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Anna CHRZAN[1], Maria MARKO-WORŁOWSKA[1], Gabriela WĄTOR[1]
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THE PINE BARK AND TOPSOIL AS AN INDICATOR OF POLLUTIONS CAUSED BY INDUSTRY AND TRANSPORT

ZASTOSOWANIE KORY SOSNY I WIERZCHNIEJ WARSTWY GLEBY DO OCENY ZANIECZYSZCZEŃ PRZEMYSŁOWYCH I KOMUNIKACYJNYCH

Abstract: Concentrations of Pb, Cd, Ni were determined in topsoil and in samples of necrotic bark of *Pinus sylvestris* L. collected along transects around the Skawina industry center and in parts of Bielansko-Tyniecki Landscape Park in Krakow (southeast Poland). The suitability of bark and topsoil for monitoring of these heavy metals and acidifying gases pollution was investigated. After comparing the concentration of heavy metals and pH value in pine bark with topsoil, it was observed that topsoil is better biomonitor for lead and nickel than bark of *Pinus sylvestris* and that bark appear to be suitable bioindicator of atmospheric deposition only for cadmium and acidifying components.

Keywords: *Pinus sylvestris* L., necrotic bark, heavy metals, topsoil, pine bark reaction, biomonitoring

Introduction

Intensive development of industry (metallurgy, burning of energetic raw materials) and steadily increasing car transport constitute the main source of contamination by heavy metals and acidic compounds (SO_2, SO_3 and NO_x) of soils adjacent to the industrial areas and traffic paved roads.

The consequence of the accumulation of metals and their toxic impact is biological deactivation of the soil subsystem. Additionally, terrestrial ecosystems productivity decreases [1-3]. Heavy metals and acidifying compounds are one of the most durable and toxic contaminates of the soil subsystem.

The anthropogenic processes that cause the emission of acidifying compounds are the cause of the spreading of many metals and the growth of their toxic impact on living organisms [4]. Respectively, the content of heavy metals (especially Pb, Ni or Cd) in soils can be treated as an indicator of the environmental degradation of different branches of the industry and car transport.

Tree bark is an ideal natural absorbent as it is dead tissue that does not grow anymore. The pine bark surface is very porous and the absence of metabolic processes makes it highly unreactive for inorganic and organic substances [5, 6]. The changes in the chemical composition of the surface layers can be documented. Kuik and Wolterbeek [7] and another [8, 9], proposed the use of tree bark samples as biomonitors of heavy metals. Monitoring of the environment with the use of bark not only enables evaluation of present layer of the accumulation of elements and polluting compounds, but also evaluation of the course of the process in the previous years. Adjacent trees are supposed to demonstrate a similar degree of pollution accumulation s and may be used consequently to determine the

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extent of the pollutants. Similarly the results on the bark of model trees analysis taken on surfaces at different distances from source emission can illustrate the problem of the spread of pollutions. Tree bark is a good bioindicator because it remains in place for an extended period of time, it is easily accessible and sampling does not damage the tree [9]. What is more, sampling and analysis of necrotic bark is fast and economical. Kuik and Wolterbeek [7] study demonstrated the potential of bark as a biomonitor on a larger scale.

The aim of the present work was the recognition of contamination by Pb, Cd and Ni and acidifying compounds of the surface soil (topsoil) and tree bark of approximately similar aged trees at localities situated at different distances from industrial and transport emitters.

Materials and methods

Characteristic of area analyzed

The samples were taken in spring 2012 at 5 different distances from the source of emission. The 3 sites (1, 2, 3) examined are situated in Skawina - a city characterized by heavy industrialization (aluminium-works, power plant and others), densely populated and situated approximately 18 km southwest from the center of Krakow and the 2 sites (4, 5) situated in the Bielansko-Tyniecki Landscape Park of Krakow - park encompassed by the Krakow city limits.

Samples collection and analysis

For evaluation of pollutions of air and soil by heavy metals and acidifying compounds necrotic pine bark (*Pinus sylvestris* L.) and topsoil from the pines' surroundings were used as the accumulative cumulative bioindicators. The temperature, soil moisture and pH of topsoil and bark were examined and the content of Pb, Cd and Ni was determined. The topsoil reaction (pH) was examined on place with a pH-meter- WTW pH 330, placed into the soil to a depth of 5 cm. The topsoil samples were taken by forcing a 5 cm diameter steel cylinder to a depth of 5 cm. At each site the 4 soil samples were taken at eastern side (before the trees) and the 40 samples of bark 3 mm thick from the trunk of 4 trees at the high of around 1.5 m from the soil, 5 in the eastern side of each tree and 5 on the western side. The trees analyzed were from 2 to 4 m distance from each other, had similar breast height diameter (35 to 40 cm) and had a similar age (around 30 years).

The samples were dried in a temperature of 65 degrees for 3 hours, then milled to a powder. One gram of powdered bark from each sample was weighed and mixed with 5 cm^3 of distilled water. After 48 hours the pH reaction was measured using a ELMETRON type CPC-401 pH-meter. Chemical analyses of heavy metals in the topsoil and bark were conducted by mapping the content of the general forms of Cd, Pb, Ni, determined by the FAAS method. Dried samples of topsoil and bark (1 g each) were mineralized. For this purpose dried samples of soil and pine bark were mixed with 3 cm^3 of 65% HNO_3, the solution was heated to a temperature of 110ºC and left for 4 hours to cool. The filtered liquid was poured into measuring flasks and filled with distilled water. In the solutions of soil and bark prepared, the content of heavy metals was determined by atomic absorption spectrometer (AAS-Cole-Parmer, BUCK 200A).

Statistical analysis

As variances showed no parametrical distribution (Shapiro-Wilk test, $p > 0.05$), we used non parametric Kruskal-Wallis ANOVA. The correlations between metal concentrations, pH and sites were calculated using the Pearson correlation coefficient and Students` test. Statistical significance was defined at $p < 0.05$. All analyses were performed using STATISTICA 12 computer program.

Results and discussions

The pH value is subjected to the quickest changes when exposed to external factors and, among others, it directly and indirectly influences many mechanisms releasing heavy metals in soils [10]. In normal conditions the pH of *Pinus sylvestris* bark is 3.5 [8], whereas the average pH of pine bark at sites analyzed indicated high acidity and fluctuated from 2.68 to 3.44. The average value of soil pH fluctuated from 4.31 to 6.04 (Table 1).

Table 1

pH value in studies sites

	Cardinal directions	**Site 1**	**Site 2**	**Site 3**	**Site 4**	**Site 5**
Pine bark pH	East	3.14 (2.98-3.24)	2.68 (2.60-2.82)	3.18 (2.63-3.94)	3.29 (3.05-3.46)	3.12 (3-3.23)
	West	3.28 (3.05-3.59)	2.99 (2.61-3.49)	3.44 (2.78-3.78)	3.14 (3.01-3.27)	3.02 (2.88-3.23)
Top soil pH	East	6.04 (5.34-6.79)	4.25 (3.79-5.47)	4.4 (4.01-5.03)	4.61 (4.37-5.05)	4.69 (4.52-5.21)

Site 1 - Skawina 700 m from the aluminium works and about 5 meters north of a heavy used road
Site 2 - Skawina 2400 m from the power plant and aluminium works
Site 3 - Skawina 1200 m from the power plant and 450m from the aluminium works and approximately 200 m from the road
Site 4 - Bielansko-Tyniecki Landscape Park 4 km north east from the power plant and 5 km from the aluminium works
Site 5 - Bielansko-Tyniecki Landscape Park 5 km north east from the power plant and 6km from the aluminium works, and around 200 m west from the ring road

Comparison of the pH reaction indicated considerably higher acidity of pine bark verses topsoil at each sites, and these differences were statistically significant (Table 2).

Table 2

Statistical significance of pH value and of heavy metals concentrations

	pH	**Pb**	**Cd**	**Ni**
Pine bark East-West	0.0040*	0.000013*	0.019198*	0.000001*
Pine bark East - Topsoil	0.000000*	0.000000*	0.000046*	0.000000*
Pine bark West - Topsoil	0.000000*	0.000000*	0.078504	0.000000*

*differences statistically significant at $p < 0.05$

The highest acidity (pH lower than 4.5) was observed in soils at sites 2 and 3. At the same time similar, almost parallel increasing or decreasing tendencies of pH of bark and topsoil were noticed regarding all sites. The pH value of pine bark on the eastern and on the western side did not differ much, however at sites 1, 2, 3 situated at the closest distance and west of industrial emitters, a slightly higher acidity on the eastern side of trunk was observed. The lowest average pH value of bark and of soil was recorded at site 2 (Table 1). It is probably that here polluted air touched with the north-east winds from the north-east part of Krakow, where is located a steelworks and electro-thermal power plant. Site 5 situated furthest away from the industrial emitters, but approximately 200 m from a ring road was characterized by high bark acidity, as well as the highest content of Pb in the topsoil (Fig. 1). This result proves a big impact of transport pollutions flowing with frequently occurred natural wind currents blowing from the ring road.

The low soil pH is negative from the ecological perspective - in acidic soil the mobility of heavy metals (mainly Cd and Ni) increases which facilitates transfer of these metals into the circulation of matter. The results of presented research indicate that the pH value of pine tree bark must be regarded as an indicator for air acidification.

The content of xenobiotic elements

Amongst the metals examined Ni is the only one that is indispensable (for humans 25-35 µg/day) for the proper functioning of the organisms. Its overdose, however, can have very negative consequences. Cd and Pb do not have any positive influences on organisms and constitute some of the most dangerous heavy metals; the accepted dose determined by the WHO is: Pb - 415-550 µg/day, Cd - 57-71 µg/day[11]. The occurrence of heavy metals in soil and plants can be treated as an indicator of the quality of the environment and *Pinus silvestris* is commonly used in fitoindication [12]. Intensity and scope of the contamination of soils and plants by trace elements depend on many factors at local conditions. Additionally, the important source of heavy metals accumulated on the surface of soils and plants is so-called long distance emission related to the spreading of pollutions over large distances.

The climatic conditions (rainfalls, temperature, direction and wind speed) play an important role in dispersion and deposition of air pollutants. For an estimation of the environmental health and threat of heavy metals, an evaluation of their mobility, that is, possibility of their transmission to biogeochemical circulation, is necessary [13]. High mobility of Cd, Ni and the relatively low mobility of Pb in soils is regulated by their pH and modified by the other soil qualities such as content of organic substances, occurrence of other metals and humidity. In oxidative environments with acidic reactions, Cd and Ni are characterized by high mobility, to the lesser extent the mobility of Pb increases as well [14]. Among metals measured in topsoil the concentration of Pb was the highest and its amount was higher than the average natural occurrence in the soils of Poland [15] (Fig. 1).

Lead - a component of commonly used, until recently, leaded petrol is the contamination attributed to transport and to various industrial activities. The other main sources of Pb emission are coal burning and metallurgical industries. It is a metal typical for low emitters and non-organized emissions. Pollutions from this source do not spread over long distances [16]. According to the literature [11] natural concentrations of this metal should not exceed 20 mg/kg for most soils. The Pb content in soils analyzed fluctuated from 29.37 mg/kg at site 4 furthest away from industrial emitters, ring road and busy road to 62.26 mg/kg at site 5 which is remote from industry, but situated close to a ring road (Fig. 1).The highest Pb content was observed in topsoil (site 5) approximately 200 m away from the ring road and in bark (at site 1) adjacent to the busy road (Fig. 1). Soils of habitats analyzed contain slightly higher amount of Pb that the natural average content in soils in Poland. However, only in soil at site 5 the amount of Pb is averagely 2 times higher than in soils of remaining sites and exceeds acceptable content according to the standards of soils and earths qualities [15]. The greatest effect of traffic Pb pollution on the soil subsystem was observed up to a distance of 200 m away from the motorway (Fig. 1), which proves higher influence of busy roads than in the results presented by Ruhling and Tyler (2004) [17]. Their studies of Pb accumulation in many plants growing next to busy roads in Sweden, show the most intensive accumulation of Pb up to 150 m from the road. Observations of Jaworska and Murowana [18] stating the impact of distance up to 300 m from the road on plants are similar to the results of presented research.

The content of Pb spanning from 2 to more than 6 times higher in soil than in bark was detected here, the exception is site 1 (Fig. 1). The highest Pb concentration in pine bark at site 1 can be explained by the proximity to the heavy traffic road. With increasing distance from the emission center (car transport and power plant) the Pb content of bark decreases. The lowest Pb content in bark as well as in topsoil, was observed at site 4 situated furthest away from roads (Fig. 1). Therefore it is probable that the main emitter of Pb on area analyzed is car transport.

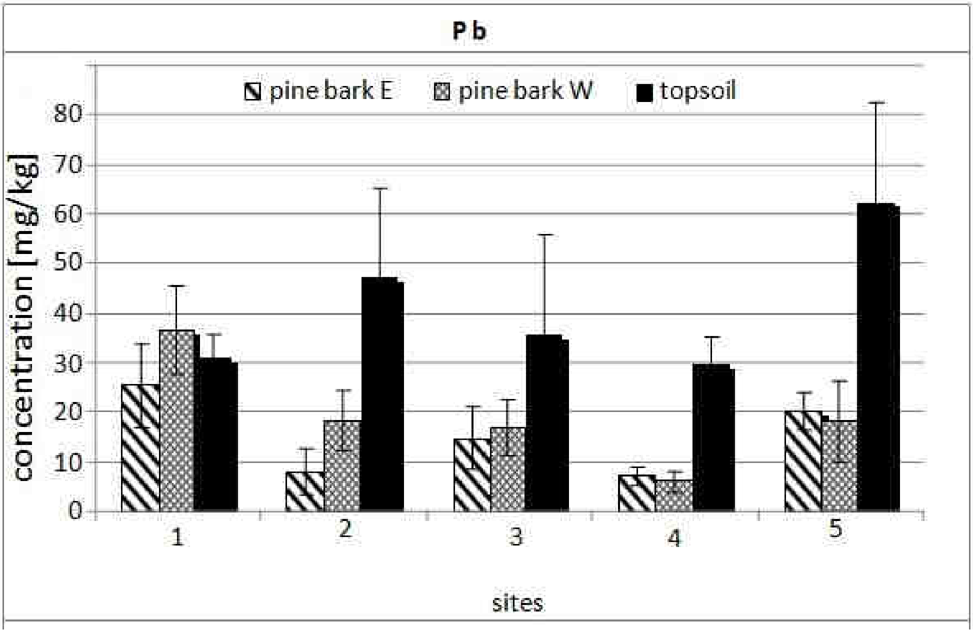

Fig.1. Pb concentrations in studies sites

Cadmium, that is emitted by metal works, is one of the most dangerous heavy metals for the environment [19]. What is more, along roads, the source of contaminations are for example greases used in vehicles, tyre abrasion and other parts of vehicles. Cd is accumulated mainly in surface soil levels and the higher the reactivity (pH) of soil, the more readily it is absorbed by it. Cadmium is more easily activated and mobile in soils of pH 4.5-5.5. With higher pH values Cd is immobilized forming carbonates [20]. In soils examined it occurs in natural amounts or slightly elevated ones and fluctuated from 0.41 to 0.97 mg/kg (Fig. 2). In 6-degree IUNG classification 0.5 mg/kg d.m. is considered as natural amount of Cd in soil. On this basis it was stated that topsoils at sites 1, 4 and 5 exceed this amount (Fig. 2). The highest Cd concentration was detected in soil with the least situated near a ring road. Whereas in tree bark the highest Cd content was detected at site (3) situated nearest to the aluminium works and power plant (Fig. 2), and the highest content of the general forms of this element was noted on the eastern side of tree-trunks. Higher Cd content on the eastern side of tree-trunk (differently than in case of Pb) can prove that the main source of emission of this element is industry. As the research indicate, Cd accumulates best in bark - according to Samecka-Cymerman et al. [21] they state that bark is a better accumulator of Cd compared to *Pinus schreberi*, whereas in soil its content is considerably lower. However in soils at sites situated near roads (1 and 5) the Cd content is similar to the content observed in barks at the same localities (Fig. 2).

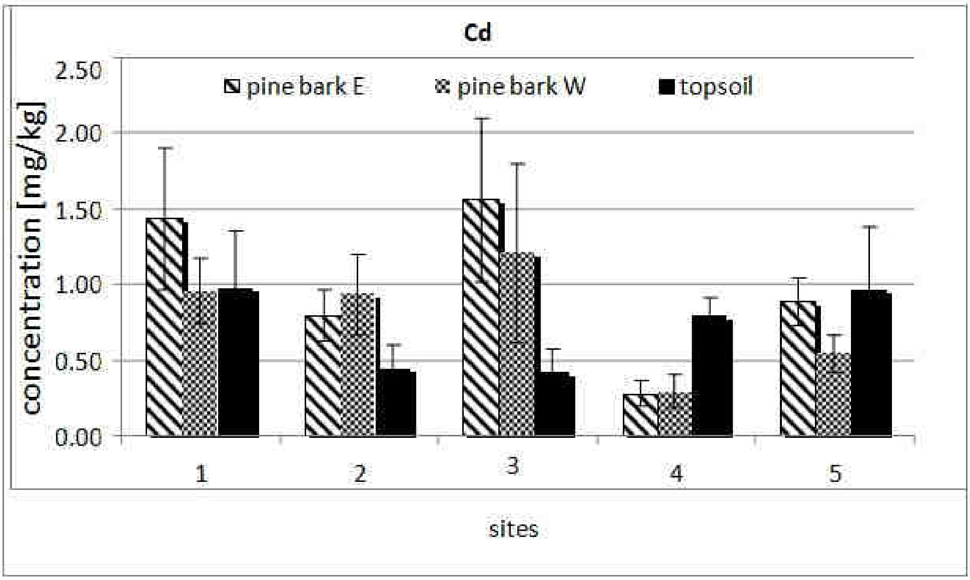

Fig. 2. Cd concentrations in studies sites

In spite of the statement presented in literature that emissions released at the height [16] can be observed in case of Cd and Ni, because they are emitted mainly from tall smokestacks. The results prove that apart from industrial emissions, car transport influences heavily the content of Cd. The results obtained by Marko-Worlowska et al. [22] confirm at the same time, that motorways are the main emitters of Pb and big emitter of Cd, in the immediate vicinity nearest and up to 200 m away from the motorway.

Nickel is emitted mainly by the metallurgical industry and during coal burning and petrol use [23]. In the case of Ni considerably higher amounts were observed in soils at all sites analyzed (from 2.73 to 4.41 mg/kg), whereas in barks the amount was from 0.4 to 1.9 mg/kg (Fig. 3).

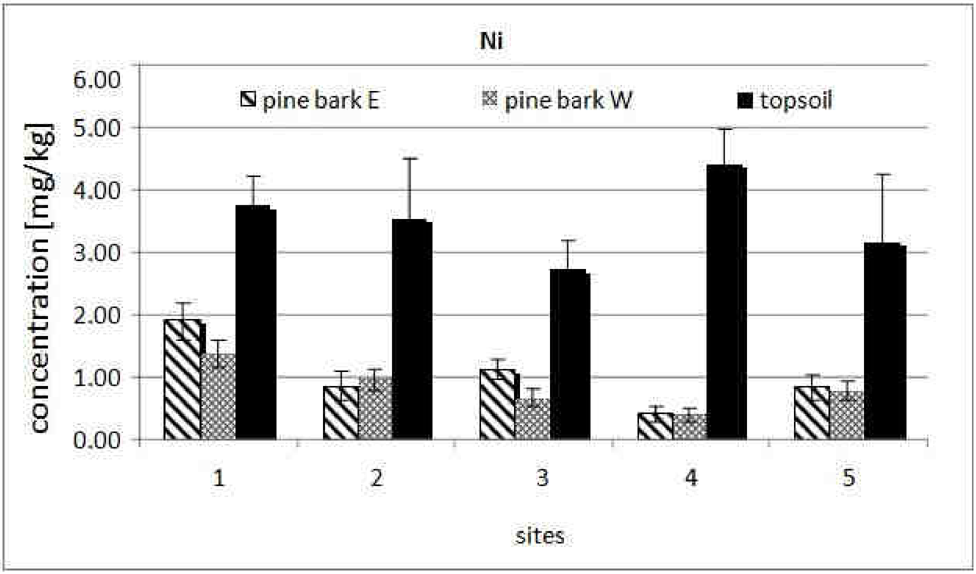

Fig. 3. Ni concentrations in studies sites

Natural concentrations of this metal in soil are 25 mg/kg d.m. [10]. In all soils analyzed its content was much lower. In tree-bark the highest content of Ni (different than in case of Pb, and similar to the case of Cd) was noted on the eastern side of the trees (Fig. 3). It proves the significant influence of industry on Ni emissions.

In most circumstances, a positive correlation is observed between lead and cadmium concentrations in soil and pine bark, which predicts the higher the lead content the higher the cadmium concentration. Concentrations of Cd and Pb in topsoil and in bark were influenced by the distance from industrial emitters and busy roads. Concentration of Ni in topsoil was not influenced by these distances, whereas concentrations of Cd, Pb, Ni in bark were not influenced by concentration of this element in soil (Figs. 1-3).

Conclusions

1. The results obtained confirm the negative impact of aluminium work, power plant and transport on quality and number of environmental pollutants at the sites situated near these industries and road with intensive traffic. Therefore, the constant monitoring of these localities is necessary.

2. Topsoil is better biomonitor for lead and nickel than pine bark.
3. Pine bark appears to be better bioindicator of atmospheric acidifying compounds and cadmium deposition and with comparison with another bioaccumulators can be suitable biomonitor for environmental pollution by heavy metals.

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ZASTOSOWANIE KORY SOSNY I WIERZCHNIEJ WARSTWY GLEBY DO OCENY ZANIECZYSZCZEŃ PRZEMYSŁOWYCH I KOMUNIKACYJNYCH

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Abstrakt: W wierzchniej warstwie gleby oraz w próbkach kory sosny zwyczajnej *Pinus sylvestris* L. zebranych wokół centrum przemysłowego w Skawinie oraz na terenie Bielańsko-Tynieckiego Parku Krajobrazowego w Krakowie, położonego w południowo-wschodniej Polsce, oznaczono stężenia takich metali ciężkich, jak, Pb, Cd, Ni. Celem badań było wykazanie przydatności kory martwicowej i wierzchniej warstwy gleby do monitorowania zanieczyszczenia środowiska tymi metalami ciężkimi i związkami zakwaszającymi. Na podstawie porównania stężenia metali ciężkich w wierzchniej warstwie gleby i korze sosny oraz wartości pH kory sosnowej stwierdzono, że gleba jest lepszym biomonitorem dla ołowiu i niklu, natomiast kora sosny zwyczajnej *Pinus sylvestris* L. wydaje się być odpowiednim bioindykatorem depozycji atmosferycznej tylko dla kadmu i składników zakwaszających.

Słowa kluczowe: *Pinus sylvestris* L., kora martwicowa, metale ciężkie, wierzchnia gleba, odczyn kory sosny, biomonitoring

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MODELLING OF THE AIR PURIFICATION FROM VOLATILE ORGANIC COMPOUNDS IN A TRICKLE-BED BIOREACTOR

MODELOWANIE PROCESU OCZYSZCZANIA POWIETRZA Z LOTNYCH ZWIĄZKÓW ORGANICZNYCH W BIOREAKTORZE STRUŻKOWYM

Abstract: The biodegradation of styrene by bacterial strain *Pseudomonas* sp. E-93486, coming from VTT Culture Collection (Finland), was studied. The kinetic experiments with the presence of styrene as the only carbon and energy source were performed both in batch and continuous cultures at optimal environmental conditions for the growth of the tested strain (pH = 7 and 30ºC). The Haldane inhibitory model was found to be the best to fit the kinetic data, and the estimated kinetic equation parameters were: μ_m = 0.119 h^{-1}; K_s = 5.984 g·m^{-3}, K_i = 156.6 g·m^{-3}. The experiments conducted in a chemostat at various dilution rate (D = 0.035-0.1 h^{-1}) made it possible to determine the value of the coefficient for maintenance metabolism (m_d = 0.0165 h^{-1}) and the maximum yield coefficient value ($(Y_{XS})_{max}$ = 0.913). The determined complete model of growth of E-93486 strain in the presence of styrene was verified by comparison of the computed and obtained in batch experiments profiles of changes in biomass and styrene concentrations. Next the tested strain was immobilized on the packing of a pilot-scale trickle-bed bioreactor operating at co-current down-flow of gas (air contaminated by styrene) and liquid (mineral solution) phases. The effect of inlet styrene concentration on its degradation was studied for initial concentration in the air changing in the range of 0.2-1 g·m^{-3}. The recirculation rate of liquid medium was 8 m^{3}h^{-1} whereas the gas flow rate was changed in the range 50-150 m^3·h^{-1}. The conversion degree depended on operational parameters and changed in subsequent experiments in the range of 75-95%.

Keywords: styrene, kinetics, trickle-bed bioreactor

Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere in large quantities from chemical and petrochemical industries. As styrene is included in this category, the economic and effective removal of styrene from waste gas and waste water from chemical plants is needed. It is released into the environmental during the manufacturing and application of its isomers including polystyrene, styrene-butadiene rubber, acrylonitrile and copolymers resins. Styrene is employed in the chemical industry as a starting material for synthetic polymers as well as a solvent in the polymer processing industry and is, therefore, present in many industrial effluents. The world production capacity of styrene amounts to about 32.5 Tg and constantly increase, on average by 2-3% a year. Such common and quantitatively big styrene consumption considerably affects its emission into the atmosphere, estimated at 25 Gg a year. In general, the concentration of styrene in industrial waste gases may reach 1 g·m^{-3} [1], and average range varies between 0.15 and 0.4 g·m^{-3} [2]. Styrene has been listed among the 189 hazardous and toxic atmospheric contaminants under Clean Air Act Amendments [3].

Chronic exposure to styrene in humans results in a variety of discomforts such as mucous membrane and eye irritations, headache, fatigue, weakness, depression, central

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nervous system dysfunction, hearing loss, and peripheral neuropathy [4]. Styrene is suspected to be potentially carcinogenic, mainly through pulmonary and percutaneous arterial absorption (solvents generally modify the cytoplasmic and external membranes). Styrene oxide, which is an oxidation product of the side chain and the major *in vivo* metabolite of styrene, may also have an immunomodulatory effect on workers exposed to gaseous emissions in an industrial setting [5]. Therefore, before discharge to the environment, both the liquid and gaseous effluents of industrial complexes should undergo an appropriate treatment to decrease the concentration of styrene to below toxic level [4, 6].

Many different methods have been used for the treatment of styrene laden waste gas streams. The use of physicochemical processes such as catalytic and thermal oxidations, wet scrubbing and activated carbon adsorption, incurs high capital and operating costs and usually results in the production of secondary effluents and does not always reduce the pollutant concentration in the air or wastewater to acceptable levels. Therefore, the biotreatment has proven to be an effective and economical technology with minimal energy requirements and low waste production among the different air pollution control techniques for reducing VOCs and odors in air.

Biotreatment provides significant advantages over conventional techniques, such as adsorption, condensation, activated carbon adsorption, and thermal and catalytic oxidation, in terms of large air volumes and low gaseous pollutant concentrations.

Biofiltration is the cost effective and reliable option in treating VOCs emitted from processes with large off-gas volume but low concentration of pollutants [7]. Three types of biofiltration such as biofilter (BF), trickle-bed bioreactor (TBB) and bioscrubber (BS) have been developed for the treatment of waste gases. A trickle-bed bioreactor (TBB) consists of an inert packed bed on which microbial biofilm grows and a nutrient-trickling system. TBBs often exhibit higher treatment performance than BFs, because more active biomass can be accumulated and reactor operation conditions can be effectively controlled. One drawback of TBBs is excess biomass accumulation on a packed bed. This produces a high pressure drop and reduces removal efficiency of the biofilter [8].

Before proceeding with the research associated with the determination of efficiency of the process of biopurification of the air from styrene, the optimal environmental conditions for growth of the selected microorganisms were examined and next kinetic equation describing both the rate of the growth of the tested strain and styrene degradation were developed. The worked out kinetic model was verified basing on our own experimental data-base, obtained in batch experiments. Than the series of experiments of biopurification of air from styrene was carried out in pilot scale trickle- bed bioreactor. The aim of the experiments was to determine the range of the operational parameters for which maximum elimination capacity was achieved.

Materials and methods

Microorganisms

The culture of gram-negative bacteria used in this study, coming from VTT Culture Collection (Finland), showed 97% homology with *Pseudomonas putida* and 97% with *Pseudomonas stutzeri* from 16SrDNA analysis. The strain, marked as E-93486, was isolated from the activated sludge enriched with styrene [9]. Proliferation of the cells and pre-incubation with styrene in the concentration of 90 g·m^{-3} was performed as described previously [10].

Analytical methods

The concentration of biomass was determined by measuring the optical density (OD) of the fluid culture (λ = 550 nm). Next, the suspension absorbance was converted into grams of dry mass of microorganisms according to the calibration curve. Styrene concentration was determined by gas chromatography using Varian 3800 (USA) chromatograph as described previously [10].

Results and discusion

Effect of temperature and pH on E-93486 growth

Before proceeding with the research associated with styrene biodegradation the effect of pH and temperature on the growth of the selected strain was examined. Pure cultures of *Pseudomonas* sp. E-93486 were inoculated into a triplicate sets of 500 cm^3 Erlenmeyer flasks containing LB medium. Part of them was adjusted to pH of 5, 6, 7 or 8 and incubated in a shaker at 30°C, another part was adjusted to pH 7 and incubated at 21, 25, 30 or 35ºC (Fig. 1). Optimal environmental conditions for the growth of tested strain were pH = 7 and 30°C and all experiments presented below were performed maintaining these parameters.

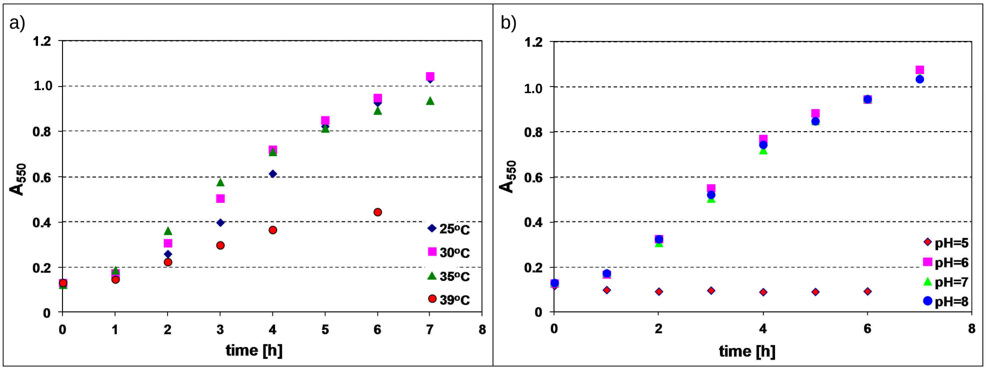

Fig. 1. The rate of growth of E-93486 strain at different temperatures (a) and pH values (b)

Kinetic experiments

The kinetic model parameters are usually obtained from batch experiments by observing the biomass growth rate with time at a different initial concentration of substrate. Microbial growth tests in the presence of styrene as the sole carbon and energy source were conducted in Biostat B fermenter (Sartorius, USA), with working volume of 2.7 dm^3, operating both in batch and continuous mode. Batch experiments were carried out for initial styrene concentration in the liquid phase changing in the range 5-90 g·m^{-3}. A $\ln X = f(t)$ graph (X [g·m^{-3}] is concentration of biomass, t [h] is time) was plotted for every experimental point. In the exponential growth phase, the dependence is a straight line of slope (μ_{net}). The compiled data-base made it possible to choose kinetic model and to determine its constants. The Haldane inhibitory model:

$$\mu_{net} = \frac{\mu_m S_l}{K_S + S_l + \frac{S_l^2}{K_i}} \tag{1}$$

was found to be the best to fit the kinetic data. In equation (1) μ_{net} [h^{-1}] is net specific growth rate, S_l [g·m^{-3}] is concentration of styrene in the liquid phase, μ_m [h^{-1}] is the model parameter, K_S and K_i are the half saturation constant [g·m^{-3}] and substrate inhibition constant [g·m^{-3}], respectively.

The kinetic equation parameters were estimated basing on the own database using the least-square error method with the help of NLReg programme, and they were: $\mu_m = 0.119$ h^{-1}; $K_s = 5.984$ g·m^{-3}, $K_i = 156.6$ g·m^{-3}.

The developed equation with a mean relative error:

$$e_Y = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\mu_{exp,i}-\mu_{calc,i}}{\mu_{exp,i}}\right| \cdot 100\% \tag{2}$$

not exceeding 5.5% approximates the experimental data. In Eq. (2) subscripts *exp* and *calc* denote experimental and calculated values, respectively.

The conducted experiments made it possible also to determine the value of the observed biomass yield coefficient ($(Y_{XS})_{obs} = 0.72$) (Fig. 2).

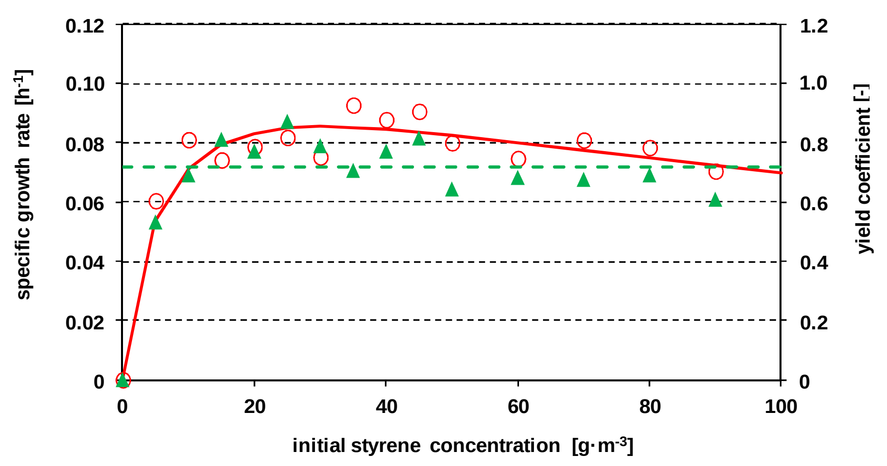

Fig. 2. Specific growth rate (circles) and observed yield coefficient (triangles) as a function of initial styrene concentration (solid line correspond to the model prediction)

The experiments conducted in a chemostat at various dilution rate ($D = 0.035$-0.1 h^{-1}) enabled us to determine the value of the coefficient for maintenance metabolism ($m_d = 0.0165$ h^{-1}) and the maximum yield coefficient value ($(Y_{XS})_{max} = 0.913$). The determined complete model of growth of E-93486 strain in the presence of styrene allows to calculate the profiles of the changes of biomass and growth substrate concentrations in the periodic cultures. For this purpose the system of differential equations must be solved:

$$\frac{dX}{\mathrm{d}t} = \left(\frac{0.119 S_l X}{5.984 + S_l + \frac{S_l^2}{156.6}} \right) \left(1 - exp\left(-\frac{t}{t_l} \right) \right) \tag{3}$$

$$-\frac{\mathrm{d}S_l}{\mathrm{d}t} = \frac{1}{0.913} \left(\frac{\mathrm{d}X}{\mathrm{d}t} \right) + 0.0165 \cdot X \tag{4}$$

where X is the concentration of cells, S_l is concentration of styrene in the liquid phase, t and t_l are time and duration of lag phase, respectively; the last term on the right hand side of Eq. (3) considers the existence of an adaptation phase of duration t_l. The above system of equations with the initial condition:

$$\text{when } t = 0, \text{ than } X = X_0 \text{ and } S_l = S_{l0} \tag{5}$$

was solved by Runge-Kutta 4th order method.

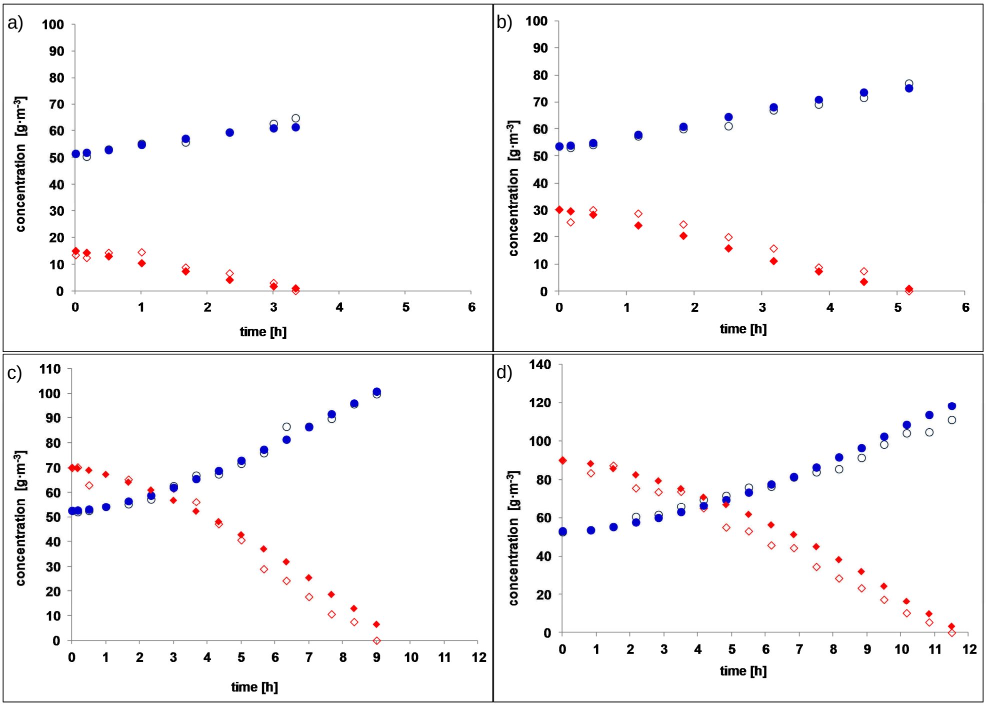

Fig. 3. Profiles of changes in concentration of biomass (circles) and styrene (diamonds) for different initial concentrations of growth substrate; *open symbols* - experimental values, *filled symbols* - values computed using set of eq. (3)-(4): a) $S_l = 15\ \mathrm{g \cdot m^{-3}}$, b) $S_l = 30\ \mathrm{g \cdot m^{-3}}$, c) $S_l = 70\ \mathrm{g \cdot m^{-3}}$, d) $S_l = 90\mathrm{g \cdot m^{-3}}$

In Figure 3 the profiles of changes in biomass and styrene concentration calculated and obtained experimentally for a few periodic cultures of *Pseudomonas* sp. E-93486 cells were compared. It is worth emphasizing that the results of numerical simulations performed using set of eq. (3)-(4) fit the experimental values with good accuracy.

Purification of the air in pilot scale trickle-bed bioreactor (TBB)

The experiments of the air purification were performed in a pilot scale installation shown schematically in Figure 4.

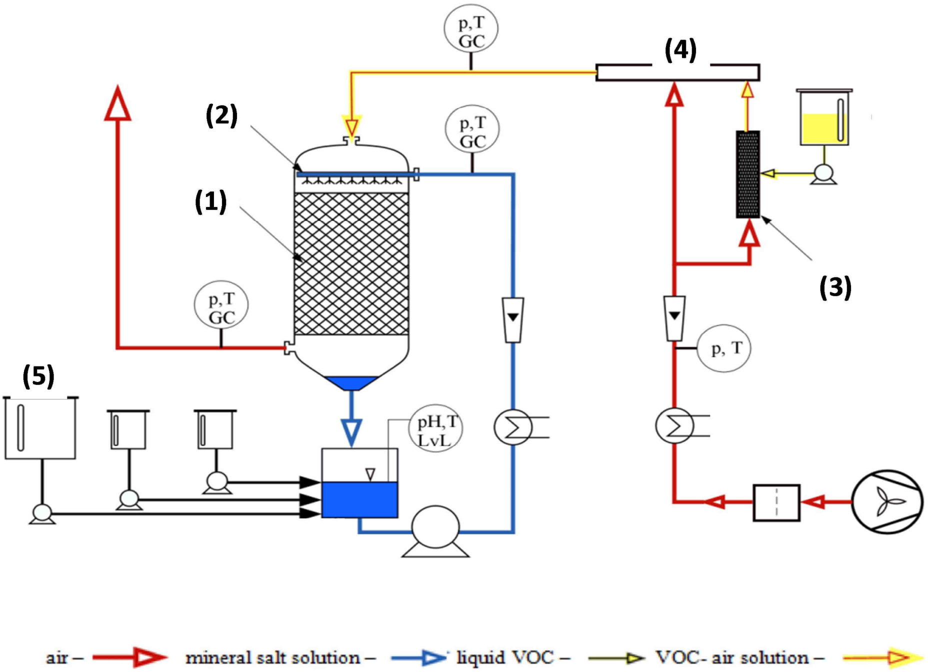

Fig. 4. Scheme of the experimental set-up: 1 - biofilter, 2 - sprinkler, 3 - vaporizer, 4 - mixer, 5 - reservoir of mineral salt solution

Its main part was a cylindrical column of 1.084 m I.D. filled with polypropylene Ralu rings up to the height of about 1.8 m. The air and liquid phases (mineral medium) flowed co-currently downward through the packing covered with a thick layer of the microorganisms. During experiments the concentration of styrene both on the inlet and the outlet of bioreactor was controlled in the gas and liquid phases. The detailed qualitative and quantitative analysis of microorganisms in the recirculating mineral solution was also performed every day. The effect of inlet styrene concentration on its degradation was studied for initial concentration in the air changing in the range of 0.2-1 $g \cdot m^{-3}$. The gas flow rate was changed in the range of 50-150 $m^3 \cdot h^{-1}$ whereas the liquid flow rate was maintained at the level 8 $m^3 \cdot h^{-1}$. The experiments were performed during the period of more than six months (Fig. 5).

It must be emphasized that conducted experiments showed high activity of examined bacterial strain in the styrene biodegradation; the conversion degree obtained for tested operational parameters changed in the range of 75-95%. It means that for the tested range of changes of pollutant load the high elimination capacity of the process was achieved; for maximum pollutant load (80 $g \cdot m^{-3} \cdot h^{-1}$) about 2500 g styrene was removed from the air every day.

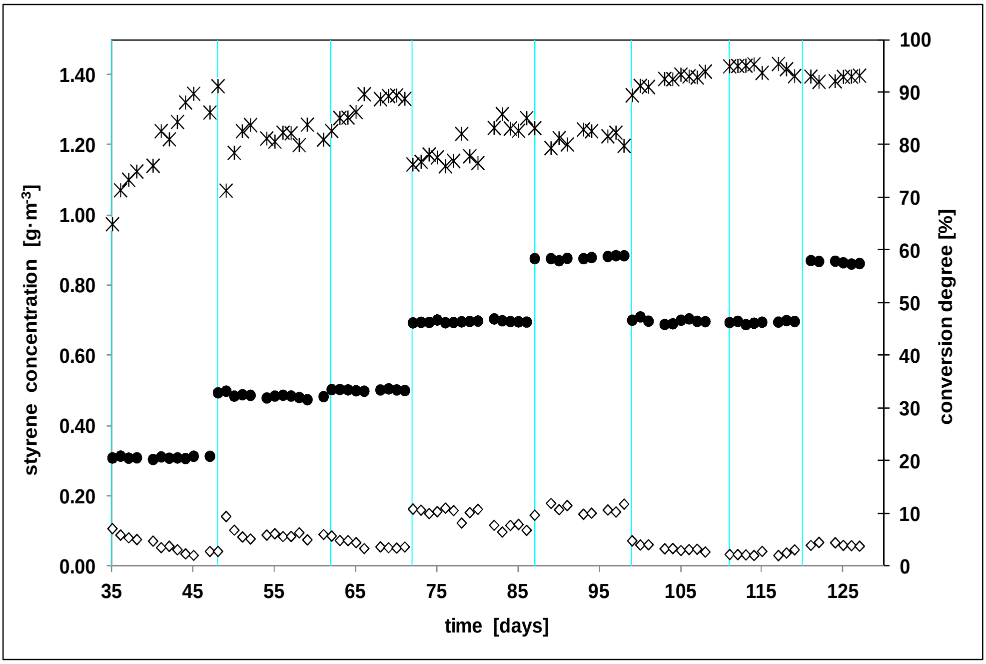

Fig. 5. Changes in the concentration of styrene in the air at the inlet (black circles) and outlet (white diamonds) of the reactor as well as conversion degree of the substrate (stars) during operation of the plant

Conclusions

The paper presents the issues associated with making use of microorganisms to remove the selected volatile organic compound which was the only source of carbon and energy for the examined strain. As a result of the kinetic experiments the equation describing the rate of the biological reaction of styrene oxidation by *Pseudomonas* sp. E-93486 bacteria were determined. The developed kinetic model was verified basing on our own experimental data base. It should be emphasized that the rate of biodegradation of the growth substrate is one of the most important stages of the processes taking place in bioreactor. The formulated relationships are necessary to verify the mathematical model of the bioreactor since drawing up mass balance of the compound removed from the air or sewage, regardless of the type of a bioreactor, always requires a knowledge of an expression determining the biodegradation rate of the removed pollutant. The tested strain was immobilized on the inert packing of TBB and for several months effectively decomposed styrene contaminating big stream of air. The created data-base will be used for verification of the mathematical model of the process of gas purification carried out in TBB.

The experiments showed high activity of tested microorganisms in the process of biodegradation of styrene and relatively low sensitivity to the inhibitory influence of styrene at higher concentrations in solution (the high value of K_i). Due to such feature, the examined microorganisms may be recommended for technical applications as biological material in the processes of removing styrene from waste air and sewages.

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MODELOWANIE PROCESU OCZYSZCZANIA POWIETRZA Z LOTNYCH ZWIĄZKÓW ORGANICZNYCH W BIOREAKTORZE STRUŻKOWYM

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Abstrakt: Badano proces oczyszczania powietrza ze styrenu, substancji zaliczanej do grupy lotnych związków organicznych (LZO), prowadzony w pilotowym bioreaktorze strużkowym (TBB). Ponieważ najważniejszym etapem procesu oczyszczania powietrza z LZO w bioreaktorze strużkowym jest biologiczna reakcja jego rozkładu, zatem, projektując proces, należy przede wszystkim starannie wyselekcjonować mikroorganizmy efektywnie rozkładające usuwane z powietrza zanieczyszczenie, określić warunki najkorzystniejsze dla ich wzrostu oraz wyznaczyć kinetykę reakcji. W wyniku testów porównawczych wyselekcjonowano szczep efektywnie wykorzystujący styren jako jedyne źródło węgla i energii. Był to, pochodzący z kolekcji VTT (Finlandia), gram-ujemny szczep z rodzaju *Pseudomonas*, oznaczony symbolem E-93486. W testach wstępnych określono najkorzystniejsze dla jego wzrostu parametry (pH 7, 30ºC, $DO = 5$ mg·dm^{-3}) i zarówno eksperymenty kinetyczne, jak i proces oczyszczania powietrza w TBB prowadzono, utrzymując wyznaczone, optymalne dla reakcji biochemicznej warunki. Pierwszą serię eksperymentów kinetycznych przeprowadzono w reaktorze okresowym, zmieniając w kolejnych eksperymentach początkowe stężenie substratu wzrostowego w zakresie 5-90 g·m^{-3}. Badania wykazały inhibitujący szybkość wzrostu mikroorganizmów wpływ substratu, stąd do opisania kinetyki wzrostu E-93486 w obecności fenolu wybrano model Haldane. Zgromadzona baza danych doświadczalnych umożliwiła estymację stałych tego równania ($\mu_m = 0{,}119$ h^{-1}; $K_s = 5{,}984$ g·m^{-3}, $K_i = 156{,}6$ g·m^{-3}). Hodowle ciągłe, prowadzone przy różnej szybkości rozcieńczania (D = 0,035-0,1 h^{-1}), umożliwiły określenie wartości współczynnika metabolizmu endogennego ($m_d = 0{,}0165$ h^{-1}) i maksymalnej wartości współczynnika wydajności biomasy ($(Y_{XS})_{max} = 0{,}913$). Otrzymane pełne równanie kinetyczne wzrostu szczepu E-93486 w obecności styrenu zostało zweryfikowane przez porównanie obliczonych i otrzymanych eksperymentalnie profili zmian stężenia biomasy i styrenu. Badania procesu oczyszczania powietrza ze styrenu przeprowadzono w pilotowej instalacji, której głównym elementem był bioreaktor strużkowy o średnicy 1,084 m, wypełniony na wysokość 1,84 m inertnym wypełnieniem (polipropylenowe pierścienie Ralu), na powierzchni którego unieruchomiony został testowany szczep. W badaniach strumień oczyszczanego gazu zmieniano w zakresie 50-150 $m^3 \cdot h^{-1}$, natomiast stężenie styrenu w powietrzu doprowadzanym do reaktora zmieniano w zakresie 0,2-1 $g \cdot m^{-3}$. Podczas trwających ponad 6 miesięcy eksperymentów uzyskano stopień konwersji styrenu rzędu 75-95%, co oznacza, że przy maksymalnym obciążeniu złoża (80 $g \cdot m^{-3} \cdot h^{-1}$) każdego dnia usuwane było z powietrza ~2500 g styrenu. Potwierdzona została w ten sposób skuteczność testowanej technologii oczyszczania powietrza z LZO.

Słowa kluczowe: styren, kinetyka, bioreaktor strużkowy

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Michał KOZIOŁ[1]

CHANGE IN SELECTED PROPERTIES OF SEWAGE SLUDGE IN MEDIUM-TERM WASTE STORAGE

ZMIANA WYBRANYCH WŁAŚCIWOŚCI OSADÓW ŚCIEKOWYCH W TRAKCIE SKŁADOWANIA ŚREDNIOOKRESOWEGO

Abstract: In recent years, a number of relatively large installations for thermal disposal of sewage sludge was built. Despite that fact, its management is still the unsolved problem for large area of the country. One of the phenomena caused, inter alia, by still underdeveloped sewage sludge management is the need of its temporary storage. Such storage occurs, for example when there is no possibility of current management of sewage sludge produced by the wastewater treatment plant. The introduction of the paper briefly outlines the issues of sewage sludge management in Poland and the genesis of the research. In the following parts, the paper focuses on the methodology of the study. The research included the use of dewatered sewage sludge, stabilized in the process of anaerobic digestion, from three municipal wastewater treatment plants. Sewage sludge was subjected to storage for six months. The storage took place on a specially constructed place, in layers with a thickness of approximately 1 meter. The study included, inter alia, the changes of the properties of sewage sludge deposited depending on the depth from which it was taken. The paper presents the results concerning the changes in selected physicochemical parameters of the sewage sludge.

Keywords: sewage sludge, storage, physicochemical parameters, experimental research

Introduction

Sewage sludge from municipal sewage treatment plants is still one of the major and unsolved problems of waste management in Poland. Difficulties in managing sewage sludge result, inter alia, from the fact that it is generated across Poland in relatively large quantities. In 2014, over 550,000 Mg of sludge dry matter was produced in Poland. Sludge has a relatively high moisture content (over 70%). Therefore, the actual weight of the waste that needs to be managed is much larger. It can be estimated that it exceeds significantly 2 million Mg per year. In addition, due to the fact that in Poland 39.4% of population live in rural areas and only 36.6% of population live in cities with population over 50,000 [1], there is significant territorial dispersion of the sources of sewage sludge generation.

Another property of the sludge, contributing to the fact that its neutralisation is troublesome, is its content of heavy metals and pathogens. Heavy metals content is significant particularly in the sludge derived from large urban agglomerations.

Currently applicable legal regulations restrict significantly the natural use of sludge and prevent their storage (from 2016 onwards). Since 2010, there have been 9 sludge thermal treatment plants constructed in Poland. Thus, at present, there are a total of 11 plants operating in the country that incinerate only sewage sludge. Other plants where sewage sludge is managed are cement kilns. In these kilns sewage sludge that has been previously dried is incinerated (there are several sludge drying plants operating in Poland).

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All in, in 2014, over 84,200 Mg of sludge dry matter was managed by thermal methods in Poland [2]. It was over 15% of the total weight of sludge generated.

Currently, in highly-developed countries, we can observe two clashing concepts of sewage sludge management. In such countries as: Norway, Denmark, the UK, over 70% of sludge is managed in a natural manner. And in such countries as the Netherlands and Switzerland, over 90% of the generated sludge weight is managed with the use of thermal methods.

However, in the case of using each method of sewage sludge management, it may be necessary to store the sludge for some time. In the case of using thermal methods, it may result from the very fact of the sludge treatment system organisation. Therefore, the need to store sludge may result, for instance, from the need to collect a larger weight of sludge derived from a small sewage treatment plant prior to its further transportation, the need to store sludge in summer time when the thermal plant (*e.g.* a heat-generating plant) does not operate or operates with smaller output. The need to store sludge may also occur as a result of a failure of a thermal sludge treatment plant.

In the case of a natural sewage sludge management, the need for the sludge storage may also occur when it is required to collect a larger quantity of sludge before transportation, but also in the periods of the absence of recipients or in winter season, when its natural management is at least hampered.

Further in the paper, the results of tests on changes occurring in the sludge stored for the period of 6 months are presented.

Testing methodology

This paper presents the results of testing conducted on three samples of sewage sludge from large municipal sewage treatment plants (with output of over 30,000 m^3/day). All sewage treatment plants were mechanical biological treatment plants. In the plant, the sewage sludge was subject to anaerobic fermentation and mechanical dewatering processes.

In testing, batches of sludge were sampled from sewage treatment plants and put in special containers. The capacity of each container was over 1 m^3. The objective of the conducted tests was to replicate the process of landfilling sludge under actual conditions, that is occurring under conditions as in industrial processes. Under such conditions, the landfilled sludge is exposed to, among others, weathering factors. For this reason, the containers were open from the top. Additionally, in order to simulate interaction of the neighbouring batches of sludge, the sides of the containers were insulated. Moreover, the effluent could flow downwards the sludge layer and farther on. This was executed with permeable layers of sand placed at the bottom of the containers. When the test was started, the thickness of the sludge layers was 1.2 m (with up to 0.05 m accuracy). Within the test, samples for laboratory determination were collected from various depths (measuring from the top surface of the sludge layer in the container), and the results presented below refer only to the samples collected from the depth of 1 meter (with tolerance as stated earlier). Samples were taken preferably from the central part of the landfilled mass of sludge (the centre of the horizontal cross section of the container). Due to the depth of sampling, the effect of meteorological conditions was included in the test as a disturbing factor.

The samples for laboratory determinations were collected in monthly intervals for a period of six months, starting with the time when landfilling sludge began. Thus, the paper presents the results related to the seven dates of sampling.

The following part of the document presents the results of the following sample analyses from the group of several determinations of parameters:

- determination of combustible matter content (determination made by gravimetric method, according to PN-G-04516:1998 [3]),
- determination of total nitrogen content (total nitrogen was determined by the Kjeldahl method [4]),
- hydrogen content (pursuant to standard PN-87/C-04301 [5]).

It should be noted that all values presented further in the paper (*e.g.* on graphs) are mean values obtained based on the threefold repetition of each determination. The mean values of analysed parameters obtained in this manner, referring to individual sludge samples, were subsequently used to determine mean values referring to all sludge samples. These values were then used for the analyses of correlation between the lapse of time and tested parameters. Determined Pearson's linear correlation coefficients were compared with critical values of the correlation coefficient for the significance level of 0.05 (for 5 degrees of freedom amounting to $r_{kr} = 0.7545$).

As part of the presented tests, tested parameters were analysed calculated to dry matter.

Test results

Figure 1 presents the results of tests on the change in time of sludge storage of its combustible matter content. The figure presents the value of combustible matter content reported in subsequent months in all samples of sludge stored. The values were used to determine mean values. For mean values, the trend line equation and the linear correlation coefficient were determined (it was similar in the case of analysis of other parameters tested).

Combustible matter content in the analysed sludge throughout testing amounted from slightly more than 51% up to about 73% (dry matter). The greatest variation range was characteristic for measurement results of combustible matter content in sample "Sludge I". Readings for this sample demonstrated nearly 4.5% variation range. It was, however, mostly due to the value of the combustible matter content reported in the third month. The value of this measurement, clearly lower than the one reported in earlier and later months, is probably the result of the heterogeneity of the sample stored. In the case of other sludge samples, the variation range was approx. 3.3%.

Table 1 presents values of tested parameters for all sludge samples at the beginning and end of tests. In addition, a ratio of the end value to the initial value is presented. As the data in the table demonstrate, differences in the case of combustible matter content amounted from the value of 0 ("Sludge I") to over 3% ("Sludge III"). In the case of mean values, the discussed difference was 1.7%.

The determined trend line for mean values had the following form: $y = 0.29x + 63.92$. The linear correlation coefficient ($r = 0.780$) leads to the conclusion that there is a correlation between the analysed values.

Figure 2 presents the results of tests on the change in time of the total nitrogen content.

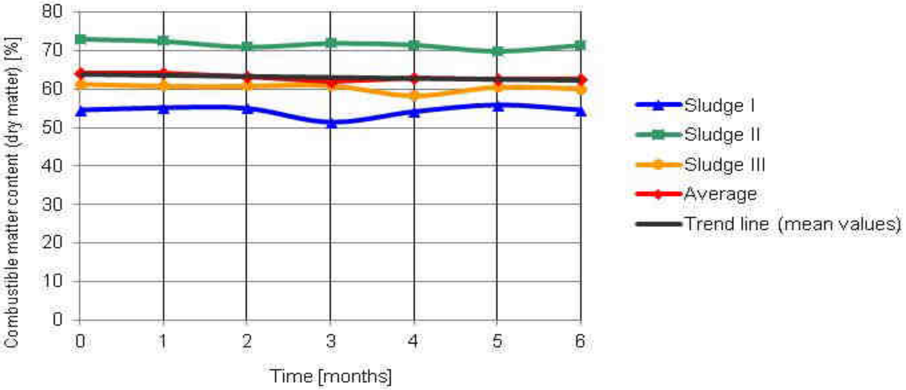

Fig. 1. Changes in time of the combustible matter content in stored sludge

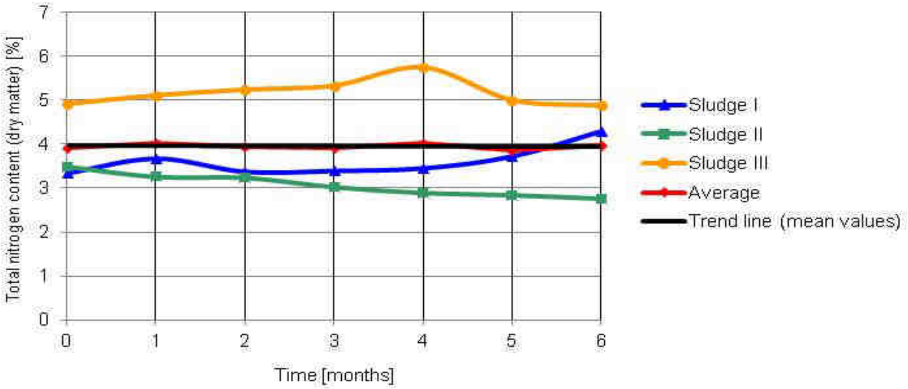

Fig. 2. Changes in time of the total nitrogen content in stored sludge

Total nitrogen content in the analysed sludge throughout testing amounted from over 2.8% up to about 5.8% (dry matter). The greatest variation range was characteristic for measurement results of total nitrogen content in sample “Sludge I”. Readings for this sample demonstrated nearly 1% variation range. For sample “Sludge II” it was 0.7%, and for sample “Sludge III” 0.9%. No correlation was confirmed between the analysed factors during testing. The mean values determined for the beginning and end of tests have nearly identical values. Table 1 presents the values of nitrogen content reported in the case of individual sludge samples at the beginning and end of the analysed testing period.

The analysis of the presented data (in the graph and in the table) leads to the conclusion that the reason for failure to confirm the correlation is large heterogeneity of sludge samples in terms of the parameter analysed. It is proved by the fact that for “Sludge I”, in the case of the last two readings, a sudden increase in the nitrogen content is clear. In the case of this sample, the total nitrogen content for the last determination is larger by over 25% than in case of the first one. And, in the case of “Sludge II” we observe for the whole time a visible downward trend of nitrogen content value during storage. And in the case of “Sludge III” for the first and last measurement, very similar values of the tested value were reported. Thus, in the case of each of the sludge sample tested, a different trend in changes of the total nitrogen content was reported during storage: drop, increase and a constant value.

Table 1

Initial and final values of analysed parameters for 3 sludge samples

Sample	**Combustible matter content [%]**		**End of testing/start of testing ratio**
	Start of testing	**End of testing**	
Sludge I	54.5	54.5	1
Sludge II	73.0	71.4	0.98
Sludge III	65.1	61.7	0.95
Share of total nitrogen [%]			
Sludge I	3.4	4.3	1.26
Sludge II	3.5	2.8	0.80
Sludge III	4.9	4.8	0.98
Hydrogen content [%]			
Sludge I	3.2	2.6	0.81
Sludge II	5.2	5.7	1.10
Sludge III	4.7	4.0	0.85

Figure 3 presents the results of tests on the change in time of the hydrogen content.

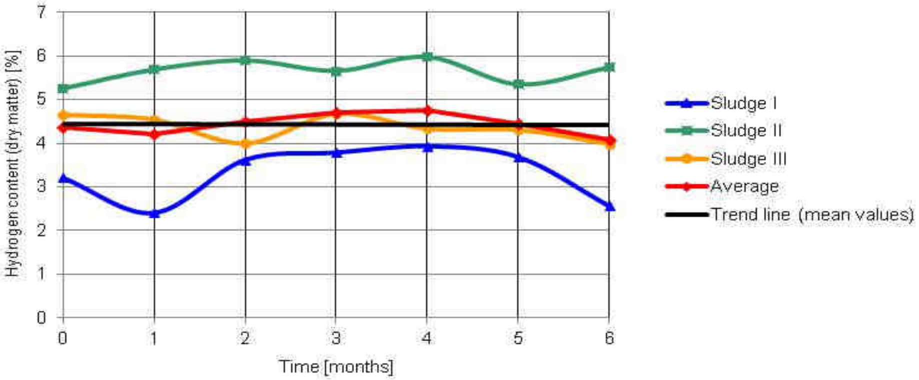

Fig. 3. Changes in time of the hydrogen content in stored sludge

The hydrogen content in the analysed sludge throughout testing amounted from nearly 2.5% up to almost 6% (dry matter). The greatest variation range was characteristic for measurement results of hydrogen content in sample “Sludge I”. Readings for this sample demonstrated the variation range of over 1.5%. In the case of other sludge samples, the variation range was approx. 0.7%. In the case of “Sludge II” the reading at the end of testing was higher than at the beginning (Table 1). No correlation was confirmed between the analysed factors during testing. It was probably caused by insignificant impact of storage time on the hydrogen content in sludge located at the depth of 1 m, as well as by the heterogeneity of sludge samples (resulting in greater variation of hydrogen content then the impact of the analysed process).

Conclusions

As it was presented in the introduction to the publication, irrespective of the management method of sewage sludge, its medium-term storage may be required.

Testing conducted leads to the conclusion that in deeper layers of the sludge stored (at the depth of 1 m), the physical and biological processes occur relatively slowly. The expected change in the combustible matter content for this period is less than 3%. In the case of other discussed parameters (total nitrogen, hydrogen content), testing conducted do not lead to the confirmation of a correlation between the storage time and a change in their value. Thus, if there are changes occurring for the period of 6 months, they are smaller than those resulting from the heterogeneity of sludge and accuracy of determinations performed.

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ZMIANA WYBRANYCH WŁAŚCIWOŚCI OSADÓW ŚCIEKOWYCH W TRAKCIE SKŁADOWANIA ŚREDNIOOKRESOWEGO

Katedra Technologii i Urządzeń Zagospodarowania Odpadów, Politechnika Śląska, Gliwice

Abstrakt: W ostatnich latach zrealizowano w Polsce szereg stosunkowo dużych instalacji termicznego unieszkodliwiania osadów ściekowych. Pomimo powyższego, ich zagospodarowanie wciąż stanowi nierozwiązany problem na znacznym obszarze Polski. Jednym ze zjawisk wynikającym m.in. z wciąż nie w pełni poprawnej gospodarki osadami ściekowymi jest konieczność ich okresowego składowania. Składowanie to ma miejsce np. w sytuacji, kiedy nie ma możliwości bieżącego zagospodarowania osadów wytwarzanych przez oczyszczalnię ścieków. We wstępie pracy krótko zarysowano problematykę zagospodarowania osadów ściekowych w Polsce oraz genezę prezentowanych badań. W dalszej części pracy omówiono metodykę przeprowadzonych badań. W ramach badań wykorzystano ustabilizowane w procesach fermentacji beztlenowej odwodnione osady ściekowe, pochodzące z trzech oczyszczalni ścieków komunalnych. Osady zostały poddane składowaniu przez 6 miesięcy. Osady składowano na specjalnie zbudowanych w tym celu stanowiskach, w warstwach o grubości ok. jednego metra. W badaniach uwzględniono m.in. zmiany właściwości składowanych osadów w zależności od głębokości, z jakiej je pobrano. W pracy przedstawiono wyniki dotyczące zmiany wybranych parametrów fizykochemicznych osadów.

Słowa kluczowe: osady ściekowe, składowanie, właściwości fizykochemiczne, badania eksperymentalne

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APPLICATION OF MEMBRANE PROCESSES IN UTILIZATION OF WASTEWATER GENERATED IN BIOMASS GASIFICATION

WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI ŚCIEKÓW POWSTAJĄCYCH W PROCESIE ZGAZOWANIA BIOMASY

Abstract: Gasification of biomass is always accompanied with the generation of highly loaded wastewater. Those streams are formed during cooling and cleaning of process gas and comprise of tars, condensed water vapor and a range of organic and inorganic compounds. Nowadays, there are no treatment systems of those wastewater, especially dedicated to small and medium size gasification plants, what is the main limitation in the technology popularization and industrial commercialization. On the other hand, conventional methods proposed for the treatment characterize with the narrow spectrum of action dedicated, mainly to the removal of tar substances. In the presented paper the possibility of utilization of biomass gasification wastewater by means of membrane processes is proposed. The technology was based on the two stage treatment system enabling the separation of tars by spontaneous sedimentation/floatation and low pressure drive aqueous phase filtration. Polymeric, ultrafiltration membranes of various cut off were investigated due to the contaminants removal effectiveness and capacity. It was shown, that the use of membrane processes assures the concentration of soluble organic contaminants to the rate enabling their recycle to the gasifier. The filtrate obtained during the process characterized with much decreased load of contaminants and after the proper polishing could be directly deposited to the environment.

Keywords: wastewater, tars, gasification, biomass

Introduction

The process of biomass gasification is energetically efficient and economically attractive thermal operation, which is regarded as one of the most promising method for renewable energy production [1-4]. The process comprises of several stages, which usually occur in one reactor, called gasifier, organized in co-current or counter-current flow, which is schematically presented in Figure 1.

The mechanism of gasification process can be defined as a series of thermochemical reactions, which occur during pyrolysis and combustion. As a results of those reaction and at the use of a proper gasification agent (air, oxygen, water vapor, hydrogen, carbon dioxide, etc.) and increased temperature (above 800°C) the conversion of solid substrates to combustible gaseous products, which is a mixture of carbon oxide and dioxide, hydrogen, methane and water vapor, takes place [5-7].

The gas obtained during the gasification process, except of the gaseous products, contains also a range of contaminants, which need to be removed in case, when further gas processing, *e.g.* in chemical synthesis or cogeneration, is predicted. Two gas cleaning methods are used for this purpose *i.e.* wet and dry. In the former method, the contaminants are usually washed out from the gas by means of water or oil absorption in scrubbers and the simultaneous cooling of gas due to its contact with the scrubbing medium occurs. In the

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latter method, the condensable contaminants present in gas stream appear in the form of aqueous-tar mixture, while solids (dusts and ashes) are usually removed on filters [8-10].

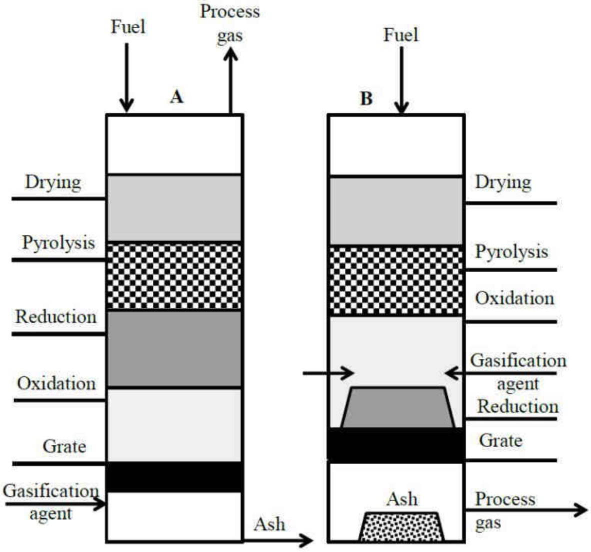

Fig. 1. Fixed bed reactor for biomass gasification: A - counter-current mode, B - co-current mode

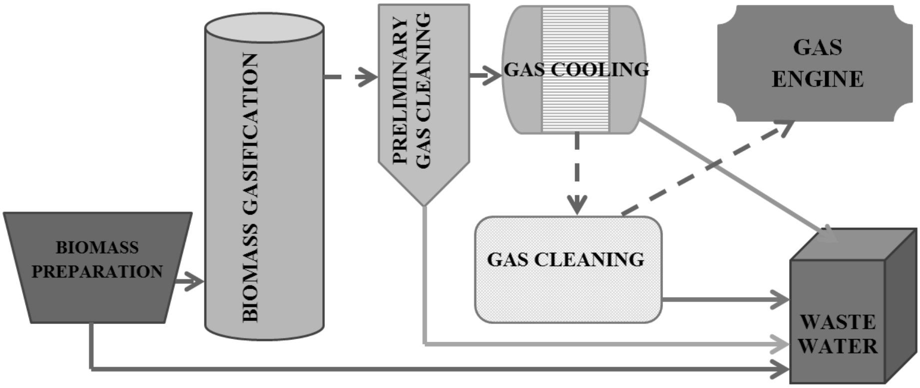

Fig. 2. Places of formation of wastewater streams generated during biomass gasification process

Regardless of gas cleaning method, the highly loaded wastewater containing tars and aqueous stream contaminated with water soluble organic compounds is formed (Fig. 2). The proper management of the stream is said to be one of the most important condition for popularization of biomass gasification, especially in case of medium and small systems. Nowadays, only large installations equipped with technologically complete wastewater treatment plants are found to be commercially available, and the lack of the method for proper utilization of smaller amount of wastewater is one of the main reason [11, 12].

In the paper, the technique for the treatment of biomass gasification wastewater obtained during the dry cleaning of gas (*i.e.* tar-water condensate) is discussed. The system was based on the membrane separation, and different types of membranes were used.

Methods

The process of membrane filtration was carried out in the laboratory installation by KOCH Membrane Systems, model KMS Cell CF1. The device is equipped with the feed tank of volume 0.5 dm^3 and two membrane cells arranged in a series of common separation area of 56 cm^2. The construction of the device enables to run the process in the cross flow mode. The scheme and the photography of the installation is shown in Figure 3.

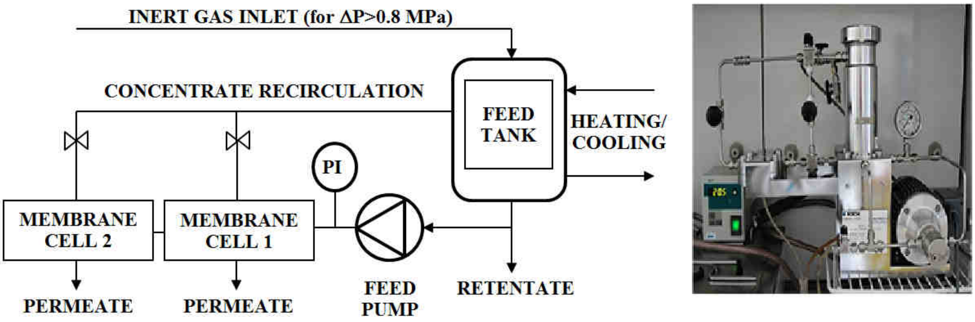

Fig. 3. The scheme and the photography of laboratory installation for membrane filtration KMS Cell CF1

In the study two types of membranes differ in membrane material and molecular weight cut off, *i.e.* polyether sulfone membrane of cut off 5 kDa (UF-PES-5) and composite membrane of cut off 1 kDa (UF-K-1), were used. The filtration of gasification condensate was preceded by both, membrane conditioning and characterization with deionized water at transmembrane pressure of 0.1 MPa as well as with removal of tars from the treated medium by means of spontaneously occurring sedimentation and floatation of the fraction. Next, the filtration of the aqueous phase of the condensate was carried out at transmembrane pressures equal to 0.2 MPa for UF-PES-5 and 1.0 MPa for UF-K-1. The difference in process pressures resulted of the dependences observed during the membrane conditioning. Both process were carried out until 80% of the feed volume was recovered in the form of permeate. After the process, the stream of deionized water was again measured, in order to evaluate the character of fouling of the membrane and possible interactions between membrane materials and contaminants present in the treated wastewater.

The feed and the filtrates obtained during the process were characterized due to the value of pH, specific conductivity, chemical oxygen demand, ammonia nitrogen and dry mass content. pH and specific conductivity were measured with the use of dedicated probes, chemical oxygen demand and ammonia nitrogen were indicated by means of

HACH Lange methodology, while dry mass content was analyzed by means of conventional thermal method at 105°C temperature.

Results and discussion

In Figure 4, the capacities of clean membranes expressed as the volumetric deionized water flux at 0.1 MPa transmembrane pressure are compared.

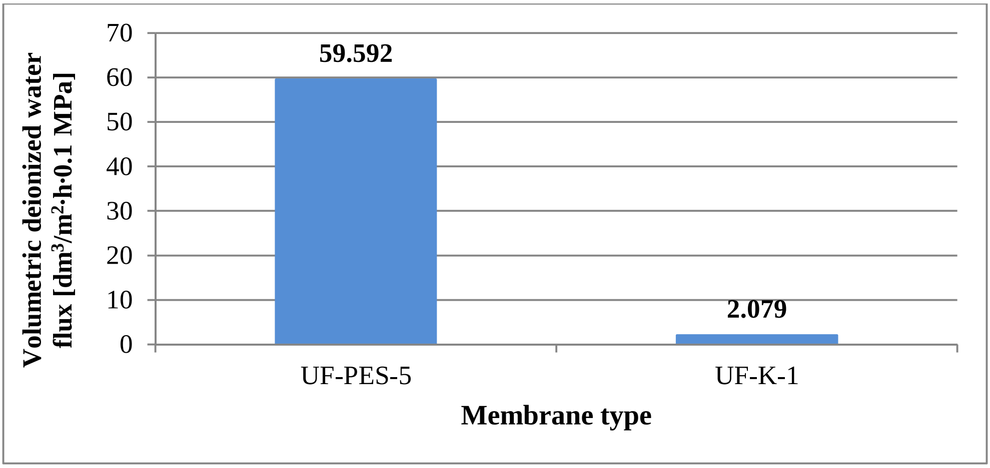

Fig. 4. The comparison of capacities determined for clean membranes

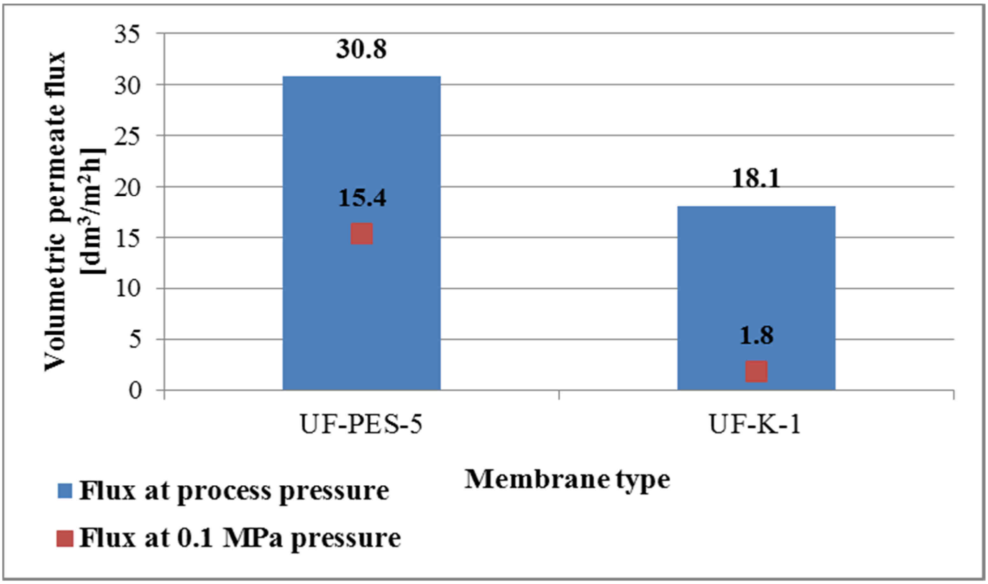

Fig. 5. The capacity of membranes obtained during biomass gasification wastewater filtration

It was noticed, that despite the small difference between particular membranes cut off (5 kDa and 1 kDa), the difference in their capacities was significant. It was explained by the hydrophilicity of particular membrane materials, which was found to be higher for polyether sulfone membrane.

In Figure 5 the results of biomass gasification wastewater filtration at 0.2 MPa pressure for UF-PES-5 and 1.0 MPa pressure for UF-K-1, as well as fluxes recalculated for 0.1 MPa transmembrane pressure are shown.

The much higher capacity at both, process and 0.1 MPa pressure, was obtained for UF-PES-5 membrane. However, when values of relative permeate fluxes, calculated as the ratio of the permeate flux to the deionized water flux, were compared, it was noticed that UF-PES-5 membrane operated at 0.25 of initial capacity, while UF-K-1 membrane at 0.87 of the initial capacity. The phenomenon was explained by both, membrane cut off responsible for fouling and membrane material hydrophilicity and affinity to compounds present in the treated membrane. The former reason resulted of the blockage of pore membranes, as probably they were wide enough, in case of UF-PES-5, to enable only the entrance of the contaminant and its remaining inside the pores. The latter reason resulted of the deposition of contaminants on the membrane surface, which protected membrane pores from the entrance of smaller particles inside the membrane. Hence, forming the washable filtration cake layer was formed. In order to confirm the described phenomena, the investigation of the change of deionized water flux was made. The results are shown in Figure 6.

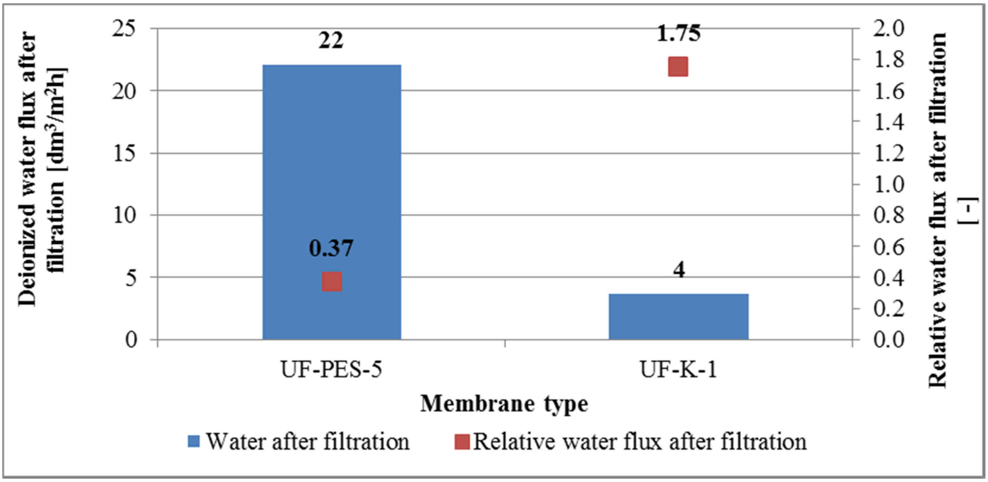

Fig. 6. The comparison of water fluxes and relative water fluxes measured for UF-PES-5 and UF-K-1 after the process

It was noticed, that despite higher capacity revealed during the wastewater filtration, it was UF-PES-5 membrane, capacity of which decreased by 63% after the process. Hence, the conclusion on the penetration of membrane pores by contaminants present in the treated medium and irreversible fouling occurrence was confirm. On the other hand, and interesting observation was made for UF-K-1 membrane, for which 175% of initial capacity was noted. It was explained by the fact, that the presence of the filtration cake, which formed on the membrane surface during the wastewater treatment, modified the membrane material and increased its hydrophilicity.

The operation of membranes was also evaluated due to the rate of contaminants removal. In Table 1 the comparison of parameters analyzed in feed and particular process filtrates is shown, while in Figures 7 and 8 the photography's of process streams and membrane after process are shown.

Table 1

The values of parameters of process streams and removal rates of contaminants

Parameter	**Unit**	**Feed**	**UF-PES-5 permeate**	**UF-K-1 permeate**	**UF-PES-5 removal rate**	**UF-K-1 removal rate**
pH	-	3.51	7.63	7.61	-	-
Specific conductivity	[mS/cm]	4.01	3.08	2.33	23.2	41.9
COD	[mg O_2/dm^3]	67 000	1049	896	65.7	70.3
$N\text{-}NH_4$	[mg/dm^3]	610	209	181	93.3	94.2
Dry mass	[mg/dm^3]	593	5	2	99.5	99.7

Fig. 7. Feed, permeate and concentrate and membrane after the process - UF-PES-5 membrane filtration

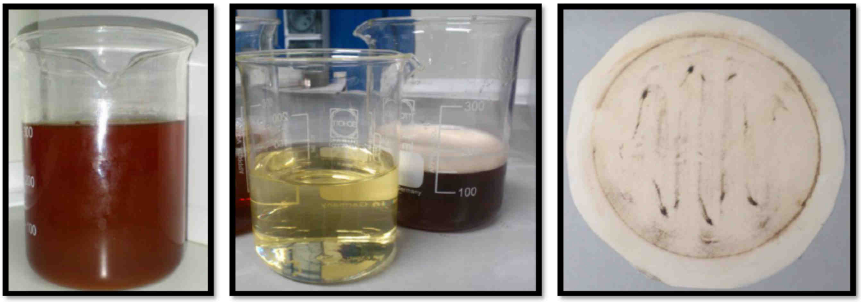

Fig. 8. Feed, permeate and concentrate and membrane after the process - UF-K-1membrane filtration

It was observed, that in both cases membrane filtration resulted in the efficient removal of organic contaminants indicated as chemical oxygen demand. The obtained removal rates were 98.4 and 98.7 for UF-PES-5 and UF-K-1 membranes, respectively. The membrane filtration also enabled the removal of suspended contaminants, as the dry mass content in the permeates was 5 and 2 mg/dm^3, for UF-PES-5 and UF-K-1 membranes, respectively, what corresponded to the removal rates above 99%. The content of ammonia nitrogen was also decreased, but only by 70 and 65%, while specific conductivity was reduced by 23 and 42%. Additionally, the pH of permeates was much higher, that the one noted for the feed, what suggested, that acidic contaminants present in the wastewater were rejected by the membranes and remained in the concentrate.

Considering both, membrane capacity, its affinity to fouling and effectiveness of contaminants removal, it is suggested, that the treatment of aqueous phase of biomass wastewater should be carried out at UF-K-1 membrane. The obtained permeate can be directed to municipal sewage system, or after polishing, by means of *e.g.* activated carbon absorption, it can be directly deposited to the environment. The retentate generated during the process, as an aqueous stream highly loaded with soluble organic compounds, can be recycle to the gasifier in order to assure both, the proper humidity of the gasified biomass and thermal decomposition of the remaining contaminants.

Summary and conclusions

The wastewater generated during biomass gasification, equipped with the dry gas cooling and cleaning system, is a highly loaded tar-aqueous mixture of a wide range of contaminants. The proper management of the stream is said to be crucial for popularization and commercialization of small and medium biomass gasification system. In this paper, a study on the treatment of aqueous phase of the stream by means of membrane filtration is discussed. The feed to the membrane process was the water fraction of the tar-water condensate, from which tar fraction was removed by means of spontaneous sedimentation and flotation. Two types of ultrafiltration membranes were used, polyether sulfone membrane of cut off 5 kDa and composite membrane of cut off 1 kDa. It was found, that both membranes effectively removed contaminants present in the process stream, and the obtained permeates could be deposited to the municipal sewage systems, or, after a proper polishing, directly deposited to the environment. Nevertheless, considering the capacity of the process and the affinity of membranes to fouling, it was concluded, that the process should be carried out at the composite membrane.

Acknowledgements

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WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI ŚCIEKÓW POWSTAJĄCYCH W PROCESIE ZGAZOWANIA BIOMASY

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Abstrakt: Proces zgazowania biomasy wiąże się z powstawanie wysoko obciążonych ciekłych strumieni odpadowych. Wody te formowane są podczas chłodzenia i oczyszczania gazu procesowego i stanowią mieszaninę smół, skroplonej pary wodnej oraz szeregu związków organicznych i nieorganicznych. Brak odpowiednich rozwiązań systemowych, przede wszystkim w przypadku małych i średnich instalacji, powoduje, że ich popularyzacja i komercjalizacja na skalę przemysłową są znacznie ograniczone. Obecnie proponowane metody utylizacji ciekłych strumieni odpadowych charakteryzują się zawężonym spektrum działania, skupiając się na jednym z aspektów problemu, jakim jest obecność substancji smolistych. W niniejszej pracy zaproponowano możliwość zagospodarowania ciekłych strumieni odpadowych z procesu zgazowania biomasy z wykorzystaniem technik membranowych. Rozwiązanie oparto o dwustopniowy system oczyszczania umożliwiający separację smół poprzez samoistnie zachodzące procesy sedymentacji i flotacji oraz niskociśnieniową filtrację membranową. W badaniach wykorzystano polimerowe membrany ultrafiltracyjne o różnych granicznych masach molowych. Wykazano, że zastosowanie procesów membranowych umożliwia zatężenie rozpuszczonych związków organicznych w stopniu pozwalającym na ich zawrócenie do reaktora oraz powstawanie filtratu o znacznie obniżonym ładunku zanieczyszczeń, który po odpowiednim podczyszczeniu może zostać odprowadzony bezpośrednio do środowiska.

Słowa kluczowe: ścieki, smoły, zgazowanie, membrany

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PRODUCTION AND OPTIMIZATION OF EXOCELLULAR LIPASES PRODUCED BY *Proteus mirabilis*

PRODUKCJA I OPTYMALIZACJA ZEWNĄTRZKOMÓRKOWYCH LIPAZ *Proteus mirabilis*

Abstract: Lipases are produced by plants, animals and microorganisms, but only those produced by the microorganisms are important to industry due to their various enzymatic properties and substrate specificity. Despite the fact, that such enzymes are synthesized by many species of microorganisms, new environmental strains able to synthesize exocellular lipases are searched for. The aim of conducted research was to assess the lipolytic activity of *Proteus mirabilis* depending on pH and temperature. The activity was analysed in the pH range between 4-9 and temperatures 5-60ºC. The lipolytic activity was assessed by means of titration and the results were presented as the amount of released µmoles of fatty acids. The analysis of pH influence showed that the highest amount of µmoles of fatty acids was released by the strain under study at pH 4 (264.75 µmol/cm^3). Synthesized lipases were most active at 35-45ºC and the amount of released µmoles of fatty acids ranged between 264.75 and 116.25 µmol/cm^3. Lipases produced by *P. mirabilis* due to their biological activity showed in the wide range of pH and temperature may be an alternative to lipolytic products currently applied in the industry.

Keywords: *Proteus mirabilis,* lipolytic activity, culturing conditions

Introduction

The global industrial enzymes market is projected to reach USD 6.30 billion by 2022 in terms of value [1]. In the forthcoming years we shall witness a significant increase in enzymes production due to their expanding application as detergents, pharmaceuticals, food and beverages. Lipases constitute third group, after proteases and carbohydrases, in terms of their total sale number [1]. Lipases catalyze the breakdown of ester bonds between glycerol and fatty acids in different lipids. The enzymes are responsible for the breakdown of triglycerides which provide energetic substances for living organisms. The reaction catalyzed by lipases is carried out between the lipid and aquatic phase, which dissolves the enzyme. The products of hydrolysis are fatty acids, diacylglycerols, monoacylglycerols and glycerol. Due to their versatile catalytic properties, lipases have wide range of industrial applications including detergent, textile, and dairy industries, oil processing, production of surfactants and synthesis of chiral pharmaceuticals [2-6].

Many different lipases have been identified in and isolated from bacteria belonging to the following species: *Acitenobacter*, *Pseudomonas*, *Bacillus*, *Geobacillus*, *Burkholderia*, *Serratia* and *Staphylococcus.* Bacterial lipases are exocellular enzymes of molecular weight 19-75 kDa [6], isolated to the growing medium in the late phase of logarithmic growth and produced in the process of submerged fermentation [2]. At present, bacterial lipases belonging to these from Family I, Subfamily I.1 and I.2 are perhaps studied most closely. Lipases from Subfamily I.1 and I.2 are nearly exclusively found in *Pseudomonas* and *Proteus* species [4, 7]. The process of their synthesis and secretion is influenced by many

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environmental factors, such as: sources of carbon and nitrate, ions, the presence of polysaccharides which are not metabolized by bacteria, temperature and pH. Therefore, the latest trend in lipase research is the development of novel and improved lipases.

The aim of the research was an assessment of different environmental factors such as: temperature, pH, incubation time on the lipolytic activity of the new strain *Proteus mirabilis* KMN16.

Materials and method

Isolation and identification

Proteus mirabilis strain KMN16 was isolated from meat waste contaminated soil. The isolation process was performed on tributyrin agar plates incubated at 30°C. Colonies showing clear zones around them were picked out and transferred to nutrition agar. The Identification of the isolate was performed with the rapid miniaturised system API ID 32GN and API 20E (bioMérieux, France), following the suppliers instructions. Complementary tests used for the final identification of the isolate were as follows: macroscopic and microscopic morphologies and biochemical analysis following Bergey's manual of determinative bacteriology.

Lipase production

The ability of *P. mirabilis* KMN16 to produce lipase was tested in tributyrin medium containing [%]: tributyrin oil 1.0, pepton 1.0, NaCl 0.5, $CaCl_2$ 0.01. The pH was maintained at 7. The strain was suspended in 5 cm^3 of sterile water and used as the inoculum for the pre culture to obtain an initial cell density to adjust the turbidity of 0.5 McFarland standard. The suspension of bacterial culture was incubated in 100 cm^3 of liquid medium on a rotary shaker at 100 rpm and incubated at 30°C. After 7 and 14 days of incubation, the culture was centrifuged at 10,000 rpm for 15 min at 4°C and the cell free culture supernatant was used as the source of exocellular lipases.

Qualitative assay

Lipolytic activity of *P. mirabilis* KMN16 was determined by the diffusion plate method in tributyrin agar medium containing tributyrin oil 1%. To perform the assay, the holes of 5 mm diameter were bored in agar and 200 mm^3 of supernatant was introduced to each. The media were incubated at different temperatures ranging from 5 to 60ºC for 7 days. Lipolytic activity of tested strain was determined by measuring the diameter of hydrolytic zones around each hole.

Assay of lipase activity

The lipase activity was assessed by means of titrimetric analysis and determined with tributyrin emulsion as a substrate. The reaction mixture contained 1 cm^3 of the enzymatic suspension, 4 cm^3 of respective buffer and 5 cm^3 of tributyrin emulsion. In the control treatment the supernatant was replaced with sterile water. The mixture was incubated for 30 minutes and the reaction was terminated by adding 10 cm^3 of acetone-ethanol (1:1) mixture. The amount of liberated fatty acids was determined by titration with 0.05 M

NaOH solution against 2% phenolphthalein as an indicator, and calculated as a subtraction between the proper treatment and the control treatment results. The result was presented as the amount of liberated µmoles of fatty acids. One lipase unit (U) was defined as the amount of enzyme which liberated 1 µmol of fatty acids per minute.

Effect of pH and temperature on lipase activity

For determination of optimal temperature of the activity, the supernatant containing the enzyme was incubated at different temperatures ranging from 5 to 60°C, at pH 7.0 (0.05 M phosphate buffer). The optimal pH was determined at 35°C in buffer solutions of pH values from 4 to 9 using different buffers (0.05 M citrate buffer pH 4-6; 0.05 M phosphate buffer pH 7-8; 0.05 M Tris-HCl buffer pH 9). Enzymatic activity was measured according to a standard titrimetric protocol.

Results and discussion

The sample of meat waste contaminated soil showed high bacterial count. The colony described as KMN16 showed maximum zone of clearance when plated on tributyrin agar. Morphological and biochemical studies were carried out on KMN16 isolate. The analysis clearly demonstrated that strain KMN16 belongs to the genus *Proteus* and exhibited maximum biochemical similarity with *P. mirabilis* (99% of biochemical similarity).

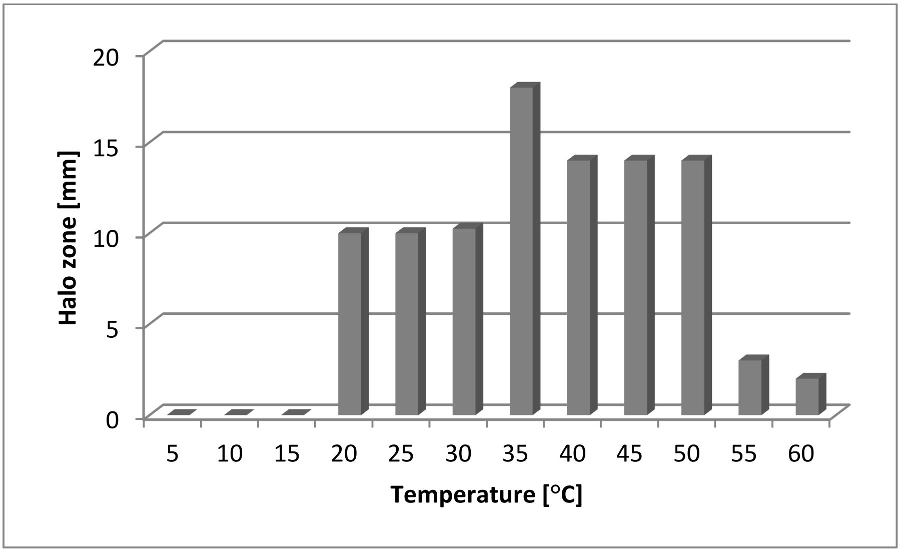

Fig. 1. Lipase activity on tributyrin agar plate after 7 days

P. mirabilis KMN16 was tested in terms of its ability to synthesize exocellular lipases in different environmental conditions concerning time, temperature and pH of the culturing medium. The first phase of the research consisted of screening tests on the medium with tributyrin incubated at temperature ranging from 5 to 60°C (Fig. 1). The ability to produce lipases by strain KMN16 was assessed according to the hydrolytic zones. They were observed only after 7 days of incubation around the holes containing supernatant. The biggest hydrolytic zone of 18 mm was obtained at 35°C. Slightly smaller zones were noted at temperatures ranging from 20 to 30°C (ca. 10 mm) and between 40 and 50°C (14 mm). At the lowest and the highest temperatures amounting 5-15°C and 55-60°C respectively the strain KMN16 did not produce lipases or synthesized them at a low amount. The differences between obtained hydrolytic zones were statistically insignificant in this case (Fig. 1).

The results obtained in screening tests proved that lipolytic activity of *P. mirabilis* KMN16 was noted after at least 7 days of culturing. Therefore, the amount of liberated µmoles of fatty acids was measured after 7 and 14 days and the most optimal conditions for culturing was 35°C and pH 7.

The analysis of lipolytic activity of *P. mirabilis* KMN16 shows that the highest amount of fatty acids was liberated under the most optimal conditions after 7 days of incubation (Figs. 2 and 3). Strain KMN16 synthesized the highest amount of µmoles of fatty acids at 35°C and pH 4 which amounted over 260 µmoles. As the pH was getting higher, the amount of fatty acids was decreasing rapidly to the amount of 107.25 µmoles at pH 5 and gained constant value of 58 µmoles in the pH range of 8-9. After 14 days of incubation, no influence of pH was noticed in the process of lipases synthesis. Analyzed range of pH showed that the amount of liberated µmoles of fatty acids remained at a constant level and mounted between 49-47 µmoles (Fig. 2). The highest amount of liberated fatty acids at pH 7 optimal for *P. mirabilis* KMN16 was noted after 7 days of incubation at 35°C and amounted over 94 µmoles. Further rise of temperature caused reduction in the amount of µmoles of fatty acids. However, in the temperature range between 40 and 45°C these differences were statistically insignificant and liberated µmoles of fatty acids amounted 90. Regardless of the incubation time, no ability to synthesize fatty acids was noted under psychrophilic conditions - below 15°C (Fig. 3).

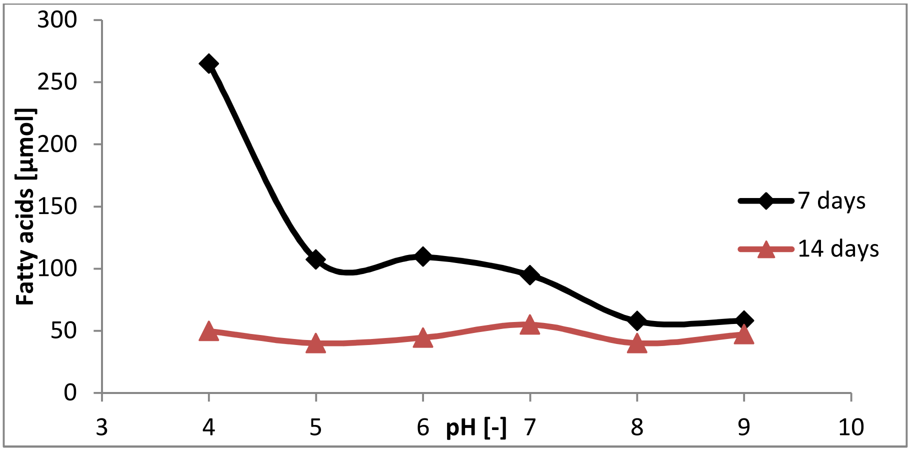

Fig. 2. Effect of different pH on lipase production by *P. mirabilis* KMN16

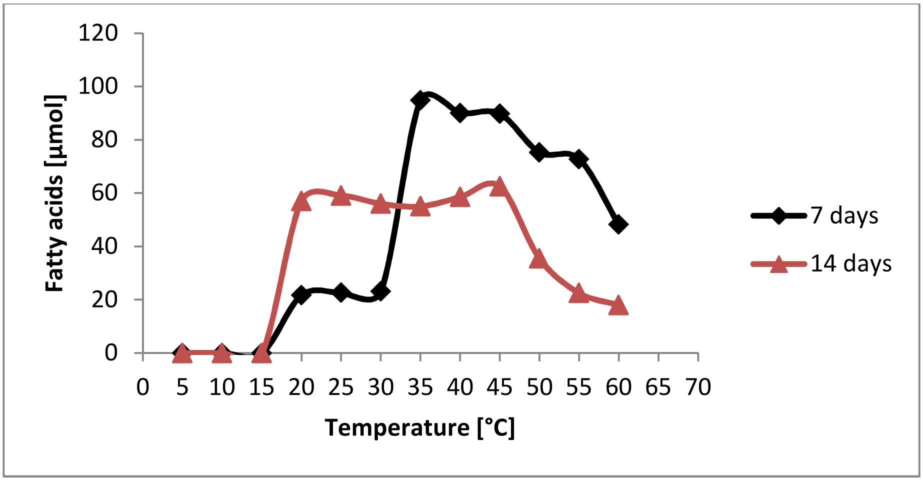

Fig. 3. Effect of different temperature on lipase production by *P. mirabilis* KMN16

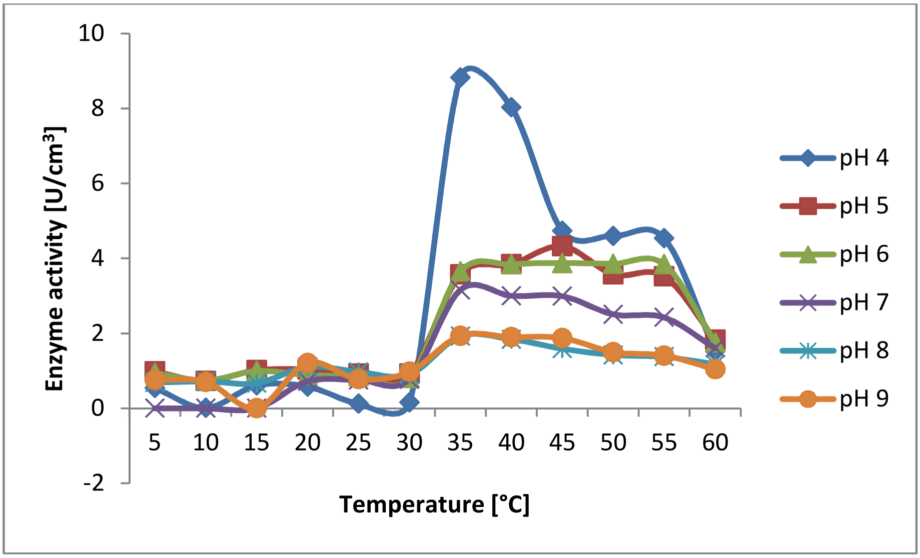

Fig. 4. Lipolytic activity of *P. mirabilis* KMN16 after 7 days incubation

In Figures 4 and 5 lipolytic activity of *P. mirabilis* KMN16 is shown in the units of lipolytic activity in the full range of analyzed both temperatures and pH. After 7 days of incubation, regardless of the pH value, in the temperature range between 5-30°C no lipolytic activity or the lowest activity was noted. The significant increase in the activity was noted at the temperature over 30°C. The strain showed the highest activity at pH 4 and temperatures between 35-40°C (8.83 U/cm^3). Under test conditions at pH between 5 and 9 and at temperature range from 35 to 55°C the enzyme was stable. The lipolytic activity measured at various pH levels (pH 5-9) was statistically insignificant (Fig. 4). After 14 days of incubation, no enzymatic activity or only low value of it was noted at the temperatures between 5 and 15°C. The results obtained in this case were ambiguous, as regardless of the pH, increased enzymatic activity was observed in the temperature range of 25 and 45°C. The highest lipolytic activity amounting 3.45 U/cm^3 was noted again at pH 4 at the lowest temperature amounting 25°C (Fig. 5).

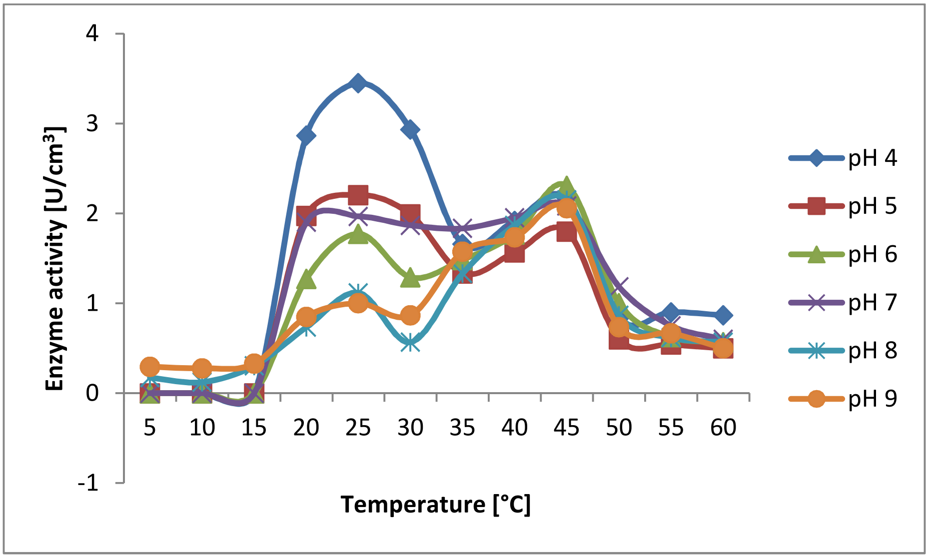

Fig. 5. Lipolytic activity of *P. mirabilis* KMN16 after 14 days incubation

On the basis of obtained results it may be concluded that optimal conditions for the strain *P. mirabilis* KMN16 to synthesize lipases is pH amounting 4 and the temperature range between 35-45°C. However, in an alkaline and thermophilic environment, strain under study KMN16 showed low lipolytic activity regardless of the incubation time.

Conclusions

The effect of pH on the lipolytic activity was determined in six different buffers covering the range of pH 4 to 9. In conducted research, the enzyme was most active at pH 4. In general, bacterial lipases are stable in a wide range of pH from 4 to 11 [9]. However, the optimum pH value will vary greatly from one enzyme to another. For example the optimum value of pH for pancreatic lipase amounts 8, for gastric lipases it ranges between 4-5 and for lipases used in the process of biodiesel production pH amounts 4.7 [10]. However, the majority of other research papers prove that the optimal pH value in the process of bacterial lipases production is neutral or alkaline. The research papers on lipases produced by strain *P. fluorescens* SIK W1 show that it prefers an acidic optimum of pH 4.8. Whereas, in the research of Bradoo et al. [11] the strains *B. stearothermophilus* SB-1 and *B. licheniformis* SB-3 retained their lipolytic activity at pH 3.0.

Bacterial lipases generally have temperature optima in the range of 30-60°C, which was proved by the authors' own research. According to Korman and Bowie [12] and Korman et al. [13] bacterial lipases from Subfamily I.1 and I.2 catalyze the hydrolysis of triacylglycerol at the temperature range between 25-45°C and are used extensively as biocatalysts. As the authors show, the lipase from *P. mirabilis* belongs to the *Proteus*/psychrophilic family of lipase Subfamily I.1 and is a promising catalyst for biodiesel production because it can tolerate high amounts of water in the reaction. In conducted research, the enzyme was most active at 35°C, which allows to include lipases produced by strain KMN16 in Subfamily I.1. An application of new psychrophilic lipase produced by *P. mirabilis* KMN16 in an industrial process of biodiesel production enables to reduce the costs as it decreases the temperature of the process and thus reduce the demand for energy.

The results obtained in this study show that the stability of *P. mirabilis* KMN16 lipase at pH 4 and at temperature 35°C have proved it to be a potential psychrophilic and acidic lipase and a candidate for industrial applications such as biodiesel production. Further studies are needed to enhance lipase production in strain KMN16.

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PRODUKCJA I OPTYMALIZACJA ZEWNĄTRZKOMÓRKOWYCH LIPAZ *Proteus mirabilis*

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Abstrakt: Lipazy są wytwarzane przez rośliny, zwierzęta i mikroorganizmy, ale tylko te pochodzenia mikrobiologicznego są ważne dla przemysłu ze względu na zróżnicowane właściwości enzymatyczne i specyficzność substratową. Mimo że enzymy te są syntetyzowane przez wiele gatunków mikroorganizmów, to nadal poszukuje się nowych, środowiskowych szczepów zdolnych do syntezy zewnątrzkomórkowych lipaz. Celem przeprowadzonych badań była ocena aktywności lipolitycznej *Proteus mirabilis* w zależności od pH oraz temperatury. Aktywność lipolityczną analizowano w zakresie pH 4-9 oraz w temperaturach 5-60ºC. Do oznaczenia aktywności lipolitycznej posłużono się metodą miareczkową, a wyniki podano jako ilość uwolnionych µmoli kwasów tłuszczowych. Analizując wpływ pH, stwierdzono, iż najwięcej µmoli kwasów tłuszczowych badany szczep uwolnił przy pH 4 (264,75 µmol/cm^3). Lipazy syntetyzowane przez badany szczep wykazywały największą aktywność, gdy reakcję prowadzono w zakresie temperatur 35-45ºC. Ilość uwolnionych wówczas µmoli kwasów tłuszczowych mieściła się w przedziale od 264,75 do 116,25 µmol/cm^3. Lipazy *P. mirabilis* ze względu na aktywność biologiczną w szerokim zakresie pH oraz temperatury mogą stać się alternatywą dla obecnych na rynku preparatów lipolitycznych stosowanych w przemyśle.

Słowa kluczowe: *Proteus mirabilis*, aktywność lipolityczna, warunki hodowli

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MODELLING OF CHLOROPHYLL-A CONTENT IN RUNNING WATERS

MODELOWANIE ZAWARTOŚCI CHLOROFILU-A W WODACH PŁYNĄCYCH

Abstract: Chlorophyll-a is one of the key parameters for assessment of trophic status of surface waters. However, Polish standard environmental monitoring procedures assume a low frequency of chlorophyll measurements in running waters, which does not provide the possibility of permanent control of eutrophication process and taking the appropriate preventive and protective measures sufficiently in advance. The article is focusing on constructing of predicting model of chlorophyll-a content based on data obtained within monitoring realized by Regional Inspectorates for Environmental Protection. Multivariate linear regression (MLR) model for chlorophyll-a content prediction was formulated on the base of chosen parameters like: pH, oxygen saturation, different forms of nitrogen and phosphorus. Formulation of the model was followed by a test of the applicability of each of the individual components of the regression equation. The main purpose was to develop an algorithm allowing for quick adaptation of model to local conditions in the rivers in order to make a reliable prediction of chlorophyll content.

Keywords: eutrophication, chlorophyll-a, running waters, prediction models

Eutrophication

Anthropogenic eutrophication is a priority global environmental problem. The negative consequences associated with this process are the disturbance of ecological balance, deterioration of water quality, loss of aesthetic properties and decline of biospheric role of aquatic ecosystems [1]. For effective prevention of eutrophication development, its control, prediction and management the properly designed monitoring procedures based on reliable methods of water trophic status assessment are essential. Classical methods for assessing of trophic status are based on the measuring of nitrogen and phosphorus content in surface waters, which are considered to be the major cause of eutrophication, as well as chlorophyll-a content which represents the level of algal biomass production and informs about ecosystem reaction on water enrichment in biogenic matter and the intensity of the process. These parameters are used most frequently in monitoring of eutrophication [2].

There are various methods for measuring the chlorophyll-a content: weight methods (Polish Norm), optical methods (*i.e.* Algaltorch©) or spatial analysis from planes or satellites. Unfortunately, measurements of chlorophyll conducting by Polish monitoring services (Regional Inspectorates for Environmental Protection - RIEP) in the frames of surface water state monitoring program are performed rarely and in small number of measuring points. The situation worsened after 2008 when the part of the measurement point was liquidated and the number of measured standard parameters was reduced. The reason was the high labor- and cost-consuming measurements of chlorophyll. This is an

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argument for developing a more pragmatic and low-cost methods for monitoring based on the results of forecasting models. Most of the forecasting statistical models are developed for the lentic systems; in the case of streams and rivers they are less common but equally necessary. The complexity of chlorophyll modelling in running waters is conditioned not only by the specifics of these ecosystems, main limiting factors and water movement, but also by the annual variations of flow intensity caused by the floods [1]. The primary objective of this study is to develop an algorithm for creation of "high-speed" model of chlorophyll-a content, based on data obtained within routine, monthly monitoring measurements carried out by RIEP. Such model is expected to predict the chlorophyll content and fill a gap in the research.

Existing solutions for modeling of chlorophyll-a

In the modern practice of modeling of chlorophyll-a content, there are the different approaches used. The first one is the determination of chlorophyll content based on images obtained from aerial or satellite photography. The second approach is the method in which the selection of the components of the model and its formulation are implemented using artificial neural networks or similar algorithms. The third approach are methods based on statistical modeling using mainly the regression analysis.

Aerial and satellite methods

Among the wide use of spatial applications there is MERIS satellite, designed to control the state of the oceans. It has also become an important tool in estimating the quantities of chlorophyll and biomass in freshwaters [3]. On the basis of satellite NIR measurements (near infrared) the direct correlation models were formulated [4] as well as the models consisting of several parameters with the construction similar to the construction of the aggregate indicators of eutrophication [5, 6]. Previously, the direct measurements were conducted with the help of satellites like: Adeos and Orbview-2 [7].

Artificial neural networks (*ANN*)

The use of artificial neural networks (ANN) is quite common in the modelling of chlorophyll-a content and other biological components in aquatic environment. In modelling process there are used the different neural networks and different methods of recognition, so there is no one universal algorithm for chlorophyll content modelling. It is popular to use the ANN in comprehensive models for predicting chlorophyll changes using the range of parameters including hydrological, hydro-morphology, meteorological data and physical and chemical parameters of the examined area [8]. Next to the neural network it is possible to use heuristic evolutionary algorithm (HEA). This algorithm could create a model that is changing in time simultaneously to environmental data changing [9]. There are also the models based on fuzzy logic co-working with neural networks and evolutionary algorithms [10].

Statistical modelling

Among the statistical models the linear regression should be distinguished. The basis of this method is the least squares method. In addition to the selection of the parameters the correlation analysis can be used (Pearson or Spearman rank) or variance inflation factor (VIF). For determining of coefficients for regression equations there is frequently used the so-called stepwise regression: backward, forward or less often bidirectional. With a limited number of suggested parameters it can be used the Akaike information criterion (AIC) [11, 12]. The formulation of statistical models of chlorophyll content can be based on Principal component analysis (PCA) and Principal component regression (PCR), in particular for the choice of model parameters [13]. There are also statistical methods based on the values of biotic indicators and their coefficient of variations allowing for the formulation of chlorophyll prediction model [14]. An interesting issue is the use of phytoplankton growth model BLOOM II to estimate the chlorophyll content [15]. According to specialist literature the ANN and statistical methods, primarily Multivariate linear regression (MLR) will finally give similar results [16]. High compliance of prediction, both for the test data values as well as for real values of parameter, gives a real possibility to use both of these methods in practice of routine monitoring.

Assessment of model adjust to real values

The basic estimation test for the convergence of prediction values with factual values is correlation analysis. The most common indicator is the Pearson coefficient, which can range from –1 to 1. The best fit is observed when its value is a positive integer and equal 1, while the minimum accepted level is usually determined individually [14]. Other parameters describing the degree of prediction reliability are: Theil Index (TI), Mean Absolute Error (MAE), Standard Uncertainty, Root Mean Square Error (RMSE), Mean Relative Error (MRE) [13, 17, 18], Occasionally Receiving Operating Characteristic (ROC) curve (AUC) [10] or even scatterplots [19].

Research area

The object of research is the river Ner, located in north-western Poland, in the province of Lodz. Together with its tributaries, such as Dobrzynka, Pisia, Beldowka and Nida the river Ner is monitored by the Regional Inspectorate for Environmental Protection (RIEP) located in Lodz city, within the framework of state monitoring. Ner is a river of abiotic type 20 - lowland gravel river. The rivers of this type are characterized by varying flow intensity, with mainly gravel and sand bottom substrate. It was necessary to select the appropriate measurement point where the measurement of chlorophyll was conducted regularly. The research was based on data obtained from monitoring provided by the Inspectorate in the period of years 1992-2014 in chosen measurement point located at 111.7 km of the Ner river, where the content of chlorophyll was measured in the period of 1993-2006. During overall multi-year monitoring the RIEP measured the values of more than 60 parameters, but there are only about 25 parameters were measured regularly every year. The main of them are: water and air temperatures, color of water, solid substances, pH value and dissolved oxygen, BOD and COD measured by two methods, total nitrogen and total phosphorus, conductivity, hardness, concentrations of chlorides, calcium and magnesium and others. The set of 25 values of regularly measured parameters was used to construct a predictive model of chlorophyll-a content.

The regression prediction model of chlorophyll-a content

Algorithm of statistical analysis

Statistical analysis was carried out in stages using Statistica software version 10.0 developed by StatSoft. The first step of the analysis was to verify the compliance of distribution of the parameters derived from the annual monitoring with the normal distribution. Confirmation of the normal character of their distribution allowed for further statistical analysis. Globally for multi-year data it was created the Pearson correlation coefficient matrix to pre-eliminate the parameters depending on each other. It assumes two methods of its creation and verification. The first method is the separation of data groups forming the model and the test group, the second method presupposes that all data will be used for construction of the model, and the whole will be verified by comparing the data for individual years. For formulation of the model the multiple stepwise linear regression (MLR) was used. Then the validity of the model elements was tested by the AIC criterion. The parameters of the model were selected using the linear regression provided the correct final model. For the assessment of conformity with factual values the Pearson's correlation coefficient and root main squared error (RMSE) were used. The elaborated algorithm applied for statistical analysis and further formulation of the model is shown in the Figure 1.

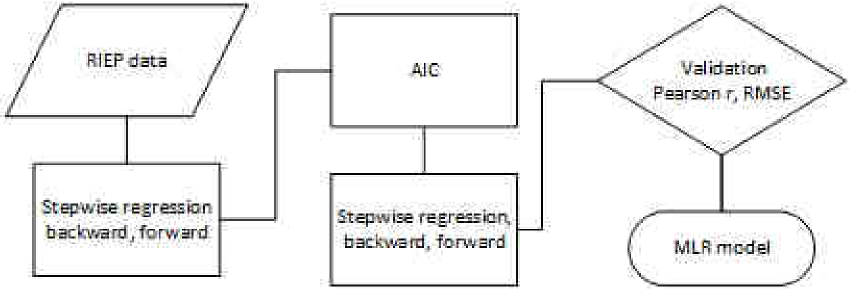

Fig. 1. Algorithm of model creation

Model calculation

The database was formed by the results of measurements of selected 25 parameters in the measurement point located at the 111.7 km of the river Ner, carried out during the monitoring period 1993-2006. In total, there were conducted 136 series of measurements and 346 values of different parameters were determined. The values of 21 parameters were selected as the model input data: chlorophyll-a, air and water temperature, water color, total suspended solids, pH, oxygen saturation, BOD_5, COD_{Mn}, $ChZT_{Cr}$, ammonia, nitrates, nitrites, total nitrogen, phosphates, total phosphorus, total hardness, sulphates, chlorides, calcium, magnesium. The data was characterized by a distribution similar to normal distribution. The highest coefficient of Pearson (r = 0.744) characterized the interdependence of chlorophyll-a and COD_{Mn} values. Then stepwise regression analysis was applied, both backward and forward. The obtained results of statistic test F (Fisher test) allowed the selection of the following parameters for model formulation: suspended solids, BOD_5, COD_{Mn}, nitrites, nitrates, total hardness, dissolved substances, sulfates, calcium and magnesium. The applied AIC analysis made it possible to rank the selected parameters in the following order of priority: sulphates, COD_{Mn}, nitrites, total suspended solids, magnesium, total hardness, dissolved substances, calcium, BOD_5. Then, the construction of appropriate model based on MLR method of five-stage backward analysis were conducted. The last stage of the analysis allowed for final selection of following parameters for model formulation: solid substances (SS), BOD_5, COD_{Mn}, nitrates ($N\text{-}NO_2$) and dissolved substances (DS) Finally the statistical model for prediction of chlorophyll content (Chl^p-a) takes the form of following equation (1):

$$Chl^{p}\text{-a} = -27.4835 + 0.1678\ SS + 3.2788\ BOD + 6.9097\ COD + (-33.6520)\ N\text{-}NO_2 + (-0.0695)\ DS \qquad (1)$$

The graph in Figure 2 shows the values of chlorophyll-a concentrations obtained by modelling during the subsequent stages of the analysis against the factual values of chlorophyll- a concentration. Table 1 shows the values of selected parameters of the model in each of five steps of statistical analysis.

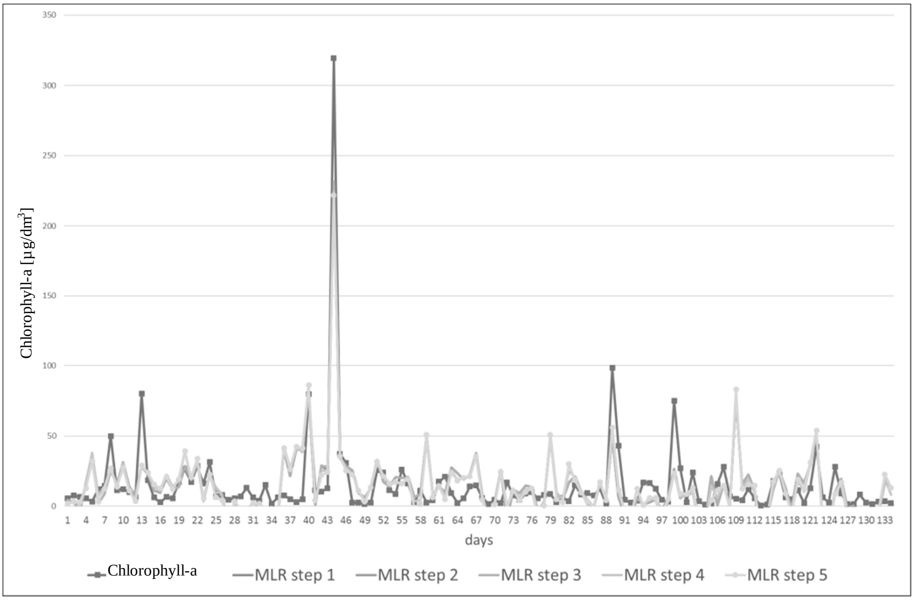

Fig. 2. Chlorophyll values - real and predicted

Using backward linear regression algorithm, with selecting the key parameters of the model using AIC criterion and using the MLR analysis it was possible to formulate the final variant of the model and to achieve the satisfactory results. Table 2 presents the values of

Pearson correlation coefficient and root main squared error RMSE. In each step they achieved a high degree of correlation between the factual values of chlorophyll-a content and the values obtained on the base of formulated model. Due to the fact that all the parameters used for the final MLR analysis are the parameters regularly monitored by RIEP, there is the possibility to formulate the predictive models based on the maximum amount of parameters. The research also justified the possibility of application of the elaborated algorithm for selection of the parameters of predictive model. The permanent application of mentioned algorithm would help to avoid the problem of remodelling and ensure the satisfactory level of model adjustment to real aquatic conditions.

Table 1

Parameters of linear regression of each step statistical analysis

MLR stages	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Step 5**
Absolute term	–46.146	–45.996	–46.061	–37.916	–27.483
Suspension	0.199	0.199	0.198	0.178	0.167
BOD	3.278	3.274	3.240	3.071	3.278
COD_{Mn}	7.271	7.269	7.284	7.127	6.909
Nitrate	–34.760	–34.840	–35.054	–30.914	–33.652
Dissolved substances	–0.092	–0.092	–0.093	–0.098	–0.069
Hardness	0.119	0.121	0.132	0.071	out
Sulphates	–0.161	–0.162	–0.159	out	out
Calcium	0.036	0.034	out	out	out
Magnesium	0.052	out	out	out	out

Table 2

The values of statistical characteristics at each step of MLR

MLR step	**Number of parameters**	**Mean deviation**	**Standard deviation SD**	**Pearson *r***	**RMSE value**
1	9	14.539	25.20	0.79	18.43
2	8	14.539	25.20	0.79	18.43
3	7	14.534	25.20	0.79	18.43
4	6	14.392	25.01	0.79	18.52
5	5	14.380	24.93	0.79	18.60

Summary and conclusions

The increasing pollution of rivers and the continuing threat of eutrophication problem forces to expand, optimize and improve water monitoring programs for eutrophication. It is therefore the prior necessity for regular control of the value of such parameters as various forms of nitrogen and phosphorus and chlorophyll-a content. Under the conditions where the key parameters of eutrophication are not subjected to routine monitoring it is the need of other ways of obtaining the necessary information. In the absence of information on the monthly values of chlorophyll-a concentrations it is possible to obtain the necessary values on the base of mathematical modelling. In order to create a model that would be readily and widely used by monitoring authorities (RIES) the model must be easy to use and based on regularly measured parameters. The elaborated algorithm of statistical analysis presented in the article allows for the selection of key model input parameters and formulation of a simple mathematical model which is characterized by high degree of reliability of the obtained results. Application of the developed algorithm of statistical analysis which provides the base for formulation of prognostic mathematical models allows the prediction of chlorophyll-a content in order to forecast the dynamics of trophic status changes and to take the appropriate decisions on the integrated management in river basins.

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MODELOWANIE ZAWARTOŚCI CHLOROFILU-A W WODACH PŁYNĄCYCH

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Abstrakt: Chlorofil-a jest jednym z kluczowych parametrów służących do oceny stanu troficznego wód. W Polsce w ramach standardowego monitoringu rzek jest jednak badany rzadko. Artykuł skupia się na skonstruowaniu modelu predykcji zawartości chlorofilu-a w oparciu o dane pochodzące z rutynowego monitoringu realizowanego przez Wojewódzkie Inspektoraty Ochrony Środowiska. W tym celu na podstawie parametrów jakości wód, takich jak pH, nasycenie tlenem oraz różne formy azotu i fosforu, został sformułowany model regresyjny, a następnie przeprowadzono test zasadności zastosowania w nim poszczególnych składników równania regresji. Ostatnim etapem było opracowanie algorytmu pozwalającego na szybkie dostosowywanie modelu do lokalnych warunków w rzekach w celu dokonania wiarygodnej prognozy zawartości chlorofilu.

Słowa kluczowe: eutrofizacja, chlorofil-a, wody płynące, modele predykcyjne

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ANALYSIS OF BIOGENIC MATTER BALANCE IN MUNICIPAL WASTEWATER IN JAWORZNO-DAB WWTP

ANALIZA BILANSU ZWIĄZKÓW BIOGENNYCH W ŚCIEKACH KOMUNALNYCH OCZYSZCZANI JAWORZNO-DĄB

Abstract: The role of municipal wastewater in the development of eutrophication processes due to high content of nutrients will be increasing correspondingly with economic development. However, treatment technologies do not always provide an effective protection of surface waters against eutrophication. Biogenic substances on their way from the place of their origin to the discharge to water receiver undergo significant transformations. The knowledge about it is essential to understand some theoretical issues and to develop the methods of protection against eutrophication. In recent decades, many countries have introduced an advanced wastewater treatment technologies for increased nutrients removal. However, regardless of the fact that load of biogenic substances was significantly reduced, the substantial successes in preventing of eutrophication processes has failed to achieve. Moreover, as research has shown, wastewater treated in conventional biological technologies can accelerate the process of eutrophication, because it characterized by a high content of mineral forms of nitrogen and phosphorus, which are easily absorbed by aquatic vegetation. European and national requirements in terms of treated wastewater quality discharged into receivers concern the contents of total nitrogen and phosphorus, while the most available to algae are their dissolved inorganic forms. Knowledge about the content of bioavailable forms of nutrients in wastewater discharged into receiver allows to make rational decisions when choosing wastewater treatment technologies, as advanced technologies of deep nutrients removal are an extremely capital-intensive investments. In view of the above considerations the research was undertaken on the content of various forms of nitrogen and phosphorus in municipal wastewater discharged from wastewater treatment plant Jaworzno-Dab, the results of which are presented in this article.

Keywords: eutrophication, municipal wastewater, biogenic matter, bioavailability of nutrients

Introduction

The assessment of influence of various wastewater types on eutrophication development in surface waters allows to conclude that municipal wastewaters have prevailing role in surface water pollution. From 50 to 90% of phosphorus compounds are delivered in that way to water receivers from which 7 to 20% represents phosphorus contented in detergents. On the other hand, detergents of older generation in 50% are composed of phosphorus [1, 2]. The role of wastewater in the acceleration of eutrophication process will increase with the economic development, still wastewater treatment technologies cannot always provide the proper protection against eutrophication.

Removing biogenic substances from wastewater become an up-to-date problem when it appeared, that conventional treatment technologies are not effective enough in the matter of nitrogen and phosphorus elimination. In the past decades in many countries the advanced technologies of wastewater treatment were implemented in order to achieve the increased removal of nutrients. However, regardless of the fact that the load of biogenic substances was significantly reduced, the substantial successes in preventing of eutrophication processes has failed to achieve. Moreover, as some researchers have shown, wastewater

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treated in conventional biological technologies can accelerate the process of eutrophication, because it is characterized by high content of mineral forms of nitrogen and phosphorus, which are easily absorbed by aquatic vegetation [3, 4]. European and national requirements in terms of treated wastewater quality discharged into receivers concern the contents of total nitrogen and phosphorus [5]. Various number of publications on eutrophication process development shows, that just dissolved inorganic forms of nitrogen and phosphorus are the most available to algae [6-9]. Different algae species have specific demands concerning bioavailable forms of nitrogen and phosphorus. For example, orthophosphate P-PO_4 is concerned to be the most assimilable form of phosphorus compounds for phytoplankton. Its content depends on water pH value. When pH value amounts 3-7 dihydrogen phosphate anion H_2PO_4 dominates, when pH = 8-12 hydrophosphate ion HPO_4 prevails. The most bioavailable nitrogen form is nitrate nitrogen which can be consumed, for example, by *Cyanobacteria* representatives like: *Anabaena variabilis*, *Nostoc paludosum* and *Nostoc coeruleum*. Such species as *Microcystis aeruginosa, Calothrix elenkini*, *Hapalosiphon fomtinalis* etc. reproduce better consuming the ammonia nitrogen [10]. The majority of green algae absorbs most actively the nitrate nitrogen. Some species of higher aquatic vegetation, for example the reed, also absorb better the ammonium nitrogen. The least assimilable form of mineral nitrogen is nitrite nitrogen.

The specificity of mineral nutrition of aquatic vegetation is not fully investigated due to the high degree of complexity of the studies, that require the interdisciplinary team of specialists involvement.

Knowledge about the content of bioavailable forms of nutrients in wastewater discharged into receiver allows to make rational decisions when choosing wastewater treatment technologies, as advanced technologies of deep nutrients removal are extremely capital-intensive investments.

In view of the above considerations the research was undertaken on the content of various forms of nitrogen and phosphorus in municipal wastewater discharged from wastewater treatment plant Jaworzno-Dab, the results of which are presented in this article.

Materials and methods

Municipal wastewater treatment plant (WWTP) Jaworzno-Dab is located between two cities Jaworzno and Chelmek in the eastern part of Silesia Region of Poland. Untreated wastewater is transported to wastewater treatment plant by two canals. There are also sanitary sewage being transported by septic tankers from the areas without access to municipal sewage system. The maximum wastewater flow rate is around 25,000 m^3 per day and the maximum load according to operative water permit equals the population equivalent PE = 87,500. Due to the modernization of sewage system the forecasting load is going to rise up to 125,000 PE [11]. Treated wastewater is discharged to the river Przemsza in the point located at km 9+518.

Jaworzno-Dab WWTP operation is based on low-loaded activated sludge technology with advanced nutrients removal and possible phosphorus chemical precipitation. The currently valid water permit [11] obligates to achieve the following parameters in discharge from the WWTP: BOD - 15 mg O_2/dm^3, COD - 125 mg O_2/dm^3, TSS - 35 mg/dm^3, total nitrogen - 15 mg N/dm^3, total phosphorus - 2 mg P/dm^3. The technological scheme of the WWTP is shown in Figure 1.

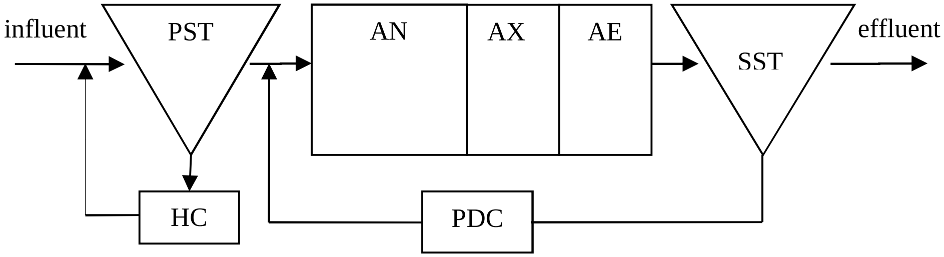

Fig. 1. Technological scheme of Jaworzno-Dab WWTP (PST - primary settling tank, HC - hydrolysis chamber, AN - anaerobic chamber, AX - anoxic chamber, AE - aerobic chamber, SST - secondary settling tank, PDC - recirculated sludge pre-denitrification chamber)

Table 1

Concentration of different forms of nitrogen and phosphorus in raw wastewater

Year	**N-NH$_4$ [mg/dm^3]**	**N-NO$_2$ [mg/dm^3]**	**N-NO$_3$ [mg/dm^3]**	**N Kj [mg/dm^3]**	**TN [mg/dm^3]**	**N$_{org}$ [mg/dm^3]**	**TP [mg/dm^3]**	**P-PO$_4$ [mg/dm^3]**
2013	41.40	0.00	0.31	64.49	64.80	23.10	8.48	6.49
2014*	43.08	0.00	0.30	71.19	71.49	24.64	11.48	8.40
2014**	41.50	0.00	0.27	69.86	70.13	21.55	10.24	7.58

*results for months I-VI with primary settling tank ON. ** results for months VII-XII with primary settling tank OFF.

Table 2

Concentration of different forms of nitrogen and phosphorus in wastewater after mechanical treatment

Year	**N-NH$_4$ [mg/dm^3]**	**N-NO$_2$ [mg/dm^3]**	**N-NO$_3$ [mg/dm^3]**	**N Kj [mg/dm^3]**	**TN [mg/dm^3]**	**N$_{org}$ [mg/dm^3]**	**TP [mg/dm^3]**	**P-PO$_4$ [mg/dm^3]**
2013	41.40	0.00	0.33	65.83	66.16	24.44	8.69	6.98
2014*	44.00	0.00	0.81	68.36	69.17	24.36	11.87	9.58
2014**	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.

n.e. - not examined

Table 3

Concentration of different forms of nitrogen and phosphorus in wastewater after biological treatment

Year	**N-NH$_4$ [mg/dm^3]**	**N-NO$_2$ [mg/dm^3]**	**N-NO$_3$ [mg/dm^3]**	**N Kj [mg/dm^3]**	**TN [mg/dm^3]**	**N$_{org}$ [mg/dm^3]**	**TP [mg/dm^3]**	**P-PO$_4$ [mg/dm^3]**
2013	0.30	0.00	7.87	1.63	9.50	1.33	0.70	0.55
2014*	0.49	0.00	8.29	1.81	10.10	1.32	0.35	0.23
2014**	2.00	0.00	7.07	2.85	9.92	0.85	0.73	0.57

Data used for analysis were obtained from the results of wastewater quality monitoring conducted by WWTP laboratory. The values of examined parameters were systematized, organized and prepared for analysis. Basis was constituted from the average annual values of concentrations, of different forms of nutrients within the period of 2013 and 2014. The analysis concerned the quality of raw wastewater, wastewater after mechanical treatment and after biological treatment. Due to the need of primary settling tank modernization it was turned off the operation in June 2014. Owing to this the parameters relating to the examined period between July-December 2014 were analyzed separately. The results of analysis on the content of different forms of biogenic substances in wastewater after different steps of treatment are shown in Tables 1-3.

After analyzing the data shown in Table 3 it can be stated, that exclusion of primary settling tank did not affect seriously on the increase of neither total nitrogen nor total phosphorus. However it brought to the changes in the structure of content of different forms of nitrogen compounds, which is especially distinct for the concentration of ammonia nitrogen and Kjeldahl nitrogen.

Taking into account, that the main objective of research is the content of mineral forms of nitrogen and phosphorus in treated wastewater, which are immediately bioavailable for water vegetation, the next step was to assess the content structure of particular bioavailable nutrient forms of biogenic compounds.

Results and discussion

Content structure of nitrogen compounds in wastewater

One of the main component of raw wastewater in Jaworzno-Dab WWTP is ammonia nitrogen (64%) and organic nitrogen (35%). It suggests that the ammonification processes had already started in sewage network. Technological system of wastewater treatment plant provides the stabile effect of total nitrogen removal, so WWTP meets the requirements of existing Regulation [12]. The average level of total nitrogen removal is about 86% and its maximum concentration in the effluent not exceeds 10 mg/dm^3.

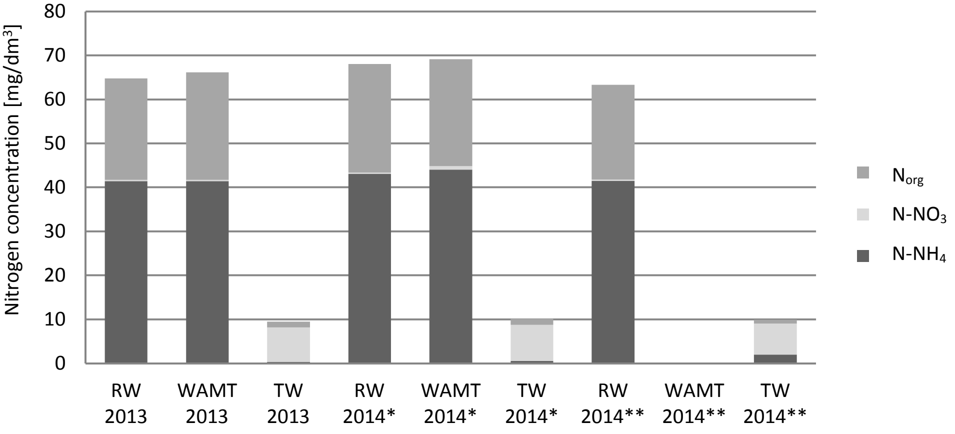

Fig. 2. Nitrogen compounds in wastewater after particular treatment stages (RW - raw wastewater, WAMT - wastewater after mechanical treatment, TW - biologically treated wastewater), * results for months I-VI with primary settling tank ON, ** results for months VII-XII with primary settling tank OFF

The percentage content of particular nitrogen compounds ($N\text{-}NH_4$; $N\text{-}NO_3$; N_{org}) in wastewater discharged to Przemsza river in 2013 is presented as follows: 3.18; 82.86; 13.95% respectively. In the first half of 2014 any severe changes were not observed and the content structure of these compounds were the following: 4.86; 82.10; 13.04. However in the second half of 2014, when the primary settling tank was turned off, the concentration of ammonia nitrogen increased and content structure of different nitrogen forms mentioned above changed as following: 20.21; 71.23; 8.56% respectively. It can be assumed that turning off the primary settling tank caused serious changes in the structure of nitrogen compounds in effluent from WWTP.

The results of analysis of wastewater quality after mechanical treatment had shown the slight increase of organic nitrogen amount, which can be an effect of a number of difficulties connected with primary settling tank exploitation. Figure 2 presents the content of nitrogen compounds in wastewater after particular treatment stages.

Content structure of phosphorus compounds in wastewater

Phosphorus in raw wastewater is generally represented by phosphates (74.59%) and organic phosphorus (25.41%). Wastewater after biological treatment consists mainly of orthophosphates PO_4 (79.07%) and organic phosphorus (20.93%). In the first half of 2014 the phosphates amount was around 66.65% and organic phosphorus - about 33.35%. After turning off the primary settling tank in June 2014 the concentration of phosphates increased to 78.66% and the concentration of organic phosphorus accordingly dropped to 21.34% (Fig. 3). Wastewater treatment technology provides the average reduction of total phosphorus up to 94% (against required min. 80%) and its maximum concentration is 0.7 mg/dm^3 which means that WWTP Jaworzno-Dab meets the requirements of current Regulation [12] in case of total phosphorus reduction.

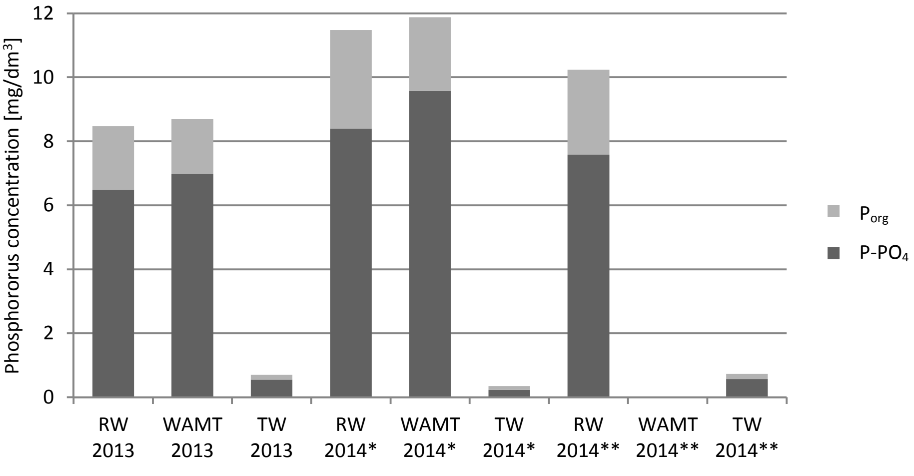

Fig. 3. Phosphorus compounds in wastewater after particular treatment stages (RW - raw wastewater, WAMT - wastewater after mechanical treatment, TW - biologically treated wastewater), * results for months I-VI with primary settling tank ON, ** results for months VII-XII with primary settling tank OFF

Amounts of immediately bioavailable nitrogen and phosphorus compounds

Results of analysis of concentrations of organic and mineral forms of nitrogen and phosphorus are presented in Tables 4 and 5. These results are relating to the period with primary settling tank operating and turned off.

Table 4

Nitrogen compounds in raw and treated wastewater

Nitrogen	**TN [mg N/dm^3]**	**N_{org} [mg N/dm^3]**	**$N_{min.}$ [mg N/dm^3]**	**N_{org} / $N_{min.}$ [%]**	**Bioavailable N [%]**	**NO_3 / $N_{min.}$ [%]**	**NH_4 / $N_{min.}$ [%]**
Raw wastewater							
2013	64.80	23.10	41.71	55.38	64.36	0.74	99.26
2014*	71.49	24.64	43.38	56.79	60.69	0.69	99.31
2014**	70.13	21.55	41.77	51.60	59.56	0.64	99.36
Biologically treated wastewater							
2013	9.50	1.33	8.18	16.21	86.05	96.30	3.70
2014*	10.10	1.32	8.78	14.99	86.96	94.41	5.59
2014**	9.92	0.85	9.07	9.36	91.44	77.90	22.10

* results for months I-VI with primary settling tank ON. ** results for months VII-XII with primary settling tank OFF

Table 5

Phosphorus compounds in raw and treated wastewater

Phosphorus	**TP [mg/dm^3]**	**P_{org} [mg P/dm^3]**	**$P_{min.}$ [mg P/dm^3]**	**P_{org} / $P_{min.}$ [%]**	**Bioavailable P [%]**
Raw wastewater					
2013	8.48	1.98	6.49	30.52	76.62
2014*	11.48	3.08	8.40	36.72	73.14
2014**	10.24	2.66	7.58	35.12	74.01
Biologically treated wastewater					
2013	0.70	0.15	0.55	26.47	79.07
2014*	0.35	0.12	0.23	50.03	66.65
2014**	0.73	0.16	0.57	27.13	78.66

* results for months I-VI with primary settling tank ON. ** results for months VII-XII with primary settling tank OFF

The analysis of data presented in Tables 4 and 5 allows to sum up, that the ratio between organic nitrogen and mineral nitrogen in treated wastewater decreased about 1.8 times during the period with operating primary settling tank and 5.5 times when it was turned off. The content of bioavailable nitrogen compounds increased 1.4 times with operating primary settling tank and 1.5 time when it was turned off. The dominating bioavailable nitrogen form in biologically treated wastewater is nitrate nitrogen, contrary to raw wastewater, where the main bioavailable form of nitrogen is ammonia nitrogen. It should also be noted, that turning off the secondary settling tank has led to the reduction of nitrite nitrogen share by 12.8% and corresponding increase of ammonia nitrogen share by 17.5% in treated wastewater.

The ratio of organic phosphorus and mineral phosphorus in raw wastewater has averaged 34.0%, while in treated wastewater in 2013 and under the settling tank turned off in 2014 it decreased slightly and accounted for an average of 26.8%. There was one exception before June 2014 when this ratio increased by 13%.

Amount of bioavailable phosphorus compounds in biologically treated wastewater increased by 3.6%, but in the first part of 2014 the share of mineral phosphorus was lower due to different content of phosphorus forms in raw wastewater. The results are presented in Figures 4 and 5.

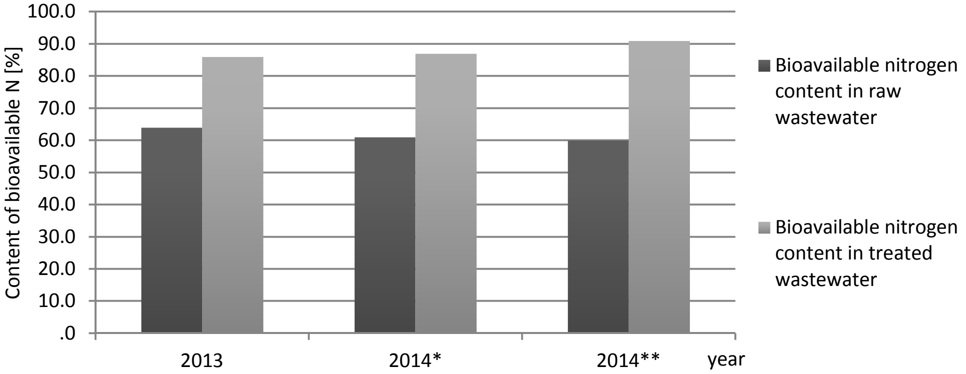

Fig. 4. Content of bioavailable nitrogen forms (sum of NO_3, NO_2 and NH_4) in raw and treated wastewater; * results with primary settling tank ON, ** results with primary settling tank OFF

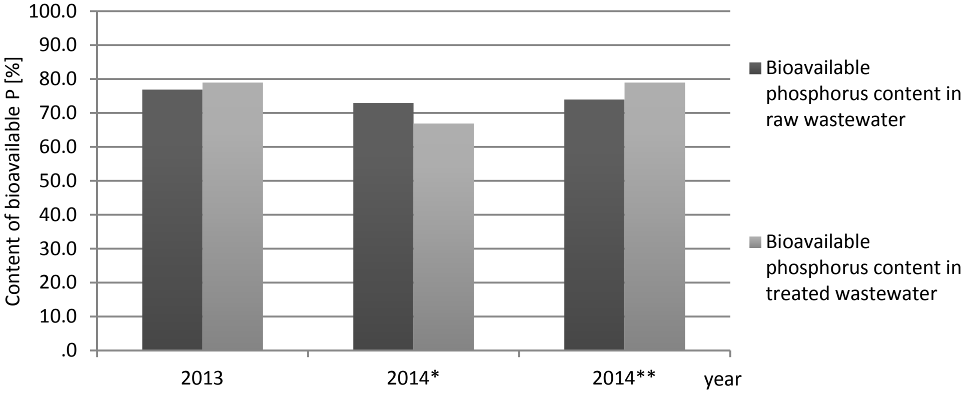

Fig. 5. Content of bioavailable phosphorus forms (PO_4) forms in raw and treated wastewater; * results with primary settling tank ON, ** results with primary settling tank OFF

Conclusions

The analysis of the state of knowledge on treated municipal wastewater impact on trophic status of receiving surface waters and analysis of wastewater quality treated in low-loaded activated sludge technology with advanced nutrients removal in Jaworzno-Dab WWTP allowed to draw the following conclusions:

- Eutrophication manifested by intensive development of aquatic vegetation is accelerated mainly by excessive amounts of mineral forms of nitrogen and phosphorus introducing into receivers together with biologically treated wastewater.
- Biologically treated wastewater, meeting the legislative requirements concerning total nitrogen and total phosphorus content, are enriched in mineral forms of these biogenic elements immediately bioavailable for aquatic vegetation.
- The above mentioned statement was confirmed by the analysis of raw and treated wastewater content from Jaworzno-Dab WWTP.
- The content of bioavailable forms of nitrogen and phosphorus in biologically treated wastewater from WWTP Jaworzno-Dab has increased correspondingly by 22% and 3.6%. This fact shows the growth of biologically treated wastewater potential for intensification of surface water eutrophication.

Further research in undertaken direction would allow the optimization of decision-making process in the sphere of wastewater treatment technologies taking into consideration the eutrophication processes mechanisms.

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ANALIZA BILANSU ZWIĄZKÓW BIOGENNYCH W ŚCIEKACH KOMUNALNYCH OCZYSZCZANI JAWORZNO-DĄB

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Abstrakt: Rola ścieków komunalnych w rozwoju procesów eutrofizacji ze względu na dużą zawartość substancji biogennych będzie wzrastać wraz z rozwojem gospodarczym, a technologie ich oczyszczania nie zawsze zapewniają skuteczną ochronę wód przed eutrofizacją. Substancje eutrofizujące na drodze od miejsca ich powstawania do miejsca zrzutu do odbiornika ulegają znacznym transformacjom, których znajomość jest bardzo istotna do zrozumienia niektórych zagadnień teoretycznych oraz opracowania sposobów ochrony przed eutrofizacją. W ostatnich dziesięcioleciach w wielu państwach wprowadzono zaawansowane technologie oczyszczania ścieków w celu wzmożonego usuwania substancji biogennych. Jednak bez względu na to, że ładunki substancji eutrofizujących znacznie się zmniejszyły, nie udało się osiągnąć znacznych sukcesów w zapobieganiu procesom eutrofizacji. Co więcej, jak pokazały badania, ścieki oczyszczone w konwencjonalnych układach biologicznego oczyszczania przyspieszają procesy eutrofizacji, ponieważ zawierają duże ilości mineralnych form azotu i fosforu, łatwo przyswajalnych przez roślinność wodną. Wymagania europejskie i krajowe w zakresie jakości ścieków oczyszczonych wprowadzanych do odbiorników dotyczą zawartości ogólnego azotu i fosforu, natomiast najbardziej dostępną dla glonów formą tych pierwiastków są ich rozpuszczone nieorganiczne formy. Wiedza o zawartości przyswajalnych form związków biogennych w ściekach, odprowadzanych do wód powierzchniowych, pozwoli na podejmowanie racjonalnych decyzji przy wyborze technologii oczyszczania ścieków, ponieważ zaawansowane technologie głębokiego usuwania substancji biogennych stanowią wyjątkowo kapitałochłonne inwestycje. Mając na uwadze powyższe rozważania, podjęto badania nad strukturą zawartości różnych form azotu i fosforu w ściekach komunalnych odprowadzanych z oczyszczalni ścieków Jaworzno-Dąb, wyniki których przedstawiono w niniejszym artykule.

Słowa kluczowe: eutrofizacja, ścieki komunalne, substancje biogenne, bioprzyswajalność

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PHYSICOCHEMICAL, THERMAL AND KINETIC ANALYSIS OF SEWAGE SLUDGE

FIZYKOCHEMICZNA, TERMICZNA I KINETYCZNA ANALIZA OSADÓW ŚCIEKOWYCH

Abstract: Sewage sludge (SS) is the residual matter generated from waste water treatment. Current treatment methods consist of mechanical dewatering and thermochemical treatment, which have become expensive, inefficient and energy consuming. Furthermore, European Union (EU) laws prohibit landfilling, agricultural and storage utilization of sewage slude (SS). Consequently, innovative and sustainable treatment, management and utilization technologies for SS are urgently required. The pyrolysis of sewage sludge can be potentially address the outlined challenges. Therefore, the main aim of this investigation was to examine the physicochemical, thermal and kinetic properties of selected sewage sludge samples (SS1 and SS2). Thermogravimetric analysis was examined to provide comprehensive description of the decomposition behaviour and kinetic characteristics of SS1 and SS2 under pyrolysis conditions at heating rates: 5, 10, 20 and 40°C/min from 30-800°C. The kinetic parameters such activation energy E_a and pre-exponential factor, A were calculated using the Kissinger model. The E_a and A values for SS1 are 205.87 kJ/mol and $9.68 \cdot 10^{14}$ whereas SS2 are 320.40 kJ/mol and $7.44 \cdot 10^{24}$. The general conclusion based on experimental studies is that the physicochemical and thermal kinetic properties of SS1 and SS2 are comparable with other pyrolysis feedstock and suitable for pyrolysis conversion.

Keywords: physical and chemical properties of sewage sludge, thermal analysis, kinetics

Introduction

Sewage sludge (SS) is the residual matter generated from the treatment of waste water plants. Currently, SS treatment methods are mechanical dewatering, biological and chemical treatment techniques [1] aimed at reducing moisture content, microbial load, hazardous substances and volume density [2]. However, the high cost, low efficiency and energy consumption of current treatment processes present significant challenges to sewage sludge management. Furthermore, European Union (EU) Sewage Sludge Directive 86/278/EEC as well as regulations on health, safety and environmental (HSE) seeks to limit landfilling, agriculture utilization and long term storage of sewage sludge [3].

Consequently, there is an urgent need to explore low cost, energy efficient and sustainable solutions for the treatment, management and future utilization of sewage sludge. There are several thermal technologies for utilizing renewable fuels to obtain useful forms of energy through the correct pre-treatment (torrefaction, slow pyrolysis, and hydrothermal carbonization processes) [4-9]. The valorisation of sewage sludge through pyrolysis can potentially address the challenges related to sewage sludge treatment and management. Pyrolysis is considered as the most practical, efficient and sustainable technology for the synthesis of liquid, solid and gaseous fuels from various feedstock [6]. However, pyrolysis

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requires comprehensive knowledge of the physicochemical, thermal and kinetic decomposition characteristics of the feedstock [10]. This is an essential requirement for assessing the feasibility of implementing thermal conversion as well as process design, engineering economics and materials considerations. In addition, feedstock properties can be used to optimize operating conditions and improve selectivity of thermal conversion products during conversion [11].

Thermal techniques, in particular thermogravimetric analysis (TG, DTG) provide information about the thermal behaviour, reactivity and kinetics of sewage sludge in a simple and straightforward way [12]. The most important applications of thermal analysis is for evaluating kinetic parameters such as activation energy E_a and pre-exponential factor A through non-isothermal solid-state kinetics [13-15]. Numerous researchers have successfully investigated the non-isothermal thermogravimetry (TG, DTG) [16, 17] and kinetic analysis of various feedstock under pyrolysis conditions. Furthermore, the characterization of the physicochemical properties, and thermal behaviour of mechanical-biologically treated SS through gasification, pyrolysis and combustion has been investigated. However, this is lack of comprehensive understanding of the properties of mechanical-biological-chemically treated SS samples. The scientific data of SS fuel properties will potentially improve the efficiency of conversion technologies [18] products optimization [19] and reduce pollutant emissions [20].

Consequently, this study aims to investigate: (a) the physicochemical properties of two types of sewage sludge (b) the thermal behaviour of the selected SS using non-isothermal thermogravimetric (TG, DTG) analysis (c) the kinetic parameters; activation energy (E_a) and pre-exponential factor (A) according to conversion degree (α) using the Kissinger method under pyrolysis conditions.

Experimental

Materials

The sewage sludge samples investigated in this study were acquired from wastewater treatment plants (WWTP) in Poland.

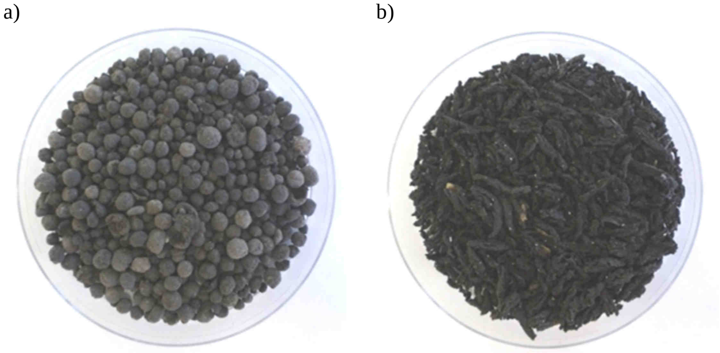

Fig. 1. Sewage sludge samples: a) Sewage sludge 1 - from mechanical and biological wastewater treatment plants (WWTP); b) Sewage sludge 2 - mechanical, biological and chemical WWTP with simultaneous phosphorus precipitation

Sewage sludge 1 (SS1) was obtained from mechanical-biological treatment while Sewage sludge 2 (SS2) was collected after mechanical-biological-chemical treatment with simultaneous phosphorus precipitation. Subsequently, the sludge was subjected to fermentation, dewatering, and drying. SS1 was dried in a cylindrical drier on shelves heated up to 260°C while SS2 was dried using hot air at 150°C in a belt drier. Therefore, SS1 appear as granules whereas SS2 as irregular thin “pasta” shaped crumbs (Fig. 1).

Methods

The chemical qualitative analysis of the dried sewage sludge samples SS1 and SS2 was examined using an automatic IR (Infra-Red) analyser to determine the concentrations of major elements: carbon, hydrogen, nitrogen, chlorine, fluorine, sulphur and oxygen. Next, physicochemical analysis was conducted to determine moisture, volatile fractions and ash content using the gravimetric standards [21-23], respectively. The higher heating value was determined by the calorimetric method while the lower heating value was calculated using the mass fractions of the major elements in the SS samples.

The thermogravimetric analyses were conducted using a Mettler Toledo TGA/SDTA 851 apparatus with accuracy 10^{-6} g. The instrument was calibrated using indium, zinc and aluminium. For each TG run, 15 mg of sample was placed in an alumina crucible and heated from ambient temperature to 800°C at constant heating rates, β = 5, 10, 20 and 40°C/min under argon atmosphere at the flow rate of 40 cm^3/min. Each sample was measured under exactly the same conditions, including temperature range, atmosphere, and heating rate, to determine the correct conditions. The TG/DTG curve for each sample was obtained as the outputs for pyrolysis processes.

The derivative thermogravimetric (DTG) is based on the rate of mass loss as deduced from the mathematical transformation ($d\alpha/dt = f(t)$, where α - mass of sample, t - time). DTG profiles present vital information such as the mass loss taking place at a given temperature during thermal conversion. Consequently, the resulting weight loss [%] and corresponding temperature was analysed and numerically computed for kinetic analyses of the SS samples using the Kissinger kinetic model.

Kissinger kinetic theory

The most important applications of thermal analysis is kinetic calculations. The kinetic parameters could be obtained by methods for analysing non-isothermal solid-state kinetics. Solid-state kinetic data are the major interest in thermal processes. In non-isothermal kinetics, the Friedman (F), Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods are the most often used isoconversional methods [14, 24-26].

The kinetics of SS1 and SS2 decomposition under pyrolysis conditions was evaluated using the *Kissinger* model. The kinetic parameters, activation energy E_a and frequency factor A can be determine using the model. The decomposition of sewage sludge (SS) during pyrolysis can be represented as:

$$Sewage\ Sludge \xrightarrow{k(T)} Volatiles + Liquid + Char \tag{1}$$

Consequently, the rate of sewage slude decomposition under pyrolysis conditions can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

Where the term $f(\alpha)$ is the reaction model for SS pyrolysis (decomposition), and $k(T)$ is the temperature dependent rate constant defined by the Arrhenius law in Eq. (3):

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

The terms E_a, A, R and T denote activation energy [kJ/mol], frequency factor [min^{-1}], universal gas constant [J/mol K] and temperature [K], respectively. Consequently, by substituting Eq. (3) into Eq. (2), an empirical model describing SS pyrolysis can be propounded Eq. (4):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{4}$$

Subsequently, Eq. (4) can be rewritten to account for Eqs. (2-4):

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{5}$$

For SS pyrolysis at multi-heating rate, the term $\beta = \mathrm{d}T/\mathrm{d}t$ must be introduced after separation of variables, therefore Eq. (5) can be rewritten as:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right) dT \tag{6}$$

By integrating Eq. (6) the function $g(\alpha)$ describing the SS pyrolysis at a given heating rate can be deduced:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \tag{7}$$

The solution to the Eq. (7) for the pyrolysis of SS at temperature, T_m yields the expression for the *Kissinger* model in Eq. (8):

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_m}\right) \tag{8}$$

The term T_m is the peak decomposition temperature obtained from the DTG curve. Consequently, the kinetic parameters; E_a and A, for SS pyrolysis can be obtained from the slope and intercept of the plot of $ln\ (\beta/T^2_m)$ against $1/T_m$ at different heating rates.

Results and discussion

Physicochemical properties

Table 1 presents the chemical qualitative characteristics of two sewage sludge (SS1, SS2) samples examined by ultimate, proximate and calorific analyses.

Analysing presented data it can be concluded that the sludge collected after mechanical-biological-chemical treatment (SS1) is characterized by the lower content of carbon, hydrogen, nitrogen, oxygen and chlorine in comparison to sludge obtained from mechanical-biological treatment (SS2). The main reason for this, is a chemical reaction of precipitation realized during the chemical stage of wastewater treatment process.

In addition, the results indicate the lower suitability of the sludge SS2 as a fuel in comparison to sludge SS1, This is based on the comparative empirical evidence from the volatile matter (VM) and ash content. The higher VM content of SS1 indicates lower ignition temperature and reactivity during pyrolysis compared to SS2. Similarly, lower ash content of SS1 points to low potent for agglomeration, and slagging during thermal conversion, Furthermore, the results submit that chemical precipitation process of wastewater treatment significantly affects on the calorific value and overall physicochemical of the properties treated SS.

Table 1

Proximate and ultimate analysis of studied sewage sludge samples

	Element/Parameter	Sewage sludge 1 (SS1)	Sewage sludge 2 (SS2)
Proximate analysis [%] (as received)	Moisture	5.30	5.30
	Volatile matter	51.00	49.00
	Ash	36.50	44.20
Ultimate analysis [%] (dry basis)	C	31.79	27.72
	H	4.36	3.81
	N	4.88	3.59
	O (by difference)	20.57	18.84
	S	1.67	1.81
	F	0.013	0.003
	Cl	0.22	0.03
Calorific value	HHV* [MJ/kg], dry basis	14.05	11.71
	LHV** [MJ/kg], dry basis	12.96	10.75

*HHV - Higher Heating Value; **LHV - Lower Heating Value

Thermogravimetric analysis

Figure 2 a,b shows the derivative thermogravimetric (DTG) profiles for sewage sludge samples (SS1 and SS2) at heating rates β = 5, 10, 20 and 40°C/min. The thermal conversion of sewage sludge under argon atmosphere takes place with mass loss. The impact of heating rate is evident for both samples, but for SS1 the differences of mass loss rate are more significant with wider endothermic peaks and higher rates of thermal decomposition.

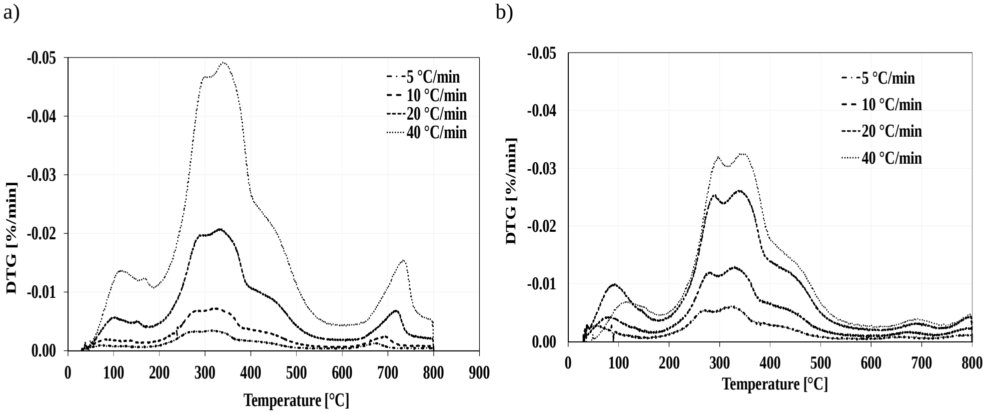

Fig. 2. DTG plots for SS1 from 5, 10, 20, 40°C/min under argon atmosphere (a) and DTG plots for SS2 from 5, 10, 20, 40°C/min under argon atmosphere (b)

The DTG curves indicate the pyrolysis of SS1 and SS2 occurred in three stages. The first stage (< 200°C) corresponds to drying and is typically attributed to the loss of moisture and devolatilization of low molecular weight compounds [27]. The moisture content of sewage sludge samples are similar which accounts for the similar mass loss, albeit at different rates. The main decomposition during the pyrolysis process is in the temperature rage 200-580°C. This is mainly attributed to the decomposition of organic matter in sewage which comprises proteins, polysaccharides, cellulose and polymers that typically decompose below 600°C. The DTG curves also indicate the devolatilization of the SS samples occurs in two stages as depicted on the dual protuberances on the devolatilization peaks in Figure 2a,b. Two main peaks appear for SS1 and SS2, with the first at approximately 290°C, and the second is at approximately 310°C indicating the occurrence of two separate but simultaneous chemical reactions. During this stage, the pyrolysis of SS and breakdown of combustible volatiles (*e.g.*, CH_4, CO, H_2) results in the release of non-condensable gases H_2, H_2O, CO_2 and CH_4 [7]. The final decomposition takes place above 580°C, for sewage sludge SS2 is not significant and slight weight loss is observed. An increase in heating rate does not significantly influence the shape of DTG curves, but weight loss rate is increasing in higher temperatures.

Kinetic analysis

The kinetic analysis of SS1 and SS2 was carried out using the Kissinger model from the plot of $\ln(\beta/T_m^2)$ against $1/T_m$ at different heating rates (β). The term T_m is the peak decomposition temperature of the samples derived from the DTG curve.

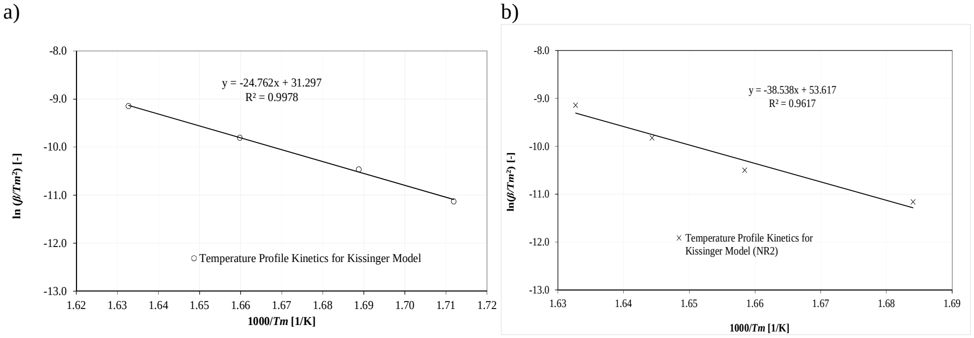

Fig. 3. Kissinger kinetic plots for: a) SS1, b) SS2

Consequently, the kinetic parameters; E_a and A, were deduced from the slope and intercept of the plots for SS1 and SS2 presented in Figures 3a,b. Table 2 presents the calculated kinetic parameters for the pyrolysis of the SS samples.

The results indicated the kinetic parameters of SS1 have lower values comparing to SS2 sample. The difference in the E_a and A values for the samples can be ascribed to the effect of chemical treatment on the SS2 sample. The chemical treatment of SS2 is clearly responsible for the loss of volatile organic matter and reactive components. Consequently, the SS1 higher proportions of reactive components aided rapid decomposition of the sample compared to SS2. This is corroborated by the higher rate of devolatilization (higher mass loss) observed for the SS1 sample in Figure 2a. Hence, it can be inferred that chemical precipitation decreases the thermochemical fuel and kinetic properties of sewage sludge as feedstock for pyrolysis. This suggests that SS for prospective utilization in pyrolysis can only undergo mechanical-biological treatment.

Table 2

Kinetic parameters of sewage sludge samples SS1 and SS2

Sample	**E_a [kJ/mol]**	**A [min^{-1}]**	**R^2**
SS1	205.87	$9.68 \cdot 10^{14}$	0.9978
SS2	320.40	$7.44 \cdot 10^{24}$	0.9617

Conclusions

The study was aimed investigating the physicochemical, thermal and kinetic properties of two types of sewage sludge SS treated via mechanical-biological and mechanical-biological-chemically methods. Thermal analysis of the sewage sludge SS was carried out under pyrolysis conditions to determine the the kinetic parameters; activation energy (E_a) and pre-exponential factor (A) using the *isoconversional* Kissinger method. The results showed the chemical precipitation treatment decreases the thermochemical fuel and kinetic properties of sewage sludge as feedstock for pyrolysis. Consequently, prospective pyrolysis of SS utilization requires mechanical-biological treated feedstock for efficient thermal conversion.

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FIZYKOCHEMICZNA, TERMICZNA I KINETYCZNA ANALIZA OSADÓW ŚCIEKOWYCH

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Abstrakt: Osady ściekowe są stałym produktem procesu oczyszczania ścieków. Obecne metody zagospodarowania osadów obejmujące mechaniczne odwadnianie oraz termiczne wykorzystanie stają się drogie, nieefektywne i energochłonne. Co więcej, prawo Unii Europejskiej ogranicza składowanie oraz wykorzystanie rolnicze osadów ściekowych. W efekcie znalezienie innowacyjnych oraz zrównoważonych metod zagospodarowania i utylizacji osadów ściekowych jest niezwykle istotne. Proces pirolizy wydaje się odpowiedni, by sprostać tym wymaganiom. Celem pracy jest określenie fizykochemicznych, termicznych oraz kinetycznych właściwości wybranych próbek osadów ściekowych (SS1 i SS2). Zastosowano analizę termograwimetryczną w celu przeprowadzenia analizy porównawczej opisującej proces przemian termicznych oraz ich kinetyki w warunkach pirolizy dla stałych szybkości grzania wynoszących 5, 10, 20 i 40°C/min w zakresie temperatur od 30-800°C. Parametry kinetyczne: energia aktywacji E_a oraz czynnik przedekspotencjalny A zostały wyznaczone przy użyciu modelu Kissingera. Wartość E_a oraz A dla osadu ściekowego SS1 wynosi odpowiednio 205,87 kJ/mol i $9{,}68 \cdot 10^{14}$, podczas gdy dla osadu SS2 odpowiednio 320,40 kJ/mol i $7{,}44 \cdot 10^{24}$. Wyniki analiz zostały porównane z innymi materiałami poddawanymi pirolizie.

Słowa kluczowe: właściwości fizykochemiczne osadów ściekowych, analiza termiczna, kinetyka

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ASSESSMENT OF ENVIRONMENTAL POLLUTION CAUSED BY EDCs FROM EVERYDAY OBJECTS

OCENA ZANIECZYSZCZENIA ŚRODOWISKA ZWIĄZKAMI EDCs POCHODZĄCYMI Z PRZEDMIOTÓW CODZIENNEGO UŻYTKU

Abstract: Endocrine-disrupting compounds (EDCs) are a specific category of chemicals that attracted a great deal of public and scientific attention in the past few decades. They are proved to interfere with the endocrine system, and thus affect the growth, reproduction, homeostasis and metabolism of living organisms. They appear as a threat not only for humans but also for the wildlife. EDCs are present in plastics such as plastic food packaging, detergents, pesticides, fire retardants, heavy metals, pharmaceuticals. They are also components of personal care products, for example cosmetics like creams, soaps or UV filters, oral contraceptives, analgesics and many more. They are not always detected and eliminated in sewage treatment plants and because of that they get to the environment and with the running water into the households. In order to eliminate different contaminants, appropriate techniques have to be chosen.

Keywords: EDCs, PPCPs, wastewater treatment

Introduction

In the past few decades a specific category of chemicals attracted a great deal of public and scientific attention. They appear as a threat not only for humans but also for the wildlife. EDCs (endocrine-disrupting compounds, endocrine-disrupting chemicals) are proved to interfere with the endocrine system, and thus, may affect the growth, reproduction, homeostasis and metabolism of living organisms [1].

In 1997 the US Environmental Protection Agency (US EPA) defined an EDC as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" [2].

The list of EDCs includes: pesticides (*e.g.* DDT - 2,2-bis-*p*-chlorophenyl-1,1,1-trichloroethane, vinclozolin, atrazine), organochlorines and organohalogens (*e.g.* dioxins and furans produced during the incineration of chlorinated aromatic compounds, paper and in production of PVC plastic, brominated fire retardants), alkyl phenols used in production of phenol resins and plastic additives (*e.g.* nonyphenol, nontlphenol etoxylate, octylphenol), bisphenol A, phthalates: higher-molecular-weight phthalates (*e.g.* DEHP - bis(2)ethylhexyl) phthalate, PVC - polyvinyl chloride, DBP - dibutyl phthalate, BBP - butyl benzyl), lower-molecular-weight phthalates (DMP - dimethyl phthalate, DEP - diethyl phthalate), heavy metals (*e.g.* Cd - cadmium, Cu - copper, Pb - lead, Hg - mercury), phytoestrogens (isoflavones, lignans), natural hormones excreted by humans and livestock (*e.g.* (E1) - estrone, (E2) - 17β-estradiol, (E3) - estriol), synthetic hormones (*e.g.* (EE2) - ethinyl estradiol) [3-6].

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Endocrine disrupting compounds

Phytoestrogens are natural products classified as endocrine-disrupting compounds - isoflavones, such as: daidzein (Dai) present in soy, genistein (Gen) found in soybeans, lupin, fava beans, kudzu and psoralca, kacmpferol (Kacm) isolated mostly from tea, broccoli, grapefruit and apples. Flavonoides: apigenin (Api) is used to dye wool, coumesterol (Coum), classified as a coumestant, is also able to bind to the estrogen receptors.

Bisphenol A (BPA) is widely used in the manufacturing of polycarbonate and other plastic products, epoxy resin-based food can liners, flame retardants, dental fillings and rubber chemicals. The annual production of bisphenol A is about 3 Tg, of which nearly 100 Mg are released to the atmosphere.

Bisphenol AF (BPAF) is used in production of polycarbonate copolymers in high-temperature composites and electronic materials.

Data shows that bisphenols are detectable in urine samples in more than 90% of the U.S. population.

Higher-molecular-weight phthalates, *e.g.* DEHP, PVC, are widely used in consumer goods, such as food packaging, plastics, detergents and resins.

Widespread exposure for these chemicals (food, air, dust and other goods) may result in adult living beings in reduced fertilization success, miscarriage, premature delivery, reduced sperm quality, gene expression and many other serious disorders [3, 4, 7-10].

Pesticides, including herbicides (*e.g.* alachlor, aminotriazole, atrazine, metribuzin, nitrofen), fungicides (*e.g.* benomyl, carbendazim, hexachlorobenzene, pyrimidine methanol, ethylidene double dithiocarbamate zinc), insecticides (*e.g.* (Endo) endosulfan, (Kep) kepone, lindane(β-666), chlordane, endosulfan, triazine), nematicides (*e.g.* temix, carbofuran, dibromochloropropane (DBCP)) are very extensively used in agriculture. Recently, the usage of herbicides and pesticide in developing countries has been increasing alarmingly. They are present in food and water, and what is the most important, some of them are proven to affect the male reproductive system and to cause cancers. Statistics show that every year there are around 20,000 deaths as a result of acute pesticide intoxications. Because of that, usage of some pesticides have been restricted or banned in industrialized countries. Unfortunately they are often exported to developing countries where such restrictions do not exist [3, 4, 9, 11].

Another group of compound interfering with estrogen receptors are metaloestrogens, commonly used in industrial mining and metallurgy, such as: cadmium, cobalt, copper, nickel, lead, zinc, mercury, tin, chrome and aluminum. Among them cadmium belongs to the most wide spread. It is used in production of batteries, dyes, plastics and is a part of cigarette smoke. Also popular nickel is able to impair the proper thyroid functioning, while zinc, lead and mercury cause reproductive disturbances [10-12].

Pharmaceutical and personal care products

Another group of EDCs, which biological effects to nontarget organisms are being currently studied is big group of pharmaceutical and personal care products (PPCPs) used for both humans and animals for daily personal care, disease treatment and prevention. They include: pharmaceutical products, such as: analgesics and anti-inflammatory drugs (*e.g.* acetaminophen, diclofenac, ibuprofen, ketoprofen and naproxen), antibiotics/antimicrobials (*e.g.* sulfonamides, chlortetracycline, tetracycline, trimetoprim, erythromycin), antiepileptics (*e.g.* carbamazepine), beta-blockers, blood lipid regulators used to lower cholesterol and triglyceride levels in the blood (*e.g.* clofibrate, bezafibrate), cytostatics, contraceptives, antiseptics - chemical agents that slow or stop the growth of microorganisms on external surfaces of the body (*e.g.* triclosan), synthetic musk fragrances commonly used in perfumery(*e.g.* nitromusks, galaxoline, tonalide), sun screen agents (*e.g.* benzophenone, methylbenzylidene camphor, octylmethoxycinnamate), parabens used as preservatives in most cosmetics and other personal care products (*e.g.* methyl-, ethyl-, propyl-, butylparagen), surfactants/alkyl phenols used in emulsifiers production [3, 10, 11, 13].

Parabens are a group of p-hydroxybenzoicacid (PHBA) widely used in cosmetic, pharmaceutical and food industries. The most common is methylparaben due to its antibacterial activity and the fact that it does not modify the physical properties of the final product, such as taste, color or texture. Parabens are found in almost all categories of cosmetics and many pharmaceuticals: soaps, lotions, shampoos, conditioners, creams, tonics, gels, toothpastes, sunscreens, make up cosmetics, ointments, syrups and aerosols. Studies have proved that long-term exposure to these compounds may affect the growth and development of cancerous tissue by absorbing into biological tissues. It can also interfere with secretion of testosterone and functioning of the females' reproductive system [14].

UV filters that provide the protection against the harmful effects of the ultraviolet radiation coming from the sun, are used not only in cosmetics, such as: creams, lotions, lip balms, hair sprays, hair dyes, shampoos, nail polishes but also in tires and inks. Sun screen agents can get into the surface waters directly by recreation activities when cosmetics are rinsed off of the skin by swimming pool or lake water. Even more important is the indirect way - some UV filters stay on clothes and towels and while washing, they get into the domestic sewage. Sun screen agents are commonly detected in samples of surface waters and freshwater fishes [15, 16].

Many of these xenoestrogens enter waste treatment plants via household and industrial waste streams, and due to their insufficient removal processes, they are released to streams and rivers, where they often resist degradation by microbes and ultraviolet light. While the toxicities of other compounds can be reduced by dilution of the effluent in surface waters, EDCs can elicit biological effects at very low concentrations. Except this one, other important factors are persistence, bioaccumulation, exposition time and mechanism of biotransformation. Some compounds in the environment after biotransformation give metabolites or by-products more harmful than the original substances. Researches show that measurable levels of hundreds of substances from pharmaceutical and personal care products are found in the $\mu g/dm^3$ range in sewage-treatment plant effluents and in the ng/dm^3 range in surface waters. A lot of endocrine disruptors are hydrophobic, have low vapor pressures, high octanol-water partitioning coefficients, partition into sediment and sewage sludge and have been detected in biosolids. Over 3 million metric tons of these biosolids are applied to agricultural fields, parks and other areas each year.

Xenoestrogens such as bisphenol-A may leach into drinking water from infant bottles and coatings in food cans. Alkylphenols, phthalates and polyaromatic hydrocarbons can get into drinking water when plastic pipes are used in supply lines [1, 3, 6, 11, 13].

Effect of endocrine-disrupting compounds on humans and environment

Endocrine disrupting compounds are widely distributed in the biosphere by precipitation, surface runoff, the usage of pesticides and through enrichment of food and drinking water. Even if the content is low, after long time of continuous exposure, the organism response can be similar to that produced by exposure to a higher dose of a single endocrine disruptor. Such compounds cause abnormal and even toxic effects. Exposure to xenoestrogens during critical periods, such as the cellular differentiation period may result in permanent character changes in the mature living beings. Children's developing systems are delicate and they may not be able to repair the damage triggered by EDCs exposure. Reports show frequent occurrence of childhood cancers and congenital malformations among children, whose parents had contact with pesticides at work. Endocrine disruptors in adults may be associated with reduced fertilization success, sperm and embryo quality, implantation failure, miscarriage, premature delivery, endometriosis, altered hormone concentrations, obesity. But xenoestrogens affect not only reproductive function, but also a range of tissues which are steroid sensitive, for instance, the central nervous system and thyroid. They can also interfere with immune system, glucose homeostasis, alter epigenetic markers and gene expression, causing breast, testicle and prostate cancers [3, 6, 9, 11].

It is evident now that exposure to endocrine disrupting compounds is almost unavoidable. Having the potential to bio-accumulate in body fat, they may be released later and enter infants during pregnancy or through breast milk. The effects associate with the presence of xenoestrogens in the environment are: reduced sperm count in males, reduction in the breakage of eggs of birds, fishes and turtles, feminization of male fishes, sexual abnormalities in alligators (due to exposure to organochlorines), reproductive problems in fishes, reptiles, birds and mammals, prostate enlargement in male mice, obesity in offspring and changes in immunologic system of marine mammals. In some cases, these disorders can lead to decline in population [1, 3, 11, 16].

Anadromous salmon population decline is an effect of exposure to anthropogenic disturbances, such as endocrine disruptors, as the salmons pass through some most polluted areas of larger rivers and estuaries during their downstream migration to the sea. The biggest threat seems to be nonylphenol (NP) which is widely used in manufacture of paper, plastic, agricultural chemicals, pesticides, commercial and household cleaning products, detergents, cosmetics, contraceptives and paints, and is commonly released to the environment. Along with other pollution and environmental disturbances, nonylphenol can elicit stress response affecting both metabolic and ion regulatory processes. What is more, polychaetes as feeders in aquatic ecosystems are likely to accumulate xenoestrogens, such 17β-estradiol, nonylphenol, bisphenol A and octylphenol, from sediment through dietary uptake. It is important, because benthic invertebrates are main food source for some bottom feeding fishes.

Another big problem is increasing resistance in the natural bacterial population due to misuse and overuse of antibiotics, their over the counter availability together with crowding and improper sewage disposal [17, 18].

Endocrine-disrupting compounds removal from wastewater

Data from recent researches shows that conventional treatment processes removal of endocrine disruptors are sufficient only in around 25% and dependent upon its intrinsic chemical properties such as molecular weight, relative hydrophobicity, aromatic carbon content and functional group composition. The hydrophobic and nonpolar nature of EDCs allows them to absorb onto particulates. This suggests that the general effect of wastewater treatment processes would be concentration of organic pollutants and their removal from the aqueous phase to primary and secondary sludge, by mechanical separation techniques. Wide range of PPCPs, pesticides and alkyl phthalates can be removed using nanofiltration or reverse osmosis. Nanofiltration membranes remove E1 by size exclusion and others by adsorption, however, the membrane retention decreases with increase in the amount of E1 accumulated on the membrane surface.

Effective is application of coagulation by cationic polyacrylamide in water supply, which enhance the removal of phthalate esters and reduce water turbidity. Flocculation is sufficient in dioctyl phthalate removal, and under optimized conditions its effectiveness reaches 82%.

More advanced water treatment technologies, such as granular activated carbon (GAC) adsorption or ozonation are recommended as better way to remove many xenoestrogens including methoxychlor, endosulfan, DDT, dioxin, polychlorinated biphenyls and many others. Even though adsorption, using granular activated carbon is sufficient in removing most organic contaminants (from 60 to 99% for estrogens 17β-estradiol and 17α-ethynylestradiol), some of them, for instance: iopromide, analgesics like ibuprofen, naproxen, dichlofenac, sulfamehtoxazole and meprobamate are recalcitrant for this method. Ozonated activated carbon would oxidize endocrine chemicals into small organic molecules, and thus increase the efficiency of GAC adsorption.

Advanced oxidation processes (AOPs) is a group of chemical-oxidative processes which are characterized by the generation of hydroxyl radicals. Hydroxyl radical, as one of the strongest radicals, is able to oxidize and mineralize almost every organic pollutant into CO_2, H_2O and mineral acids. Light oxidation techniques are those which are characterized for the use of UV radiation and the presence of oxidants as hydrogen peroxide and ozone. UV/H_2O_2 and titanium dioxide photocatalysis are efficient in removing up to 98% of estrogens, bisphenols and antiepileptics. Ozonation as a dark oxidation treatment eliminates 90% of estrogens, antibiotics, pesticides, anti-inflammatories and antiepileptics from wastewaters. Ozone is considered to be more efficient for PPCPs control than ClO_2 or Cl_2 which are used in the most widespread conventional treatments.

Activated sludge biological treatment, commonly used in large cities, as numerous studies showed that the majority of endocrine disruptors are biodegradable, is considered as the cheapest available process of removing and degrading compounds. Conventional biological processes, such as activated sludge, biofiltration and soil aquifer treatment exhibit some degree of EDCs removal. They are more efficient in disposing of alkylphenols, bisphenol A and natural estrogens from the aqueous phase than primary treatment. Data indicates that this process can remove around 85-88% of βE2, 85% EE2, up to 95% of E3, however, the removal performance for E1 appears to be less and more variable. Further studies show that the highest removal rates of estrogenic activity were obtained at plants with comprehensive treatment technologies, for instance combined biological and chemical ones [3, 5, 9, 11, 19].

Conclusions

This paper presented that most of the everyday objects, such as cosmetics, pharmaceuticals, plastic food packaging, pesticides and many more are sources of compounds interfering with natural endocrine system, causing diverse disorders. Due to the inefficient wastewater treatments, they are widely released to the environment, and even in "acceptable" concentrations, resulting in abnormal changes in wildlife. In order to eliminate different contaminants, appropriate techniques have to be chosen. That is why control and proper removal of endocrine disrupting compounds from sludge should be further studied.

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OCENA ZANIECZYSZCZENIA ŚRODOWISKA ZWIĄZKAMI EDCs POCHODZĄCYMI Z PRZEDMIOTÓW CODZIENNEGO UŻYTKU

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Abstrakt: Związki modulujące pracę hormonów estrogenowych są grupą związków chemicznych, które przez ostatnich kilka dekad zwróciły uwagę zarówno społeczeństwa, jak i naukowców. Dowiedziono, że substancje te ingerują w prawidłową pracę układu hormonalnego i zaburzają rozwój, reprodukcję, homeostazę i metabolizm żywych organizmów. Zagrażają nie tylko ludziom, ale także wszystkim żywym organizmom. Są obecne w: plastikach, między innymi plastikowych opakowaniach na żywność, detergentach, pestycydach, tworzywach ognioodpornych, metalach ciężkich, a także farmaceutykach i produktach codziennej higieny, takich jak kosmetyki - kremy czy mydła, filtry UV, doustne środki antykoncepcyjne i przeciwbólowe, a także w wielu innych produktach. Nie zawsze są wykryte i usunięte ze ścieków, a w ten sposób dostają się do środowiska i gospodarstw domowych wraz z bieżącą wodą. W celu eliminacji powyższych substancji zanieczyszczających muszą być użyte odpowiednie techniki oczyszczania ścieków.

Słowa kluczowe: związki modulujące pracę hormonów estrogenowych, farmaceutyki i produkty codziennej higieny, oczyszczanie ścieków

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APPLICATION OF PERVAPORATION IN GASOLINE DESULFURIZATION - VARIOUS SULFUR COMPOUNDS REMOVAL EFFICIENCY

ZASTOSOWANIE PERWAPORACJI DO ODSIARCZANIA BENZYNY - EFEKTYWNOŚĆ USUWANIA RÓŻNYCH ZWIĄZKÓW SIARKI

Abstract: In order to adapt to new and more rigorous requirements and to satisfy higher environmental expectations, specifications on sulfur content in gasoline demands a reduction of its level to 10 ppm. Sulfur in gasoline is a considerable source of sulfur oxides emissions. SO_x, which are formed during the combustion of sulfur-containing fuels, are sulfates precursors, which contributes to the formation of acid rains and further acidification of soils and surface water. Since sulfur is present in gasoline in a form of different compounds (such as thiophene and its derivatives, mercaptans and sulfides) and different sulfur species show different affinity with membrane materials, it is very important to investigate the efficiency of their removal separately. The aim of this research was to recognize the influence of typical chosen sulfur compounds present in gasoline on membrane pervaporation behavior and the efficiency of sulfur species separation. The influence of process parameters such as feed temperature, feed concentration and downstream pressure on the efficiency of thiophenes removal from model *n*-octane/sulfur compound mixtures by means of vacuum pervaporation method was also examined. During the test, the hydrophobic PDMS-based composite membrane were applied. Binary mixtures of thiophene/*n*-octane and 2-methylthiophene/*n*-octane were used as a model gasoline. The content of sulfur from thiophenes varied from 0.05 to 0.13 mas. %. Feed temperature was ranged from 30 to 50ºC. The feed flow rate (80 dm^3/h) was kept at constant level.

Keywords: vacuum pervaporation, desulfurization, thiophenes, gasoline

Introduction

Nowadays a lot of attention is being paid to the reduction of sulfur concentration in transportation fuels. In order to adapt to new and more rigorous requirements and to satisfy higher environmental expectations, specifications on sulfur content in gasoline demands a reduction of its level to 10 ppm [1].

Sulfur oxides, which are formed during the combustion of sulfur-containing fuels, are sulfates precursors which contributes to the formation of acid rains and further acidification of soils and surface water, as well as the formation of photochemical smog. Moreover, their presence in exhaust gases from vehicles contributes to the larger emission of NO_x and VOC's caused by the reduction of low-temperature catalytic converters activity.

Trade gasoline is a blend of gasoline fractions coming from various refinery processes such as light straight run, catalytic reforming, isomerization and fluid catalytic cracking (FCC). Streams derived from reforming and isomerization processes are generally characterized by low sulfur content, as feedstocks for those units are light fractions from the atmospheric distillation of crude oil [2]. Sulfur organic compounds tends to accumulate in higher-boiling fractions like atmospheric residue and fractions obtained from vacuum

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distillation, which are feedstocks for FCC units. Therefore, FCC gasoline is the main contributor of organosulfur compounds [3]. Although sulfur is present in gasoline in the form of different compounds, it occurs mainly in thiophenes, sulfides, mercaptans and disulfides [2, 3].

A lot of effort is now spent on developing novel and efficient hydrogen and non-hydrogen desulfurization technologies, such as selective extraction, catalytic extraction, selective oxidation, biodesulfurization, alkylation-extraction, improved selective hydroprocessing and pervaporative desulfurization (PVDS) [4, 5]. It should be noted, that some of them, including pervaporation, has already progressed beyond the lab-scale tests stage. In comparison with the traditional and other non-hydrogen separation processes, membrane separation offers many advantages including lower energy consumption and operating cost, simple operation and control scheme, easy scale up and adaptability to changes in process streams [6].

Pervaporation is a membrane technique, in which a first-order phase transition takes place. In pervaporation separation a dense non-porous membranes are applied. The liquid feed is contacted with the surface of the membrane and a specific compound is preferentially dissolved and transported across the membrane and then removed as vapour at the downstream side of the module. As a result of the separation, feed solution is divided into permeate and retentate streams. The vapour permeate is enriched in the component selectively transported through the membrane, while the liquid retentate in the component retained by the dense separation barrier. The vacuum pervaporation is carried out by maintaining the downstream pressure, lower than the saturation pressure of the permeating liquid solute at operating temperature [7]. The overall accepted mechanism explaining the mass transport across the dense membrane is solution-diffusion model [8].

Separation in the case of pervaporation is based on the affinity between compound being removed and membrane material. According to the mass transport model, pervaporation process can occur only when a certain amount of a compound is dissolved in the membrane material in the first stage of pervaporation separation. In the second stage, diffusion through the membrane combined with plasticization of its amorphous parts takes place. Diffusion step with a step of the sorption determine the selectivity of the process. The permeated compounds are then removed on the opposite side. The driving force for the separation process *i.e.* the partial pressure gradient between feed and permeate site, is maintained by constant withdrawn of the permeated compounds from the membrane [8].

To ensure the efficient process performance, the material of an active layer needs to show high affinity toward removed component. Hence, solubility parameter δ ((MPa)$^{1/2}$) and membrane polarity are the two main factors used for the preliminary evaluation of the interaction between the polymeric membrane and components of the mixture, as well as development of the novel membrane materials. The more similar the solubility parameters of the polymer and solvent, the more soluble solvent in the polymer [9]. In order to remove a specific component or group of compound from a mixture, the polarity of those species must be close to the polarity of the polymeric material used [10].

The aim of this research was to recognize the influence of typical chosen sulfur compounds present in gasoline on membrane pervaporation behavior and the efficiency of sulfur species separation. The influence of process parameters such as feed temperature, feed concentration and downstream pressure on the efficiency of thiophenes removal from model *n*-octane/sulfur compound mixtures by means of vacuum pervaporation method was also examined.

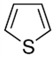
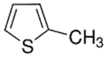
Experimental

Materials

To prepare the model gasoline, thiophene (99.5%, extra pure, benzene free) obtained from Acros Organics, 2-methylthiophene (98% purity) obtained from Sigma-Aldrich and *n*-octane (pure p.a.) obtained from Chempur were used. The physical and chemical characteristics of the investigated are listed in Table 1. Composite membranes consisting of a porous support with thin and dense poly(dimethylsiloxane) separating layer were obtained from PERVATECH, Netherlands.

Table 1

The physical and chemical characteristics of the investigated

Compound		**Structural formula**	**Molecular weight [g/mol]**	***Bp* [°C]**	**Vapour pressure [hPa]**	**δ [(MPa)$^{1/2}$]**
Hydrocarbon	*n*-octane	$CH_3(CH_2)_6CH_3$	114.23	125	14.7	15.5
Sulfur compound	thiophene		84.14	84	53^{a}	20
	2-methylthiophene		98.17	113	63.4^{b}	18.6

Bp - boilling point; δ - Hansen solubility parameter

Feed and permeate samples analysis

During studies, SRI 8610C Instruments Gas Chromatograph equipped with a dual FPD/ FID (flame photometric/flame ionization detector) detector and a Restek DB-1 MTX capillary column company (0.5 μm, 0.53 mm × 60 m) was used. The sample volume was 0.6 μm^3. Samples were injected manually using a SGE Analytical Science micro-syringe with a capacity of 5 μm^3. Retention time for thiophene was 3.45 min, for 2-methylthiophene was 6.73 min. The retention time for *n*-octane presented in samples from PV desulphurization process was 7.98 min. The temperature of the injector and detectors was 100 and 200°C, respectively. The column was conditioned each time before starting analysis. To ensure high purity of gases, additional air and hydrogen filters were installed.

Pervaporation experiments

The Sulzer lab-scale pervaporation setup, equipped with a test module with a diameter of 9 cm and a membrane effective area of 55 cm^2 was used for vacuum pervaporation measurements (Fig. 1). To prevent the mechanical damage of a membrane, it was kept on highly porous stainless steel support. The feed solution, maintained at a constant temperature by a thermostat (Thermo Electron Co., model Haake DC 30), was circulated to the upstream side of the cell using a recirculation pump. The permeated vapours were condensed by a cold traps cooled by immersion in Dewar flasks filled with liquid nitrogen, while retentate was returned to the feed tank. Permeates were collected within a specified time interval. The cold traps were then brought to room temperature prior to measure their weight using a balance (RadWag PS 210/C/2). The membrane upstream side was kept at atmospheric pressure. A vacuum pump (Alcatel, model Pascal 2015 SD) was used to create a vacuum in the downstream side of the module and to ensure the pressure gradient across the membrane. The temperature was controlled through a PID controller device (Greisinger Electornics GTH 1100/2 DIF). Sufficient feed flow rate was maintained using a circulation pump. Total downstream pressure was measured by an electronic vacuum gauge (Vacuubrand DRV 2).

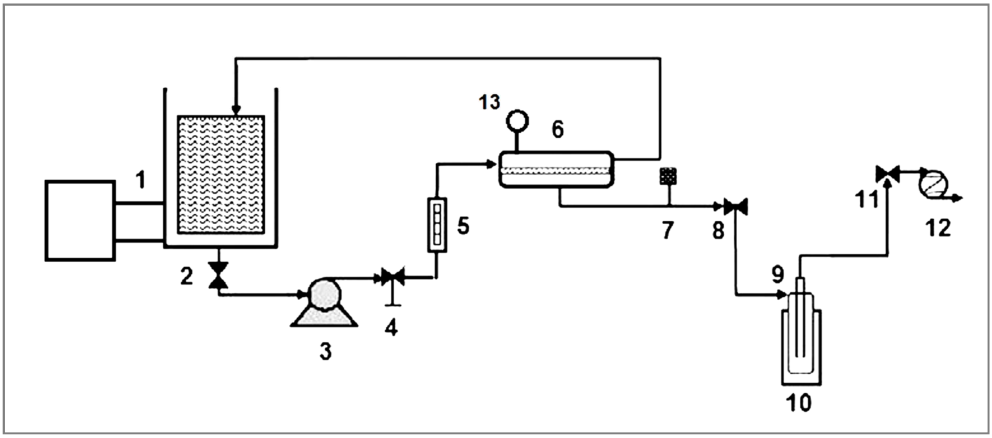


Fig. 1. Schematic diagram of the pervaporation system: 1 - thermostat, 2 - feed tank, 3 - circulation pump, 4 - pump regulator, 5 - rotameter, 6 - membrane module, 7 - vacuum pressure gauge, 8 - valve, 9 - cold trap, 10 - liquid nitrogen bath, 11 - valve, 12 - vacuum pump

Efficiency and selectivity of sulfur removal were evaluated basing on the dimensionless separation factor β (2). Yield of the pervaporation process was evaluated on the basis of the permeation flux determined as total and partial one:

$$J_m = \frac{m_p}{S_m \cdot t} \tag{1}$$

where: m_p - permeate weight [kg], S_m - membrane effective area [m^2], t - time [h].

$$\beta = \frac{\boldsymbol{w_T^p / w_O^p}}{\boldsymbol{w_T^f / w_O^f}} \tag{2}$$

where: w_T^P, w_H^P - weight fractions of thiophenes and hydrocarbon, respectively, in the permeate [-], w_T^F, w_H^F - weight fractions of thiophenes and hydrocarbon, respectively, in the feed [-].

Results and discussion

Effect of sulphur content in feed

Differences in crude oil sulfur content mined from various sources made it very important to investigate the impact of the concentration of this element on membrane's selectivity and transport properties and in consequence - on the efficiency of sulfur compound removal.

Two of typically presented in gasoline sulfur species, *i.e.* thiophene and 2-methylthiophene, were selected to investigate the different sulphur compound removal efficiency from *n*-octane/sulfur species mixtures with PDMS-based composite membranes. The effect of sulfur concentration in the feed on the pervaporation performance was investigated in the range of 0.05-0.13 mas. %.

The impact of thiophenes concentration in model gasoline on the total permeate flux for both binary *n*-octane/sulfur specie mixtures at the feed temperature of 30°C and permeate-side pressure of 100 Pa is shown in Figure 2. As it can be seen, the variation in thiophenes concentration in the feed had practically no influence on the transport of permeating compounds through the membrane. This relationship resulted most likely from the narrow scope of the concentration of thiophene and the fact, that the thiophene concentration was very low as compared to hydrocarbon content. Taking into account the solution-diffusion theory, the separation in pervaporation process is determined by the first two stages, *i.e.* the sorption and diffusion of mixture components [7]. Most likely the concentration of sulfur compound was beyond the range, where the effect of swelling caused by thiophene surpass the swelling phenomena resulted from hydrocarbon sorption in PDMS layer [10, 11]. Nonetheless, partial fluxes of sulfur compounds were proportional to the sulfur concentration, which leads to nearly unchanged values of thiophenes separation factor (Fig. 3).

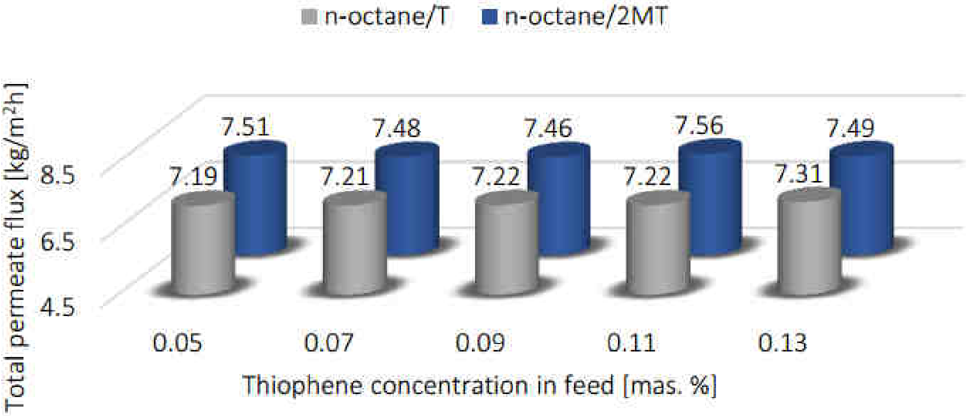


Fig. 2. Effect of feed concentration on the total permeate flux at feed temperature of 30ºC and permeate pressure of 100 Pa

Experimental results also showed, that PDMS membrane is more selective to thiophene than to 2-methylthiophene (Fig. 3) and it may be mainly because of the difference in molecular size and structure but also due to the difference in partial vapour pressure, which is lower for 2-methylthiophene. Furthermore, thiophene shows higher chemical affinity to the poly(dimethylsiloxane), from which the membrane active layer was made (the solubility parameter for thiophene is $\delta = 20.0$ (MPa)$^{1/2}$, for 2-methylthiophene is

δ = 18.6 (MPa)$^{1/2}$ and for PDMS is δ = 21.1 (MPa)$^{1/2}$). Obtained results correspond with results presented in the literature [11, 12].

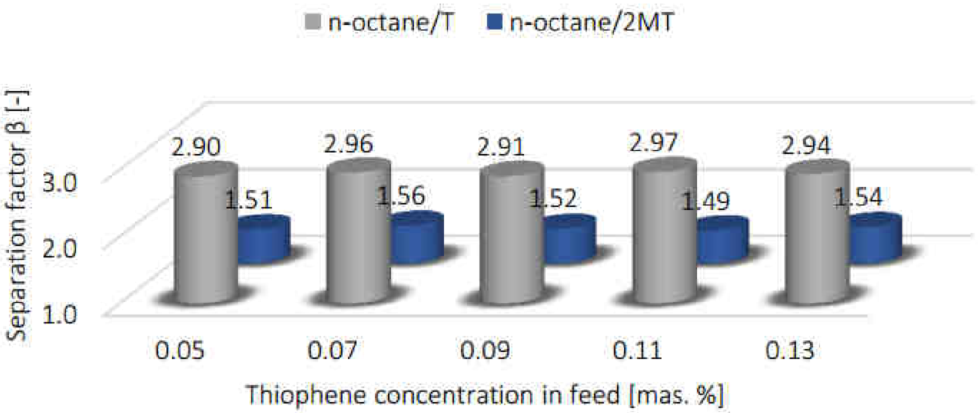


Fig. 3. Effect of feed concentration on the separation factor at feed temperature of 30ºC and permeate pressure of 100 Pa

Effect of feed temperature

The effect of operating feed temperature on the efficiency of thiophene and 2-methylthiophene separation from model binary mixtures was investigated in the range of 30-50°C. Temperature dependence of total permeate flux and partial fluxes of individual compound for model mixtures are illustrated in Figures 4-6.

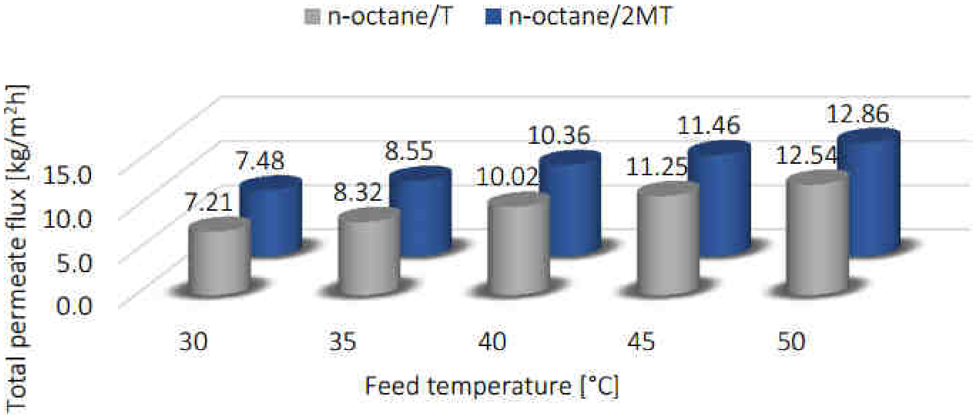


Fig. 4. Effect of feed temperature on the total permeate flux at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

Experimental data indicated an increase in the total flux (Fig. 4) and partial fluxes (Fig. 6) with the rise of the feed temperature. In Figure 5, separation factors decline with the increase of feed temperature for both *n*-octane/sulphur compound mixtures. During the pervaporation experiments, a trade-off phenomenon between flux and selectivity was observed - as the feed temperature increased, the total flux increased but the sulfur separation factor shows a digressive trend.

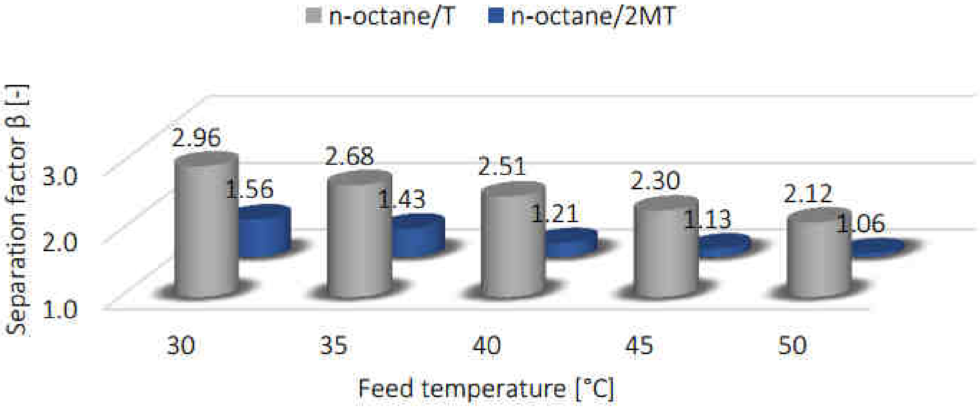


Fig. 5. Effect of feed temperature on the separation factor at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

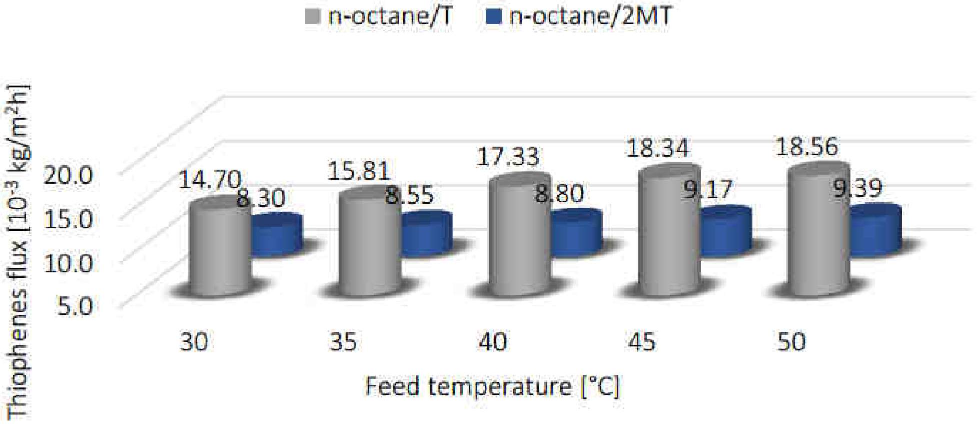


Fig. 6. Effect of feed temperature on thiophenes flux at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

Above mentioned relationships are thought to be a consequence of two simultaneously occurring phenomena [7]. First, operating temperature affects the driving force for the mass transfer - the increase in the temperature results in higher partial vapour pressure of components in the upstream side of the membrane and provide a greater driving force for the permeation of components since the downstream pressure remains practically unaltered. Secondly, rise of the temperature additionally enhance the swelling of the membrane active layer, which, on the one hand is a "natural" consequence of feed components dissolution and on the other - can be responsible for the decrease in thiophene separation factor.

Effect of downstream pressure

Since the driving force of components permeation in pervaporation is the difference between the vapour pressure at feed and permeate side of the membrane, the downstream pressure is an important parameter that affects the performance of the PV process. On the basis of the above statement, it can be expected, that partial fluxes will increase with the decrease of the downstream pressure. It also determined the component concentration in the permeate stream and affected the membrane selectivity [7]. Downstream pressure impact on the total permeate flux and sulfur separation factor for model mixtures are illustrated in Figures 7 and 8.

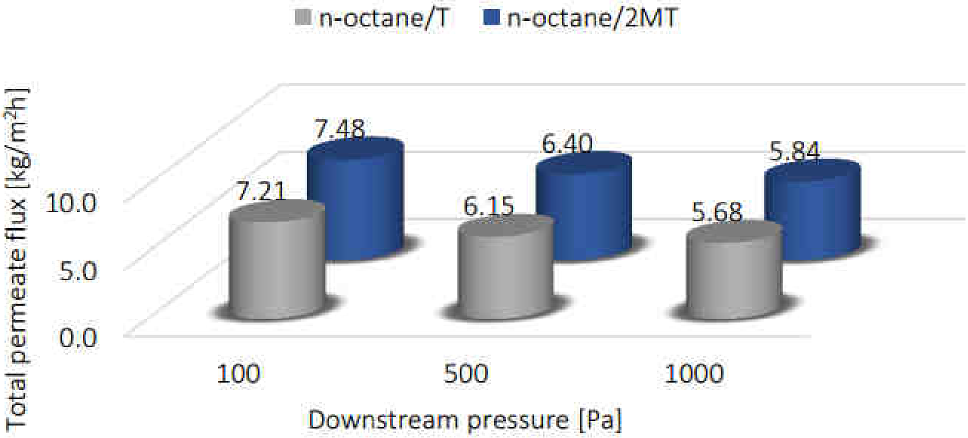


Fig. 7. Effect of downstream pressure on the total flux at thiophenes concentration of 0.07 mas. % and temperature of 30ºC

The influence of permeate-side pressure on the pervaporation performance at 30ºC and thiophenes concentration of 0.07 mas. % was investigated in the range of 100-1000 Pa. Experimental results indicated, that maximum partial pressure gradients obtained for the minimum downstream pressure was the most beneficial. As the permeate pressure of *n*-octane/thiophene and *n*-octane/2-methylthiophene mixtures was increased, the total flux decreased significantly. At the same time, the sulfur separation factor was declined more gently. Figures 7 and 8 indicates, that high vacuum (low downstream pressure) had a greater impact on total flux in comparison with sulfur separation factor.

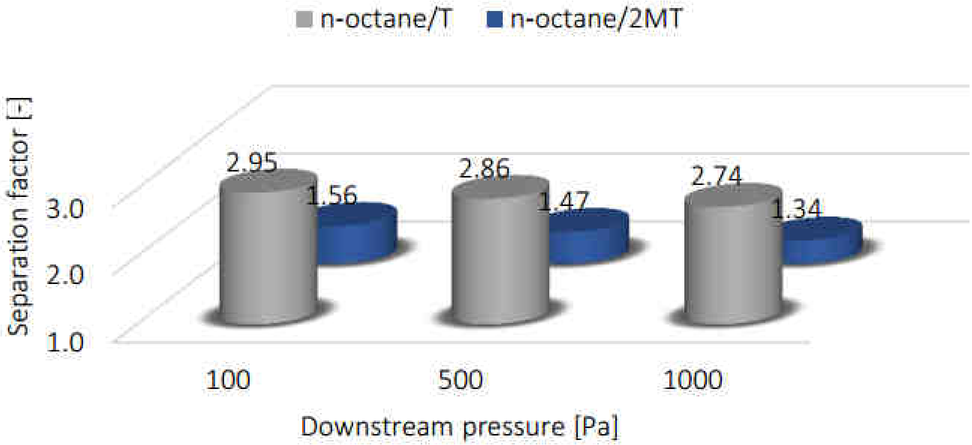


Fig. 8. Effect of downstream pressure on the separation factor at thiophenes concentration of 0.07 mas. % and temperature of 30ºC

Conclusions

- Experimental results indicated, that higher feed temperature yielded higher total flux and lower sulfur separation factor.
- Simultaneously, the increase in total permeation flux resulted in the separation factor decrease, which was caused by the decrease in the selectivity of the active layer resulted from its enhanced swelling.
- Partial fluxes of thiophenes were proportional to its concentration in the feed. However, the variation of thiophenes concentration had almost imperceptible impact on the total flux and selectivity.
- Differences of chemical affinity of the investigated thiophenes to poly(dimethylsiloxane) leaded to various selectivities thereof within PDMS membrane for both separated mixtures.
- As the permeate pressure in desulfurization of *n*-octane/thiophenes using a PDMS was increased, the total flux was decreased significantly while the sulfur separation factor was declined gently.

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ZASTOSOWANIE PERWAPORACJI DO ODSIARCZANIA BENZYNY - EFEKTYWNOŚĆ USUWANIA RÓŻNYCH ZWIĄZKÓW SIARKI

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Abstrakt: Ze względu na rosnącą świadomość ekologiczną dużą uwagę poświęca się jakości paliw transportowych, w tym zawartości siarki. Spalanie związków siarki obecnych w benzynie stanowi źródło emisji SO_x. Co więcej, obecność tlenków siarki w spalinach przyczynia się do zwiększonej emisji NO_x i lotnych związków organicznych (VOC), spowodowanej obniżeniem się niskotemperaturowej aktywności katalizatorów. Dlatego regulacje prawne wprowadzone w krajach UE wymagają redukcji poziomu siarki w benzynie do 10 ppm. Jako że siarka występuje w benzynie w postaci różnych związków (takich jak tiofen i jego pochodne, merkaptany i siarczki) oraz różne związki siarki wykazują różne powinowactwo względem materiału membrany, bardzo ważne jest, aby zbadać efektywność ich usuwania oddzielnie. Celem badań było określenie wpływu typowych wybranych związków siarki obecnych w benzynie na selektywność membrany oraz wydajność separacji związków siarki w procesie perwaporacji próżniowej. Zbadano również wpływ parametrów procesu, takich jak temperatura nadawy, stężenie usuwanych zanieczyszczeń i ciśnienie po stronie odbioru permeatu na skuteczność usuwania tiofenów z modelowych mieszanin *n*-oktan/związek siarki. W czasie badań stosowano hydrofobowe membrany kompozytowe na bazie poli(dimetylosiloksanu). Nadawę stanowiły dwuskładnikowe mieszaniny *n*-oktan/tiofen i *n*-oktan/2-metylotiofen. Zawartość siarki obecnej w tiofenach wahała się granicach od 0,05 do 0,13% mas. Wpływ temperatury nadawy zbadano w zakresie 30-50°C. Przepływ nadawy (75 dm^3/h) utrzymywano na stałym poziomie.

Słowa kluczowe: perwaporacja próżniowa, odsiarczanie, tiofeny, benzyna

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NITROGEN REMOVAL FROM FISH FARMS WATER BY *Lemna minor* AND *Wolffia arrhiza*

USUWANIE AZOTU Z WODY GOSPODARSTW RYBNYCH Z WYKORZYSTANIEM RZĘSY DROBNEJ I WOLFII BEZKORZENIOWEJ

Abstract: It is extremely important for the productive fish farming with closed water systems to treat the water to the level allowing its reuse for fish production. This paper presents studies considering the possibility of water embryophyte application to assimilation of pollutants (mainly nitrogen compounds) solute in water of recirculation systems in fish farms. The results of experimental studies covering ammonium nitrogen removal from polluted water of fish farms by the tested *Lemnoideae* representatives (*Lemna minor* and *Wolffia arrhiza*) were presented. The obtained results confirmed the usefulness of phytoreactors application in wastewater treatment plants in fish farms.

Keywords: pollution of water in fish farms, nitrogen removal, *Lemnoideae* in water treatment

Introduction

The general tendency of decrease in aquatic resources resulting in decreased fishing, numbers and diversity of fish as well as amount of fishless water reservoirs in the environment stimulates the development of aquaculture in the artificial water reservoirs, especially a fishing farms utilizing re-use of water (RAS, Recirculation Aquaculture Systems). Ukraine may be characterized by relatively low volumes of industrial fish breeding which is related to the general unsatisfactory state of economy and production in the country as well as the general archaic attitude towards fish farming [1, 2]. But on the other hand, problems related to fish and seafood import, caused by money devaluation, stimulate the development of domestic production and justify the advisability of creation of the highly-productive fish farms based on the modern technologies of production.

The successful fish production in RAS requires the proper living and feeding conditions [3, 4], so the main factors influencing the farming efficiency are composition and amount of feed and characteristics of water reservoir - the quality of water available for fish farming and effectivity of its treatment for possible re-use. Thus, omitting the economic factors and availability of water sources, the main problem of RAS is the quality of aquatic environment for fish farming - assuring treatment for water allowing its reuse.

The main tasks of RAS' treatment plants is removal of solute and non-reconstituted nutrients, especially ammonium and phosphates [5-7]. In order to remove the undissolved pollutants the mechanical filters are used. Removal of solute pollutants and the fine-grained dispersed phase, which is unable to be filtered, is performed due to application of biological

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methods of treatment [8-10]. Concentration of nitrogen compounds may be treated as the main indicator for water treatment quality assessment in RAS because most of the pollutants is available as ammonium nitrogen [11].

Biotechnologies allowing transformation of nitrogen compounds due to bacterial microflora (by nitrification and denitrification) present several negative issues for RAS. The most important are: required considerable amounts of nitrificators and denitrificators for bioreactors, necessity of the outside carbon sources (*e.g.* methanol) for denitrification and required stabilization of water parameters [5, 8, 9, 11-15]. The application of embryophyte is more perspective manner of nitrogen removal from water in fish farms [16-19]. There are known several advantages of such treatment, as related to the processes using nitrobacteria: resistance to higher concentrations of nitrogen compounds, direct assimilation of ammonium nitrogen without the intermediate processes and high ratio of metabolism in favourable process conditions [17, 18, 20].

The experience with embryophyte application to RAS water treatment was gained by European and Asian countries. In our opinion, in case of Ukrainian conditions, the application of the freely floating plants to RAS water treatment may be quite effective. Validity of embryophyte application in order to restore the required quality of water in RAS is justified by typical characteristics of fish farming in artificial and controlled aquatic ecosystems. The ability of plants to consume nutrients may be assessed basing on their composition and dynamics of biomass growth. The assurance of the optimal farming conditions, including the proper lighting and the optimal temperature for given species, is the important condition for the maximum growth ratio of plants. So, it is important to utilize plants characterized by the rapid growth and capable to adjust to artificial conditions of farming.

Thus, the aim of presented research covered determination of possible application of *Lemnoideae* (*Lemna minor* and *Wolffia arrhiza*) to breeding water treatment in fish farms of water closed circuit.

Materials and methods

The experiments of *Lemnoideae* cultivation included in this paper were performed during 10 weeks in tilapia (*Oreochromis aureus*) fish farm and under the laboratory conditions. The cultivation was located in phytoreactor integrated with the unit of biologic treatment of wastewater from the fish farm. The dimensions of the reactor were 130x55x40 cm. Two lamps of 36 W of power each were applied as lighting devices. The time duration of water detention in the device was equal to 35-40 min.

During the parallel experiment under the laboratory conditions the reservoirs of 45 dm^3 volume operating in the sequential layout were used. The untreated water from RAS after *Oreochromis ureus* and *Clarias gariepinus* breeding was used. The laboratory setup was not additionally illumed. The cultures of studied plants *Lemna minor* L. and *Wolffia arrhiza* (L.) Horkel ex Wimm developed under the artificial conditions were dosed into all tested volumes. The weighing of raw plants' mass was performed daily using electronic scale TBE (0.21-0.001 accuracy EN ISO 45501-2) with 0.001 h of error. Ammonium, nitrites an nitrates content were determined by the laboratory ion meter I-160-M equipped with the ion selective membrane electrodes.

Results

The results of our studies confirmed the rapid increase in biomass of *Lemnoideae* under the favourable conditions (which can be created) in phytoreactor for treatment of wastewater RAS (Fig. 1). *Lemna minor* and *Wolffia arrhiza* placed in the flow reservoirs increased their mass approx. twice (88-110%) during 24 hours.

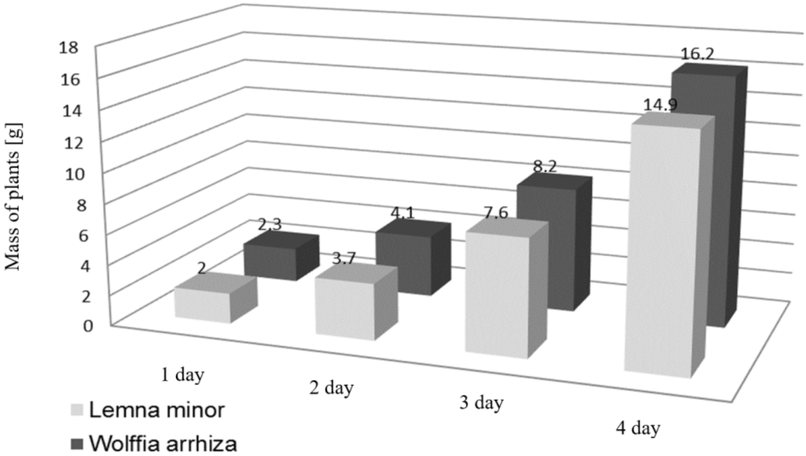

Fig. 1. Dynamics of *Lemnoideae* growth under conditions of flow phytoreactor

The studied species were resistant to presence of different forms of nitrogen in water. In one of the tested samples the noted concentration of ammonia was equal to 32 mg/dm^3, while usually the ammonium concentration in samples at the outflow from the reservoirs of fish farming was 0.6-2.8 mg/dm^3. The range of presented concentrations is acceptable for most of floating plants, especially *Lemnoideae*. Thus, no problems related to their cultivation under the flow and stationary conditions were noted. The predicted ratio of plants growth was unchanged, which was related to the constant concentration of pollutants at the inflow from farming tanks.

The parallel series of experiments under the stationary conditions was performed in volume of 45 dm^3 reservoirs of bioreactors. The initial concentrations of ammonia nitrogen at the inflow to bioreactor was 30-32 mg/dm^3, while nitrates and nitrites were observed in the lower concentrations (0.8 and 11.5 mg/dm^3, respectively).

During the experiment four technological lines were used, two of them were used as the frame of reference - one without aeration, the second one intensively aerated by the air compressor. The remaining two were used to determine the dynamics of nitrogen removal by *Lemna minor* and *Wolffia arrhiza* (Fig. 2).

The presented results confirmed the possibility of partial ammonia nitrogen removal due to intensive aeration of the tank. It was also observed that the high concentration of ammonia nitrogen in water had no negative influence on living conditions and plants biomass increase.

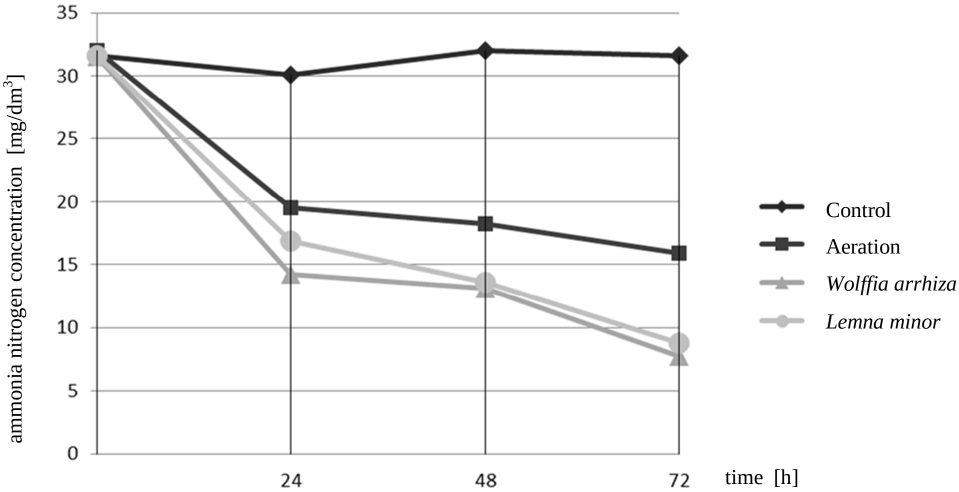

Fig. 2. Changes of ammonia nitrogen concentration in static conditions

Only the partially decrease in nitrate concentration in the aerated samples was observed. Generally, aeration allowed to reduce ammonia nitrogen concentration for approx. 50%. Despite the positive effect of reduction of ammonia concentration in water, the intensive aeration may present some serious disadvantages, including the considerable energy consumption and changes in heat balance. Moreover, in order to ensure the process operation, the usage of appropriate devices (air compressors, fittings, valves and pipelines) is required. The increase of ammonia nitrogen in unaerated sample, by approx. 2.5 mg/dm^3 after 48 hours may be explained by transformation of fine grained pollutants into the solute phase. Under the conditions of RAS water treatment for which the efficiency of dispersed phase removal no filters may reach the level of 45-80%, the fine suspended phase is usually present.

Determination of water treatment efficiency (as related to ammonia nitrogen presence) of the phytoreactor with aquatic embryophyte may be performed basing on the results of the presented experiment an theoretical data concerning morphology and biochemistry of plants. According to the experimental studies 1 g of *Lemna minor* and *Wolffia arrhiza* is capable to remove from 2.6 to 6.0 mg NH_4^+ per day, under the conditions of the bright daily light, without artificial illumination. Basing on the data concerning nitrogen content in dry mass of plants, in range of 4.2-6% (at water content in the plants reaching the level of 90%) and possibility to double its mass during time of 1-2 days, it may be assumed that daily nitrogen assimilation capability may reach the level of 2-6 g per 1 kg of raw mass, which reflects 1.64-4.94 g of ammonium. The obtained experimental data proved the theoretical calculations. However it should be noted that maximum possible capability of nitrogen assimilation may be obtained only at favorable temperature (24-30°C) and under the required light as well as presence of macro- and microelements.

Summary and conclusions

The tested plant species *Lemna minor* and *Wolffia arrhiza* showed good accommodation to the conditions of flow phytoreactor used in RAS waste water treatment. The experimental studies concerning *Lemnoideae* cultivation in phytoreactor treating circulating RAS water confirmed the high capability of these plants in ammonium nitrogen removal. The ability of ammonia ion assimilation may vary in a quite wide range and results from the conditions of the specific phytoreactor. But it may be approximated as 2 g NH_4^+ daily for 1 kg of raw mass.

The efficiency of phytoreactor in ammonia nitrogen assimilation may be highly dependent to biomass of the cultivated plants (as a process factor). But the settlement density of several types of *Lemnoideae* inside the phytoreactor is limited by their biological characteristics. Under the artificial conditions, with the intense artificial illumination, the settlement density of *Lemna minor* and *Wolffia arrhiza* may reach the value of 5-8 kg per 1 m^2. So, the ammonium assimilation capability of *Lemnoideae* phytoreactor may reach the level of 16 g NH_4^+ daily at the area of 1 m^2 of the device.

Determination of the boundary load of the tested water treatment may be performer by the experimental method - measurement of main pollutants concentration before and after the treatment, as well as the theoretical one - using recommendations for loads proportional to amount and quality of applied feed. However, the results of theoretical determination may be only treated as preliminary and approximate. To remove the solute pollutants introduced to water with the 1 kg of dosed feed containing 40% of proteins, 10-20 kg of raw plants mass are required, corresponding to the area of phytoreactor equal to 0.7-2 m^2.

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USUWANIE AZOTU Z WODY GOSPODARSTW RYBNYCH Z WYKORZYSTANIEM RZĘSY DROBNEJ I WOLFII BEZKORZENIOWEJ

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Abstrakt: Dla wydajnej hodowli ryb w układach z zamkniętym systemem obiegu wodnego niezwykle ważne jest właściwe oczyszczanie wody do poziomu, który pozwala na jej ponowne wykorzystanie. W opracowaniu przedstawiono możliwość zastosowania wyższych roślin wodnych do asymilacji zanieczyszczeń rozpuszczonych w wodzie, głównie związków azotu. Zaprezentowane wyniki badań eksperymentalnych dotyczą usuwania azotu amonowego z zanieczyszczonej wody gospodarstw rybnych przedstawicielami rzęsowych (*Lemnoideae*) rzęsą drobną i wolfią bezkorzeniową. Wyniki te potwierdzają zasadność wykorzystania fitoreaktorów w obiektach oczyszczalni gospodarstw hodowli ryb.

Słowa kluczowe: zanieczyszczenia wody gospodarstw rybnych, usuwanie azotu, *Lemnoideae* w oczyszczaniu wody

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THE USE OF BARK OF SCOTS PINE IN ENVIRONMENTAL IMPACT ASSESSMENT OF CEMENT AND LIME DUST

WYKORZYSTANIE KORY SOSNY ZWYCZAJNEJ DO OCENY ODDZIAŁYWANIA NA ŚRODOWISKO PYŁÓW CEMENTOWO-WAPIENNICZYCH

Abstract: The study analysed bark of Scots Pine exposed to alkaline pollution from the cement factory Chelm. The range of impact of cement-lime dust on environment was determined based on water extracts of bark. Relationships between pH_{H2O} of bark and the distance from the dust emitter were studied using analysis of regression and linear correlation. These results were referred to the results from a forest control plot free of alkaline pollution. Precipitation of cement-lime dust decreased with the distance from the source of pollution, which was confirmed by the values of pH_{H2O} of pine bark. The greatest impact on environment of dusts from the cement factory Chelm was recorded at NE, ES and SW directions, where pH of the bark was < 6.0 at 3 km or even 5 km from the emitter. Multiple correlation coefficient between the distance from the emitter and the dust precipitation was from –0.66 to –0.98%.

Keywords: pine bark, cement-lime dust, bioindicators

Introduction

A cement factory emits gases and dusts to environment. Cement dusts that get to soil in excess enrich their genetic levels in calcium carbonate, which causes many consequences in phytocenoses [1]. Oligotrophic communities of pine forests are especially sensitive to even small changes. The range of the effect of alkaline deposition depends on *e.g.* the source and type of emission, distance from emitters, land relief, frequency and direction of winds [2]. Assessment of deterioration in the quality of forest environment caused by cement industry includes determination of the range of dust deposition and its amount that exceed the norm, and identification of qualitative and quantitative changes in the studied ecosystem. Bark is a good indicator of air pollution with cement-lime dust, as shown by papers of Sporek [2] and confirmed by other authors [3, 4]. But in the literature of the topic pine bark is mentioned mainly as a bioindicator of air pollution with compounds that cause acidification, mainly of sulphur and nitrogen, and of heavy metals [5-9]. The study was aimed to determine the range of impact on environment of the cement factory Chelm using pine bark as a bioindicator.

Material and methods

Bark of the Scots Pine (*Pinus sylvestris* L.) collected within 12 km from emitters of the cement factory Chelm was analysed. Fifty five sites were selected along eight directions of the wind rose, with the cement factory accepted as the middle in calculations. Bark was collected using draw-knife at the height of 1.50 m, according to the method of Sporek [2].

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Samples were collected at each site from five trees using the envelope method. The distance from the central tree was 10 m. In total, 275 samples were collected from standing trees. Additionally, a 0.25 ha plot exposed to strong effect of the cement work was delimited, where samples of bark were collected from 83 trees.

Bark was dried in room temperature, washed with deionised water and dried in a drier at 65°C for 24 hours. Dried plant material was ground in a mortar and milled into a powder in a percussion grinder. From each sample 4 g of the bark powder was taken, weighted with 0.001 g accuracy, placed in a beaker and filled up with 40 cm^3 of distilled water. After 48 hours the content of each beaker was mixed and its pH_{H2O} was measured up to two digital places. The electrode was calibrated using two buffer solutions of pH 4 and 7.

The relationships between pH_{H2O} of bark and the distance from the source of dust emission were studied using analysis of regression and linear correlation. These results were referred to the results from the forest control plot free of alkaline pollution. The control plot was an experimental area in Niemodlin forests where monitoring of pollution to forest ecosystem has been conducted since 1996. Fifty five-years-old pine stands at this plot, which grows on podzols, is of good condition and correct height, without clear anthropogenic effects. Samples of bark for comparative studies were collected from 50 standing trees.

Results and discussion

Bark of the Scots Pine collected at the control plot had natural pH_{H2O} in the range 3.2-3.97 and low coefficient of variation v = 6.07%. The increment of this trait was 0.77 of the pH unit. The mean of these measurements was 3.60 $pH_{H2O,}$ and the mode was 3.63 (Table 1). These values are typical of pine bark from areas free of industrial imissions [2, 5, 10].

Table 1

Variation in reaction (pH_{H2O}) of bark of the Scots Pine at the control plot (Bory Niemodlinskie) and at the plot polluted with alkaline dusts (near cement factory Chelm)

Parameter	Plots	
	control	polluted
pH_{H2O} range	3.2-3.97	7.12-7.76
$\bar{x}_{pH}$	3.63	7.38
SD	0.22	0.18
Median	3.63	7.36
Mode	3.64	7.24
CV%	6.07	2.47
n	50	83

The pine stand at the plot exposed to strong anthropogenic pressure was in bad health condition. Despite similar age as at the control plot, pines at the study plot had weaker growth and considerable defoliation of canopies. The reaction of pine bark in 83 samples from a uniform plot is shown at Figure 1. Both the control and the polluted plots had common features such as low coefficient of variation and small standard deviation of the bark reaction. But the plots differed in reaction by 4 pH unit. At the polluted plot pH was in the range 7.12.-7.76, the mean pH was 7.38, and the coefficient of variation was 2.47%

(Table 1). The distribution of pH values of bark was right-skewed and showed that measurements were above 7.36 (median) for 50% of the samples. Other authors [2, 3] obtained similar distributions of bark pH.

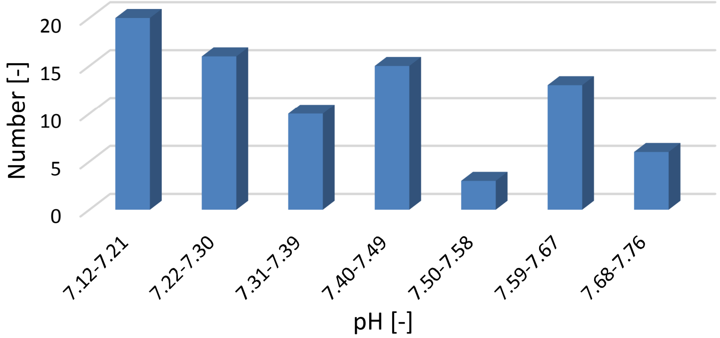

Fig. 1. Distribution of the reaction of bark of Scots Pine at the plot exposed to strong anthropogenic pressure from the cement factory Chelm

Comparison of the control plot free of alkaline pollution with the plot polluted with alkaline dusts (Table 1, Fig. 1) confirmed that the reaction of pine bark is with no doubt a bioindicator of air pollution with alkaline dusts. Thus it can be used to draw isolines of the range of impact of the cement factory on environment.

Based on that, sites for collecting samples of bark were chosen within 12 km from emitters of the cement factory Chelm. Precipitation of cement-lime dust decreased with the distance from the source of pollution. The distances of impact of alkaline dusts from the cement factory Chelm were determined based on the criterion of the reaction of bark by Sporek [2]. According to this author [2] pH of bark within the range 4.1-4.9 should be considered as vestigial. Swiercz [3] determined a similar range and distinguished ecotone zone where pH_{H2O} of bark is in the range 4.0-4.9. Alkalinisation of forest habitats occurs when pH of bark is ≤ 5.0. Values ≥ 4.0 pH are accepted as a lack of alkaline pollution.

Table 2

Distances at which dust precipitated determined according to changes in the reaction of pine bark

Directions	**Areas**	**The range of effect of alkaline dusts [m]**			**Multiple correlation coefficient**	**Coefficient of determination**
		trace	**clear**	**prominent**		
		pH_{H2O}				
		5.0	**5.5**	**< 6.0**	***r***	**r^2**
NE	I	7400	5000	2700	–0.66	0.43
EN	II	5800	4300	2700	–0.83	0.68
ES	III	7400	6000	4400	–0.90	0.81
SE	IV	5300	4300	3300	–0.96	0.91
SW	V	8100	6200	4600	–0.66	0.43
WS	VI	4300	3100	1900	–0.83	0.68
WN	VII	4400	3500	2500	–0.90	0.81
NW	VIII	4100	3500	2900	–0.96	0.91

Analysis of the collected material showed a correlation between the distance from the emitter and the precipitation of dust determined from bark reaction. The multiple correlation coefficient was from –0.66 to –0.98% (Table 2). The coefficient of determination showed that participation of dusts from the cement factory Chelm in the qualitative changes was 43 to 91%, according to this indicator (Table 2).

Meteorological data (from the Institute of Meteorology and Water Management) shows that in the vicinity of Chelm winds that blow from west to east, (W-E), from northwest (NW) to southwest (SW) and from southwest (SW) to northeast (NE) are the most frequent. Thus the wind rose has an irregular half-oval shape. The largest distance of the impact of dust from the cement factory Chelm on environment was recorded at NE, ES and SW directions. The departure of distribution of dust pollution from the wind rose was caused by location of other sources of unorganised emission in the aras, *e.g.* heaps, mines, access roads to mines, and by a lack of trees that would isolate these emitters from the surroundings. Analysis of regression and correlation showed that compact forest areas reduce movements of dusts from ca 12 km to *ca* 1 km.

Conclusions

1. Isolines of the zones of eutrophic effect in forest habitats can be drawn based on changes of bark reaction, which may be applied in determination of damage caused by deposited cement dust and in assessment of the quality of forest habitat.
2. Forest areas reduce movements of dusts from ca 12 km to ca 1 km. The negative impact of the cement factory on the vicinity can be reduced and even eliminated by appropriately located tree belts.

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WYKORZYSTANIE KORY SOSNY ZWYCZAJNEJ DO OCENY ODDZIAŁYWANIA NA ŚRODOWISKO PYŁÓW CEMENTOWO-WAPIENNICZYCH

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Abstrakt: Analizie poddano korę sosny zwyczajnej znajdującej się pod presją zanieczyszczeń alkalicznych cementowni Chełm. Na podstawie wodnych wyciągów z kory określono zasięg oddziaływania pyłów cementowo-wapienniczych na środowisko. Zależności pomiędzy pH_{H2O} kory a odległością od źródła emisji pyłów badano metodą analizy regresji i korelacji liniowej. Wyniki badań odnoszono do wyników uzyskanych na leśnej powierzchni kontrolnej - wolnej od zanieczyszczeń alkalicznych. W miarę oddalania od źródła zanieczyszczeń opad pyłów cementowo-wapienniczych obniża się, co jest zrozumiałe, i znajduje potwierdzenie w zmiennych wartościach pH_{H2O} kory sosny. Najsilniej odnotowano presję w kierunku NE, ES i SW, gdzie w odległości 5 km od emitora pH kory było wyższe od 6,0. Współczynnik korelacji wielorakiej pomiędzy odległością od emitora a opadem pyłu wynosił od –0,66 do –0,98%.

Słowa kluczowe: kora sosny, pył cementowo-wapienniczy, bioindykator

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Paulina STANKOWSKA[1], Julia STANDERA[1] and Adam KWIATKOWSKI[1]

ANALYSIS OF THE SEWAGE TREATMENT SYSTEM OF THE SILESIAN AGGLOMERATION

ANALIZA SYSTEMU OCZYSZCZANIA ŚCIEKÓW MIASTA AGLOMERACJI ŚLĄSKIEJ

Abstract: The construction of the technological treatment plant is closely related to the amount and physicochemical parameters of incoming sewage. The economic aspects and the principles of sustainable development also should be taken into account at the stage of sewage treatment plant construction planning. Moreover, in large cities, there is often greater number of sewage treatment plants, which should create an effective system for wastewater treatment. Municipal wastewater treatment system should not disturb the ecological balance of the area and cannot contribute to the deterioration of the living conditions of people (especially those living in the immediate vicinity of the sewage treatment plant). The paper compares the process lines of three wastewater treatment plants located in the city of Bytom: "Centralna" plant, "Miechowice" plant and "Bobrek" plant. The paper also compares the main indicators of the efficiency of the described wastewater treatment plants and the selected parameters of the sewage sludge. Based on the above data, an attempt was made to assess the proper operation of the sewage treatment system in the city of Bytom.

Keywords: wastewater treatment plant, efficiency of wastewater treatment technology

Introduction

The issue of sewage treatment is one of the most important problems of contemporary water and sewage management. According to the definition, a sewage treatment plant is a system of technical and biological facilities whose function is to remove and neutralise sewage.

The most common division of sewage treatment plants, in terms of the treatment methods used, is the distinction of mechanical, chemical, biological treatment plants and plants with increased biogene removal. In practice, these systems are operated in specific combinations, often concurrently, as complementary methods. This leads to the increase in the effectiveness of the sewage treatment process. Currently present technologies, such as A2/0 or UCT, allow for the reduction of the pollution load size in sewage. Basic pollutions present in sewage include: organic compounds and nutrients (nitrogen and phosphorus compounds) [1]. In the Polish law, the level of sewage pollution reduction is governed by the Regulation of the Minister of Environment on the conditions to be met when discharging sewage to water or to soil and on substances which pose a special hazard to aquatic environments [2].

Bytom is a city located in the southern Poland and belonging to the Silesian agglomeration. The area of the city is 6944 ha and population density amounts to 2516 inhabitants per km^2. The percentage of population using sewerage system in 2012 amounted to 90.1%, which places Bytom on the 32nd position among the cities with district rights in Poland [3].

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First references to the sewerage system network of the city date back to the 19th century; however, the construction of a developed sewerage system took place in the period 1900-1904. Along with the construction of the network, the construction of the city sewage treatment plant was also commenced. The plant was designed for the needs of 70,000 people. Treated sewage was discharged to the Bytomka River. With an increase in the city population, starting from 1933, the treatment plant was being modernised. In the subsequent years, there were 10 new smaller treatment plants established, frequently located within city districts.

At present, Bytom Municipal Company supervises the water and sewage management of the city of Bytom. The main investment of the recent years, supported with the EU funds, was the project “Improvement of the water and sewage management of the city of Bytom”. Under the project, in the period 2004-2010, inter alia, the sewage treatment system was modernised. Instead of five treatment plants: “Centralna”, “Miechowice”, “Bobrek”, “Rozbark” and “Stolarzowice”, the first three are currently operated. They were subject to substantive extension and modernisation. In lieu of “Rozbark” treatment plant, the main sewage pumping station was created [4, 5].

The treatment plants existing in the city: “Centralna”, “Miechowice” and “Bobrek”, differ both in terms of their size and the sewage treatment technology used.

Further in the paper, process systems of three Bytom sewage treatment plants are presented and their effectiveness is analysed.

Sewage treatment technologies of the city of Bytom

“Centralna” sewage treatment plant is the largest treatment plant in Bytom. It is situated near the Szarlejka River. Its total area is about 11 ha, and the design flow rate is equal to 30 thousand m^3/d. There is also a laboratory at the premises of the treatment plant.

The process line is composed of a typical mechanical part (encapsulated grates; grit chamber; horizontal flow, radial primary sedimentation tank) and a biological part (three activated sludge chambers in the form of oxidation ditches with partly immersed aeration brushes) with increased treatment of nutrients (additional dephosphatation by adding PIX coagulant to oxidation ditches). Primary and excess sludge produced in the process is concentrated separately and then it is combined and subject to fermentation. There are 3500 m^3 of biogas generated in “Centralna” treatment plant daily. The obtained methane is first subject to desulphurisation, and then it is transferred to two power generators. The sludge remaining after fermentation is transported to filter presses and then it is sanitised with lime and exported outside the treatment plant.

Treated sewage is discharged to the Szarlejka River. The total time of sewage flow through the treatment plant amounts to about 24 h [6].

“Miechowice” sewage treatment plant is the second largest treatment plant in Bytom, occupying the area of about 6 ha, with sewage design flow rate of 12 thousand m^3/d. The total amount of sewage entering the treatment plan is derived from Miechowice district, and the average sewage flow rate is 3.5-8 thousand m^3/d.

Like “Centralna” treatment plant, it belongs to mechanical and biological treatment plants with increased treatment of nitrogen, phosphorus and carbon compounds. Downstream the classic mechanical part, biological reactors are used in the form of radial

Biomixes where denitrification and nitrification processes occur subsequently. Moreover, the dephosphatation process is supported by the addition of PIX coagulant upstream the reactors. A sedimentation chamber serves as the secondary settlement tank. The produced sludge is subject, in sequence, to aeration and dewatering, which leads to the form of sludge that can be used for agricultural purposes or for waste land reclamation. After treatment, sewage is transported to Row Miechowicki.

“Bobrek” treatment plant is the smallest and at the same time the oldest operating treatment plant in Bytom. The sewage entering that treatment plant comes from Bobrek - one of the smallest districts of Bytom; thus, the flow rate designed for that treatment plant has much smaller values in comparison to other treatment plants in Bytom - 800 m^3/d.

The process line is based on basic elements of the mechanical and biological treatment plant: a system of a sieve and grit chamber; Imhoff tank; three-chamber biological reactors. Settled sludge is transported to the sludge dewatering station, sanitised and then exported to the storage yard.

Treated sewage, as in case of “Miechowice” treatment plant, is discharged to Row Miechowicki [4].

Analysis of basic operating parameters of the treatment plant

Table 1 below presents requirements for efficiency in the reduction of selected pollutions in sewage acc. to [2].

Table 1

Minimum percentage of pollution reduction [2]

Indicator name	**Minimum percentage of pollution reduction [%]**		
	“Centralna”	**“Miechowice”**	**“Bobrek”**
COD	75	75	75
BOD_5	90	90	90
N_{total}	85	80	70-80
P_{total}	90	85	80
Total suspended solids	90	90	90

As part of the presented testing, two basic parameters were analysed determining the effectiveness of the treatment plant operation: COD and BOD_5. The analyses were conducted for the period January-June 2014. Data used for analyses purposes were obtained from “Centralna” and “Miechowice” treatment plants [4].

Table 2

COD and BOD_5 indicators of raw and treated sewage in “Centralna” and “Miechowice” treatment plants [4]

Month	**“Centralna”**				**“Miechowice”**			
	Raw sewage		**Treated sewage**		**Raw sewage**		**Treated sewage**	
	COD	**BOD_5**	**COD**	**BOD_5**	**COD**	**BOD_5**	**COD**	**BOD_5**
	[mg/dm^3]	**[mg/dm^3]**	**[mg/dm^3]**	**[mg/dm^3]**	**[mg/dm^3]**	**[mg/dm^3]**	**[mg/dm^3]**	**[mg/dm^3]**
January	1732	446	48.9	6	1137	627	61.7	16
February	1270	535	32	5	1062	351	19.1	4
March	822	275	49.1	7	2268	637	34.1	5
April	1100	323	57.5	6	1172	421	42.1	5
May	1019	453	71.3	13	670	308	19	2
June	1300	346	34.8	7	898	341	16.6	2

Figure 1 presents in a graphic form COD values for raw and treated sewage determined in the case of both analysed treatment plants.

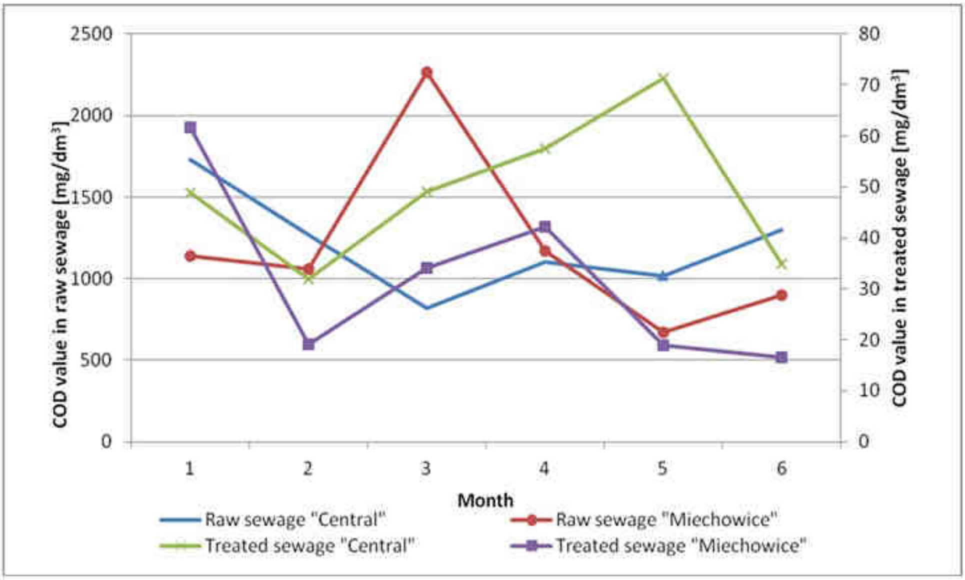

Fig. 1. COD values for raw and treated sewage determined in the case of both analysed treatment plants

The highest value of COD in raw sewage in "Centralna" treatment plant was recorded in January (1732 mg/dm^3), and the lowest one of 822 mg/dm^3 in March. The mean parameter value at inlet amounted to 1207 mg/dm^3. The maximum BOD$_5$ value occurred in February - 535 mg/dm^3 and the minimum one in March - 275 mg/ dm^3. The average amount of BOD$_5$ was 376 mg/ dm^3. While compiling analogically parameter values at outlet we obtain: the highest COD value in sewage in "Centralna" treatment plant in May (71.3 mg/dm^3), and the lowest one in February (32 mg/dm^3). The mean parameter value amounted to 48.9 mg/dm^3. The maximum BOD$_5$ value occurred in May - 13 mg/dm^3 and the minimum one in February - 5 mg/dm^3. The average amount of BOD$_5$ was 7.3 mg/ dm^3.

The above considerations demonstrate that in each of the months analysed, the indicator of reduction in COD and BOD$_5$ was higher than the one required in [2]. The mean value of COD reduction indicator amounted to 95.63% and of BOD$_5$ to 98.7%. Sewage parameters of "Miechowice" treatment plant were subject to a similar analysis. The highest value at inlet, amounting to 2268 mg/dm^3 was reached in March, and the lowest one, amounting to 670 mg/dm^3 - in May; the mean was 1201.2 mg/dm^3. The maximum BOD$_5$ value at inlet was 637 mg/dm^3 (March), and the minimum one - 308 mg/dm^3 (May). The mean value was 447.5 mg/dm^3. The maximum COD value at outlet was 61.7 mg/dm^3 (January), and the minimum one - 16.6 mg/dm^3 (June). The mean value was 32.1 mg/dm^3. The maximum BOD$_5$ value at outlet amounted to 16 mg/dm^3 (January) and the minimum one was 2 mg/dm^3 (May and June). The mean value was 5.67 mg/dm^3.

The above indicates that in each of the months analysed, the percentage reduction in COD and BOD_5 was higher than the one required under regulations [2]. The mean indicator value for COD amounted to 97.2% and for BOD_5 to 98.9% [4].

For other main indicators, “Centralna” and “Miechowice” treatment plants obtain reduction levels higher than those provided for in regulations.

Conclusions

The sewage treatment system of the city of Bytom is based on the functioning of three sewage treatment plants: “Centralna”, “Miechowice” and “Bobrek”, which are characterised by the following flow capacities, respectively: 30 thousand m^3/d, 5.5 thousand m^3/d, 800 m^3/d. Process lines of each treatment plant are based on the mechanical and biological part, and the two largest of these treatment plants are adapted to increased removal of nutrients.

In the analysed period (January-June 2014), “Centralna” and “Miechowice” treatment plants obtained the reduction level of main parameters characterising sewage that was higher than the standard one.

And the current management of sewage sludge from the sewage treatment plants of Bytom cannot rather be seen as a target solution. In the case of large city agglomerations, such as the city of Bytom, neutralisation of sewage sludge should not be based on agricultural use or on storage (unacceptable from 2016 onwards), but on thermal methods.

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ANALIZA SYSTEMU OCZYSZCZANIA ŚCIEKÓW MIASTA AGLOMERACJI ŚLĄSKIEJ

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Abstrakt: Budowa ciągu technologicznego oczyszczalni jest ściśle powiązana z ilością i parametrami fizykochemicznymi dopływających ścieków. Na etapie planowania należy rozważyć także kryteria zrównoważonego rozwoju oraz aspekty ekonomiczne. Ponadto, w dużych miastach na skuteczny system oczyszczania ścieków składa się często większa liczba oczyszczalni. Miejski system oczyszczania ścieków nie może zakłócać równowagi ekosystemowej danego obszaru ani przyczyniać się do pogorszenia warunków bytowania ludzi (szczególnie tych mieszkających w bezpośrednim sąsiedztwie oczyszczalni ścieków). W artykule porównano ciągi technologiczne trzech oczyszczalni ścieków znajdujących się na terenie miasta Bytom: Oczyszczalni „Centralna”, Oczyszczalni „Miechowice” oraz Oczyszczalni „Bobrek”. Zestawiono także główne wskaźniki efektywności oczyszczania oraz niektóre parametry osadu czynnego. Na podstawie powyższych danych podjęto próbę oceny prawidłowego funkcjonowania systemu oczyszczania ścieków w Bytomiu.

Słowa kluczowe: oczyszczalnia ścieków, skuteczność technologii oczyszczania ścieków

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SIMPLIFIED SAMPLING OF BENTHIC MACROINVERTEBRATES FROM SMALL STREAMS

UPROSZCZONE POBIERANIE PRÓBEK MAKROFAUNY BEZKRĘGOWEJ Z NIEWIELKICH STRUMIENI

Abstract: European Union legislation requires achievement of good ecological status of European streams and rivers. Because of that, the ecological status of all streams has to be assessed and evaluated. If there is a status identified less than good the remedial measures must be applied. For effective remediation it is necessary to find the cause of worse than good status classification. In urbanized areas is a number of urban drainage outlets with consequences in a necessity of very detailed biomonitoring. Due to time and money demands of such detailed monitoring, it is not possible to make standardized macroinvertebrates field sampling and processing to evaluate the ecological status. Therefore, admissible simplification of field sampling of macroinvertebrates compared to the standard AQEM method was searched for. Both the effect of the subjectivity of multihabitat sampling and the effect of the reduction of the number of sampling points and their uncertainties were studied with help of field experimental work and probabilistic Monte Carlo simulations. It was proved, that a substantial reduction of the number of sampling units (from 20 sampling units requested by European protocol AQEM) is possible only for ASPT and saprobity index (7 sampling units is sufficient) and diversity (9 sampling units is sufficient). A certain reduction (to 14 sampling units) is also possible for the number of individuals, % EPT and IBI index but no reduction can be applied in case of number of taxa and BMWP, where already the replicate 20 unit samples were biased by an unacceptable uncertainty.

Keywords: benthos, macroinvertebrates, sampling method, screening, uncertainties

Introduction

European Union legislation - Water Framework Directive 2000/60/EC [1] requires achievement of good ecological status of European streams and rivers. For this reason, the ecological status of all streams has to be assessed. The assessment of ecological status is based on several indicators, benthic macroinvetebrates being one of them. However, the realization of extensive macroinvertebrates monitoring programs requires a lot of effort and time. Thus, it is not always possible to evaluate the ecological status by the detailed macroinvertebrates field sampling and processing [2-4]. For this reason, studies searching for a simplification of this procedure are necessary and urgent [5].

The biomonitoring process contains several steps, which can be simplified to save time, and hence money: field sampling, laboratory processing and taxonomical identification. Most studies of possible simplification have focused on the laboratory processing by subsampling when only a part of the sample is processed. However, the minimum number of individuals that has to be taken into account to obtain a valid result varies widely between 100 and 700 [6, 7]. Little attention has been paid to the possibilities of the field sampling simplification. Only Vlek et al [3] studied the effect of the sample size

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on individual benthic metrics and final bioassessment of the streams. Metrics dependent on the absolute abundance were more sensitive to the sample size than those dependent on the relative abundance. Also the effect of the variability of multihabitat samples has not been investigated systematically. Lorenz and Clarke [4] studied the similarity of replicate samples on one sampling site and found out that it varied 83-100%.

Comparing various countries, field sampling protocols differ substantially. Some methods require multihabitat sampling when the sampling site is covered by sampling units distributed relatively to the microhabitats occurrence. Other methods doesn’t use a certain number of sampling points but the sampling is performed for a certain time, *e.g.* 3 minutes AQEM [8], PERLA [9]. In 2006 the comparison and intercalibration of the national methods within EU with the AQEM one was performed in the STAR project [10]. This project found that some methods were compatible with AQEM and their variance was < 10% (*e.g.* Czech method PERLA) [9].

Thus, in our study on admissible simplification of field sampling of macroinvertebrates of standard AQEM method was searched for including both the effect of the subjectivity of the multihabitat sampling and the effect of the reduction of the number of sampling points and their uncertainties.

The requirements on the uncertainties imposed by the simplification of the sampling method are that the simplified sampling must be able to reveal stream disturbances caused by discharges from the urban drainage system. A site is considered to be significantly disturbed by urban drainage if the difference in total abundance from reference conditions (usually a site upstream of the disturbance source) is higher than 30% or the difference in number of taxons greater than 20% or 3 or more species with at least mean abundance or one highly abundant species do not overlap [11]. For other metrics the uncertainty of about 15% reflects the natural variability [12]. Thus, the relative error of the simplified sampling method compared to the standard method must be lower than these values.

Materials and methods

Seven streams of different morphological quality were sampled. Three of the streams were in urban areas affected by combined sewer overflows, four were natural streams. The stream morphological status was assessed according to the Swiss methodology [12].

In order to find the multihabitat sampling subjectivity the AQEM procedure (reach length 20 m at least, multihabitat sampling, 9 seconds per unit) was applied with the exception of the number of units. Contrary to 20 units required by AQEM, 34 to 41 units were sampled in individual streams. It allows both to determine the uncertainty of the subjective selection of 20 sampling units in the AQEM method and to study the possibility of a further simplification in a screening method.

Organisms from each sampling unit were collected, kept separately and preserved in 90% ethanol. In the laboratory all organisms were identified to the lowest practicable level (usually species) except Oligochaeta, Nematoda, Turbellaria, Acarina, Chironomidae, Ceratopogonidae, Psychodidae which were not identified any further.

In order to identify uncertainties introduced by the reduction of sampling units, Monte Carlo method was used. In each simulation (randomization) a desired number of sampling units x was randomly chosen and benthic metrics were calculated. The randomization was repeated y times (y = 500). It resulted in y possible values of each benthic metrics, which were statistically analyzed to obtain probability density functions (PDF) (log-normal distribution was considered).

The process described was applied to x values ranging from 8 to 20 in order to find a relation between the number of sampled units and the uncertainty of individual metrics. The values of metrics from the original sample (*i.e.* from all sampled units) served as a reference.

In order to ensure that selected sampling units are not similar (as a biologist selects different representative habitats) criteria restricting the selection were implemented. A maximum difference of 40% from the original sample was set for all criteria (*e.g.* in case 30% of sampling units in the original sample had flow velocity of 1 m/s, then 18-42% of units had to be in the same category in the reduced sample). To allow a comparison of this restricted selection with a non-restricted one, a second run of simulations was done for the random selection without restrictions.

Eight metrics were evaluated: number of individuals, number of taxa, metrics describing general degradation: % of EPT taxa and diversity, and metrics characterizing organic pollution: Si (Saprobity Index), ASPT (the Average Score per Taxon) and BMWP (Biological Monitoring Working Party) [7]. Also B-IBI (Benthic Index for Biological Integrity) describing general and morphological degradation was calculated [13].

Results and discussion

In our study on admissible simplification of field sampling of macroinvertebrates of standard AQEM method was searched for. Both the effect of the subjectivity of multihabitat sampling and the effect of the reduction of the number of sampling points and their uncertainties were studied with help of field experimental work and probabilistic Monte Carlo simulations.

Simulations showed that the restriction criteria applied on the sampling units selection had only a minor influence on results as they caused less than a 3.5% decrease of uncertainty (less than 2% in most cases). Therefore, the results of random selections are presented.

Figure 1 shows two typical patterns of behavior of benthic metrics: 1. nearly no effect of the systematic error, and 2. a pronounced effect of the systematic error (*i.e.* a systematic under- or overestimation of the metrics due to the insufficient number of sampled units). Number of individuals, Saprobic Index, diversity and ASPT belong to the first group as they are not affected by a systematic error larger than 2%. Percentage of EPT taxa is systematically overestimated by up to 4% and IBI shows no systematic error until 15 sampling units (if the number of sampling units is further reduced, the systematic underestimation increases). Number of taxa and BMWP are representatives of the second group as they are highly affected by the systematic error caused by the increased probability of missing rare species when number of sampling points is reduced.

The full line in Figure 1 represents the mean value of metrics in unrestricted simulations, dotted line mean value of metrics in restricted simulation, dashed lines mean random error as 90% uncertainty of unrestricted simulations. Relative uncertainty of 0% corresponds to the reference value of metrics (*i.e.* from all sampled units).

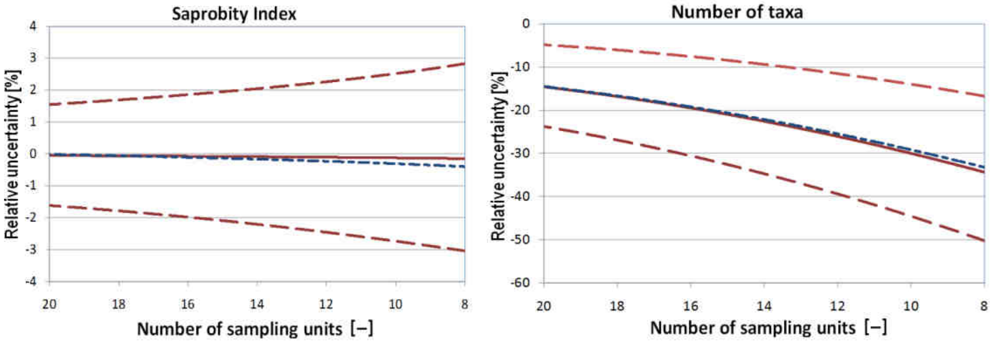

Fig. 1. Course of metrics uncertainties in relation to the decrease of the number of sampled units for one stream sampled

The minimum number of sampling units needed to meet the criteria for the relative uncertainty of individual metrics can be derived from the courses of uncertainties of the individual metrics (Table 1).

Table 1

Number of sampling units needed to meet criteria for relative uncertainty

Metrics	**Tritrubecky**	**Cerveny**	**Obecnice**	**Sazavka**	**Hloucela**	**Rokytka**	**Botic**	**Mean value**	**Standard deviation**	**90% conf. interval**
Individuals	13	20	11	12	13	16	10	13.6	3.2	19
Taxa	20	20	20	20	20	20	20	20.0	0.0	20
%EPT	6	16	6	8	11	20	20	12.4	5.8	~20
Saprobity index	6	11	6	6	6	6	6	6.7	1.7	10
ASPT	6	6	6	6	6	8	6	6.3	0.7	8
BMWP	20	20	20	20	20	20	20	20.0	0.0	20
Diversity	6	20	6	6	9	7	6	8.6	4.8	17
IBI	7	20	6	6	6	20	19	12.0	6.7	~20

Conclusions

No sampling simplification is admissible for the number of taxa and BMWP, where already the replicate 20 units samples were biased by an unacceptable uncertainty. On the other hand, only 7 sampling points are in average necessary for ASPT and Si and 9 points for the diversity. 14 sampling points should be in average sufficient for the number of individuals, % EPT and IBI. However, standard deviations of the necessary number of sampling units are quite high for some metrics (especially IBI, % EPT and diversity).

Benthic metrics studied exhibited a different dependency on the samples size as also confirmed by [3, 7, 10]. A further reduction of the number of sampling units is possible for metrics, for which the calculated relative uncertainty based on the 20 units sample is lower than the requested uncertainty. Thus, a substantial reduction of the number of sampling units is possible only for ASPT and saprobity index, which are very robust. A certain reduction is also possible for diversity, number of individuals, % EPT and IBI index. However, in case of the number of taxa and BMWP the average uncertainties are higher than the requested ones even for replicate 20 units samples no reduction can be applied.

As a conclusion, no screening method of the field sampling reducing the number of sampling units from the original 20 unites used in the AQEM method can be recommended.

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UPROSZCZONE POBIERANIE PRÓBEK MAKROFAUNY BEZKRĘGOWEJ Z NIEWIELKICH STRUMIENI

Abstrakt: Normy legislacyjne Unii Europejskiej (Ramowa Dyrektywa Wodna 2000/60/WE) wymagają osiągnięcia dobrego statusu ekologicznego rzek i strumieni na obszarze państw członkowskich. Z tego też powodu status ekologiczny rzek i strumieni krajów Unii powinien być określony i oceniony. W przypadku gdy status ten zostanie oceniony jako mniej niż dobry, powinny zostać podjęte odpowiednie środki zaradcze. Dla wdrożenia efektywnych działań polepszających stan ekologiczny strumieni należy najpierw zidentyfikować powody, dla których jest on niezadowalający. Na terenie obszarów zurbanizowanych zlokalizowanych jest zwykle wiele wylotów z systemów odprowadzających wody opadowe, które powinny być poddane odpowiednim procedurom biomonitoringu. Ze względu na znaczne nakłady finansowe i czasochłonność nie jest możliwe prowadzenie standardowych procedur pobierania i analizy próbek makrofauny bezkręgowej dla każdego z tak licznych punktów wraz z wymaganą oceną statusu ekologicznego. Stąd też poszukiwane są sposoby dopuszczalnego uproszczenia metod pobierania próbek makrobezkręgowców w odniesieniu do standardowych metod AQEM. W ramach przeprowadzonych badań, za pomocą terenowych prac eksperymentalnych oraz symulacji z wykorzystaniem metody Monte Carlo, analizowano efekty subiektywnego próbkowania siedlisk wielogatunkowych oraz zmniejszenia liczby punktów pobierania próbek powiązane z niepewnością próbkowania. Dowiedziono, że znaczne zmniejszenie liczby próbek (z 20 wymaganych w protokole AQEM) jest możliwe tylko dla indeksu ASPT i indeksu saprobowości (wynosi 7 próbek) oraz indeksu różnorodności (wystarczająca liczba 9 próbek). Zauważalne zmniejszenie liczby (do poziomu 14 próbek) jest możliwe również dla ilości osobników oraz % EPT i indeksu IBI. Jednakże niemożliwe jest zmniejszenie liczby próbek w celu prawidłowego określenia liczby taksonów oraz wartości BMWP, gdzie już w przypadku liczby powtórzeń na poziomie 20 próbek wynik obarczony jest wysokim poziomem niepewności.

Słowa kluczowe: bentos, makrobezkręgowce, testy przesiewowe, niepewność pomiarów

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EXAMINATION THE HEAVY METAL CONTAMINATION OF MUNICIPAL WASTE INCINERATOR AND M3 MOTORWAY IN BUDAPEST

PORÓWNANIE ZANIECZYSZCZENIA ŚRODOWISKA METALAMI CIĘŻKIMI PRZEZ SPALARNIĘ ODPADÓW ORAZ AUTOSTRADĘ M3 W BUDAPESZCIE

Abstract: Soil is one of humanity's most valuable treasure, which is a biotope for plants, animals and humans. There are two big threats for the soil resources: the soil degradation and soil pollution. The accumulation of a variety of harmful and/or toxic substances in the soils is well-known. This includes heavy metals, as well. Many of these heavy metals are indispensable, however some of them may be toxic even at low concentrations. The heavy metals may come to contact with the living beings through the food chain. The metals in the soil are in balanced state. This balance depends on the type of the metal, the pH value, the cation binding ability of the soil, and also on the redox conditions and the concentration of the cations within the soil. In order to be able to handle with the metal contaminated soils, it is important to examine the form of metal contaminants, the possible extent of its within the soil, and the magnitude of the concentration. Only with the help of detailed and thorough investigations can one form a description of the state of the environment (soil, plants, pollutant sources, etc.) and design the necessary interventions. In the present study, a comparison was made about the problem what is more dangerous to the environment: heavy metal content from the traffic of from the waste incineration? For the sampling spots the surroundings of the Budapest Municipal Waste Incinerator and the area around the introductory section of M3 motorway were chosen. 22 suspected contaminated soil samples were taken from the area of Budapest Municipal Waste Incinerator, by use of the point sampling method. Along the M3, "linear emission area sampling" methods were used, and 18 soil samples were taken. The GPS coordinates of the sampling points have been determined, and can be used later on as a basis for further researches and comparative studies. In the samples, the concentrations of six heavy metals were measured: lead, cadmium, zinc, copper, manganese and iron. During the measurement preparation process, the samples were digested by a Milestone 1200 Mega Microwave Digestion System. The determination of the concentrations of the heavy metals was performed with an ATI UNICAM 939 FAAS device. For both the soil samples, that were taken along the Budapest Municipal Waste Incinerator and those which are from the area of M3 it is valid, that the copper and zinc concentrations were low, the manganese concentration is average, while the cadmium, lead and iron concentrations were high.

Keywords: heavy metals, municipal waste, monitoring, effect of motorway

Introduction

The disposal of waste by burning is a one and a half century old procedure. In USA was burned "municipal solid waste (MSW) since the 1880s" [1].

The burning decreases the volume of the settlement waste to one third of its initial value, while 4000-6000 m^3 waste gas is created pro 1 metric ton, containing air-polluting and dangerous materials. The most important are the following ones: dust, carbon-monoxide, nitrogen-oxide, chlorine- and fluorine compounds, sulphur-dioxide and -trioxide, mercury and cadmium from heavy metals [2, 3], polichrolized dibenzo-dioxine and - furans (PCDD, PCDF), polychrolized biphenyl (PCB), poliaromatic hydrocarbon (PAH).

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The economic development of a country or a part of its, fundamentally depends on traffic conditions and expansion of the transport networks. During planning and building the motorway constructions and buildings, the specialists paid and are paying special attention to the protection of the environment. During determination of places of the traffic paths and institutions, the designer is in a strong cooperation with the competent environmental authorities. In the areas, which are sensitive from the point of view of the environment, the planning of the conservation - and environmental buildings and the protecting actions are realized on the base of environmental impact assessments.

Building up of a motorway is also not without disadvantages. The most of the problems are caused by different contamination types and environment destroying effects. The poisonous materials emitted by vehicles (sulphur-dioxide, nitrogen-oxides, volatile organic compounds, carbon-dioxide, smut, heavy metals [4, 5], etc.) accumulate on the riding-surfaces, and arrive into the environment being washed down by precipitates or arrive directly into soils, atmosphere or living waters, where they cause difficult loads.

The heavy metals are recognized as dangerous environment pollutants and big efforts are made for their questing, indication and decontamination of the environment from them. The examinations [6] are rarely oriented to detecting of only one type of heavy metals, but usually concentrations of 3-4 (or even more) metals are indicated in the given medium. The most of the available data are about lead (Pb), because its concentration, mobility and biological availability were mainly investigated due to its toxic character. Besides, the analyses have also been extended to cadmium (Cd), copper (Cu), nickel (Ni), chrome (Cr), zinc (Zn) and other metals, too.

The Budapest Municipal Waste Incinerator in Rákospalota, Budapest, Hungary, as well as the M3 motorway (part of the all motorways in Budapest) could also be potential waste sources. This fact has motivated us to investigate the heavy metal content of the soil in our surrounding. Accordingly, we collected soil samples in the 1 km zone of the incinerator and the introductory sector of the M3 motorway. We would like to compare, if the heavy metal content emitted from waste incineration or those emanating from traffic (*i.e.* the matter emitted by cars) are more dangerous from the point of view of the environment.

Materials and methods

Sampling

Sampling of different soil samples

First sampling place (Fig. 1)

Fig. 1. Soil sampling sketch diagram near Budapest Municipal Waste Incinerator

The contaminant source (chimney of Budapest Municipal Waste Incinerator (BMWI)) was considered as center, the sampling was made along concentric circles [7] according to the main and extension compass points. The center, the polluter source was drawn onto a map with 1:10,000 scales.

Second sampling place (Fig. 2)

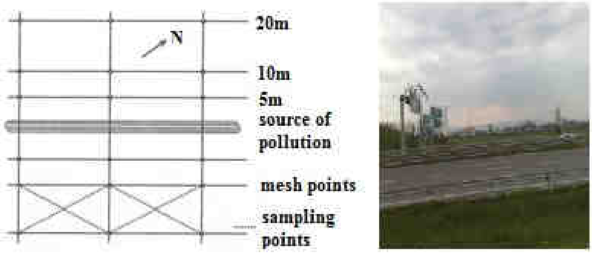

Fig. 2. Soil sampling scheme near motorway M3 in Budapest

Linear emission sampling was applied near motorway M3 (part of all motorway in Budapest) [7].

Sample preparing

Soil samples

Preparation of soil: in order to remove pieces of root, the samples were sifted with sieve (diameter: 2 mm). Then these were left to dry.

Moisture content and pH determination: determination of moisture content and pH were made according to standards No. MSz-08-0205-1978; MSz-08-0206/2-1987.

All analytical measurements were done in 3 replicates.

Determination of soil pH value

The pH value characterized the acidity of the soil’s liquid phase. A lot of Hungarian and National standards specify 2.5:1 liquid soil rate for water suspensions, and this is used in the present method, too. The advantage of using 1 mole/dm^3 KCl suspension is that the result values are more permanent and more reproducible. The acidity caused by H_3O^+ ions is the real or actual acidity in distilled water medium and the potential acidity can be measured in neutral saline solution (source).

6 g air dry soil was used for the determination of KCl and distilled water pH in test tubes. Soil was measured into 4 test tubes, then 10 cm^3 distilled water was put into 2 test tubes and 10 cm^3 1 mole/dm^3 KCl solution was given to 2 test tubes, then these were homogenized and the method was repeated for all samples. The samples were let to stay 12 hours at room temperature. The measurement was done with ADWA AD8000 pH meter. WTW Technical Buffer (T = 25°C, pH = 4.01), HANNA Instruments HI7007 (T = 25°C, pH = 7.01), HANNA Instruments HI7010 (T = 25°C, pH = 10.01) were used for three point calibration.

Digestion of the soil samples by Milestone 1200 Mega Microwave oven

Soil microwave digestion: The samples were digested by a MILESTONE 1200 Mega Microwave Digester with the following process:

Digestion of soil samples: about 0.5 g dry matter soil was put into each bomb. Then 5 cm^3 65% HNO_3 and 2 cm^3 30% H_2O_2 were added and let to stay in the solution for half an hour and then put the bombs into the microwave oven for half an hour. After that, the bombs were put into water cooled for half an hour and when they cooled down, they opened under a fume hood. The suspension made was filtered into 25 cm^3 standard flask, then it was filled up with high purity distilled water. The samples were stored in refrigerator until the instrument measuring. The digestion was done according to the „Cook-book" recipe of Milestone mega 12000 microwave oven. Table 1 contains the recipe of digestion in microwave oven.

Table 1

Digestion program for soil samples

Steps	Time [min] - Soil	Process [Watt] - Soil
1.	5	Digesting, 250
2.	2	Ventilation
3.	5	Digesting, 400
4.	5	Digesting, 250
5.	7	Digesting, 700

Heavy metal detection

The concentration of measured heavy metals was determined by atomic absorption spectrometry (Soil: "ATI Unicam 939 FAAS") with standard addition method.

Statistical analysis

Statistical analysis was done by SPSS 19.0 for Windows.

Results and discussion

The pH value of the soil samples was examined and the results are given in Table 2. All the pH values of spoils were between 6.60 and 9.78. Generally it is true, that mobility of the heavy metals increase in soil, if pH is more acidic, and more available for the plants. It can be said, that the acidic pH is not favorable environmental point of view. But in this case, the pH value is rather neutral or basic.

Table 2

The pH value of the soil samples

Number of soils	pH_{KCl}	pH_{H2O}
M3-1	7.58	7.91
M3-2	7.12	7.03
M3-3	7.66	7.35
M3-4	7.3	7.44
M3-5	7.94	7.85
M3-6	7.12	6.93
M3-7	7.20	6.99

Number of soils	pH_{KCl}	pH_{H2O}
M3-8	7.28	7.28
M3-9	7.40	7.26
M3-10	7.06	6.92
M3-11	6.64	6.60
M3-12	7.64	7.51
M3-13	7.26	7.17
M3-14	6.62	6.68
M3-15	7.16	6.93
M3-16	7.20	7.09
M3-17	7.68	7.70
M3-18	7.02	7.12
BMWI-1	7.83	7.69
BMWI-2	8.05	7.98
BMWI-3	8.22	7.98
BMWI-4	8.05	7.92
BMWI-5	7.74	7.68
BMWI-6	7.87	7.80
BMWI-7	7.87	7.69
BMWI-8	7.94	9.78
BMWI-9	7.86	7.51
BMWI-10	8.03	7.87
BMWI-11	7.48	7.32
BMWI-12	7.78	7.94
BMWI-13	7.6	7.39
BMWI-14	7.88	7.89
BMWI-15	7.56	7.38
BMWI-16	7.88	7.77
BMWI-17	7.81	7.69
BMWI-18	7.74	7.68
BMWI-19	7.7	7.60
BMWI-20	8.00	7.89
BMWI-21	7.96	7.84
BMWI-22	7.64	7.72

Cadmium concentration in soil samples

According to ANOVA, the cadmium concentration does not depend significantly on sampling place ($p = 5\%$). $LSD_{5\%} = 0.34$.

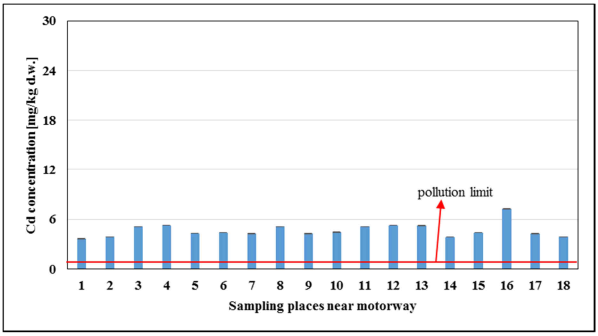

Fig. 3. Cadmium concentration in soil samples near M3 motorway

Figures 3 and 4 show cadmium concentration in different sampling places in soil samples is near M3 and near BMWI and the pollution limit value according to Hungarian regulation ("6/2009. (IV. 14.) KvVM-EüM-FVM"). The pollution limit for cadmium is 1 mg/kg dry weight (d.w.). In all cases was the Cd concentration over the pollution limit value. There were not any differences in Cd concentration at two sampling places.

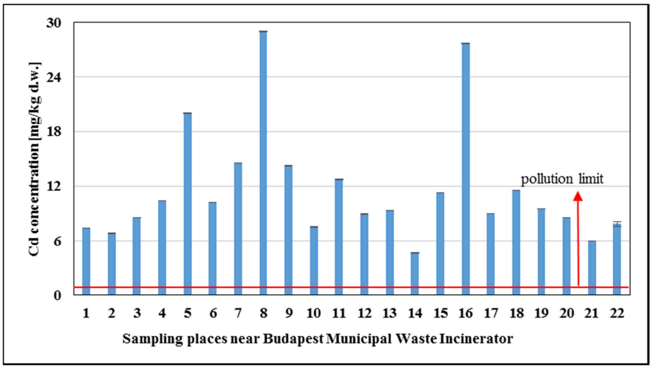

Fig. 4. Cadmium concentration in soil samples near Budapest Municipal Waste Incinerator

Copper concentration in soil samples

According to ANOVA, the copper concentration depends significantly on sampling place ($p = 5\%$). $LSD_{5\%} = 2.30$. Figures 5 and 6 show Cu concentration in different sampling places in soil samples near M3 and near BMWI. The pollution limit for Cu is 75 mg/kg d.w. (according to Hungarian regulation: "6/2009. (IV. 14.) KvVM-EüM-FVM"). In all cases the Cu concentration was under the pollution limit value. There were significant differences in Cu concentration in two sampling places. It was found higher Cu concentration near M3 (average concentration was 35.24 mg/kg d.w.) than near BMWI (average concentration was 31.15 mg/kg d.w.)

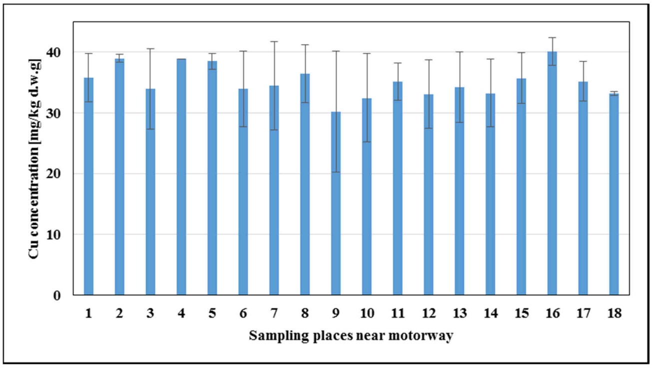

Fig. 5. Copper concentration in soil samples near M3 motorway (pollution limit is 75 mg/kg dry weight)

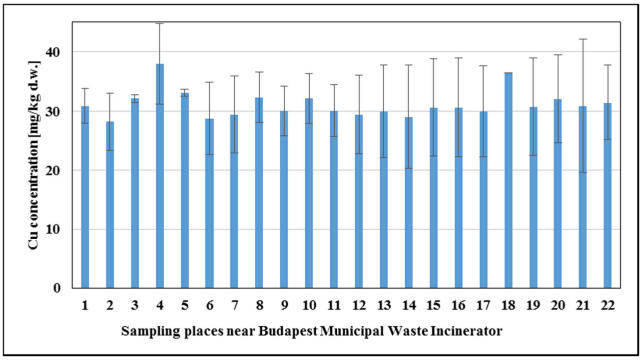

Fig. 6. Copper concentration in soil samples near Budapest Municipal Waste Incinerator (pollution limit is 75 mg/kg dry weight)

Zinc concentration in soil samples

According to ANOVA, the Zn concentration does not depend significantly on the sampling place (p = 5%). LSD$_{5\%}$ = 2.82.

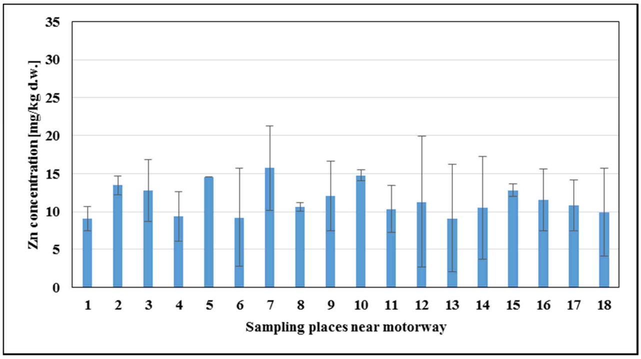

Fig. 7. Zinc concentration in soil samples near M3 motorway (pollution limit is 200 mg/kg dry weight)

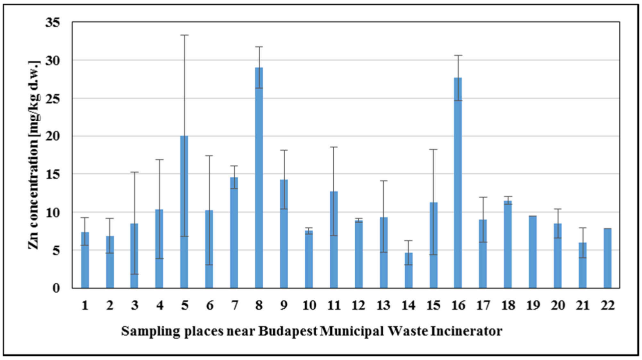

Fig. 8. Zinc concentration in soil samples near Budapest Municipal Waste Incinerator (pollution limit is 200 mg/kg dry weight)

Figures 7 and 8 show Zn concentration at different sampling places in soil samples is near M3 and near BMWI and the pollution limit value according to Hungarian regulation (“6/2009. (IV. 14.) KvVM-EüM-FVM”). The pollution limit is for Zn 200 mg/kg d.w. In all cases the Zn concentration was under the pollution limit value. There were not any differences in Zn concentration in two sampling places.

Lead concentration in soil samples

According to ANOVA, the Pb concentration depends slightly on sampling place (p = 5%). $LSD_{5\%}$ = 6.67. Figures 9 and 10 show Pb concentration in different sampling places in soil samples near M3 and near BMWI and the pollution limit value according to Hungarian regulation (“6/2009. (IV. 14.) KvVM-EüM-FVM”). The pollution limit is for Pb 100 mg/kg d.w. Near M3 the average Pb concentration was: 99.77 mg/kg d.w. (almost the limit value). Near the BMWI the average Pb concentration was 92.87 mg/kg d.w. It can be seen from the results: near the motorway the Pb concentration was slightly significantly higher. This result can be explained, that the cars used earlier leaded gasoline (it was banned in 01.04.1999). The lead dropped to the ground next to the highway, but it has not cultivated these lands. This would be necessary, because in many places produce plants or grazing animals, therefore the food may still lead.

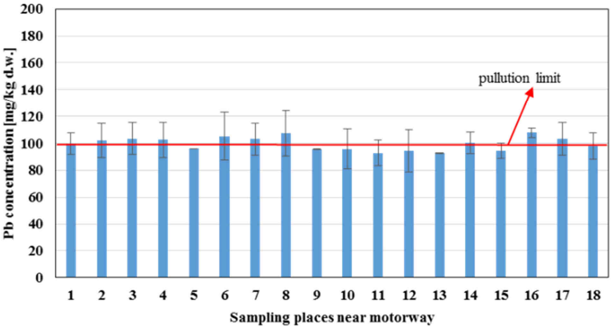

Fig. 9. Lead concentration in soil samples near M3 motorway

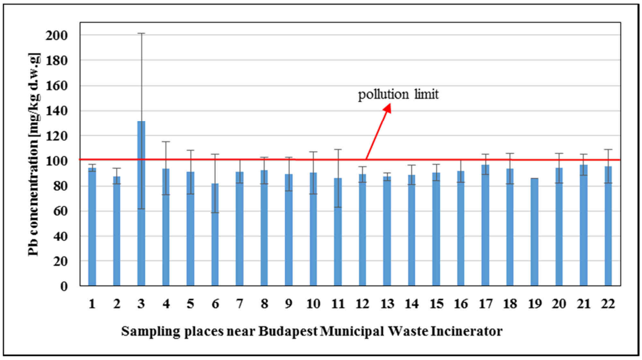

Fig. 10. Lead concentration in soil samples near Budapest Municipal Waste Incinerator

Conclusions

All the soil samples near BWMI and M3 have low Cu and Zn concentrations and relative high Pb concentration and very high Cd concentration. All the soil samples have Zn and Cu concentrations under limit value according to the Hungarian role ("6/2009. (IV. 14.) KvVM-EüM-FVM"). The examined area is not polluted by Zn and Cu.

Unfortunately, this cannot be said for the content of cadmium and lead in the soil samples. The cadmium pollution limit values set out all the soil samples exceeded most of the contamination was five-fold and seven-fold, as well.

If we compare the Pb concentration in soil samples derived immediate area of BMWI and M3 than it can be said, that Pb concentration depend significantly on the place ($p = 5\%$; $LSD_{5\%} = 6.67$). The Pb concentration derived from the closest area of the M3 has significantly higher Pb concentration (average Pb concentration is 95.48 mg/kg d.w.), than the samples from BMWI (average Pb concentration is 84.15 mg/kg d.w.). It can be said about similar in case of Cu concentration. Cu concentration depends significantly on the place ($p = 5\%$; $LSD_{5\%} = 0.96$), if the closest soil samples to M3 and BMWI are compared. The Cu concentration derived from the closest area of the M3 has significantly higher Cu concentration (average Cu concentration is 38.04 mg/kg d.w.), than the samples from BMWI (average Pb concentration is 32.65 mg/kg d.w.).

The pollution emanating from the vehicles is higher than in case of BMWI in case of Pb and Cu, which was confirmed of ANOVA.

Since the soil samples have very high Cd concentration and relative high Pb concentration that is why should forbid the agricultural production. Therefore, the heavy metals cannot get into food chain. The final solution could be the cleaning of the soils.

Acknowledgements

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PORÓWNANIE ZANIECZYSZCZENIA ŚRODOWISKA METALAMI CIĘŻKIMI PRZEZ SPALARNIĘ ODPADÓW ORAZ AUTOSTRADĘ M3 W BUDAPESZCIE

Abstrakt: Gleba jest jednym z najważniejszych skarbów ludzkości, będącym biotopem dla roślin, zwierząt i ludzi. Istnieją dwa wielkie zagrożenia dla gleby: degradacja oraz zanieczyszczenie. Akumulacja różnych groźnych i/lub toksycznych substancji w glebie jest dobrze znana. Do tych substancji zaliczają się również metale ciężkie. Wiele z nich jest niezbędnych, jednak część z nich może być toksyczna nawet w niskich stężeniach. Metale ciężkie mogą mieć kontakt z organizmami żywymi poprzez łańcuch pokarmowy. Metale w glebie znajdują się w stanie równowagi. Ta równowaga zależy od typu metalu, wartości pH, zdolności wiązania kationów w glebie, jak również od warunków redoks i stężenia kationów w glebie. Aby móc kontrolować ich zawartość w zanieczyszczonych glebach, niezbędne jest zbadanie formy tych zanieczyszczeń, możliwy zasięg w obrębie badanej gleby oraz wartość stężenia. Tylko z pomocą szczegółowej i dogłębnej analizy można stworzyć opis stanu środowiska (gleba, rośliny, źródła zanieczyszczeń itd.) oraz zaprojektować niezbędne działania. W tej pracy porównano zagrożenia środowiska stwarzane przez metale ciężkie pochodzące z ruchu drogowego i ze spalania odpadów. Próbki do badań pobrano dookoła spalarni odpadów komunalnych w Budapeszcie oraz w okolicy zjazdu na autostradę M3. Przy użyciu metody próbkowania punktowego zebrano 22 próbki potencjalnie zanieczyszczonej gleby z obszaru spalarni odpadów komunalnych w Budapeszcie. Wzdłuż autostrady M3 użyto metod „próbkowania liniowego obszaru emisji” i zebrano 18 próbek. Wyznaczono współrzędne GPS miejsc pobierania próbek, które mogą być wykorzystane w późniejszym czasie jako baza do dalszych badań czy badań porównawczych. W próbkach oznaczono stężenia sześciu metali ciężkich: ołowiu, kadmu, cynku, miedzi, manganu oraz żelaza. Podczas przygotowania do badań próbki zostały zmineralizowane przy użyciu systemu mikrofalowego Milestone 1200 Mega. Oznaczenia stężeń metali ciężkich wykonano przy użyciu aparatu FAAS ATI UNICAM 939. Dla próbek pochodzących z obydwóch obszarów stwierdzono niskie stężenia miedzi i cynku, średnie stężenia manganu oraz wysokie stężenia kadmu, ołowiu i żelaza.

Słowa kluczowe: metale ciężkie, odpady komunalne, monitoring, wpływ autostrady