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Proceedings of ECOpole

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Stanisław LEDAKOWICZ[1] and Lucyna BILIŃSKA[1]

APPLICATION OF FENTON REAGENT IN THE TEXTILE WASTEWATER TREATMENT UNDER INDUSTRIAL CONDITIONS

ZASTOSOWANIE ODCZYNNIKA FENTONA DO OCZYSZCZANIA ŚCIEKÓW WŁÓKIENNICZYCH W WARUNKACH PRZEMYSŁOWYCH

Abstract: Application of reactive dyes is very popular in textile industry as these dyestuffs are characterized by good fastness properties. Constapel et al estimated the production of this type dyes for over 140,000 Mg/year. The reactive dyes are mostly (50%) employed for coloration of cellulosic fibers, however they can be also applied on wool and nylon. Unfortunately, they possess a low degree of fixation (50÷90%), since the functional groups also bond to water, creating hydrolysis and the excess of dyes applied cause a colored pollution of aqueous environment. Moreover, dyeing process requires the use of: electrolytes in the form of aqueous solutions of NaCl or Na_2SO_4 in the concentration up to 100 g/dm^3, alkaline environment (pH > 10) and textile auxiliary agents (among others detergents). Therefore, the wastewater generated during the reactive dyeing processes are characterized by high salinity, pH value and color, and due to low value of the ratio BOD_5/COD are non-biodegradable. The successful methods of the textile wastewater treatment could be an advanced oxidation processes (AOPs), amongst which the Fenton reagent seems to be the most perspective as it is the cheapest and easy in use. Based on the newest literature survey it was found that many successful tests with Fenton reaction were performed mainly in decolorization. However, not enough attention was devoted to decolorization of real industrial wastewater containing dyes, detergents and salts NaCl, or Na_2SO_4. The experiments carried out in lab scale were focused on the impact of NaCl and textile auxiliary agent (liquid dispersing and sequestring agent) on an inhibition of decolorization process by Fenton reagent. The objects of the investigation were the synthetic mixtures simulating the composition of real textile wastewater as well as the real industrial wastewater generated in the reactive dyeing. The inhibition of the Fenton decolorization in the presence of NaCl and liquid dispersing and sequestering agent was demonstrated.

Keywords: Fenton reagent, textile wastewater, decolorization, inhibition

A full range of bright colors, stable covalence bond to the fiber, providing a good fastness of dyeing and relatively easy synthesis - these properties make reactive dyes so popular in textile industry [1]. Constapel et al [2] estimated the annual production of these type of dyestuff for over 140,000 Mg (tones), while Ahmed and El-Shishtway [3] announce, that 50% of all cellulose fibers is dyed with reactive dyes, and only 17% with vat dyes, 16% with direct dyes, 7% with sulfur dyes, also 7% with indigo dyes and 3% with glacial dyes. Reactive dyes are mostly used to dye cellulose fibers, however there are also groups of reactive dyes dedicated for wool and polyamide. Unfortunately, despite those advantages and common use, reactive dyes are marked by low degree of fixation, between 50 and 90%, depending on the assortment. It means, the excess of dye, used in industrial dyeing process, does not bound to the fibers and in the hydrolyzed form is expelled to the sewage, causing higher contamination of aqueous environment. The fact, that the process of reactive dyeing requires special technology, also has to be taken into consideration. A fixation of reactive dye onto fiber is possible, when an electrolyte NaCl or Na_2SO_4 is used in dye bath, strong alkaline pH is produced and auxiliary *surface active agents* (SAA)

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are applied. The consumption of dyestuff in process of reactive textile dyeing amounts on average 0.5÷80 g/kg textiles, organic auxiliary agents up to 30 g/kg textiles, inorganic auxiliary agents 30÷250 g/kg textiles, electrolyte 90÷1500 g/kg textiles. Therefore, the wastewater generated in reactive dyeing process is marked by high salinity and coloration, high pH value and SAA presence. Moreover, textile wastewater is characterized by high *Chemical Oxygen Demand* (COD) value and low *Biological Oxygen Demand* (BOD) value, what makes it non-biodegradable.

A way of purification of this kind of wastewater could be AOPs methods (advanced oxidation processes), amongst which the Fenton reagent is worth of consideration, as it is not expensive and easy in use. Fenton's reagent is a method of generating hydroxyl radicals ($HO^{\bullet}$) by using reaction of hydrogen peroxide decomposition catalyzed by ferrous ions Fe^{2+}. The application of oxidizer with high redox potential (for $HO^{\bullet}$ 2.81 V) generated under *in situ* conditions, with Fenton's reaction, enables decomposition of low biodegradable substances, including dyestuff used in textile industry.

According to the newest literature report a lot of successful tests were performed, mostly in discoloration of dye solution used in textile industry, not only of reactive dyes. Xu et al [4], Papić et al [5], Kusić et al [6], Tantak and Chaudhari [7] and Arslan-Alaton et al [8] worked on discoloration of reactive dye solution with use of Fenton reagent. Wang et al [9], Gulkaya et al [10], Bianco et al [11] worked on discoloration of real industrial wastewater. These studies were focused on optimization of the method regarding color reduction, reduction of *Total Organic Carbon* (TOC) and comparison of working effects of Fe^{2+}/H_2O_2 and $Fe^{2+}/H_2O_2/UV$.

The aim of the present publication is to show the inhibition impact of NaCl and SAA, present in real industrial wastewater, on their discoloration. Similar tests have already been performed by Alnuaimi et al [12], Riga et al [13] and Arslan-Alaton et al [14] and reveled the inhibition impact of salt on Fenton's reaction. Those tests included the impact of different kinds of salts on discoloration process of dye solution with Fenton's reagent, however the impact of SAA has not been examined yet. Moreover, the highest salt concentration (NaCl) used in these tests was 15 g/dm^3, while in industrial practice of dyeing process it can reach up to 100 g/dm^3. Therefore, conducting further study on this matter, including higher salt concentration and SAA presence, concentrated on examination of both synthetic mixtures simulating the composition of real textile wastewater and real wastewater generated in reactive dyeing process, seems to be justified.

Experimental

The experiment has been carried out with the use of a black dye commonly used in industrial practice - C.I. Reactive 5 known in trade form as Setazol Black DPT supplied by Setas Kimya. Chemical formula of the dye is presented in Figure 1. Molecular weight of Reactive 5 is 991.82 g/mol and the maximum absorbance for this dye was observed for $\lambda = 596$ nm. Furthermore, $FeSO_4 \cdot 7\,H_2O$, perhydrol - H_2O_2 conc. 30%, H_2SO_4 conc. 94% - aqueous solution 1:10, NaOH, NaCl, Perigen LDR supplied by Textilchemie Dr Petry GmbH - liquid dispersing and sequestering agent based on naphthalene sulphonic acid condensate and carboxylates have been used. The aqueous solutions of dyes and auxiliary agents have been prepared by Dosorama machine provided by Technorama. The dyestuff in a hydrolyzed form has been used, since it is present in this form in textile wastewater. The hydrolysis of dye solution has been performed in water bath at temperature 80°C during 2 hours, at pH 12. Initial dye concentration in the simulated industrial wastewater mixtures has been fixed, basing on earlier experiments, on 200 mg/dm^3.

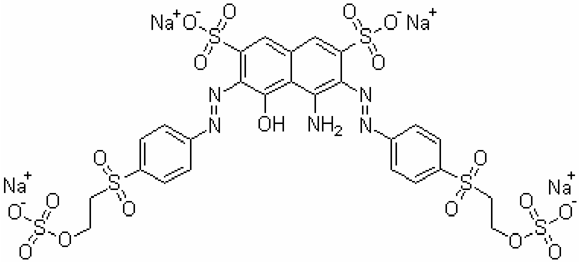

Fig. 1. C.I. Reactive 5 (trade form - Setazol Black DPT) chemical formula

The color of the dye water solution has been measured by defining the absorbance with maximum absorbance of the dye. The kinetics of discoloration of water dye solution with Fenton's reagent has been examined by measuring the absorbance with transient absorption spectrophotometer Helios, delivered by Thermo company, with constant, automatic tests collection and flow cell. Discoloration has been carried out for the three objects: aqueous solutions of BDPT dye only, simulated lab mixtures imaging the composition of real wastewater (BDPT dye solution with NaCl and Perigen LDR) and for real wastewater after dyeing process. Tests have been taken in textile testing laboratory under conditions of normal alternative climate according to ISO 139:2005, point 3.2 standards.

Results and discussion

Effect of pH

Natural pH value after discoloration process reaches 11, or even 12. However, the decomposition reaction of H_2O_2 is catalyzed most efficiently by Fe^{2+} ions in water solutions with pH value between 2 and 3. In order to verify this the discoloration of BDPT dyestuff was proceeded for pH values equal to 2 and 3. Comparatively also for two other reactive azo dyestuff (YKHL - Synozol Yellow KHL and YHB - Synozol Yellow HB) the same test was proceeded, what has been presented in Figure 2. The discoloration with Fenton's reagent for all examined dyestuff solutions proceeded the fastest with pH value equal to 3. Therefore, further tests have been performed with pH value equal to 3. In all tests the pH value of examined samples was set with H_2SO_4 1:10 solution.

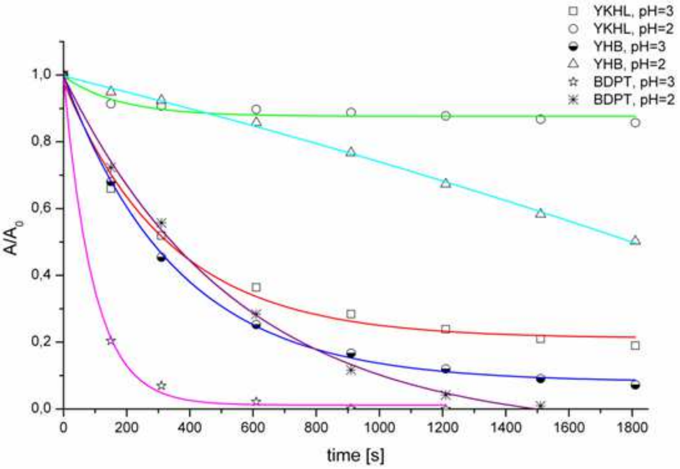

Fig. 2. Discoloration of aqueous solutions of dyestuffs: YKHL, YHB, BDPT with dyestuff concentration 200 mg/dm^3 and 75 mg Fe^{2+}/ 750 mg H_2O_2 at pH value equal to 2 and 3

Effect of ferrous dosage and Fe^{2+} : H_2O_2 ratio

In order to find an optimal dosage and reagent ratio assuring effective discoloration process tests for aqueous solution of BDPT have been performed. The concentrations of $FeSO_4$ within the range 25÷100 mg/dm^3 and reagent ratio $FeSO_4$: H_2O_2 1:5 and 1:10 have been applied. The results gained for the solutions have been presented in Figure 3. In each case higher degree of color reduction has been noticed for the reagents ratio 1:10, which has been chosen for the further tests of BDPT discoloration with $FeSO_4$ concentration amounting 75 mg/dm^3. The degree of color reduction of aqueous solution of BDPT exceeded 99%.

Effect of NaCl and Perigen LDR addition

The same conditions of Fenton reaction as for aqueous solution of BDPT (75 mg/dm^3 $FeSO_4$ and reagent ratio $FeSO_4$:H_2O_2 1:10) have been used for discoloration of dyestuff solution BDPT containing 1, 5, 10, 20, 40, 80 g NaCl /dm^3. As it can be observed in Figure 4 only for 1 g/dm^3 NaCl no meaningful decrease of discoloration efficiency appeared compared with tests without NaCl. However, the color reduction for a sample including 10 g NaCl /dm^3 amounted already 63%, and for the one including 80 g NaCl /dm^3 - 40% after 45 min.

The NaCl impact on discoloration efficiency can be explained as follows. In the presence of excess Cl^- ions due to reaction of $HO^\bullet$ radicals with Cl^- ions the ion-radicals $Cl_2^{-\bullet}$ are produced which possess much lower oxidative potential than $HO^\bullet$ radicals [15]:

$$HO^\bullet + Cl^- \longleftrightarrow HOCl^{\bullet-}$$

$$HOCl^{\bullet-} + H^+ \longrightarrow H_2O + Cl^\bullet$$

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^{-\bullet}$$

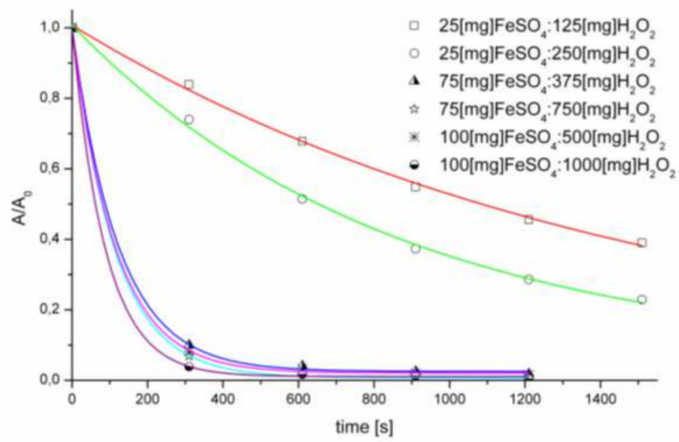

Fig. 3. Dependence of discoloration extent of dyestuff BDPT aqueous solutions on $FeSO_4$ dose

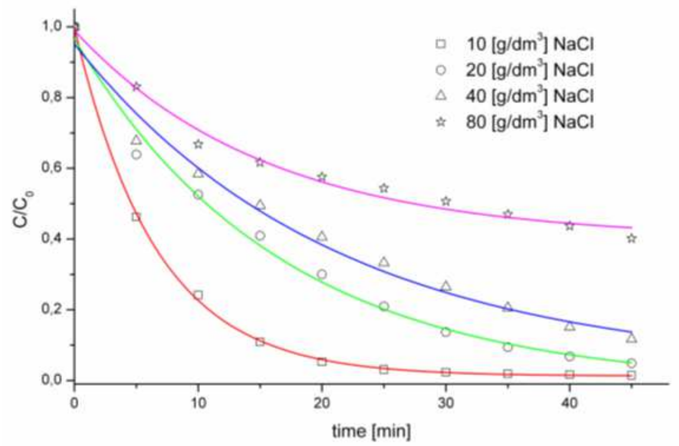

Fig. 4. Dependence of discoloration extent of dyestuff BDPT aqueous solutions on NaCl concentration

After increasing the $FeSO_4$ dose up to 200 mg/dm^3 and keeping the ratio $FeSO_4$:H_2O_2 = 1:10 the test has been repeated for samples of BDPT solution containing 0.5, 1.0, 2.0 g/dm^3 of auxiliary agent - Perigen LDR. In the case of samples containing 0.5 and 1.0 g/dm^3 Perigen LDR the Fenton reaction enabled 99% color reduction, however for the samples containing 2.0 g/dm^3 LDR the degree of color reduction decreased to 75% after 45 min, what was shown in Figure 5. The presence of surfactants in the concentration above the *Critical Micelle Concentration* (CMC) causes emulsification of dyestuff molecule shielding it against the attack of radicals, which in consequence decreased the efficiency of discoloration.

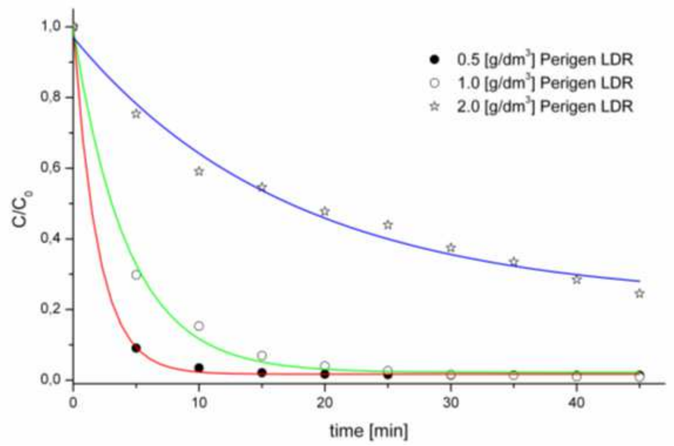

Fig. 5. Time dependence of discoloration of BDPT in the presence of surfactant Perigen LDR

Discoloration of simulated wastewater and real industrial textile effluents

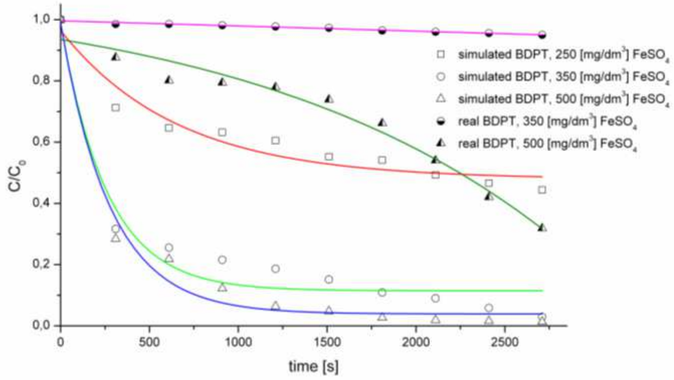

Fig. 6. Comparison of discoloration of simulated textile wastewater with real industrial one of the same reagents concentration

In the next experiment an aqueous solution with concentration of 200 mg/dm^3 BDPT containing 80 g/dm^3 NaCl and 0.5 g/dm^3 Perigen LDR, simulating the composition of real textile wastewater has been subjected to discoloration with Fenton's reagent. The doses of reagent amounting 250, 350, 500 mg/dm^3 $FeSO_4$ with the ratio $FeSO_4$:H_2O_2 = 1:10 were used. As it is seen in Figure 6 satisfactory degree of color reduction above 90 and 97% both for $FeSO_4$ dose 350 mg/dm^3 and 500 mg/dm^3 was achieved.

Finally the corresponding test for a real industrial wastewater after dyeing process with 350, 500 mg/dm^3 $FeSO_4$ and reagent ratio $FeSO_4$:H_2O_2 = 1:10, pH value equal to 3 has been performed. Unexpectedly the results of discoloration were incomparable with that obtained for the simulated wastewater. In the case of usage of 350 mg/dm^3 $FeSO_4$ almost none color reduction was observed, however for 500 mg/dm^3 $FeSO_4$ 70% of color was reduced during

45 min. It is difficult to explain these results of discoloration of real industrial wastewater, what needs further investigation. One can conclude that simulated textile wastewater is not the same as real wastewater generated during reactive dying in industrial scale.

Conclusions

Fenton reagent appeared to be very effective method in degradation of aqueous solution of many dyestuffs. Inhibition effect of NaCl presence in textile wastewater on discoloration has been found: the higher content of NaCl the poorer is discoloration degree. The emulsification effect of surfactants present in textile wastewater in the concentration above critical micelle concentration causes a decrease of discoloration rate.

Simulated textile wastewater are not the same with respect to discoloration by Fenton reagent as real wastewater generated during reactive dying in industrial scale.

It was proved, that nearly 5 times more reagent dose had to be used to discolor a mixture simulating the composition of real textile wastewater, than it is in the case of dyestuff solution without any additional substances. Moreover, to discolor real wastewater generated in industrial reactive dyeing process 500 mg/dm^3 $FeSO_4$: 5000 mg/dm^3 H_2O_2 reagent dosage, ie 7 times higher dose than in case dyestuff solution, have to be applied.

It becomes legitimate to make further study concerning discoloration of model wastewater including dyestuffs, NaCl, auxiliary agents and real wastewater, with Fenton's reagent as well as with other deep oxidation techniques.

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ZASTOSOWANIE ODCZYNNIKA FENTONA DO OCZYSZCZANIA ŚCIEKÓW WŁÓKIENNICZYCH W WARUNKACH PRZEMYSŁOWYCH

Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka

Abstrakt: Barwniki reaktywne wyróżnia szereg cech, które sprawiają, iż są one powszechnie stosowane w praktyce przemysłu włókienniczego. Constapel i in. oszacowali roczną produkcję tego typu barwników na ponad 140 000 Mg. Przy czym barwniki reaktywne są w większości (50%) stosowane do barwienia włókien celulozowych, jednakże mogą one być również stosowane do wełny i poliamidu. Niestety, barwniki reaktywne wyróżnia niski stopień wyczerpania z kąpieli, wynoszący od 50 do 90%. Oznacza to, iż w przemysłowych procesach barwienia używany jest nadmiar barwnika, który nie wiąże się z włóknem i w postaci hydrolizatu trafia do ścieków, stanowiąc obciążenie dla środowiska. Procesy barwienia reaktywnego wymagają użycia elektrolitu w postaci: roztworu NaCl lub Na_2SO_4 o stężeniu do 100 g/l, wytworzenia silnie alkalicznego pH oraz użycia środków powierzchniowoczynnych - SPC. To sprawia, iż ścieki generowane w procesach barwienia reaktywnego charakteryzuje: wysokie zasolenie i zabarwienie, wysoka wartość pH, obecność SPC. Ponadto te ścieki ze względu na niski stosunek BZT_5/ChZT są mało podatne na procesy biologicznego oczyszczania. Alternatywą dla oczyszczania tego typu ścieków mogą być metody AOP, wśród których na uwagę ze względu na niskie koszty i łatwość stosowania zasługuje odczynnik Fentona. Na podstawie przeglądu najnowszych doniesień literaturowych można stwierdzić, iż zostało przeprowadzone wiele udanych prób głównie dekoloryzacji roztworów. Niewiele natomiast uwagi poświęcono odbarwianiu ścieków rzeczywistych czy symulowanych mieszanin zbliżonych składem do ścieków rzeczywistych, czyli zawierających barwniki oraz NaCl, Na_2SO_4, SPC, (Sun i in. 2009; Arslan-Alaton i in. 2008). Eksperymenty przeprowadzone w skali laboratoryjnej były ukierunkowane na analizę wpływu NaCl i włókienniczych środków pomocniczych (środki dyspergujące i sekwestrujące) na hamowanie procesu odbarwiania odczynnikiem Fentona. Przedmiotem badań były zarówno syntetyczne ścieki symulujące skład rzeczywistych ścieków włókienniczych, jak również rzeczywiste ścieki powstałe w procesie barwienia reaktywnego. Wykazano zjawisko hamowania odbarwiania odczynnikiem Fentona w obecności NaCl, jak i środków dyspergujących i sekwestrujących.

Słowa kluczowe: odczynnik Fentona, ścieki włókiennicze, odbarwianie, inhibicja

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Mariusz BARAŃSKI[1], Iwona ZAWIEJA[1] and Lidia WOLNY[1]

EFFECT OF THERMO-ULTRASONIC DISINTEGRATION OF EXCESS SLUDGE ON THE EFFECTIVENESS OF ANAEROBIC STABILIZATION PROCESS

WPŁYW TERMICZNO-ULTRADŹWIĘKOWEJ DEZINTEGRACJI OSADÓW NADMIERNYCH NA EFEKTYWNOŚĆ PROCESU STABILIZACJI BEZTLENOWEJ

Abstract: It is estimated that processing of sewage sludge absorbs ca 70% of utilization costs. Subjecting initial and secondary sludge to aerobic stabilization, regarded as environment-friendly and economical technology contributes to a considerable minimization of the mass of the sludge. Biogas production is an essential factor which improves the profitability of the process of methane fermentation since it allows for partial recovery of costs incurred for maintenance of mesophilic conditions of fermentation. Methane fermentation is a process which occurs slowly and necessitates a long period of retaining sludge. The degree of fluidization of insoluble organic polymers to soluble form, available for microorganisms, has essential effect on the rate of sludge biodegradation. Disintegration of excess sludge affects the increase in dispersion of sludge particles, which determines acceleration of the process of hydrolysis which limits the course of anaerobic stabilization. Increase in the speed of production of VFAs and increase in their level over consecutive days of acid fermentation preconditions biogas production efficiency. This paper presents the results of the investigations concerning the effect of disintegration by means of a hybrid method on the efficiency of 25-day anaerobic stabilization *ie* the degree of sludge fermentation and intensification of biogas production. Application of thermal-ultrasound excess sludge processing caused the increase in the degree of sludge fermentation, where ca 60% removal of organic dry mass was reported with respect to anaerobic stabilization of raw sludge. Moreover, the increase in intensity of biogas production was observed, expressed in the value of unit biogas production, which amounted to 4.64 dm^3/g of organic dry mass for the sludge subjected to modification by the hybrid method, whereas this value for raw sludge amounted to 1.1 dm^3/g of organic dry mass.

Keywords: excess sludge, ultrasound-thermal disintegration, anaerobic stabilization, degree of sludge fermentation, unit biogas production

Disintegration of sewage sludge consists in destruction of the structure of the sludge through application of external forces which affect changes in their physicochemical parameters and the character of the structure. Due to the origins of implementation of the energy supplied into the system, one can distinguish between mechanical disintegration, which includes the method using ultrasound effect, with sludge particles subjected to shear forces and pressure which cause stress in the structure of sludge and non-mechanical disintegration, eg thermal processing [1].

The effect of ultrasound field and thermal processing on a medium produces the results of mechanical sonochemical nature. Acute conditions (high temperature and pressure) in the area of cavitation explain the changes in physicochemical properties in sonicated systems. The effect of excess sludge conditioning is disintegration, which, apart from dispersion of solid phase in the sludge, causes destruction of cell membranes in microorganisms and release of the substrates contained in the cells to sludge liquid, which

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is essential for further biochemical decomposition of organic compounds. The degree of destruction of the structure of sludge depends on the method, amount of energy supplied and sludge properties [2].

As a result of the process of disintegration, the amount of organic matter which can be processed into biogas is increased. "Killing" the organisms resistant to anaerobic conditions in activated sludge accelerates and intensifies sludge fermentation in fermentation chamber. After the process of anaerobic stabilization, the sludge with lower content of organic matters is obtained. Properly fermented sludge, with low content of organic matter, allows for easier mechanical dehydration. Application of disintegration gives in effects better stabilization and dehydration of the sludge. As a result of decomposition of more organic mass in the sludge into biogas in the process of fermentation, overall amount of sludge for final use is obtained.

The most advanced methods which are used on an industrial scale in sewage treatment plants today include the methods of mechanical disintegration, ultrasounds and thermal sludge treatment [1]. Degree of destruction of sludge structure depends on the applied method, energy and properties of the sludge [3].

In the case of the process of anaerobic stabilization of sewage sludge, an important energy-related problem is intensification of biogas production. Application of pre-conditioning of sewage sludge allows for increase in the degree of fermentation of the sludge subjected to physical modification as well as intensification of biogas production [4].

The processes of anaerobic stabilization contribute to: substantial reduction in the amount of compounds which release unpleasant odour, reduction in the amount of organic matter in the sludge, facilitation of the processes of sludge dehydration and reduction in the amount of pathogens [5, 6].

The aim of the investigations was to determine the effect of initial treatment of excess sludge by means of ultrasound field and the combined (hybrid) ultrasound-thermal method of disintegration on the course of the process of anaerobic stabilization ie the degree of sludge fermentation and biomass production.

Material and methods

A basic substrate for the study was excess sludge (90%), and fermented sludge (10%) which was used for inoculation. The sludge was sampled from the Warta Central Sewage Treatment Plant in Czestochowa. General characteristics of raw excess sludge are presented in Table 1.

Table 1

General characteristics of raw excess sludge

Parameters / **Type of sludge**	**Hydration**	**Dry mass**	**Dry org. mass**	**Dry min. mass**	**Volatile Fatty Acids (VFAs)**	**Chemical Oxygen Demand (COD)**
	[%]	**[g/dm^3]**	**[g/dm^3]**	**[g/dm^3]**	**[mg CH_3COOH/dm^3]**	**[mg O_2/dm^3]**
Excess sludge	98.75	9.51	6.52	2.99	68	120

During the first stage of the investigations, changes in COD were adopted as a criterion of assessment of physicochemical and biomechanical changes which occur in sludge as a result of application of physical methods of conditioning. During the second stage, these parameters were used for determination of the most favourable conditions of conditioning of the sludge with ultrasound field and hybrid ultrasound-thermal method for the process of 1-day and 25-day anaerobic stabilization.

The choice of the most advantageous parameters of disintegration with ultrasound field was made using VCX 1500 disintegrator manufactured by SONICS (USA) with automated tuning. Maximal output power of this generator amounts to 1500 W, with the frequency of sonication of 20 kHz. Sonotrode in this disintegrator was submerged in a container with the diameter of 10 cm containing sludge at the depth of 5 cm from the container's bottom. The volume of the conditioned samples will amount to 0.5 dm^3. In the case of the hybrid ultrasound-thermal method, the sample, after the use of ultrasound field, was closed in laboratory flask with glass plug equipped in fermentation pipe and placed in water bath with automated shaking for the period of 1.5 hours at the temperature of 70ºC.

The sludge prepared in this manner, in the amount appropriate to the process of anaerobic stabilization, was cooled under natural conditions to the temperature of 37ºC, and then inoculated with fermented sludge at the amount of 10% of the whole volume. The mixtures of sludge obtained with this method were very well mixed and used in the process of 10-day acid fermentation carried out in laboratory flasks ($V = 0.5$ dm^3), which played the role of fermentation chambers, closed with glass plug with fermentation pipe and placed in a thermostat at the temperature of 37ºC. The process of 25-day stabilization was carried out in fermentation chamber with effective capacity of 7 dm^3. The system is equipped in the installation which ensures constant temperature of the process, the equipment which provides optimal mixing rate and installation for biogas sampling. There is a water jacket on the outside of the system, which is used for heating the sludge in the chamber. The required temperature of 37ºC was provided by platinum thermoelectrode placed inside the chamber. Biogas was captured by means of the system which included the cylinder with capacity of 2 dm^3, filled with saturated solution of sodium chloride and compensation bottle with capacity of 5 dm^3. The cylinder allows for reading the amount of generated biogas. The biogas collected in the cylinder lifts the excess liquid from cylinder to the compensation bottle. The control over the course of fermentation was carried out every day based on the measurement of the amount of generated biogas.

On each day of the process (10 days), before the process (0-day) and after fermentation chamber (25th day), the levels of dry mass, organic dry mass and mineral dry mass were determined. Levels of *Chemical Oxygen Demand* (COD) were measured based on dichromate method using spectrophotometer HACH 2100N IS, whereas *Volatile Fatty Acids* (VFAs) levels were measured using the method of distillation with water vapour in supernatant liquor.

Discussion

Initial sludge treatment before the process of fermentation was aimed at disintegration of sludge particles, destruction of microorganisms in excess sludge and release of the organic compounds and enzymes. Based on the results obtained during initial investigations, with consideration of the changes in COD levels in sludge liquor for excess sludge disintegrated with ultrasound field, the most favourable amplitude and conditioning time was determined. In the case of the hybrid method, time of sludge preparation in water bath after the use of ultrasound field was also determined. It was adopted after the analysis of the obtained results that the most favourable time of sludge preparation with ultrasound field was 10 min, with vibration amplitude of 80% (≈31.4 μm). In order to carry out the process of anaerobic stabilization by means of the hybrid method, the sludge was additionally prepared at the temperature of 70ºC for 1.5 hours in water bath, after the use of ultrasound field.

Changes in parameters for the methods of sludge conditioning discussed above after the process of anaerobic stabilization are presented in Table 2.

Table 2

Selected physical and chemical parameters of physically pretreatment sludge

Fermentation time [d]	**Parameters**	**Unit**	**Raw sludge**	**Ultrasonic field 80% - 10 min**	**Hybrid method 80% - 10 min + 70ºC - 1.5 h**
0	Dry mass	[g/dm^3]	11.2	12	13.6
	Dry org. mass	[g/dm^3]	8.15	8.4	8.6
	COD	[mg O_2/dm^3]	160	2768	3714
	VFAs	[mg CH_3COOH/dm^3]	85	137	124
10	Dry mass	[g/dm^3]	7.25	7.6	8.8
	Dry org. mass	[g/dm^3]	5.71	4.5	5.3
	COD	[mg O_2/dm^3]	145	761	1648
	VFAs	[mg CH_3COOH/dm^3]	51	360	582
25	Dry mass	[g/dm^3]	6.65	6.9	7.7
	Dry org. mass	[g/dm^3]	4.67	3.9	3.6
	COD	[mg O_2/dm^3]	120	300	386
	VFAs	[mg CH_3COOH/dm^3]	42	154	240

The highest level of COD (3714 mg O_2/dm^3) was observed before the process of anaerobic stabilization in the case of hybrid method (mixture C). The recorded level of COD was 23-time higher compared with excess sludge without conditioning (mixture A), with its value reaching 160 mg O_2/dm^3. On the 10th day of methane fermentation, value of COD for sludge conditioned with ultrasound field (mixture B) and hybrid method amounted to, respectively, 761 and 1648 mg O_2/dm^3. After the process in fermentation chamber (25th day), level of COD was 300 and 386 mg O_2/dm^3, respectively for the sludge subjected to ultrasound field and using hybrid method. Figures 1 and 2 present levels of COD and VFA registered on individual days of the process of anaerobic stabilization.

The highest value of VFA which amounts to 1782 mg CH_3COOH/dm^3 was found for the 4th day of anaerobic stabilization of excess sludge disintegrated with hybrid method. In the case of sludge conditioned with the same ultrasound field, the maximal value of 1508 mg CH_3COOH/dm^3 for VFA parameter was obtained on the second day of the process. Comparing the obtained results to sludge which is not physically conditioned, with the highest level of VFA of 497 mg CH_3COOH/dm^3 reported on 4th day, a 3- and 3.5-time rise in VFA level can be observed in the case of ultrasound field and hybrid method, respectively.

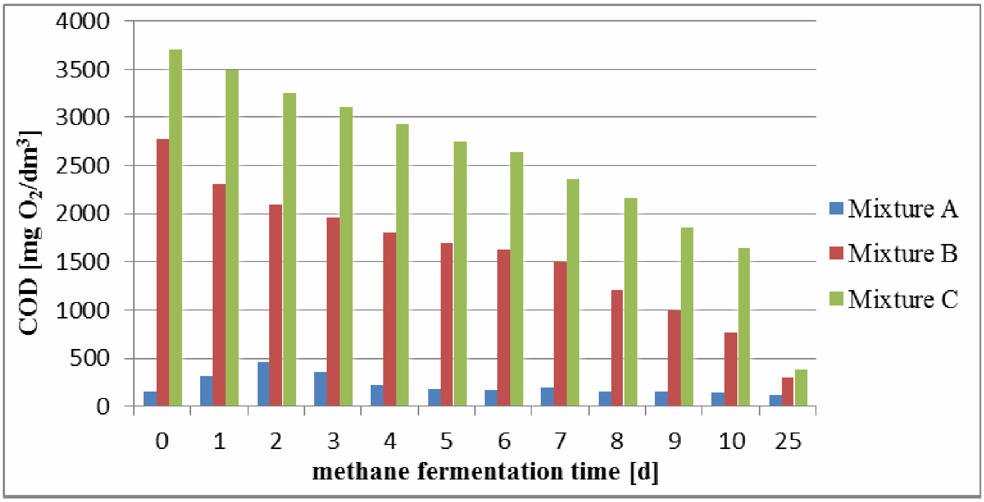

Fig. 1. Changes in the COD level observed in sludge liquor as a function of methane fermentation time

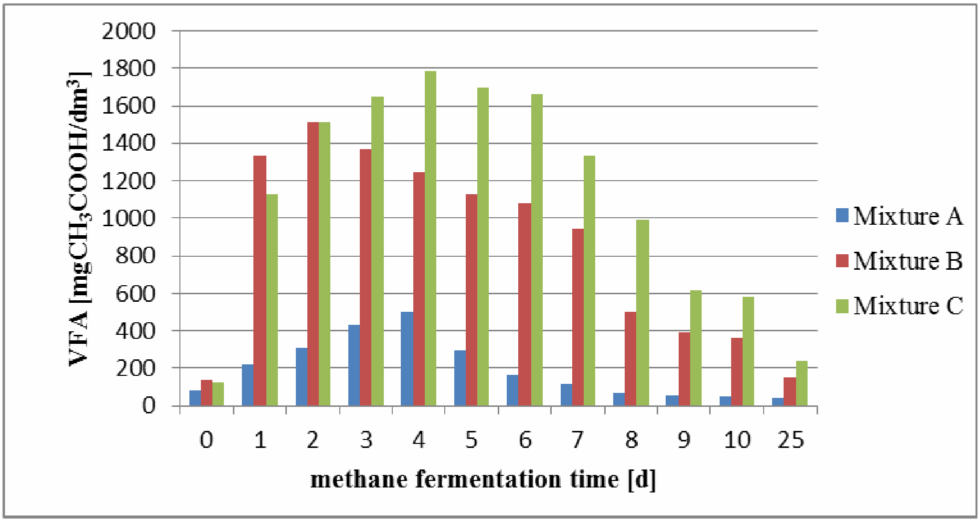

Fig. 2. Changes in the VFAs level observed in sludge liquor as a function of methane fermentation time

For the processes of anaerobic stabilization, the degree of sludge fermentation was also determined based on depletion of organic matter. The obtained levels of dry mass and organic dry mass on consecutive days of the process are presented in Figures 3 and 4.

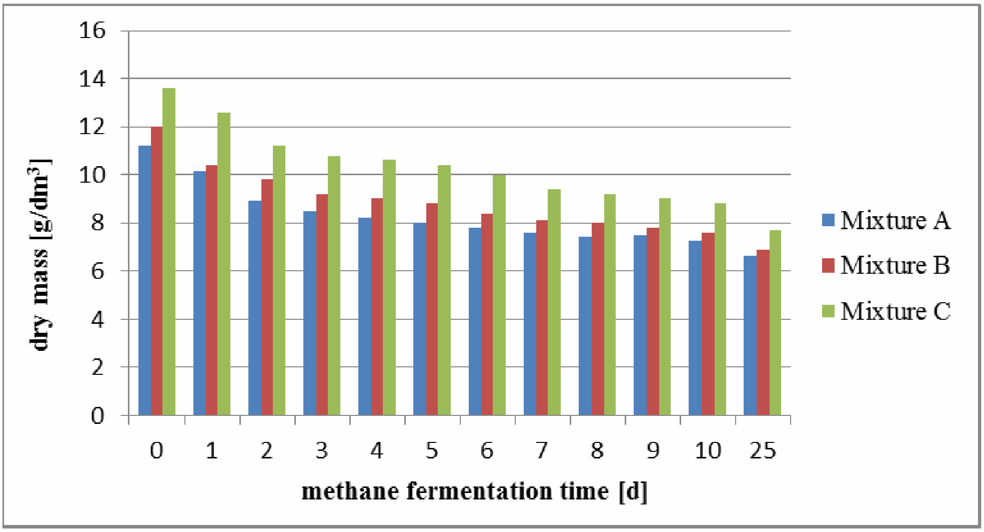

Fig. 3. Changes in the dry mass level observed in sludge liquor as a function of methane fermentation time

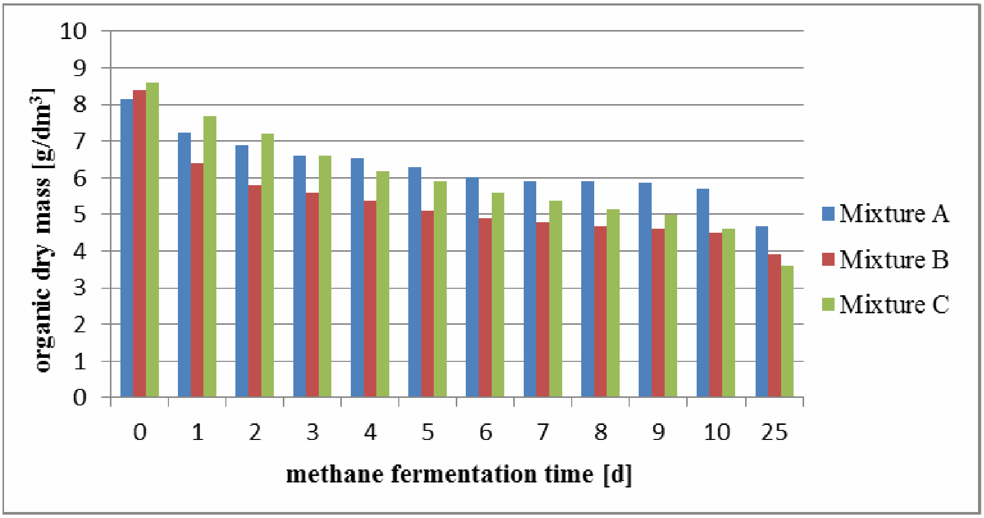

Fig. 4. Changes in the dry organic mass level observed in sludge liquor as a function of methane fermentation time

The highest degree of sludge fermentation using the hybrid method (mixture C) (ca 60%) was obtained after the process of 25 day anaerobic stabilization, whereas in the case of the sludge conditioned with ultrasound field (mixture B), a 53% decrease in organic dry matter was reported. The degree of fermentation for the non-prepared sludge amounted to 42%.

Furthermore, the degree of fermentation after the process of 10-day anaerobic stabilization amounted to 29, 46 and 47% for A, B and C mixture, respectively. Essential effect in terms of economics of the process of anaerobic stabilization is from the amount of generated biogas, which can be exchanged into electricity or used for heating fermentation chambers. This causes considerable reduction in the costs of maintaining sewage treatment plants. The highest total biogas production of 23.23 dm^3 was observed during the process of hybrid method carried out in fermentation chamber (25 days).

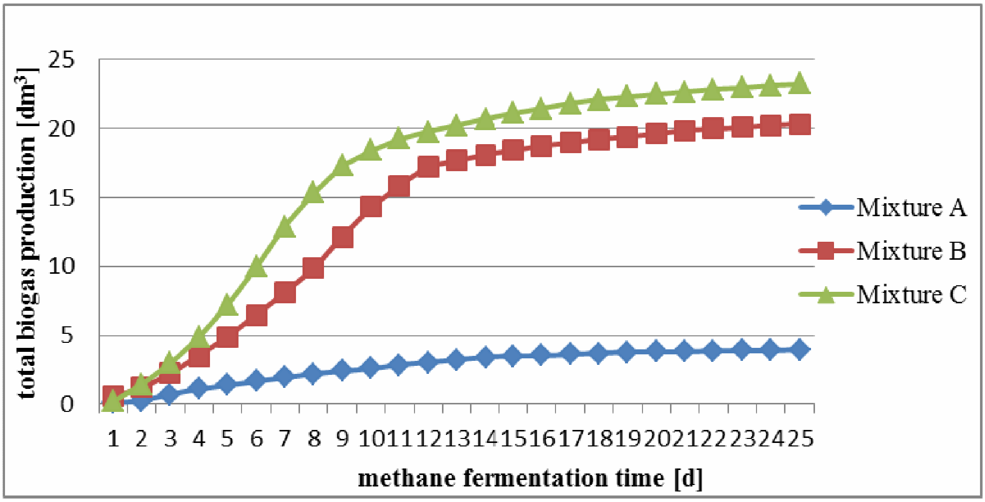

Fig. 5. The total biogas production in anaerobic stabilization process

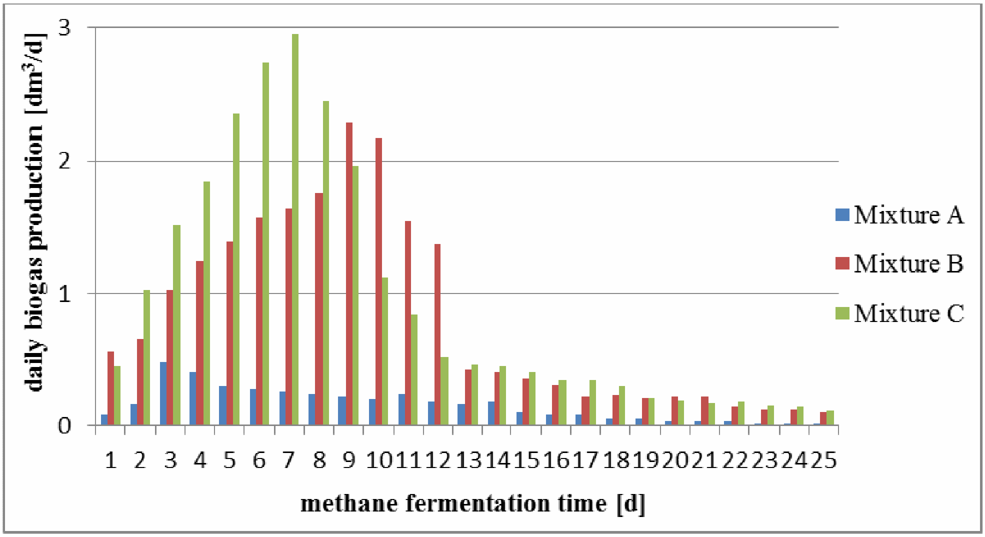

Fig. 6. Daily biogas production in anaerobic stabilization process

In the case of sludge conditioned with ultrasound field (mixture B), the total value of the obtained biogas amounted to 20.31 dm^3, whereas this value for non-prepared sludge was only 3.94dm^3. Total biogas production is compared in Figure 5.

The highest daily biogas generation (2.95 dm^3/d) was observed on the 7th day of the process for the sludge subjected to preparation with the hybrid method. In the case of the sludge conditioned with ultrasound field, the highest level of daily biogas generation (2.28 dm^3/d) was reported on the 9th day of the process. For non-conditioned sludge, the highest level of biogas generation per day was 0.48 dm^3/d. Daily biogas generation levels are presented in Figure 6.

A unit biogas generation was also calculated based on biogas generation. The highest value of unit biogas generation of 4.64 dm^3/g of *organic dry mass* (o.d.m.) was obtained in the case of hybrid method. Similar high value of unit biogas generation was observed in the sludge conditioned with ultrasound field (4.51 dm^3/g o.d.m.). Raw excess sludge exhibited unit biogas generation at the level of (1.13 dm^3/g o.d.m.).

Conclusions

The process of initial conditioning leads to an increased degree of excess sludge disintegration, which is reflected by an increase in concentration of organic compounds in sludge liquor. Increase in concentration of soluble organic matter contributes to intensification of hydrolytic phase of the process of methane fermentation. With an increase in the degree of fragmentation of solid phase of the sludge, their susceptibility to biodegradation is substantially increased.

The following conclusions can be drawn based on the results obtained in the study:

- Application of conditioning before the process of anaerobic stabilization facilitates operation of the separated chambers of fermentation, which provides benefits in the form of increased biogas generation, higher degree of sludge fermentation and shortening the process of methane fermentation.
- Both in the case of conditioning of sludge with ultrasound field and hybrid method, a considerable degree of fermentation and intensification of biogas production can be obtained.
- The investigations carried out using a hybrid method, where the highest levels of COD and VFA, degree of fermentation and increased biogas production were observed confirm the legitimacy and effectiveness of the selected method.

Acknowledgments

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WPŁYW TERMICZNO-ULTRADŹWIĘKOWEJ DEZINTEGRACJI OSADÓW NADMIERNYCH NA EFEKTYWNOŚĆ PROCESU STABILIZACJI BEZTLENOWEJ

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Abstrakt: Szacuje się, że przeróbka osadów ściekowych pochłania ok. 70% kosztów eksploatacyjnych oczyszczalni. Poddanie osadów wstępnych i wtórnych stabilizacji beztlenowej, uważanej za technologię zarówno przyjazną środowisku, jak również ekonomiczną, przyczynia się do znacznej minimalizacji masy osadów. Produkcja biogazu stanowi istotny czynnik zwiększający rentowność prowadzonego procesu fermentacji metanowej, ponieważ pozwala na częściowy odzysk kosztów ponoszonych na utrzymanie mezofilowych warunków fermentacji. Fermentacja metanowa to proces przebiegający wolno oraz wymagający długiego okresu zatrzymania osadów. Stopień upłynnienia nierozpuszczalnych polimerów organicznych do postaci rozpuszczonej, dostępnych dla mikroorganizmów, ma znaczący wpływ na szybkość biodegradacji osadów. Dezintegracja osadów nadmiernych wpływa na wzrost dyspersji cząstek osadów, co determinuje przyspieszenie procesu hydrolizy, limitującej przebieg stabilizacji beztlenowej. Zwiększenie szybkości wytwarzania LKT oraz wzrost ich wartości w kolejnych dobach kwaśnej fermentacji warunkuje bezpośrednio efektywność produkcji biogazu. W artykule przedstawiono wyniki badań dotyczące wpływu dezintegracji prowadzonej metodą hybrydową na efektywność 25-dobowej stabilizacji beztlenowej, tj. wzrost stopnia przefermentowania osadów oraz intensyfikację produkcji biogazu. Zastosowanie termiczno-ultradźwiękowej obróbki osadów nadmiernych wpłynęło na wzrost stopnia przefermentowania osadów, gdzie odnotowano ok. 60% usunięcie s.m.o. w odniesieniu do stabilizacji beztlenowej osadów surowych. Ponadto zaobserwowano wzrost intensywności produkcji biogazu, czego wyrazem była wartość jednostkowej produkcji biogazu wynosząca dla osadów poddanych modyfikacji metodą hybrydową 4,64 dm^3/g $s.m.o_u$, natomiast dla osadów surowych 1,1 dm^3/g $s.m.o_u$.

Słowa kluczowe: osady nadmierne, dezintegracja termiczno-ultradźwiękowa, stabilizacja beztlenowa, stopień przefermentowania osadów, jednostkowa produkcja biogazu

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CONCENTRATION OF BUTANOL-ETHANOL-ACETONE-WATER USING PERVAPORATION

ZATĘŻANIE UKŁADU BUTANOL-ETANOL-ACETON-WODA ZA POMOCĄ PERWAPORACJI

Abstract: The purposes, objectives and technology pathways for alternative energy are biofuels. The main interest so far has been focused on bioethanol due to the availability of raw materials as well as developed methods for separation and purification. Butyl alcohol can also be regarded as a potential biofuel, and used for internal combustion engines. Butanol can be obtained by means of chemical reaction as well as by fermentation of biomass well know as acetone-butanol-ethanol (ABE) fermentation. Separation of butanol from fermentation broth is a very difficult technical problem. The distillation process traditionally used is economically unprofitable. Review of methods for product recovery from fermentation broth indicates that pervaporation is a modern membrane technology which allows for the separation and concentration of the product during a single process. This work presents results of research on biobutanol separation from the acetone-butanol-ethanol-water system by pervaporation. The concentration of biobutanol was changed in the 0.25÷3 wt. % range. The quaternary system was prepared similarly to that obtained from the ABE fermentation process. The process was carried out on a flat, hydrophobic, commercial membrane at steady state conditions. The pressure at the permeate side was 30 mbar, the temperature range was 50÷70°C and feed flow rate was 20, 40 and 60 dm^3/h. The chemical constitution of permeate and retentate was analyzed by gas chromatography. Based on experiments, separation and enrichment factors of the organic phase for individual components were obtained. The mass fraction of individual components in the output flux was determined as well. Satisfactory performance of the analyzed system on the selected membrane was obtained.

Keywords: biobutanol, ABE fermentation, pervaporation

Biofuels are one of the alternative sources of energy. They have been used in the past since in the case the inception of the automotive industry, however low prices of crude oil lead to the reduction of use of biofuels. At present, the ever-increasing prices of crude oil and necessity of greenhouse emission reduction from fossil fuels shift the interest back to biologically produced biofuels. Biomass quality is not directly related to fuel calorific value but it affects the cost of manufacture. The main interest so far has been focused on bio-ethanol due to the availability of raw materials and well developed methods for separation and purification. Butyl alcohol can also be regarded as a potential biofuel, and used for internal combustion engines. As its properties are similar to petrol (see Table 1) butanol can be used as petrol additive. Relatively low heat of vaporization is one of its advantages as it facilitates engine start up at low temperatures. It is less susceptible to separate from petrol in the presence of water than ethanol [1]. Moreover, it contains less oxygen per mass unit and thus can be added to petrol at higher volumes. Typical blends of ethanol with petrol contain 5÷20% ethanol, while blends with butanol contain 8÷32% butanol.

Butanol can be obtained by means of chemical reaction as well as by fermentation of biomass well known as *Acetone-Butanol-Ethanol* (ABE) fermentation. Typical raw

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materials include sugar cane, corn or wheat but other cellulose containing materials could also be used such as wood waste, which would greatly decrease the cost of biobutanol production. The product of ABE fermentation is the acetone:butanol:ethanol aqueous solution with the 3:6:1 mass ratio, as a result of which butanol of the concentration of up to 3 wt. % is obtained. Separation of butanol from fermentation broth is a very difficult technical problem [2]. The distillation process traditionally used is not economically viable. Review of methods for product recovery from fermentation broth indicates that pervaporation is a modern membrane technology which allows for the separation and concentration of the product during a single process.

Table 1

A comparison of the properties of engine fuels [3]

Fuel	**Calorific value**	**Enthalpy of vaporization**	**Motor Octane Number**
	[MJ/dm^3]	**[MJ/kg]**	**[-]**
Petrol	32	0.4	81÷89
Butanol	29	0.7	78

Pervaporation is a separation technique which involves phase change combined with mass transfer across non-porous composite membrane. This technique, used for the dehydration of ethanol, involves hydrophilic membrane and water transport across the membrane [4]. In the case of ABE post-fermentation product, the organic fraction, mainly biobutanol is the component transported across the hydrophobic membrane. Literature provides examples of studies into *n*-butanol separation and recovery from aqueous solutions by *pervaporation* (PV) [5-8].

Materials and methods

The experimental part of the study presents results of research on biobutanol separation from the acetone-butanol-ethanol-water system by pervaporation. The model feed consisted of aqueous solution of three organic components, namely butanol, ethanol and acetone. The quaternary system was prepared similarly to that obtained from the ABE fermentation process (acetone:butanol:ethanol 3:6:1). The concentration of biobutanol was changed in the range of 0.25÷3 wt. %. The process was carried out on a flat, hydrophobic, commercial membrane PERVAP 4060 [9] using Sulzer Chemtech laboratory apparatus at steady state conditions (Fig. 1). The pressure at the permeate side was 3 kPa, the temperature range was 50÷70°C and the flow rate of feed was 20, 40 and 60 dm^3/h [10].

The chemical constitution of permeate and retentate was analyzed by gas chromatography using ThermoFinnigan apparatus and BTR-CW column. In most cases, due to the low solubility of *n*-butanol in water of approximately 8 wt. %, the permeate obtained was separated into two phases: lower, aqueous phase and upper, organic phase. To measure the concentration, the sample was additionally diluted with 5% aqueous methanol solution that was at the same time used as the internal standard, to the final *n*-butanol content of max. 10 wt. %. The obtained one-phase solution was examined by chromatography.

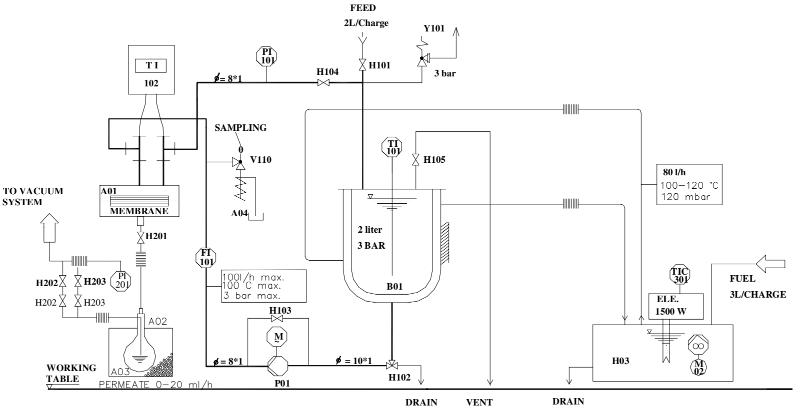

Fig. 1. Schematic diagram of the pervaporation equipment

Results

Based on the experiments, permeate weight and mass fractions of individual components in the permeate (w_{ip}) were obtained. The data was used to determine the total permeate flux (J_{tot}) and the mass fraction of individual components (J_i) in the output flux, according to the following formula:

$$J_i = J_{tot}\, w_{ip} \left[\frac{\text{kg}}{\text{m}^2\text{h}}\right] \tag{1}$$

where: J_i - partial flux of component i [kg (m^2 h)$^{-1}$], J_{tot} - total flux [kg (m^2 h)$^{-1}$], w_i - mass fraction of component i in the permeate (p) or feed (F) [-].

The separation (α_i) and enrichment (β_i) factors define membrane selectivity and allow for the comparison of pervaporation results on various membranes. The separation and enrichment factors of the organic phase for individual components were calculated using the following formulas:

$$\alpha_i = \frac{x_{ip}}{x_{iF}} \cdot \frac{1 - x_{iF}}{1 - x_{ip}} \tag{2}$$

$$\beta_i = \frac{x_{ip}}{x_{iF}} \tag{3}$$

where x_i - mole fraction of component i in the permeate (p) or feed (F) [-].

During the experiments, due to the varying mass content of the organic phase in the feed (with acetone:butanol:ethanol 3:6:1 ratio maintained at all times), various concentrations of the permeate were obtained. Figure 2 presents an exemplary relationship between the mass content of a selected component of the organic phase in the feed and the mass content of the same component in the permeate. Higher concentrations may be observed for lower content of the organic phase in the feed. Additionally, it was found that butanol tends to concentrate better (up to 25 wt. %) at lower temperatures and feed flow rates, as shown in Figure 3. The remaining components of the organic phase also diffused across the membrane. For acetone, the results were much more distributed for higher feed content of the component than for ethanol.

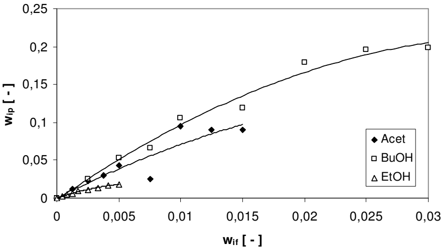

Fig. 2. Organic phase content in the permeate (w_{ip}) depending on its feed content (w_{if}) for processes carried out at T = 70°C and u = 20 dm^3/h

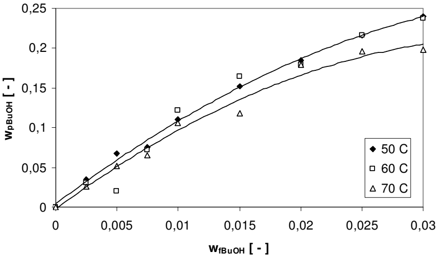

Fig. 3. Butanol content (BuOH) in the permeate (w_{pBuOH}) depending on its feed content (w_{fBuOH}) at various temperatures and feed flow rate of u = 20 dm^3/h

Total permeate flux increases with the increase of mass flow rate, feed temperature and feed content of butanol (Fig. 4). Figure 5 presents butanol fluxes in relation to the mass content of organic phase (butanol) in the feed averaged for several feed flow rates. Also here the fluxes are higher at higher operating temperatures and for the increased feed content of organic phase.

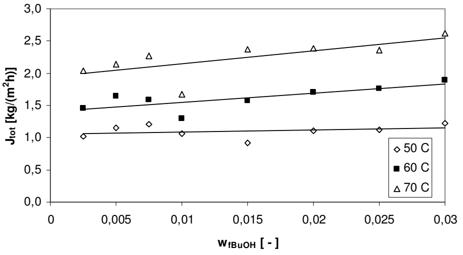

Fig. 4. Total mass flux of permeate (J_{tot}) depending on mass content of butanol in the feed for u = 60 dm^3/h

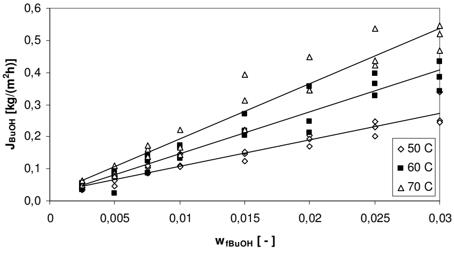

Fig. 5. Mass flux of butanol (J_{BuOH}) depending on mass content of butanol in the feed for various feed flow rates

Separation coefficient (α_i) for butanol calculated based on experimental data, and averaged for various feed flow rates ranges from 11÷15.5 at operating temperature of 50°C, 10÷14 at 60°C and 8.7÷12 at 70°C. The values are lower for other components. The mean selectivity for acetone, initially high for low content of the component and similar to the selectivity for butanol, significantly decreases with the increase of its content in the feed. Separation factor for ethanol remains virtually constant over the entire range of concentrations. Figure 6 presents the average separation factor of the organic phase (α_i) for various temperatures and flow rates depending on butanol mass content in the feed. The figure shows that the rate of permeation of individual components across the membrane was found to be in the order of butanol>acetone>ethanol. Butanol is thus the component which is preferentially diffused across the membrane.

The above results lead to the following conclusions concerning pervaporation process conditions: higher concentrations of organic components in the feed (butanol 2÷3 wt. %) ensure better separation of butanol from acetone. However, at the same time enrichment factor (β_i) is decreased with average values for butanol, acetone and ethanol of 10.5; 11.8 and 5.7, respectively. Feed flow rate had no decisive influence on result analysis.

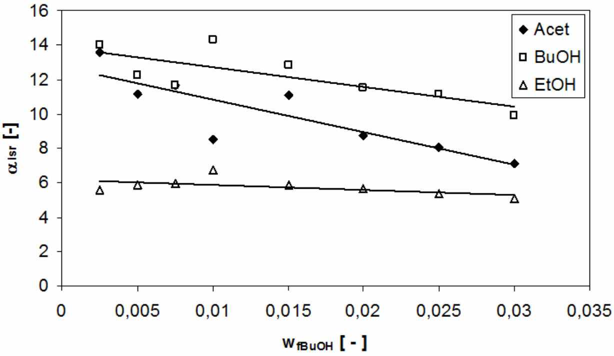

Fig. 6. Mean separation factor of the organic phase (α_i) for various temperatures and flow rates depending on butanol mass content in the feed

Conclusions

The experiments involving concentration of the model biobutanol system were aimed at analyzing pervaporation process to determine performance of the commercial membrane as regards the separation of aqueous and organic phases. The results analyzed within the range of butanol 0.25÷3 wt. % in the feed prepared at the same mass ratios of all of the components, namely acetone/butanol/ethanol/water confirm the dependence on flow rate and operating temperature. Transfer of organic phase, including butanol, across the membrane is higher for its lower content in the feed and lower temperatures despite higher fluxes. The studies into PERVAP 4060 membrane performance as regards pervaporative transfer and separation capabilities confirm its usability for the concentration of butanol following ABE fermentation.

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ZATĘŻANIE UKŁADU BUTANOL-ETANOL-ACETON-WODA ZA POMOCĄ PERWAPORACJI

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Abstrakt: Jednym z rodzajów alternatywnych źródeł energii są biopaliwa. Główna uwaga do tej pory skupiana była na bioetanolu ze względu na dostępność surowców i dobrze opracowane metody wydzielania i oczyszczania. Alkohol butylowy może być również traktowany jako potencjalne biopaliwo i wykorzystany do silników wewnętrznego spalania. Butanol można otrzymać zarówno z paliw stałych, jak również przez fermentację biomasy. Produktami fermentacji ABE jest wodny roztwór acetonu, butanolu i etanolu. Wydzielanie butanolu z brzeczki fermentacyjnej jest bardzo trudnym problemem technicznym. Tradycyjnie stosowana destylacja jest procesem energetycznie i ekonomicznie nieopłacalnym. Poszukiwane metody odzysku produktu z brzeczki fermentacyjnej wskazują na nowoczesną technikę membranową, jaką jest perwaporacja, która umożliwia separację i koncentrację produktu w trakcie pojedynczego procesu. Niniejsza praca pokazuje badania perwaporacyjnego zatężania biobutanolu z modelowego czteroskładnikowego układu aceton-butanol-etanol-woda, przygotowanego zgodnie z informacjami o produkcie po procesie fermentacji ABE w zakresie stężeń 0,25÷3% mas. butanolu. Proces prowadzony był na płaskiej, hydrofobowej membranie komercyjnej w sposób ciągły, w warunkach ustalonych, z ciśnieniem po stronie permeatu wynoszącym 30 mbar, w zakresie temperatur 50÷70°C i z natężeniem przepływu nadawy 20, 40 i 60 dm^3/h. Skład permeatu i retentatu był analizowany za pomocą chromatografii gazowej.

Słowa kluczowe: biobutanol, fermentacja ABE, perwaporacja

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EVALUATION OF EFFECTIVENESS OF BISPHENOL A REMOVAL ON DOMESTIC AND FOREIGN ACTIVATED CARBONS

SKUTECZNOŚĆ USUWANIA BISFENOLU A NA KRAJOWYCH I ZAGRANICZNYCH WĘGLACH AKTYWNYCH

Abstract: Wide use of bisphenol A (BPA) in production of polycarbonates and plastic food packaging cause increase of concentration of BPA in the environment. Both in surface water, underground water and seawater BPA was frequently detected in different concentrations. Emerging problem is adsorption of BPA on sewage sludge, because it could be considered as an additional source of pollution if it is used as a fertilizer in agricultural sectors. Absorbed BPA on sewage sludge stays persistent in the environment and generates adverse biological effects in endocrine system. Because of ecological safety, exploration of potential techniques to remove BPA to the level, which does not give adverse effect on natural environment is necessary. In this study the adsorption of BPA from simulated water onto commercial activated carbons was investigated. On the basis of experimental data the kinetics and type of sorption were determined.

Keywords: micropollutants, sorption, activated carbons

In recent years, increasing attention is focused on the presence of xenoestrogens in the aquatic environment, that degrade its quality and cause disturbances in endocrine system of living organisms. Among xenoestrogens one of the most prevalent is *bisphenol* A (BPA), which occurrence in the environment is connected with anthropogenic activity. BPA is mainly used for production of epoxy resin and polycarbonate plastics. Therefore, industrial and municipal wastewater and landfill leachates have to be considered as point sources of BPA. In recent works the presence of BPA have been documented in different matrices such as sewage sludge, effluents from wastewater treatment plant, river water and sediments soil. The results provided by Gibson et al from Mexico City wastewaters showed concentrations of BPA ranged from 0.77 to 2.5 μg/dm^3 [1]. The study conducted in Toronto reported widely divergent concentration of BPA in wastewater from different industrial sectors. Concentration of BPA ranged 0.08÷91.27 μg/dm^3, 0.75÷43.45 μg/dm^3, 0.1÷0.48 μg/dm^3 for wastewater from chemical products industry, commercial laundries, textile and clothing industries, respectively. Yamamoto et al determined concentration of BPA in some samples from hazardous waste landfill leachates with median concentration 269 μg/ dm^3 [2]. Latter publications reported concentration of BPA in municipal landfill leachates in the range 26÷8400 μg/dm^3 [3].

The significance of the problem of BPA in the environment is intensified by physicochemical properties of this compound such as low solubility, high hydrophobicity characteristics. These properties suggest that BPA has low biodegradability and accumulates in living organisms.

The influence of BPA presence even at low concentration in the environment can cause feminization of aquatic organisms, decrease in population fertility and survival of

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progeny. Wide ranging global studies have demonstrated that exposure to BPA, interfere endocrine system in diverse range of concentrations and the effects can be very unpredictable as a consequence of its ability to initiate numerous responses.

According to U.S. *Environmental Protection Agency* (EPA) BPA has been identified as an "exogenous" agent, that interfaces with synthesis, secretion, transport, binding action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction or behaviour.

Given the ecological safety it is advisable to develop effective technology of removal of BPA to the level, excluding their negative impact on the environment. Some investigations have indicated, that nanofiltration and reverse osmosis are efficient techniques to remove bisphenol A [4-7]. Adsorption is one of the simplest and widely used methods that can be applied to removal micropollutants from water. Adsorption potential of selected activated carbons were tested and found that BPA was effectively removed from aqueous solution [8, 9].

The aims of the study were (1) to compare the effectiveness of removal of BPA using selected activated carbons (2) determine adsorption behaviour of BPA (3) fit two kinetic models to analyze the experimental data.

Materials and methods

Characterization of the activated carbons

Two kinds of commercial powder activated carbons were tested. Carbon AKPA-22 (Gryfskand, Poland) and SX2 (Norit (R), USA) were used for the comparative adsorption experiments. Both of them are being used for water conditioning. The sorbents used in this study did not subject any extra treatment in order to replicate their application in commercial water treatment processes. BPA (purity > 99%) was purchased from Sigma-Aldrich (Poznan, Poland).

Adsorption experiments

In order to determine kinetics and isotherms, batch experiments in an orbital shaker at 180 r/min were conducted. In the adsorption kinetics experiments, the concentration of activated carbon was equalled at 30 mg/dm^3 and the initial concentration of BPA was at the level of 5 mg/dm^3. At predetermined time intervals, the samples were filtered in order to separate sorbents from solution of BPA.

Isotherms studies can be investigated by varying the initial concentration of adsorbate [10] or the sorbent amount [11]. In this study, the sorbent concentrations were changing in the range from 10 to 120 mg/dm^3 and the initial concentration of BPA was equalled at 15 mg/dm^3. The experiments were conducted under ambient conditions. The flasks were put in a shaker for 3 h. After finishing experiments, sorbents were separated from BPA solution. The concentration of BPA was determined using phenol cell test (photometric method, MERCK). The amount of BPA absorbed onto activated carbons was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot v}{m} \tag{1}$$

where q_e [mg/g] is equilibrium adsorption amount, C_0 and C_e [mg/dm^3] are the initial and equilibrium concentration of BPA, and m [g] is the mass of sorbent.

Results and discussion

Removal efficiency of BPA

In this part the efficiency of BPA removal for AKPA-22 and SX2 was compared. The results of this comparative study were illustrated on the Figure 1. The removal efficiency of BPA was in the range 9.6÷85.7 and 12.6÷82.7% at the dosage change from 10 to 110 mg/dm^3 for AKPA-22 and SX2, respectively. In lower dosages of sorbents using SX2 showed little higher level of removal of BPA than AKPA-22. However in high dosages of sorbents reverse tendency was observed, higher removal of BPA was observed on AKPA-22 than on SX2. Overall, this study shows that both sorbents have ideal performance for removal bisphenol A from aqueous solutions.

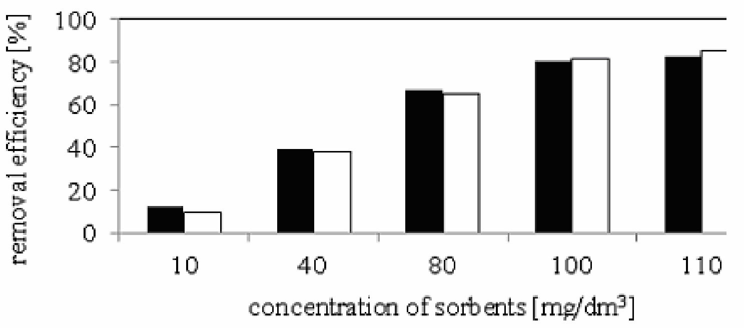

Fig. 1. The removal efficiency of BPA depending on dosage of sorbents (AKPA-22 (□), SX2 (■))

Adsorption kinetics of BPA

In order to determine the adsorption kinetics of BPA, the experimental data were analyzed using pseudo-first-order and pseudo-second-order kinetic models, which were given in the equation (2) and (3) respectively:

$$\frac{\ln(q_e - q_t)}{q_e} = -K_1 t \tag{2}$$

$$\frac{t}{qt} = \frac{1}{K_2 q_{e2}^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the amount of BPA adsorbed at equilibrium and at time (t), K_1 and K_2 are the pseudo-first-order and pseudo-second-order constants respectively. Furthermore on the basis pseudo-second-order model were calculated the half adsorption time ($t_{1/2}$) and the initial adsorption rate (h) according to following equations:

$$t_{\frac{1}{2}} = \frac{1}{k_2 \cdot q_e} \tag{4}$$

$$h = k_2 q_e^2 \tag{5}$$

Figure 2 shows adsorption of bisphenol A onto selected activated carbons versus time. Both curves resemble the same trend, however the equilibrium time of BPA onto AKPA-22 was shorter than onto SX2 and were equalled 180 min and 270 min, respectively. This means that addition of BPA onto surface of AKPA-22 was faster than SX2. The Figures 3 and 4 present the results of fitting experimental data with kinetic models. The adsorption kinetic parameters listed in table 1 show that the pseudo-second-order model fitted better the experimental data than pseudo-first-order model both for AKPA-22 and SX2. The adsorption capacity calculated from pseudo-second-order model ($q_{e(cal)}$) also corresponds well with the experimental data ($q_{e(exp)}$). The higher rate constant, lower time required for half of q_e of BPA to be absorbed of AKPA-22 confirm better adsorption of BPA than SX2.

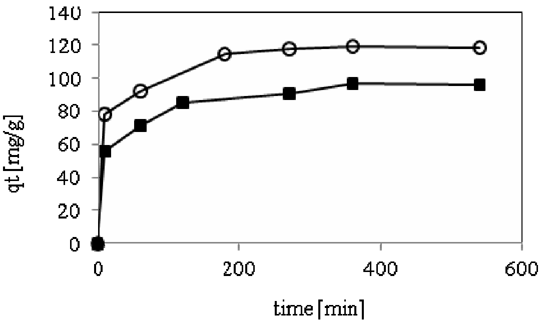

Fig. 2. Time-resolved uptake of BPA onto AKPA-22 (○) and SX2 (▪)

Table 1

Adsorption rate constants rate for two kinetic models

Adsorbent	**Pseudo-first-order equation**				**Pseudo-second-order equation**			
	K_1 [1/min]	**R^2**	**K_2 [g/(mg·min)]**	**$q_{e2(exp)}$ [mg/g]**	**$q_{e2(cal)}$ [mg/g]**	**$t_{1/2}$ [min]**	**h [mg/(g·min)]**	**R^2**
AKPA-22	0.0106	0.921	0.001	118.7	120.48	8.3	14.51	0.9992
SX2	0.0019	0.8049	0.00085	97	98.03	12	8.16	0.9981

Adsorption isotherms of BPA

The isothermal data were fitted to Freundlich and Langmuir models according to their linear equation. The equations are as follows:

The Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where K_F [mg(dm^3/mg)$^{1/2}$/g] is the Freundlich constant reflects the bonding energy, the parameter $1/n$ with value between 0÷1 describes adsorption intensity or surface heterogeneity; q_e [mg/g] and C_e [mg/dm^3] are the uptake capacity and the equilibrium concentration, respectively.

The Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{7}$$

where q_e [mg/g] and C_e [mg/dm^3] are the uptake capacity and the equilibrium concentration respectively. K_L [dm^3/mg] is the Langmuir constant and q_m [mg/g] is the maximum adsorption capacity.

The parameters of models are summarized in Table 2 only for AKPA-22 because in case of SX2 bad fitting was obtained. This indicated that Langmuir and Freundlich models are not sufficient to describe adsorption of BPA onto SX2 and the another mixed models were needed for this isotherms. Compared with Langmuir model, Freundlich model fitted the experimental data better because the R^2 values were higher for Freundlich than Langmuir models for sorbent AKPA-22. The Langmuir theory assumes monolayer adsorption where molecules interact only with the surface of sorbent. On the other hand Freundlich theory describes multilayer coverage where molecules interact with the surface of sorbent and then with each other. The high value of R^2 demonstrates that BPA forms multimolecular layer on the surface of AKPA-22. The $1/n$ value was less than 1 indicating a favorable adsorption system and heterogenity of the sorbent adsorption sites.

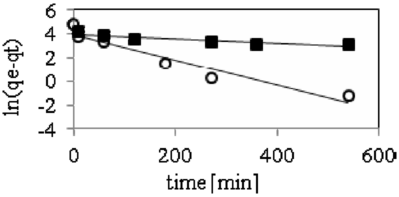

Fig. 3. Simulation of BPA adsorption onto AKPA-22 (○) and SX2 (▪) by means of pseudo-first-order kinetics

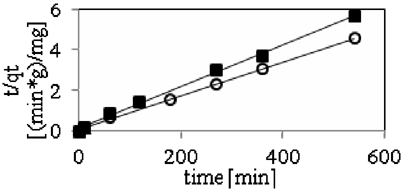

Fig. 4. Simulation of BPA adsorption onto AKPA-22 (○) and SX2 (▪) by means of pseudo-second-order kinetics

Table 2

Fitted parameters using Freundlich and Langmuir models for adsorption of BPA by AKPA-22 and SX2

Adsorbent	**Freundlich model**		**Langmuir model**	
	K_F **[mg(dm^3/mg)$^{1/2}$/g]**	**1/*n***	K_L **[dm^3/mg]**	q_m **[mg/g]**
AKPA-22	97.49	0.12	2.37	131.57

Conclusions

1. The study indicated high removal efficiencies of BPA using both sorbents (AKPA-22, SX2).
2. The kinetics data fitted better with the pseudo-second-order model than pseudo-first-order model fitted.
3. Adsorption of BPA on AKPA-22 was much faster than on SX2.
4. Adsorption isotherms fitted better with the Freundlich model than the Langmuir model.

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SKUTECZNOŚĆ USUWANIA BISFENOLU A NA KRAJOWYCH I ZAGRANICZNYCH WĘGLACH AKTYWNYCH

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Abstrakt: Masowe wykorzystywanie *bisfenolu* A (BPA) do produkcji tworzyw sztucznych i opakowań na żywność powoduje wzrost stężenia tego związku w środowisku. Zarówno wody powierzchniowe, podziemne, jak i morskie ulegają coraz większemu skażeniu bisfenolem A. Niepokojący jest fakt, że BPA obecny w ściekach w znacznym stopniu ulega sorpcji na kłaczkach osadu czynnego, co wskazuje na dodatkowe źródło zanieczyszczenia środowiska tym związkiem. Zasorbowany na osadzie bisfenol A trwale pozostaje w środowisku, wywołując niekorzystne efekty biologiczne głównie o charakterze hormonalnym. Zagrożenie, jakie stanowi ten związek, powoduje konieczność poszukiwania efektywnych metod jego usuwania. W pracy podjęto próbę usunięcia BPA z roztworów wodnych na krajowych i zagranicznych węglach aktywnych. Na podstawie danych doświadczalnych wyznaczono kinetykę i typ procesu sorpcji.

Słowa kluczowe: mikrozanieczyszczenia, sorpcja, węgle aktywne

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Aleksandra PŁATKOWSKA-SIWIEC[1] and Michał BODZEK[1]

INFLUENCE OF NATURAL ORGANIC MATTER (NOM) ON FOULING AND ULTRAFILTRATION MEMBRANES PROPERTIES - AFM ANALYSIS

WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN ULTRAFILTRACYJNYCH - ANALIZA AFM

Abstract: Low pressure membrane processes *ie* microfiltration and ultrafiltration are widely applied in water and wastewater treatment. The main exploitation problem connected with those technologies is the decrease of membrane capacity during the process caused by blocking of membrane pores with organic and inorganic substance (so-called fouling). The performance of atomic force microscopy analysis enables quantitative determination of membranes roughness and allows to characterize membrane surface before and after fouling. The paper discuss results of filtration of three surface waters differ in properties, mainly in specific UV absorbance ($SUVA_{254}$).

Keywords: fouling, ultrafiltration, natural organic matter, atomic force microscopy

Ultrafiltration is one of the low pressure membrane techniques applied in drinking water production. The method allows to remove colloids and high molecular weight substances from treated medium. However, a decrease of the permeate flux during the membrane filtration is one of the most important operating problems. *Natural Organic Matter* (NOM) interacts with membrane surface and pores and induces its fouling [1].

Except for organic substances, the type of a membrane also has a significant influence on fouling extent. Both, adsorption properties connected with hydrophobicity and electrostatic repulsion forces resulted from membrane material and foulant charges are considered [2].

Specific UV absorption (SUVA) can be used as a parameter describing hydrophobicity or aromaticity of NOM present in water [3]. However, chemical parameters of water ie pH, ionic strength and concentration of calcium ions can affect SUVA value [4]. The low value of SUVA indicates great concentration of non-humic fraction of organic matter present in water. The high value of SUVA indicates great concentration of aromatic compounds [5, 6].

To determine the structure of a membrane various microscopic techniques are used [7, 8] eg *Scanning Electron Microscope* (SEM), *Transmission Electron Microscope* (TEM), *Field Emission Scanning Electron Microscopy* (FESEM) and *Atomic Force Microscopy* (AFM). The performance of atomic force microscopy analysis enables quantitative determination of membranes mean roughness (R_a) and mean square roughness (R_q). It allows to characterize membrane surface before and after fouling occurrence [9].

The wettability with distilled water is the significant membrane parameter. Hydrophobicity/hydrophilicity can be described by the measurement of the contact angle

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between the water drop and the membrane surface [5]. It is stated that the membrane is highly hydrophilic if the contact angle equal to 0° (complete wetting) and highly hydrophobic for the contact angle above 90° (no wetting) [10, 11]. To sum up, the greater contact angle the more hydrophobic membrane.

The aim of the study was to determine the influence of NOM on both, ultrafiltration membranes properties and the intensity of fouling. The effect of NOM on the retention coefficients of organic contaminants was also investigated.

Materials and methods

Experiments were carried out in MilliporeCDS10 (Millipore&Amicon), dead-end type stirred UF cell, using a feed volume of 2000 cm^3. The process pressure was maintained at 0.1 MPa and temperature was 20°C. The diameter of the membrane disc was 76 mm.

The experiments were conducted using *polyether-sulphone* (Millipore) (PES), *polyacrylonitrile* (PAN), *polysulphone* (PS), *poly(vinylidene fluoride)* (PVDF) (KOCH Membrane Systems) and *cellulose acetate* (GE Osmonics Labstore) (CA) membranes. The nominal molecular weight cut off (MWCO) was 10, 20, 10, 30 and 20 kDa for PES, PAN, PS, PVDF and CA, respectively.

Measurements of contact angle were performed using the goniometer (Pocket Goniometer PG-1) and the sessile drop method was applied. The angle between drop of water, membrane surface and air was measured according to Yoon et al [12]. The obtained contact angles were 73.1 ± 5°, 65.7 ± 4.5°, 63 ± 2.4°, 49.6 ± 4.9° and 39.1 ± 5° for PES, PAN, PS, PVDF and CA, respectively. This allowed to classify membrane materials as ranging between strongly hydrophobic and strongly hydrophilic. CA membrane was found to be the most hydrophilic and PES membrane as the most hydrophobic.

Pictures of membranes surface were made using contact atomic force microscope. Membranes, after preliminary drying were placed on a metal plate which was next placed in the microscope. Pictures were registered for sectors of dimensions 50x50 µm and 5x5 µm. The setpoint varied at ranges 5.725÷–2.725, –4.65÷–2.5, –2.475÷0, –4.075÷–3.050 and –3.875÷–3.3V for CA, PVDF, PS, PAN and PE membranes, respectively. The scan rate was equal to 5.086 Hz for all membranes.

Prior to the first use, the membranes were conditioned according to the manufacture protocol using Milli-Q water. The new membrane was used for each filtration. Fluxes of distilled water J_m (t = 20°C) were 98.7÷311.2, 52.4÷81.0, 39.92÷105.72, 44.6÷70.71 and 32.7÷39.6 dm^3/m^2h for PES, PAN, PS, PVDF and CA, respectively.

In the membrane filtration three different surface water samples were used. Zabie Doly - "Zabie D" is a nature and landscape protected area in the centre of the highly-urbanized region of Upper Silesia (Poland). The second water "Lasek S" was sampled from a lake located in the forest (Piasniki district in Swietochlowice, Upper Silesian Region). The third water sample "Las P" originated from a lake located in the forest in the town of Poraj (near Czestochowa, Poland). The lake is a hydrographic basin of the surrounding forest.

The concentration of NOM in the feed and permeate was measured as TOC (*Total Organic Carbon*), DOC (*Dissolved Organic* Compounds) and by UV absorbance at λ = 254 nm (UVA_{254}). SUVA was calculated as the ratio of UVA to DOC. The conductivity and pH were also measured.

Moreover, in order to measure the particulate fouling potential of feed waters for low pressure membranes, the *Unified Membrane Fouling Index* (UMFI) was determined. UMFI value can be assigned from the dependence between normalized membrane specific flux and unit permeate capacity, regardless of hydrodynamic process conditions [13, 14].

Results and discussion

The pH, UVA, DOC and SUVA of natural waters are shown in Table 1.

Table 1

Feed water characteristics

Sample	**pH**	**κ[μS/cm]**	**DOC [mg/dm^3]**	**TOC [mg/dm^3]**	**UVA$_{254}$ [1/cm]**	**SUVA [m^2/gC]**
Zabie D	6.90±0.02	907.7±2,5	13.40±0.22	13.40±0.31	0.099±0.000	0.74
Lasek S	6.96±0.03	260.8±2.5	10.65±0.24	12.67±0.07	0.240±0.001	2.25
Las P	6.52±0.03	82.6±2.5	8.90±0.24	18.10±0.35	0.304±0.002	3.43

The water from Las P (SUVA values close to 4) indicated that NOM is dominated by high molecular weight, hydrophobic humic acid fractions. For water form Lasek S, SUVA ratio was in the range 2-4, what means that NOM is dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights, humic and fulvic acids. For raw waters with SUVA below 2 (Zabie D), NOM is normally dominated by mostly non-humic, low molecular weight substances of low hydrophobicity [3].

Table 2

Retention coefficients of TOC and DOC

Sample	**Zabie D**					**Las S**					**Las P**				
Membrane	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA
R_{TOC} [%]	7.79	22.95	10.99	9.00	12.51	37.43	27.53	37.18	32.68	26.04	58.92	48.02	58.37	64.30	45.98
R_{DOC} [%]	8.13	23.23	11.32	8.75	12.84	18.55	21.08	21.34	18.11	19.46	12.41	8.55	11.24	4.16	29.30

The highest retention of organic compounds was obtained for Las P water regardless the membrane applied, next for Las S water and the lowest for Zabie D water (Table 2). It was probably caused by the highest difference between TOC and DOC concentration of Las P water (Table 1). The retentions of DOC did not exceed 30%. Similar values were obtained during filtration of Las S water (characterized with the most heterogenic composition) regardless the membrane used. Moreover, these were the greatest values of R_{DOC} obtained for particular membranes. The only exception was the retention of DOC obtained for Las P water during filtration with CA membrane. The highest value of retention coefficient was probably caused by the adsorption of positively charged particles on negatively charges membrane surface.

The main advantage of using UMFI over other fouling indices is its universality *ie* it is independent of filtration scale or mode [14]. Figure 1 depicts the values of UMFI for each filtration. In case of Zabie D and Las S waters the fouling of membranes follows the trends: PES>PS>PVDF>CA. This is in agreement with pervious consideration of Zularisam et al [2] for membrane-foulant interactions. The hydrophobic membranes (PES) tended to foul more than hydrophilic membrane (CA). It was ascribed to the electrostatic interaction occurring between negatively charged functional group of NOM and the membrane (positively) charged polymer [15, 16] of hydrophobic membrane (PES, PAN). Natural organic matter present in Las P water caused the smallest fouling of intensity comparable for all membranes. It could result from a significant share of non-dissolved organic compounds, which deposited on the membrane and acted as a protective layer for membrane pores. The highest fouling was observed in all cases for Las S water. The SUVA value calculated for this water indicated the content of both aromatic and aliphatic substances, which confirmed the significant influence of foulant-foulant interaction on fouling.

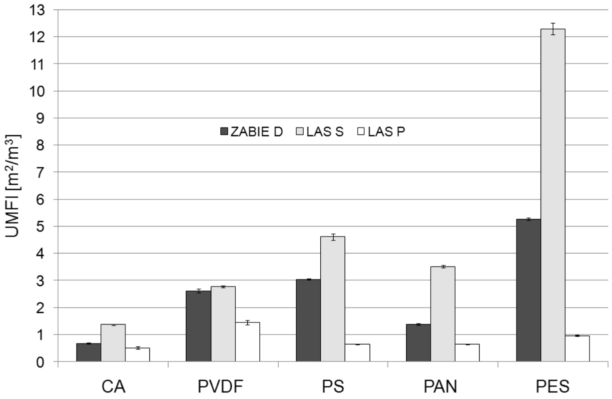

Fig. 1. Calculated UMFI indexes

Mean roughness (R_a) and mean square roughness (R_q) of clean and used membranes measured for both sectors (50 x 50 μm) are shown in Figure 2. The highest values of both, mean roughness and mean square roughness were obtained for PAN membrane. Its surface was the most diversified considering geometry, thus the smaller membrane sectors (5 x 5 μm) showed unrealistic pictures (Fig. 3). For this reason, membrane sectors of 50 x 50 μm were used for analysis. The smallest roughness was observed for PES membrane. However, irregularities sporadically appearing on its surface could have been seen.

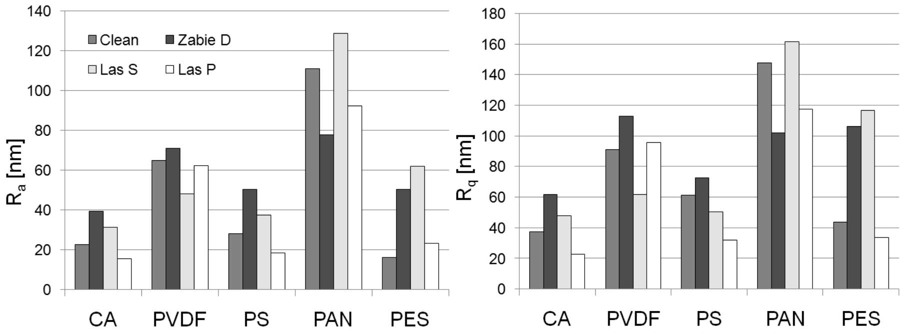

Fig. 2. R_a and R_q of new and used membranes sector 50 x 50 μm

The increase of both, mean roughness and mean square roughness was observed after filtration of Zabie D water for all membranes except for PAN membranes. Zabie D water characterized with high content of mineral substances (Table 1), which could partially crystallize on membranes surface increasing the roughness. In case of PAN membranes those compounds could penetrate its irregular surface and caused its smoothing. Moreover, non-aromatic organic compounds present in Zabie D water could also adsorb on membrane surface. The smoothing of membranes surface and the decrease of mean square porosity were observed after filtration of Las P water except for PES membrane. Non-dissolved organic compounds affected the irregularity of more rough membranes, on the other hand caused the roughness increase of the smoother membrane (PES), thus its surface became more uniform (lower R_q). The filtration of Las S water resulted in the increase of R_a and R_q of CA, PAN and PES membranes. The increase of R_a was also observed for PS membranes, however its surface became more uniform than before the filtration (lower R_q). The surface of PVDF membrane became smoother and more uniform. The differences between changes in membranes surface can result from water heterogeneity.

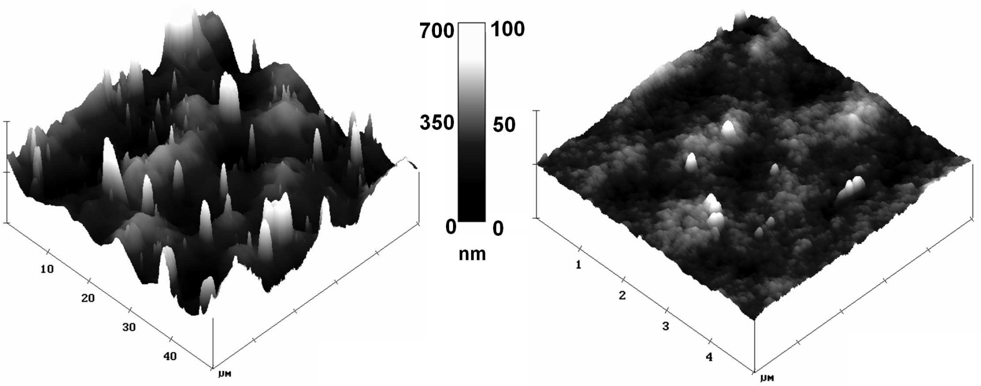

Fig. 3. The comparison of surface for different sectors of PAN membrane

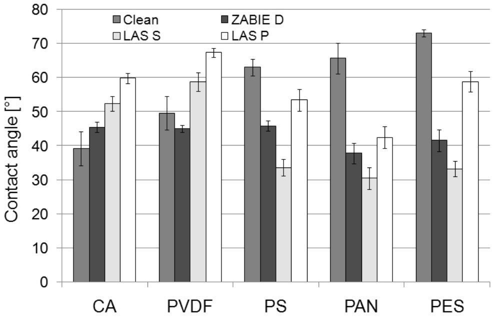

Fig. 4. Changes of contact angle of the new and used membranes

Fouling affected also membranes wettability. The observed changes in contact angle values are shown in Figure 4. The increase of hydrophobic character of membranes for which the initial contact angle was below 50° was stated regardless the water type. Opposite phenomenon was observed for membranes of contact angle above 63°.

Conclusions

The mechanism of spherical exclusion is significant during TOC removal, while for DOC removal foulant-folulant interaction and adsorption on the membrane are of the greatest importance.

Hydrophobic membranes (eg PES) tends to foul more than hydrophilic ones (eg CA). Such a tendency is not observed for waters in which the difference between TOC and DOC content is high. Such waters caused smaller fouling as non-dissolved particles deposit on membrane surface forming a protective layer for membrane pores. The highest fouling is caused by water for which SUVA value indicates the presence of both aromatic and aliphatic substances, what confirmed the significant impact of foulant-foulant interactions on fouling.

Substances retained on a membrane significantly affect its properties ie wettability and roughness. Depending on water and initial membrane properties the roughness can increase or decrease. Membranes of small roughness reveal the greatest ability to foul during filtration of low and medium SUVA value waters. In case of Las P water the difference between TOC and DOC content seems to be the more important property than the type of organic substance. This water causes the greatest fouling of membrane of high mean roughness and medium mean square roughness.

Acknowledgements

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WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN - ANALIZA AFM

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Abstrakt: Niskociśnieniowe techniki membranowe, ultrafiltracja i mikrofiltracja, stosowane są do oczyszczania i uzdatniania wody. Głównym problem eksploatacyjnym jest zmniejszanie wydajności membrany w trakcie procesu, związane z blokowaniem porów przez substancje organiczne i nieorganiczne (tzw. fouling). Analiza mikroskopem sił atomowych (AFM) umożliwia ilościowe określenie chropowatości powierzchni membrany, co pozwala scharakteryzować powierzchnię membran przed i po foulingu. W artykule przedstawiono wyniki filtracji trzech wód powierzchniowych różniących się głównie specyficzną absorbancją w nadfiolecie ($SUVA_{254}$).

Słowa kluczowe: fouling, ultrafiltracja, naturalne substancje organiczne, mikroskop sił atomowych

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APPLICATION OF MEMBRANE PROCESSES IN TREATMENT OF SLURRY FROM HIGH-DENSITY PIG FARMING

ZASTOSOWANIE PROCESÓW MEMBRANOWYCH DO OCZYSZCZANIA GNOJOWICY POCHODZĄCEJ Z WIELKOPRZEMYSŁOWEJ HODOWLI TRZODY CHLEWNEJ

Abstract: The aim of the study was to determine the effectiveness of integrated system: ultrafiltration and two-step reverse osmosis to recover water from pig slurry. The natural separation *ie* sedimentation and floatation were used to prepare feed for membrane treatment. Obtained supernatant was introduced to pilot scale installation for membrane filtration equipped with ceramic UF membrane of pore size 5 nm. The cleaned stream was polished on polyamide RO membranes. The capacity of the process and the quality of cleaned streams were used to evaluate the effectiveness of the treatment. Washing of the ceramic membrane via back flushing with water and chemicals ie 0.5% solutions of sodium hydroxide and nitric acid was also performed. The study revealed that proposed system was suitable to recover water from pig slurry. The final product is of good quality and can be reused on farms eg for washing of animals, farmhouses or in heating/cooling systems. The additional advantage is the concentration of organic compounds and nutrients in the form of retentate, which can be still used for fertilization or agricultural biogas production.

Keywords: pig slurry, ceramic ultrafiltration, reverse osmosis, slurry treatment

Slurry is produced during non-bedding livestock farming on industrial farms. It is a liquid mixture of animal feces, urea and technological water [1, 2]. Slurry properties are depended on various factors among which number and age of animals, type of a feed, amount of water used for washing of farmhouses and animals, storage method, season and atmospheric conditions are the most important [3, 4].

Slurry management and utilization methods need to be developed and improved. Nowadays, slurry is mainly used for fertilizing purposes (ca 30% of total production), and, in much lower extent, for biogas and compost production. The attention of slurry management methods discussed in literature is usually focused on nutrients ie nitrogen and phosphorus or organic matter recovery [5-7], while the possibility of water production is omitted. The amount of water in slurry can reach up to 99%, thus it can be considered as a source of useable water. Such an assumption can be pursued with the application of membrane processes, which are already widely used in water and wastewater treatment [8, 9]. Low-pressure membrane processes *ie* micro- and ultrafiltration practically guarantee the rejection of microorganisms, what results in production of sanitary safe fertilizing stream. Moreover, their combination with high-pressure membrane techniques ie nanofiltration and reverse osmosis can result in the recovery of water of useable quality [10-13].

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The aim and the methodology of the study

The aim of the presented study was to determine the effectiveness of integrated system comprised of ultrafiltration and two-step reverse osmosis to recover water from pig slurry. The natural separation processes *ie* sedimentation and floatation were used to prepare feed for membrane treatment. Obtained supernatant was introduced to the pilot scale installation for membrane filtration. The system was equipped with ceramic, tubular, ultrafiltration membrane of separation area 0.2 m^2 and pore size 5 nm (by Pall).The process was carried out at the pressure 0.3 MPa. The cleaned stream *ie* permeate was next introduced to laboratory membrane installation KMS Cell CF1 (by Koch) and polished on flat sheet, polyamide reverse osmosis membranes of effective separation area 28 cm^2 (by Koch). The polishing operation comprised of two-steps which were carried out at pressure 2.0 MPa. The capacity of the process and the quality of cleaned streams were used to evaluate the effectiveness of the treatment. Additionally, washing of the ceramic membrane via back flushing with water and chemicals *ie* 0.5% solutions of sodium hydroxide and nitric acid was performed and the initial flux recovery was established.

Following parameters were determined in all process streams: pH, conductivity, dry mass, COD, TOC, TC, N_{tot}, $N\text{-}NH_4^+$, $P\text{-}PO_4^{3-}$, Cl^-, SO_4^{2-}. COD, concentrations of $P\text{-}PO_4^{3-}$, N_{tot} and $N\text{-}NH_4^+$ were determined according to Hach Lange methodology. Concentrations of Cl^- and SO_4^{2-} were measured using ionic chromatograph DX 120 by Dionex. Particular forms of carbon were analyzed with the use of Multi N/C analyzer by Jena Analytic.

Results and discussion

Membranes performance

In Figures 1-3 the comparison of water and slurry fluxes measured for membranes (1) before the slurry treatment (deionized water) (2) during treatment (slurry) (3) after treatment (deionized water) (4) after chemical cleaning (deionized water - only for ceramic membrane) is shown.

It was observed that the filtration of slurry caused a significant decrease of UF membrane capacity (the ratio of slurry flux to initial deionized water flux - 0.7%) (Fig. 1). The measurement of water flux after the treatment process preceded with 1-hour backflushing with water showed 12% recovery of the initial value. It indicated on the irreversible character of membrane fouling caused mainly by the deposition of impurities in membrane pores. Thus, the membrane was cleaned chemically using 0.5% solutions of, first, sodium hydroxide and, next, nitric acid. Every washing step was carried out for 15 minutes. It allowed to recover 70% of the initial membrane capacity.

The filtration of permeate from UF also caused the decrease of 1st step RO (*Reverse Osmosis*) membrane capacity (23% of initial value) (Fig. 2). However, simple flushing of membrane with water enabled the total capacity recovery. Moreover, the measured water flux after the process was higher than the initial one. It could have been caused by several reasons. Firstly, only the reversible membrane fouling occurred and impurities were deposited on membrane surface forming washable filtration cake. Secondly, adsorption of some compounds (either organic or inorganic) could have modified membrane surface increasing the hydrophilicity of membrane material. Thirdly, the diffusion of compounds through the membrane could loosen its polymeric structure.

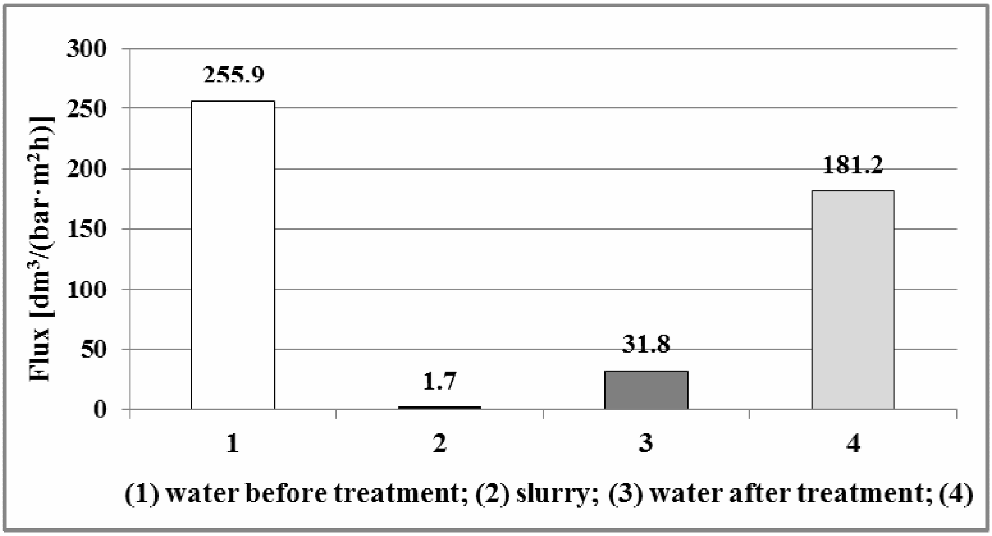

Fig. 1. Fluxes measured for ceramic UF (ultrafiltration) membrane

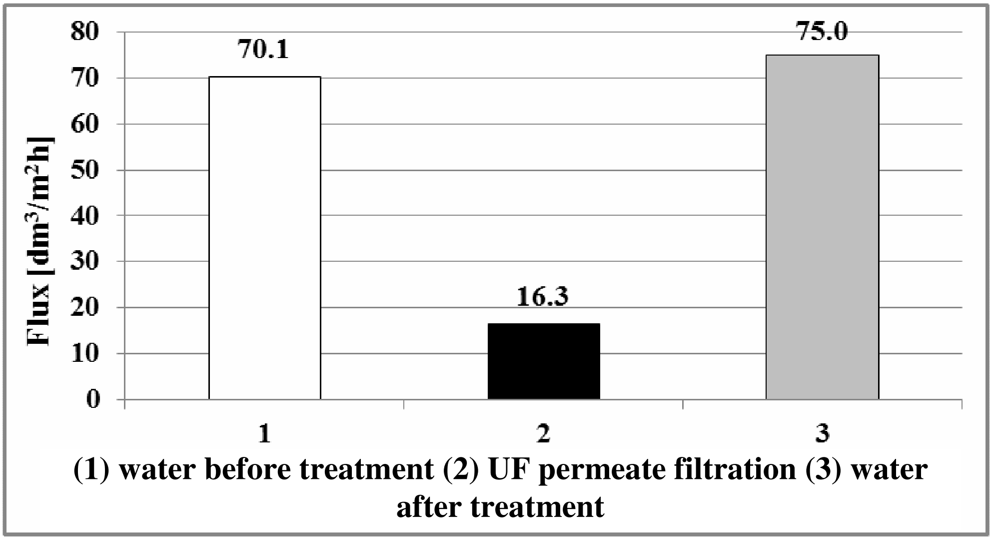

Fig. 2. Fluxes measured for polyamide 1st step RO membrane

The final polishing of treated slurry via 2nd step RO caused the lowest decrease of membrane capacity (83% of initial value) (Fig. 3). The flushing of membrane with water enabled almost 98% of initial capacity recovery. In case of this membrane, water flux after the process was slightly lower than at the beginning. As higher molecular weight compounds were already removed during the 1st step RO treatment the formation of protective filtration cake layer was limited. Besides, smaller particles did not affect membrane structure. Thus, slight membrane fouling occurred.

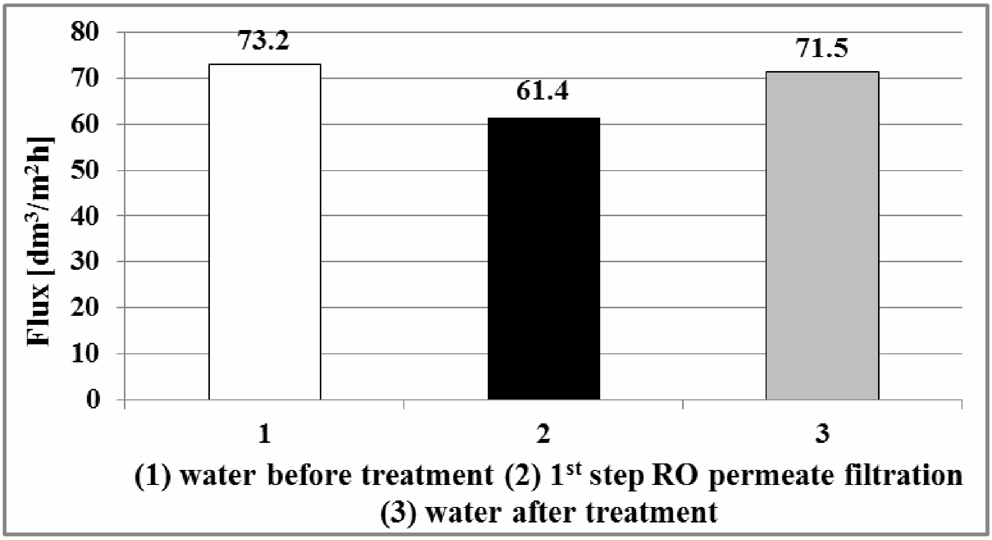

Fig. 3. Fluxes measured for polyamide 2nd step RO membrane

Quality of process streams

In Table 1 the comparison of crude slurry, supernatant and cleaned process streams including retention rates is shown.

Table 1

Comparison of process streams parameters

Parameter	Unit	CS	SN	R [%]	UF P	R [%]	RO1 P	R [%]	RO2 P	R [%]
pH	-	5.98	6.08	-	6.37	-	6.47	-	8.65	-
Cond.	[mS/cm]	18.8	18.1	-	16.3	-	1.6	-	0.062	-
COD	[g/dm^3]	38	29	23	18	39	0.953	95	<5	99
$N\text{-}NH_4$	[mg/dm^3]	2095	1961	6	1490	24	126	92	7.8	94
N_{tot}	[mg/dm^3]	2550	2367	7	1560	34	178	89	9	95
$P\text{-}PO_4$	[mg/dm^3]	695	578	17	354	39	5.2	99	0	100
Cl^-	[mg/dm^3]	1022	1004	2	951	5	164	83	2	99
SO_4^{2-}	[mg/dm^3]	300	294	2	284	3	8	97	0	100
TC	[mg/dm^3]	11871	8904	25	4390	51	227	95	4.24	98
TOC	[mg/dm^3]	11508	8779	24	3821	56	202	95	2.1	99
d.m.	[%]	4.2	1.4	67	0.7	51	n/a	n/a	n/a	n/a

CS - crude slurry, SN - supernatant, P - permeate, R - retention rate, n/a - not analyzed; d.m. - dry matter

It was found that natural separation processes *ie* sedimentation and flotation already caused the reduction of COD, phosphates and carbon concentrations. Ultrafiltration influenced mainly on organic compounds and phosphates content. Besides, the decrease in ammonium nitrogen was observed what was related to the emission of the compound during the treatment. The retention rates obtained for 1st RO step were in the range of 83% (Cl^-) to 99% ($P\text{-}PO_4$). Despite such high impurities rejection the quality of the permeate was still poor, thus it was decided to polish it via 2nd RO step. The retention rates obtained in the finial treatment process varied form 94% ($N\text{-}NH_4$) to 100%. The final product quality was found to be satisfactory considering its further use on farms *ie* washing of animals and farmhouses, fields irrigation or heating/cooling purposes.

Conclusions

The study discussed the possibility of application of integrated membrane processes *ie* ultrafiltration/two step reverse osmosis for recovery of water from pig slurry. It was found that the proposed system was suitable for that purpose. The final product was good quality, sanitary safe water that could be successfully reused on farms. The ratio of 2nd RO step permeate volume to crude slurry volume was equal to 15%.

The highest decrease in membranes capacity was observed for UF membrane, next for 2nd RO and finally for 1st step RO. The fouling of UF membrane was significant and irreversible *ie* washing of membrane via backflushing with water did not improve significantly its capacity. The cleaning of membrane with chemicals ie 0.5% solutions of NaOH and HNO_3 enabled to recover membrane capacity up to 70% of the initial one. In both RO processes the decrease of membranes capacity was observed, however simple flushing of membranes with water enabled the total recovery of the initial water flux. Moreover, in the 1st RO process the increase of capacity was observed. It could have been caused by several reasons ie the occurance of only reversible membrane fouling, adsorption of some compounds (both, organic and inorganic) that modified membrane surface increasing its hydrophilicity or the diffusion of compounds through the membrane loosen its polymeric structure.

Acknowledgements

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ZASTOSOWANIE PROCESÓW MEMBRANOWYCH DO OCZYSZCZANIA GNOJOWICY POCHODZĄCEJ Z WIELKOPRZEMYSŁOWEJ HODOWLI TRZODY CHLEWNEJ

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Abstrakt: Celem przeprowadzonych badań było określenie efektywności zintegrowanego systemu ultrafiltracja/dwustopniowa odwrócona osmoza do odzysku wody z gnojowicy trzody chlewnej. W celu przygotowania nadawy do procesu oczyszczania wykorzystano procesy naturalnej separacji, tj. sedymentację i flotację. Otrzymaną ciecz nadosadową wprowadzono na pilotową instalację do filtracji membranowej wyposażoną w ceramiczne membrany ultrafiltracyjne firmy Pall o rozmiarze porów 5 nm. Strumień oczyszczony był następnie doczyszczany na poliamidowych membranach osmotycznych firmy Koch. Efektywność procesu oceniano na podstawie wydajności oraz jakości oczyszczonych strumieni. Zbadano także wpływ mycia membran ceramicznych za pomocą płukania wstecznego wodą oraz środkami chemicznymi (0,5% roztwory wodorotlenku sodu i kwasu azotowego) na przywrócenie początkowej wydajności membran. Badania wykazały, iż proponowany system może zostać zastosowany do odzysku wody z gnojowicy. Jakość końcowego produktu pozwala na jego ponowne wykorzystanie np. do mycia zwierząt i obiektów hodowlanych czy w systemach grzewczo-chłodzących. Dodatkową zaletą jest zatężenie składników odżywczych w formie retentatu, który wciąż może zostać użyty do celów nawozowych lub też w produkcji biogazu rolniczego.

Słowa kluczowe: gnojowica świńska, ceramiczna ultrafiltracja, odwrócona osmoza, oczyszczanie gnojowicy

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FUNCTIONAL RELATIONSHIPS BETWEEN SELECTED FUEL PARAMETERS OF SEWAGE SLUDGE AND THE TIME OF ITS STORAGE

ZALEŻNOŚCI FUNKCYJNE POMIĘDZY WYBRANYMI PARAMETRAMI PALIWOWYMI OSADÓW ŚCIEKOWYCH A CZASEM ICH SKŁADOWANIA

Abstract: Sewage sludge is waste whose disposal causes a number of problems in many countries (including even highly developed ones). The paper presents the genesis, methodology and results of conducted tests. The study presents results of research conducted for 4 samples of sludge stored for the period of 3 months each in a pile, in conditions similar to natural ones (eg exposed to the atmospheric conditions). The paper discusses test results of sludge samples derived from various depths of their location in the pile. In the research the stabilized by anaerobic fermentation processes and dehydrated wastewater sludge was used, which was derived from large, municipal wastewater treatment plants. The paper focuses on the results pertaining to the sludge fuel parameters, including combustible and volatile matter, calorific value, elemental composition.

Keywords: sewage sludge, fuel properties, experimental research, changes in time

Sewage sludge from municipal sewage treatment plants is one of the major problems of waste management. This waste is troublesome in management due to a number of its properties. The major of them include, inter alia: a large volume of its production and its moisture content. For example, in the second half of the first decade of the 21st century, there were from 900 000 to over 1 100 000 Mg of sludge dry matter generated annually in Poland (in that period there were 2 050 000 Mg of sludge dry matter generated in Germany, 1 770 000 Mg in Great Britain, approx. 1 060 000 Mg of sludge dry matter in Spain, France and Italy) [1]. At the same time, most frequently, the moisture of sewage sludge at the treatment plant outlet ranged from 70÷85%. Thus, the actual weight of the waste that needs to be managed is several times larger than the specified quantities of dry matter.

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.

Therefore, for a number of years we can observe an increasing importance of thermal methods in the treatment of sewage sludge in highly-developed countries. In Poland, however, until 2008 there was de facto only one technologically advanced thermal treatment plant of sewage sludge management. It was the fluidized-bed incineration plant, put into operation in 1998 in Gdynia-Debogorze. Until 2008 a series of studies on the sludge co-combustion process in grate furnaces were undertaken, and even for some time such process was conducted, on a small scale, in one of the sewage treatment plants.

The sludge co-combustion in cement kilns may be also considered a modern method of thermal sludge treatment, which has been used in Poland already for a long time. However, this method started to be widely used after 2005.

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In recent years in Poland, thermal methods of sludge treatment in plants constructed only for this purpose have been developed intensely. After 2008, plants in the following cities were built or are still under construction: Lomza, Olsztyn, Bydgoszcz, Gdansk, Kielce, Krakow, Lodz, Warszawa, Zielona Gora.

Moreover, several sludge drying plants operate in Poland. Sludge from such plants is used for firing cement kilns.

The main advantages of thermal processes include:

- waste weight reduction (for dry sludge - 55÷70%, for wet sludge - over 90%);
- complete neutralisation of the sludge in terms of biological threats;
- possibility to dispose of large quantities of waste.

The disadvantages of sewage sludge combustion in plants dedicated exclusively for that purpose include:

- the necessity to incur high capital expenditures;
- the necessity to incur high operating costs;
- the necessity to manage the solid, post-process residue.

The sludge co-combustion processes in power and cement plants are free from the above defects. In these processes the already existing plants are used and the post-process residue is built in the material that leaves the process (cement kilns) or managed along with the residue after the combustion of coal (due to the negligible sludge content it does not have a substantial effect on the properties of slag and ashes).

However, both for the co-combustion and independent combustion, an important problem affecting the operating costs are fuel parameters of the sludge, and in particular, its moisture content. Furthermore, due to temporary outages and seasonality of the implementation of certain processes in the power industry (heating season), as well as the distance from the potential sources of sewage sludge generation and plants for its thermal treatment, the necessity of periodic sludge storage may arise.

Further in the paper, changes in the basic properties of sludge occurring during a 3-month storage in the autumn and winter period (October - January) are presented.

Testing methodology

This paper presents the results of testing conducted on four samples of sewage sludge from a large municipal sewage treatment plant (with capacity above 30 000 m^3/day). The sewage treatment plant was a mechanical biological treatment plant. In the plant, sewage sludge was subject to anaerobic fermentation and mechanical dewatering processes.

Under testing, batches of sludge with a volume of over 2 m^3 were taken and placed in two special containers with a capacity of over 1 m^3 each. During testing, the conditions of sludge storing in natural conditions - storing in a pile - were simulated. Thus, the containers were open at the top and exposed to the atmospheric conditions. Sides of the containers were insulated and the bottom of the container enabled the leachate drainage. Sludge subject to testing was stored in layers with thickness of about 1.2 m. As part of testing, from the sludge stored in such manner samples were taken for analytical determinations. Samples were taken from the depth of approx. 1 m (hereinafter "Sludge bottom") and 0.20 m ("Sludge top II") - measured from the surface layer of the stored sludge. The atmospheric conditions in the presented tests were found to be disturbing factors.

The aim of testing the sludge derived from one source but stored separately was to determine the scatter of results arising from the fact of the natural, various dynamics of phenomena occurring in the stored material in similar conditions.

Samples for analytical determinations were taken at the beginning of the sludge storing process and then they were taken at two-week intervals for the period of 12 weeks. Altogether, the article presents the results concerning seven dates of sample taking (at present, tests are still in progress).

Within the framework of conducted tests, ten-odd parameters were determined, including: gross calorific value, moisture content, fraction of combustible and volatile matter, elemental composition, aggressive substance content. Further in the paper the results of the following analyses are presented:

- determination of volatile matter content (determination made by gravimetric method, according to PN-G-04516:1998 [2]),
- carbon and hydrogen content (determination made by Sheffield's method, according to PN-C-04301:1987 [3]).

It should be noted that all values presented further in the paper (eg on graphs) are average values obtained based on the threefold repetition of each determination. Average values obtained in this manner were used (in different configurations) 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 (amounting for 5 degrees of freedom to $r_{kr} = 0.7545$).

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

Test results

As mentioned above, testing concerned the determination of the properties of several parameters. Below exemplary results for two of them are presented.

Figure 1 shows the observed changes in the volatile matter share, occurring in the top layers of the stored sludge. Figure 2, on the other hand, presents similar results for the bottom layers of the sludge.

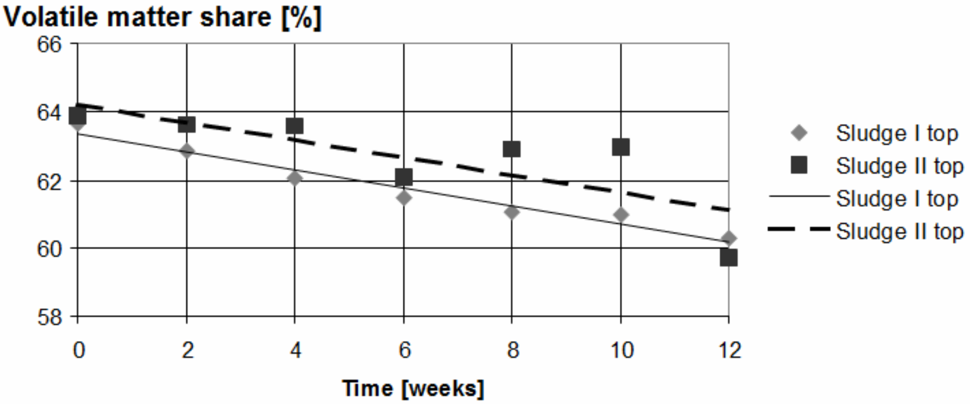

Fig. 1. Changes in time of volatile matter share in sludge derived from top layers

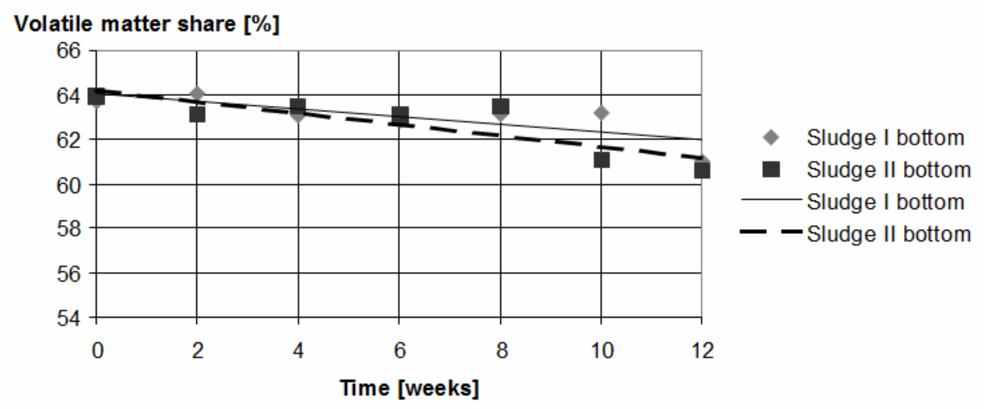

Fig. 2. Changes in time of volatile matter share in sludge derived from bottom layers

As illustrated in the charts, in all cases, the determined trend line indicates a decreasing volatile matter share in time, and in case of sludge derived from the top layers, the declines are larger, approx. 3.5÷4% (in sludge from bottom layers the declines amount to approx. 2.5÷3%).

The determined linear correlation coefficients are as follows:

- Sludge I top, $r = 0.977$;
- Sludge II top, $r = 0.777$;
- Sludge I bottom, $r = 0.777$;
- Sludge II bottom, $r = 0.837$.

Thus, in the case of the parameter in question, the correlation was found in sludge derived from all analysed points of their collection from containers.

The scatter of results between volatile matter shares derived from similar collection points ranged from 0.23 to 2.12%. The average difference between values obtained for sludge derived from two containers, from analogous collection points (at the same time) amounted to:

- at the top - 1.08%,
- at the bottom - 0.67%.

At the same time, the average standard deviations were as follows:

- at the top - 0.26%,
- at the bottom - 0.27%.

Thus, the obtained mean differences are as much as 4.15 times larger at the top and 2.50 times larger at the bottom than the average standard deviation.

The regression line equations for the obtained results took the following form:

- Sludge I top, $y = -0.266x + 63.372$;
- Sludge II top, $y = -0.260x + 64.245$;
- Sludge I bottom, $y = -0.172x + 64.024$;
- Sludge II bottom, $y = -0.253x + 64.192$.

Figure 3 shows the observed changes in carbon element content, occurring in the top layer of stored sludge samples. Figure 4, on the other hand, presents similar results for the bottom layers of the sludge. These figures present also trend lines for each analysed sludge.

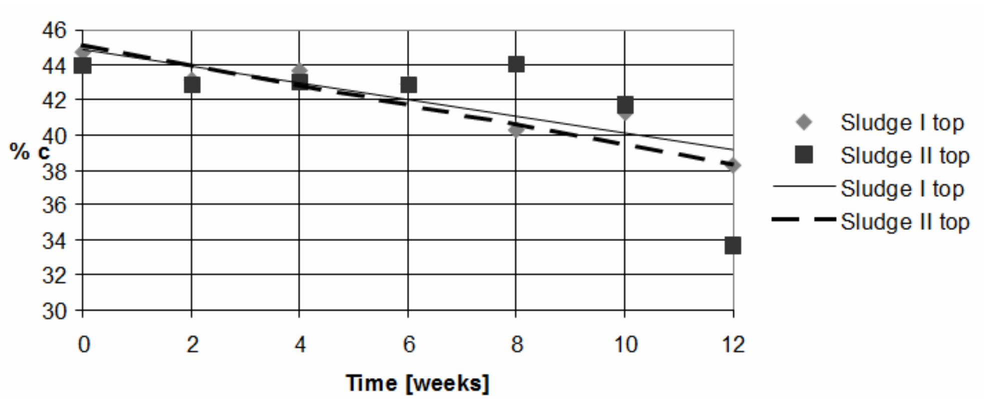

Fig. 3. Changes in time of carbon share in sludge derived from the top layer

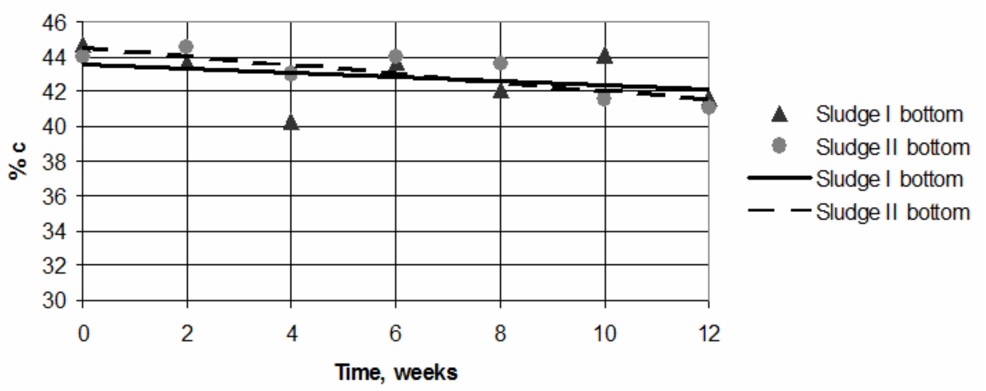

Fig. 4. Changes in time of carbon share in sludge derived from the bottom layer

As illustrated in the charts, in all cases, the determined trend line indicates a decreasing carbon share in time. And changes are more dynamic in the case of samples derived from the top sludge layers. In the top layers the declines of about 3÷5% and in bottom - of 2.5÷3% were observed.

The determined linear correlation coefficients are as follows:

- Sludge I top, $r = 0.919$;
- Sludge II top, $r = 0.679$;
- Sludge I bottom, $r = 0.317$;
- Sludge II bottom, $r = 0.822$.

Thus, a correlation can be found only in two cases: “Sludge I top” and “Sludge II bottom”.

The difference between carbon shares derived from similar collection points in both containers (at the same time) ranged from 0.07 to 4.55%. With the largest differences occurring in the case of determinations characterised by the largest standard deviations.

The average difference between values obtained for sludge derived from two containers amounted to:

- at the top - 1.52%,
- at the bottom - 1.33%.

At the same time, the average standard deviations for sludge stored in two containers were as follows:

- at the top - 1.64%,
- at the bottom - 0.64%.

Thus, the obtained mean differences are smaller at the top than the average standard deviation and at the bottom they are 2.1 times larger.

The regression line equations for the results obtained in the case of measurement series allowing to find a correlation, took the following form:

- Sludge I top, $y = -0.476x + 44.906$;
- Sludge II bottom, $y = -0.25x + 44.600$.

Conclusions

Sewage sludge is still a major problem of waste management in Poland and around the world. Although in recent years a few large plants for the thermal sludge treatment were established in Poland, still on a large part of the territory of our country sewage sludge management is solved in a provisional manner, at most. Much of the sludge, before being subject to the final treatment, is stored for a certain period of time. Hence, it becomes important to know the processes of changes occurring in the stored sludge.

During the tests presented in the article, it was found that in the 3-month period, in the sludge subject previously to biological stabilization processes, processes resulting in the decrease in volatile matter share of 3.5÷4% and the decrease in carbon share of 2÷5% occur. Moreover, it was found that in the top layer of the stored sludge, processes progress in a more dynamic manner (observed declines in analysed shares are larger).

When comparing the sludge stored separately, the obtained differences between similar measurements - except for one case - were significantly higher than the average standard deviations.

In case of finding a correlation between the tested values and the time of storage, regression line equations are presented in the article.

Acknowledgements

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ZALEŻNOŚCI FUNKCYJNE POMIĘDZY WYBRANYMI PARAMETRAMI PALIWOWYMI OSADÓW ŚCIEKOWYCH A CZASEM ICH SKŁADOWANIA

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Abstrakt: Osady ściekowe stanowią odpad, którego unieszkodliwienie nastręcza szereg problemów w wielu krajach (w tym nawet w państwach wysokorozwiniętych). W pracy przedstawiono genezę, metodykę oraz wyniki przeprowadzonych badań. Zaprezentowano także wyniki badań przeprowadzanych dla 4 próbek osadów składowanych każdorazowo przez okres 3 miesięcy w pryzmie w warunkach zbliżonych do naturalnych (m.in. narażonych na wpływ czynników atmosferycznych). Omówiono również wyniki badań próbek osadów pochodzących z różnych głębokości ich położenia w pryzmie. W badaniach wykorzystano ustabilizowane w procesach fermentacji beztlenowej i odwodnione osady ściekowe pochodzące z dużych komunalnych oczyszczalni ścieków. Skupiono się na wynikach dotyczących parametrów paliwowych osadów, m.in.: wilgotności, części palnych i lotnych, wartości opałowej, składu pierwiastkowego.

Słowa kluczowe: osady ściekowe, właściwości paliwowe, badania eksperymentalne, zmiany w czasie

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ANALYSIS OF THE POSSIBILITY OF THE SEWAGE SLUDGE THERMAL TREATMENT

ANALIZA MOŻLIWOŚCI ENERGETYCZNEGO WYKORZYSTANIA OSADÓW ŚCIEKOWYCH

Abstract: Promoting of the renewable energy is one of the priorities of the Polish energy policy until the year of 2030. It is believed that the co-combustion of sewage sludge in the Polish conditions is especially attractive. The paper contains two parts of research. The first one concerns a theoretical analysis of the possibility of direct co-combustion of solid municipal sewage sludge with hard coal in power station boilers. Numerical simulation of indirect co-combustion process of gas from sewage sludge gasification in coal-fired boiler has been done in the second part of the work. The conclusions show that the thermal methods of sewage sludge utilisations provide a great opportunity for application in Polish conditions.

Keywords: co-combustion, sewage sludge

According the Polish Regulation and the objectives of the National Waste Management Plan 2014 [1] and the National Urban Wastewater Treatment Program [2] the quantity of sewage treated in Poland is systematically increasing. Currently, the predominant method for the disposal of sewage sludge is its storage and agricultural application [3]. The main problems are the high percentage of stored sewage sludge and a lack of installations for its thermal utilization. Thermal processes can be used for the conversion of large quantities of sewage sludge (eg, in large urban areas) into useful energy. There is a wide range of analysed and proposed solutions for municipal sewage sludge utilization. Nevertheless, there are serious legal constraints determining this choice. One of the most important Regulation is the Regulation of the Minister of Economy and Labour [4], which introduced a ban of the storage of sewage sludge from the date of January 1, 2013.

In view of the presented facts, there is a large and pressing need for the development of thermal methods (combustion, co-combustion, gasification and pyrolysis) of disposal of sludge.

Taking into consideration Polish specificity of the power engineering sector which is based on the coal-fired boilers, the most promising method of sewage sludge treatment in Poland is co-combustion. Basically, it is mainly possible to distinguish the use of sewage sludge in fossil fired power plants in three different co-combustion concepts, which are as follows:

1. Direct co-combustion: Sewage sludge and coal are burned in the same boiler or gasifier, using the same or separate mills and burners, depending principally on the sewage sludge fuel characteristics. Coal and sludge can be mixed before milling or coal and sludge are fed and milled by separated supply chains.

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2. Indirect co-combustion: In gasifier sewage sludge is converted into a fuel gas, which after cooling and cleaning can be burned in the coal boiler furnace. As an alternative the produced syngas can also directly be burnt in a joint steam boiler without further cooling or cleaning.

The aim of the work is - first of all - theoretical analysis of the possibility of direct co-combustion of solid municipal sewage sludge with hard coal in power station boilers (WR-25, CFB-420 and OP-230) and - secondly - numerical simulation of indirect co-combustion process of gas from sewage sludge gasification in coal-fired boiler.

Methods and materials

First part of the present work consist theoretical analysis of the possibility of the direct co-combustion of dried sewage sludge in different types of the coal-fired boilers (fluidized bed boiler CFB-420, stoker fired boiler WR-25 and pulverized coal boiler OP-230). The analysis takes into consideration wide range of mass fraction of sewage sludge (0÷20%) in the fuel (hard coal) mixture and wide range of air excess ratio in the combustion chamber (1.1÷1.5). Boiler efficiency in all analysed examples was calculated. Energy balance of all analysed boilers was done. Composition of the analysed fuels blends are presented in Table 1.

Table 1

Composition of analysed fuel mixtures [5]

Mass fraction of main components in mixture	**Mass fraction of sewage sludge in fuel mixture [%]**				
	0	**5**	**10**	**15**	**20**
C	0.6867	0.6542	0.6246	0.5977	0.5730
H	0.0083	0.0087	0.0091	0.0094	0.0097
S	0.0466	0.0468	0.0469	0.0470	0.0472
O	0.0849	0.0932	0.1070	0.1076	0.1141
N	0.0178	0.0205	0.0230	0.0252	0.0272
H_2O	0.0493	0.0517	0.0539	0.0559	0.0577

Equilibrium calculations of fuel mixtures complete combustion in analysed boilers were done. Energy balance illustration is presented in Figure 1.

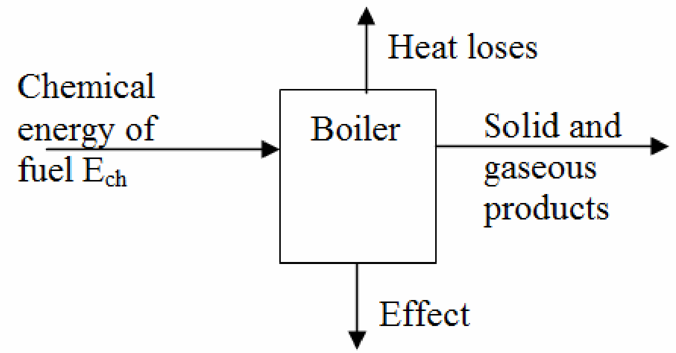

Fig. 1. Illustration of energy balance

Energy balance solution using real operating parameters of all analysed boilers (capacity, operating temperatures and pressures etc.) leads to determination of the flow of combusted fuel $\dot{P}$. Thanks to it, boilers efficiency using eq. (1) can be determined:

$$\eta = \frac{\text{Effect}}{E_{ch}} = \frac{\dot{Q}}{\dot{P}\cdot W_d} \tag{1}$$

where: $\dot{Q}$ - boiler capacity [kW], $\dot{P}$ - flow of the fuel [kg/s], W_d - lower heating value [kJ/kg].

In the second part of the work, numerical simulation of the indirect co-combustion of sewage sludge gasification gas in coal-fired boiler NO_x reduction efficiency has been calculated. The calculations were modelled using the GRI-Mech 2.11 mechanism, plug flow reactor model. The molar flow rate ratio of the additional fuel to the whole exhaust was assumed to be 5.0, 7.5, 10.0, 12.5 and 15.0%. The simulations were conducted at a constant pressure equal to 1atm and at temperatures ranging from 600 to 1400ºC, with typical residence times of 0.0÷0.4 s and local air excess ratio ranging from 1.0 to 2.0.

Results and discussion

Direct co-combustion

The calculated values of boiler efficiency are presented in Table 2. Analyzing those results it can be concluded that, taking into consideration constant value of boiler capacity, both increasing of mass fraction of sewage sludge in fuel mixture and increasing of air excess ratio causes decreasing of boiler efficiency. Nevertheless, it should be emphasis that this decrement is not very high and mainly causes by high value of exhaust loss. It can be concluded, that direct co-combustion of sewage sludge in different types of coal-fired boilers does not negative affect on boiler efficiency.

Table 2

Efficiency of analysed boilers

λ	**WR-25**					**CFB-420**					**OP-230**				
	Mass fraction of sewage sludge in fuel mixture [%]														
	0	**5**	**10**	**15**	**20**	**0**	**5**	**10**	**15**	**20**	**0**	**5**	**10**	**15**	**20**
1.10	90.8	90.8	90.7	90.7	90.6	92.6	92.5	92.5	92.5	92.4	82.7	82.6	82.5	82.4	82.3
1.15	90.5	90.5	90.4	90.4	90.4	92.3	92.3	92.3	92.2	92.2	82.0	82.0	81.8	81.8	81.7
1.20	90.2	90.2	90.1	90.1	90.1	92.1	92.1	92.0	92.0	92.0	81.4	81.3	81.2	81.2	81.1
1.25	90.0	89.9	89.9	89.8	89.8	91.9	91.9	91.8	91.8	91.8	80.8	80.7	80.6	80.5	80.4
1.30	89.7	89.6	89.6	89.6	89.5	91.7	91.6	91.6	91.6	91.5	80.2	80.1	80.0	79.9	79.8
1.35	89.4	89.4	89.3	89.3	89.2	91.5	91.4	91.4	91.4	91.3	79.6	79.5	79.4	79.3	79.2
1.40	89.1	89.1	89.0	89.0	89.0	91.2	91.2	91.2	91.1	91.1	79.0	78.9	78.7	78.7	78.6
1.45	88.9	88.8	88.8	88.7	88.7	91.0	91.0	90.9	90.9	90.9	78.3	78.2	78.1	78.0	78.0
1.50	88.6	88.5	88.5	88.4	88.4	90.8	90.8	90.7	90.7	90.6	77.7	77.6	77.5	77.4	77.3

Indirect co-combustion

In Figure 2, relative amount of NO_x as a function of temperature is shown. NO reduction efficiency of the gasification gas is strongly dependent on temperature. Temperature in the additional fuel injection zone is a key variable in the process because it determines the degree of conversion of the additional fuel and thus the formation of hydrocarbon radicals, as well as the rates of important reactions involved in the reburning mechanism. The reduction of NO increases with increasing temperature - presumably through its reaction with CH_i - until it reaches a maximum. At temperatures between 600 to 800ºC, the sewage sludge-derived syngas does not affect the NO concentration. At higher temperatures, the reburning efficiency of the analysed reburning fuel increases. The strongest NO reduction occurs at temperatures higher than 1000ºC; however, the best temperature for the reburning process is 1200ºC. In general, as seen in Figure 2, increasing the molar ratio of reburning fuel results in a decrease in the temperature for optimal NO reduction.

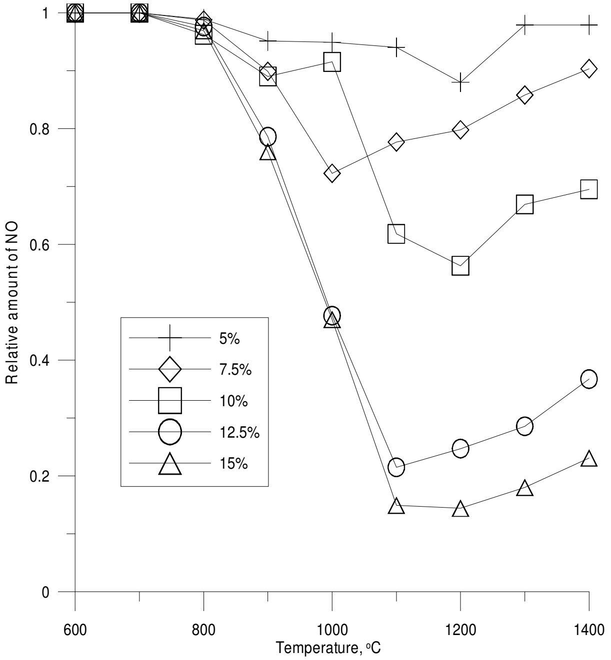

Fig. 2. Relative amount of NO_x as a function of the temperature for different values of the molar ratio of reburning fuel; λ - 1.1; τ = 0.4 s

Figure 3 shows the dependence of relative amount of NO as a function of the air excess ratio for a reburning zone temperature and residence time of 1200ºC and 0.4 s. As shown in this figure, an air excess ratio equal to 1.0, reburning fuel has no influence on the reduction of NO. The reduction of NO increases up to a maximum as the stoichiometry becomes more fuel-rich. Such conditions favour the formation of CO and CO_2 via the oxidation mechanism of the reburning fuel instead of the formation of hydrocarbon radicals active in NO reduction.

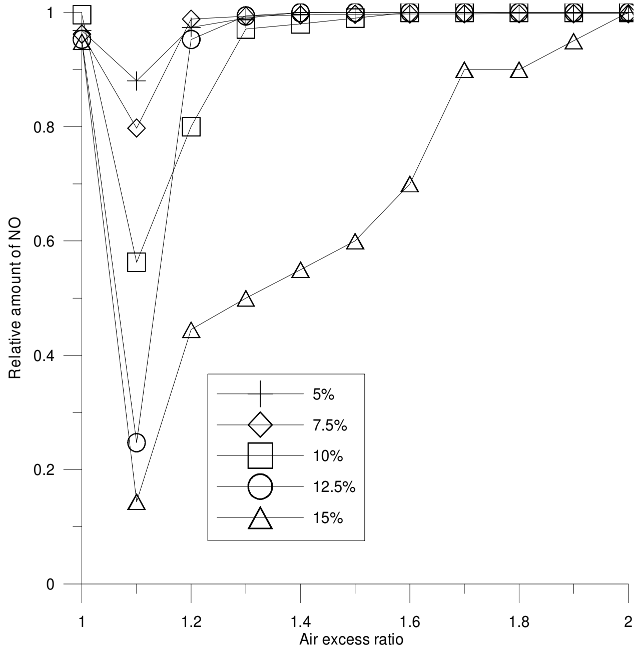

Fig. 3. Relative amount of NO_x as a function of the air excess ratio for different values of the molar ratio of reburning fuel; $t = 1200°C$; $\tau = 0.4$ s

For each molar ratio of reburning fuel, the relative amount of NO initially decreases at the beginning as the air excess ratio begins to increase. As seen in this figure, there is a value of the air excess ratio for which the efficiency of the NO reduction reaches a maximum. Above this value, NO reduction decreases.

Conclusions

Alternative methods for the thermal utilization of sewage sludge are an important element in the wider problem of sludge disposal. Their undoubted advantage, in addition to the disposal of sludge, is that it becomes possible to obtain a product that can be effectively used for the generation of energy. Polish conditions also appear to present a good opportunity to utilize this group of waste-disposal technologies.

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ANALIZA MOŻLIWOŚCI ENERGETYCZNEGO WYKORZYSTANIA OSADÓW ŚCIEKOWYCH

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Abstrakt: Promowanie wykorzystania odnawialnych źródeł energii jest jednym z priorytetów polskiej polityki energetycznej do roku 2030. Uważa się, iż współspalanie osadów ściekowych w warunkach polskich zasługuje na szczególną uwagę. W pracy zaprezentowano dwa główne nurty badawcze. Pierwszy z nich dotyczy analizy możliwości współspalania komunalnych osadów ściekowych z węglem kamiennym w obiektach energetyki zawodowej. Drugi nurt dotyczy symulacji numerycznych procesu współspalania gazu ze zgazowania osadów ściekowych w kotle opalanym węglem kamiennym. Wnioski wskazują, iż energetyczne sposoby wykorzystania osadów ściekowych dają duże szanse na zastosowanie w polskich warunkach.

Słowa kluczowe: współspalanie, osady ściekowe

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INFLUENCE OF COPPER ON SUPEROXIDASE DYSMUTASE ACTIVITIES IN RATS EXPOSED TO CADMIUM

WPŁYW MIEDZI NA AKTYWNOŚĆ DYSMUTAZY PONADTLENKOWEJ U SZCZURÓW ZATRUWANYCH KADMEM

Abstract: The aim of this study was to evaluate the influence of copper supplements on superoxide dismutase (SOD) activities in the kidneys and liver of rats exposed to moderate doses of cadmium chloride. SOD activities were measured weekly for a period of 28 days. The examinations involved male Wistar rats divided into three groups. Rats in group I were considered the controls whereas rats in group II and III were administered intragastrically for 7 d, 14 d, 21 d, and 28 d a water solution of cadmium chloride corresponding to 10 mg Cd/kg diet. All rats fed a standard laboratory chow LSM (Agros Motycz, Poland) containing 5 mg Cu/kg except for the rats in group III in which animals were fed an LSM diet supplemented up to 50 mg Cu/kg. The experimental procedure included evaluation of water and feed intake, body weight gains, liver, kidneys, testicles, heart and spleen to body ratio, and hepatic and renal SOD activities measured after 7 d, 14 d, 21 d, and 28 d exposure to cadmium or cadmium plus copper. Results indicated that SOD activity in cadmium or cadmium plus copper groups changed in comparison with the control values. Supplements of copper increased significantly hepatic and renal SOD activities after 21 and 28 d of exposure when compared to those found in the controls and cadmium exposed rats. Moreover, rats fed the copper supplement diet improved body weight gain in comparison with that in the cadmium exposed rats. Results suggest that copper may stimulate a protective activity against toxic action of cadmium given at doses resembling its concentrations in the areas contaminated with this metal.

Keywords: copper, cadmium, superoxide dismutase, rat

Cadmium is constantly released into the atmosphere with an estimated 4 000 to 13 000 Mg (tons) coming from human activities. The cadmium present in the environment does not break down. Consequently, plant, animal and human exposure to and intoxication with cadmium continues to occur [1]. Following exposure, cadmium is readily distributed to all organs and tissues where it proceeds toxic activities [2]. Its participation in biological functions may lead to oxidative stress causing the loss of membrane integrities in biomolecules including lipids and proteins [3].

Animal studies have provided evidence that several factors may affect the absorption and toxicity of cadmium [4-6]. For example, Fox [7] discussed the effects of dietary nutrients in increasing or decreasing risks from cadmium toxicity. It was found that a diet deficient in copper and iron caused increased mortality and reduced growth in chicks whereas copper supplements decreased mortality and increased haematocrit of anaemic Japanese quail fed cadmium in the diet. Moreover, it was reported that rats fed a copper fortified diet (10 times the level in a standard diet) increased cadmium content in metabolically significant organs including liver and kidneys [8]. However, the increases in cadmium content were associated with improved body gains suggesting that the toxic action within the body of rats exposed to cadmium was limited.

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It worth noting that relationships between cadmium and copper seems to be significant not only during metabolism but also when enzyme activities are considered [6].

The aim of these studies was to evaluate the effect of copper supplements on the renal and hepatic activity of *superoxide dismutase* (SOD) in rats exposed to dietary doses of cadmium. The studies included SOD activities because this enzyme constitutes one of the main defense mechanisms against the oxidative stress produced by cadmium.

Material and methods

Experiments involved male Wistar weighing 207 ± 12 g. After a one-week acclimatization period rats were randomly assigned to three groups (45 animals per group). Animals in group I (control) were fed a standard laboratory diet LSM (Fodder Manufacture Motycz, Poland) and drunk tap water whereas rat in groups II and III were exposed daily for 28 days (except weekends) to a water solution of cadmium chloride containing cadmium at a concentration corresponding to 10 mg Cd/kg of diet. Cadmium chloride was administered intragastrically using a stainless gavage. Rats in groups II were fed the LSM diet containing 5 mg Cu/kg (according to the manufacture's procedure) whereas rats in group III the LSM diet supplemented with copper chloride up to 50 mg Cu/kg. The experimental procedure included evaluation of water and feed intake, body weight gains, organ to body ratios, and renal and hepatic SOD activities measured according to Marklund's method [9] after 7 d, 14 d, 21 d, and 28 d intoxication with cadmium. Rats were killed by immersion in gaseous carbon dioxide.

Statistical analysis of results based on 5 rats killed at each point time. Mean values were compared by Student's *t*-test at $P < 0.05$.

Results

Rats in all groups demonstrated a similar feed and water intake. The body weight gains measured after 28-day intoxication with cadmium were visibly lower in rats fed a standard diet and exposed to cadmium as compared with those in the controls and group III. However, the differences were not statistically significant (Table 1). Further, the organ to body ratio for the liver, spleen, heart, and kidneys was similar in the three groups examined except for the testicles showing a statistically significant decrease in group III in comparison with the value in the controls.

Table 1

Body weight gains and organ to body ratio measured after a 28-day intoxication

Groups	Initial weight [g]	Final weight [g] after 28 d exposure	Liver to body ratio	Kidneys to body ratio	Testes to body ratio	Heart to body ratio
Control	190 ± 12	348 ± 45 (87%)	3.36 ± 0.32	0.71 ± 0.06	1.13± 0.14	0.23 ± 0.03
Group II	202 ± 12	325 ± 21 (61%)	3.76 ± 0.37	0.73 ± 0.06	0.85 ± 0.09	0.26 ± 0.02
Group III	208 ± 12	366 ± 44 (78%)	3.92 ± 0.38	0.68 ± 0.06	0.79 ± 0.11*	0.27 ± 0.03

* means statistically significant differences at $P < 0.05$

The effect of increasing doses of cadmium on superoxide dismutase activities in the liver and kidneys were shown in Tables 2 and 3. A gradual increase in the renal and hepatic activities of SOD was observed in the controls, cadmium, and cadmium plus copper treated rats. Maximum values were noted after 21 days in the controls and cadmium treated rats whereas in the rats exposed to cadmium and supplemental copper peak values were seen at 28 days. It should be also stressed that SOD activities in groups II and III were a little lower after 7 days intoxication with cadmium. No significant differences in SOD activities were found between groups I and II. However, rats exposed both to cadmium and supplemental copper demonstrated significant increases in renal and hepatic SOD activities after 21 days in comparison with those in the controls and significant increases after 28 days as compared to those found in the controls and cadmium exposed group.

Table 2

Hepatic SOD activities in rats exposed to cadmium and copper

Intoxication [days]	**Control (Group I)**	**Cadmium (Group II)**	**Cadmium and copper (Group III)**
7	48.26 ± 14.56	40.37 ± 13.76	45.88 ± 13.56
14	53.57 ± 18.12	56.96 ± 20.09	100.61 ± 23.81
21	77.33 ± 17.89	85.27 ± 22.43	134.93 ± 31.50^{a}
28	56.54 ± 14.32	69.49 ± 17.67	140.09 ± 29.69^{ab}

Explanations: a - means statistically significant differences between group III and groups I at $P < 0.05$, b - means statistically significant differences between group III and groups II at $P < 0.05$

Table 3

Renal SOD activities in rats exposed to cadmium and copper

Intoxication [days]	**Control (group I)**	**Cadmium (group II)**	**Cadmium and copper (group III)**
7	38.77 ± 12.93	31.56 ± 12.74	35.08 ± 11.85
14	39.63 ± 15.08	51.16 ± 16.07	72.02 ± 16.12
21	56.15 ± 17.29	68.62 ± 16.94	127.69 ± 25.84^{a}
28	47.46 ± 17.02	62.66 ± 15.67	136.96 ± 27.06^{ab}

Explanations as in Table 2

Discussion

The cadmium doses given to rats in this experiment corresponded to 10 mg Cd/kg diet. The toxicological consequence of cadmium given at such dose for relatively short time is not well known. Examinations of the kidneys, testicles and liver of rats exposed to similar amounts of cadmium failed to show any anatomopathological alterations in these organs (not yet published). Several authors reported no responses in growth, feed and water consumption in ewes, lambs and pigs given cadmium at concentrations up to 30 mg/kg [10, 11]. However, it should be stressed that in the present studies the relative weight of testicles decreased significantly in rats exposed both to cadmium and copper. The toxicity of cadmium to the male reproductive system has been extensively investigated in animals. It was reported that long-term treatment with moderate doses of cadmium for several months did not give rise to any toxicity to testicles [12]. A drop in relative testicular weight in the case of concomitant supplemental copper administration may correspond to reports by Chattopadhyay et al [15] who found significant reduction of testicular and accessory sex organs (seminal vesicle, ventral prostate) weight after intraperitoneal injection of copper chloride at doses of 2 and 3 mg/kg body weight/day for 26 days.

Cadmium may cause indirectly prolonged generation of *reacitive oxygen species* (ROS) which promote necrosis. Superoxide dismutase is an essential cellular component of antioxidative defense system as it dismutates two oxygen radicals to oxygen and water.

In the present studies the activities of SOD in the liver and kidneys of rats exposed cadmium and cadmium plus copper decreased after 7 day exposure. A drop in SOD activities on day 7 may reflect an enhancement in lipids peroxidation with concomitant impairment in the antioxidative defence mechanism [14]. However, continuous exposure to cadmium and copper for a longer time stimulated a steady-state increase in SOD activities on days 14, 21, 28. These increases in SOD activities seems to be attributed to the supplements of copper and confirmed findings of others who also found enhanced SOD activities in patients fed a diet fortified with this element [16].

On the basis of the results presented here, it can be concluded that copper supplements given to rats exposed to a moderate level of dietary cadmium improve the body weight gain within the exposure period. Moreover, an increase in SOD activities may indicate an increased protection from oxidative stressed produced by cadmium.

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WPŁYW MIEDZI NA AKTYWNOŚĆ DYSMUTAZY PONADTLENKOWEJ U SZCZURÓW ZATRUWANYCH KADMEM

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Abstrakt: Celem pracy było określenie wpływu diety wzbogaconej w miedź na aktywność *dysmutazy ponadtlenkowej* (SOD) w wątrobie i nerkach szczurów szczepu Wistar eksponowanych na umiarkowane dawki chlorku kadmu. W badaniach uwzględniono 3 grupy zwierząt: grupę I stanowiły zwierzęta kontrolne, grupę II zwierzęta eksponowane na kadm podawany dożołądkowo w ilościach odpowiadających 10 mg Cd/ kg paszy oraz grupę III, w której kadm podawano tak jak w grupie II, a ponadto zwierzęta eksponowane były na chlorek miedzi podawany w paszy LSM (Agros Motycz, Polska) w stężeniu 50 mg Cu/kg. Stężenie miedzi w standardowej paszy LSM podawanej zwierzętom w grupach I i II wynosiło 5 mg Cu/kg. W doświadczeniu określano spożycie paszy i wody, przyrosty masy ciała, masy względne wątroby, nerek, serca, śledziony i jąder oraz aktywność SOD po 7, 14, 21 i 28 d podawania kadmu. Wyniki badań wskazują, że zatruwanie szczurów chlorkiem kadmu zmieniało aktywność SOD w wątrobie i nerkach w porównaniu z danymi w grupie kontrolnej. Dodatek miedzi do paszy zwiększył statystycznie istotnie aktywność SOD po 21 i 28 dniach ekspozycji na kadm w porównaniu z danymi w grupie kontrolnej i grupie eksponowanej tylko na kadm. Warto także podkreślić, że dodatek miedzi do paszy szczurów zatruwanych kadmem powodował zwiększone przyrosty masy ciała w porównaniu z danymi uzyskanymi od zwierząt karmionych standardową paszą i eksponowanych na kadm. Uzyskane wyniki sugerują, że miedź może mieć ochronne działanie u zwierząt eksponowanych na kadm drogą pokarmową w ilościach, które mogą być obecne w paszy na terenach skażonych tym metalem.

Słowa kluczowe: miedź, kadm, dysmutaza ponadtlenkowa, szczur

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STUDY OF DIOXIN LEVELS IN RAW MILK OF COWS AND GOATS IN POLAND

BADANIE POZIOMÓW DIOKSYN W SUROWYM MLEKU KRÓW I KÓZ W POLSCE

Abstract: Dioxins due to their toxic properties may pose health risks. These compounds comprise seven congeners of polychlorinated dibenzo-*p*-dioxins (PCDDs), 10 polychlorinated dibenzofurans (PCDFs) and 12 dl-PCBs. Because the main source of human exposure to dioxins is food of animal origin, the goal of the studies was to assess the levels of 29 congeners of dioxins in cow and goat's milk from Poland. High resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS) were used to analyze more than 120 samples in the period of 2006 to 2011. In 94 samples of raw cow's milk an average concentration of PCDD/PCDFs was 0.84 ± 0.60 pg WHO-TEQ/g fat whereas the sum of 29 congeners was 1.35 ± 0.89 pg WHO-TEQ/g fat. The concentrations of dioxins and dl-PCBs were low (30% of limits for whole milk) and the samples met the requirements of the national and European legislation. Within the period of examinations two samples of cow's milk demonstrated the concentrations of PCDD/PCDFs at the action level (2 pg WHO-TEQ/g fat) whereas only one sample revealed the concentration exceeding the permissible content of PCDD/PCDFs (3 pg WHO-TEQ/g fat). Raw goat's milk contains generally higher concentrations than those found in cow's samples tested (PCDD/PCDFs and dl-PCBs) and the average concentration of PCDD/PCDFs was 1.49 ± 0.97 pg WHO-TEQ/g fat. Of the 33 examined goat's milk samples, 6 demonstrated the concentrations of dioxins at the "action level" whereas in 1 sample the content of dioxins exceeded the acceptable limits. The obtained results allow to conclude that cow and goat's milk contains generally low levels of dioxins. High concentrations of dioxins found could be a result of improper feeding of food producing animals.

Keywords: dioxins, furans, PCBs, milk, cows, goats

Introduction

Dioxin is the name generally given to a class of very toxic chemicals, the chlorinated dioxins and furans, formed as a by-product of the manufacture or burning of organic chemicals and plastics that contain chlorine. These compounds comprise seven congeners of *polychlorinated dibenzo-p-dioxins* (PCDDs), 10 *polychlorinated dibenzofurans* (PCDFs) and 12 *dioxin like PCBs* (dl-PCBs). Dioxins due to their toxic properties may pose health risks. They are everywhere in nature because they get carried by wind to all parts of the globe. Remain on pastures, plants and grains that form part of the food chain for food producing animals. Over 90% of human exposure to dioxin and related compounds occurs via food ingestion, primarily meats, fish and dairy products [1]. Like the other organochlorine compounds dioxin accumulates in the fat cells of the animals, and re-appears in meat and milk.

Food safety in addition to its nutritional value is one of the most important factors affecting human health. Monitoring of food is a fundamental way which enables estimation of care for the population. Since 2006 Polish General Veterinary Inspectorate has

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undertaken a program to monitor the national food supply for dioxin and dioxin-like compounds. Because the results of initial milk goat testing suggested higher dioxin levels in subsequent years the number of goat milk samples was increased [2].

This paper reports the survey for PCDD, PCDF and dl-PCB in raw cow and goat's milk collected from 2006 to 2011. The purpose of this survey was to assess the levels and congener profiles of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs) in the general milk supply.

Materials and methods

Sample collections

For the official food control program raw cow and goat's milk samples were collected by veterinary inspection and sent to the National Veterinary Research Institute in Pulawy, Poland for chemical analysis. Number of yearly tested samples was set according to the Commission Recommendation 2006/794/EC [3]. Milk samples were collected also by national export dairies. Sample collections followed the requirements of the official food control standards [4]. From 2006 to 2011, 127 of raw milk samples were analyzed: 94 cow milk samples and 33 goat milk samples.

Chemical and instrumental analysis

Analyses were carried out in an accredited laboratory. The concentration of seventeen 2,3,7,8-substituted PCDDs and PCDFs congeners and 12 individual congeners dl-PCBs (non-*ortho* PCBs 77, 81, 126, 169 and mono-*ortho* PCBs 105, 114, 118, 123, 156, 157, 167, 189) were determined using gas chromatography coupled with high resolution mass spectrometry [4].

Briefly, chemical analysis based on a modified AOAC and EPA 1613 method. Two hundred and fifty milliliter of sample was freeze and lyophilized. Amount of 5 g dry milk was fortified with all of interest ^{13}C labeled standards and extracted by *accelerated solvent extraction* (ASE 300), with a solvent mixture of n-hexane/dichloromethane/methanol (5/2/1, v/v/v) under pressure of 10 MPa and temperature of 100°C. After removal of solvents the lipid content of each sample was determined gravimetrically. The samples were further cleaned up by column chromatography utilizing multi-layer acid silica column (22 and 44%). PCBs were separated from the dioxins/furans using Florisil column. Carbon/Florisil column was used for purification and separation mono-*ortho* from non-*ortho* PCB and carbon column was used for purification of dioxins/furans fraction. Collected fractions were concentrated to small volume and fortified by recovery/syringe standards before instrumental analysis. All compounds were analyzed using the isotope dilution method with GC connected with MAT 95XP (Thermo Scientific, Germany) operated in *electron impact* ionization (EI) mode. The chromatographic separation was achieved by splitless injection on a capillary column with length of 60 m, i.d. 0.25 mm and 0.1 µm thickness stationary phase film (Agilent J&W Scientific, USA). The MS was used in the SIM mode with the two most intensive ions of the molecular ion cluster monitored in specific windows. *Limits of Quantitation* (LOQs) and *Limits of Detection* (LODs) were estimated during validation process (Tables 1 and 2). Laboratory procedures for measuring dioxins and dioxin-like compounds in animal fat matrices developed in our laboratory can be found in the paper of Lizak at al [2].

Analytical procedures yielded three synthetic figures per sample: the concentrations of PCDD/PCDFs, dl-PCBs and the total TEQ concentration (the sum of PCDD/PCDFs and dl-PCBs) using WHO-TEF$_{1998}$. Results were expressed in pg WHO-TEQ/g fat and interpreted according to the thresholds recommended by the European Union regulations [5].

Table 1

PCDD/PCDFs. Limit of detection (LOD) and quantitation (LOQ) in raw milk

Congener	**LOD [pg/g]**	**LOQ [pg/g]**
2378-TCDD	0.05	0.13
12378-PeCDD	0.05	0.13
123478-HxCDD	0.06	0.15
123678-HxCDD	0.06	0.15
123789-HxCDD	0.06	0.15
1234678-HpCDD	0.20	0.50
OCDD	0.50	1.25
2378-TCDF	0.05	0.13
12378-PeCDF	0.05	0.13
23478-PeCDF	0.05	0.13
123478-HxCDF	0.06	0.15
123678-HxCDF	0.06	0.15
234678-HxCDF	0.06	0.15
123789-HxCDF	0.06	0.15
1234678-HpCDF	0.10	0.25
1234789-HpCDF	0.10	0.25
OCDF	0.50	1.25

Table 2

Dioxin like PCBs. Limit of detection (LOD) and quantitation (LOQ) in raw milk

Congener	**LOD [pg/g]**	**LOQ [pg/g]**
3,3',4.4'-TeCB (77)	1.00	2.50
3,4,4',5-TeCB (81)	0.50	1.25
3.3',4,4',5-PeCB (126)	1.00	2.50
3,3'4,4',5,5'-HxCB (169)	1.00	2.50
2,3,3',4,4-PeCB (105)	0.20	0.50
2,3,4,4',5-PeCB (114)	0.05	0.13
2,3',4,4',5-PeCB (118)	0.40	1.00
2',3,4',5-PeCB (123)	0.05	0.13
2,3,3',4,4',5-HxCB (156)	0.05	0.13
2,3,3',4,4',5'-HxCB (157)	0.05	0.13
2,3',4,4',5,5'-HxCB (167)	0.05	0.13
2,3,3',4,4',5,5'-HpCB (189)	0.05	0.13

Quality assurance (QA) and quality control (QC)

QA/QC was performed through the analysis of procedural blanks, a duplicate sample and a *standard reference material* (CRM) for each set of samples. Additionally, the method performance was assessed through *interlaboratory studies* (PT study). Expanded uncertainty was estimated at the level of interest and was established below 20% for both WHO-PCDD/PCDFs and WHO-PCDD/PCDF/dl-PCB. Concentrations of PCDD/PCDFs and dl-PCBs are expressed as pg WHO-TEQ/g on a lipid basis.

Results and discussion

Dioxin concentration from this study is shown in Tables 3 and 4. For all results, the lipid-adjusted concentrations were converted to the 2, 3, 7, 8-TCDD *toxic equivalence* (TEQ) using the WHO *Toxic Equivalence Factor* (WHO-TEF$_{1998}$). The results were calculated using upper-bound concentration, *ie* all analytes under the limit of determination would be equal to that limit [4].

Table 3

Dioxin levels in cow and goat's milk

Milk samples	**pg WHO-TEQ/g fat**				
	PCDD/PCDF ($x_{Av.}$ ± std dev.)	**Limit**	**dl-PCB** ($x_{Av.}$± std dev.)	**PCDD/PCDF/ dl-PCB** ($x_{Av.}$ ± std dev.)	**Limit**
Cow n = 94 Range	0.84 ± 0.60 0.37÷4.88	3	0.51 ± 0.35 0.12÷3.05	1.35 ± 0.89 0.67÷7.93	6
Goat n = 33 Range	1.49 ± 0.97 0.51÷4.64		0,87 ± 0,47 0.32÷2.07	2.35 ± 1.27 0.88÷5.08	

Table 3 displays the average concentration PCDD/PCDFs, dl-PCBs, average sum of PCDD/PCDF/dl-PCB in cow and goat's milk samples and the concentration range. The samples with higher level of tested compounds are presented in Table 4. The European Union (EU) has established maximum limits for these undesirable substances in food including milk, as well in feed aiming to ensure that food is safe for consumer. As specified in EC Regulation 1881/2006 the maximum permissible milk levels for human consumption are of 3 and 6 pg/g toxic equivalents (WHO-TEQ), for PCDD/PCDFs and PCDD/PCDFs plus dioxin-like PCBs compounds, respectively. The data here showed that the concentrations of both group of contaminants in most samples tested were below the legal limits. There were only two samples exceeding legal permit level (sample no. 049/2008 and 026/2008) and eight samples close to the action level (Table 4).

Dioxin and furans congeners were the dominant chemicals in milk tested (over 60% of the PCDD/PCDFs and 40% of dl-PCBs). The percentage of dominating congeners are presented in Figure 1. In goat and cow milk samples, highest contribution to the toxicity of the matrix resulted PCB-126 about 31%, 2,3,4,7,8-PeCDF - 21%, 1,2,3,7,8-PeCDD - 13%, and 2,3,7,8-TCDD - 11%.

Table 4

Samples exceeding permit levels. Results are presented as a mean X ± U (uncertainty)
*2006/88 EC, ** 1881/2006/ EC

Material		**Year**	**Sample No.**	**REGION**	**X ± U**			**Action level (A)* Maximum limit (ML)** [pg WHO-TEQ/g fat]**		
					PCDD/F	**dl-PCB**	**PCDD/F/ dl-PCB**	**PCDD/F**	**dl-PCB**	**PCDD/F/ dl-PCB**
1	Cow milk	2007	076/2007	Podlaskie	3.09 ± 0.49	1.15 ± 0.26	4.24 ± 0.96	**A - 2 ML - 3**	**A - 2**	**A - 4 ML - 6**
2		2008	049/2008	Mazowieckie	**4.87 ± 0.78**	**3.05 ± 0.69**	**7.93 ± 1.8**			
3		2009	048/2009		2.88 ± 0.46	0.87 ± 0.20	3.75 ± 0.85			
4	Goat milk	2008	026/2008	Lubelskie	**4.64 ± 0.74**	**0.44 ± 0.10**	**5.08 ± 1.15**			
5		2009	067/2009		2.75 ± 0.44	0.67 ± 0.15	3.43 ± 0.78			
6		2010	012/2010	Malopolskie	2.86 ± 0.46	1.78 ± 0.40	4.64 ± 1.05			
7		2010	035/2010		2.67 ± 0.43	1.46 ± 0.33	4.14 ± 0.94			
8		2010	036/2010		2.64 ± 0.42	1.49 ± 0.34	4.13 ± 0.94			
9		2010	066/2010	Lubelskie	2.61 ± 0.42	0.93 ± 0.21	3.54 ± 0.80			
10		2011	036/2011		3.01 ± 0.48	2.07 ± 0.47	5.08 ± 1.15			

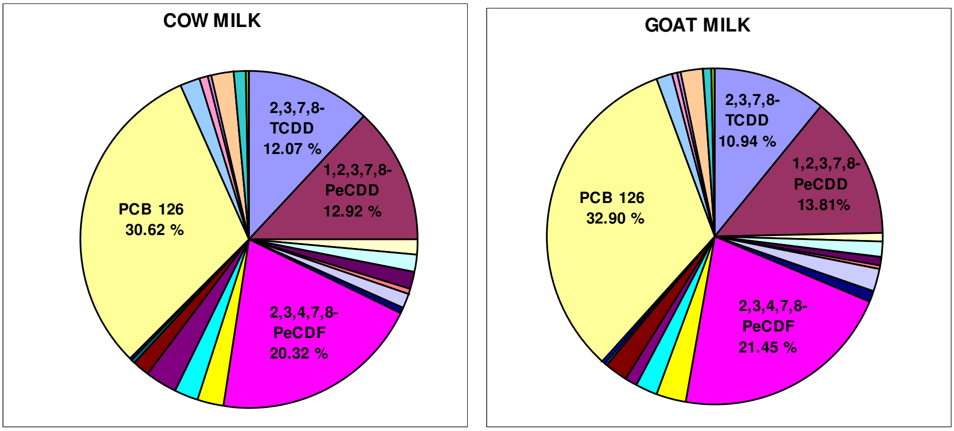

Fig. 1. Percentage of PCDD/F/dl-PCB congeners contribution in matrix toxicity. Cow and goat's milk

Milk fat and dairy foods contribute from 5.2 to 80% to the total daily exposure of general population, depending on the eating habits [6-8]. In this study it was found that dioxins, furans and dl-PCBs levels were very low, and only two milk samples were non-compliant with EC legislation. The higher values of dioxin in milk could be due to an increase in the burning of various materials, in particular chlorine-containing plastic wastes, burnt illegally near the pastures where the cows and goats graze as well as contaminated mixed feed or accidentally contamination. The milk levels were in agreement with those reported in other countries in areas with similar background levels of exposure. Congener levels and profiles of PCDDs, PCDFs, and PCBs in feedstuffs and milk samples that were compared describe congener-specific transfer behavior [9-17]. In 2010 EFSA has shown in Scientific Report "Results of the monitoring of dioxin levels in food and feed", that the level of PCDD/PCDFs and dl-PCBs, found within national cow's milk surveys in Europe is about 1.05 pg WHO-PCDD/F-TEQ/g fat and 2.42 pg WHO-PCDD/F-PCB-TEQ/g fat [18].

In conclusion, this survey shows a low concentration of PCDD/PCDFs and dl-PCBs in cow and goat's milk in Poland. Higher concentrations of dioxins found could be also a result of improper feeding of food producing animals (contaminated feed). As food contamination is directly related to feed contamination the integrated approach must be adopted. Persistent, bioaccumulative and toxic pollutants, including dioxins, bioaccumulate through the food chain and ultimately result in low-level contamination in most animal fats. It is important to understand the levels in milk, as milk fat may be one of the highest dietary sources of dioxin exposure.

Monitoring of dioxins in milk could provide information for contamination of milk itself or other associated food (milk products). Analysis of milk also allows the opportunity to investigate geographic variability, relations between environment and area were milk is produced and distributed. It is essential to reduce dioxin and dioxin like compounds in food and feed.

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BADANIE POZIOMÓW DIOKSYN W SUROWYM MLEKU KRÓW I KÓZ W POLSCE

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Abstrakt: Dioksyny ze względu na właściwości toksyczne mogą stanowić zagrożenie dla zdrowia. Do grupy tej należy 7 kongenerów *polichlorowanych dibenzo-p-dioksyn* (PCDD), 10 *polichlorowanych dibenzofuranów* (PCDF) oraz 12 dl-PCB. Ponieważ głównym źródłem narażenia ludzi na dioksyny jest żywność pochodzenia zwierzęcego, celem pracy była ocena poziomów 29 kongenerów dioksyn w mleku krowim i kozim pochodzącym z terenu kraju. Metodą wysokorozdzielczej chromatografii gazowej sprzężonej z wysokorozdzielczą spektrometrią mas (HRGC-HRMS) analizowano w latach 2006-2011 ponad 120 próbek. W 94 próbkach surowego mleka krowiego średnie stężenie PCDD/PCDF wynosiło 0,84 ± 0,60 pg WHO-TEQ/g tł., zaś suma 29 kongenerów 1,35 ± 0,89 pg WHO-TEQ/g tł. Zawartość dioksyn i dl-PCB była niska (do 30% dopuszczalnych limitów dla mleka pełnego) i próbki spełniały wymagania przepisów krajowych i unijnych. W badanym okresie jedynie w dwóch próbkach mleka krowiego stwierdzono stężenie na poziomie progu podejmowania działań (2 pg WHO-TEQ/g tłuszczu) oraz w 1 próbce stężenie przekraczające dopuszczalną zawartość PCDD/PCDF (3 pg WHO-TEQ/g tłuszczu). Surowe mleko kozie generalnie zawierało wyższe niż krowie stężenia badanych związków (zarówno PCDD/PCDF, jak i dl-PCB) i średnia dla PCDD/PCDF wynosiła 1,49 ± 0,97 pg WHO-TEQ/g tłuszczu. W 6 spośród 33 badanych próbek mleka koziego stężenia dioksyn znajdowały się na poziomie „action level", zaś w jednej próbce zawartość dioksyn przekroczyła dopuszczalne limity. Uzyskane wyniki pozwalają na stwierdzenie, że mleko zawiera niskie poziomy dioksyn, jakkolwiek zdarzały się incydenty wynikające najprawdopodobniej z błędów żywieniowych zwierząt hodowlanych (karma zawierająca dioksyny).

Słowa kluczowe: dioksyny, furany, PCB, mleko, krowy, kozy

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ENDOCRINE DISRUPTING COMPOUNDS (EDCs) - ENVIRONMENTAL HAZARDS AND THEIR PHOTOCHEMICAL DEGRADATION

KSENOESTROGENY - ŚRODOWISKOWE ZAGROŻENIA I ICH FOTOCHEMICZNA DEGRADACJA

Abstract: Some of xenoestrogens presented in aqueous environment can mimic or/and block natural hormones (Endocrine disrupting compounds - EDCs). Those hazardous contaminants consist of many natural and synthetic organic compounds, but are mostly man-made substances such as pharmaceuticals and additives for personal care products. The presence of EDCs in the aquatic environment at low concentrations, coupled with their toxicity to microbe cause that the classical method of water purification, including biodegradation are ineffective. Removal of EDCs from the aquatic environment can be effectively carried out by oxidation using advanced oxidation processes and photosensitized oxidation. Applications of photochemical processes permit to obtain a high degree of reduction of EDCs in relatively short time. Photosensitized oxidation, that has shown satisfactory results, has an unquestionable advantage in being able to use oxygen from the air and the energy of sunlight. The paper presents the application of several photochemical methods for degradation of phenolic compounds belonging to the EDCs - parabens, chlorophenols, phenylphenol.

Keywords: endocrine disrupting chemicals - EDCs, advanced oxidation processes, photosensitized oxidation

The scientific studies provide data that some chemical compounds *endocrine disrupting compounds* (EDCs) found in the surface waters can influence on animal and human endocrine systems. It is well-established that aquatic wildlife in marine and freshwater is exposed to natural and synthetic EDCs which are able to interfere with the hormonal system, thus possibly causing adverse effects on the intact physiology of organisms [1]. EDCs are highly diverse and include synthetic chemicals used as plasticizers, detergents, pesticides, and pharmaceuticals, natural and synthetic hormones. Widespread use of these compounds can cause their accumulation and the occurrence of irreversible changes in nature. Generally EDCs are present in water at low levels concentration (1 ng/dm^3 - 1 μg/dm^3) which makes their removal in conventional sewage treatment plant inefficient. Many pharmaceuticals, pesticides and other compounds that demonstrate estrogenic effects are not removed by physical methods. Research conducted over the degradation of EDCs using biological methods are relatively slow and indicate low efficiency [2]. The degradation of EDCs in aerobic and anaerobic sludge permitted on the above 90% concentration reduction of contaminant, but this process took over 30 days [3]. For this reasons EDCs are emerging as a major concern for water quality.

The use of UV light for disinfection of water has been known for several decades. The absorption of light energy may result in photodegradation, but some of molecules are recalcitrant to photolysis. Chemical methods like advanced oxidation processes (AOP) are very effective in removing pollutants present in wastewater at low concentrations. Mainly AOP rely on the formation of reactive and short-lived oxygen intermediates such as

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hydroxyl radicals ($^{\bullet}OH$). The hydroxyl radicals are a powerful, non-selective chemical oxidant (the redox potential is 2.80 V [2]). In literature several AOPs have been described: UV combined with H_2O_2, UV combined with ozone (O_3), O_3 in combination with H_2O_2, UV combined with O_3 and H_2O_2. Apart from a direct reaction of ozone with the organic pollutants, aqueous solutions of ozone especially at high pH lead to ozone transformation to hydroxyl radicals give reactions. Other methods, like heterogeneous photocatalysis (eg TiO_2/hυ or ZnO/hυ) are based on the use of wide-band gap semiconductors (3.2 eV for TiO_2) [4]. Homogeneous photo-Fenton produces $^{\bullet}OH$ in the reaction of H_2O_2 with dissolved iron salts [5]. Both processes can occur under UV-Vis radiation and after some modification can be indicated by the solar light. Although AOPs have been shown to be effective, removal of pollutant from wastewater is a process with high energy consumption, where cost and efficiency are the key limit for their potential application. Introduction of AOPs before a biological treatment process may be likely because of the chemical/photochemical oxidation renders recalcitrant EDCs more biodegradable and less toxic, and improves their degradation in the following treatment process. To reduce the cost of energy consumed in the AOP, generally available solar energy should be applied for the degradation of compounds. However, among the advanced oxidation methods, many of them are unsuitable for degradation of pollutants in the environment with the use of solar energy. Only photocatalysis and photo-Fenton reaction under modification can use the solar radiation.

Another possibility of removing the water pollutants using solar light is the photosensitized oxidation. The main reactant formed in this process is very reactive species - molecular singlet oxygen. Photochemical oxidation, particularly using molecular oxygen, is unquestionable one of the most important of photochemical methods, since it does not formed any additional pollutant. Important issue in this process is to find the proper photosensitizer characterized by high efficiency in initiating oxidation processes. Photosensitized oxidation may occur in homogeneous and heterogeneous systems. Disadvantage of the homogenous process is the necessity of removing photosensitizer from the solution as the reaction has been completed. This problem can be overcome by using immobilized photosensitizers which show the advantage of easy operation, but sometimes demonstrate a reduced rate of reaction due to mass transfer effects.

The best results for removing EDCs from wastewater gain method combining the characteristics of strong oxidants and UV or VIS radiation. The most effective methods employing photochemical reactions include: photocatalysis with titanium peroxide (TiO_2/UV), ozonolysis or/and hydrogen peroxide with UV radiation (O_3/UV, H_2O_2/UV*)*, photo-Fenton process (Fe^{2+}/H_2O_2/UV), photolysis and photosensitized oxidation or photocatalysis [6-9].

The paper presents the application of several photochemical methods for degradation of phenolic compounds belonging to the EDCs - parabens (Fig. 1), phenylphenols (Fig. 2), and chlorophenols (Fig. 3).

Parabens

The literature about degradation of parabens is rather scarce. The degradation of *n-butylparaben* (BP) by direct irradiation using UV (254 nm) was inefficient [8]. In turn, the application of H_2O_2/UV system for BP decomposition was proved to be extremely efficient [10]. Oxidation using chlorine resulted in a reduction of BP and *benzylparaben* (BeP) concentration after 15 min by 67 and 71%, respectively [11]. However in this process chlorinated byproducts appeared in the reaction solution [11, 12]. The use of solar radiation for BP and BeP degradation did not give satisfactory results [12]. Parabens were also degraded by photocatalysis and ozonation processes. Heterogeneous reaction in the system TiO_2/UV caused 90% (pH 6) and 100% (pH 9) reduction of metylparaben concentration in 120 min, and 180 min, respectively [2]. Degradation with ozone at pH 6.9 was the most effective method of removal parabens - 99% decomposition after 12 min [13]. Photosensitized oxidation was successfully applied for decomposition of BP and BeP with the successful effect as well in homogenous and heterogeneous systems. Both of pollutants were completely removed from the solution after 120 min [14, 15].

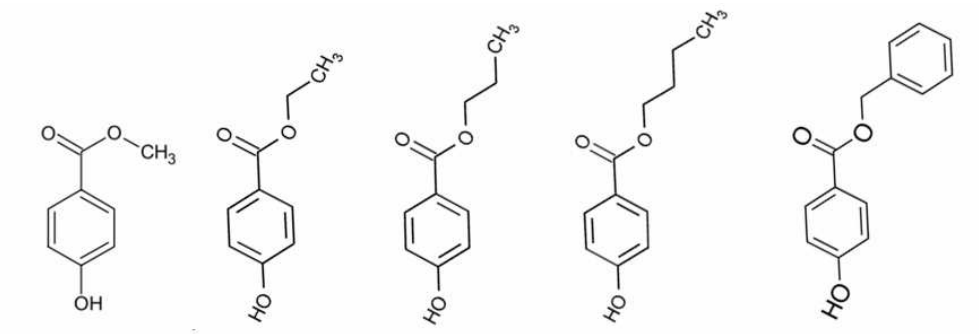

Fig. 1. General chemical structures of a parabens: metylparaben, etylparaben, propylparaben, butylparaben, benzylparaben

Phenylphenols

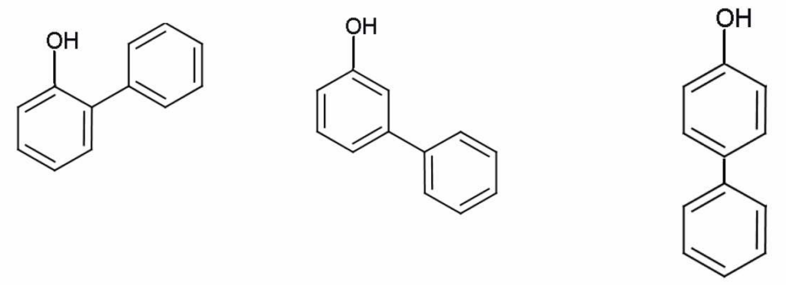

Fig. 2. General chemical structures of a phenylphenols: *orto*-phenylphenol, *meta*-phenylphenol, *para*-phenylphenol

There are a limited number of literature data on the degradation of phenylphenol isomers in an aqueous solution. Among the tested biodegradation processes two methods can be distinguished by using enzymes [16, 17] and activated sludge [18]. Enzymatic degradation of phenylphenol proceeds relatively quick however the preparation of enzymes to the process are very tedious and expensive. Photocatalytic degradation of *para*-phenylphenol in the presence of TiO_2 leads to the formation of bicyclic aromatic compounds [19]. Sarakham et al studied the photosensitized oxidation of *meta*- and *para*-phenylphenol [20]. These compounds were total removed from the solution after 50 min, but the received final product was identified as oligomers of phenylphenols. Photocatalytic degradation of *2-phenylphenol* (2-PP) irradiated between λ = 300 and 450 nm was examined. The use of ZnO caused the 80% reduction of 2-PP concentration during 7 h, while the use of TiO_2 in the same time removed 50% of 2-PP. In both cases, the main identified photoproducts were hydroquinone, *p*-benzoquinone, phenylhydroquinone, phenylbenzoquinone, 2,2- and 2,3-dihydroxybiphenyls [21]. During ozonation process at neutral solution 2-PP was completely removed just after 250 s [22].

Chlorophenols

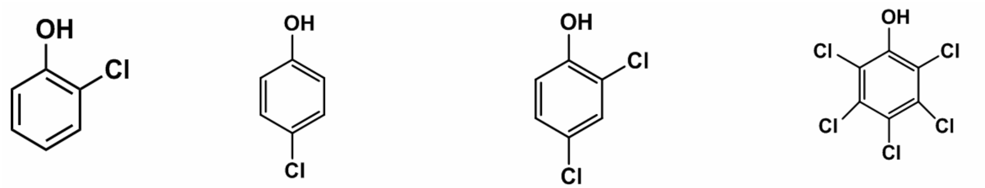

Fig. 3. The molecular structures of chlorophenols which are belonging to EDCs: 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and pentachlorophenol

Chlorophenols are a group of contaminants whose degradation was most extensively studied. Several methods were successfully applied for chlorophenol degradation: UV radiation [23], photochemical methods (using hydrogen peroxide, Fenton reaction, ozone [24, 25]), electrochemical methods [26] and photocatalysis with TiO_2 [27-29]. Photodegradation of chlorophenols using singlet oxygen in a homogeneous system has been also thoroughly studied [30-33]. The level of chlorination of phenol molecule influenced on the efficiency of all photodegradation methods and higher substituted phenols demonstrated lower reactivity. The efficiency depended also on the position of chlorine substituent in the aromatic ring.

Summary

Applying AOPs for effective water pollutants degradation, they had several disadvantages. The application of photocatalytic technology with TiO_2 to wastewater treatment is limited to the wavelength range of radiation. Modification of TiO_2 leading to its activation under visible radiation can lead to the broad employment of this method [27]. The drawbacks of H_2O_2/UV process consist in the high energy requirements associated with the use of UV lamps and the need of the use of high H_2O_2 concentrations [34]. Disadvantages of photo-Fenton reactions are connected with the necessity of acidic reaction condition and the difficulty in removing the sludge containing iron ions after the treatment [35].

AOPs are effective methods for removing EDCs from water solution, but the costs of the processes are high due to the use expensive reagents such as H_2O_2 and O_3 and electric energy when UV radiation is applied. For this reason interesting option among the photochemical processes seems to be the use of photosensitized oxidation. The main advantage of this process is the use of visible light or solar energy and using oxygen from air.

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KSENOESTROGENY - ŚRODOWISKOWE ZAGROŻENIA I ICH FOTOCHEMICZNA DEGRADACJA

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Abstrakt: Niektóre ksenoestrogeny występujące w środowisku wodnym mogą naśladować lub/i blokować naturalne hormony (EDCs). Do grupy tych groźnych substancji zaliczyć można wiele naturalnych i syntetycznych organicznych związków, ale głównie są to substancje stworzone przez człowieka, takie jak farmaceutyki czy środki higieny osobistej. Obecność EDCs w środowisku wodnym w niewielkich stężeniach i często toksycznych wobec mikroorganizmów powoduje, że klasyczne metody oczyszczania wód łącznie z biodegradacją są nieefektywne. Usuwanie EDCs ze środowiska wodnego może być skutecznie realizowane na drodze utleniania poprzez zastosowanie *zaawansowanych technik utleniania* (AOP) oraz fotosensybilizowanego utleniania. Zastosowanie procesów fotochemicznych pozwala na uzyskanie wysokiego stopnia redukcji EDCs w relatywnie krótkim czasie. Metoda fotosensybilizowanego utleniania posiada niekwestionowaną zaletę, jaką jest możliwość wykorzystania tlenu z powietrza i energii światła słonecznego. W pracy przedstawiono zastosowanie szeregu fotochemicznych metod do degradacji związków fenolowych zaliczanych do EDCs - parabenów, chlorofenoli, fenylofenoli.

Słowa kluczowe: ksenoestrogeny, zaawansowane metody utleniania, fotosensybilizowane utlenianie

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PHOTOCATALYTIC DEGRADATION OF THE SELECTED SULFONAMIDES IN WASTEWATER

FOTOKATALITYCZNA DEGRADACJA WYBRANYCH SULFONAMIDÓW W ŚCIEKACH

Abstract: Sulfonamides are antibacterial drugs, the most commonly used in veterinary prophylaxis. To the environment, these drugs are being introduced in several ways. Sulfonamides have the capacity to accumulate in various organisms, for which they may be toxic. Even low concentrations of these drugs may lead to the formation of microbial drug resistance. The aim of this study was to determine the applicability of the process of photocatalysis for the degradation of selected sulfonamides applied to real wastewater and optimization of this method. The process of photocatalytic degradation was studied in real municipal wastewater, synthetic sewage and in distilled water. The process was carried out in open reactors that were UV-A irradiated, with the participation of TiO_2-P25, a mixture of $FeCl_3$ and $TiO_2/FeCl_3$. It was found that use of the $TiO_2/FeCl_3$ mixture brings the best results in the removal of selected sulfonamides. Influence of selected wastewater treatment processes, pH and concentrations of reagents on the efficiency of degradation of sulfonamides from wastewater has been determined. In addition, orders were designated as well as kinetics of studied reaction.

Keywords: photocatalysis, sulfonamides, wastewater

Environment is an essential part of human's life. Therefore, it is very important to avoid pollution of water, soil and air. In most cases, progressing pollution of the environment is a result of human's activity. The main sources of environmental pollution are mostly households, industry and agriculture, where various organic compounds can pass to wastewater. However, after treatment, the wastewater can become a serious threat to a whole biosphere. Ones of the particularly hazardous components of these wastewater are drugs and their metabolites. *Sulfonamides* (SNs) are an example of such compounds. It is estimated that most of them is stable in the environment, and some are also highly toxic, or ecotoxic [1, 2].

The threat caused by antimicrobial drugs is mainly based on the fact that even in trace amounts, they may generate drug resistance in microorganisms [3, 4]. Then, the resistance genes can be transferred between different strains of bacteria, for example by conjugation.

In consequeance, these genes may occur in pathogens in ecosystems not previously exposed to contact with antibiotics [4]. According to the authors of the National Programme for the Protection of Antibiotics [5], relatively few pathogenic microorganisms through acquired resistance mechanisms may be major factors threatening the health and human life. In result, diseases commonly considered to be "defeated" may be re-spread again.

The above discussed reasons cause that different methods to remove of these compounds from wastewater have been intensively studied in recent years. The efficiency

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of traditional methods, eg, biodegradation, coagulation and sedimentation, is often low or very low [1, 6-8]. Researchers have high expectations with regard to *advanced oxidation processes* (AOP) such as a photocatalytic degradation [9-15]. The use of this technique for treatment of municipal and domestic wastes enables the degradation of organic substances, including drugs, as a result of oxidation by hydroxyl radicals (HO•) generated in the reaction medium. Partially treated wastewater without pharmaceuticals and their metabolites could be used for example to fertilize the fields.

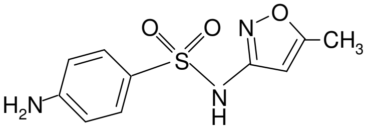
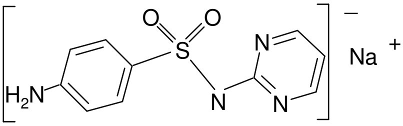
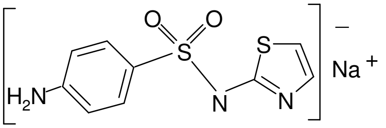
The aim of this study was to determine the possibility of the use of photocatalytic process for degradation of the selected sulfonamides added to real wastewater and this method optimization.

Materials and methods

The investigated SNs are characterized in Table 1.

Table 1

The characteristics of the used SNs

Sulfonamides	**Abbr. in text**	**Structure**	**Manufacturer**	**Initial concentration in samples [mmol dm^{-3}]**
Sulfamethoxazole	SMX		Sigma	0.050
Sulfadiazine (natrium salt)	SDZ		Sigma	0.025
Sulfathiazole (natrium salt)	STZ		Sigma	0.025

Titanium oxide (IV) (TiO_2-P25) from Evonic Degussa GmbH and ferric chloride ($FeCl_3$) from POCH were used as photocatalysts. They were selected based on the results of previous studies on the photocatalytic degradation of sulfonamides in aqueous solutions. If necessary, the HCl was added to samples in order to decrease the pH values.

Wastewater samples

The characteristics of wastewater used in experiments are presented in Table 2. Wastewater samples were stored for 1 hour at room temperature before their use in experiments. The investigated drugs at concentrations above the limit of detection were not detected in wastewater. The determination of wastewater parameters were performed according to the standard operating procedures for water and wastewater.

Table 2

The characteristics of the used wastewater samples

	Wastewater[a]	**Influent II**[b]	**Wastewater from septic tank**	**Landfill leachate**	**Effluent after WWTP**[b]
Collection date	04.2009	09.2009-02.2010	29.12.2010	8.06.2010	09.2009-02.2010
pH	7.63	7.58÷7.92	8.69	8.37	7.10÷7.66
COD [mg O_2 dm^{-3}]		611÷902	820	>2000	137÷774
BOD_5 [mg O_2 dm^{-3}]		152÷199	368	360	60÷89
Conductivity [mS cm^{-1}]	0.799	0.508÷1.789	2.56	8.25	1.204÷1.722
Turbidity [FTU]	117	40÷145	352	-	4÷50
Absorption λ = 254 nm		0.380÷0.752	1.77	-	0.196÷0.346

a) illegal discharge of wastewater drain into the river Bobrek, Sosnowiec (Poland), b) from sewer system that convey domestic and urban waste to wastewater treatment plant (WWTP) Zagorze, Sosnowiec (Poland)

Before the irradiation process, a mixture of SNs (Table 1), solid TiO_2 and / or $FeCl_3$ were added to wastewater samples (100 cm^3). They were irradiated with 4 UV lamps (Philips TL W/05). During irradiation, samples were mixed using magnetic stirrers and had free contact with air.

Determination of drugs in samples

The concentration of selected drugs in samples were determined by HPLC method [16] (Waters detector - TAD-486, wavelength - 254 nm, pump - Knauer 64, column Supelcosil LC-18, 250x4.6 mm, grain - 5 μm, mobile phase: buffer containing 20 mmol dm^{-3} K_2HPO_4, pH 8.2: acetonitrile - 95:5, flow - 1.0 cm^3/min, sample volume - 20 cm^3).

In order to estimate the efficiency of the investigated photocatalytic reactions, the dynamics of changes in SNs concentrations during the irradiation was compared in relation to the stock solutions prepared according to previously described procedure (without the addition of catalysts and before the beginning of irradiation). On this basis, the percentage degree of the removal of SNs after a definite, in the experiment, irradiation time of their solutions was determined. *The degree of removal* (*DR*) was calculated according to the equation:

$$DR = \left(1 - \frac{C_i}{C_o}\right) \cdot 100\%$$

where C_i/C_o is the ratio of determined and initial concentration of each sulfonamide.

The average degree of removal of SNs in a mixture was calculated as a weighted average value of DR.

Studied the kinetics of photocatalytic processes were evaluated based on the value of the regression coefficients

$$\ln\frac{C_i}{C_o} = -k^I t + b \quad \text{(for the first-order reaction)}$$

$$\frac{1}{C_i} = k^{II} t + b \quad \text{(for the second-order reaction)}$$

where t is the irradiation time, b is the intercept.

The half-life time ($T_{1/2}$) was determined by the graphical method.

Dynamics of photocatalytic reaction

The process of photocatalytic degradation of SNs was studied in the presence of TiO_2 (0.5 g dm^{-3}) and $FeCl_3$ (1.0 mmol dm^{-3}) and mixtures containing these two compounds. Their used concentrations and the pH of the irradiated solutions was established in preliminary studies using the SNs solutions in distilled water. Figure 1 shows the average half-times of SNs to added to wastewater samples during irradiation in the presence of TiO_2 and / or $FeCl_3$. Additionally, the results obtained in processes carried out in distilled water are presented in Figure 1.

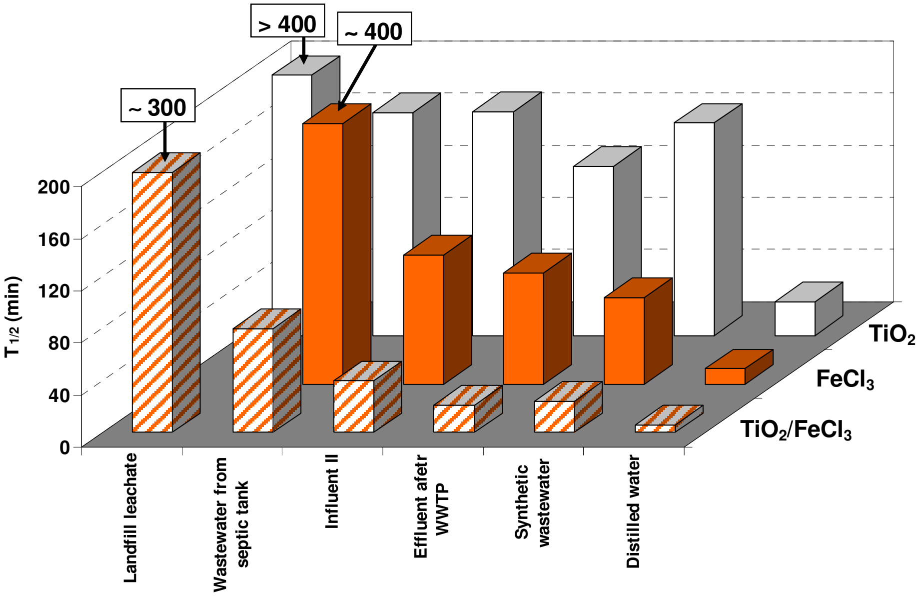


Fig. 1. The average half-times of SNs added to samples during irradiation in the presence of TiO_2 (0.5 g dm^{-3}) and/or $FeCl_3$ (1.0 mmol dm^{-3})

Before the beginning of irradiation, a slight decrease in SNs concentration (about 10%) was observed in all samples at pH ~3. Further decrease in SNs concentration occurred during the irradiation of samples. It can be an evidence of the drugs degradation. As expected, the values of $T_{1/2}$ determined for SNs in wastewater samples are much longer than in distilled water. It means that in order to carry out an effective degradation of drugs in wastewater, the irradiation time should be prolonged.

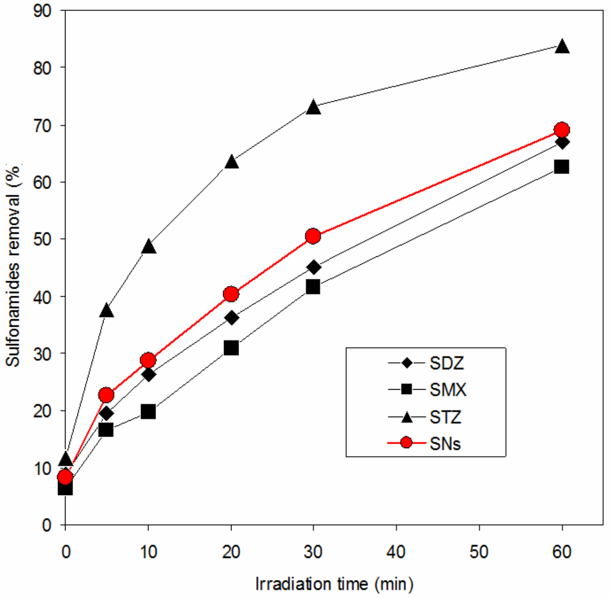


Fig. 2. The dynamics of the SNs degradation in influent in the presence of $TiO_2/FeCl_3$ mixture

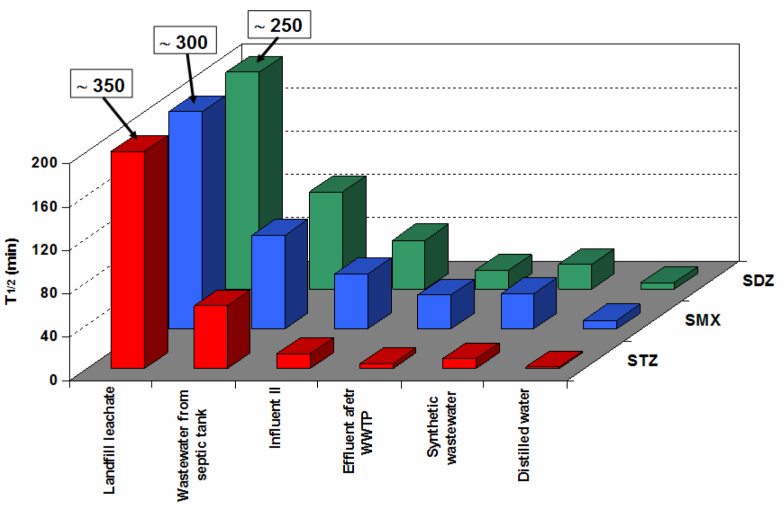


Fig. 3. The half-life times of SNs in wastewater samples and in distilled water. The values were determined during the photocatalytic degradation carried out in the presence of a mixture of TiO_2 (0.5 g dm^{-3}) and $FeCl_3$ (1.0 mmol dm^{-3})

By comparing the half-times of individual SNs, the mixture $TiO_2/FeCl_3$ was settled as the optimal photocatalyst in this process (Fig. 1). This mixture has high initial rate of photodegradation, especially in the case of sulfathiazole (STZ) and the process occurs most likely in accordance with the second-order reaction kinetics (Fig. 2). In all other cases, the process of photodegradation follows the first-order kinetics.

Figure 3 presents the weighted average of $T_{1/2}$ determined for all SNs in the investigated samples.

It was found that all investigated SNs, added to wastewater samples underwent the photocatalytic degradation. However in practice, the photocatalysis has only little use in the case of leachate from landfills because it proceeded much slower than in the other wastewater studied.

Additionally, the effect of concentration of individual components of the most active photocatalytic system ($TiO_2/FeCl_3$) and the pH of the irradiated samples on the $T_{1/2}$ value of SNs added to the influent II were also determined. The results obtained were similar to those observed in distilled water. It was found that in wastewater the photocatalytic degradation of SNs carried out at pH = 3 and at concentrations of TiO_2 and $FeCl_3$ established in earlier experiments was the most preferred process. However, the results obtained for STZ differed from the others. For example, the efficiency of STZ degradation increased with increasing concentration of TiO_2 above 0.5 g dm^{-3} and at $pH < 3$. It means that the reaction mechanisms for SDZ, SMX and STZ may vary.

Conclusions

1. Sulfonamides (SNs) added to wastewater, may be removed by the photocatalytic degradation process.
2. Photocatalytic degradation of SNs is ineffective in the case of leachate from landfills.
3. The process of photocatalytic degradation is the most favourable when a mixture of $TiO_2/FeCl_3$ and pH = 3 are used.
4. Photocatalytic reaction mechanisms may vary in the case of individual SNs.

Acknowledgements

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FOTOKATALITYCZNA DEGRADACJA WYBRANYCH SULFONAMIDÓW W ŚCIEKACH

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Abstrakt: Sulfonamidy są lekami przeciwbakteryjnymi najczęściej używanymi w profilaktyce weterynaryjnej. Do środowiska leki te dostają się różnymi drogami. Sulfonamidy mają zdolność kumulowania się w różnorodnych organizmach, wobec których mogą okazać się toksyczne. Nawet małe stężenie tych leków może prowadzić do wytworzenia się lekooporności drobnoustrojów. Celem pracy było określenie możliwości zastosowania procesu fotokatalizy do degradacji wybranych sulfonamidów aplikowanych do rzeczywistych ścieków oraz optymalizacja tej metody. Proces fotokatalitycznej degradacji badany był w rzeczywistych ściekach komunalnych, w ściekach syntetycznych oraz w wodzie destylowanej. Proces prowadzony był w otwartych reaktorach, które były naświetlane promieniowaniem UV-A, przy udziale TiO_2-P25, $FeCl_3$ i mieszaniny $TiO_2/FeCl_3$. Stwierdzono, iż zastosowanie mieszaniny $TiO_2/FeCl_3$ przynosi najlepsze efekty w usunięciu wybranych sulfonamidów. Określono wpływ wybranych procesów oczyszczania ścieków, pH oraz stężeń reagentów na efektywność degradacji sulfonamidów ze ścieków. Zostały wyznaczone ponadto rzędy badanych reakcji oraz ich kinetyka.

Słowa kluczowe: fotokataliza, sulfonamidy, ścieki

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RESEARCH OF HEAVY METALS DISTRIBUTION IN BOTTOM SEDIMENT OF LAKE TALKŠA (LITHUANIA)

BADANIA PRZESTRZENNEGO ZANIECZYSZCZENIA METALAMI CIĘŻKIMI OSADÓW DENNYCH Z JEZIORA TALKŠA (LITWA)

Abstract: The intensification and development of industrial processes has harmful effects of human activities on nature and entire environment. Having performed the assessment of contamination of environmental components, especially geological environment, it is possible to make a quantitative evaluation of the scope of anthropogenic influence and often the hazardousness of such influence on biota and people. This paper presents study results on accumulation of heavy metals in different layers of Talkša Lake. For the sampling of intact structure of the sediment, the turf borer from the ice was used. After the preparation and examination of samples, Pb, Ni, Cr, Zn and Cu concentrations were identified in the laboratory. Concentrations of these heavy metals in sapropel layers were determined in the extracts of sapropel prepared by means of atomic absorption spectrometry. The results showed that sapropel stratifying on the northern shores of Talkša Lake in terms of LAND 20-2005 should be classified as sludge of Category II. That was determined by maximum concentrations of Cr (257.5 mg/kg) detected in the upper horizon of the sludge. Within other horizons, sapropel is not contaminated with heavy metals, and metal concentrations within it could be treated as amount of valuable trace elements. Due to different mixing layers, sapropel recovered from this part of the lake would become valuable excavation widely used for the purposes of economic needs.

Keywords: heavy metals, lake clean, lake sediments, sapropel

Lakes are a great national treasure, they are important from the natural and economic point of view. Lakes are a source of fresh water. They are also used for modern fishculture, development of hunting economy, water sports, recreational and tourism purposes. Therefore, recovery of silted lakes is very important. On the other hand, sapropel is a valuable lake product. In agriculture it is suitable for soil fertilization and as addition to food for animals, and is a good raw material for chemical and even building industry or medicine and in the energy sector because of the matter's chemical and physical properties [1-4].

Lithuania has about 2850 lakes each covering over 0.5 hectare and around 3150 lakes of under 0.5 hectare each. In total, they cover the territory of 91360 hectares [1]. Eutrophication makes lakes decline, and they accumulate sludge, lakeshores get covered with excess vegetation and, consequently, all this entails a serious ecological problem. The process of declining lakes may also be natural, yet anthropogenic contamination adds to a fast-paced silting up of lakes [5-7]. Sapropel may be of different colors: its color is very important as it discloses the quantities of organic and non-organic matters. Jade color shows that sapropel includes chlorophyll, pink means sapropel has carotene, blue color reveals that sapropel includes vivianite, grey means lime addition and black color or a quickly darkening shade means sapropel includes iron. After being pumped out of a lake, sapropel undergoes fast oxidation and loses its natural shade [2, 6].

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The aim of this article is to survey the concentration of heavy metals in sapropel in Lithuanian Lake Talkša and determine whether or not sapropels of such consist qualifies as an agricultural fertilizer.

Materials and methods

Sapropel samples have been taken from Lithuanian the Lake Talkša. The Lake is located 1 km from the center of Šiauliai town. The lake covers 56.2 hectares, it is 2 km long, and its maximum width reaches 550 m. The northern part of Lake Talkša is connected with Lake Ginkūnai covering 16 hectares via 150 m-long and 5 m-wide Kulpė canal covered with reed. Overgrowth of vegetation covers almost all shores of the lake. The samples of lake sediments were taken in winter with a 50 cm-thick ice cover. Having drilled the ice cover to different depths of bottom sediment samples were taken by peat type drills.

To examine the impurity of samples with heavy metals and to find out other settings of sludge, the analysis of the composition of their trace elements is carried out. Impurity of sludge in Lithuanian lakes is usually measured according to the requirements for the use of sludge wastewater for fertilization and reclamation set in LAND 20-2005 (Table 1).

Table 1

Maximum limit values for concentration in sludge

Sludge category	**Quantities of heavy metal [mg/kg]**				
	Pb	**Ni**	**Cr**	**Zn**	**Cu**
1st	≤ 60	≤ 45	≤ 60	≤ 200	≤ 60
2nd	61÷165	45÷100	61÷130	201÷660	61÷200

With reference to LAND 20-2005, the sludge which can be used for fertilization and reclamation of quarries is classed to I category of sludge. It is forbidden to use the sludge of II-IV category as fertilizer in the areas which are intended for growing vegetables and fruit trees, but it is allowed to grow field crops within one year after the promulgation on the sowing surface. In case of intention to fertilize the soil with the sludge of II-IV category for the first time, it is necessary to identify the indicators of soil quality: the content of heavy metals (Pb, Cd, Cr, Cu, Ni, Zn and Hg), granulometric composition and pH [8].

Micro-quantities of sapropel heavy metals were analyzed in lined-up solutions from sapropel (extracts) by Atomic Absorption Spectroscopy with the use of Atomic Absorption Spectrophotometer Buck Scientific 210 VGP with acetylene-air flame. 0.5 g of each sapropel sample were digested with a mixture of HNO_3 (65%) and H_2O_2 (37%) at the microwave digester *Milestone ETHOS*. The solution was poured in flasks of 50 cm^3 and diluted with deionised water to the mark of 50 cm^3.

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples [9].

Results and conclusions

According to its chemical composition, sapropel can be organic, calcareous, siliceous, and mixed (organic-calcareous and organic-siliceous). The quantitative chemical composition of sapropel varies within a wide range depending on maturity, lying depth and formation conditions [1, 9-12].

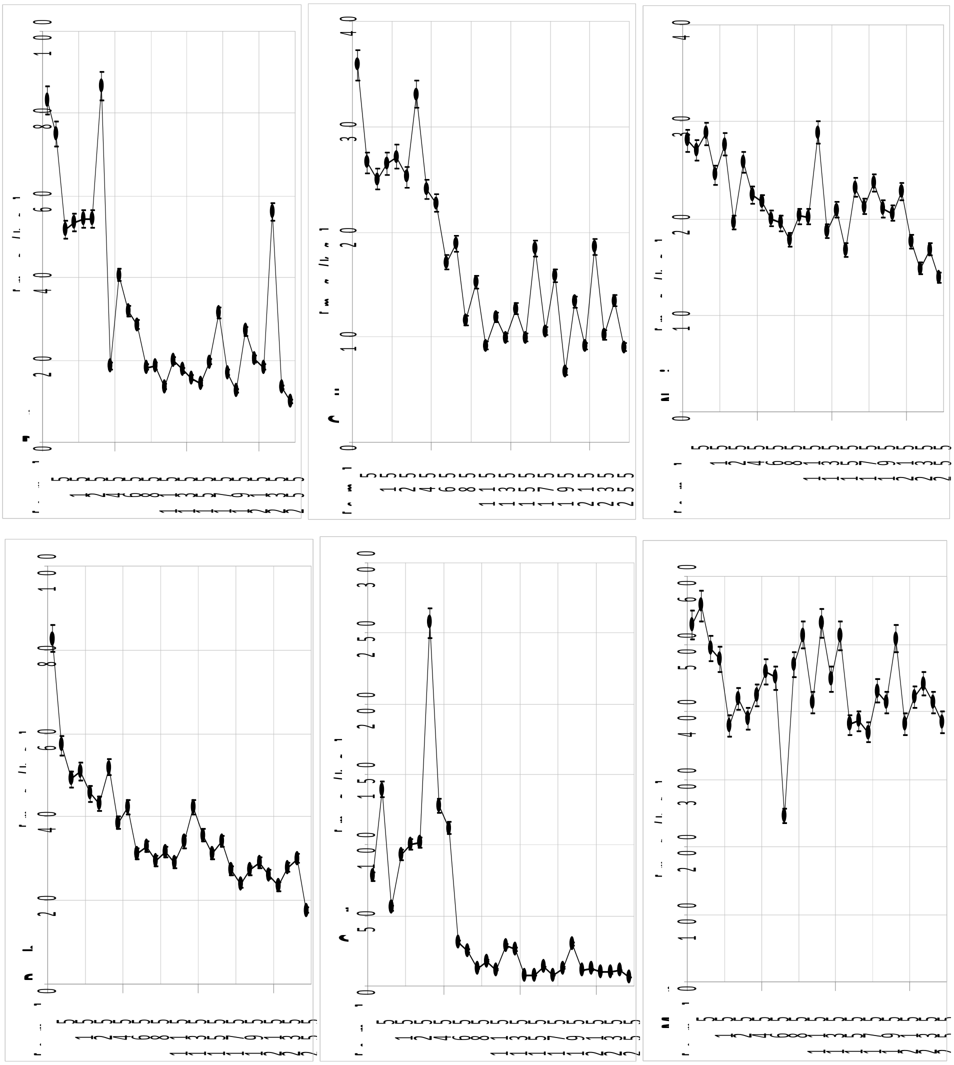

Fig. 1. Variations of heavy metal concentration in the sapropel of Lake Talkša (in vertical profile)

Other studies of *heavy metals* (HM) with the lake sapropel have shown different results. When assessing sapropel in Talkša Lake according to LAND 20-2005, maximum concentration of Cr (257.5 mg/kg) in the upper layer of sludge determined its assign to the sludge of category II. However, mean concentration of Cr (105.3 mg/kg) in the upper layer like the concentrations of others explored, HM of other metals would be classed as sludge of category I. Sapropel in the second horizon is not polluted with heavy metals, and the metal concentrations contained therein can be treated as a content of valuable trace elements.

Vertical section of sapropel in the lake contains horizons which are more polluted with heavy metals, but the following concentration within different depths decreases and does not have great effect on the whole sapropel layer. Assessment report on environmental impact of complex arrangement of Talkša Lake and its approach and installation of international rowing base prepared in Šiauliai in 2003 indicates that the lake sludge is classed to the category I of sewage sludge.

In the past, Talkša Lake experienced significant anthropogenic load. Impact of the "Elnias" leather processing plant on the composition of trace elements of sapropel of the lake is especially significant. Leather processing industry determined the increase in concentrations of pollutants such as Cr and Mn in sapropel. Also, essential influence on the composition of trace elements of bottom sediment had urban wastewater which gets into the lake. Increased amounts of Cr and Zn are formed by the urban wastewater. Transport exhaust gas also has close association with the increase in Pb concentrations. Particulate matter (dust), which are deposited directly, or get into the lake with rainwater drain, also change the natural content of trace elements and their associations.

When assessing sapropel of the northern shore of Talkša Lake under LAND 20-2005, the upper horizon of the sludge is classed to the sludge of category II. In the second horizon, sapropel is not polluted with heavy metals and the metal concentrations contained therein can be seen as the content of valuable trace elements. Sapropel recovered from this part of the lake, due to different mixtures of layer, would become valuable excavation widely used for purposes of economic needs. Researches of heavy metal concentration levels in lakes in Lithuania have revealed that content of sapropel is different in individual cases; and in order to start an expansive use of sapropel it is indispensable to carry out thorough analysis of the matter.

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BADANIA PRZESTRZENNEGO ZANIECZYSZCZENIA METALAMI CIĘŻKIMI OSADÓW DENNYCH Z JEZIORA TALKŠA (LITWA)

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Abstrakt: Intensywność oraz rozwój przemysłu ma szkodliwy wpływ na człowieka, przyrodę, a także całe środowisko. Po przeprowadzeniu oceny zanieczyszczenia komponentów środowiska, zwłaszcza środowiska geologicznego, możliwe jest dokonanie oceny zakresu oddziaływań antropogennych i często niebezpieczeństwa takiego wpływu na żywe organizmy. W pracy przedstawiono wyniki badań dotyczących akumulacji metali ciężkich w różnych warstwach jeziora Talksza. Próbki były pobierane zimą, do ich pobrania został użyty chwytacz rurkowy. Przygotowane próbki zostały zbadane w laboratorium, stężenia metali ciężkich (Pb, Ni, Cr, Zn i Cu) w różnych warstwach sapropelu wyznaczono za pomocą atomowej spektrometrii absorpcyjnej (AAS). Wyniki analizy wykazały, że według klasyfikatora LAND 20-2005 sapropel pochodzący z północnego brzegu jeziora Talksza należy do II kategorii szlamu. Maksymalne stężenie Cr (257,5 mg/kg) zostało wykryte w górnej części osadu, natomiast stężenia innych metali ciężkich występowały w badanych rdzeniach tylko w ilościach śladowych. Stwierdzone w sapropelu zawartości pierwiastków śladowych nie stanowią przeszkody w wykorzystaniu do celów rolniczych oraz rekultywacyjnych.

Słowa kluczowe: metale ciężkie, osady denne, oczyszczenie jeziora, sapropel

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MOBILITY AND PHYTOAVAILABILITY OF LEAD IN URBAN SOILS

DOSTĘPNOŚĆ OŁOWIU DLA ROŚLIN NA TERENACH UPRZEMYSŁOWIONYCH

Abstract: Lead belongs to a group of the most commonly man distributed heavy metals. The reason lies in a dynamic development of transportation but also in development of industry and municipal economy. In bibliography it is referred as a chemical element which is relatively stable in soil - captured in surface layers, and in a high reaction conditions with good sorption qualities it is almost unavailable for live organisms. The paper proves that the problem is more complicated due to various geneses and man's pressure towards soil. Only small anthropogenic pressure affects lead content and mobility. Soils under big anthropogenic pressure - urban, industrial and those within communication route areas - can be characterized for their increased lead content, its solubility and phytoavailability.

Keywords: heavy metals, lead, plants, industrial zones

Lead is a chemical element often referred in bibliography. This is definitely a result of prevalence on Earth and its potential toxicity for organisms [1-4].

The communication used to be recognized as the main source of this element - lead petrol which ceased to be used not a long time ago [5, 6], industry - mainly steel industry, metallurgy, power engineering [7, 8], municipal economy, wastes, landfill effluents, wastewaters and sludge, composts [8]. Sometimes, attention is directed to installations and other elements of infrastructure [5, 9]. Effects from particular sources have changed in time, which illustrates the typical history of development of the most of European cities. Until the 19th century first there were farming and craftsmen's settlements with a great part of activities focused on gardening. In the 19th century and the first part of the 20th century their character changed into typically industrial. In the end of the 20th century industry fell substituted by development of services and dynamic growth of city areas followed by an increase of the number of cars.

In the majority of references lead mobility is described as relatively low, which results from this element chemical and replacement sorption in soils [10]. Many authors also stress a great importance of other soil qualities, mainly reaction. High, neutral or alkaline reaction is indicated as a factor immobilizing lead in soil environment which causes that it becomes practically unavailable to live organisms [1, 11, 12]. Researchers also point at the phenomenon of accumulation of this element in surface soil levels, rich in organic matter. Most of these observations have already been reflected in border figures fixed for lead content in particular elements of natural environment.

As long as researchers' analyses concerning lead behavior are generally right, they rarely touch the problem of time necessary for permanent absorption of this element. Not

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often do they indicate disturbances in soil profile structure being a result of urban pressure as a potential reason for variation of sorption performed. Important within this context is behavior of the constantly mobile part of soil lead. The tests carried out in Zielona Gora by the authors of this paper show that lead deposition in urban soils is often a result of the history of their transformations, and not of a directly treated surface deposition (for example, industrial or communication).

In Europe the problem of lead sorption by plants growing in urban areas has two meanings. One is a result of the condition of decorative plants in urban green areas [13, 14]. The other issues from growing fruit and vegetable in urban vegetable gardens which are then designed for human consumption [15, 16]. Recently, as part of waste management, attention is also focused upon the so called green wastes generated by plant care. The latter problem is related to the possibility of using compost made of urban plant residue as a fertilizer [8, 14].

Methods

The tests were carried out in the commune of Zielona Gora in the areas used for farming, agriculture and forests, in the outskirts and within the town of Zielona Gora (120 thousand inhabitants, west of Poland, Lubuskie Region). Sample collection locations were chosen in the areas illustrating particular stages of human pressure made on natural environment - 105 soil profiles at the depth of 150 cm (samples from each of the genetic levels) + 32 collective surface samples (area of approximately 20 m^2 each, samples from humus levels). In total, 562 samples were subject to the tests. Soils were classified according to the classification of the WRB [17]. Lead content in soil samples was determined by means of atomic absorption FAAS (Varian, $\lambda = 283.3$ nm, 0.7 mm slit).

Extracts in aqua regia ($3HCl:HNO_3$) were made by burning 10 g of airy dry soil in a furnace at temperature of 550°C (12 hours), and then at a sand bath by heat digesting ash in aqua regia (20 cm^3) [18]. Extracts in 0.1 M HCl - the fraction potentially available to plants [19] was prepared by cool digesting airy dry soil in 100 cm^3 of the solution and by shaking for 1 hour. *Cation Exchange Capacity* (CEC) was determined by the Kappen method, pH in 0.01 M $CaCl_2$ potentiometrically, Ca content according to the flame photometry in aqua regia extract and the humus content by means of the Tiurin method.

Leaves were collected in the places with versatile urban, industrial and transportation pressure. The samples included: Black Locust (*Robinia pseudoacacia* L), Small-leaved Lime (*Tilia cordata* L), Wild Privet (*Ligustrum vulgare* L) and grasses (*Graminae*). Collection of leaves was carried out in July and October 2007 (in total 80 samples). Tree leaves were collected from the level of 1.5÷2 m above the ground, whereas leaves of shrubs were collected at the height of approximately 1 m above the ground. Grass was cut when the leaves were approximately 20 cm long. For the tests only well-formed leaves were selected that did not show any damages or disease symptoms. Leaf lead content analysis was carried out in an extract obtained by burning 5 g of dry matter in a furnace at the temperature of 550°C (12 hours), and then by heat digesting ash in aqua regia.

Statistic analysis was made using the software Statistica for Windows 9.1a. The basic statistic figures were defined together with correlations between soil condition indices at levels $\alpha = 0.01$ and 0.05.

Results and discussion

The average lead content in the Lubuskie Region soils is approximately 11.3 mg·kg^{-1} (at the range of 0.6÷81.8 mg·kg^{-1}). About 1.0% of the samples from out-of-town areas show anthropogenic increase of the overall Pb content - 20÷70 mg·kg^{-1}, the other fall within the geochemical background - below 20 mg·kg^{-1} [20]. As far as Zielona Gora is concerned, higher concentrations of this element are noted in the soils within the city as well as in its suburbs (Table 1).

Table 1

Lead content and its potential availability in out-of-town, urban and suburban areas

Description of the area and soils	**Lead form (dissolved in:)**		**0.1 M HCl / aqua regia ratio**	**pH in 0.01 M $CaCl_2$**	**CEC**
	0.1 M HCl	**aqua regia**			
	[mg·kg^{-1}]		**[%]**		**[cmol·kg^{-1}]**
Out-of-town areas					
Haplic Podzols	2.40÷7.00	3.97÷9.88	63.43÷70.85	4.10÷4.91	1.18÷4.92
Haplic Arenosols	2.40÷5.86	7.62÷10.20	32.48÷57.45	3.52÷4.22	1.97÷8.96
Cambic Arenosols	2.80÷16.80	6.47÷24.11	43.28÷69.68	4.62÷5.12	3.48÷8.22
Suburban areas					
Haplic Podzols	3.19÷17.32	4.40÷59.20	7.89÷72.50	5.57÷7.24	3.36÷26.30
Technosols	3.20÷27.13	4.14÷90.40	4.50÷77.30	6.92÷7.42	2.00÷24.71
Urban areas					
Urbi-Anthropic Regosol	1.80÷6.31	4.76÷22.80	19.76÷59.43	7.21÷7.49	14.02÷24.04
Anthropic Regosol	3.20÷23.18	7.27÷57.00	44.01÷90.33	6.04÷6.59	3.32÷13.21
Cumulic Anthrosol	4.35÷9.09	6.20÷17.40	31.79÷84.44	6.84÷7.31	16.36÷27.77
Anthrosols	3.53÷6.20	8.20÷197.20	2.93÷42.99	6.71÷6.90	2.07÷21.60
Technosols	4.83÷18.85	6.90÷52.40	17.63÷93.93	5.31÷6.80	3.18÷21.83
Technosols	3.19÷36.09	4.40÷171.40	21.06÷72.50	6.80÷8.01	3.88÷25.05
Technosols	4.82÷16.55	22.00÷48.00	21.93÷62.69	6.30÷7.28	9.75÷24.94

When comparing samples from out-of-town areas with those experiencing strong urban pressure we can note several regularities. Enriching soils with various foreign materials, including wastes, results in transferring their reaction and sorption qualities. The dependence among those factors is referred to by numerous researchers, among others: [1, 11, 12]. Others, like Dragovic et al [21], did not show any relation between lead content and soil pH, however indicated a strong correlation between lead content and CEC. This also means a new approach towards the problem of lead mobility in soils. The results of the present paper indicate, that soil sorption along with bringing calcium carbonate into soil are a condition for lowering Pb solubility, which was proved statistically (Figs. 1-3). This is especially clear with respect to strongly limed garden soil/hortisoles, which is referred to in the works of, among others: [22] and [23].

Soil genesis as well as the range and type of transformations they have undergone are very diversified, thus a particular soil cannot be related automatically to an increased or decreased lead content. Furthermore, the test results also show that a factor conditioning lead content, solubility as well as bioavailability in urban soils can be time of soil form occurrence - shorter in anthropogenic transformed areas, especially within a young territory of a developing city. This was also indicated by Bretzel and Calderisi [10].

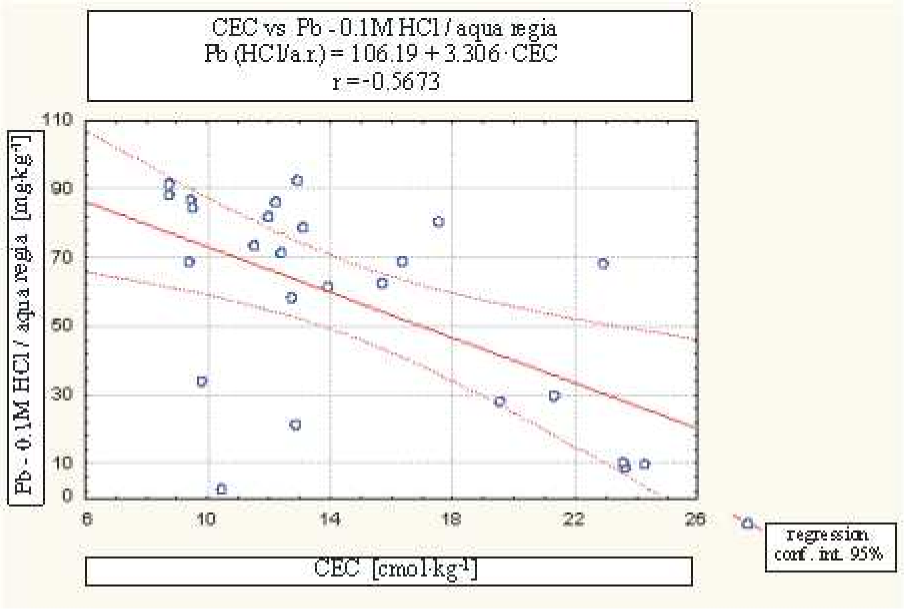

Fig. 1. Effect of CEC on potential Pb availability in urban soils

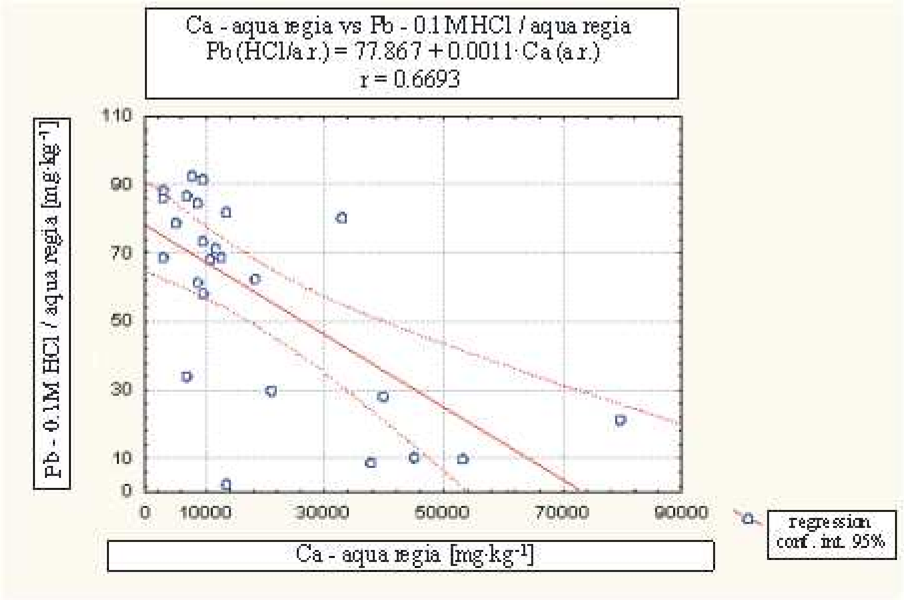

Fig. 2. Effect of Ca content on potential Pb availability in urban soils

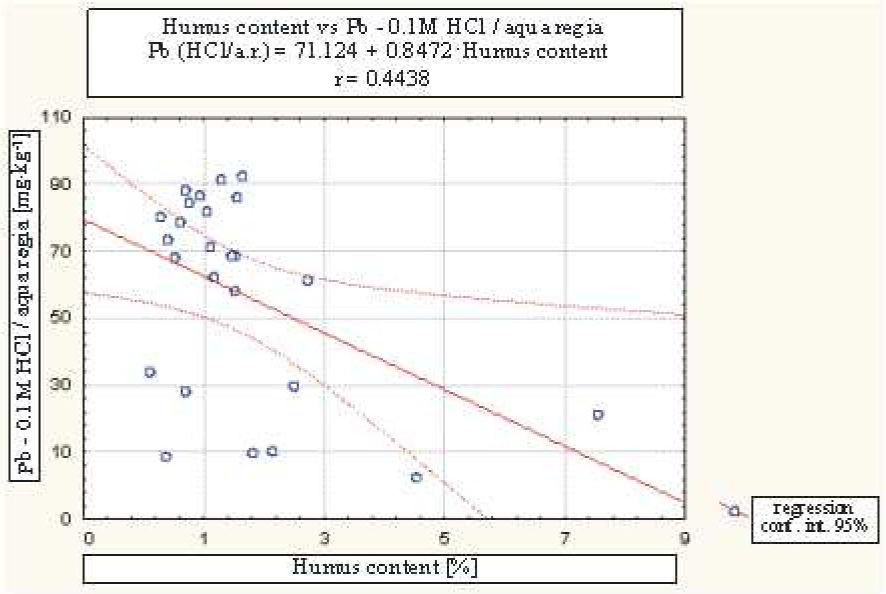

Fig. 3. Effect of humus content on potential Pb availability in urban soils

City is a complex system as far as paths of lead expansion is concerned. This results in both an area surface deposition, as well as in a unit underground deposition - "hot points"! It has been found out that in many parts of cities it is difficult to maintain decorative plants. Only a few of them, however, have a direct relation with emission of toxins, including heavy metals. The majority of problems result from incorrect, other than settlement and microclimate, conditions. Nevertheless, it was noticed that plants of different species and different growth character vary in lead absorption. As far as trees often grown in the cities of Eastern Europe, Small-leafed Lime absorbs more lead than Black Locust. One of the most commonly grown hedge shrubs - Wild Privet - shows the average quantity of Pb absorption in comparison with the above-mentioned tree species. On the other hand, grass specimens have a very wide reaction spectrum.

Table 2

Lead content in leaves of plants from urban green areas

Location	Black Locust	Small-leaved Lime	Wild Privet	Grasses (Grass mix)
	[mg·kg^{-1}]			
Centre	3.82÷7.98	7.36÷31.50	4.26÷12.74	3.54÷24.28
Areas along transit routes	4.58÷15.22	5.64÷21.94	4.36÷20.16	1.76÷17.62
Areas along city roads	7.32÷31.30	9.14÷24.60	9.28÷16.50	3.00÷27.08
Housing estates	3.98÷13.88	6.86÷22.20	3.44÷15.26	9.30÷18.94
Parks	1.10÷11.98	7.94÷28.00	3.42÷13.56	6.80÷18.72

It is quite interesting to compare lead absorption by plants growing along newly constructed roads (transit roads built in 1980-2007) and along old routes (city roads built before 1980). Lead absorption, as it is shown, is bigger in the latter situation. It is a clear picture of plant growth under conditions in which soil has been recently transformed along new communication routes (reference to Urbi-Anthropic Regosol and Cumulic Anthrosol). As far as the old roads are concerned, their surroundings used to be for a long time exposed to immissions at the time when the basic fuel was leaded petrol. This also illustrates a new technology of road building based on clear mineral materials. In the past roads were constructed on the foundation made from waste materials. Smaller lead content is presented by plants growing in some housing estates or park locations, however, also here big diversification can be noticed. This partially depends on the period of time in which housing estates and parks were built, thus on various approaches towards forming their soils and a different time of their deposition.

Conclusions

1. Behavior of lead in urban soils depends on their sorption capacity and reaction.
2. Due to a strong diversification of the genesis and the qualities of urban soils, potential lead availability from soils varies within wide range.
3. It is not possible to indicate automatically a biological risk resulting from lead deposition in a real place in a city, relating it with a form of use or taxonomic soil unit.
4. Absorption of lead by plants depends, to a great extent, on age of the soil cover and an approach to its formation.

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DOSTĘPNOŚĆ OŁOWIU DLA ROŚLIN NA TERENACH UPRZEMYSŁOWIONYCH

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Abstrakt: Ołów należy do grupy metali ciężkich najbardziej rozpowszechnionych przez człowieka. Przyczyną takiego stanu rzeczy jest dynamiczny rozwój transportu, przemysłu i gospodarki komunalnej. W literaturze jest przedstawiany jako pierwiastek stabilny w glebach - kumulowany głównie w wierzchnich warstwach, gdzie w warunkach wysokiego odczynu i dobrych właściwości sorpcyjnych jest właściwie niedostępny dla żywych organizmów. W artykule zwrócono uwagę na fakt, że problem jest jednak bardziej skomplikowany, głównie ze względu na genezę i antropopresję, która, jak się okazuje, podnosi zawartość ołowiu, a także zwiększa jego rozpuszczalność i fitoprzyswajalność.

Słowa kluczowe: metale ciężkie, ołów, rośliny, strefy przemysłowe

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SCREENING OF THE SPATIAL DISTRIBUTION OF RISK METALS IN TOPSOIL FROM AN INDUSTRIAL COMPLEX

ROZKŁAD PRZESTRZENNY METALI TOKSYCZNYCH W GÓRNEJ WARSTWIE GLEBY TERENU PRZEMYSŁOWEGO

Abstract: For the sustainable development of urban areas, it is necessary to identify if environmental pollution exists and where hot spot pollution sources lie. In this study, 280 topsoil samples were collected from an industry estate in Zlin (the Czech Republic). In these samples, the presence of toxic metal was analyzed by wave dispersed X-Ray fluorescence (ED-XRF), and statistical analysis revealed that the major anthropogenic contaminants in the topsoil were Pb, Zn and Sn. Further contaminant analysis by atomic absorption spectrometry (AAS) determined the maximum contents of 28558.47 mg/kg for Pb, 1132.35 mg/kg for Sn and 2865.22 mg/kg for Zn in selected topsoil samples. According to soil pollution index results, the main proportion of topsoil is contaminated, with the possible sources of contamination being traffic and a nearby municipal heating plant. This study proves that the combination of preliminary ED-XRF topsoil analysis, a multivariative statistical approach, AAS analysis and the geographical information system (GIS) is effective and together form a powerful tool for mapping topsoil contamination and conducting an environmental risk assessment.

Keywords: industrial urban soil, pollution, heavy metals, multivariative statistics, cluster analysis, ED-XRF, AAS, GIS

Introduction

Soil has been perceived by human beings as a source of building materials and as the medium for farming, ergo the lowest component of the food chain. However, from an environmental point of view, soil should be perceived as an ecosystem, the quality of which is influenced positively or negatively by the mutual interaction of individual (animate and inanimate) components. For that reason, soil has to be considered an animate, dynamic and vitally important part of the ecosystem. Its quality should support the desirable development of plants and animals, as well as biological productivity, and should not be hazardous to human health [1-3].

According to the EU COM (2006) 232 directive proposal for soil protection, the member states of the EU have to identify localities where proven hazardous substances occur, as a consequence of human activities, in such quantities that represent a significant risk to human health or the environment. The risk must be quantified by taking present and future approved land use into consideration [3, 4]. Incidentally, a group of EU member states undertook the systematic monitoring of the quality of agricultural and forest soil in the past, which has been integrated into their legislation. However, the monitoring of urban soils has been neglected.

Even though the Czech Republic joined the European Union in 2004, soil quality monitoring was actually carried out in 1990-1993. Most attention was paid to risk elements

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(As, Cd, Cr, Ni, Pb) and persistent organic pollutants (PAH, PCDD/PCDF, DDT and styrene). It was found that only 2% of the total land mass of the Czech Republic (78,865 km^2) was contaminated. The pollution was limited to small areas and tended not to indicate diffuse sources. The areas in the northern part of the Czech Republic (municipal heating and power plants, surface mining, the chemical industry), northern Moravia (heavy industry), and Prague and its environs (traffic emissions) as well as fluvial soil in the alluvium of large rivers (the Labe, the Morava) were very affected by both pollutant groups [3, 5].

In the Czech Republic, Sanka [6] carried out a study to identify the sources of soil contamination and their impact on the health of the population of Brno. Soil and plant samples were analyzed for the presence of heavy metals (Cd, Cu, Cr, Ni, Pb, Zn) and PAH (*polyaromatic hydrocarbons*). The results displayed a significant difference between pollutant content in plants growing in an urban and suburban environment. Furthermore, it was discovered that the traffic in an urban environment is the major source of soil contamination by the elements of Zn, Cu, Pb. These conclusions corresponded with an earlier study of lead accumulation from petrol combustion on Californian roads, which was conducted between the years of 1976-1990. Due to the lead content of petrol being reduced from 0.4 to 0.15 g/dm^3 in 1986, the atmospheric deposition of lead fell by approximately 50% and no doubt there was a reduction in the deposition of airborne lead into soil.

The aim of this pilot study is to identify major inorganic hazardous metals which contribute to the heavy metal content in topsoil on an industrial estate. The employment of multivariate statistical techniques is used for determining the lithologic and anthropogenic origin of major inorganic pollutants, this in addition to visualizing their spatial distribution via GIS. The results of this study shall be the basis for topsoil monitoring over the long term and the environmental risk assessment support system used for area sustainability.

Methods

Site description

Sampling the 280 topsoil samples was carried out on an industrial estate that once served the SVIT shoe production company. This is located near the centre of Zlin (the Czech Republic) in a part of the city lying at the bottom of a valley, through which the Drevnice river flows. The industrial estate and its surroundings are in area formed from Paleogenic rocks - Maguras flysch of the Racans tectonic unit, where lime clay alternates with glauconitic sandstone. In the fluvial plain of the River Drevnice, the bedrocks are covered with alluvial sediment up to a thickness of 3-4 m. The terrain's surface contains various types of anthropogenic backfill, as well as tiled and concreted areas [7].

Soil sampling, analysis and data processing

The sampling points were all at accessible public places on the industrial estate. The points were located by a GPS. The 0.5 kg bulk samples were transferred into sealable polypropylene plastic sample boxes and transported to the laboratory for analysis. The screening analysis of inorganic contamination was carried out according to the European norm EN 15309:2007 for the characterization of waste and soil by XRF. According to the

XRF's measurement results, multivariative and cluster analysis was accomplished and samples containing potential contaminants were selected for analysis via AAS. Raw data (GPS coordinates, the intensity of XRF spectral lines, contaminant amounts in the leachates and the intensity of the photonic dose equivalent) were stored on the MS Access® database. The statistical evaluation was conducted by the Statistica 6® program, which is able to carry out the multivariative, correlation and cluster analysis that can assess the relationships between the soil contaminants found and their origin. Areal contaminant distribution was visualized by ArcGIS 9.3.1 software, which contains the extension for Inverse Distance Weighted interpolation.

Results and discussion

Pollutant identification

The identification of potential contaminants was conducted via cluster analysis. Four groups of elements are present in the dendrogram obtained (Fig. 1). It is supposed that, with a higher dendrogram position (from Sb to Ca), there is a decrease in the degree of anthropogenic origin and an increase in the degree of lithologic origin in topsoil. According to the geological map of the Czech Republic, the rocks belonging to the most recent geological era (Cenozoic middle Eocene - lower Oligocene) - glauconitic sandstone, calcareous claystone, sandstone, conglomerates and minor claystone exist in the study area. Therefore, it may be assumed that Ca, Mg, Fe, Si, Al, K and Na are the main lithologic elements of uncontaminated topsoil.

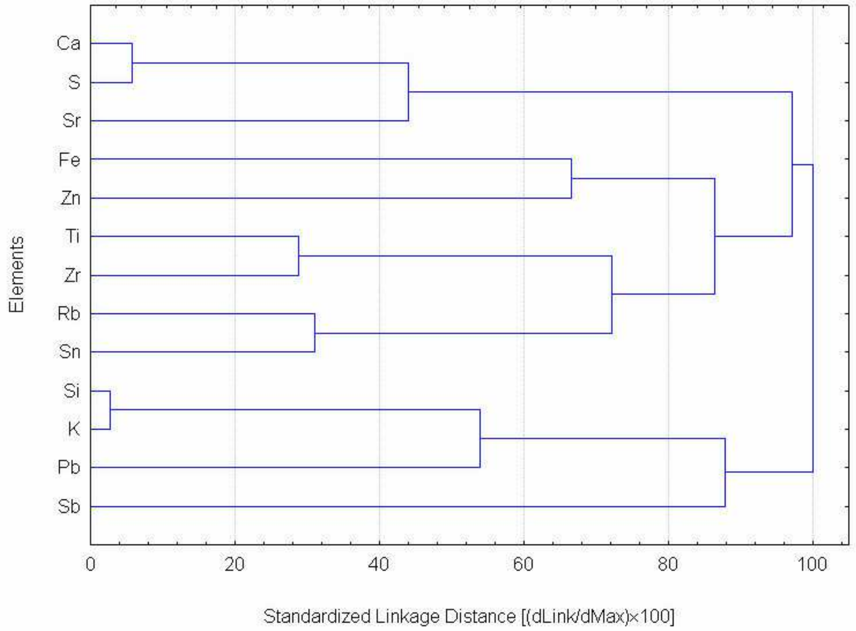

Fig. 1. Dendrogram of elements in soil samples based on ED-XRF spectral analysis

Taking into account the results of preliminary screening by XRF, the geological structure and mineralogical composition of rock in this particular environment, the foremost risk metals can be classified as Pb, Zn, Sn, Fe and Ca in the topsoil samples. However, for a qualified decision on whether the enumerated metals represent such topsoil contamination, it is necessary to compare the metal content of samples with the valid legislated regulatory levels of the country.

Spatial distribution of pollutants

The comparison of potential risk metals with regulatory levels from the Czech Ministry of the Environment - methodical directive No. 8/1996 [8] - is presented in Table 1. The topsoil limit levels for Pb, Sn and Zn were exceeded and, for that reason, attention shall now be focused on these metals.

Table 1

Czech regulatory levels and descriptive statistics of element content in soil samples and *soil pollution index* (SPI)

	Unit	**Minimum**	**Maximum**	**Median**	**SD**	**RL**
Pb	[mg/kg]	10.19	28558.47	38.56	2640.66	250
Sn	[mg/kg]	1.19	1132.35	20.50	14.63	200
Zn	[mg/kg]	16.73	2865.22	521.27	193.86	1500
SPI	[-]	0.02	39.83	0.52	2.38	< 1

As can be seen from Figure 2, the spatial distribution of Pb, Sn and Zn significantly differs. The highest topsoil content of Pb is concentrated in the southwest part between the road, railway and Building No. 122 (highest content = 28558.47 mg/kg), where the value of the limit has been exceeded more than hundredfold. It is more than probable that here the remediation of lead has to be conducted. A likely source of contamination can be found near Building No. 122, where a car repair workshop and a scrapyard firm are placed. It is there that used lead batteries from cars, containing PbO_2 and $PbSO_4$, are replaced or repurchased.

Nevertheless, the greater content of Sn and Zn occurred unevenly, distributed throughout the entire area. However, identifying the source proves difficult in the case of Sn. Figure 2 shows that highest content of Sn (1132.35 mg/kg) was discovered in front of Building No. 31 (a hospital car park), with increased concentration alongside roads. The amount of Sn oscillates around the mid value of 521.27 mg/kg in the study area, so it can be supposed that a sizeable source exists there. For that reason, thought was paid to the local heating plant. At present, a mixture of black and brown coal is combusted in a fluidized bed; for gaseous combustion products, a desulphurization process is applied. Nevertheless, until 1995, the products of combustion were freely released into the air. Danihelka et al [9] have found through analyzing the type of Czech coal used for combustion in heating plants that the Sn content in coal ranges between 0.9÷2.4 mg/kg. After combustion of the coal, and following product analysis, the content of Sn in particular emissions was 1÷85 mg/kg, in fly ash 2.5÷7.7 mg/kg, and in bottom ash 1.6÷3.7 mg/kg. Based on these results, it can be supposed that the Sn content in topsoil is probably residual, because the new technology now in place at the heating plant does not allow products of combustion to be dispersed in the air.

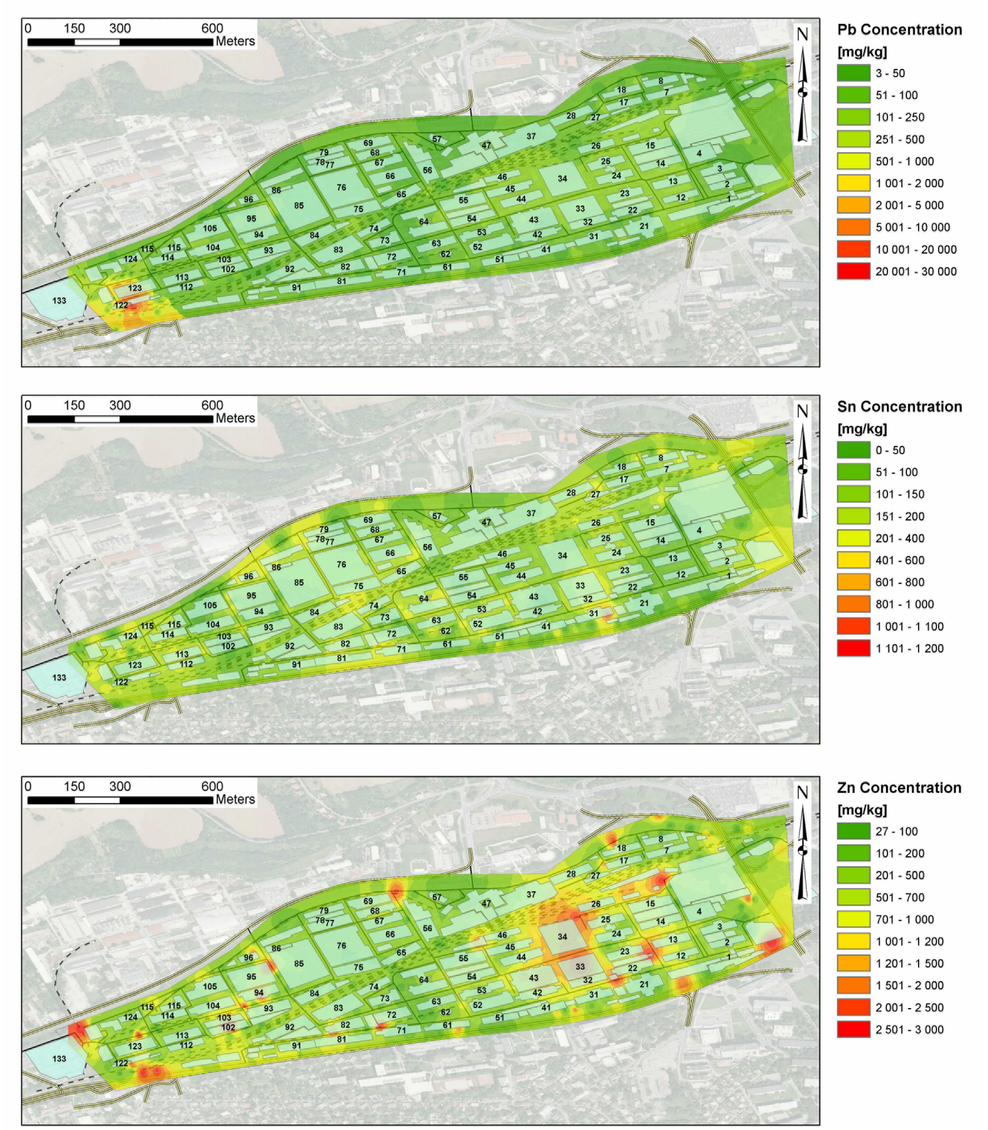

Fig. 2. Spatial distribution maps of Pb, Sn, and Zn

The last metal to be studied was Zn, of which higher concentrations have been found primarily beside roads and railways. The maximum Zn content of 2865.22 mg/kg was determined near Building No. 122 (a car repair workshop), but a high amount - as much as 2000 mg/kg - was discovered by many other buildings, as can be seen in Figure 2. Near to buildings number 122 and 34, a railway track traverses the roads and could cause the higher Zn content in topsoil found there. This assumption confirms the geochemistry study of urban surface soil by Anderson et al [10], or Pratt and Lottermoser [11], who investigated the mobilization of traffic derived trace metals. It has been discerned that the Zn in the sediments alongside roads orginates from tires, road signs and/or railings.

Another possible source of Zn can be shoe production, which took place at the SVIT industrial estate until 1990. A paper by Malik et al [12] focused on the study of soil contamination in the city of Sialkot (Pakistan) shows that a potential source of Zn was the zinc salts used for tanning. Another possible Zn source is rubber processing for tires and shoes, in which zinc oxide is used as an additive. Data from an archive revealed that plastic and rubber production for shoes was carried out in buildings numbered 43-46, 95 and 104. In shoe production technology, chromium tanning and various rubber types were utilized. Due to this, the possible major sources of Zn might be the railway lines and traffic, in association with a minor Zn source of past shoe production.

Conclusions

In the urban topsoil, a large amount of heavy metals, lithologic as well as anthropogenic in origin (traffic, industry, etc.), can be found. For that reason, knowledge of contaminated sites is necessary for their removal. The results of this work will be used as a basis for detailed and long-term monitoring of risk metals in the topsoil of the studied area.

The combination of multivariate statistical approaches, cluster analysis and GIS visualization seems to be very useful for interpreting soil environmental data sets. The use of multivariate analyses (CM and CA) by ED-XRF result processing helps to quickly identify the major anthropogenic elements (Pb, Sn and Zn) present in topsoil. In the selected samples, the exact content of risk elements was determined via the AAS method. It was found that in the western part of the industrial estate, the Pb content in topsoil reaches the extreme amount of 28558.47 mg/kg, whilst, in the opposite eastern side, the content of Zn was 2865.22 mg/kg and that of Sn was 1132.35 mg/kg, which indicates they were in excess of Czech regulatory limits. The visualization of spatial metal distribution and SPI was conducted by GIS. The maps created show that the distribution of contamination is not regular but depends on the kind of production process at specific sites. According to the SPI results, the places requiring immediate decontamination were identified, too.

Acknowledgements

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INITIATING BIODEGRADATION OF POLYVINYLPYRROLIDONE IN AN AQUEOUS AEROBIC ENVIRONMENT

ZAINICJOWANIE BIODEGRADACJI POLIWINYLOPIROLIDONU W ŚRODOWISKU WODNO-POWIETRZNYM

Abstract: A synthetic polymer, Polyvinylpyrrolidone (PVP - E 1201) primarily finds applications in the pharmaceutical and food industries due to its resistance and zero toxicity to organisms. After ingestion, the substance passes through the organism unchanged. Consequently, it enters the systems of municipal wastewater treatment plants (WWTP) without decomposing biologically during the waste treatment process, nor does it attach (through sorption) to particles of activated sludge to any significant extent, therefore, it passes through the system of a WWTP, which may cause the substance to accumulate in the natural environment. For this reason the paper investigates the potential to initiate aerobic biodegradation of PVP in the presence of activated sludge from a municipal wastewater treatment plant. The following agents were selected as the initiators of the biodegradation process - co-substrates: acrylamide, N-acethylphenylalanine and 1-methyl-2-pyrrolidone, a substance with a similar structure to PVP monomer. The biodegradability of PVP in the presence of co-substrates was evaluated on the basis of biological oxygen demand (BOD) as determined via a MicroOxymax $O_2/CO_2/CH_4$ respirometer. The total substrate concentration in the suspension equaled 400 $\text{mg}\cdot\text{dm}^{-3}$, with the ratio between PVP and the co-substrate being 1:1, while the concentration of the dry activated sludge was 500 $\text{mg}\cdot\text{dm}^{-3}$. Even though there was no occurrence of a significant increase in the biodegradation of PVP alone in the presence of a co-substrate, acrylamide appeared to be the most effective type of co-substrate. Nevertheless, a recorded decrease in the slope of biodegradation curves over time may indicate that a process of primary decomposition was underway, which involves the production of metabolites that inhibit activated sludge microorganisms. The resulting products are not identified at this stage of experimentation.

Keywords: polyvinylpyrrolidone, biodegradation, activated sludge, aqueous environment

Polyvinylpyrrolidone (PVP) is a synthetic polymer that dissolves very well in water. From a chemical perspective, it is a polymer lactam with an internal amide bond and ranks amongst poly-*N*-vinylamides (Fig. 1). The diverse forms produced commercially are differentiated through the K-number denoted (eg PVP K12, K17, K25 and K30), indicating average molecular weight. With regard to monomer unit structure, PVP exhibits an amphoteric characteristic, due to it containing an amide group of high polarity and non-polar methylene groups in its main chain and ring, which indicates its hydrophilic and polar properties and hydrophobic properties, respectively.

Due to its physical, chemical and biological properties (bio- and hemocompatible, physiologically inactive), PVP finds applications in a range of technological processes. Due to its resistance and zero toxicity to organisms, the compound is mainly used in the pharmaceutical and food industries (in the European Union soluble PVP is labeled E 1201,

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within the system of E-numbers, when utilized in food supplements, pills and sweeteners). After ingestion, the substance passes through the organism unchanged [1]; consequently, it enters the systems of municipal *wastewater treatment plants* (WWTP) without decomposing biologically during the waste treatment process, according to most recent studies [2-4]; nor does it attach (through sorption) to particles of activated sludge to any significant extent [5]. Therefore, it passes through the system of a WWTP, which may cause the substance to accumulate in the natural environment.

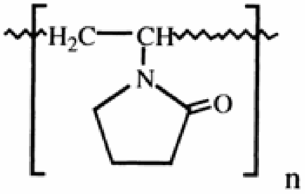

Fig. 1. The chemical structure of polyvinylpyrrolidone

However, some studies do not completely reject its biodegradability, pointing out the importance of experimental conditions and the microbial cultures used. Abd El-Mohdy and Ghan [6], describe biodegradation of PVP in a soil environment (soil burial test). Their findings of a decrease in mass does not evidence the complete resilience of pure PVP, as regards decomposition, with such mass dropping to about 10% after 6 months. Marusincova [7] also notes some positive findings on eliminating PVP (Mr ~ 10 kDa) from a municipal WWTP by using anaerobic sludge; increased production of CH_4 was recorded for samples containing PVP after 24 days of testing compared with the endogenous production of CH_4.

As mentioned in the introduction, PVP contains a lactam ring in its structure, this being γ-lactam, a substance that may be subject to attack by γ-lactamase (an enzyme). Therefore, from both a theoretical and practical perspective, it would be of interest to use microorganisms producing the aforementioned γ-lactamase as a cornerstone for biologically decomposing PVP. Indeed, a number of microorganisms have been identified very recently, such as *Pseudomonas fluorescens* [8], *Microbacterium hydrocarbonoxydans* [9], *Sulfolobus solfataricus MT4*, *Rhodococcus* sp. *ENZA1*, *Aureobacterium* sp. *ENZA25*, *Pseudomonas solanacearum ENZA20*, *P. cepaecia* and *P. fluorescens ENZA22*, and *Comomonas acidovorans* [10]. Among other things, the work of Line et al [11] also found that some soil bacteria producing γ-lactamase are able to utilize *N*-acyl as a sole source of carbon and energy [11], while the study of Hickey et al [12] revealed increased activity by γ-lactamase in the presence of acrylamide substrate. This theoretically suggests that *N*-acethylphenylalanine or acrylamide might initiate the production of γ-lactamase in some types of microorganisms.

The literature study shows that the ultimate fate of PVP within a WWTP and subsequently in the environment has not been widely explored, so reiterating presumptions that PVP does not pose an environmental problem is not really an option. This paper investigates the potential to initiate aerobic biodegradation of PVP in the presence of mixed microbial cultures, in the form of activated sludge from a municipal wastewater treatment plant, with the following agents selected as the initiators of the biodegradation process - co-substrates: 1-methyl-2-pyrrolidone, a substance with a similar structure to PVP monomer, as well as acrylamide [12] with *N*-acethylphenylalanine [11], this based on literature research.

Materials and methods

The materials used for tests were commercial products that are currently available: polyvinylpyrrolidone K15 (Mr ~ 10 kDa), the Aldrich Chemical Company; 1-methyl-2-pyrrolidone (1M-2P), acrylamide (AC) and N-acethylphenylalanine (APhA), at a purity of 98%, the Aldrich Chemical Company. Others chemicals employed were of analytical purity, produced or delivered by the Lachema Co., Brno, the Czech Republic.

A mixed microbial culture in the form of activated sludge from a municipal *wastewater treatment plant* (WWTP Zlin-Malenovice, the Czech Republic) was applied as the inoculum (biological material). Prior to such testing, the aerobic sludge was first centrifuged at 4,500 rpm^{-1} for 10 minutes at 20°C. After removing the supernatant, the biomass was suspended in the biomedium [13] and then aerated for 24 hours.

Biodegradability was determined using a respirometer, a MicroOxymax $O_2/CO_2/CH_4$. The sample tested (PVP or PVP + co-substrate) was the sole source of organic carbon and energy in the environment. The conditions of the test were as follows: suspension volume 50 mL, dried sludge 500 $\mathrm{mg \cdot dm^{-3}}$, concentration of PVP 200 $\mathrm{mg \cdot dm^{-3}}$, concentration of the co-substrate 200 $\mathrm{mg \cdot dm^{-3}}$, temperature 25±1°C and pH = 7. At the beginning and end of the experiment, sludge solids, pH and reference DOC (*Dissolved Organic Carbon*) were determined for all samples. Allylthiourea as an inhibitor of nitrifying processes was not dosed when studying the biodegradation of PVP alone, even though the substance studied contains organically bound nitrogen. This procedure was chosen with regard to the work of Marusincova [7], where aerobic biodegradation of PVP *via* ordinary wastewater treatment plant culture was not underway and, furthermore, the addition of allylthiourea was causing the process to become inhibited. All measurements were taken three times in parallel.

The course of biodegradation was evaluated on the basis of determining *Biochemical Oxygen Demand* (BOD) [13], expressed as the ratio of the biological oxygen demand measured vs *Theoretical Oxygen Demand* - BOD/TOD [%], according to equation:

$$\text{Biodegradation of PVP} = \frac{\left(\dfrac{\mathrm{BOD}_{\mathrm{PVP/COSUBSTRATE}} - \mathrm{BOD}_{\mathrm{COSUBSTRATE}}}{c_{\mathrm{PVP}}}\right)}{\mathrm{TOD}_{\mathrm{PVP}}} \times 100 \qquad (1)$$

where $\mathrm{BOD}_{\mathrm{PVP/COSUBSTRATE}}$ and $\mathrm{BOD}_{\mathrm{PVP/COSUBSTRATE}}$ are experimentally found values pertaining to biological oxygen demand of PVP biodegradation in the presence of the co-substrate, respectively merely the co-substrate, (all in $[\mathrm{mg \cdot dm^{-3}}]$),TOD is theoretical oxygen demand (for PVP = 2020 $\mathrm{mg \cdot g^{-1}}$), and c_{PVP} is the concentration of PVP in the suspension tested in $[\mathrm{g \cdot dm^{-3}}]$.

Results and discussion

The first part of the work focused on observing the biodegradability of PVP and each of the co-substrates. The results of these measurements were then used to evaluate the impact of the co-substrates on the biodegradation of PVP. Due to the fact that the retention time of wastewater in WWTP aeration tanks is in the order of several hours (depending on the type of WWTP facility), testing was carried out only for 30 days.

The BOD_{max}/TOD values for each co-substrate (data not presented) revealed that the substances are highly biologically degradable. Acrylamide decomposed from 100% within as little as 170 hours of testing, the lag phase being 60 hours. Similarly, 1M-2P was fully decomposed after 300 hours, with the lag phase equaling 30 hours. As regards APhA, 83% biodegradation was achieved after approximately 200 hours, with the lag phase being 30 hours. BOD attributable to the decomposition of PVP alone, without any additional co-substrate, progressed almost at the level of endogenous respiration. Despite the above, about 3.19 ± 2.91% of biodegradation was achieved. Nonetheless, this value cannot be considered significant due to its high standard deviation, and it may be assumed that under the given conditions decomposition occurs only through the production of unreacted *N*-vinylpyrrolidone, a monomer contained in commercial PVP.

Figures 2 and 3 show the impact of the co-substrate on the biodegradation of PVP alone. It should be emphasized that each curve (Fig. 2) and column (Fig. 3), as shown in the diagrams, are based on the BOD value for merely PVP, ie after deducting oxygen consumption attributable to the decomposition of the co-substrate itself and endogenous respiration of activated sludge.

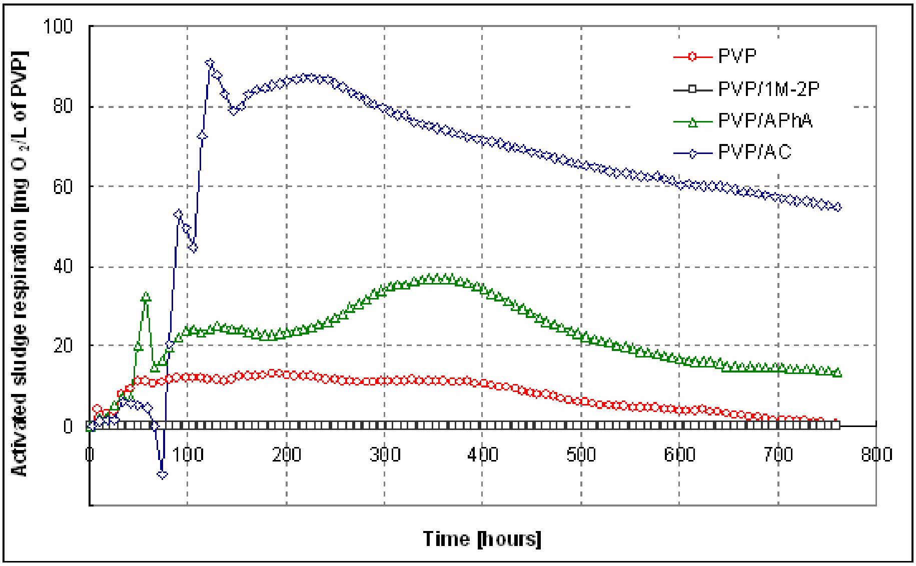

Fig. 2. The course of PVP biodegradation in the presence of co-substrates expressed as the respiration of activated sludge per instance of decomposition of PVP alone; that is after deduction of endogenous respiration and respiration attributable to the decomposition of merely the co-substrate

The most significant influence on the degradation of PVP was that of acrylamide. The biodegradation curve showing the combination of PVP and acrylamide was located above the curve of merely the co-substrate. The difference between both curves pertains to the biodegradation of PVP alone (about 20% of biodegradation). Nevertheless, the sample containing PVP + the co-substrate showed a stagnation of BOD values over time compared with endogenous respiration, which resulted in a drop in the biodegradation curves (Fig. 2). The results displayed in Figure 2 thus indicate that there might be primary decomposition of PVP accompanied by the production of metabolites inhibiting microorganisms in the activated sludge.

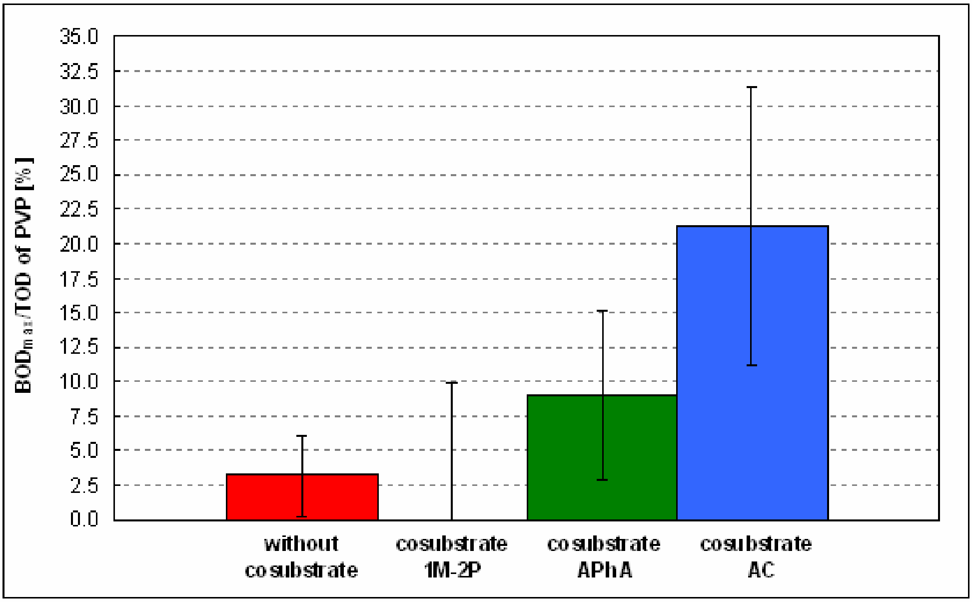

Fig. 3. The percentage of PVP biodegradation expressed as BOD_{max}/TOD; ± standard deviation

Adding APhA to the PVP sample did not induce the presumed support of decomposition of the latter (Fig. 2). The values of biological oxygen demand attributable to the decomposition of PVP in the presence of APhA varied only slightly to those of BOD attributable to the decomposition of the co-substrate alone. As with acrylamide, there was also a reduction in the biodegradation curves over time in this case.

Although 1M-2P is a substance with a structure greatly resembling that of PVP monomer, there was clearly no formation of γ-lactamase or other enzymes capable of decomposing PVP throughout the biodegradation process. Concurrently, adding 1M-2P suppressed the decomposition of merely PVP (Fig. 2).

The results imply (Fig. 3) that the aerobic environment is probably one in which partial PVP lactam ring cleavage has the potential to occur through the activities of microorganisms and influence of the AC and APhA co-substrates, and which may not be accompanied by polymer chain decomposition; it was not studied whether this is caused by γ-lactamase production or not. The declining trend of the curves indicates the aforementioned production of metabolites inhibiting microorganisms in the activated sludge. Any resulting intermediates were not identified at this stage of experimentation.

Conclusions

1. The results of this preliminary research need to be viewed with reservation (due to the high values of standard deviations). However, in light of the knowledge obtained, it can be concluded that the biodegradation of PVP is influenced by the presence of other substances. Toxic metabolites may form during the PVP decomposition process. This fact will require verification in future research using advanced instrumental techniques (GC or HPLC with MS detection). At the same time it would be appropriate to extend the testing period.
2. None of the selected co-substrates proved a significant accelerator of PVP biodegradation. The efficacy per co-substrate may be arranged as follows: AC > APhA > 1M-2P, with an astonishing 20% of biodegradation achieved in the case of acrylamide.

Acknowledgments

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UTILIZATION OF LIGHT ENDS OF CHLOROORGANIC WASTES FROM PVC PRODUCTION WITH APPLICATION OF FERRIC-CHROMIC CATALYST

UTYLIZACJA FRAKCJI LEKKIEJ ODPADÓW CHLOROORGANICZNYCH Z PRODUKCJI PVC Z UDZIAŁEM KATALIZATORA ŻELAZOWO-CHROMOWEGO

Abstract: The subject of the investigation was the model solution containing 50 g/dm^3 waste light ends from PVC production dissolved in the ethanol-water (1:1) mixture. Granular ferric-chromic catalyst (TZC 3/1) was used in the investigation. The temperature range applied in experiments was 400÷600°C and the contact time was 0.27 s. Gaseous products of the reaction were analysed in order to determine among others concentration of chlorine, formaldehyde, oxygen, carbon monoxide and dioxins. The content of total organic carbon (TOC), chloride ions and formaldehyde was determined in a condensate. Oxidation of the mixture proceeded in the all temperature range with high efficiency in regard to initial TOC value in the solution. The concentration of dioxins in the combustion gases obtained in the process carried out in temperature 450°C amounted to 0.027 ngTEQ/m^3, and was significantly lower than the admissible value of 0.1 ngTEQ/m^3.

Keywords: ferric-chromic catalysts, liquid chloroorganic wastes, thermocatalytic oxidation, ethanol, dioxins

Waste chloroorganic compounds generated in three states of matter during polyvinyl chloride production, are utilized by combustion in the temperature of about 1350°C. This process, for example carried out in Anwil S.A. in Wloclawek, consists in total oxidation of organics and conversion of chlorine contained in organics into dry hydrogen chloride or commercial hydrochloric acid [1, 2]. The application of proper catalysts enables a decrease in a temperature of total oxidation of chloroorganic compounds to the range of 300÷600°C. Moreover, this usually enables a decrease in process costs [3-6]. The first aim of our investigations was to determine an effect of a temperature on catalytic oxidation efficiency of a mixture containing chloroorganic wastes, ethanol and water. The second aim was to determine the content of polychlorinated dibenzo-*p*-dioxins and dibenzofuranes (PCDD/Fs) in the combustion gases, characterized by *toxic equivalent quality* (TEQ). These compounds are highly toxic, mutagenic and cancerogenic, especially congener - *2,3,7,8-tetrachlorodibenzo-p-dioxin* with *toxic equivalent factor* (TEF) of 1 [7-11]. The admissible value of TEQ for combustion gases sample from waste incinerating plant in Poland and Europe is 0.1 ng TEQ/m^3 [12].

Experimental

A model solution containing 50 g/dm^3 waste light ends from industrial PVC production was the object of the investigation. Its main components were as follows: trichloromethane, tetrachloromethane, chloroethanes and chloroethenes (Table 1) dissolved

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in ethanol-water mixture (1:1). Air and substrate flow rate was 300 dm^3/h and 16 g/h, respectively. The temperature range applied in experiments was 400÷600°C. Granular ferric-chromic catalyst (TZC 3/1) containing 42.27% Fe, 5.40% Cr and 1.78% Cu was obtained from Fertilizer Research Institute in Pulawy. It was applied in the investigations, which were carried out in an apparatus presented in the paper [5]. The contact time was 0.27 s. Gaseous products of the reaction were analysed in order to determine among others concentration of chlorine, formaldehyde, oxygen, carbon monoxide and PCDD/Fs. The content of *total organic carbon* (TOC), chloride ions and formaldehyde was determined in a condensate. Analysis of combustion gases in order to determine the content of PCDD/Fs was carried out according to the standard EN-1948-3-2006 in Laboratory of Environment Protection in the Institute of Biopolymers and Chemical Fibers in Lodz. PCDD/Fs content was determined with the application of high performance gas chromatography coupled with mass spectrometry [13].

Table 1

Average composition of light ends of chloroorganic wastes from PVC production [% w/w]

Components of the light ends	**[% w/w]**
Ethylene	0.1918
Chloromethane	0.0386
Vinyl Chloride	0.3301
Chloroethane	2.0408
Vinylidene Chloride	0.8461
Trans-1,2-dichloroethene	0.8058
1,1-dichloroethane	6.1695
Chloroprene	0.0075
Cis-dichloroethene	1.3788
Trichloromethane	72.735
1,2-dichloroethane	1.6667
2-chloroethanol	0.0095
Benzene	0.0001
Tetrachloromethane	10.7792
Trichloroethene	0.0020
1,1,1-trichloroacetaldehyde	0.0001
1,1,2-trichloroethane	0.0001
Tetrachloroethene	0.0002
Other light ends	2.9936
Other heavy ends	0.0045

Results and discussion

Selected results of the experiments are presented in Figures 1, 2 and Table 2.

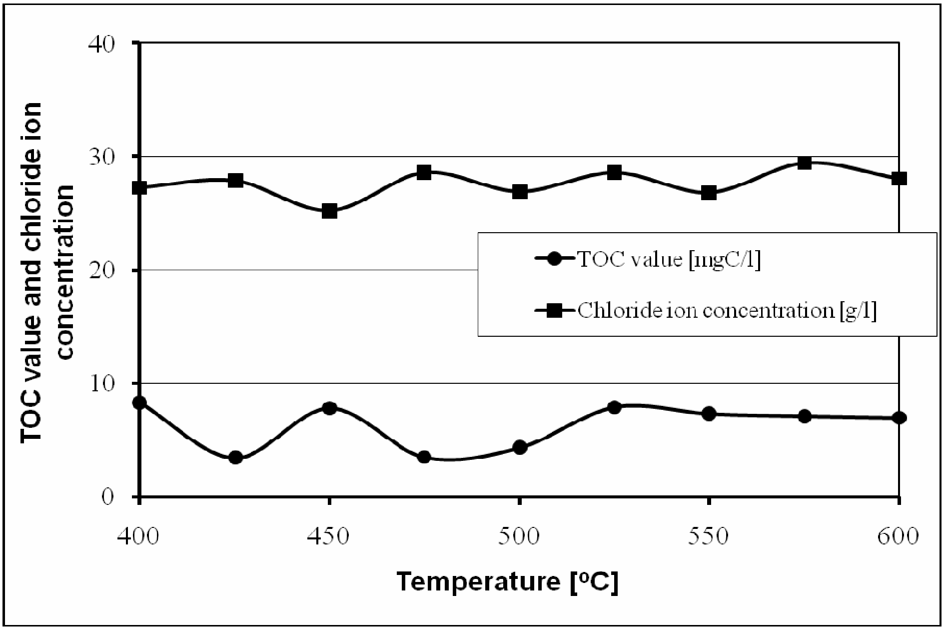

Fig. 1. A dependence of TOC value and chloride ion concentration in the condensate obtained during substrate oxidation on process temperature in the range of 400÷600°C

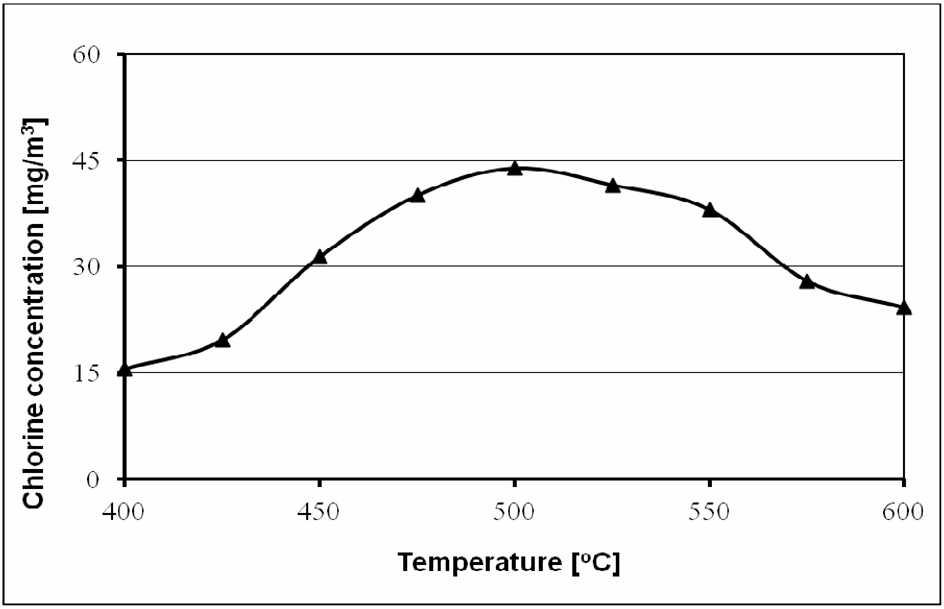

Fig. 2. A dependence of chlorine concentration in the combustion gases obtained during substrate oxidation on process temperature in the range of 400÷600°C

Table 2

Analysis results of condensate and combustion gases from the oxidation process lasting 50 h in the presence of TZC 3/1 catalyst and in the process temperature of 450°C

Reaction products	Average value of parameter
TOC [mgC/dm^3]	6.637
X_{TOC} [%] X_{TOC} - TOC decrease	≥ 99.99 (min.)
Formaldehyde in condensate [mg/dm^3]	0.61
Chloride ions in condensate [g/dm^3]	28.89
Formaldehyde in combustion gases [mg/m^3]	0÷0.31 (value range)
Chlorine in combustion gases [mg/m^3]	32.34
Hydrogen chloride in combustion gases [mg/m^3]	≤ 18 (max.)
Carbon monoxide [ppm]	1
Oxygen [%]	18.58
Carbon dioxide [%]	1.73
TEQ of PCDD/Fs in combustion gases [ng TEQ/m^3]	≤ 0.027 (one analysis)

Figure 1 presents a dependence of TOC values and chloride ions concentrations in a condensate on temperature of reaction furnace in the oxidation of the substrate solution, with the application of TZC 3/1 catalyst. These parameters varied with the increase in temperature in the range from 400 to 600°C, probably due to methodology of the investigation. TOC value was in the range from 3.433 to 8.307 mg C/dm^3 and chloride ions concentration varied from 25.21 to 29.42 g/dm^3. Hydrogen chloride, carbon dioxide and water vapour were the final products of the solution oxidation with the application of the catalyst. The final (mostly reactive) products were as follows: formaldehyde, chlorine, carbon monoxide and dioxins. Figure 2 presents a dependence of chlorine concentration in combustion gases on the temperature changed in the above-mentioned range during the oxidation of the mixture containing the wastes. The maximal concentration of chlorine (43.9 mg/m^3) was achieved in the temperature of 500°C.

Table 2 presents average concentrations of products obtained in the substrate oxidation with the application of catalyst in the optimal temperature of 450°C in the process carried out for 50 hours. The conversion of liquid products of the reaction, calculated as a change in TOC value of the oxidized solution (initial value of 192 000 mg C/dm^3) was very high and exceeded 99.99%. The condensate and combustion gases contained trace amounts of products of non-complete oxidation of the initial mixture, ie, carbon monoxide and formaldehyde. Combustion gases sampled during the reaction carried out in the temperature of 450°C were analysed in order to determine total content of dioxins (PCDD/Fs) which was presented as toxic equivalent quality (TEQ). The obtained result of 0.027 ng TEQ/m^3 was significantly lower than the admissible value of 0.1 ng TEQ/m^3 [12].

Conclusions

Oxidation of the chloroorganic wastes at the concentration of 50 g/dm^3 in the ethanol-water (1:1) mixture proceeded in the temperature range of 400÷600°C with the efficiency of 99.99% in regard to initial TOC value in these solutions. Water vapour, carbon dioxide and hydrochloric acid were the final products of the substrates oxidation. The intermediate products in the substrates oxidation were as follows: components including formaldehyde responsible for total organic carbon content in the condensate, as well as formaldehyde, chlorine and carbon monoxide present in the combustion gases. The concentration of PCDD/Fs in the combustion gases obtained in the process carried out in the optimal temperature, ie 450ºC, amounted to 0.027 ng TEQ/m^3 and was significantly lower than the admissible value of 0.1 ng TEQ/m^3.

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UTYLIZACJA FRAKCJI LEKKIEJ ODPADÓW CHLOROORGANICZNYCH Z PRODUKCJI PVC Z UDZIAŁEM KATALIZATORA ŻELAZOWO-CHROMOWEGO

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Abstrakt: Przedmiot badań stanowił roztwór modelowy 50 g/dm^3 frakcji lekkiej odpadów z produkcji PVC w mieszaninie etanol-woda (1:1). Stosowano ziarnisty katalizator żelazowo-chromowy TZC 3/1. Zakres temperatury doświadczeń wynosił 400÷600ºC, a czas kontaktu 0,27 s. W gazowych produktach reakcji oznaczano m.in. stężenie chloru, formaldehydu, tlenu i tlenku węgla oraz dioksyn, natomiast w kondensacie zawartość ogólnego węgla organicznego (OWO), jonów chlorkowych, formaldehydu. Utlenienie badanej mieszaniny zachodziło bardzo wydajnie w całym zakresie temperatury doświadczeń względem początkowego OWO tego roztworu. Stężenie PCDD/Fs w spalinach w procesie realizowanym w temperaturze 450ºC wynosiło 0,027 ng TEQ/m^3 i było znacznie niższe od wartości dopuszczalnej 0,1 ng TEQ/m^3.

Słowa kluczowe: katalizatory żelazowo-chromowe, ciekłe odpady chloroorganiczne, utlenianie termokatalityczne, etanol, dioksyny

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WASTEWATER PURIFICATION FROM COLORANT BY FLOTATION AND BIO-COAGULATION

USUWANIE BARWNIKA ZE ŚCIEKÓW W PROCESACH FLOTACJI I BIOKOAGULACJI

Abstract: The aim of this work is to study the effect of wastewater treatment by flotation and biocoagulation from toxic compounds (colorants), depending on the concentration and parameters of activated sludge in the treated water as well as the duration of flotation and colorant concentration. During the researches, size of sludge layer during flotation process was observed, together with effect of purification changing in time. The samples of activated sludge from purification plant of linen factory wastewater were used in our experiment. Samples were taken at the outflow from secondary sedimentation tank. At the laboratory, the sludge was used to prepare the model solutions of process factor of various concentrations. The obtained results showed time varying effect of purification with different concentration of activated sludge and a constant concentration of colorant as well as with the different concentration of colorant and a constant concentration of activated sludge.

Keywords: wastewater treatment, activated sludge, colorant, flotation, biocoagulation, sorption

Literature reports show that removal of colorant from wastewater is also possible by biological methods [1-6]. Samples of activated sludge from purification plant of linen factory were used for the experiment presented in this paper. Nowadays, this purification plant is also used as a wastewater treatment plant (WWTP) for urban sanitary sewage. Samples of activated sludge were taken at the outflow of the secondary sedimentation tank. At the laboratory, sludge was used to prepare the model solutions of process factor of varied concentrations.

A toxic colorant used in the linen factory was applied as a treated pollutant in our experiment [3-5, 7]. Name of colorant is “a straight brown”, it is water-soluble and it has an active anion. The composition of used colorant includes the molecules of sulfonic acid which contain groups SO_3H. The chemical nature of azo dyes is organic matter, painting process is carried out in aqueous solution. These dyes are used in the textile industry for dyeing knitting yarn and products made of various fibers: natural, artificial and synthetic. Manufacturer of colorant is corporation “Factory of fine organic synthesis - Barwa”, Ivano-Frankivska oblast, Ukraine. This type of colorant is popular in factories in Ukraine, so it was used in our experiments [7, 8]. Using common industrial impurities and activated sludge, we checked a process of wastewater treatment by biological method in presence of toxic chemical compound [3, 6, 8-10]. As the world’s literature show [11-16] such way of municipal and industrial wastewater treatment is applied around the world. Also, there is the possibility of purification processes control by the bioindication methods [16-20].

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The concentration of activated sludge was calculated by the weight method. To determine the concentration of sample with the colorant solution, we used the proportion:

$$V_1 \cdot C_1 = V_2 \cdot C_2 \tag{1}$$

$$C_2 = \frac{(V_1 \cdot C_1)}{V_2} \tag{2}$$

where: V_1 - volume of activated sludge, C_1 - concentration of activated sludge in the water selected for the experiments, V_2 - volume of activated sludge with the colorant solution, C_2 - concentration of activated sludge in sample.

The group of experiments was conducted to study the removal process of colorant, dissolved in water, with activated sludge by the biological treatment methods - biocoagulation and sorption, with the pressure of saturation of colored solution - 2 at and the duration of saturation 4 min in laboratory conditions [6, 10].

The results of our research showed dependence of the flotation and biocoagulation process, namely the volume and height of the sludge, the degree of illumination, and the effect of treatment on the duration and concentration of the activated sludge [1, 2]. Characteristics of sample solutions used in experiments are presented in Table 1.

Table 1

Characteristics of model solutions

Number of sample	**Amount of water with activated sludge V_1 [cm^3]**	**Amount of water [cm^3]**	**Amount of solution with the colorant V_2 [cm^3]**	**The concentration of activated sludge in the sample C [g dm^{-3}]**
1	500	-	500	0.22
2	250	250	500	0.16
3	125	375	500	0.12
4	62.5	437.5	500	0.08

The laboratory installation and experiment

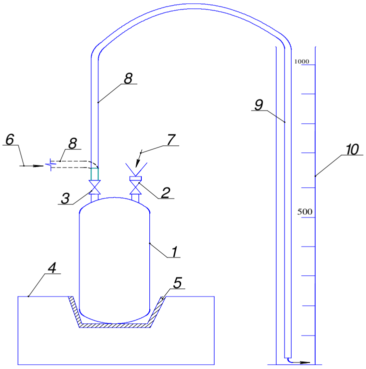

Fig. 1. Scheme of laboratory installation: 1 - pressure tank, 2 - flush valve, 3 - valve for pressure regulation and air compressor, 4 - vibrator, 5 - rubber gasket, 6 - inlet from air compressor, 7 - supply of water to dilute, 8 - rubber tube, 9 - glass tube, 10 - scaled cylinder

The laboratory installation applied to our experiment consists of the following elements: stainless steel, capacity of 1 dm^3, pressure tank (1) equipped with a flush valve for tank filling and releasing water-mixture into a measuring cylinder (2); pressure regulation valve of saturated water-air and air from the compressor (3); vibrator for the better saturation of water-air mixture (4); glass graduated cylinder (10) of 1 dm^3 capacity, with a pipe (9) for a mixture of water-intake and sampling to cylinder (Fig. 1).

Experiment No. 1, p = 2 atm

Pressure tank capacity of 1 dm^3 was filled with 500 cm^3 of the tested colorant solution. Then, all the valves were closed and the tank was supplied with air from the compressor, the saturation pressure was set to 2 at. Further, pressure tank was installed on mini table vibrator for better mixing and dissolution of air in the water, applied duration of vibrating - 4 min. Then the water-air mixture was served through the tube into 1 dm^3 cylinder volume, which was already containing 500 cm^3 of the tested activated sludge and where the process of flotation and biocoagulation occurred. After a time interval which is given in Table 2 the height of slurry [cm], and the volume of slurry [cm^3] were measured. Experiment lasted 60 minutes.

To determine the flotation rate V [cm min^{-1}] from each subtracts of sludge, its height was measured and compared with the difference in the duration of flotation time.

To determine the effect of color solution changes, after a certain period selected for this initial trial and after 20, 30 and 60 min (end of test duration), the volume of test solution was taken. After filtering the selected volumes through a filter paper, the effect of illumination on the colorimeter was determined. Photoelectric colorimeter CFC-2, manufactured by Co Ltd “Hemical procurement” (Himsnabzhenie), Kharkov, Ukraine was used. Application of photo-colorimeter allowed possibility to change a length of light wave and color of light filter. Light of wavelength equal to λ = 440 nm, green filter and 10 mm wide cuvette were used in our experiment.

Cleaning effect of solution was determined by the formula:

$$\eta = \frac{s_1 - s_2}{s_1} \cdot 100 \tag{3}$$

where: η - cleaning effect, s_1 - initial color of the solution, s_2 - final color of the solution.

Table 2

Results of experiment No. 1

The concentration of activated sludge [g dm^{-3}]	**0.16**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	28.0	18.5	17.5	16.0	15.5	14.0	13.0
Volume of slurry [cm^3]	780	505	480	430	415	395	360
Lifting speed [cm min^{-1}]	1.9	0.2	0.3	0.05	0.1	0.06	-
Effect of purification [%]	-	-	-	82.0	82.0	-	82.0
Concentration of colorant [g dm^{-3}]	-	-	-	0.11	0.11	-	0.1

The results of experiment No. 1, at the concentration of activated sludge equal to 0.16 g dm^{-3} in volume of 250 cm^3, the colorant saturation pressure 2 at and the duration of saturation of 4 min are presented in Table 2.

Experiment No. 2, p = 2 atm

Saturation of water and water-air mixture in the cylinder was similar as in case of experiment No. 1, but concentration of activated sludge was equal to 0.12 g dm^{-3}. In addition, the same time interval was considered during the measurement of the height and volume of the sludge. The results are presented in Table 3.

Table 3

Results of experiment No. 2

The concentration of activated sludge [g dm^{-3}]	**0.12**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	10.0	9.0	8.0	7.0	6.5	6.2	6.0
Volume of slurry [cm^3]	265	230	220	185	180	165	145
Lifting speed [cm min^{-1}]	0.2	0.2	0.2	0.05	0.02	0.01	-
Effect of purification [%]	-	-	-	70.8	79.1	-	79.1
Concentration of colorant [g dm^{-3}]	-	-	-	0.14	0.10	-	0.10

Experiment No. 3, p = 2 atm

Saturation of water and water-air mixture in the cylinder was similar as in experiments No. 1 and No. 2. Concentration of activated sludge was equal to 0.08 g dm^{-3}. The results of the experiment are presented in Table 4.

Table 4

Results of experiment No. 3

The concentration of activated sludge [g dm^{-3}]	**0.08**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	5.3	4.3	3.7	3.5	3.2	2.8	2.5
Volume of slurry [cm^3]	150	120	100	95	90	75	65
Lifting speed [cm min^{-1}]	0.2	0.12	0.04	0.03	0.02	0.02	-
Effect of purification [%]	-	-	-	70.8	70.8	-	77.1
Concentration of colorant [g dm^{-3}]	-	-	-	0.14	0.14	-	0.11

The next three experiments were conducted with different concentrations of colorant, but with the same initial concentration of activated sludge in all three samples (0.16 g dm^{-3}).

Experiment No. 4, p = 2 atm

Saturation of water and water-air mixture in the cylinder was similar as in the previous experiments. Concentration of colorant was equal to 0.22 g dm^{-3}. Results of the experiment are shown in Table 5.

Table 5

Results of experiment No. 4

The concentration of colorant [g dm^{-3}]	**0.22**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	24.0	20.0	17.9	15.0	14.7	14.5	13.0
Volume of slurry [cm^3]	600	530	470	410	400	390	360
Lifting speed [cm min^{-1}]	0.8	0.40	0.58	0.03	0.01	0.1	-
Effect of purification [%]	-	-	-	63.6	63.6	-	70.4
Concentration of AS [g dm^{-3}]	-	-	-	0.08	0.08	-	0.065

Experiment No. 5, p = 2 atm

Saturation of water and water-air mixture in the cylinder was similar as in the previous experiments. Concentration of colorant was equal to 0.33 g dm^{-3}. Results of the experiment are presented in Table 6.

Table 6

Results of experiment No. 5

The concentration of colorant [g dm^{-3}]	**0.33**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	13.6	11.5	11.2	10.5	9.0	8.5	7.5
Volume of slurry [cm^3]	360	320	300	280	250	220	210
Lifting speed [cm min^{-1}]	0.42	0.06	0.14	0.15	0.03	0.03	-
Effect of purification [%]	-	-	-	83.3	83.9	-	84.8
Concentration of AS [g dm^{-3}]	-	-	-	0.055	0.053	-	0.050

Experiment No. 6, p = 2 atm

Saturation of water and water-air mixture in the cylinder was similar as in case of the previous experiments. Concentration of colorant was equal to 0.44 g dm^{-3}. Results of the experiment are shown in Table 7.

Table 7

Results of experiment No. 6

The concentration of colorant [g dm^{-3}]	**0.44**						
Duration of flotation [min]	5	10	15	20	30	45	60
Height of slurry [cm]	22.0	17.5	16.0	15.0	13.5	12.5	11.5
Volume of slurry [cm^3]	580	470	430	400	360	330	310
Lifting speed [cm min^{-1}]	0.9	0.3	0.2	0.15	0.07	0.07	-
Effect of purification [%]	-	-	-	81.9	82.5	-	82.9
Concentration of AS [g dm^{-3}]	-	-	-	0.085	0.082	-	0.08

Based on the data obtained during the experiments, the graphical interpretation, presented at Figure 2 was prepared.

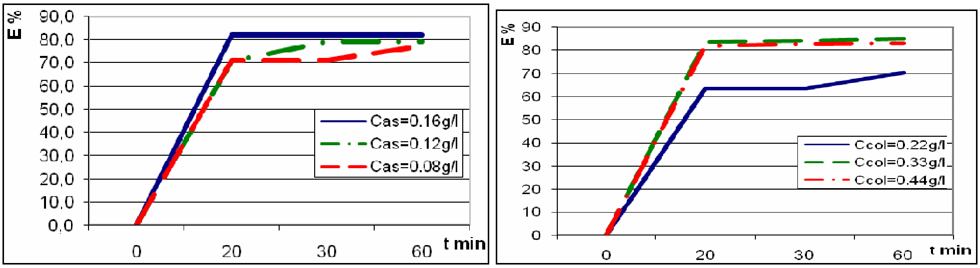

Fig. 2. Effect of purification with different concentrations of activated sludge and a constant amount of colorant (left), effect of purification with different concentrations of colorant and a constant amount of activated sludge (right)

Summary and conclusions

Based on our studies, it is possible to present the following conclusions:

- Process of purification, independent and dependent on activated sludge concentration, can be divided in two phases - exponential and plateau phase.
- The most efficient phase of exponential growth occurs during the first 20÷30 minutes from the start of experiment. During the next 30÷40 minutes, process becomes stable (plateau phase).
- Effectiveness of purification process depends on activated sludge concentration. Increase of activated sludge concentration results in enhanced process effectiveness, from 70 to 80%.
- Effectiveness of purification process revealed dependence of colorant concentration at constant concentration of activated sludge. The process can be also divided in two phases - exponential and plateau.
- Process of purification is most effective during the first 20 minutes (exponential phase). During the next 40 minutes, colorant extraction process occurs extremely slowly.
- Our observation showed that, the process reaches its highest effectiveness for activated sludge and colorant concentration equal to, respectively, 0.08 g dm^{-3} and 0.22÷0.33 g dm^{-3}. The increase of colorant concentration to 0.47 g dm^{-3}, decreased the process effectiveness by 20%. Thus, selection of the optimal concentrations of activated sludge and colorant allows reaching the maximal effectiveness of sorption.

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OCZYSZCZANIE ŚCIEKÓW Z BARWNIKA W PROCESACH FLOTACJI I BIOKOAGULACJI

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Abstrakt: Przedstawiono efekty usuwania barwnika ze ścieków za pomocą procesów biokoagulacji i flotacji. Przeanalizowano wpływ stężenia osadu czynnego wykorzystywanego jako czynnik procesowy oraz czasu biokoagulacji i flotacji na uzyskiwany efekt końcowy. Podczas eksperymentu badano grubość powstającej warstwy osadów oraz zmniejszanie się stężenia barwnika w oczyszczanej objętości ścieków. Do badań wykorzystano osad czynny pobrany z wylotu osadnika wtórnego oczyszczalni ścieków przemysłu włókienniczego. Wspomniany osad wykorzystano do sporządzenia roztworów z czynnikiem procesowym o różnych stężeniach. Uzyskane wyniki pierwszej serii badań pokazują zmieniające się w czasie stężenia barwnika dla różnych stężeń osadu czynnego przy jednakowym stężeniu zanieczyszczeń na początku eksperymentu. Wyniki drugiej serii przedstawiają wpływ oczyszczania w wybranych etapach eksperymentu przy stałym stężeniu czynnika procesowego i zmieniającym się stężeniu barwnika na początku eksperymentu.

Słowa kluczowe: oczyszczanie ścieków, osad czynny, barwniki, flotacja, biokoagulacja, sorpcja

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DYNAMICS OF *Opiliones* AND *Acarina* OCCURRENCE IN SOIL CONTAMINATED WITH OIL DERIVATIVES DURING BIOREMEDIATION PROCESS

PRZEBIEG DYNAMIKI WYSTĘPOWANIA KOSARZY (*Opiliones*) I ROZTOCZY (*Acarina*) W GLEBIE SKAŻONEJ ROPOCHODNYMI W TRAKCIE PROCESU BIOREMEDIACJI

Abstract: The investigations were conducted to determine the effect of oil derivatives (petrol, diesel fuel and used engine oil) during the process of their bioremediation on dynamics of *Opiliones* and *Acarina* occurrence. No negative effect of applied oil derivatives on the occurrence of representatives of epigeal *Opiliones* or *Acarina* arachnid order on the soil surface was stated. Applied bioremediation of soil polluted with petrol contributed to a reduction in *Opiliones* occurrence, particularly during the first month after it was conducted, whereas a positive effect of this measure on the presence of epigeal *Acarina* was registered in the third month after soil contamination.

Keywords: oil derivatives, soil, bioremediation, *Opiliones, Acarina*

Arachnids are counted to animals which fast respond to all changes in the environment caused by human activity, therefore their role as potential bioindicators has been emphasized [1-4]. Important groups among *Arachnida* are *Opiliones* and *Acarina*. Both play a crucial role in organic matter decomposition in soil.

Natural ground reclamation in result of extremely serious pollution with oil derivatives may take between several to several hundred years. Application of modern biotechnological methods using selected microorganisms allows to shorten the time of reclamation to several months. Such acceleration of oil derivatives decomposition process may affect soil invertebrates.

The work aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of *Opiliones* and *Acarina* occurrence.

Materials and methods

The investigations were conducted at the Experimental Station of the University of Agriculture in Krakow situated in Mydlniki near Krakow. The experiment, conducted in four replications, comprised the following objects in two series (with bioremediation and without bioremediation): 1. Control - unpolluted soil (C); 2. Soil artificially polluted with petrol (P); 3. Soil artificially polluted with diesel fuel (DF) and 4. Soil artificially polluted with used engine oil (EO). In autumn 2009, the indigenous soil was placed in 1 m^3 (1 m/1 m/1 m) containers specially adapted for this purpose. The containers were dug into the ground. Doses of 6 000 mg of oil derivative per 1 kg soil d.m. were applied in June

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2010. After one week a half of the containers with experimental soil was subjected to bioremediation using a biopreparation containing selected prokaryotic microorganisms, mainly bacteria. Detailed description of experiment was presented in other paper [5]. During the period from June to October 2010, epigeal fauna was trapped using Barber's traps (a 0.9 dm^3 jar dug in level with the ground surface and covered against rainfall water by a plastic roof) placed in the central part of each container. The traps were emptied once a week. Statistical computations were conducted using Statistica 9.0 PL programme. Means were differentiated using LSD (*least significant differences*) Fisher test on significance level $\alpha = 0.05$.

Results and discussion

Opiliones were the most rarely trapped in conditions of control soil on which biopreparation was used (Fig. 1). During the first month after the moment of soil contamination these arachnids were most frequently trapped in conditions of soil polluted with petrol, without bioremediation. Their number was significantly higher than on the unpolluted soil (both with and without biopreparation) and on the non-remediated soil contaminated with diesel fuel. Statistical analysis for the subsequent months passing from the moment of soil pollution did not reveal any marked effect of the analyzed pollutants or applied bioremediation on the occurrence of *Opiliones*. A higher average number of trapped *Opiliones* was registered for the whole period of the experiment in conditions of soil contaminated with petrol and diesel fuel without the use of bioremediation than in conditions of control soil on which the biopreparation was poured, however the differences were insignificant for the unpolluted soil without the biopreparation (Fig. 4). A decreased number of trapped *Opiliones* was noted in conditions of soil contaminated with petrol and subjected to bioremediation as compared with the same object without biopreparation applied.

Data on the effect of pollutants on these arachnids are diverse. The research on the influence of soil contamination with oil derivatives in result of a serious road accident revealed that three years after the moment of pollution, *Opiliones* were trapped in greater numbers in the polluted area [6]. On the other hand, pollution with oil derivatives, whose source were seasonal floodwaters of streams polluted with these substances, limited the numbers of both *Opiliones* and *Acarina* in the investigated area [7]. The differences may be due to the size of polluted area. In the presented investigations the soil was polluted with individual kinds of oil derivatives within a limited area, but usually soil pollution with oil derivatives are point source pollutions. In research on the effect of sulphur pollutants on soil invertebrates, the representatives of both *Opiliones* and *Acarina* caught using Barber's traps were classified to groups which did not show changes in their numbers under the influence of this factor [8].

Acarina occurred in greatest numbers in the initial period of the experiment, *ie* at the turn of June and July (Fig. 2). Later their number increased again in September. No significant effect of oil derivatives on epigeal *Acarina* occurrence was noticed for the two first months after the soil pollution (Fig. 3). Slightly bigger number was trapped on unpolluted soil but the differences fell within the range of experimental error. In the third month of the experiment more numerous *Acarina* presence was noticed in conditions of soil contaminated with petrol and subjected to bioremediation than in the same object but without bioremediation.

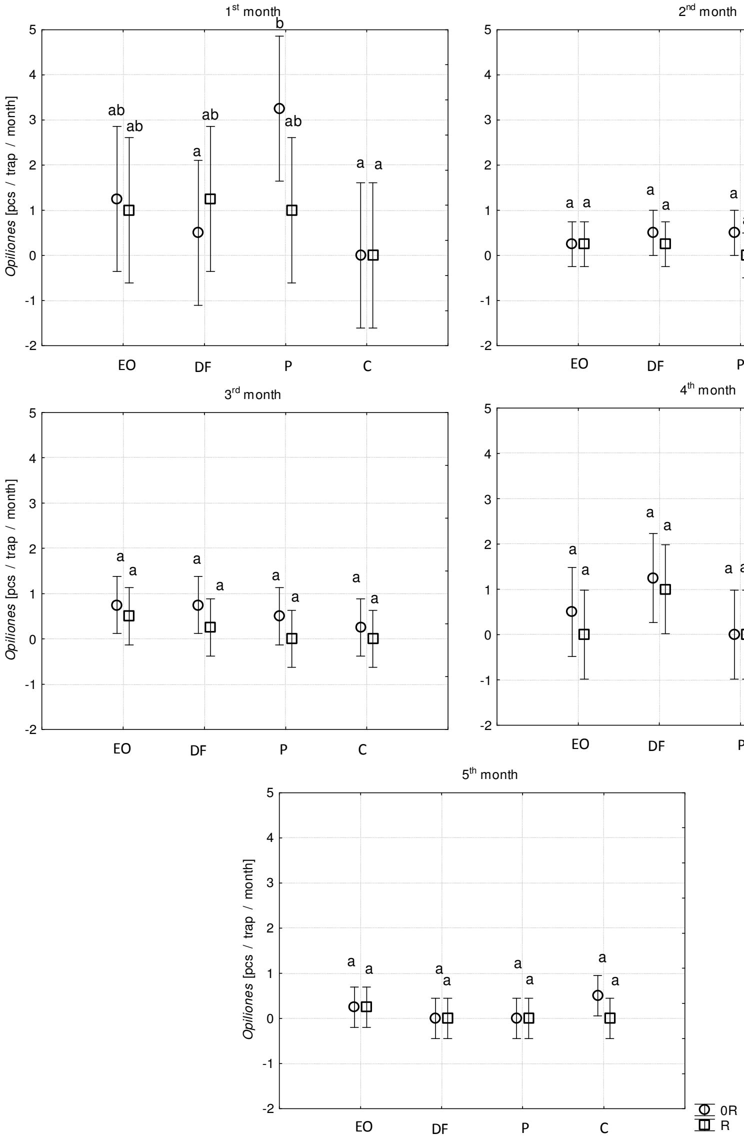

Fig. 1. Occurrence of *Opiliones* trapped using Barber's traps in individual months after soil contamination. EO - soil contaminated with used engine oil, DF - soil contaminated with diesel fuel, P - soil contaminated with petrol, C - unpolluted soil, 0R - series without bioremediation, R - series with bioremediation. Means marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ± 0.95 confidence interval

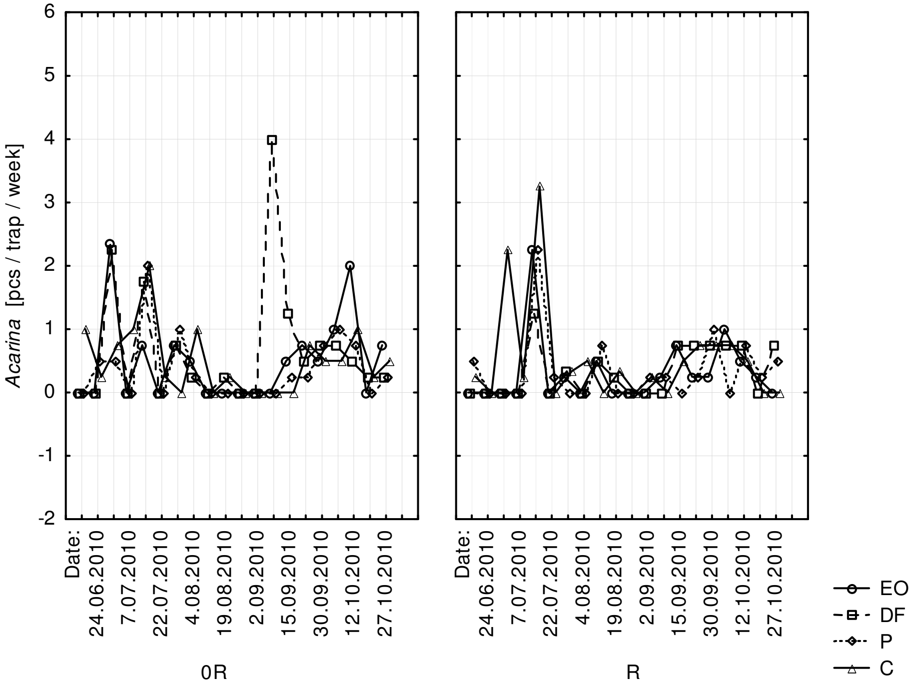

Fig. 2. Course of dynamics of *Acarina* occurrence trapped using Barber's traps. The symbols as in Figure 1

In the subsequent months number of *Acarina* in individual objects fluctuated, *ie* after 4 months the largest number of these invertebrates were spotted on soil contaminated with diesel fuel and non-remediated, while after 5 months on the soil contaminated with engine oil and also without bioremediation. On average for the whole investigated period significant differences in the number of trapped *Acarina* were registered only between the object where the soil was contaminated with engine oil, in the series subjected to bioremediation (the least number of *Acarina*) and the object with soil polluted with diesel oil, where bioremediation was not applied (the highest number of *Acarina*) (Fig. 4). *Oribatida* are one of the more numerous groups among soil *Acarina*. After 2 and 3 years from the moment of soil contamination with oil derivatives in result of road disaster slightly bigger number of these invertebrates were caught in the unpolluted area, although the differences were not statistically proved [6]. According to some authors [3, 9] use of oribatid mites as bioindicators in agroecosystems or polluted areas must incorporate information on life history traits and habitat profiles for species. Khalil et al [3] did not find relationship between metal pollution and total density of oribatids but there were differences in occurrence of selected species. Reports on the effect of various kinds of anthropogenic factors on the occurrence of soil *Acarina* are diversified. Research on the influence of various kinds of fertilization on soil *Acarina* presence demonstrated their increased number when low doses of liquid manure were applied but reduced occurrence at too high doses, particularly if they contained sodium hydroxide and calcium hydroxide supplements [10].

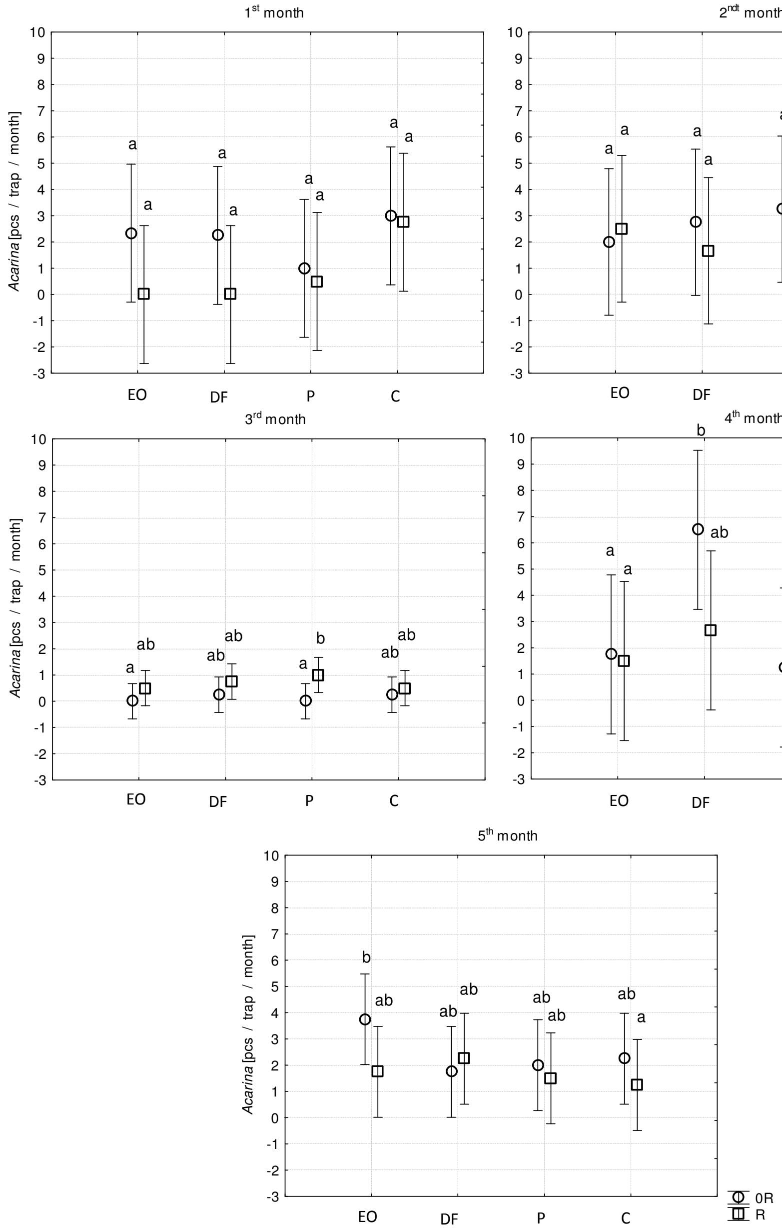

Fig. 3. Occurrence of *Acarina* trapped using Barber's traps in individual months after soil contamination. The symbols as in Figure 1

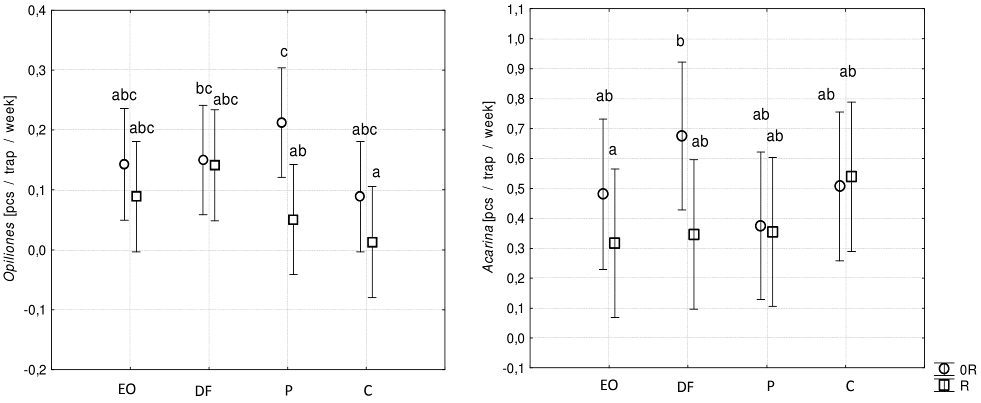

Fig. 4. Occurrence of *Opiliones* and *Acarina* trapped using Barber's traps mean during experiment. The symbols as in Figure 1

Conclusions

1. No negative effect of applied oil derivatives on the occurrence of representatives of epigeal *Opiliones* or *Acarina* arachnid order on the soil surface was stated.
2. Applied bioremediation of soil polluted with petrol contributed to a reduction in *Opiliones* occurrence, particularly during the first month after it was conducted, whereas a positive effect of this measure on the presence of epigeal *Acarina* was registered in the third month after soil contamination.

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PRZEBIEG DYNAMIKI WYSTĘPOWANIA KOSARZY (*Opiliones*) I ROZTOCZY (*Acarina*) W GLEBIE SKAŻONEJ ROPOPOCHODNYMI W TRAKCIE PROCESU BIOREMEDIACJI

Katedra Ochrony Środowiska Rolniczego, Uniwersytet Rolniczy w Krakowie

Abstrakt: Celem pracy było zbadanie oddziaływania substancji ropopochodnych (benzyny, oleju napędowego, zużytego oleju silnikowego) w trakcie procesu bioremediacji gleby na przebieg dynamiki występowania kosarzy i roztoczy. Nie stwierdzono ujemnego wpływu zastosowanych substancji ropopochodnych na występowanie na powierzchni gleby przedstawicieli pajęczaków naziemnych z rzędu kosarze oraz roztocza. Zastosowana bioremediacja gleby zanieczyszczonej benzyną przyczyniła się do ograniczenia występowania kosarzy, szczególnie w ciągu pierwszego miesiąca po jej przeprowadzeniu, natomiast odnotowano korzystny wpływ tego zabiegu na obecność roztoczy naziemnych w trzecim miesiącu po skażeniu gleby.

Słowa kluczowe: ropopochodne, gleba, bioremediacja, *Opiliones, Acarina*

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ANTIFUNGAL ACTIVITY OF *Bacillus* spp. AGAINST *Fusarium* spp.

AKTYWNOŚĆ PRZECIWGRZYBOWA BAKTERII Z RODZAJU *Bacillus* spp. WOBEC *Fusarium* spp.

Abstract: The aim of the study was to assess the fungistatic activity of supernatants obtained from 4, 6, 8, 10 and 24-hour culture of *Bacillus* KF2 and *Bacillus* BK2 against *Fusarium* spp. The antagonistic activity was evaluated on the basis the rate index of fungal growth on Czapek-Dox and PDA media. The rate index of *Fusarium* spp. growth on PDA medium was 5-fold and 3.5-fold slower than in the control, after application of supernatants obtained from the 24-hour culture (respectively for *Bacillus* KF2 and *Bacillus* BK2). Similarly, a high antifungal activity of the tested strains was observed on Czapek-Dox medium. The growth of *Fusarium* spp. was 6-fold and 3.5-fold slower after application of supernatants obtained from 6-hour culture, respectively, for *Bacillus* KF2 and *Bacillus* BK2. Supernatants obtained from the culture of both strains showed fungistatic activity against *Fusarium* spp., although the *Bacillus* KF2 strain showed a stronger impact than *Bacillus* BK2 strain. The inhibitory properties of *Bacillus* species was depended on the age of the bacterial culture and/or strains of *Bacillus*, and the composition of the medium. The experimental results exhibit the fungistatic activity of *Bacillus* strains and indicate the possibility of use their as antifungal agents against *Fusarium* spp.

Keywords: *Bacillus* spp., antifungal activity, *Fusarium* spp.

Bacillus spp. and relatives or their metabolites present an ecofriendly alternative to use of synthetic chemicals for plant growth enhancement in many different applications. Extensive research has demonstrated that these microorganisms could have an important role in agriculture and horticulture in improving crop productivity [1-3]. Direct mechanisms of these bacteria include the provision of bioavailable phosphorus for plant, nitrogen fixation, production of siderophores, production of phytohormones like cytokinins, auxins and gibberellins. Indirect mechanisms used by *Bacillus* spp. include reduction of iron available to phytopathogens bacteria, synthesis of fungal cell wall-lysing enzymes (cellulase, chitinase, β-1,3 glucanase), antibiotic production (phospholipides, lipoprotein) and protection against pathogenic fungi. The major antibiotics that play a vital role in the suppression of plant pathogens by *Bacillus* spp. (eg *B. cereus*, *B. subtilis*, *Paenibacillus polymyxa*, *B. circulans*, *B. coagulans*) are grouped into non-volatile (eg lipopeptides: iturins, fengycins, surfactins) and volatile antibiotics (eg hydrogen cyanide) [2, 4-8]. These metabolites have antibacterial and antifungal activity against phytopathogenic microorganisms (eg *Rhizoctonia* spp., *Pythium* spp., *Aspergillus* spp., *Botritis cinerea*, *Sclerotina sclerotinum*) [1, 9-11]. Antibiotics production is strongly conditioned by factors such as the strain microorganism, chemical composition of the medium and the incubation conditions (incubation time, agitation, pH and temperature). The main purpose of the study was to assess the antifungal activity of the *Bacillus* strains KF2 and BK2 on *Fusarium* spp.

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Materials and methods

The involvement of antifungal compounds produced by the *Bacillus* strains KF2 and BK2 in the inhibition of fungal growth was confirmed by the ability of cell-free culture filtrate of these strains to inhibit of hyphal growth of *Fusarium* spp. The *Bacillus* strains were inoculated into a flask containing the nutrient broth and incubated at 30°C for various times to give 4, 6, 8, 10 and 24-hour culture (working culture). The *Fusarium* spp. strain was cultivated on Czapek-Dox medium at 25°C for 5 days. Each experiment was run in triplicate. The antagonistic activity of the tested *Bacillus* strains was evaluated as the rate index of fungal growth.

Determination of influence of Bacillus strains on mycelium growth. Fungal mycelial-disks (diameter of 10 mm) obtained from growing cultures of tested fungal isolates were placed in the centre of Czapek-Dox and PDA media that containing 0.5 cm^3 (mL) working cultures of *Bacillus* strains (in four replications). A control was made only with fungal mycelial-disks on both media without bacteria. After incubation at 27°C for 14 days, plates were observed at 2 days intervals and estimated as the rate *index of fungal growth* (*Ifg*) using the formula [12]:

$$Ifg = \frac{A}{D} + \frac{b_1}{d_1} + \ldots + \frac{b_x}{d_x}$$

where A is the mean from colony measurement, D is the experiment duration (days), $b_1 \ldots b_x$ is the increase a colony diameter from lasted measurement, $d_1 \ldots d_x$ is the number days from lasted measurement.

Results and discussion

The antifungal activity of *Bacillus* strains KF2 and BK2 grown on 2 different media was evaluated towards tested *Fusarium* spp. as the rate index of fungal growth. The antifungal activity of these strains was depended on the strains of *Bacillus* spp. and also age of the culture applied and the growth media used. This might be due to the secretion of metabolites produced by these strains, diffused and dissolved into the culture media. Figure 1 shows the results obtained on the Czapek-Dox medium.

In this experiment 4, 6, 8, 10 and 24-hour culture of the *Bacillus* strains were used as an inhibition factor. It was observed that the rate index of *Fusarium* spp. growth was the slowest after application of the supernatants obtained from 6-hour culture compared with the control, around 72÷82%, for *Bacillus* BK2 and *Bacillus* KF2 respectively. Whereas the 24-hour culture of both these strains showed a very little inhibitory properties, although in case of *Bacillus* KF2 it was a quite high and amounted to 73%, but in case of *Bacillus* BK2 amounted only 9%.

The high antifungal activity the tested strains was also observed on PDA medium (Fig. 2).

It is appear that inhibitory activities of *Bacillus* KF2 was higher than *Bacillus* BK2. The growth of *Fusarium* spp. was strongly inhibited by both these strains, when were applied as 24-hour culture and amounted to 70÷78%, for *Bacillus* strains BK2 and KF2 respectively. However the *Bacillus* BK2 showed very little inhibitory properties as a 6-hour culture and even small stimulatory properties in case of 4-hour culture. *Fusarium* spp. was also the less sensitive to metabolites produced by 4-hour culture of *Bacillus* KF2, and the suppress of its growth was still a quite big (about 59%) compared with the control.

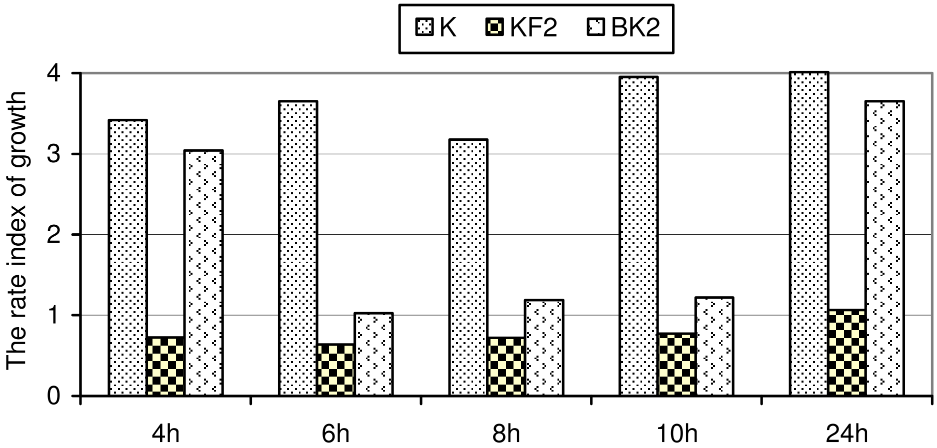

Fig. 1. Antifungal activity of *Bacillus* KF2 and *Bacillus* BK2 on Czapek-Dox medium against *Fusarium* spp.

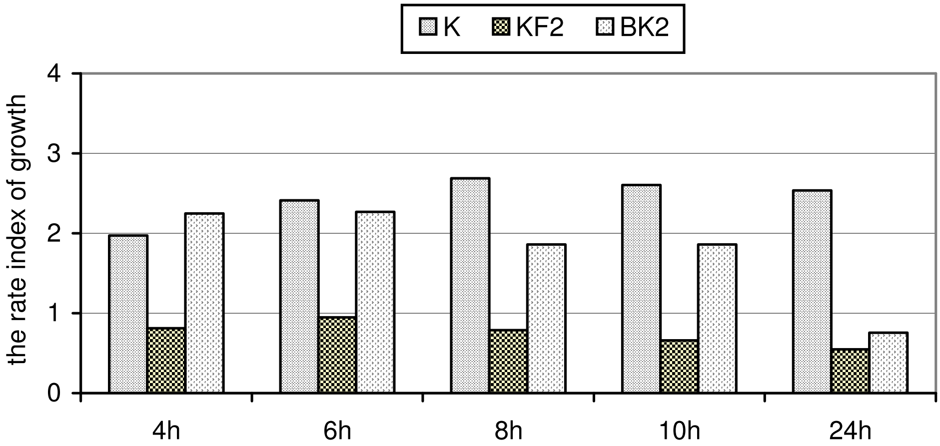

Fig. 2. Antifungal activity of *Bacillus* KF2 and *Bacillus* BK2 on PDA medium against *Fusarium* spp.

With these observations agree some authors, who evidenced that the different sensitivities of the fungi to the various *Bacillus* genus might be due to the secretion of secondary metabolites at different concentrations and dependent on the fungi membrane composition. Besides, the appearance of secondary metabolites in bacterial cultures is often confined to a certain growth phase. Production of most antibiotics begins by the end of the log phase and occurs throughout the stationary phase [11, 13].

Therefore, an interest of these microorganisms is increasing and possibility theirs application as biological control agent are investigated extensively and conducted in many countries around the world [1, 3, 4].

Conclusions

1. The inhibitory properties of *Bacillus* species was depended on the kind of the ones: the age of the bacterial culture and/or strains of *Bacillus*, and the composition of the medium.
2. Supernatants obtained from the culture of both strains showed fungistatic activity against *Fusarium* spp, although the *Bacillus* KF2 strain showed a stronger effect than *Bacillus* BK2 strain.
3. The growth of *Fusarium* spp. was strongly inhibited on PDA medium by 4-hour culture of both *Bacillus* strains, while on Czapek-Dox medium by 6-hour culture.
4. The experimental results demonstrated the fungistatic activity of the tested *Bacillus* strains and indicate the possibility of using theirs as antifungal agents against *Fusarium* spp.

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AKTYWNOŚĆ PRZECIWGRZYBOWA BAKTERII Z RODZAJU *Bacillus* spp. WOBEC *Fusarium* spp.

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Abstrakt: Celem podjętych badań była ocena aktywności fungistatycznej supernatantów otrzymanych z 4-, 6-, 8-, 10- i 24-godzinnych hodowli *Bacillus* KF2 i *Bacillus* BK2 wobec *Fusarium* spp. Ocenę właściwości antagonistycznych metabolitów bakteryjnych przeprowadzono metodą hodowlano-płytkową z zastosowaniem podłoży Czapka i PDA. Tempo wzrostu *Fusarium* spp. na podłożu PDA było 5-krotnie oraz 3,5-krotnie wolniejsze niż w próbce kontrolnej, po zastosowaniu supernatantów uzyskanych z 24-godzinnej hodowli, odpowiednio dla *Bacillus* KF2 i *Bacillus* BK2. Podobnie dużą aktywność przeciwgrzybową badanych szczepów stwierdzono na podłożu Czapka. Indeks tempa wzrostu *Fusarium* spp. był 6-krotnie oraz 3,5-krotnie wolniejszy po zastosowaniu supernatantów z 6-godzinnej hodowli, odpowiednio dla *Bacillus* KF2 i *Bacillus* BK2. Supernatanty otrzymane z hodowli obu szczepów wykazały działanie fungistatyczne wobec *Fusarium* spp. przy czym silniejszy wpływ wykazał *Bacillus* KF2. Stopień zahamowania wzrostu *Fusarium* spp. zależał od gatunku bakterii, wieku jej hodowli, rodzaju podłoża i czasu trwania hodowli. Uzyskane wyniki badań wykazały aktywność fungistatyczną szczepów *Bacillus* spp. i wskazują na możliwość wykorzystania ich jako środków przeciwgrzybiczych wobec *Fusarium* spp.

Słowa kluczowe: *Bacillus* spp., aktywność przeciwgrzybowa, *Fusarium* spp.

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DISTRIBUTION OF CARABID BEETLES (*COLEOPTERA*, *CARABIDAE*) IN THE URBAN AREA OF LUBLIN

ROZMIESZCZENIE BIEGACZOWATYCH (*COLEOPTERA*, *CARABIDAE*) NA TERENACH ZURBANIZOWANYCH MIASTA LUBLIN

Abstract: The composition and distribution of ground beetles species in the different urban green areas of the Lublin city, Eastern Poland was studied. Carabids were collected since the end of April till the late July 2011 using pitfall traps. In total 67 carabid species were found during of the study period. The number of species varies from 54 in valley of Bystrzyca to 5 on the lawns along street. The highest species richness (5.94) had the studied floodplain of river Bystrzyca in comparison with other green territories. All studied green areas were distinguished by considerable individuality. Our results support the thesis that despite of the sizeable areas of the lawns and flowerbeds, their role in the diversity maintenance and preservation is minimal.

Keywords: species richness, urban green areas, *Carabidae*

The populated areas extension and transformation of the landscapes are important characteristics of second half of the 20th century. The expansion of cities is accompanied by a reduction of proportion between green and residential zones.

In view of this many publications appeared that deal with diversity of insects in urban landscapes [1-13]. It was showed that considerable moving of urban green areas (parks, squares, flowerbeds, grass spots and water bodies) away from the surrounding cities of ecosystems leads to reduction of biodiversity [14]. The building-up of river valleys that perform the function of migration tracks becomes an obstacle for animals and plants penetration into the green zones of towns.

According to the modern trends the townspeople become isolated from the nature most of the time. The citizens' isolation from nature in megalopolises has been accompanied by psychological discomfort [15]. This is why nowadays the importance of green areas as places with relaxing action is obvious. Present development projects aim more and more at combining the residential functional areas with green areas. However this task can be fulfilled in two ways: by construction of artificial green zones on place of natural ones or by conservation of native landscapes fragments amidst buildings. What type of green areas is able to keep up the sufficiently high level of biodiversity is still the question, which requires detailed research.

In this article the results of studies of the ground beetles species composition and distribution in various types the green areas of the Lublin city are presented.

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Material and methods

Four urban green areas of different types, within the city of Lublin, were selected for study. The valley of river Bystrzyca (around Lublin University of Technology), the valley of drained tributary (region of T. Zana Street), the Saski Park (city centre) and a number of lawns were studied. All studied territories are under considerable human impact. The section of the valley of river Bystrzyca and Park Saski were characterized by wide variety of habitats.

In the valley of the Bystrzyca were studied the floodplain meadows on both riversides (stations B1-B3), plot of land with ruderal vegetation (B5) and small lake (B4), bank of floodplain lake (B7) situated on the Bystrzyca left side, old park (B8), and also tree-shrub brushwood (B9). In the Saski Park the samples were taken on six various stations situated on the slopes of an artificial stream (S1-S4), in shrubs (S5, S7) and on the grass-plots (S6). In the valley of dried tributary were studied bottom of the ravine overgrown with herbaceous vegetation (T1) and the shrubs on the ravine slopes (T2). Also the objects of investigation were lawns with single trees and shrubs located along the Nadbystrzycka Street.

The survey was conducted since April till July 2011. From five to nine pitfall traps (plastic containers with 90 mm in diameter and 130 millimeters of height) per station were installed depending on the size of study object. No preservation liquid was added to the traps. Sampling was conducted every day.

Average activity density of carabid species (individuals per trap and day) was used in statistical analyzing. The index of species richness by Margalef was used. The degree of difference between the studied urban greenery was evaluated using cluster analysis (on the Ochiai index similarity as distance measure and single linkage as method) based on the quantitative data of the ground beetles and also calculation of the index of similarity by Sörensen based on the qualitative data of the ground beetles. Calculations were conducted with the Diversity 3.0 and PAST 1.81 packages [16].

Results and discussion

In general during of the research period 868 individuals were captured, belonging to 67 species (29 genera). The number of species found in four of Lublin urban green zones varied from 54 (in Bystrzyca river valley) to 5 (on the lawns) (Fig. 1). Alone 36 species from 16 genera were registered in the Bystrzyca floodplain: *Acupalpus meridianus* L., *Agonum fuliginosus* Panz., *A. marginatum* L., *A. versutum* Sturm, *A. viduum* Panz., *Amara aenea* Deg., *A. communis* Panz., *A. plebeja* Gyll., *A. tibialis* Payk., *Anisodactylus binotatus* F., *A. signatus* Panz., *Badister dorsiger* Duft., *Bembidion articulatum* Panz., *B. dentellum* Thunb., *B. doris* Panz., *B. quadrimaculatum* L., *B. quadripustulatum* Aud.-Serv., *B. semipunctatum* Don., *B. tetracolum* Say, *B. varium* Ol., *Carabus granulatus* L., *Chlaenius nigricornis* F., *C. nitidulus* Schrnk., *Clivina collaris* Hbst., *C. fossor* L., *Dyschirius aeneus* Dej., *Dyschirius tristis* Steph., *Elaphrus riparius* L., *Oodes helopioides* F., *Patrobus atrorufus* Stroem, *Pterostichus anthracinus* Ill., *P. nigrita* Payk., *P. oblongopunctatus* F., *P. strenuus* Panz., *Stenolophus mixtus* Hbst., *Trechoblemus micros* Hbst. Also exclusively in the Saski Park 6 species from 5 genera were found: *Amara familiaris* Duft., *A. littorea* Thoms., *Badister unipustulatus* Bon., *Calathus erratus* Sahlb., *Poecilus lepidus* Leske, *Stomis pumicatus* Panz. The species *Calathus mollis* Marsh., *Harpalus progrediens* Schaub., *H. xanthopus winkleri* Schaub. were exclusively detected in the valley of drained tributary. Whereas *Badister bullatus* Schrnk. and *Harpalus rubripes* Duft. were not registered anywhere except of the lawns along the street.

Such species richness is quite high for the urbanized territory. This confirms the comparison with other city researches data. For example, in the studied of green zones of Warsaw - parks, green plots of land around the houses, forestry - 64, 55 and 54 species were found, respectively [1, 2]. 68 species from 26 genera were registered in the two riverbanks in the town of Sumy (Ukraine) [6]. The similar quantity - 55 species from 19 genera were found on the shores of lakes and artificial water reservoirs in the Kyiv (Ukraine) [10]. On the territories of three parks in the Donetsk (Ukraine) there were 77 species [17], and in two woodland parks of the town Lviv (Ukraine) - 48 species has been found [18]. In the reserve and woodland park in the territory of Olsztyn were found 37 and 48 species respectively [19]. Also on the territory of three woodlands of the Debrecen city (Hungary) a 50 species of carabid beetles were found [20], and 26 species - in the forests of Helsinki (Finland) [21]. According to described studies the general environmental tendency of increasing the number of species with the growth of the studied areas which is inherent in the natural biogenesis still persists on the urban territories. Despite the uniformity of conditions in green areas the homogenization of species composition is not observed in urban areas [22].

Our study showed that highest value of Margalef species richness index was in the section of the Bystrzyca river valley (5.94) and the lowest value of index (0.83) on the lawns in the city center (Fig. 1). The species richness in the valley of drained tributary and the Saski Park reached the level of the 2.01 and 2.07 respectively (Fig. 1).

The investigated sites of urban areas are located in the Bystrzyca river valley and its two tributaries. This suggests that in the past the populations of ground beetles of this area were similar according to species composition and level of diversity. Based on Sorensen's similarity coefficient we can estimate the degree of impact of territory development on the diversity of carabid assemblages of the studied green areas by the results of their comparison. The species composition similarity between all studied green areas is quite low (Fig. 2), which indicates significant changes taken place in their communities' structures.

All studied green areas were distinguished by a considerable individuality, which is proved with the results of the cluster analysis (Fig. 3). The cluster analysis shows considerable differences between the green areas in the city center, united into a one cluster, and the floodplain of the Bystrzyca, the river valley which is a corridor linking the urban green areas with the natural habitats outside the city. The results showed that the most of the habitats have a low level of similarity; this indicates the high structuring of Lublin city environment.

At the territories of green areas genetically connected with natural landscapes (residual fragments of natural landscapes) much higher level of biological diversity was preserved in comparison with artificial greenery. However it cannot be denied that artificial green areas supplement the diversity of ecological niches, and this favors the increase of overall diversity level of urban territory. In confirmation of the importance of preserving in the towns the landscape elements which have genetic relation with original natural landscape, one can cite the fact that protected species - *Carabus granulatus* L. and *C nemoralis* Müll.

together with species from the Red List [23] - *Oodes helopioides* F. were found in the valley of Bystrzyca. It should be noted that *C. nemoralis* Müll. also occurs in the Saski Park.

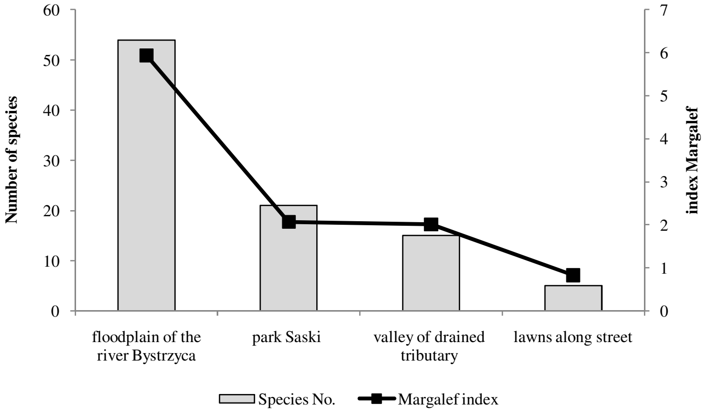

Fig. 1. The Margalef's species richness index calculated for urban green areas of the Lublin city

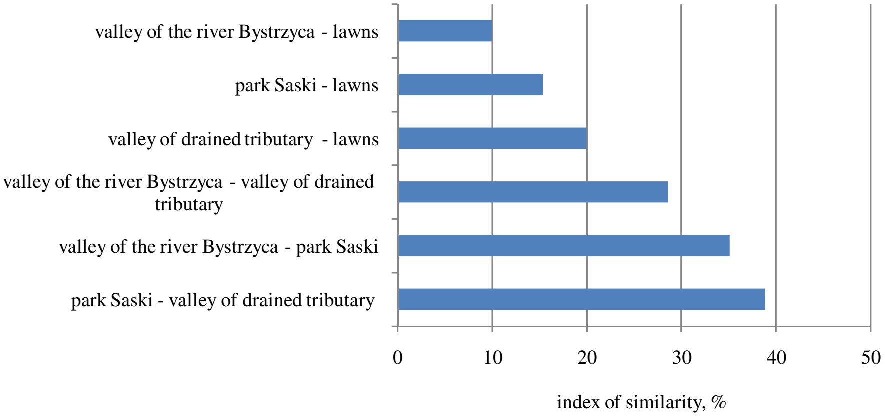

Fig. 2. Species composition similarities (Sörensen index) between the studied green areas of the Lublin city

However, for the preservation of biological diversity on the urban territories not only the conservation of residual natural complexes is important, but also the development of the infrastructure of artificial green zones, which are often represented by open habitats. The both habitat types (open and closed) are represented in our research. The floodplain meadows and ruderal vegetation in the Bystrzyca valley belong to the open habitats; the Saski Park and wooden vegetation in the floodplain of Bystrzyca belong to closed habitats.

The importance of preservation of exactly open habitats for maintenance of high level of the species richness and conserve of indigenous carabid beetles is confirmed by a number of researchers [24].

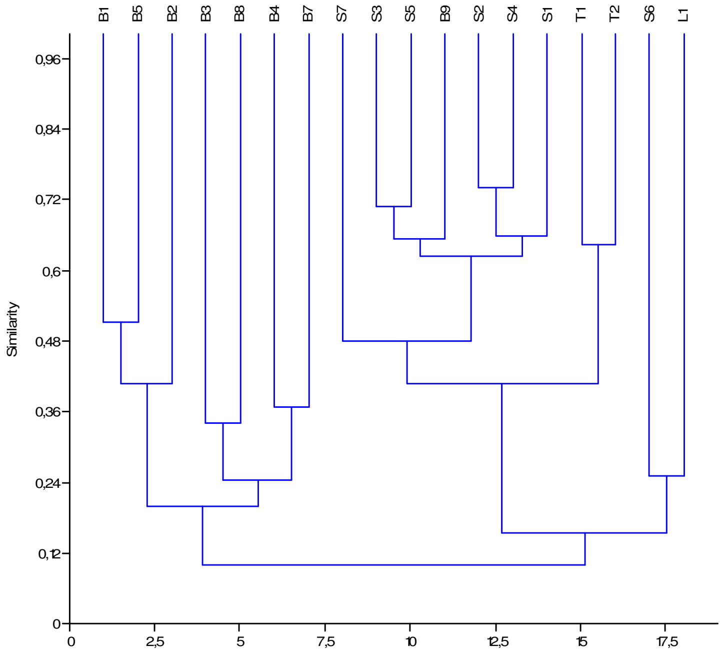

Fig. 3. Cluster analysis of the carabid species composition in the stations of the four studied green areas using Ochiai index as similarity measure and the paired group as linkage method. Code of stations (see also Material & methods): B1-B9 - the floodplain of river Bystrzyca, T1-T2 - the valley of drained tributary, S1-S6 - the park Saski, L - lawns allow street

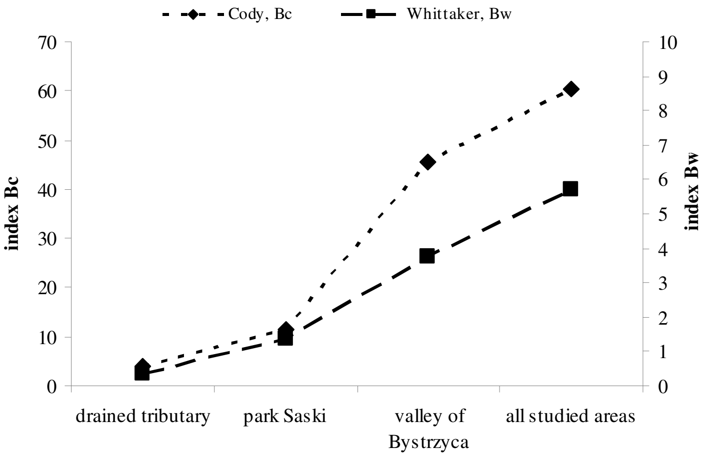

Fig. 4. The beta-diversity indices calculated for each studied green area separately and in total

The considerable increase of the total level of biodiversity in the presence of various types of green areas in the town boundaries shows the diagram in the Figure 4. Although the highest values of beta-diversity indices are registered in the Bystrzyca river valley, however the total index of diversity considerably increases due to the presence of green areas in the city center.

Conclusion

Our studies proved the exceptional importance of the preservation of different elements of floodplain landscape within town boundaries for the conservation of the biodiversity. Quite high level of biodiversity remains in a city park and the drained tributary of Bystrzyca, despite of their location in the residential zone. Even though the lawns and flowerbeds occupy here sizable areas, their role in the diversity maintenance and preservation is minimal.

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ROZMIESZCZENIE BIEGACZOWATYCH (*COLEOPTERA*, *CARABIDAE*) NA TERENACH ZURBANIZOWANYCH MIASTA LUBLIN

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Abstrakt: W pracy omówiono wyniki badań dotyczących składu gatunkowego zgrupowania biegaczowatych na różnych obszarach zieleni miejskiej w Lublinie (Polska). Badania prowadzone były od końca kwietnia do końca lipca 2011 roku; odłowy biegaczowatych prowadzono za pomocą pułapek naziemnych. W czasie przeprowadzonych badań odłowiono łącznie 67 gatunków biegaczowatych. Liczba gatunków stwierdzonych podczas badań kolejnych obszarów wahała się od 54 do 5. Największą wartością wskaźnika bogactwa gatunkowego Margalefa (5.94) charakteryzował się teras zalewowy rzeki Bystrzycy w porównaniu do innych obszarów zieleni miejskiej. Na podstawie składu gatunkowego poszczególnych stanowisk można stwierdzić znaczne różnice między nimi. Wyniki wskazują również, że pomimo znaczących obszarów trawników na terenie miasta Lublin ich rola w utrzymaniu i ochronie różnorodności biegaczowatych jest minimalna.

Słowa kluczowe: bogactwo gatunkowe, tereny zurbanizowane, *Carabidae*

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INFLUENCE OF INTENSIVE FARMING ON NUMBER AND VERTICAL DIVISION OF *Galinsoga parviflora* CAV. SEEDS IN ARABLE SOIL LAYER

WPŁYW UPRAWY INTENSYWNEJ NA LICZEBNOŚĆ I ROZDZIAŁ PIONOWY NASION *Galinsoga parviflora* CAV. W ORNEJ WARSTWIE GLEBY

Abstract: The degree of soil pollution with vital seeds of weeds depends on many factors, such as amount and species biodiversity of the habitat of weeds inhabiting in the crop, type of crop, method of cultivation as well as the level of nutrients supply in soil and its physicochemical properties. Various species of weeds differ from each other in possibilities to produce seeds. Differences between actual and potential seed production are significant, which is determined by environmental conditions in which plant vegetation takes place. At the population level weeds have the ability to produce such quantities of seeds, which largely compensate reduction in their appearance. This ability makes it significantly difficult to reduce the degree of their presence in the crop. In order to identify the impact of the above technology of cultivation on the amount and vertical distribution of *Galinsoga parviflora* Cav seeds in arable layer, pot experiments were carried out, in which soil samples taken twice from winter wheat fields were subjected to detailed analysis. The results indicate that the technology of plant cultivation significantly affects the number of seeds of weed species and their distribution in the arable layer of soil.

Keywords: soil weed seed bank, mechanical tillage, weed seed emergence, ecological weeding

In agrocenoses of intensive farming system as a result of disrupted biodiversity there do not function (or function very badly) natural self-regulation mechanisms of plant groups. Increased level of fertilisation and applied farming simplifications namely direct drilling or ploughless sowing increase the number of weed species in the cultivated plant field, and facilitate greater share of dominant species [1].

Weeding infestation of corn field depends, among others, on intensive chemical protection, therefore on number and accuracy of performed herbicide treatment, on a kind of applied herbicidal preparation, active ingredient dose size, time of its application, weather conditions etc. [2].

The most significant element of field weed infestation are segetal weeds that adapt to growth conditions of cultivated plants and ruderal weeds that grow in not cultivated areas. The source of weed infestation is diaspore reserve in soil called by Harper [3] "seed bank". It is supplemented every year mostly by annual weeds, which account for 95% or more of seeds found in the soil [3].

Smallflower galinsoga (*Galinsoga parviflora* Cav.) is a weed that often appears in vegetable and root crops plantations. It comes from South America, from where it was brought to botanical garden in Prague by a scientific expedition. At present it is the most annoying weed of segetal and ruderal form found in the gardens all over Europe and Asia [4]. It prefers clayey soil and humus soil and soil rich in nitrogen. During its vegetation period in favourable conditions it may produce several generations, because it needs from 4 to 6 weeks to reach full growth [5].

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Methods

The experiments were conducted on soil samples taken in year 2000 from a field located in Opole-Polwies. The soil for laboratory examination was taken at twice: in spring and in autumn. In both cases at depth of 0÷10 and 10÷20 cm.

Plant emergence and growth in vases was observed in few time periods (cycles), of which each lasted for roughly 6 weeks. After each period an analysis of weed concentration was conducted to determine species spectrum, number of emergence and development phase. In order to facilitate emergence after each analysis the soil in vases was mixed. After the fifth analysis fallowing was applied, during which watering factor was limited. The research was conducted with optimal photoperiod and relative moisture [6].

In the taken soil samples pH were determined and the amount of humus and macro and microelements was determined.

Results

The field of which soil samples were taken was located in the western part of Opole town. Plant production technique was involved a conventional way of farming vegetables (cucumber, beans, cabbage, peas) partitioned every second year with Jawa variety winter wheat. Plant production was conducted in intensive farming system, namely, there applied 395 kg NPK/ha and full chemical protection from pest. In vegetable farming mineral fertilisation was optimal, however in winter wheat there applied the following doses: 160 kg N, 110 kg P_2O_5 and 120 kg K_2O/ha. Winter wheat was sowed using ploughless tillage and together with sowed fertiliser it was covered with disc harrow.

The research was conducted on chernozem fen soil, IIIa valuation class of good wheat complex.

Very high amount of magnesium, phosphorus and potassium and high amount of manganese, zinc and average amount of iron was determined as a result of the analysis in the examined soil (Table 1).

Table 1

The results of the analyses of soil samples

Soil layer [cm]	**pH (1 N KCl)**	**Humus [%]**	**P_2O_5**	**K_2O**	**Mg**	**B**	**Mn**	**Cu**	**Zn**	**Fe**
			[mg/100 g soil]			**[mg/kg]**				
0÷10	8.5	2.10	67.0	33.5	13.6	4.4	307.0	7.6	20.1	1682
10÷20	8.6	1.80	65.3	25.3	13.6	4.3	291.0	7.5	20.9	1415

During both collection times of soil samples using frame method there were determined species content of weeds present in the field. As a result of the analysis there were determined the presence of 6 weed species, of which the most numerous were: *Chenopodium album* L - 81% and *Galinsoga parviflora* Cav. - 11% (Table 2).

As a result of conducted vase experiments *Galinoga parviflora* emerged in total number of 1480 piece/m^2, of which on soil samples taken in spring it accounted for 43% and on soil samples taken in autumn 57% (Fig. 1).

Table 2

Analysis of the weed field

Plant species	**Number of weeds [piece/m^2]**
Lamb`s quarters *Chenopodium album* L.	40
Common chickweed *Stellaria media* (L.) Vill.	1
Shepherd`s purse *Capsella bursa pastoris* (L.) Med.	1
Field violet *Viola arvensis* Murray	1
Smallflower galinsoga *Galinsoga parviflora* Cav.	5
Green amaranth *Amaranthus retroflexus* L.	1
Total score	49

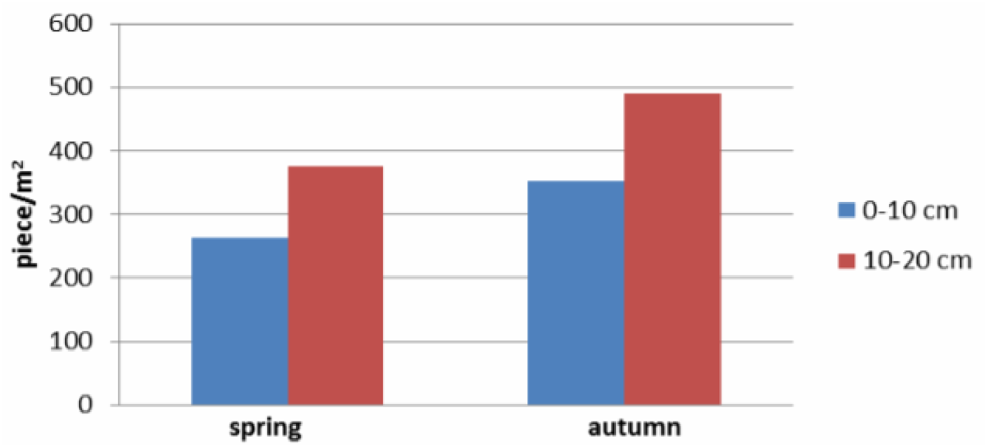

Fig. 1. Emergence concentration of *Galinsoga parviflora* Cav. on soil samples taken in spring and autumn

At both times the most numerous emergence of smallflower galinsoga was noted at soil samples taken at depth 10÷20 cm. In spring they accounted for 59% and on samples taken in autumn they accounted for 58%.

Table 3

Emergence dynamics of *Galinsoga parviflora* Cav. on a spring soil

Soil layer [cm]	**Number of cultivation**																		
	1-4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
	[piece/m^2]																		
0÷10	145	28	0	11	11	6	11	0	17	0	11	11	0	0	11	17	6	0	6
10÷20	216	0	6	28	39	17	6	17	6	17	11	0	0	0	6	0	0	0	6

This species reacted in different ways to soil reversing and mixing applied during the examinations. In spring samples the highest emergence was noted after first 4 cultivations, after which there emerged 55.1% in a soil layer of 0÷10 cm and 57.6% of plants in a soil layer of 10÷20 cm (Table 3).

The isolation of all vital seeds of smallflower galinsoga from the above-mentioned samples required application of 7 cycles of examination, namely 23 treatments, which total time of emergence account for 1008 days.

In autumn soil the highest emergence was characterised by first 5 cultivations, after which there emerged 58.2% in soil layer of 0÷10 cm and 60.4% plants in a layer of 10÷20 cm (Table 4).

There isolation of all vital seed of *Galinsoga parviflora* from soil samples required performing 6 cycles of examination, namely 22 treatment lasting for total 921 days.

Table 4

Emergence dynamics of *Galinsoga parviflora* Cav. in autumn soil

Soil layer [cm]	**Number of cultivation**																	
	1-5	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
	[piece/m^2]																	
0÷10	205	0	14	10	5	0	0	14	14	14	14	7	0	0	0	7	0	0
10÷20	29	54	20	20	5	4	7	0	14	14	20	7	7	0	0	15	0	7

Summary

The presented outcome achieved during the conducted research show that vital seeds of *Galinsoga parviflora* Cav. were quite numerous in a soil seed bank. This species could, therefore, create some kind of danger for winter wheat crops. *Galinsoga parviflora* and *Chenopodium album* are taxons, which do not appear, or rarely appear in crops cultivation. Their presence in soil was a result of forecrop cultivation, which were vegetables. Ploughing applied after their harvest displaced smallflover galinoga and lamb`s quarters seeds cumulated in surface layer to deeper layers. Therefore, we noted their increased amount in the layer of 10÷20 cm. The application of intensive farming system facilitated more numerous weed growth. Weeds, however, appeared in limited number of species, what was proven by results achieved in field conditions. In case of extensive and conventional farming system, the way of cultivation influences positively not only number, but also species biodiversity of habitat [6]. With ploughless sowing and monoculture of cultivated plant, weed seeds in the soil, due to limited number of mechanical cultivations, did not have adequate emergence conditions, especially from deeper layers, therefore it was difficult to elaborate an effective programme that limits their amount.

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WPŁYW UPRAWY INTENSYWNEJ NA LICZEBNOŚĆ I ROZDZIAŁ PIONOWY NASION *Galinsoga parviflora* CAV. W ORNEJ WARSTWIE GLEBY

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Abstrakt: Stopień zanieczyszczenia gleby żywotnymi nasionami chwastów zależy od wielu czynników, takich jak: liczebność i bioróżnorodność gatunkowa siedliska chwastów bytujących w uprawie, rodzaj uprawy, sposób gospodarowania oraz poziom zasobności gleby w składniki pokarmowe i jej właściwości fizykochemicznych. Poszczególne gatunki chwastów różnią się między sobą możliwościami wytwarzania nasion. Różnice między faktyczną i potencjalną produkcją nasion są znaczne, o czym decydują warunki środowiska, w jakich odbywa się wegetacja rośliny. Na poziomie populacji chwasty mają zdolność do produkcji takiej ilości nasion, która w znacznym stopniu kompensuje zmniejszenie ich nasilenia. Zdolność ta w znaczny sposób utrudnia stopień ograniczania ich obecności w łanie rośliny uprawnej. W celu rozpoznania wpływu technologii uprawy na liczebność i rozdział pionowy, w warstwie ornej, nasion żółtlicy drobnokwiatowej przeprowadzono doświadczenia wazonowe, w których szczegółowej analizie poddano próbki glebowe pobrane w dwóch terminach z pól z uprawą pszenicy ozimej. Uzyskane wyniki wskazują, że technologia uprawy roślin w dużym stopniu wpływa na ilość nasion gatunków chwastów oraz na ich rozmieszczenie w ornej warstwie gleby.

Słowa kluczowe: glebowy bank nasion chwastów, uprawa mechaniczna gleby, nasilenie wschodów chwastów, ekologiczna walka z chwastami