European countries in water. Therefore, underground water intakes are the main source of water. They are used by smaller and larger settlement units and industrial plants. In order to get out this type of water, it is necessary to build appropriate infrastructure and pressure systems (Dowigałło 2002, Raport Kraków 2014).

The composition of groundwater depends on many factors, including geological features of the aquifer, depth of water occurrence, length of the aquifer, size of the surface and time of water contact with rock matter, relation with soil surface and surface waters – including the manner of land management on the surface (Skoczko 2019). Unlike surface waters, groundwater is characterized by a constant physical and chemical composition, shaped by physical, biological and mainly biochemical processes, such as:

- oxidation and reduction,
- dissolving (leaching) and precipitation,
- hydration and hydrolysis,
- airing,
- adsorption, desorption, ion exchange and membrane processes,
- migration (dispersion),
- biochemical processes (Skoczko et al 2017).

The most common groundwater pollutants of natural origin are iron and manganese salts. They mainly come from the dissolution and leaching of magma or sedimentary rocks (Nawrocki 2000, Skoczko 2018). Iron and manganese ions are a potential hazard for drinking water and economic use as they cause overgrowth of water supply systems and household installations with iron and manganese scale. They also worsen the organoleptic properties of water, increase its colour and turbidity and change its taste. They must be absolutely removed from water in most industrial processes, especially in the case of their use in the agri-food, textile and pulp and paper processing industries (Szpindor 1998).

Water treatment processes

Groundwater needs to be properly prepared before being transferred to water supply systems. Due to its different levels of pollution before it is consumed or used in industrial processes, it should be treated. The technologies used today for water treatment based on solutions developed decades ago. Depending on the chemical composition of water, different variants of treatment processes are applied, which can be grouped according to the scheme below:

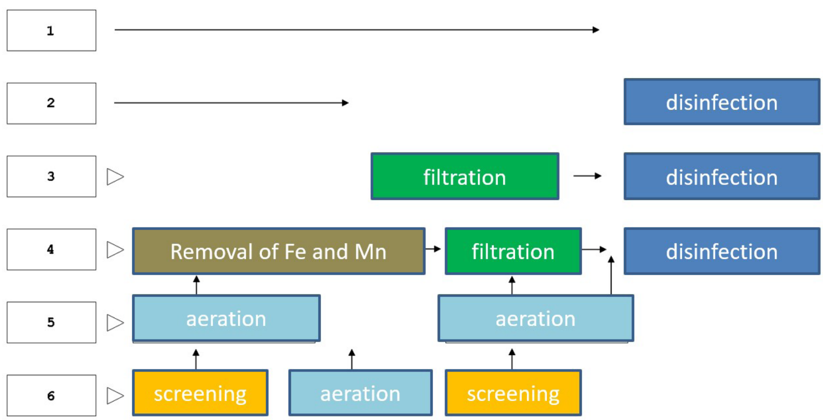

Fig. 1. Processes used in groundwater treatment [source: own study]

In most cases, there is no water of such quality in nature that it is suitable for direct use without prior treatment. Pre-treatment is therefore most often required. It is based on groups of processes taking different forms – from mechanical purification, filtration, disinfection to softening and demineralisation. Therefore, in order to decide which processes water should be subjected to, it is necessary to adopt suitability criteria for a specific application in advance.

The basic processes used in groundwater treatment are mechanical filtration and chemical final oxidation called disinfection. It should be noted that these technologies require considerable financial resources and constant service by qualified personnel. It is caused mainly by the use of preparations from the group of strong oxidizers showing a risk of improper implementation of the technology. Filtration is usually carried out on washed quartz sand or gravel of various grain sizes, which fills pressure or gravity filters. It happens that it is preceded by a coarse mesh filter installed at the beginning of the water treatment line. The filtration process ensures that only mechanically suspended, sedimenting or flotating particles are removed from the water. It allows to reduce turbidity and the amount of suspended solids and to slightly reduce the colour. However, underground water is often contaminated with excessive amounts of iron and manganese ions. Therefore, the process of iron and manganese removal is usually applied in the treatment plants. For this purpose, most often dedicated filter media with oxidative or catalytic properties are used, which allow to convert the degree of iron oxidation from Fe(II) to Fe(III) and manganese from Mn(II) to Mn(IV). In reality, however, one can find such treatment plants which do not use masses for iron and manganese removal. Instead, sand filtration is followed by aeration, which oxidizes the inorganic forms of Fe(II) with atmospheric oxygen. This method, however, is not possible to reduce the concentration of manganese. Therefore, in order to ensure the quality of the treated water, it is necessary to combine all these unit processes into a uniform treatment system. In view of the above, research is constantly being carried out into the use of methods to assist in the removal of iron and manganese salts from groundwater (Skoczko 2014, Niewulis 2017).

Water quality

The legal regulations on the quality of water intended for consumption are specified in the Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption (Journal of Laws 2017 item 2294). It states that water is safe for human health if it is free from pathogenic microorganisms and parasites, various substances in concentrations that pose a potential threat to human health and does not have aggressive corrosive properties. It should meet basic microbiological and chemical requirements as well as organoleptic, physical and radiological requirements specified in the Annexes.

Basic physical indicators include

- Turbidity – is caused by organic suspensions such as humus and inorganic compounds such as hardly soluble metal hydroxides i. e. $Fe(OH)_3$, $Mn(OH)_2$, clay, etc. The turbidity of water intended for human consumption should not exceed 1.0 NTU (nephelometric turbidity units) in the treated water.
- Colour – Chemically pure water is colourless. Under natural conditions, it takes on a shade of blue in thick layers. Contaminated waters take their colour from the chemical compounds dissolved in it. This is usually a green-yellow colour. The colloidal aqueous solution of platinum (1 mg / L = 10 platinum scale) is taken as the reference system.
- Taste and smell – these are the parameters tested organoleptically. Taste and smell are given by inorganic compounds dissolved in water, such as salts, acids, gases and organic compounds – most often products of the metabolism of organisms living in water in natural conditions. The Ministry of

Health defines these requirements as "acceptable to consumers and without inappropriate changes".

- Temperature – is a function of the energy of particles. This parameter is of fundamental importance in thermal technology (refrigeration) as well as in the food industry [http://beta.chem.uw.edu.pl/people/AMyslinski/cw3/ins3.htm].

Chemical indicators of water quality are: pH, COD, content of nitrogen, chlorides, sulphates, phosphates, iron, manganese, silicon, magnesium and calcium (hardness), alkalinity, dry residue, dissolved gases, etc.[beta.chem.uw.edu.pl/people/AMyslinski/cw3/ins3.htm].

- pH – This indicates whether the water is acidic or alkaline. The pH of most natural waters ranges from 6.8 to 8.5 pH.
- Alkalinity – This is the property of water caused by the presence of hydroxides, bicarbonates and carbonates Ca^2+, Mg^2+, K+, Na+. Therefore, alkalinity may be of bicarbonate, carbonate and hydroxide origin. There are two types of alkalinity:
- of the 'p' type by titration of HCl against phenolphthalein as an indicator (transition pH = 8,2...8,3),
- of the 'm' type by titration of HCl against methyl orange as an indicator (transition pH = 4,6...4,3). The alkalinity of the p-type is induced by hydroxides, the m-type is the sum of alkalinity induced by carbonates, bicarbonates, monohydrogen phosphates, dihydrogen phosphates, etc. up to pH = 4,3. Natural waters show alkalinity only to methyl orange. In the boiler technology the so-called alkaline number LA = p 40 is also determined, where: p – alkalinity to phenolphthalein.
- COD – It is used conventionally to determine the organic substances contained in water. It is determined by several methods. The COD value determined by the permanganate method is conventional, because only about 60% of the organic substances contained in water are oxidized. When the amount of Cl-ion is less than 300 mg/dm3 , COD is determined in an acidic environment. If the content of chlorides exceeds 300 mg/dm3, the determination in the alkaline environment should be carried out.
- Hardness – this is the content of calcium and magnesium ions in the water. The hardness is expressed as the amount of millial calcium and magnesium ions in the cubic decimetre of water. The so called hardness grades are also used to express it:
- German hardness grade (n) corresponding to calcium and magnesium salts equivalent to 10 mg CaO in 1 L of water,
- a French degree of hardness (f) corresponding to a calcium and magnesium salt content equivalent to 10 mg $CaCO_3$ in 1 L of water,

– English hardness grade (Clark) corresponding to calcium and magnesium salts equivalent to 14,3 mg $CaCO_3$ in 1 L of water.

Water intended for consumption and economic use should, above all, be safe for human and animal health and, clean and tasty. It must not contain bacteria, e.g. Escherichia coli. Furthermore, the water must not contain more than 0.050 mg/L of manganese and less than 0.200 mg/L of iron. The content of microelements is desirable. The presence of calcium and magnesium salts – up to a total of 500 mg/L per $CaCO_3$ – is therefore permitted. In the group of dissolved gases, methane, ammonia and hydrogen sulphide must be completely eliminated. The permissible content of dissolved CO_2 must not exceed 2 mg/L. Water for the food industry should generally meet the same criteria as water intended for human consumption. Exceptions are plants that heat water solutions to temperatures above 60 °C, e.g. breweries or distilleries. In this case, the water should contain less dissolved salts responsible for the hardness, i.e. it should be soft. Dairy feed water, on the other hand, must not contain dissolved oxygen, not even trace amounts of microorganisms, iron or manganese.

For the preparation of water for human consumption and for the needs of the various branches of the food industry, the sanitary requirements set out above shall be taken into account in particular. However, for other industrial processing technologies, the chemical composition of water and its physical parameters play an essential role. The technological requirements are varied. The composition of purified water also varies from solutions containing only selected indicators to ultra-pure water. It depends on the type of production technology as well as quality requirements of products and raw materials. The water supplied to the metallurgical industry should be different, the water supplied to the electronic industry should be different, and the water supplied to the cosmetics or pharmaceutical industries should be different. Water should have a constant temperature, regardless of the season. It must not contain solid impurities of organic and inorganic origin. It should also often be soft and not contain dissolved salts and gases.

In view of the above, the objective of the research was to analyze the effectiveness of water treatment at a water treatment plant in a selected locality in Podlaskie Province. The plant was modernized by changing the treatment system. The effect of water treatment before and after modernization was compared.

Material and methods

As part of the research carried out, there were undertaken the analysis covered the water treatment plant in Pelele in the municipality of Punsk.

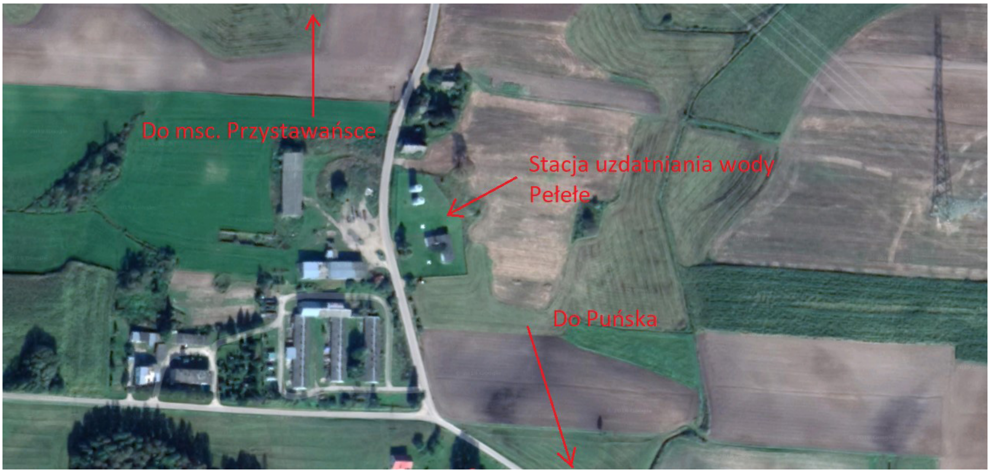

Fig. 2. Localisation of modernized water treatment station in Pełele

Source: [https://www.google.pl/maps].

a) Analytical methods

Raw water samples taken directly from deep wells at the water treatment plant were the starting material for the study. Raw water samples before modernization were analysed every 3 days in 2017 year. Raw water was picked up directly from the well intake. Modernization had place in 2018. Than purified water at the old and new stations were analysed. The results obtained from water tests before and after modernization of the station were compared. The following parameters were analysed: colour, turbidity, pH, iron (Fe), Manganese (Mn), pH. The tests were carried out in accredited laboratories in accordance with Polish standards.

Statistical analysis were conducted using software Statistica 10 (StatSoft Polska). Shapiro-Wilk test were used for variables verification for calculation of normal distribution. Evaluated parameters are presented as average value and average deviation.

Chemical composition of raw water is presented in the Table 1.

Tab. 1. Chemical composition of raw water grom deep well in Pelele (municipality of Punsk)

Water parameter	Unit	Results
Colour	mg/L	5-15
Turbidity	NTU	14-35
pH	-	7-7.8
Flavour	-	Accepted
Taste	-	Accepted

Water parameter	Unit	Results
Conductivity	μS/l	500-750
$N\text{-}NH_4$	mg/L	0.05-1.09
Total Manganese	mg/L	0.125-0.350
Total iron	mg/L	1.7 – 3.5
Chlorides	mg/L	10-60
$N\text{-}NO_2$	mg/L	<1,0
N-NO3	mg/L	<0.05
Total Hardness	$mgCaCO_3/L$	350-500

Source: Own elaboration.

b) Technological methods

At the studied water treatment station before modernization such treatment processes were conducted as:

- Mechanical filtration with mesh filters,
- Aeration,
- Quartz sand filtration,
- Disinfection.

The station needed to be modernized because the equipment, which had not been changed for 30 years, was in operation there. There was an old mechanical mesh filter, a Venturi type aerator and a quartz sand filter. The apparatus was supplemented by a hydrophore. After a full quality inspection of the station It turned out that the mechanical filter is damaged. The screen, which was used as the first stage of cleaning, was cracked in many places. The Venturi operator does not aerate the water effectively, due to the significant irregularity of the flows. At low flows there was no suction of air and the raw water flowed to the filter without enriching it with the oxygen necessary to reactions with iron. The last device sand filter was largely clogged with iron sediments. Biofilm developed on the sludge, causing an intrusive reduction of iron compounds and the formation of unpleasant odours.

The station absolutely required modernization. As part of the research efforts, a new water purification system was designed. The technology of the station is based on a two-stage water treatment system. Raw water directly from the intake is fed to a closed aerator where it is accurately oxygenated. Next, it reaches the 1st stage of treatment, which are filters filled with quartz sand beds of various fractions, on which filtration, mainly of iron compounds, precipitated during aeration takes place. Then the water reaches the second treatment stage, where are pressure filters filled with brauchtin and pyrolusite deposits, also called active mass of G-1 or catalytic mass of manganese dioxide, which is aimed at reducing manganese concentration.

Results and disscusion

The basic processes used in water treatment in small towns and villages is iron and manganese removal. They are carried out by aeration of water contaminated with manganese and iron, which results in the precipitation of hydroxide residues, which are then removed by filtration in appropriate filters. An increase in pH by adding $Ca(OH)_2$ results in a faster process. Groundwater often contains iron in the form of Fe^{2}+ ions. This is the result of the CO_2 reaction of $Fe(HCO_3)_2$ iron bicarbonate or $FeSO_4$ iron sulphate. If the iron content exceeds 0.2 mg/L, the water must be purified. Iron in the form of bicarbonate easily hydrolyses to $Fe(OH)_2$ and then oxidizes with oxygen from the air to $Fe(OH)_3$. The process takes place in an inert and alkaline environment. If $pH < 7$, the CO_2 must be preliminarily removed by aeration or liming (Anorganicum 1989).

Water containing iron in the form of $FeSO_4$ requires liming:

$$FeSO_4 + Ca(OH)_2 ==> Fe(OH)_2 + CaSO_4 \quad (1)$$

The next process is as above. Manganese accompanies iron as $Mn(HCO_3)_2$ bicarbonate or $MnSO_4$ sulphate. Carbonate is precipitated similarly to iron, sulphate and requires the use of a properly formed manganese bed. These are ceramic fillings coated with manganese dioxide MnO_2 [http://beta.chem.uw.edu.pl/people/AMyslinski/cw3/ins3.htm].

In connection with the extensive program of modernization of the water treatment plant, an analysis of the operation of the modernized system of the plant in Pełele was carried out. The station in Pełele, established more than thirty years ago. The technology of the station was based on a two-stage filter system.

Despite their years of operation, the equipment continued to operate, as evidenced by the correct water results presented in Table 2. The facility required modernization due to leaks from used technological systems and poor technical condition of the building. In 2018, PALWOD Company carried out a comprehensive modernization of the water treatment plant for the commune of Puńsk, the facility is located in Pełele.

At the station two-stage filtering systems with aerator were used. At the first stage after the aeration iron compounds are removed, while at the second stage manganese is removed. Raw water from the deep well is collected by a deep well pump and pumped to the treatment plant. Then it is aerated in the central aerator and subjected to two-stage filtration on two independent sequences of fast pressure filters filled with mixed deposits. The treated water is directed to two equalisation tanks with a capacity of 100 m^3 each. From there, with a 2nd stage pumping set, it is directed to the water supply system. Water disinfection is performed periodically when bacteriological contamination of water is found, by dosing sodium hypochlorite to the water fed to the tank or directly to the system, behind the second stage hydrophoric set. After storing and clarifying in the settling tank, the water from the washing of the filters is discharged through the collectors to the receiver. At the modernized water treatment plant in Pełele, the Commune of Puńsk tested the quality of water approximately 20 days after the plant was put into operation. The results showed that the permissible content of manganese and iron was exceeded. Despite the fact that the station was commissioned in accordance with the procedures, the filters did not ensure adequate water parameters after the planned capacity of Q hmax=72 m^3/h was reached. Iron in raw water oscillated at 4 033 µg/L, while manganese at 498 µg/L. On the basis of these parameters, raw water could be considered difficult to treat. In order to improve water parameters, at the beginning the amount of air in the aeration chamber was increased from the designed amount of 4 m^3/h to 6 m^3/h. The station has been operating at maximum capacity since the start-up date, due to the drought in Poland in 2018. In addition, the area served by the station is dominated by dairy farms. As a result, the demand for water was enormous.

After the changes were made, the water was re-examined. The iron level decreased to an acceptable level and oscillated between 50µg/L and 105.2µg/L, while the manganese level was exceeded. The reason for this was the huge demand for water and the high content of iron in the raw water, which oxidation consumed the given oxygen. In order to achieve proper water parameters, it was necessary to supplement the 2nd degree filters by 2000 kg of G1 catalytic bed, instead of the filter top layer preventing the washing out of the bed. It was only after these procedures that the water parameters required by the regulation were achieved. In order to reach the correct parameters, it was necessary to perform a comprehensive adjustment and wait for the catalytic filter to work out at the second stage of treatment. Water intake in the Pełele station was subject to large fluctuations during the day and year. Daily changes in water demand occur due to the agricultural character of the area supplied by the station, whereas the annual water demand increases due to the tourist character of the area. Such a state of fluctuations in water demand and the associated periodical downtime in individual wells, and then increasing their efficiency, resulted in a temporary deterioration of water supply parameters (excess iron and manganese) and contamination of the water system in the area supplied by the stations. Daily irregularity also adversely affects the quality of water stored in retention reservoirs. The water in the reservoirs may be exposed to the development of bacterial flora, the situation worsens in winter when the demand for water in the region significantly decreases. It is necessary to periodically rinse the network in order to remove sediments and refresh the water supply at the station.

The chemical composition of the water was tested and compared with the tests performed earlier (before the modernization of the station). After the modernization of the station, water parameters are presented in Table 2.

Tab. 2. The quality of raw and treated water in studied water treatment station before and after modernization

Pollution parameter	Unit	Rawa water	Treated water before modernization	Treated water after modernization
Colour	mg/L	5-15	9	
Turbidity	NTU	14-35	5	
pH	-	7-7,8	7,5	
Flavour	-	Accepted	Accepted	Accepted
Taste	-	Accepted	Accepted	Accepted
Conductivity	µS/L	500-750	580	530
$N\text{-}NH_4$	mg/L	0,05-1,09	0,67	0,5
Total Manganese	mg/L	0,125-0,350	0,052	0,059
Total iron	mg/L	1,7 – 3,5	0,15	0,05
Chlorides	mg/L	10-60	55	49
$N\text{-}NO_2$	mg/L	<1,0	<1,0	<1,0
N-NO3	mg/L	<0,05	<0,05	<0,05
Total Hardness	$mgCaCO_3/L$	350-500	470	

Source: Own elaboration.

Conclusions

1. Commonly used technologies in water treatment are expensive in building, exploitation and modernization. In spite of their simple construction which let them be exploded for many years, some disadvantages are mentioned which are difficult to solve.
2. Increasing water demand and its high fluctuations are the cause to project and design of new water treatment systems and methods.
3. Water pollution parameters in Pełele water treatment station exhibit other disadvantages of used water treatment technologies. It is the lack of process stability which need time for regulation and adaptation of used materials for filtration.
4. It becomes compulsory to add extra equipment to support water treatment process. Other solution it combination with replacement devices when breakdowns and stagnations of water treatment station are reported.

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Wioleta Saczko, Małgorzata Krasowska

Bialystok University of Technology
Faculty of Civil and Environmental Egineering
m.krasowska@pb.edu.pl

HOUSEHOLD SEWAGE TREATMENT AS AN ELEMENT DECIDING ABOUT THE DEVELOPMENT OF THE GARDEN

keywords: hydrophyte sewage treatment plants, drainage, garden, hydrophytes

Abstract:

Household sewage treatment plants are an excellent alternative to septic tanks (cesspools). Currently there are several solutions of such sewage treatment plants on the market, therefore potential investors can tailor such a solution to their own needs in accordance with legal requirements. Household sewage treatment plants are economical, ecological and can be a decorative element of the garden. This paper presents the concepts of plot development with drainage system and a with a root-bed deposit. It was found that the selection of plant species for the purposes of the study is wide, and the most possibilities for development is provided by the constructed wetlands. In the very concept of its functioning is the appropriate selection of plants (hydrophytes), which in consequence, through appropriate design, integration into the environment and use, can be a decorative element of the garden.

Introduction

Collective sewage in rural areas is often impossible due to economic reasons, therefore, it is necessary to build a household sewage treatment plant. Single-family houses not connected to a collective sewage system may discharge sewage into septic tanks (cesspools) or use household sewage treatment plants, which are an excellent alternative to reservoirs [4]. The use of so-called cesspools is a temporary solution due to the fact that it does not lead to the disposal of sewage, but only to storage [5, 16]. In contrast, a household sewage treatment plant is a device that treats sewage and allows it to be discharged into the environment in a purified state [6,8]. In recent years, there has been a growing interest in the construction of single-family houses on the outskirts of cities, while more and more often, residents are moving to the countryside in search of peace and rest. The consequence of this is greater interest in wastewater treatment systems. At the same time, companies dealing with this aspect of environmental engineering constantly improve engineering solutions and respond to market demand. There are several technical solutions for household sewage treatment plants that can be used depending on the permeability of soil on our plot and the level of groundwater (Fig.1). In addition, the selection of the right solution determines the requirements for the location, construction and operation of the household sewage treatment plant are included in many legal provisions: Construction law, water law, environmental protection, act on maintaining cleanliness and order in the municipality, regulations on the technical conditions of buildings and their location, conditions of entry sewage to the environment and acts of local law [1, 2, 7, 22].

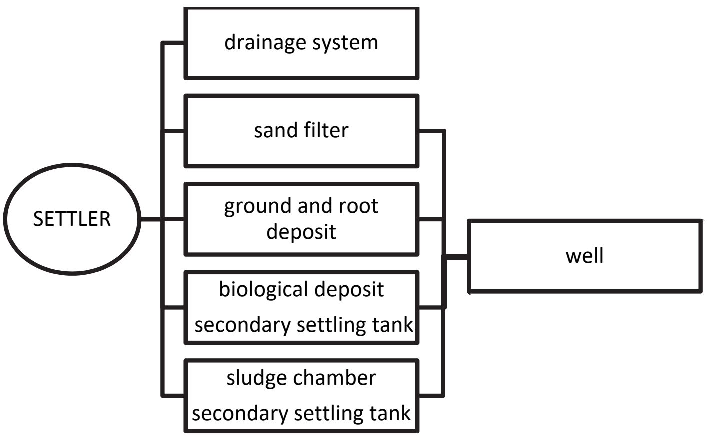

Fig. 1. Household sewage treatment
Source: [own elaboration based on: 5, 15, 19].

The installations of the household sewage treatment plant must consist of at least two stages of wastewater treatment. The first one is mechanical cleaning in the septic tank, in which the process of anaerobic stabilization of sediments also takes place. Until the second stage, in which oxygen treatment of sewage takes place, among other things, drainage, sand filter, biological beds, activated sludge equipment, hydrophyte sewage treatment plants [7, 17, 21].

One of the types of household treatment plants that has been enjoying particular interest over recent years is the hydrobotanic (hydrophyte) treatment plant. It is an ecological system that is used to treat municipal sewage in your own garden. The treated wastewater is suitable for re-use in nature. In order to achieve this, the scheme should be based on a simple and failure-free technology of wastewater treatment, it should also be easy to operate and cheap to use, as well as resistant to uneven quantity and changing quality of wastewater. In garden wastewater treatment (in constructed wetlands), only natural processes taking place in the environment are used, which is why it is a reliable system [1, 3, 9]. The most important element of the constructed wetlands is a plant composition composed of plant species adapted to local hydro-climatic conditions. Therefore, in addition to usable values, the garden plant can be an integral part and decoration of the landscape. In this paper, it was assumed that garden elements with technical and engineering functions, properly planned, designed and used can harmonize with the surroundings and provide the aesthetic value of the garden. Therefore, an attempt was made to develop a garden with a household sewage treatment plant, and in order to compare the concept, a backyard garden with a hydrophyte sewage treatment plant and a drainage system was designed.

Garden development with a household treatment plant

The development of the biologically active garden area with the house sewage treatment plant assumed the selection of suitable plants, the design of paths, driveways, lawns, paved surfaces and elements of small architecture. Plant species adapted to local climatic and environmental conditions should be used in constructed wetlands. In addition, they should have adequate capacity to accumulate nitrogen and resistance to contaminants contained in wastewater. They should be plants that are easily replanted and characterized by the ability to grow quickly and reproduce. The purification process also includes the reduction of biogenic compounds, i.e. phosphorus and nitrogen compounds, which pose a threat to surface waters [1, 3, 12].

When designing a backyard garden with a wastewater treatment plant with a drainage system or hydrophytic plant, it should be remembered that it is important to select the appropriate plant species. Not all plants can cover the area occupied by the drainage system that distributes the pre-treated sewage, because the area around the filter drainage is often wet. The places under which the drainage pipes are located can only grow on plants with a very shallow root system, which does not surpass the geotextile that protects the drainage layer, and therefore it is mostly grass The areas that surround the drainage system can be used for higher perennials, grasses and shrubs that favor moist soils [14, 17]. Tables 1, 2, 3 contain the species proposed for planting at the garden sewage treatment plant. Attention is paid to their tolerances, partial flooding with water and the required position.

Tab. 1. Species of perennials and grasses

Species	Tolerance for partial flooding	Height [m]	Place
Iris pseudoacorus	x	0,8 -1,0	sunny, partially shaded
Iris siberica 'Big Blue'	x	0,8-1,0	sunny, partially shaded
Iris x brabant 'Baria'	x	0,8-0,1	sunny, partially shaded
Hosta fortunei		0,3-0,75	partially shaded
Hosta undulata		0,3-0,75	partially shaded
Hosta Sieboldiana		0,3-0,75	partially shaded
Astible x arendsii		0,5-1,5	
Primula florindae	X	0,1-0,15	sunny, partially shaded
Primula bulesiana	x	0,1-0,15	sunny, partially shaded
Pulmonaria saccharta		0,3	sunny, partially shaded
Ligularia dentata		1-1,5	partially shaded
Ligularia hessei		1-1,5	partially shaded
Lisymachia punctata	x	0,8	sunny, partially shaded
Alchemilla molis	x	0,5-1	sunny, partially shaded
Phalaris arundinaceae 'Picta'	x	0,7-1,0	sunny
Stipa capillata		0,2-1,0	sunny
Glyceria maxima	x	0,7	partially shaded
Spartina pectinata		1,5	partially shaded
Deschampsia cespitosa		0,5	partially shaded
Carex muskigumensis	X	0,6-1,0	sunny, partially shaded
Carex disticha	x	0,6-1,0	sunny, partially shaded

Source: [own elaboration based on: 18].

Tab. 2. Species of shrub

Species	Tolerance for partial flooding	Height [m]	Place
Salix purpurea 'Nana'	x	1,5	sunny
Salix integra 'Pendula'	x	3	partially shaded
Salix caprea 'Kilimarnocka'	x	9,0	sunny
Corylus avellana 'Aurea'		5,0	sunny partially shaded
Viburnum opulus 'Roseum'	x	4,0	sunny, partially shaded
Cornus sericea 'Kelsevi'	x	1,5-3,0	sunny, partially shaded
Cornus alba 'Siberica'	x	1,5-3,0	sunny, partially shaded

Source: [own elaboration based on: 18].

Tab. 3. Species of deciduous and coniferous trees

Species	Tolerance for partial flooding	Height [m]	Place
Fraxinus padus	x	10,0	sunny
Alnus glutinosa 'Aurea'	x	6,0-10,0	sunny, partially shaded
Alnus incana 'Pendula'	x	20,0	sunny, partially shaded
Acer pensylvanicum	x	10,0	partially shaded
Ouercus palustris	x	20,0	sunny
Tsuga canadensis 'Pendula'		15,0	sunny, partially shaded, shaded
Metasequoia glyptostroboides		7,0-35,0	sunny, partially shaded

Source: [own elaboration based on: 18].

In wetlands (ground-root) plants, plant species are used, whose root system during the growing season absorbs and neutralizes pollutants. Such species include mainly common reed, willow and cattail. Water coming from the home treatment plant is not 100% purified and contains some amounts of nitrogen and phosphorus. It can be used again for watering ornamental plants and lawns, however, due to the possibility of occurring in treated wastewater dangerous for health bacteria, you can not water them fruits or vegetables. However, it should be emphasized that the garden treatment plant does not produce an unpleasant smell because the sewage flows a few centimeters below the surface of the ground [10, 20].

The process of wastewater treatment in the case of the two analyzed solutions follows the diagrams shown in figures 2 and 3. Drainage treatment plants consist of a septic tank and a drainage system. They work on the basis of natural processes occurring in nature: anaerobic digestive decomposition by fermentation in a settling tank and physical-biological processes during further polishing during infiltration through the ground. Due to the fact that sewage treatment is in the ground, these plants can be used only in appropriate soil and water conditions (soil permeability, groundwater level) and typographic (plot area, slope direction) [14, 15].

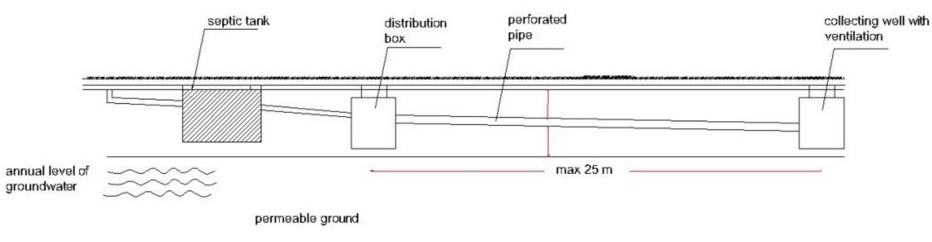

Fig. 2. Scheme of a household treatment plant with drainage

Source: [own elaboration based on: 7].

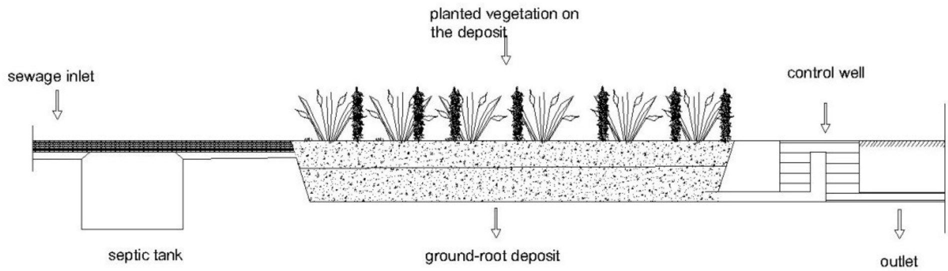

Fig. 3. Scheme of a household treatment plant with a ground-root deposit
Source: [own elaboration based on: 7].

Constructed wetlands are high efficiency biological wastewater treatment systems that are modeled on natural swamp ecosystems. They occur in processes similar to those that occur in natural wetlands, such as sedimentation, filtration, vegetation plants and the activity of bacteria and microorganisms causing the removal of, among others, carbon, nitrogen and phosphorus compounds. The hydrophyte deposit is distinguished by aerobic, anaerobic and reduction zones, which occur in the entire volume of the bed around the roots of plants, which creates ideal conditions for the development of various microorganisms. Occurrence of zones with different oxygen content allows simultaneous oxygen processes such as nitrification and anaerobic, eg denitrification, it increases the efficiency of such a treatment plant. Proper design and construction of such facilities ensures high control and intensification of processes, eg the ability to control the number of incoming and outgoing sewage creates even more favorable conditions, allowing for more efficient cleaning of pollutants compared to natural wetland systems. The individual properties of the constructed wetlands, such as the presence of specific macrophytes, the composition of inflowing sewage, environmental and hydraulic conditions, affect the biochemical processes occurring in these systems. Their knowledge and understanding are necessary for the proper design of such objects and their failure-free operation [3, 9].

Wastewater treated in a household sewage treatment plant can be spread into the ground or drained into a river or drainage ditch, without fear of their negative impact on the environment.

Taking into account the guidelines for the design of household wastewater treatment plants, a concept for the development of a plot of land with a detached house was created. Two projects were prepared for the needs of the work: with a sewage treatment plant with drainage system (Fig. 4) and with ground-root deposit (Fig. 5).

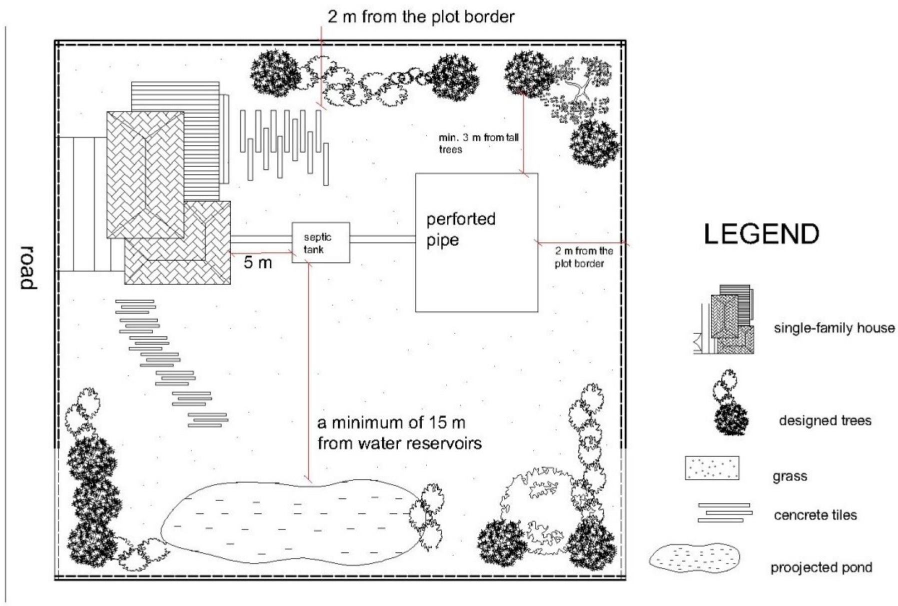

Fig. 4. The concept of garden development with a sewage treatment plant with a drainage system
Source: [own elaboration].

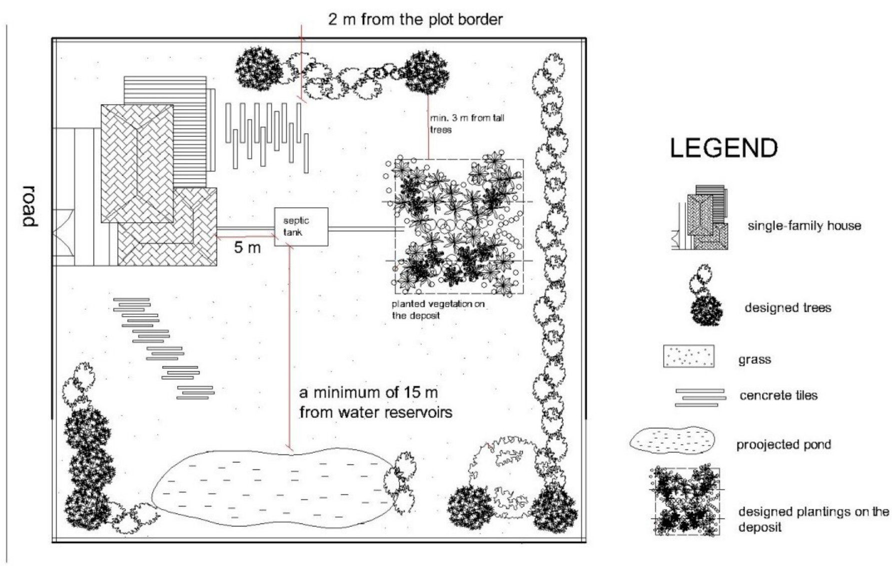

Fig. 5. The concept of garden development with a sewage treatment plant with a ground-root deposit
Source: [own elaboration].

Both schemes show the possibilities of developing a similar plot, at the same time taking into account the guidelines regarding minimum distances from trees, water reservoirs or the border of the plot. In the case of a project with a plant-soil treatment plant, hydrophyte plantings in the form of a butterfly were designed, which can diversify the aesthetic values of the garden (Fig. 6).

The use of the constructed wetlands provides greater opportunities for the development of the plot. More and more often, various projects are observed and special shapes are added to the aboveground parts of the wetfield deposit. An example of this solution is the turtle-shaped wetland purification plant at the didactic-museum center of the Polesie National Park in Stary Zaucz or the butterfly-shaped treatment plant on the island of Koh Phi Phi in Thailand.

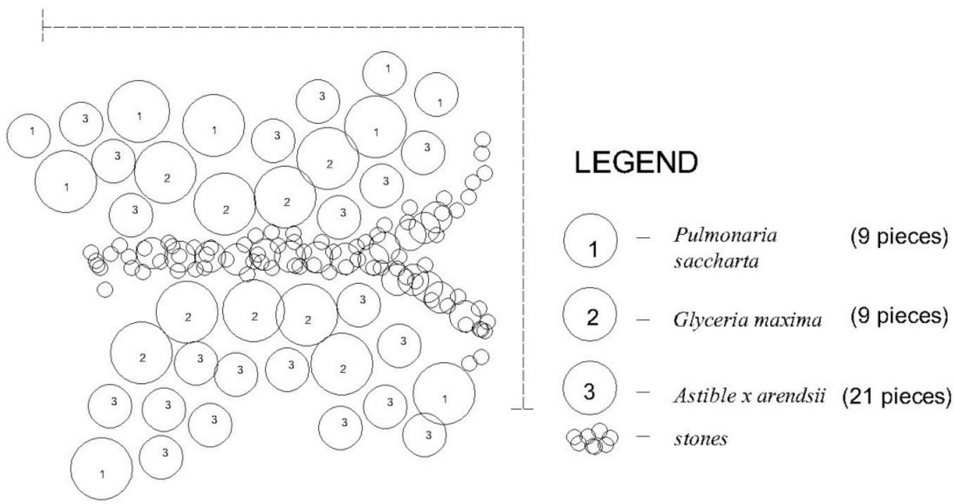

Fig. 6. Project of plantings on a ground-root deposit
Source: [own elaboration].

Summary

Domestic sewage treatment plants, especially those with drainage or a constructed wetlands, require the investor to have quite a large area on the plot, because they can not be located anywhere, and the legal regulations in this matter are very strict. Despite various restrictions, these purifiers enjoy interest and are a good alternative to septic tanks. In addition, as shown in the paper, they can be an element that fits in with the surroundings and harmonizes with the garden's management. The place on the plot, where technical elements of household sewage treatment plants are located, do not have to be excluded from the development, and on the contrary, properly designed and maintained, can be a decorative element. It is important to combine technical and engineering solutions with elements of landscape architecture.

Due to the fact that social awareness regarding environmental protection has increased in recent years, it can be assumed that there will be an exchange of existing cesspools for household wastewater treatment plants, which (as the producers of such solutions state) not only simple exploitation, durability, failure-free operation charaterize but also aesthetics and convenience, which is part of the assumption of rational water management and sustainable development [11, 13].

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