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Artykuły

Proceedings of ECOpole

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Katarzyna BŁASZCZYK[1] and Teresa KRZYŚKO-ŁUPICKA[1]

MICROBIAL DIVERSITY OF SEWAGE SLUDGE[*]

RÓŻNORODNOŚĆ MIKROBIOLOGICZNA OSADÓW ŚCIEKOWYCH

Abstract: Sewage sludge may be a cluster of different groups of microorganisms, including potential pathogenic, therefore processing of sludge should be conducted in a manner that protects workers and the environment from the sanitary risks. The aim of the study was to assess quantitatively and qualitatively the microbial diversity of the municipal sewage sludge, from the food industry and from the coke after the treatment, with the addition of flocculant and/or lime. Research material consisted of samples taken directly from the wastewater treatment plant. Quantitative and qualitative assessment of mesophilic and psychrophilic bacteria, yeasts, filamentous fungi and potentially pathogenic microorganisms was performed by a culture method. Techniques for treatment sewage sludge towards their hygenisation and reduce the amount of sediment by supporting flocculants and/or liming affect the quantitative and qualitative microorganisms composition. In the studied sewage sludge dewatered using a flocculant, with the exception of sediments from the food industry, there was the highest total number of microorganisms, both meso- and psychrophilic bacteria, yeast, filamentous fungi and potentially pathogenic bacteria. However, in the sediments of the food industry increase in the number of bacteria was observed only after simultaneous application of liming. Among the isolated microorganisms, depending on the origin of the sludge there was a domination of gram negative rods, with the exception of coke sediments without a flocculant. The municipal and from the food industry sediments were dominated by fungi: *Aspergillus niger* and *Cladosporium sp.,* in coke sediments *Aspergillus amstelodami*, *Paecilomyces javanicus* and *Acremonium sp*. In these latter was also observed the greatest diversity of yeasts.

Keywords: sewage sludge, microbiological determination, microbial diversity

Sewage sludge is a complex ecosystem of microorganisms that are involved in the treatment process and are supplied to the wastewater treatment plant with flowing sludge. The microbiological composition varies according to the type of treatment and pre-treatment methods [1]. They may be a cluster of different groups of microorganisms, including pathogens and their spores [2, 3]. Sludge should be conducted in a manner that protects workers and the environment from the sanitary risks [4]. In order to reduce the amount of sludge, dewatering with chemicals called flocculants is commonly used [5]. A way to reduce an epidemiological risk is hygienisation sludge by using *eg* lime. These activities are designed to prepare an environmentally safe waste before export from a wastewater treatment plant.

Aim of the study

The aim of the study was to assess quantitatively and qualitatively the microbial diversity of the municipal sewage sludge, from the food industry and from the coke after the treatment, with the addition of flocculant and/or lime.

Material and methods

Material consisted of samples taken directly from the wastewater treatment plant:

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- dewatered sewage sludge from the food industry and municipal sewage treatment plant without/with the addition of lime: 1.5 kg/Mg d.m. of sludge and 200 kg/Mg d.m. of sludge, respectively;
- nondewatered and dewatered sludge from coke sewage treatment plants.

In order to dewater sewage sludge the cationic flocculant was added (acrylamide copolymer) in an amount of 2-3 kg/Mg d.m. The dry matter content in the nondewatered sediment was about 5%, whereas in dewatered sludge about 20%.

Quantitative and qualitative assessment of mesophilic and psychrophilic bacteria, yeasts, filamentous fungi and potentially pathogenic microorganisms was performed by culture method (Koch's decimal dilutions method) on media:

- Nutrient agar - mesophilic and psychrophilic bacteria,
- YPD - yeasts,
- Czapek - filamentous fungi,
- Hektoen, Endo - bacteria of the Enterobacteriaceae family,
- Parker - *Staphylococcus ssp.,*
- Enterococcus agar - *Streptococcus ssp.* (fecal streptococci).

Mesophilic and potentially pathogenic bacteria (Enterobacteriaceae family, *Staphylococcus* and *Streptococcus* genus) were incubated 24-48 h at 35°C, psychrophilic bacteria - 48-72 h at 20°C and yeast at a temperature of 30°C. The filamentous fungi were incubated for 7 days at 25°C. After incubation, the colonies which grew were counted and the result was given in [lg CFU/g d.m.]. Simultaneously, the bacteria were differentiated by the Gram stain and morphologically divided into groups. Filamentous fungi were identified on the basis of morphological features according to the identification keys [6-8].

Discussion of the results

In wastewater treatment plants are carried out different treatment techniques towards their hygienisation and reduce the amount of sediment. Frequently, dewatering with chemicals (flocculants) and/or liming are used.

In the case of sediments from the coke wastewater treatment plant the addition of flocculant to the raw waste affects the growth of the total number of bacteria. The municipal waste and sediment samples from the food industry were initially dewatered (with flocculant) and/or limed. Hygienisation the sludge with lime decreased the number of bacteria in municipal sediments and caused an increase in sediment samples from food industry compared to the non-limed ones (Fig. 1).

Pre-treatment of sewage also affects the quantitative and qualitative diversity of microorganisms. Dewatering of sludge with the flocculant had an impact on the numbers of meso- and psychrophilic bacteria. The presence of a flocculant in sewage sludge from coke industry caused an increase in the number of meso- and psychrophilic bacteria, yeasts and filamentous fungi compared to the nondewatered sediment (Figs. 2 and 3). On the other hand, in municipal sludge a decrease and in sediments from the food industry- an increase could be seen in the number of these groups of bacteria after liming (Fig. 2). However, the number of yeast and filamentous fungi in this sewage sludge was decreased (Fig. 3). In municipal sediments, there was no yeast, in sediments from the food industry - one type of yeast, while in the coke sludge in the presence of flocculant - three types of yeast. In the municipal and from food industry sediments dominated fungi: *Aspergillus niger* and *Cladosporium sp.*, whereas in coke wastewater - *Aspergillus amstelodami, Paecilomyces javanicus* and *Acremonium sp.*

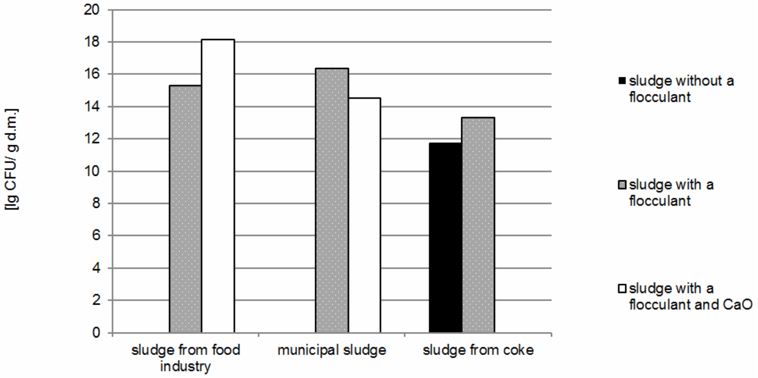

Fig. 1. The total number of bacteria [lg CFU/g d.m.] in the studied sewage sludge

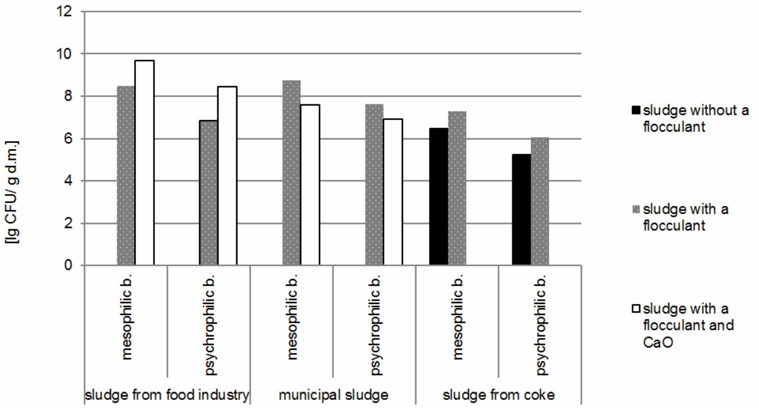

Fig. 2. The total number of mesophilic and psychrophilic bacteria [lg CFU/g d.m.] in the studied sewage sludge

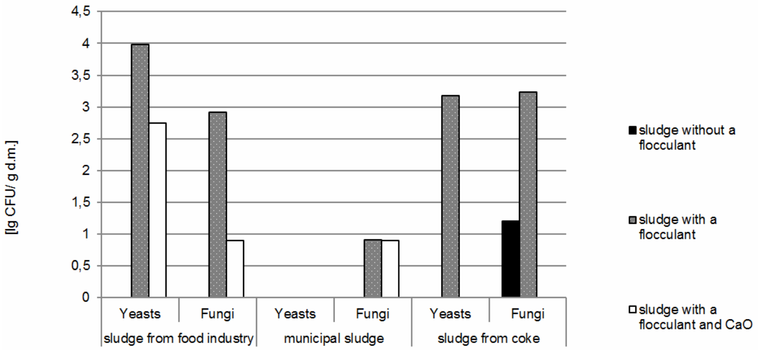

Fig. 3. The total number of yeast and filamentous fungi [lg CFU/g d.m.] in the studied sewage sludge

Among the isolated microorganisms, depending on the origin of the sludge was found the dominance of the various morphological groups of bacteria (Fig. 4). The highest number in the studied sediments were gramnegative rods, with the exception of coke sludge without flocculant (dominated grampositive rod-shaped cocci) (Fig. 4).

In the coke sludge with the presence of a flocculant an increase in the number of potentially pathogenic bacteria was observed compared to the raw one. In samples of sewage sludge with a flocculant although the liming an increase in the number of potentially pathogenic bacteria was also observed (Fig. 5).

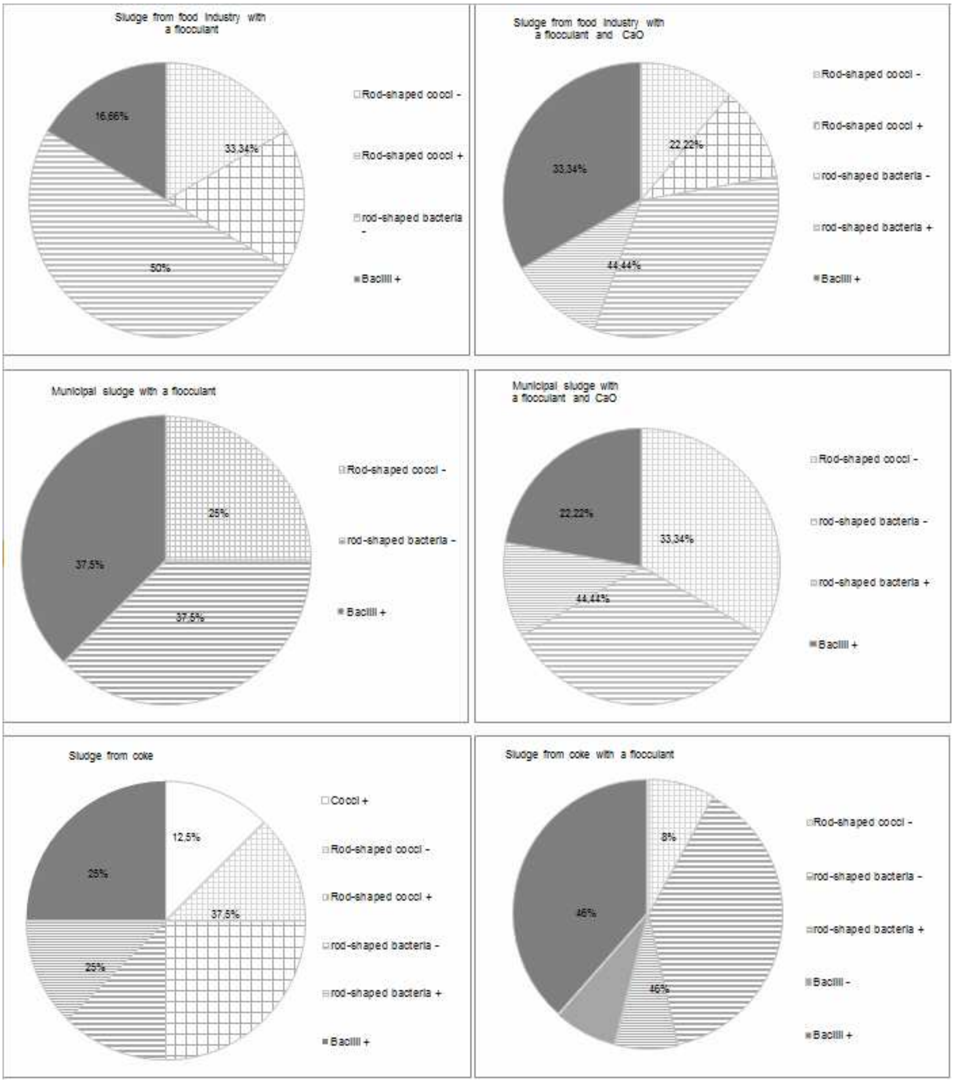

Fig. 4. The composition of the bacterial population [%] in the studied sewage sludge

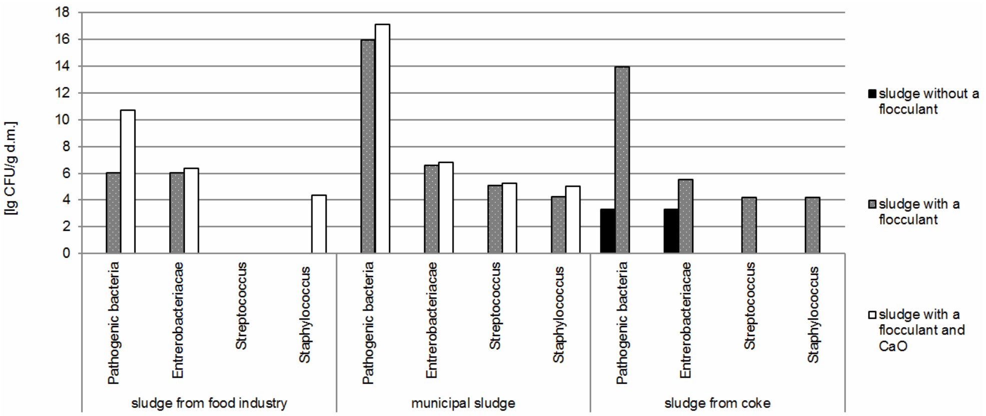

Fig. 5. The total number of potentially pathogenic bacteria [lg CFU/g d.m.] in the studied sewage sludge

Conclusions

Techniques for sewage sludge treatment towards their hygienisation and reduce the amount of sediment supporting by flocculants and/or liming affect the quantitative and qualitative composition of microorganisms. In the dewatered sludge with a flocculant, with the exception of sediments from the food industry, there was the highest total number of microorganisms, both meso- and psychrophilic bacteria, yeast, filamentous fungi and potentially pathogenic bacteria. However, in the sediments from food industry an increase in the number of bacteria was observed after simultaneous application of liming. Among the isolated microorganisms, depending on the origin of the sludge was found the dominance of gramnegative rods, with the exception of coke sludge without a flocculant (dominated grampositive rod-shaped cocci).

In the municipal and from food industry sewage dominated fungi: *Aspergillus niger* and *Cladosporium sp.* and in coke sediments - *Aspergillus amstelodami, Paecilomyces javanicus* and *Acremonium sp.* In these latter the greatest variety of yeasts was also observed.

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RÓŻNORODNOŚĆ MIKROBIOLOGICZNA OSADÓW ŚCIEKOWYCH

Samodzielna Katedra Biotechnologii i Biologii Molekularnej, Uniwersytet Opolski

Abstrakt: Osady ściekowe mogą być skupiskiem różnych grup mikroorganizmów, w tym potencjalnie chorobotwórczych, dlatego ich przeróbka powinna być prowadzona w sposób chroniący pracowników i środowisko przed zagrożeniem sanitarnym. Celem badań była mikrobiologiczna ocena ilościowa i jakościowa osadów ściekowych komunalnych i pochodzących z przemysłu spożywczego oraz koksowni po przeróbce z dodatkiem flokulantu i/lub wapna palonego. Materiał badawczy stanowiły próbki pobrane bezpośrednio z oczyszczalni ścieków. Ocenę ilościową i jakościową bakterii mezofilnych i psychrofilnych, drożdży, grzybów strzępkowych oraz mikroorganizmów potencjalnie chorobotwórczych przeprowadzono metodą hodowlaną. Techniki przeróbki osadów ściekowych w kierunku ich higienizacji oraz zmniejszenia ilości osadów poprzez wspomaganie flokulantami i/lub wapnowanie miały wpływ na skład ilościowy i jakościowy mikroorganizmów. W badanych osadach ściekowych odwadnianych flokulantem, z wyjątkiem osadów z przemysłu spożywczego, występowała najwyższa ogólna liczba mikroorganizmów, zarówno bakterii mezo-, jak i psychrofilnych, drożdży i grzybów strzępkowych oraz bakterii potencjalnie chorobotwórczych. Natomiast w osadach przemysłu spożywczego wzrost liczebności bakterii obserwowano dopiero po równoczesnym zastosowaniu wapnowania. Wśród wyizolowanych mikroorganizmów, w zależności od pochodzenia osadu ściekowego, stwierdzono dominację pałeczek gram-ujemnych z wyjątkiem osadów koksowniczych bez flokulantu. W osadach komunalnych i pochodzenia spożywczego dominowały grzyby: *Aspergillus niger* oraz *Cladosporium sp.*, a w osadach koksowniczych *Aspergillus amstelodami*, *Paecilomyces javanicus* i *Acremonium* sp. W tych ostatnich obserwowano również największą różnorodność drożdży.

Słowa kluczowe: osad ściekowy, ocena mikrobiologiczna, różnorodność mikrobiologiczna

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Jolanta BOHDZIEWICZ[1], Gabriela KAMIŃSKA[1] and Sara PESZKE[1]

ADVANCED TREATMENT OF MUNICIPAL WASTEWATER IN NANOFILTRATION. EFFECT OF MEMBRANES AND OPERATING PARAMETERS ON PERFORMANCE*

POGŁĘBIONE OCZYSZCZANIE ŚCIEKÓW W NANOFILTRACJI. WPŁYW MEMBRANY I WARUNKÓW PROWADZENIA PROCESU NA JEGO EFEKTYWNOŚĆ

Abstract: In recent years, increasing attention is focused on the presence of endocrine disrupting chemicals (EDCs) in the aquatic environment that degrade its quality. These substances and derivatives of their incomplete oxidation, even at low concentrations discharge with effluent streams into natural reservoirs, strongly degrade water quality and pose a serious threat to aquatic ecosystems. Among EDCs, which presence even in trace amount is adverse for biological equilibrium in aquatic environment to which belong inter alia xenoestrogens (*ie* bisphenol A). The aim of this study was to polish wastewater constituting effluent from municipal WWTP in the nanofiltration process. Two types of membranes were used, differ in molecular weight cut-off and material (cellulose acetate, polyethersulphone). The nanofiltration process was carried out in pressure installation enabling conduction of the process in the dead-end mode on membrane area of 0.44 m^2. Polishing effectiveness was evaluated on the base of the reduction degree of typical pollution indicators (COD, TOC, phenolic compounds, total nitrogen) and bisphenol A. Obtained results show that removal efficiency of phenolic compounds in case of applied membranes was comparable. Overall it was found that membranes characterized of diversified hydraulic permeability and resistance to fouling, what constitute important factor during exploitation of membrane processes.

Keywords: EDCs, nanofiltration, wastewater treatment

Pollutions incorporated with effluent streams from *wastewater treatment plant* (WWTP) pose serious threat for purity of surface waters. It was proved many times, that biologically treated municipal wastewater did not fulfil required standards of purity [1, 2]. Particularly noxious are streams coming from municipal WWTP, because they are also often receiver of wastewaters coming from industrial plants, and they do not possess technology suitable for degradation of highly toxic compounds. Therefore many groups of micropollutants get into environment, among which particularly dangerous are heavy metals, polycyclic aromatic hydrocarbons, polycyclic biphenyls and compounds with *estrogenic biologic activity* (EDCs).

The aim of this work was polishing of real wastewater coming from effluent from municipal wastewater treatment plant in nanofiltration process. Studies determined influence of membrane polymer, pH of wastewater and operating parameters (transmembrane pressure) on effectiveness of the process.

Materials and methods

The object of study was wastewater constituting effluent from municipal wastewater treatment plant. The physico-chemical characteristics of wastewater introduced to membrane installation was shown in Table 1.

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Table 1

Characteristics of wastewater

Parameter	Value
COD [mg O_2/dm^3]	160
N-NH_4 [mg N-NH_4/dm^3]	1.1
N-NO_3 [mg N-NO_3/dm^3]	2.49
N_{Tot} [mg N/dm^3]	6.6
P-PO_4 [mg P-PO_4/dm^3]	0.4
Phenolic index [mg/dm^3]	0.29
TC [mg/dm^3]	80.7
TOC [mg/dm^3]	35.57
IC [mg/dm^3]	45.13
pH	7.2

The nanofiltration process was carried out in membrane reactor (volume 0.4 dm^3, membrane filtration area 0.44 m^2), working in dead-end mode at the *transmembrane pressure* (TMP) 2 MPa. The experiments were conducted using two kinds of flat sheet membranes, varied in polymer and *molecular weight cut-off* (MWCO). Prior to the first application, the membranes were conditioned by means of filtration of demineralized water. The characteristic of membranes was presented in Table 2.

Table 2

Characteristic of nanofiltration membranes

	Manufacturer	
	Microdyn Nadir	**GE Osmonics**
Symbol	NP010	CA
Polymer	Polyethersulfone	Acetate cellulose
Molecular weight cut-off	1000	150-300
Retention coefficient NaCl [%][1]	35	74
Retention coefficient $MgSO_4$ [%][1]	64	96
Contact angle (θ)	54	54
Zeta potential [mV]	pH 4 = –2; pH 7 = –5; pH 10 = –8[2]	pH 4 = +1; pH 7 = –7; pH 9 = –9[3]
Isoelectric point at pH	3.5[2]	4.4[3]

[1] Concentration of NaCl and $MgSO_4$ solution 1 g/dm^3, TMP = 2 MPa

[2] According to data [3]

[3] According to data [4]

Temperature of wastewater equalled 15±2°C and pH was adjusted using 1M HCl and NaOH solutions. The effectiveness of polishing was determined on the basis of typical parameters (COD, N_{Tot}, N-NH_4, N-NO_3, TOC, IC, Cl^-) characterizing feed and permeates. Additionally phenolic index to evaluation of impact of other factors on process efficiency was used. It is a number defining the concentration of different phenol compounds in sample. Considering that municipal wastewater biodegrade during treatment on WWTP, it is obvious that compounds consisting in wastewater submit various conversions leading to forming both their less toxic metabolites and more durable derivatives. Determination of phenolic index include the whole amount of phenolic micropollutants such as phenol, alkylophenols (bisphenol A, nonylphenol), nitrophenols, chlorophenols and another derivatives, which resultant through fragmentary degradation or transformation. After each filtration of wastewater, demineralized water was refiltrated, in order to evaluate relative permeate (α_p) and demineralized water (α_w) fluxes. Measurement data have been calculated according to equations in Table 3.

Table 3

Equations to evaluate transport and separation properties of membranes

Property	Parameter	Unit	Equation
Transport	Permeate flux J_v (J_w - demineralized water)	[dm^3/m^2·s]	$J_v(J_w) = \frac{V}{F \cdot t}$
	Relative permeate flux α_p	-	$\alpha_p = \frac{J_v}{J_w}$
	Relative demineralized water α_w	-	$\alpha_w = \frac{J_{wv}}{J_w}$
Separation	Retention coefficient R	[%]	$R = \left(1 - \frac{C_p}{C_n}\right) \cdot 100\%$

V - volume of permeate [dm^3], F - membrane area [m^2], t - time [s], C_p - concentration in permeate [mg/dm^3], C_n - concentration in feed [mg/dm^3], J_{wp} - demineralized water flux after filtration of wastewater [dm^3/m^2·s].

Results and discussion

Transport characteristic of membranes

In Figure 1 was shown demineralized water flux (J_w) and permeate flux (J_v) depending on time, assigned during filtration of wastewater at TMP 2 MPa.

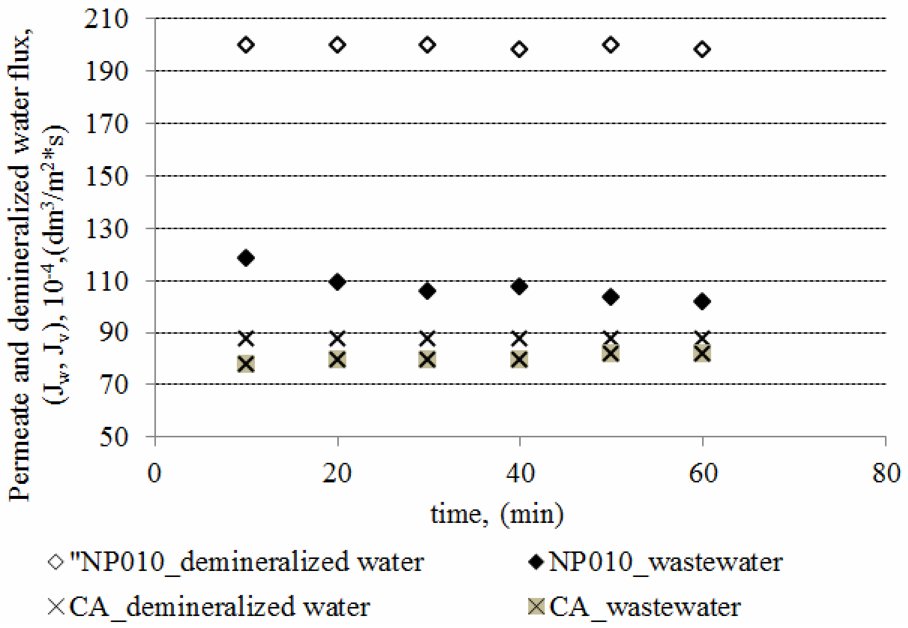

Fig. 1. Fluxes (J_v, J_w) versus time for TMP = 2 MPa

Presented magnitudes are mean value from 10 measurements. Membrane prepared from acetate cellulose (CA) characterized less hydraulic capacity in comparison with membrane NP010, what is proved less permeate and demineralized water flux. This effect could be explained by more extended structure of NP010, which enable more yield in comparison with closed structure of CA. In case of filtration of wastewater permeate flux was only lower by about 10% than demineralized water, what indicated on high fouling resistance of this membrane. For membrane NP010 maximum demineralized water equalled 0.02 $dm^3/m^2 \cdot s$, whereas maximum permeate flux was almost about half lower. Decrease of permeate flux for demineralized water flux of NP010 indicated on fouling. In order to precise description impact of fouling to transport properties of membrane relative permeate flux (α_p) were calculated. Additional intensity of fouling was evaluated on the basis of value of relative demineralized water flux (α_w), which is lower with increasing impact of fouling on membrane hydraulic performance [12].

Coefficient α_p and α_w were presented in Table 4. These values confirmed previous observation, it could be noticed that, membrane CA characterized high fouling resistance and pores of membrane NP010 gave in to substantial locking. Therefore it is obvious, that for membrane CA was recovered 100% of the initial capacity ($\alpha_p = 1$), and for membrane only NP010 65% ($\alpha_p = 0.65$).

Table 4

Relative flux α_p and α_w for membrane after polishing at TMP = 2 MPa

Membrane	**Relative permeate flux (α_p)**	**Relative demineralized water flux (α_w)**
NP010	0.27	0.65
AC	0.91	1

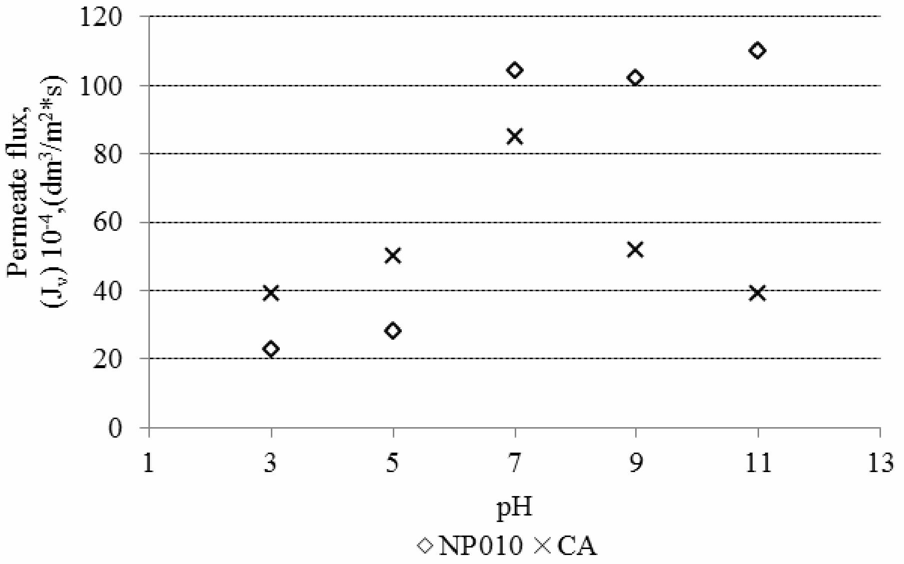

Fig. 2. Permeate fluxes versus pH of wastewater

It was also found that permeate flux was dependant on pH of wastewater (Fig. 2). Hydraulic permeability of both membranes was the lowest during filtration of acid wastewater (pH 3 and 5). This effect could be explained by significant impact of filtrated medium pH on zeta potential of membrane. The literature data [3] indicated that at acid reaction, membrane NP010 had positive charge or weak negative charge (Table 2) which was insufficient to repulse negative charged molecules of micropollutants occurring in wastewater. It caused their adsorption on membrane surface and in pores, leading to partial membrane locking and decrease of permeability. Similar mechanism was also reason of low permeate flux of CA membrane at acid wastewater. This theory was also confirmed in study, in which microscopic images proved that acid reaction of industrial wastewater (pH = 3) caused membrane locking and forming of filter cake on NP010 membrane. Whereas increase of permeate flux at pH = 7 and higher was caused by two phenomena. First was connected with increase of membrane zeta potential in alkaline reaction, leading to increase of electrostatic repulsion between dissociated sulphone groups on membrane surface and dissociated ingredients in wastewater. Molecules of micropollutants did not adsorb on membrane surface but was rejected in retentate. Second, in alkaline pH sulphone groups on membrane surface were dissociated in high rate and repulse mutually, acting membrane structure more open and more permeable.

The effectiveness of polishing wastewater

The effectiveness of polishing of wastewater in nanofiltration process depended on type of membrane (Fig. 3).

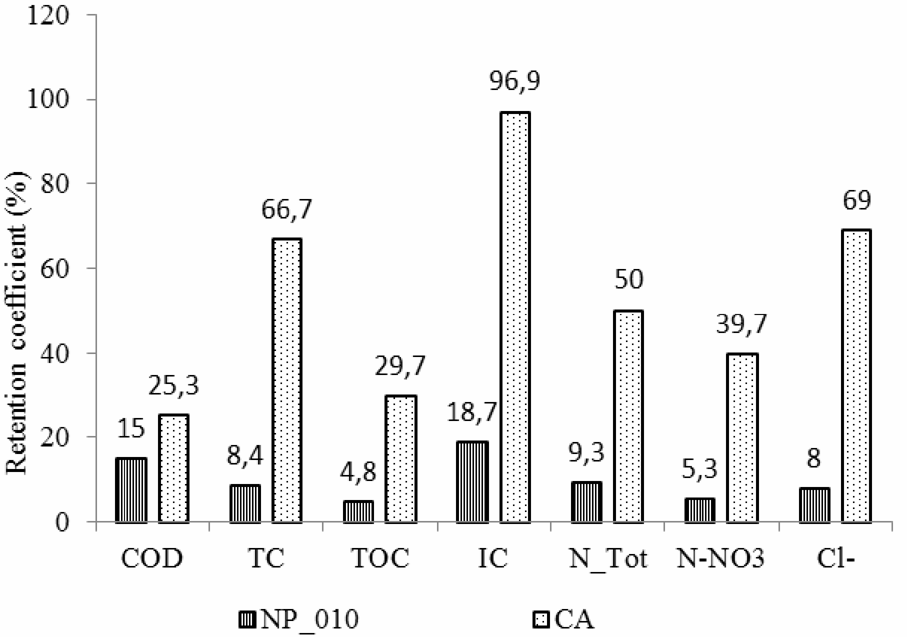

Fig. 3. Impact of membrane on retention coefficient

The removal of organic compounds expressed by COD and TOC were respectively about 40 and 84% higher on CA membrane than NP010. Concentration of total nitrogen, chlorine and inorganic compounds in permeates after filtration on CA membrane was lower in comparison with results for NP010. Low retention of pollutions on NP010 followed mainly from more open structure of this membrane in comparison with CA membrane. Molecular weight cut-off of NP010 was 10 times higher from CA membrane, it means that in case of some non-ionic pollutants, separation mechanism based on sieving effect.

Conclusions

- Considering the efficiency of the process, the susceptibility to fouling and especially quality of obtained permeates, the better membrane was CA.
- Permeate flux obtained at alkaline reaction of wastewater was three times higher in comparison with acid wastewater. It was connected with high rate of dissociation of sulphone groups, that mutually electrostatic repulse and make membrane more open and permeable.
- Highest rate of polishing was obtained for permeate after filtration on CA membrane.

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POGŁĘBIONE OCZYSZCZANIE ŚCIEKÓW W NANOFILTRACJI. WPŁYW MEMBRANY I WARUNKÓW PROWADZENIA PROCESU NA JEGO EFEKTYWNOŚĆ

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Abstrakt: Celem niniejszej pracy było pogłębione oczyszczenie ścieków rzeczywistych stanowiących odpływ z komunalnej oczyszczalni ścieków w procesie nanofiltracji. Zastosowane membrany nanofiltracyjne różniły się graniczną masą molową i materiałem, z jakiego je wykonano (octan celulozy i polieterosulfon). Proces filtracji membranowej odbywał się w ciśnieniowym urządzeniu przystosowanym do prowadzenia procesu w układzie filtracji jednokierunkowej (dead-end), na membranie o powierzchni czynnej 0,44 m^2. Efektywność procesu doczyszczania została określona na podstawie stopnia obniżenia bisfenolu A i typowych wskaźników zanieczyszczeń (COD, TOC, IC (węgiel nieorganiczny), $N_{og.}$). Uzyskane wyniki wskazują, że stopień usuwania mikrozanieczyszczeń na badanych membranach był porównywalny. Badane membrany nanofiltracyjne charakteryzowały się zróżnicowaną wydajnością hydrauliczną i odpornością na foulingu, co jest istotne z punktu widzenia eksploatacji procesów.

Słowa kluczowe: EDCs, nanofiltracja, oczyszczanie ścieków

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KINETICS OF BUTYL ACRYLATE BIODEGRADATION BY SELECTED STRAIN OF MICROORGANISMS[*]

KINETYKA BIODEGRADACJI AKRYLANU BUTYLU PRZEZ WYSELEKCJONOWANY SZCZEP MIKROORGANIZMÓW

Abstract: The subject of research in the present study was biodegradation of butyl acrylate. Tests of microbiological degradation of this compound by selected environmental and laboratory strains were conducted. The *Pseudomonas fluorescens* PCM 2123 strain utilized the growth substrate most intensively and was selected for further research. Optimal growth conditions and toxic dose of the utilized substrate were determined for the selected strain. The research into kinetics of butyl acrylate biodegradation by *Pseudomonas fluorescens* PCM 2123 bacteria included a series of experiments conducted for different initial concentrations of acrylate in a batch reactor. The influence of initial substrate concentration on the specific growth rate was described by Haldan's equation. Constants of the equation were estimated on the basis of experimental data.

Keywords: biodegradation, batch culture, growth kinetic

The rapid development of civilization in the recent centuries caused a significant increase in the amount of the produced waste exceeding the self-purifying possibility of the environment. The development of methods of water treatment and waste-gases purification to eliminate pollution at its source, is the protection against the unfavourable for the environment phenomenon of waste accumulation. Methods based on the processes of biological decomposition of waste play a great role in such methods.

The processes of biodegradation are very common in the natural environment. Creating conditions different from natural ones aims at accelerating the process. A great advantage of biological methods is the fact that they do not shift pollution to another phase, which is the case in absorption and adsorption processes, but degrade it completely at relatively low investment and operating costs of the process.

The subject of analysis in the present study is the process of biological degradation of butyl acrylate. Acrylates - acrylate acids esters - are compounds widely used in industry. About 80% of the produced acrylate acid is converted to esters. 3.3 million Mg of acrylate acid esters [1] were produced in 2004, whereas in 2009 their production was 1.28 million Mg in China alone, out of which methyl and butyl acrylates made 320 000 Mg. A 4.3% increase in the consumption of acrylate acid esters is estimated in the years 2010-2015 [2].

Butyl acrylate is a colourless liquid having an unpleasant pungent odour. It dissolves in ethanol, diethyl ether and acetone. Its solubility in water at the temperature of 20ºC is 0.14 % vol. [3]. Butyl acrylate is used to obtain various types of polymers, to produce paints, lacquers, inks, glues as well as in leather and paper industries and in stomatology [1, 4]. The main ways in which butyl acrylate penetrates the body are breathing and digestive

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systems and skin. Acrylate vapours can irritate respiratory tracts, eyes and mucosa of nose. When the concentration is high they can cause narcosis and edema of lungs. Butyl acrylate, due to its irritating pungent odour, can cause headaches, dysmnesia, hyperexcitability, arterial pulse drop, cholesterol growth and contact allergic skin inflammation among people exposed to work with this compound (among others dentists, printing-houses workers, chemical industry workers, workers in contact with glues [5, 6]. Accumulation of butyl acrylate has not been found in soil or living organisms according to literature reports. After penetrating surface water part of the substance is degraded by microorganisms and part is released into the air. According to US EPA classification butyl acrylate was classified in the group of easily biodegradable and moderately toxic substances [7].

Although acrylates are relatively easily biodegradable and do not cause great threat to human life and health, because of its characteristic unpleasant odour cause a problem to the people who live in the area where industrial plants producing acrylate acid esters or using such compounds during production are located. At the same time they are a problem to industrial plants workers employed to produce acrylates or process them and being subject to a long-lasting contact with these compounds. Increasing the comfort of work in the production processes using substances with pungent unpleasant odour involves applying proper ventilation systems, which carry away the air containing pollutants. The question is what to do with the air containing the undesirable substances whose penetration of the air makes the quality of living of the neighbouring people lower? Currently a bill regulating the emission of noxious odours is being elaborated. As a result, the regulations of quality assessment of air as regards the contents of odorous substances and standards will be introduced whose not obeying will result in a variety of sanctions [8].

Shortly, every plant (also those whose production deals with acrylates) will be forced to limit the emission of noxious substances/odours by modernizing the production process or introducing innovative ways of removal of compounds which are noxious from ventilated air or waste gases. Taking the above into consideration, it seems purposeful to work out efficient ways of biopurification of big streams of industrial gases polluted with substances noxious for the environment. Butyl acrylate is undoubtedly one of them.

The choice of microorganisms for which butyl acrylate will be the growth substrate and the determination of the kinetics of this growth must be the first stage of research.

Materials and methods

Microorganism

No study was found in literature which would show that microorganisms degrade butyl acrylate effectively. The aim of this stage of the study was the selection of a microorganism for which the degraded compound would be the growth substrate. The tests were conducted on two strains of microorganisms isolated from the soil samples collected on the site of a Chemical Company Dwory S.A. in Oświęcim, Poland and two laboratory strains. The environmental strains, as a result of biochemical tests, were identified as belonging to *Pseudomonas putida* species. The following laboratory strains underwent tests: *Pseudomonas fluorescens* PCM 2123 from the collection of Institute of Immunology and Experimental Therapy in Wroclaw, Poland and a strain from the *Pseudomonas* genus (showed 97% homology with *Pseudomonas putida* and 97% with *Pseudomonas stutzeri* from 16S r DNA analysis), coming from VTT Culture Collection (Finland). The research procedure whose aim was to appoint the strain which uses the degraded substrate most effectively was presented in the earlier study [9]. Among the tested microorganisms the *Pseudomonas fluorescens* PCM 2123 strain used butyl acrylate as the only source of carbon and energy most effectively and was appointed for further tests. The activity of the chosen strain was tested at changing in a vast range of pH values, temperature and the concentration of butyl acrylate in the solution.

They made it possible to determine the most favourable for the growth of microorganisms conditions (pH = 7, T = 303 K) and the toxic dose of the utilized pollution. Testing toxicity confirmed that the utilised compound may be degraded by *Pseudomonas fluorescens* PCM 2123 strain even in very big doses (up to 10 000 ppm).

Preparation of inoculum

Pure strain of *Pseudomonas fluorescens* PCM 2123 bacteria chosen to biodegrade butyl acrylate, stored in a lyophilized form, was activated during a 24-hour culture on the nutrient agar foundation (King B) - on Petri dishes. Next the bacteria which grew on the dishes are carried to test tubes (Falcon type) containing 5 cm^3 of LB medium. After 24 hours the suspension was carried to hermetic flasks filled with 10 cm^3 of mineral salts solution. Butyl acrylate (3 mm^3), an organic compound introduced into the solution, was the source of carbon and energy for the culture. The composition of the mineral medium used for cultivation was (g/dm^3 distilled water): 0.067 $CaCl_2x2H_2O$, 0.2 EDTA-Na, 0.58 $MgSO_4x7H_2O$, 1 $(NH_4)_2SO_4$, 3.4 KH_2PO_4, 4.5 $Na_2HPO_4x12H_2O$ and 1 ml trace elements and vitamin solution. After another 24 h, the suspension was carried to a hermetic bottle replenished with mineral medium to 100 cm^3, and 30 mm^3 of butyl acrylate was added. In subsequent days, the absorbance was measured, and 52 mm^3 of substrate was added every day. Cultures were renovated every week. The adaptation of PCM 2123 to butyl acrylate lasted ~5 weeks.

Batch experiments

Experiments were conducted in Biostat B fermenter (Sartorius, USA) with working volume of 2 dm^3. The tests were conducted at 303.2 K, pH = 7, and stirred speed 300 rpm. A constant value of pH was maintained by feeding a 10% solution of KOH or KH_2PO_4. The following procedure was performed before every experiment. The sterile biostat was filled with mineral medium and centrifuged and washed out with deionized water cells. Butyl acrylate grown bacteria were inoculated into the biostat in the amount which enables the start of each culture at a similar concentration of cells in the solution (0.2 absorbance at λ = 550 nm). After the process parameters had been stabilized, a proper doze of liquid butyl acrylate (S_{L0}), as the only source of carbon and energy for bacteria, was introduced into the solution. During the experiments, at regular intervals (15 min), biomass, growth substrate and intermediate products (acrylic acid and butanol) concentrations were determined.

The experiments were performed for the initial concentration of butyl acrylate changed within the range of 5-50 mg/dm^3 by 5 mg/dm^3.

Analytical methods

The concentration of biomass was determined by measuring the optical density (OD) of the fluid culture ($\lambda = 550$ nm). Next the suspension absorbance was converted into grams of dry mass of microorganisms according to the calibration which was performed earlier.

Butyl acrylate and intermediate products concentrations were determined by gas chromatography using Varian 3800 (USA) chromatograph with a 30-m length CP-wax 52CB column and a flame ionization detector (FID). Helium was used as the carrier gas.

Every experimental point was repeated three times in identical conditions, and the values were averaged to get the true experimental value.

Results

Figure 1 shows, as an example, the course of changes in concentration of the analyzed components during one individual experiment.

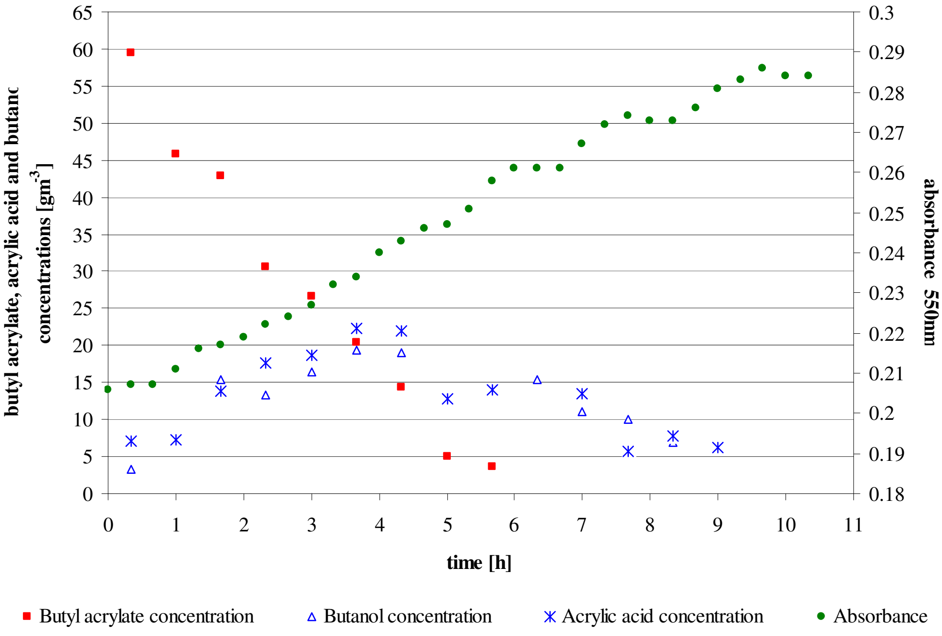

Fig. 1. Variation of butyl acrylate, acrylic acid and butanol concentrations as well as biomass for aerobic biodegradation of butyl acrylate in a batch laboratory reactor (for $S_0 = 50$ gm^{-3})

For the exponential growth phase, where the specific growth rate of biomass remains constant, the growth rate of biomass is first order and can be defined as:

$$\frac{dX}{dt} = \mu_{net} X \qquad (1)$$

Integration of Equation (1) with boundary conditions $X = X_0$ at $t = 0$ yields:

$$\ln X = \mu_{net} \cdot t + \ln X_0 \tag{2}$$

For every experimental point, that is, for every initial dose of substrate, the graph representing the dependence ln$X = f(t)$ is expected to take the form of a straight line whose slope is μ_{net}.

A data base making it possible to draw up a diagram of the $\mu_{net} = f(S_0)$ dependence and the choice of the form and estimation of kinetic equation constants can be obtained by changing, in the following experiments, the initial concentration of the growth substrate. The diagram of the $\mu_{net} = f(S_0)$ dependence shown in Figure 2 indicates the inhibition of biomass growth by increasing concentration of the substrate. Thus, the Haldane model was used to describe the growth kinetics of *Pseudomonas fluorescens* PCM 2123 strain on butyl acrylate and kinetic equation parameters were estimated using last-square error method with the help of NLREG - nonlinear regression analysis program - yielding the dependence:

$$\mu = \frac{0{,}1515 \cdot S}{8{,}5591 + S + \dfrac{S^2}{16{,}2144}} \tag{3}$$

Equation (3) with the mean percentage error not exceeding 5% approximates the experimental data.

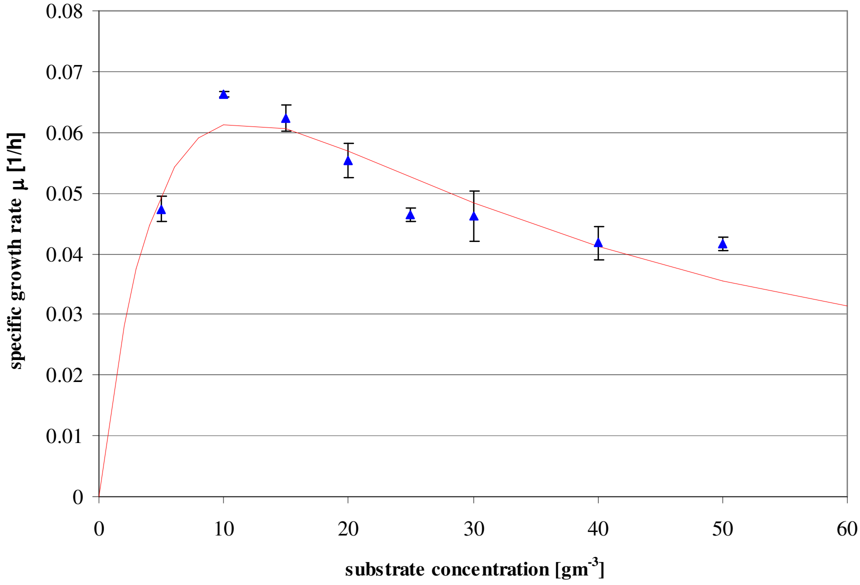

Fig. 2. Effect of initial butyl acrylate concentration on specific growth rate

Conclusions

A bacteria strain using effectively the utilized pollution as a growth substrate was selected. Optimal for the selected strain growth conditions and its kinetics were determined.

The Haldane model, in the form presented in equation (3), was used to describe the dependence of the specific growth rate of *Pseudomonas fluorescens* PCM 2123 strain on the initial concentrations of butyl acrylate. Research into the process of purifying air polluted with butyl acrylate in biotrickling filter using *Pseudomonas fluorescens* PCM2123 will be the next step. Kinetic data determined in the presented work will be used in the mathematical model of the reactor.

Symbols

μ_{net} - specific growth rate [h^{-1}]
S_0 - initial substrate concentration [g m^{-3}]
t - time [h]
X - biomass concentration [g m^{-3}]

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KINETYKA BIODEGRADACJI AKRYLANU BUTYLU PRZEZ WYSELEKCJONOWANY SZCZEP MIKROORGANIZMÓW

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Abstrakt: Celem prezentowanej pracy było wyselekcjonowanie szczepu bakterii, który efektywnie mineralizuje akrylan butylu, oraz określenie kinetyki tego procesu. Testy porównawcze przeprowadzono dla czterech gram-ujemnych szczepów bakterii. Szczep EC3_2001 był wyizolowany z próbek gleby, pobranych w Oświęcimiu z terenu firmy chemicznej Synthos S.A., szczep *Pseudomonas fluorescens* PCM 2123 pochodził z Polskiej Kolekcji Mikroorganizmów (Wrocław), natomiast szczepy *Pseudomonas putida* mt-2 i szczep E-93486 zakupiono w Finlandii z Kolekcji VTT. Wszystkie testowane szczepy posiadały zdolność do wykorzystania akrylanu butylu jako jedynego źródła węgla i energii w procesie aerobowym. Głównym kryterium selekcji mikroorganizmów była szybkość produkcji biomasy, a tym samym konwersji substratu. Badania prowadzono w kolbach, zawierających 300 cm^3 roztworu soli mineralnych i zaadaptowany do biodegradacji akrylanu butylu szczep bakterii. Do kolb co 24 godziny dodawano określone dawki substratu. Kolby były termostatowane (30°C) i mieszane (130 rpm). Szczep *Pseudomonas fluorescens* PCM 2123 najefektywniej degradował akrylan butylu, zatem dla tego szczepu wyznaczono kinetykę biodegradacji. Badania kinetyczne prowadzono w bioreaktorze Biostat B firmy Sartorius, w stałych i optymalnych dla wybranych bakterii warunkach (temperatura, pH, natlenienie, skład pożywki). Podczas pojedynczego eksperymentu wyznaczano krzywe wzrostu mikroorganizmów oraz konsumpcji substratu. Zgromadzona baza danych eksperymentalnych umożliwiła wybór postaci równania kinetycznego (model Haldana) oraz estymację parametrów tego równania.

Słowa kluczowe: akrylan butylu, biodegradacja, hodowla okresowa

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MEASUREMENTS OF ^{222}Rn ACTIVITY IN THE BUILDINGS OF THE OPOLE UNIVERSITY*

POMIARY AKTYWNOŚCI ^{222}Rn W BUDYNKACH UNIWERSYTETU OPOLSKIEGO

Abstract: The aims of this study were the analysis of the risk arising from the activity of ^{222}Rn in the buildings of the Opole University. The ^{222}Rn activity measurements were made using a portable spectrometer Alphaguard in five buildings of Opole University. The study was conducted at different levels/floors of the buildings (building on the Kominka street, the Main Building lobby, the Department of Physics (Wing of Main Building) the *Collegium Biotechnologicum* and *Collegium Chemicum*), and in classrooms in *Collegium Biotechnologicum*. The obtained results showed no potential health risk from radon contamination. However it was observed that humans staying on the lower floors are more vulnerable to radiation associated with ^{222}Rn decays, due to the physical properties of this element.

Keywords: ^{222}Rn, activity concentration, spectrometer, Alphaguard

Natural radionuclides gets into the human body mainly by ingestion, like uranium, thorium and its decays products as well as potassium ^{40}K. Radon and thoron is transported into body through the respiratory system [1].

Radon (^{222}Rn) is a colorless, odorless, alpha radioactive noble gas produced during decays of ^{226}Ra [2]. It is the first gaseous element in ^{238}U decay series and because radium occurs ubiquitously in rocks, soils and sediments with broad range of concentrations it can be found almost everywhere [3, 4].

^{222}Rn easily diffuse into air and gets into water solution during water-rock interactions with bedrock that contains ^{226}Ra [5].

The decay of radon is the largest source of ionizing radiation on Earth [6, 7]. According to the Polish Central Statistical Office radon accounted 36.4% of the annual effective dose of ionizing radiation per inhabitant in Poland in 2012 [8]. The activity concentration of radon and their progeny in buildings are largely influenced by factors such as topography, type of house construction, building materials. It penetrates into building from the soil through the cracks in the walls and floors and also with water (when the water is aerated) and natural gas [9, 10]. Even small pressure differences between the soil under the foundation and the interior space causes that the building draws radon from the ground [11].

The ^{222}Rn and its decay products are one of the major causes of lung cancer [12]. In the U.S. it is the second cause of this disease, after smoking cigarettes [13]. Radon itself is not a serious threat, however decay products such as polonium, bismuth and lead easily create a radioactive aerosol depositing on the mucous membranes of the respiratory system creating significant threat to the health [14]. The WHO recommends that the ^{222}Rn activity

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in closed rooms should not exceed 200 Bq/m^3 [15] while The International Commission on Radiological Protection gives two reference values (for dwellings), 400 Bq/m^3 for houses already built and 200 Bq/m^3 for newly built homes [16].

The aims of this study were the analysis of the risk arising from the activity of ^{222}Rn in the buildings of the Opole University.

Material and methods

Measurements were performed at five buildings at the Opole University. These objects were on the Kominka street (K), the Main Building lobby (M), the Department of Physics (Wing of Main Building) (F) and, newer than the former, buildings of the *Collegium Biotechnologicum* (CB) and *Collegium Chemicum* (CH). The study was conducted at different floors and levels of the building and in an enclosed rooms in the *Collegium Biotechnologicum* that were located on the floor -1 (I), 1 (II), 3 (III). The analysis was carried out in the morning before lectures and in the afternoon, after didactical activities.

Determination of radon activity concentrations in air were performed using the portable spectrometer Alphaguard, located at about 1.5 m above the ground level.

Results and discussion

The averaged results of measurements in each building are shown in Figure 1. The highest values were recorded in the building at Kominka street, which is a small building equipped with limited air exchange system. Buildings CB, M and CH were characterized by radon concentration at similar low levels. The comparable measurements results in these facilities were due to the efficient ventilation system in buildings.

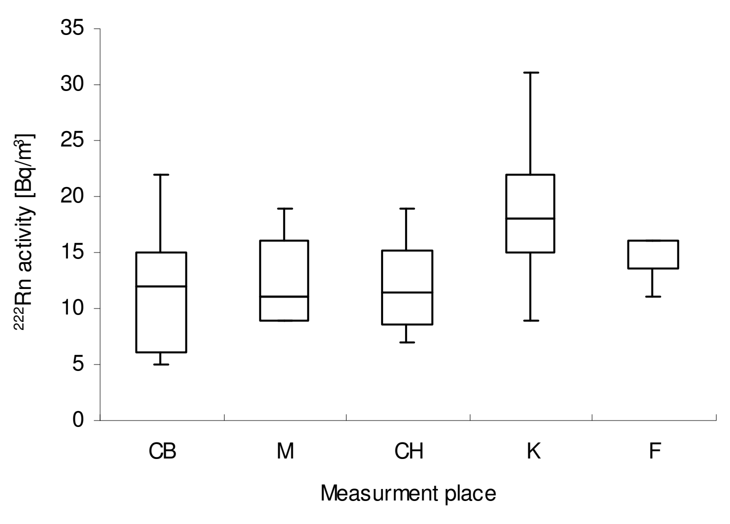

Fig. 1. The concentration of ^{222}Rn in the particular measurement places

The results of measurements carried out in enclosed rooms are shown in Figure 2. The relatively high activity concentrations of ^{222}Rn in the air were recorded on the lower floors, as a result of radon specific density bigger than that of air. At -1st floor these values ranged between 18 and 35 Bq/m^3 with the mean of 27 Bq/m^3, while at 3rd floor the mean activity concentration of ^{222}Rn in the air was 21 Bq/m^3.

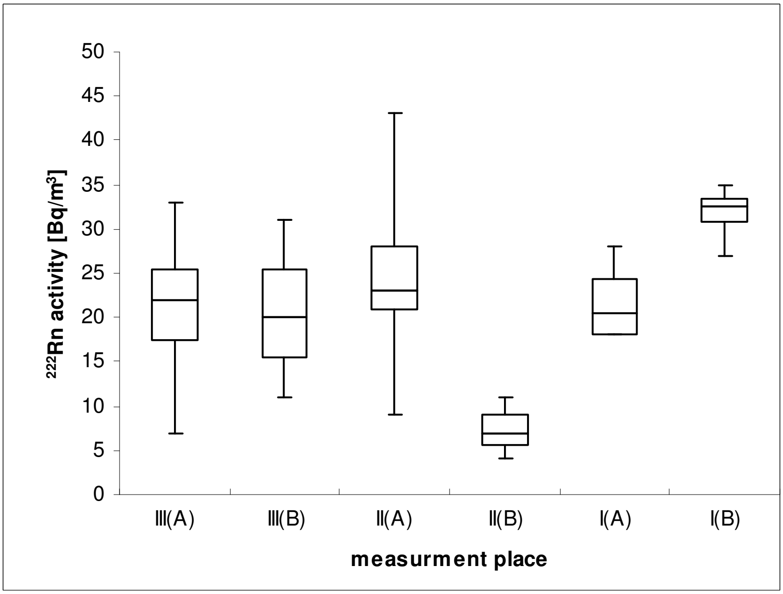

Fig. 2. The concentration of ^{222}Rn in a confined spaces on selected floors CB. The results marked by A were obtained in the morning and the ones obtained in the afternoon by B

Measurements carried out in the afternoon in the hall III showed no differences between the measurements results which were performed in the morning. In the case of the room II there was a significant decrease in the concentration of radon in the air - from 24 Bq/m^3 recorded in the morning to 7 Bq/m^3 in the afternoon. The cause of such strong decrease was the mechanical ventilation of the room, which took place between measurements. In the I room there was a reverse process - the values of activity concentration increased from 22 to 32 Bq/m^3.

Results obtained in the room I are linked with the daily changes of the ^{222}Rn concentration and specific density, which causes accumulation of ^{222}Rn in the lower places in the buildings.

Further analysis was carried out under three assumptions proposed by Moskal in 2012 [17]: (1) the hypothetical person stays in the room all day, (2) the person inhales 1 liter of air in one breath, (3) the lungs of this person weight 1 kg.

In order to determine the ^{222}Rn radiation dose inhaled with the air Formula (1) and (2) were used:

$$R = \frac{2433 \cdot Er \cdot a \cdot c}{m} \tag{1}$$

$$E = R \cdot w_t \cdot w_r \tag{2}$$

where: R - the energy of the ^{222}Rn decay in the ambient air over the year [J/kg]; Er - the energy released during a single decay of ^{222}Rn (5.5 MeV); a - the amount of ^{222}Rn decays per second [Bq/m^3]; c - the conversion factor [eV/J]; m - the mass of the lung [kg]; E - radon radiation dose inhaled with the air [Sv]; w_t - tissue weighting factor; for lung = 0.12; w_r - radiation weighting factor; for radiation α = 20.

The calculated radiation doses are shown in Figure 3.

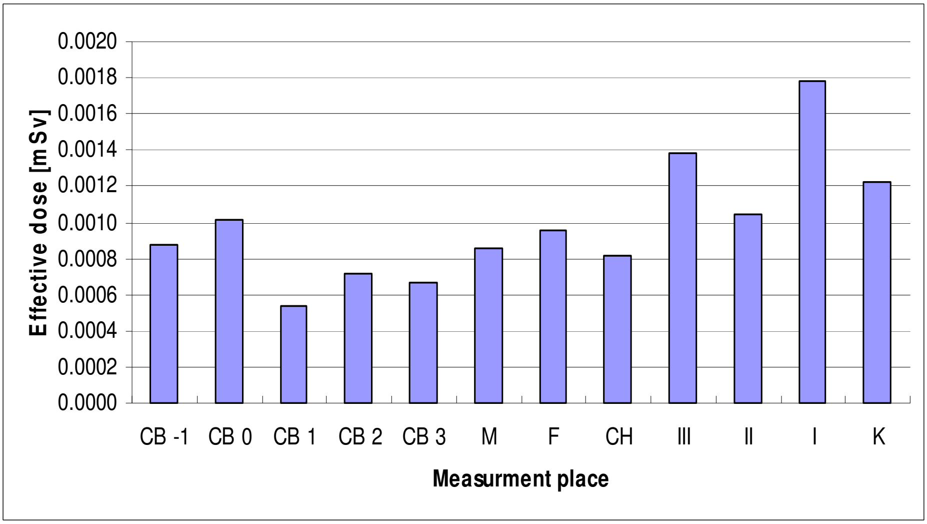

Fig. 3. The radiation dose from ^{222}Rn inhaled with air

The lowest dose of radiation will be received by the person located on the first floor of the *Collegium Biotechnologicum*, while the highest one will be received by people staying in a room on floor –1. Contributions of calculated radiation doses from radon in annual effective dose of ionizing radiation are shown in Table 1.

Table 1

The radiation dose from inhaled radon and its percentage of the total annual dose of radiation

	CB –1	**CB 0**	**CB 1**	**CB 2**	**CB 3**
Dose [mSv]	0.0009	0.0010	0.0005	0.0007	0.0007
Percent of annual dose	0.03	0.03	0.02	0.02	0.02
	M		**F**	**CH**	**K**
Dose [mSv]	0.0009		0.0010	0.0008	0.0012
Percent of annual dose	0.03		0.03	0.02	0.04
	III		**II**	**I**	
Dose [mSv]	0.0014		0.0010	0.0018	
Percent of annual dose	0.04		0.03	0.05	

The doses received by people in closed rooms are much higher than those obtained in the residence halls and corridors of buildings. Radiation doses absorbed from inhaled ^{222}Rn did not exceed 1% of the total annual effective dose of ionizing radiation for an inhabitant of Poland (3.3 mSv/year).

Conclusions

Radon activity in the buildings changes with the intensity of air movements, similar conclusions gives Dołhańczuk-Śródka et al [18] and Obed et al [19]. The activity concentration of ^{222}Rn in *Collegium Biotechnologicum* is much higher in an enclosed area and there was a small effect of the construction method on the concentration of radon in buildings. On the base of the research conducted in CB it can be concluded that people staying on the lower floors of the building are more susceptible to radiation associated with radon decay. The measurements have also shown a lack of potential risks to health from radon inhalation in buildings at the Opole University.

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POMIARY AKTYWNOŚCI ^{222}Rn W BUDYNKACH UNIWERSYTETU OPOLSKIEGO

Samodzielna Katedra Biotechnologii i Biologii Molekularnej, Uniwersytet Opolski

Abstrakt: Celem przeprowadzonych badań była analiza ryzyka związanego z aktywnością ^{222}Rn w budynkach Uniwersytetu Opolskiego. Pomiarów aktywności ^{222}Rn dokonano za pomocą przenośnego spektrometru Alphaguard w pięciu budynkach Uniwersytetu Opolskiego. Badania przeprowadzone na różnych poziomach budynków (*Collegium Biotechnologicum, Collegium Chemicum,* budynek przy ulicy Kominka, budynek Wydziału Fizyki oraz budynek główny), a także w klasach na terenie *Collegium Biotechnologicum*. Uzyskane wyniki wykazały brak potencjalnego zagrożenia zdrowia wynikającego z zanieczyszczeniem radonem. Jednocześnie zaobserwowano, że pracownicy przebywający na niższych piętrach są bardziej narażeni na promieniowanie związane z jego rozpadami, co wynika z właściwości fizycznych tego pierwiastka.

Słowa kluczowe: ^{222}Rn, aktywność, spektrometr, Alphaguard

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EFFECT OF SOIL CONTAMINATION WITH HEAVY METAL MIXTURES ON IRON CONTENT IN BROAD BEAN (*Vicia faba* L.) PODS AND SEEDS[*]

WPŁYW SKAŻENIA GLEBY MIESZANINAMI METALI CIĘŻKICH NA ZAWARTOŚĆ ŻELAZA W STRĄKACH I NASIONACH BOBU *(Vicia faba* L.)

Abstract: The investigations were conducted to determine the effect of soil contamination with mixtures of: lead, copper and cadmium with zinc and nickel on two levels of pollution (acc. to II and III pollution class in IUNG classification) on iron concentrations in broad bean pods and seeds. Broad bean, White Windsor c.v. was cultivated in a control soil with natural heavy metal concentrations (Control and Control+NPK) and in the soil contaminated with the mixtures of heavy metals (Ni+Zn, Ni+Cd, Ni+Pb, Ni+Cu, Zn+Cd, Zn+Pb, Zn+Cu) applied in two doses, or with single heavy metals (Cd, Cu, Ni, Zn and Pb) used in a higher dose. Most of the analyzed heavy metal mixtures did not affect significantly iron concentrations in broad bean pods. Soil contamination with cadmium according to the dose established on the III pollution level acc. to IUNG classification and with a mixture of Ni with Cu and Zn with Cd acc. to the dose corresponding to II level of pollution in IUNG classification led to a decrease in iron concentrations in broad bean seeds.

Keywords: heavy metals, broad bean, accumulation, Fe

Iron is an element crucial to plants for their proper functioning. It participates in the photosynthesis, stimulates chlorophyll formation, takes part in nucleic acid metabolism and regulates oxidation-reduction reactions [1]. There is a considerable interdependence of iron and heavy metals metabolic activity [2]. Excess of metals may cause disturbances in the acquisition and transfer of iron, which in consequence influences development, chemical composition and nutritional value of plants. Pulse seeds are very valuable source of protein and vitamins from groups B and C, so they should be more frequently consumed by people [3]. Broad bean pods are also valuable source of important minerals like potassium, calcium and iron [4]. Heavy metals jointly present in soil often show a different effect upon plant than when occurring singly. Because out of the five heavy metals (Pb, Cd, Cu, Zn and Ni) analysed so far and applied separately, zinc and nickel revealed the strongest (negative) effect on broad bean plants growth and also caused considerable changes in macroelement concentrations in plants, including iron, it seemed purposeful to test the effect of soil contamination with mixtures of the above mentioned metals on two levels of pollution (acc. to II and III pollution class in IUNG classification) on iron concentrations in broad bean plants.

Materials and methods

The experiment was conducted on degraded chernozem developed from loess with acid reaction and organic carbon content 1.13%. Broad bean, White Windsor c.v. was

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cultivated in a control soil with natural heavy metal concentrations (Control and Control+NPK) and in the soil contaminated with the mixtures of heavy metals (Ni+Zn, Ni+Cd, Ni+Pb, Ni+Cu, Zn+Cd, Zn+Pb, Zn+Cu) applied in two doses (marked respectively "II" and "III" corresponding to II and III class of pollution acc. to the classification suggested by IUNG [5], or with single heavy metals (Cd, Cu, Ni, Zn and Pb) used in a higher dose ("III"). The metal mixtures were used for the soil contamination in the same year when the plants were sampled for analysis, whereas in case of single metals the soil which was contaminated in the year preceding the experiment, *ie* in 2007 was used (it was marked respectively "(1)"). Doses of metals corresponding to II class were as follows: Cd - 2.25 mg · kg^{-1} d.m., Cu - 65 mg · kg^{-1} d.m., Pb - 175 mg · kg^{-1} d.m., Ni - 62.5 mg · kg^{-1} d.m., Zn - 350 mg · kg^{-1} d.m. and to III class respectively: Cd - 4 mg · kg^{-1} d.m., Cu - 85 mg · kg^{-1} d.m., Pb - 530 mg · kg^{-1} d.m., Ni - 110 mg · kg^{-1} d.m., Zn - 1000 mg · kg^{-1} d.m. Detailed data about the way in which metals were supplied to the soil and applied fertilization were presented in previous paper [6]. The samples for chemical analyses were collected at the seed full maturity. Plant material was washed in tap and in distilled water, dried in 105°C to a constant weight and ground to fine powder, then mineralized and dissolved in 10% HNO_3. After filtration Fe content was measured using Flame Atomic Absorption Spectrometry (FAAS) [7, 8]. The quality of the analytical procedure was controlled by using samples of the reference material in each series of analysis (Certified Reference material CTA-OTL-1 Oriental Tobacco Leaves). The data were processed using software Statistica to compute significant statistical differences between samples ($p < 0.05$) according to Tukey's multiple range test.

Results and discussion

Some of tested heavy metal mixtures led to a significant limiting of plant growth, which could be seen in average weight of single seeds (Fig. 1). Particularly strong negative effect was observed for mixtures of cadmium and lead with nickel and zinc applied in a dose according to III class of pollution acc. to IUNG classification (Fig. 1). Much smaller than control were also broad bean seeds collected from plants cultivated in the soil contaminated with mixture of zinc and nickel in a dose established according to II class of pollution. On the other hand, metals used separately did not cause any significant differences in the weight of seeds with reference to the control. Weakening of broad bean growth under conditions of soil contaminated with zinc in a higher dose used separately and zinc in mixture with cadmium, resulted in non-formation of seeds by these plants. Zinc and nickel were supplied to the soil in the form of sulphate. Sulfur helped to lower the pH of soil, which had a negative impact on plant growth and also increased solubilization of heavy metals [9]. This may in turn lead to increased accumulation of heavy metals by plants [10].

Iron concentrations fluctuated from 20 to 34 mg · kg^{-1} d.m. in pods and from 7 to 31 mg · kg^{-1} d.m. in seeds of broad bean (Figs. 2 and 3). Iron concentration in bean pods reported by Kabata-Pendias [2] was 84 mg · kg^{-1}d.m., whereas in pea seeds 86 mg · kg^{-1} d.m. Average content of this element in common bean grains ranged between 34 and 89 mg · kg^{-1} d.m. [11, 12]. There is also a diversification in iron concentrations in various plant organs [13]. Iron concentrations in shoots and leaves of broad bean fluctuated from 73 to 318 mg · kg^{-1} d.m. depending on the analyzed objects, and in roots ranged from 164 to 666 mg · kg^{-1} d.m. [14], so they were much higher than in pods and seeds. In a majority of objects with contaminated soil no significant changes were observed in iron concentrations in pods (Fig. 2). It reached the highest value in broad bean pods exposed to contamination with copper or with a mixture of nickel and copper, both in a lower and higher dose. The uptake of iron (Fe) changed during Cu stress in *Prunus persica* L. Batsch grafted onto two different rootstocks [GF677 (p. perscia x P. amygdalus) and Mr.S2/5 (*P. cerasifera*)] when grown in the presence of 0.1, 10 or 100 µM copper sulphate ($CuSO_4$) [15].

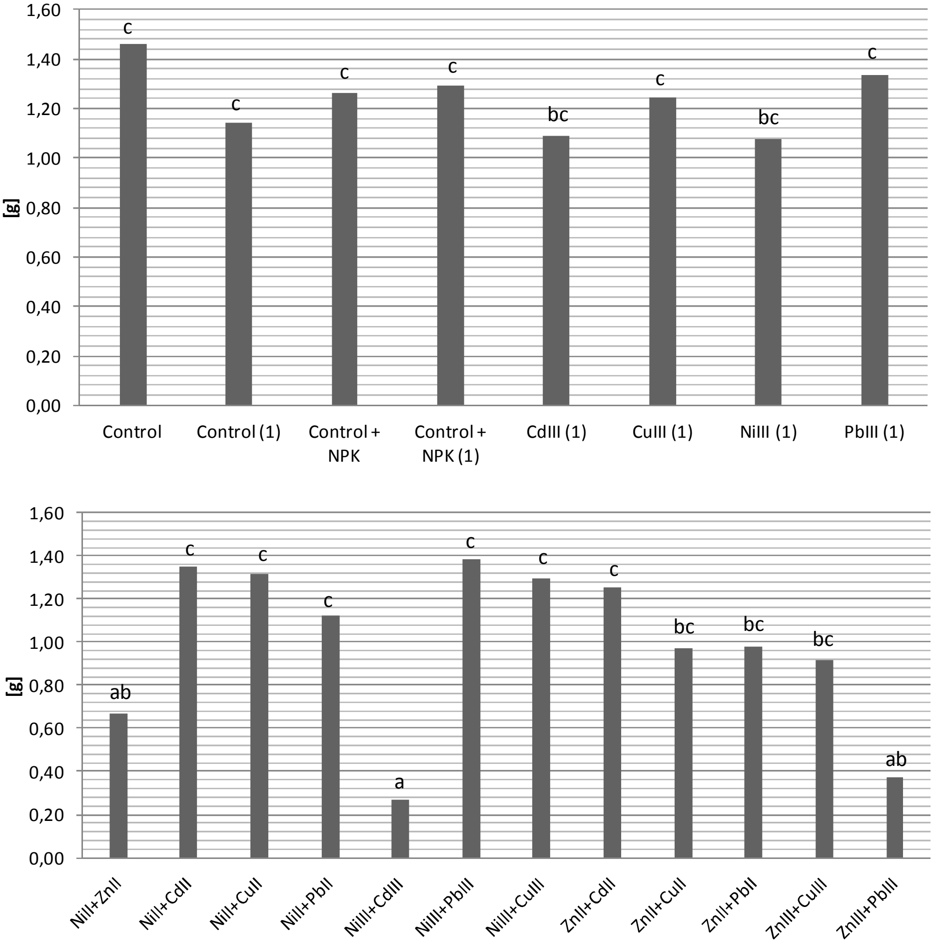

Fig. 1. Average weight of single seed of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control+NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$

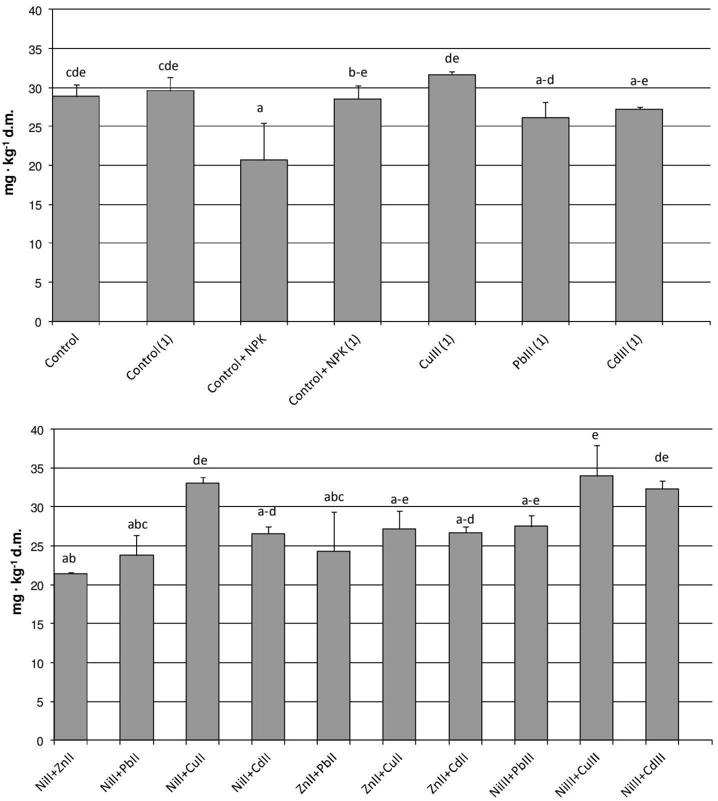

Fig. 2. Iron content in pods of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control+NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$

It proved impossible to gather a sufficient quantity of seeds for analysis from all treatments due to a phytotoxic effect of the applied metals [16]. A decrease in iron content was noted in seeds collected from contaminated plants. The most obvious decline (*ca* 5-fold) was registered in the object contaminated with a mixture of copper and nickel in a lower dose (Fig. 3). A significant decrease in iron content in comparison with the control plants was observed also in seeds collected from the plants growing in conditions of soil contaminated with a higher dose of cadmium and polluted with a mixture of zinc and cadmium in a dose calculated acc. to II level of pollution in IUNG classification. Iron deficiency may result from its complex joint effect with other elements in soil. Nickel is mentioned as one of the metals whose excess in soil leads to reduced absorption and translocation of iron, although a considerable decline in iron in seeds from plants polluted with a mixture of copper and nickel was not connected with a decreased level of this element in other plant parts [14]. However, iron does not migrate easily in plant tissues, so its deficiency appears in the first place in young plant tissues and in generative parts. The consequences of iron deficiency are disturbances of metabolic processes leading to reduced yield. In plants from the object polluted with a mixture of copper and nickel seed yield was 3-fold lower than obtained from the control plants receiving mineral fertilization. In the other objects, where metal mixtures were used, seed yield was twice lower than in the control plants [16]. A decline in iron content in broad bean seeds was registered also under the influence of swine liquid manure fertilization, although on the contrary, in leaves this measure caused increased content of iron and other heavy metals (Cd, Cu, Mn and Zn) [17]. The authors associated this with a decrease in the soil pH under the influence of this factor.

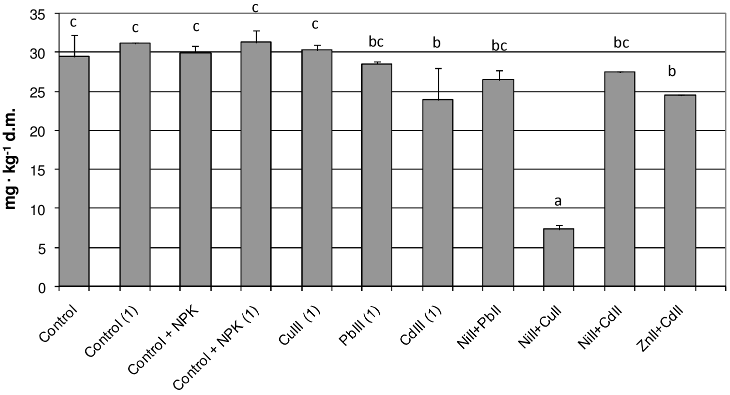

Fig. 3. Iron content in seeds of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control+NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$

Conclusions

1. Broad bean pods and seeds are characterized by lower iron concentrations than roots and shoots.
2. Most of the analyzed heavy metal mixtures did not affect significantly iron concentrations in broad bean pods. A slight increase in this element content was registered in the presence of Cu in soil or when mixtures of Ni and Cu and Ni and Cd were applied. On the other hand, on the other treatments Fe content was similar to the control object receiving mineral fertilizers.
3. Soil contamination with cadmium according to the dose established on the III pollution level acc. to IUNG classification and with a mixture of Ni with Cu and Zn with Cd acc. to the dose corresponding to II level of pollution in IUNG classification led to a decrease in iron concentrations in broad bean seeds.

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WPŁYW SKAŻENIA GLEBY MIESZANINAMI METALI CIĘŻKICH NA ZAWARTOŚĆ ŻELAZA W STRĄKACH I NASIONACH BOBU *(Vicia faba* L.)

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Abstrakt: Celem pracy było określenie wpływu skażenia gleby mieszaninami metali ciężkich: ołowiu, miedzi i kadmu z cynkiem i niklem na dwóch poziomach zanieczyszczenia (wg II i III klasy zanieczyszczenia zgodnie z klasyfikacją IUNG) na zawartość żelaza w strąkach i nasionach bobu. Bób odmiany Windsor Biały był uprawiany w glebie o naturalnej zawartości metali ciężkich (Kontrola i Kontrola+NPK) oraz w glebie skażonej mieszaninami metali ciężkich (Ni+Zn, Ni+Cd, Ni+Pb, Ni+Cu, Zn+Cd, Zn+Pb, Zn+Cu), zastosowanymi w dwóch dawkach, lub pojedynczymi metalami ciężkimi (Cd, Cu, Ni, Zn i Pb) zastosowanymi w wyższej dawce. Większość z badanych mieszanin metali ciężkich nie wpłynęła istotnie na zawartość żelaza w strąkach bobu. Skażenie gleby kadmem wg dawki ustalonej na poziomie III stopnia zanieczyszczenia wg klasyfikacji IUNG oraz mieszaniną Ni z Cu i Zn z Cd wg dawki ustalonej na poziomie II stopnia zanieczyszczenia wg klasyfikacji IUNG prowadzi do obniżenia zawartości żelaza w nasionach bobu.

Słowa kluczowe: metale ciężkie, bób, akumulacja, Fe

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Andrzej GROSICKI[1]

INFLUENCE OF MAGNESIUM ON THE CARCASS RETENTION OF CADMIUM IN RATS*

WPŁYW MAGNEZU NA RETENCJĘ KADMU W KORPUSIE SZCZURÓW

Abstract: The purpose of these studies was to evaluate the bioavailability of cadmium in rats supplemented with magnesium via drinking water. Male Wistar rats divided into 2 groups (25 individuals each) were exposed intragastrically to water solution of cadmium chloride (labelled with ^{109} Cd) daily at a dose resembling 10 ppm of cadmium in diet. Rats in group I and II were maintained in plastic cages (4 rats per cage) at 22 to 24°C with free access to commercial rodent chow and tap water. Rats in group II were additionally supplemented with magnesium via drinking water (500 mg Mg/dm^3). Carcass counting techniques were used to estimate cadmium absorption. The carcass retention of cadmium 109 was counted in a semiconductor german detector (Camberra Packard) with a multichannel analyzer after 1-, 2-, 3-, and 4-week administration. The rats in the two groups revealed a steady state decline with time in the percentage of cadmium 109 in the carcass. However, rats in group II demonstrated a lower cadmium retention throughout the whole experimental period in comparison to that in rats not supplemented with magnesium. The differences were statistically significant after a 4-week exposure. Unlike the percentage content, the total amount of cadmium in the carcass increased with time of exposure. Results indicate that supplements of magnesium reduce gastrointestinal uptake of cadmium. It may be suggested that the beneficial action of magnesium on cadmium reduction in the body increases with the length of time of the two metal co-administration.

Keywords: magnesium and cadmium interaction, retention, carcass, rat

Cadmium considered a toxic metal is not essential for biological function in humans and animals [1-3]. The presence of cadmium in the environment results from various natural sources including volcanic activity and weathering of rocks, and anthropogenic releases such as non-ferrous metal production and fossil fuel combustion [4, 5]. In spite of obvious improvements in controlling cadmium release through low-emission process technologies and cleaning of off-gases and wastewater in developed countries, literature data provide evidence that cadmium retention in human and animal bodies may be still high in several countries [4, 5]. Excessive intake of cadmium may result in numerous health problems including osteomalacia, emphysema, and renal disfunction in human and animals [4]. The uptake, distribution and elimination of cadmium in the body are influenced by the route of cadmium exposure [1]. However, the intake of cadmium through food is most important for the people and animals do not industrially exposed to this element [6, 7]. It is estimated that food or feed provides over 90% of the total intake irrespective of dietary habits. In most countries, agricultural crops account for most of the intake of cadmium [4]. The bioavailability of dietary cadmium is an important determinant of the potential risk of this toxic metal. Recent works indicate that cadmium bioavailability may be influenced by nutritional status including trace elements [8-10]. It is believed that if the general nutritional status of minerals is low in the consumer, then cadmium absorption may be enhanced [8]. Unlike zinc, calcium, selenium or iron [11, 12], magnesium is a trace element which

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interaction with cadmium has not been studied in detail and much remains to be elucidated [12].

Studies to determine effects of magnesium on cadmium distribution and toxicity are limited. Earlier works reported that feeding magnesium deprived or magnesium supplemented diet failed to affect cadmium metabolism in mice [13]. More recent reports showed that magnesium pretreatment protects kidneys against toxic action of cadmium. The effect of magnesium supplements on the bioavailability of acute doses of cadmium in rabbits and mice have demonstrated that magnesium modifies the organ redistribution of cadmium especially in the kidneys [14-18].

The aim of the present study was to examine how magnesium supplements given concomitantly with moderate cadmium doses to rats affect the whole-body cadmium retention after 1-, 2-, 3-, and 4-week co-administration.

Materials and methods

Forty male Wistar rats weighing from 230 to 255 g were used. The animals were randomly assigned into two dietary groups each of 50 rats after an acclimatisation period of one week. All rats fed a standard commercial rodent chow LSM *ad libitum* (Fodder Manufacture Motycz, Poland) containing about 190 mg Mg/kg according to the manufacturer. Rats in group I were offered a tap water (containing about 19 mg Mg/dm^3) whereas rats in group II drunk the same water supplemented with magnesium to bring the total to 500 mg/dm^3. The animals were maintained in plastic cages at 21-23°C. The total daily magnesium intake in rats in group II was about 25 times higher that that offered to rats without magnesium supplements. The consumption of feed and tap water was recorded daily. Stock solutions of cadmium chloride (Acros Organics) were prepared in deionized water and ^{109}Cd (The Institute of Atomic Energy, POLATOM, Poland) was added to prepare dosing solutions of known specific activity. Rats in the two groups examined were given through a gastric tube doses of cadmium chloride corresponding to 10 mg Cd/kg diet in a 0.5 cm^3 water solution comprising about 20 kBq/rat/daily. After 7 day-, 14 day-, 21 day-, and 28 day-exposure to cadmium or cadmium and magnesium the rats were killed by immersion in gaseous carbon dioxide. The feed and water intake were assayed daily whereas body weight gains and organ to body ratios were recorded weekly during the 28-day feeding period. The content of cadmium 109 was measured in the carcass (the whole body without the gastrointestinal tract with the contents) in a semiconductor german detector (Canberra Packard) with a multichannel analyzer. The peak energy for cadmium 109 was 88 keV. Reference standards for quantification of carcass radiocadmium were prepared by intraperitoneal injection of the appropriate solution to 10 rats which were killed 45 min thereafter. The carcass distribution of cadmium 109 in the two groups examined was compared as the percentage or amounts of the final retained dose. The area under the curves (AUC) of cadmium 109 carcass content versus time points was calculated by the trapezoidal rule. Data were analysed statistically using Student's *t*-test at $P < 0.05$.

Results

All rats showed similar feed and water intake although distinctly higher water consumption was observed in animals supplemented with magnesium. Moreover, the animals supplemented with magnesium demonstrated higher body gains; the differences were statistically significant after 4-week exposure. No differences were found in the relative weight of the liver, kidneys, heart, spleen and testicles in all examined rats.

Table 1

Body gains of rats during exposure to Cd or Mg plus Cd [g]

Period of Cd or Mg and Cd exposure	**0**	**1- week**	**2-week**	**3-week**	**4-week**
Cd	243 ± 11	269 ± 24	301 ± 32	332 ± 29	361 ± 24
Mg plus Cd	235 ± 25	307± 32	341 ± 36 (30)	381 ± 39	421 ± 33*

Explanations: * - means statistically significant differences at $P < 0.05$

The results of the carcass distribution of cadmium during the 4-week experimental period and expressed as percentage of the retained cadmium 109 in the two groups tested are shown in Figure 1.

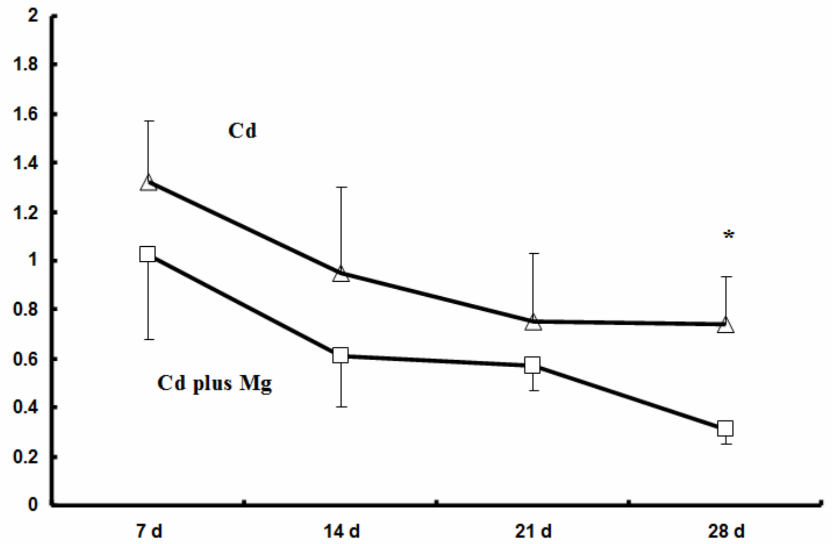

Fig. 1. Total carcass distribution (% of total dose) of cadmium 109 in rats fed with cadmium or cadmium plus magnesium; * - means a statistically significant difference at $P < 0.05$

The percentage of retained cadmium 109 in the carcass was estimated by dividing the carcass activity of cadmium 109 by the total radioactivity of cadmium 109 administered to rats. The highest percentage of cadmium 109 was found after a 1-week exposure in the two groups examined (1.32 and 1.02% of the dose, respectively) and then its content decreased steadily to 0.74 and 0.31% after 4 weeks, respectively. Although the two groups of rats revealed a similar pattern of cadmium disappearance from the body the cadmium plus magnesium fed rats continued to retain less cadmium during the 1st, 2nd , 3rd, and 4th week of exposure as compared to those treated only with cadmium. These differences were visible but not significant during the first three weeks of exposure. However, after 4 weeks, rats exposed to cadmium and magnesium showed a statistically significant reduction in cadmium retention in comparison to that in the rats exposed only to cadmium.

Figure 2 shows the total amount of cadmium deposited in the carcass calculated in micrograms within the 4-week experimental period. The results indicated that the amount of cadmium in the carcass was lowest in groups I and II after 1-week administration (26 µg and 20 µg, respectively) and then increased steadily in group I to 0.74 µg after the 4-weeek administration. On the other hand, the total amounts of cadmium in group II rose (up to 34 µg) throughout the first 3 weeks of administration and then decreased to 25 µg after the 4-week of administration. The total content of cadmium was found to increase whereas the percentage of the total dose retention decreased (Fig. 2). The calculated AUC values showed that the retention of cadmium in rats supplemented with magnesium was lower by about 35% in comparison with that in cadmium exposed group.

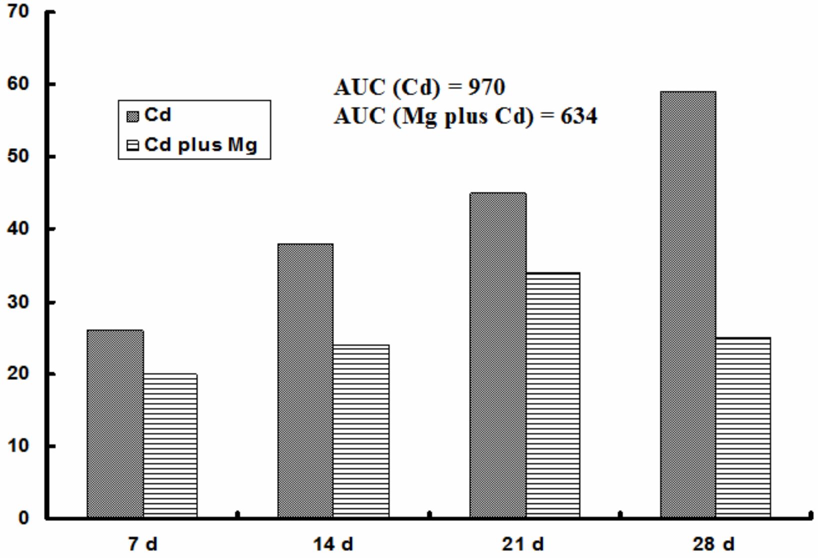

Fig. 2. Cadmium content [µg] in the rat carcass. Explanation as in Figure 1

Discussion

An increase in body gains found in animals exposed to magnesium and cadmium indicates that co-administration of magnesium with cadmium may reduce toxic action of this heavy metal [18]. Moreover, it should be stressed that magnesium protect kidneys from cadmium accumulation [13].

The whole-body counting techniques have been used to determine cadmium absorption [8]. The results of the present studies including the carcass retention of cadmium in rats not supplemented with magnesium within the 4-week period indicate a low gastrointestinal absorption of cadmium ranging from 1.32 to 0.74%. The results generally agree with those reported that dietary cadmium absorption both from single and chronic exposure in several species is low and may vary from 0.5 to 3%. However, in humans the absorption of cadmium may be higher and vary according to dietary habits: diets rich in fibre and meat from marine animals are associated with high dietary cadmium intake ranged from 5 to 7% [4].

This study demonstrated the effect of magnesium supplements via drinking water on cadmium retention in the carcass of rats exposed to moderate cadmium doses resembling those reported in the areas contaminated with the metal [2, 4, 19]. A comparison of the carcass retention of cadmium in the two groups tested indicated that less cadmium was entering the rat's body in the animals supplemented with magnesium. This finding confirmed a beneficial action of magnesium on reducing the retention of cadmium from dietary sources in acute or prolonged cadmium exposure [15, 18]. The mechanism of the gastrointestinal absorption of heavy metals including cadmium has not been elucidated in detail. However, present knowledge indicates that cadmium is transferred from the intestinal lumen into the circulation by two distinct steps involving cadmium binding to mucosal surface and then subsequent release into the entering circulation [22]. There are reports postulated that magnesium may influence cadmium transport from intestinal lumen to portal blood [15, 23]. A significant reduction in cadmium body retention found in the fourth week of cadmium and magnesium co-administration may indicate that the amount of cadmium absorbed from the gastrointestinal tract may be distinctly influenced by the length of time the rats were exposed to the two metals. The finding may also suggest, at least in the present experimental design, that the longer the rats are exposed to concomitant cadmium and magnesium administration the lower is cadmium bioavailability from the gastrointestinal tract. This evidence may seem to some extend inconclusive with an earlier report demonstrating visible but not a significant decrease in the hepatic and renal retention of cadmium in rats intoxicated with cadmium and supplemented with magnesium [11]. However, the report mentioned above did not include cadmium retention in the bones (as it was in the present study) that may concentrate large amounts of cadmium which may decrease when animals were exposed concomitantly to cadmium and magnesium [23].

Conclusion

Results indicate that the diet fortified with magnesium may be an affective factor against cadmium intake to the body and cadmium toxic activities with regard to body gains. The beneficial influence of supplements of magnesium seems to be more pronounced with the length of time of the two metals co-administration.

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WPŁYW MAGNEZU NA RETENCJĘ KADMU W KORPUSIE SZCZURÓW

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Abstrakt: Celem badań była ocena przyswajania kadmu (radiokadm 109) u szczurów eksponowanych na wodę pitną zawierającą dodatkowe ilości magnezu. Szczurom samcom szczepu Wistar podzielonych na 2 grupy zawierające po 25 zwierząt podawano codziennie dożołądkowo za pomocą stalowej sondy wodny roztwór chlorku kadmu (znakowany kadmem 109) przez 1, 2, 3 i 4 tygodnie w dawce odpowiadającej 10 mg Cd/kg diety. W grupie I zwierzęta pojone były wodą z kranu, zaś w grupie II wodę z kranu wzbogacano w chlorek magnezu (500 mg Mg/dm^3). Podczas doświadczenia określano spożycie karmy i wody oraz przyrosty masy ciała. Po 1, 2, 3 i 4 tyg. zwierzęta usypiano w atmosferze dwutlenku węgla, a następnie określano masy względne narządów. W tym samym czasie oznaczano także zawartość kadmu 109 w korpusie, z którego uprzednio usunięto przewód pokarmowy z treścią. Pomiary radiometryczne korpusu wykonano za pomocą półprzewodnikowego detektora germanowego (Camberra Packard) wyposażonego w wielokanałowy analizator. Rozmieszczenie kadmu w korpusie wyrażone w postaci procentu aplikowanych dawek wykazywało tendencję spadkową przez cały okres badań w obu grupach zwierząt. W grupie zwierząt pojonych wodą z dodatkiem magnezu procentowa zawartość kadmu w korpusie była wyraźnie mniejsza w porównaniu z zawartością u zwierząt nieeksponowanych na magnez. Po 4 tygodniach różnice były statystycznie istotne. W odróżnieniu od procentowej zawartości całkowita ilość kadmu w korpusie wzrastała wraz z długością czasu ekspozycji. Uzyskane wyniki wskazują, że dodatek magnezu do diety szczurów zmniejszał przyswajanie kadmu podawanego drogą pokarmową. Warto również zasugerować, że skuteczność oddziaływania magnezu na zmniejszenie przyswajanego kadmu zwiększała się wraz z upływem czasu ekspozycji na oba te metale.

Słowa kluczowe: interakcja magnezu z kadmem, retencja, korpus, szczura

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RADIONUCLIDES CONTENT IN SELECTED MINERAL FERTILIZERS AVAILABLE IN POLAND[*]

ZAWARTOŚĆ RADIONUKLIDÓW W WYBRANYCH NAWOZACH MINERALNYCH DOSTĘPNYCH NA POLSKIM RYNKU

Abstract: Mineral fertilizers, commonly used in agriculture, contain natural radionuclides. Fertilizers are responsible both for external and internal exposure to human beings. They supply the soil and are consumed by plants, therefore, they pose one of the main source of radionuclides in the human diet. Moreover, due to the storage of large amount of fertilizers in warehouses they can be responsible for the external exposure. The gamma spectrometric measurements of radioactive isotopes content (potassium ^{40}K, uranium ^{238}U, thorium ^{232}Th) and the measurements of gamma dose rate for over a dozen types of mineral fertilizers available in Poland, were performed. The measurements were conducted in fertilizer warehouses by means of portable gamma spectrometers with BGO detectors. The results were registered as potassium content K [%], equivalent uranium content eU [ppm], equivalent thorium content eTh [ppm] and absorbed dose rate $D_{K,\,U,\,Th}$ [nGy h^{-1}] generated by radionuclides of uranium and thorium decay series as well as potassium ^{40}K. Radium ^{226}Ra, thorium ^{232}Th and potassium ^{40}K activities range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively.

Keywords: radionuclides, mineral fertilizers, gamma spectrometry

Mineral fertilizers are commonly used in agriculture. They enrich the soil mainly in nitrogen N, phosphorus P and potassium K. Various types of fertilizers with various concentrations of these chemical compounds are available [1].

Fertilizers contain also naturally occurring radionuclides, such as radioisotopes of uranium ^{238}U and thorium ^{232}Th decay series as well as the isotope of potassium ^{40}K. The concentration of these radionuclides in fertilizers is related to the raw material used for manufacturing the fertilizer. In the case of phosphate fertilizers an important raw material is phosphate rock. It can be enriched with naturally occurring radionuclides coming from uranium ^{238}U and thorium ^{232}Th decay series as well as from potassium ^{40}K. Thorium ^{232}Th and potassium ^{40}K concentrations in phosphate rocks are similar to those observed naturally in soil. But uranium ^{238}U concentration is connected with the origin of the rock and can be enhanced in phosphate deposits of sedimentary origin [2]. A typical concentration of uranium ^{238}U in sedimentary phosphate rocks is 1500 Bq kg^{-1} [3]. A direct correlation between P_2O_5 concentration and uranium concentration in various mineral fertilizers has been noticed [2, 4].

The knowledge of uranium, thorium and potassium concentrations in fertilizers is relevant due to the fact that these radionuclides can reach human beings via various pathways and affect them. Fertilizers are responsible both for external and internal exposure to human beings. Radionuclides contained in fertilizers are consumed by plants and subsequently by man. They can also get into the water and finally cause the internal radiation exposure of the people [4]. Both, the internal (related to radon activity

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concentration in the air) and the external exposure, can occur in warehouses where large amount of fertilizers are stored [5].

To reflect an external exposure rate and to evaluate a radiation risk, an activity concentration index (*I*) is commonly used [1, 4, 7, 8]. It includes combined activities of natural radioisotopes and is defined by the following formula:

$$I = A_1 C_{Ra} + A_2 C_{Th} + A_3 C_K \tag{1}$$

where: A_1, A_2, A_3 are coefficients representing different impact factors and C_{Ra}, C_{Th}, C_K are activities of uranium ^{238}U, thorium ^{232}Th decay series and potassium ^{40}K, respectively.

Various values of A_1, A_2, A_3 coefficients are acceptable in different countries. In Poland they are equal to 1/300, 1/200 and 1/3000, respectively. An activity concentration index (*I*) should not exceed the value equal to 1 which was established on the basis of the assumption that the gamma dose rate should not exceed the value equal to 1 mSv a^{-1} over the natural background radiation dose [6].

To assess a radiation risk, also the total gamma dose rate [mSv a^{-1}] is used. According to European Commission [6] the excess of 0.3-1 mSv a^{-1} of gamma dose rate over the natural background radiation dose is acceptable.

The main aim of the survey was to evaluate the radionuclides content in selected mineral fertilizers available and used in Poland and to estimate their radiological impact on human beings.

Method

The measurements were conducted by means of portable gamma spectrometers RS230 with BGO detectors and automatic gain stabilization based on thallium ^{208}Tl emission at 2615 keV. The results were registered as potassium content K [%], equivalent uranium content eU [ppm], equivalent thorium content eTh [ppm] and absorbed dose rate $D_{K,\ U,\ Th}$ [nGy h^{-1}] generated by radionuclides of uranium and thorium decay series and potassium ^{40}K [9]. Because of the fact that uranium ^{238}U is not a gamma emitter, its content is estimated on the basis of gamma photons emitted by bismuth ^{214}Bi which is a product of uranium ^{238}U decay. This procedure is based on the assumption of the equilibrium within uranium ^{238}U decay series and uranium ^{238}U content obtained in this way is denoted as equivalent uranium eU. Similarly thorium ^{232}Th content is estimated on the basis of gamma photons emitted by thallium ^{208}Tl and thorium ^{232}Th content is denoted as equivalent thorium eTh.

87 measurements on 14 various types of fertilizers were performed in fertilizer warehouses. The devices were located at the top of piles of fertilizers placed loose directly on the floor of warehouses or packed into the bags.

Results

The average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (in [Bq kg^{-1}]) and average dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) with the respective standard deviations have been calculated for particular investigated types of mineral fertilizers. Summary of the results is presented in the Table 1.

Table 1

Mean activity concentration [Bq kg^{-1}] of Ra-226, Th-232 and K-40 and dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) for various types of mineral fertilizers

Ferti-lizer	**No of measure-ments**	**N**	**P**	**K**	**Activity concentration [Bq kg^{-1}]**			**Dose rate**	
		composition [%]			**Ra-226**	**Th-232**	**K-40**	**[nGy h^{-1}]**	**[mSv a^{-1}]**
F 1	3	27.5	0	0	17.4±1.2	9.2 ± 2.1	141.6 ± 35.0	19.8 ± 14.4	0.2 ± 0.1
F 2	10	0	40	0	827.0±90.1	38.9 ± 5.0	922.3 ± 148.8	426.6 ± 12.9	3.7 ± 0.1
F 3	5	3	22	0	416.7±30.5	14.3 ± 2.5	267.0 ± 25.4	202.5 ± 48.9	1.8 ± 0.4
F 4	12	4	12	12	347.9±61.3	32.4 ± 9.3	3494.1 ± 265.1	323.7 ± 31.0	2.8 ± 0.3
F 5	5	3.5	8	15	31.1±4.2	29.7 ± 5.1	4089.8 ± 362.4	209.6 ± 40.4	1.8 ± 0.4
F 6	3	16	16	16	37.3±8.6	35.0 ± 3.8	3610.4 ± 189.5	193.3 ± 56.9	1.7 ± 0.5
F 7	5	4	10	17.5	151.9±6.2	29.0 ± 2.3	4702.7 ± 333.7	288.2 ± 26.0	2.5 ± 0.2
F 8	3	0	12	20	328.6±27.7	27.8 ± 2.5	7028.7 ± 464.4	464.9 ± 45.4	4.1 ± 0.4
F 9	5	5	16	24	71.6±9.7	34.4 ± 2.0	7142.0 ± 995.6	361.3 ± 2.4	3.2 ± 0.02
F 10	5	5	10	25	144.5±15.8	31.0 ± 1.8	8422.3 ± 631.9	446.5 ± 35.2	3.9 ± 0.3
F 11	5	9.5	25	25	32.3±5.2	44.9 ± 3.7	7057.0 ± 1220.5	347.6 ± 82.7	3.0 ± 0.7
F 12	3	5	15	30	61.7±2.6	16.6 ± 3.7	6209.5 ± 569.5	305.6 ± 37.1	2.7 ± 0.3
F 13	10	0	0	40	65.2±77.1	19.1 ± 5.8	10743.0 ± 1678.7	504.3 ± 16.0	4.4 ± 0.1
F 14	13	0	0	60	62.0±9.0	24.2 ± 4.3	12068.2 ± 1898.3	564.1 ± 10.8	4.9 ± 0.1

Also minimum, maximum and average radionuclides concentrations and dose rate for all of the fertilizers have been estimated (Table 2). Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in investigated mineral fertilizers range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively with the average of 22.1 ± 257.2, 28.2 ± 10.1 and 6081.6 ± 4176.9 Bq kg^{-1}, respectively. The dose rate range between 0.2-6.7 mSv a^{-1} with the average of 3.3 ± 0.4 mSv a^{-1}.

Table 2

Minimum, maximum and average activity concentrations [Bq kg^{-1}] of Ra-226, Th-232 and K-40 and minimum, maximum and average dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) for investigated mineral fertilizers

	Activity concentration [Bq kg^{-1}]			**Dose rate**	
	Ra-226	**Th-232**	**K-40**	**[nGy h^{-1}]**	**[mSv a^{-1}]**
Min	16.2	7.0	121.4	18.0	0.2
Max	973.4	50.9	16777.9	762.9	6.7
Average	22.1 ± 257.2	28.2 ± 10.1	6081.6 ± 4176.9	377.4 ± 142.3	3.3 ± 0.4

The frequency distributions (Fig. 1a-c) prepared for ^{226}Ra, ^{232}Th and ^{40}K activities showed that the majority of the results are placed between the ranges 0-100, 20-40 and 0-4000 Bq kg^{-1}, respectively.

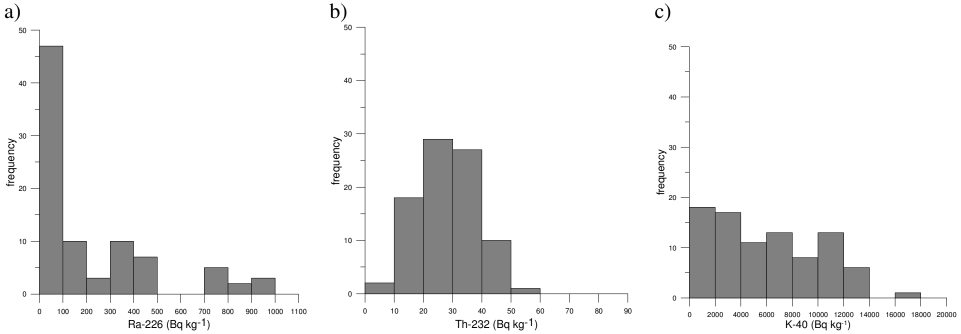


Fig. 1. Frequency distribution of radium ^{226}Ra (a), thorium ^{232}Th (b) and potassium ^{40}K (c) activities for all the investigated mineral fertilizers

Assessment of radiation hazard

To assess a radiological impact on human beings, the activity concentration index (*I*) was calculated for all types of investigated fertilizers (Table 3).

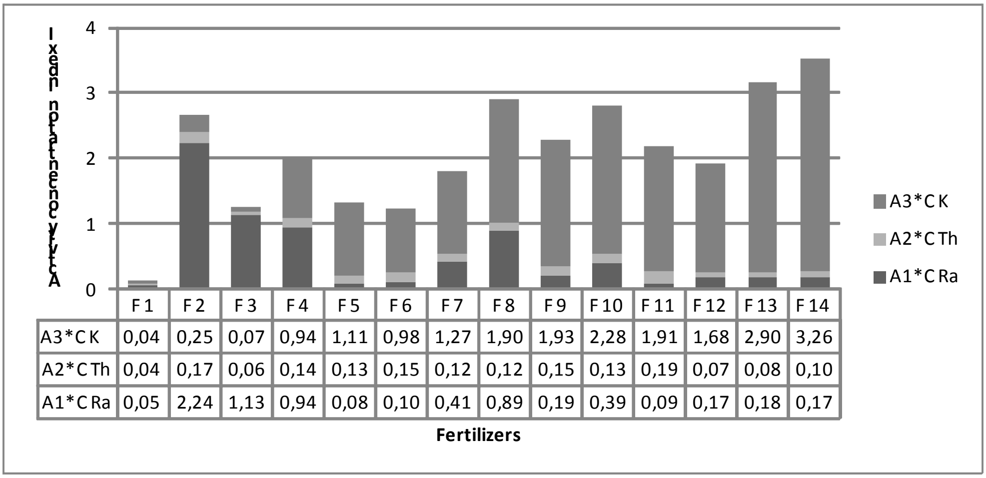
Table 3

The activity concentration index (*I*) for various types of mineral fertilizers

Fertilizer	**N**	**P**	**K**	**Activity concentration index (*I*)**
	composition [%]			
F 1	27.5	0	0	0.1
F 2	0	40	0	2.7
F 3	3	22	0	1.3
F 4	4	12	12	2.0
F 5	3.5	8	15	1.3
F 6	16	16	16	1.2
F 7	4	10	17.5	1.8
F 8	0	12	20	2.9
F 9	5	16	24	2.3
F 10	5	10	25	2.8
F 11	9.5	25	25	2.2
F 12	5	15	30	1.9
F 13	0	0	40	3.2
F 14	0	0	60	3.5

The activity concentration index ranges between 0.1-3.5 (Table 3). In 13 of 14 surveyed fertilizers the activity concentration index (*I*) exceeds the value equal to 1. The most significant values of these two indices are observed in the case of typically potassium fertilizers (F 13 and F 14) and they can pose a radiation hazard if they are stored in large amount.

Analyzing the contribution of the radioisotopes in forming the activity concentration index (*I*) it has been noticed that radionuclides of uranium decay series play the most significant role in the case of typical phosphate fertilizers (Fig. 2, fertilizer F 2) and NP fertilizers (Fig. 2, fertilizer F 3). In the case of NPK fertilizers (Fig. 2, fertilizers F 4-F 12, without F 8), PK fertilizers (Fig. 2, fertilizer F 8) and typical potassium fertilizers (Fig. 2, fertilizers F 13 and F 14), naturally occurring ^{40}K has the main participation in forming the activity concentration index (*I*). Radioisotopes of thorium decay series has a minor contribution to the radioactivity of mineral fertilizers (Fig. 2).



	F 1	F 2	F 3	F 4	F 5	F 6	F 7	F 8	F 9	F 10	F 11	F 12	F 13	F 14
A3*C K	0,04	0,25	0,07	0,94	1,11	0,98	1,27	1,90	1,93	2,28	1,91	1,68	2,90	3,26
A2*C Th	0,04	0,17	0,06	0,14	0,13	0,15	0,12	0,12	0,15	0,13	0,19	0,07	0,08	0,10
A1*C Ra	0,05	2,24	1,13	0,94	0,08	0,10	0,41	0,89	0,19	0,39	0,09	0,17	0,18	0,17

Fig. 2. The contribution of radioisotopes in forming the activity concentration index (*I*) for particular types of mineral fertilizers

In some cases of investigated fertilizers (Table 1) also the annual gamma dose rate generated by radionuclides present in fertilizers exceeds the limit value 1 mSv over the natural background radiation dose (2.4 mSv a^{-1}).

Conclusions

1. Activity concentrations of Ra-226, Th-232 and K-40 in mineral fertilizers available in Poland range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively with the average of 22.1 ± 257.2, 28.2 ± 10.1 and 6081.6 ± 4176.9 Bq kg^{-1}, respectively.
2. The annual dose rate range between 0.2-6.7 mSv with the average of 3.3 ± 0.4 mSv.
3. Calculated activity concentration index for investigated mineral fertilizers range between 0.1-3.5.
4. Some types of fertilizers stored in a large amount can pose a radiological hazard for human beings.

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ZAWARTOŚĆ RADIONUKLIDÓW W WYBRANYCH NAWOZACH MINERALNYCH DOSTĘPNYCH NA POLSKIM RYNKU

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Abstrakt: Nawozy mineralne, powszechnie stosowane w rolnictwie, zawierają naturalne pierwiastki promieniotwórcze. Środki te stanowią zarówno zewnętrzne, jak i wewnętrzne źródło napromieniowania człowieka. Nawozy zasilają glebę i pobierane są przez rośliny, przez co stanowią jedno z głównych źródeł radionuklidów w ludzkiej diecie. Natomiast na skutek składowania dużych ilości nawozów w magazynach może dojść do narażenia na promieniowanie zewnętrzne. Przeprowadzono gamma spektrometryczne pomiary zawartości izotopów promieniotwórczych (potasu ^{40}K, uranu ^{238}U i toru ^{232}Th) oraz pomiar mocy dawki promieniowania dla kilkunastu nawozów mineralnych dostępnych na polskim rynku. Pomiary wykonano w magazynach nawozów mineralnych za pomocą przenośnych gamma spektrometrów z detektorami BGO. Wyniki badań były rejestrowane jako zawartość potasu K [%], równoważne zawartości uranu eU [ppm] i toru eTh [ppm] oraz moc dawki pochłoniętej $D_{K,\ U,\ Th}$ [nGy h^{-1}] generowanej przez radionuklidy szeregów uranu i toru oraz potas ^{40}K. Zawartość radu ^{226}Ra, toru ^{232}Th i potasu ^{40}K w nawozach wahała się w granicach odpowiednio 16.2-973.4, 7.0-50.9 i 121.4-16777.9 Bq · kg^{-1}.

Słowa kluczowe: radionuklidy, nawozy mineralne, gamma spektrometria

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VARIABILITY OF MERCURY SPECIATION FORMS IN SOIL EXPOSED TO WASTEWATER FROM OLEOCHEMICAL PRODUCTION*

ZMIENNOŚĆ FORM SPECJACYJNYCH RTĘCI W GLEBIE PODDANEJ DZIAŁANIU ŚCIEKÓW Z PRODUKCJI OLEOCHEMICZNEJ

Abstract: The results of four-year research concerning variability of mercury speciation forms, contained in soil, subject to treated wastewaters from low-tonnage oleochemical production were analyzed in this paper. Doses of sewage directed to experimental patches were limited by total nitrogen concentration, with the total doses not exceeding the limit of 170 kg · (ha · year)$^{-1}$. Every year, the experimental patches were sown with plants; in the subsequent years these were: oats, rape, triticale and mustard. Then, the plants were put into soil as green fertilizers in the whole weight. After an analysis of the fractional composition in soil samples handled with treated wastewater in the experimental period, a gradual decline of the exchangeable fractions was found. Moreover, an increase of the fraction connected with carbonates and stability of the fraction connected with hydrous iron and manganese oxides and the so-called organic connections fraction, and remaining fraction was found.

Keywords: fractional composition of mercury in soil, irrigation with wastewater, fertilization with wastewater, oleochemical production

Introduction

One of the main parameters limiting the implementation of sewage from the so-called biodegradable sector in agroutilization is the contamination with heavy metals including mercury in soil, where they could be directed [1-5]. The concentration of metals limits the suitability of the appropriate type of soil for agricultural use of sewage, including their quantity and the dose of pollutant load [1-5]. In literature, there are many examples concerning the agroutilization of sewage from vegetable or animal fats production, including the aspect of the change of total heavy metals concentrations caused by agroutilization [6-17]. However, there is no information about variability of individual fractional fields during many years of experiments with fertilization and irrigation of soils such as sewage. This question seems to be essential as the total metal concentration does not reflect changes taking place with their participation and components of wastewater pollution during long-term delivery of these substances into soil [4, 5]. Low-tonnage production processes of animal or vegetable fats manufactured for the technical issues are inextricably linked to formation of effluents, which after pretreatment can be used in agriculture for irrigation and as fertilizers because they belong to the biodegradable category [1-5]. Technological wastewaters from production of vegetable fats are usually rich in phosphorus forms but lack nitrogen compounds, whereas, technological wastewaters from production of animal fats are rich in nitrogen and potassium compounds and lack

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*Contribution was presented during ECOpole'13 Conference, Jarnoltowek, 23-26.10.2013 phosphorus compounds [2, 3]. A significant amount of fat, suspensions and colloids which are frequently in form of stable dispersions impose the necessity of the physico-chemical pretreatment [4, 5].

Experimental part

The details of the physico-chemical pretreatment of wastewaters from oleochemical production are provided in works [4, 5]. Doses of sewage directed to plots were limited by the total concentration of nitrogen with the total doses not exceeding the limit of 170 kg · (ha · year)$^{-1}$. Every year experimental patches were sown with plants, and in the subsequent years these were: oats, rape, triticale and mustard, which in form of green fertilizers were in the whole weight implicated to soil. Samples of soil (light soils classified as Ap-Bw-Ck [18] from two experimental plots, (with the surface of 50.0 acres each)) irrigated and fertilized with defatted mixed crude and pretreated waste, were taken in accordance with PN-ISO 10381-2 from the subsurface layers of 0.0-0.20 m. The pH of the soil samples was determined using the methodology specified in PN-ISO 10390:1997. The soil material for analysis of the total mercury content was collected for 4 years at equal intervals. Air-dried soil samples underwent mineralization and extraction with a mixture of acids (HCl $\rho = 1.183$ kg · dm^{-3} and HNO_3 $\rho = 1.341$ kg · dm^{-3} in a volume ratio of 3 : 1) according to the standard of PN-ISO 11047:2001. Concentrations were determined by atomic absorption spectrometry technique AAS (devices: BUCK Scientific 210 VGP and Spectr AA Varian 220 SS according to the methodology of PN-ISO 16772:2009). Soil samples taken from the areas of the experimental plots also underwent the sequential extraction according to Tessier's methodology [19], using the air-dried sample weight (about 0.04 kg) which were treated with extracting solutions of increasing power according to the procedures given in [4, 5]. The results of the averaged content and the variation analysis concerning individual fractions of mercury speciation over four years of running the experiments are presented in Figure 1.

Results and discussion

The literature presents different aspects connected with implementation wastewaters from the production of vegetable and animal fats for agroutilizational purposes [6, 7, 12-17]. However, there is a lack of information concerning variation in speciation of metals including mercury during the long-term agroutilization. It could be the matter of high importance to crops technology and usability of plants grown on those irrigated areas. The presented results are continuation of the previous work [4, 5] which purpose was quantitative identification of dynamic fractional variation of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn), taking place in the surface layer of soil (0.0-0.20 m) during four-year utilization of defatted raw and physico-chemically pretreated mixed wastes from oleochemical production. To compare changes taking place over time, the area of plots was irrigated and fertilized separately with mixed crude wastes after defatting and with wastes pretreated using the method described in [4, 5]. In the experimental period, the range of values of the basic parameters for the mixed crude wastes developed in accordance with the values given in Table 1 [4, 5].

Table 1

The basic parameters of crude wastes and physico-chemically pretreated wastes
from low-tonnage oleochemical production

Item	Parameter	Unit	Raw wastewater	Pretreated wastewater
1	Reaction	pH	3.9-5.0	8.4-9.3
2	Total nitrogen	$[mg \cdot dm^{-3}]$	175.3-720.9	88.8-170.7
3	Total phosphorous	$[mg \cdot dm^{-3}]$	60.7-220.8	11.3-40.8
4	Potassium	$[mg \cdot dm^{-3}]$	149.4-606.2	66.9-483.7
5	Ether extract	$[mg \cdot dm^{-3}]$	703.3-5999.0	3.7-27.3
6	Total suspended solids	$[mg \cdot dm^{-3}]$	477.3-2530.0	18.9-42.7
7	Chemical oxygen demand	$[mg \cdot dm^{-3}]$	3348.9-10201.6	809.6-4405.7
8	Biochemical oxygen demand	$[mg \cdot dm^{-3}]$	905.8-4593.9	467.9-2067.8

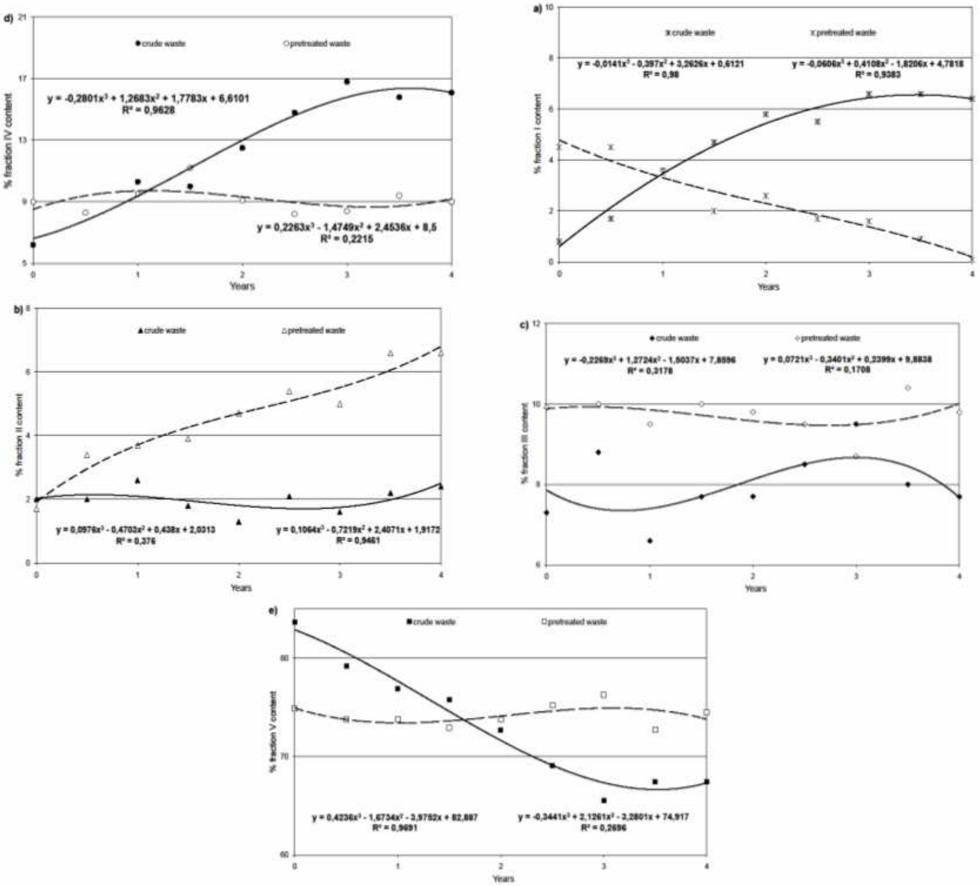

Fig. 1. Changing the fractional composition of mercury (Hg) in the surface layer of soil from the plots irrigated and fertilized with mixed waste from the oleochemical plant - crude wastes (solid trend line) and pretreated wastes (dashed trend line) ($C_{0(Hg)}$ - 0.5±0.3 $mg \cdot kg^{-1}$ TS). The individual fractions are given in diagrams: a) I exchangeable, b) II carbonate, c) III associated with hydrated oxides of manganese and iron, d) IV organic, e) V remaining

On the basis of the analyses of soil samples, it was found that the total concentration of mercury at the level of the natural background of these soils. In the case of soil irrigated with defatted crude wastes in accordance with a polynomial equation $C_{Hg}(t) = 0.0001 \cdot t^2 - 0.005 \cdot t + 0.4987$ ($R^2 = 0.1378$) (where: C_{Hg} - the total concentration of mercury indicated by AAS technique, and the parameter t is the experimental time in units of month). However, in the case of the soil irrigated with treated wastewaters, it was done with some approximation in accordance with the polynomial equation $C_{Hg}(t) = 9\text{E-}05 \cdot t^2 - 0.0052 \cdot t + 0.5019$ (Fig. 1) [4]. Registered in the experimental period, the mercury concentration did not exceed the level of 1.0 mg $\cdot$ kg^{-1} TS and remained within the statutory limits prescribed for light soils by 0.8 mg $\cdot$ kg^{-1} TS [1]. Slight variations of concentrations registered in the near surface indicate changes resulting from the vegetation processes of the sown plants.

Despite the usage of pretreated wastewater at pH = 7.8-8.8 over the four-year experiment no significant changes were found in soil from the experimental plots, since the level of this parameter was within the range pH ≈ 6.7 ± 0.2, during the whole period. Thus, it is the pH level at which the ionic mercury forms have a natural preference to form sparingly soluble forms of hydroxide - like $M(OH)_{n(s)}$. The effect of this phenomenon was the gradual decrease in the content of fraction I which was recorded in the experimental period in the case of soil samples handled with treated wastewater. However, for the soil samples treated with defatted crude wastes, the acidification was found to change over the time of the experiment from the starting level $pH_0 \approx 6.7 \pm 0.3$ to the final value $pH_K \approx 5.9 \pm 0.4$ (no liming the plot was carried out, and after degreasing crude wastes had pH ≈ 3.9-5.0). This caused an increase in the content of the exchangeable fraction (Fig. 1a). This phenomenon can be caused by the fact that there appear suitable conditions for releasing the soluble forms, possibly in the form of aqua complexes $[M(H_2O)]^{+m}$ and organic products of changes in soil, especially in the low molecular weight acids in time of vegetation (eg. deriving from micro and mycological soil transformations of polysaccharides and oligosaccharides, *eg* glycogen provided from wastes). This group contains both complex constructions $[M(R)]^{+m+n}$ (where: R - organic ligands, *eg* products of poly sugar hydrolysis: monosaccharides or dextrins; soil metabolism products: low-molecular acid, poly acid, low molecular condensation products etc., a m and n - mercury load and organic ligands) as well as different organic, non-coordinating soluble forms [5, 20-22]. Creating metal-organic connections is also justified by the constant supply of organic substance delivered to the soil, and in consequence increasing transformation processes with the participation of those substances and products of their decomposition, especially during vegetation [20-22]. In the case of fraction II (mercury connected with carbonate forms), no significant changes are found. Whereas, in the case of samples handled with treated wastes, an obvious increase of this fraction content can be seen (Fig. 1b). In the case of fraction III (associated with the hydrated forms of oxides of manganese and iron) for soil samples handled with defatted crude wastes, high stability of this fraction was found, understood as a permanent tendency to maintain a similar level of the content to the natural background in the course of the experiment (Fig. 1c). This indicates that substance composition contained in the wastewater has no effect on total changes of concentration in this fractional pool. However, in the case of soil samples handled with pretreated waste, no statistical tendency or trend providing the course possible to define the nature of the change was registered. This indicates high instability of the content of this fraction; it can also be the result of composition changes or may be the result of different vegetation processes of plants grown on the soil. Defatted crude technological wastes and pretreated wastes from the oleochemical production is free from heavy metals, and in pollution loads there are mainly low molecular weight soluble substances of vegetable origin (for example: proteins, lecithin, glycerides, sterols, tocopherols, aldehydes, ketones, lactones) or animal origin (for example, amino acids, protein degradation products, simple sugars and oligosaccharides) [12, 15]. On the basis of the obtained research results it can be concluded that they have no quantitative impact on the fractions III, which should be regarded as a desirable effect of agroutilizing impact of wastes on soil quality. In the cases of analyzed soil samples handled with defatted crude wastes, an obvious increase of fraction IV content was estimated (so-called: the combination of organic substances). This increase was recorded at the level of ca 280% (Fig. 1d). Certainly, the dynamics and the nature of humification processes involving organic external substances supplied with wastes affected such a significant change in relation to the initial conditions. The dynamics of change in the concentration of this fraction in the case of soil samples handled with pretreated wastes was shaped differently - no increase in content of this fraction was found (Fig. 1d). Analyzing the fractional composition of the soil samples treated with wastes, definitely the highest percentage recorded in this case is the so-called remaining fraction (fraction V). In the case of fraction V, which is the remaining pool for soil samples treated with defatted crude wastes in the case of mercury, there is a quantitative reduction in content registered at the time of 20-35% (Fig. 1e). Fraction V is the least defined pool in terms of the qualitative and structural composition and its properties depend to the high extent on soil formation and the local environmental conditions, which makes it difficult to describe the interpretation only on the basis of quantitative changes in time. To sum up, it can be suggested that in the case of soil samples handled with pretreated wastes no obvious evidence of a significant change in the quantitative relations concerning individual fractional pools resulted from the increase of properties and the buffer capacity of the soil presented, for which no significant changes in pH were recorded (except for periodic minimal variations - 0.3 values), and this parameter is important in the case of almost all chemical and biochemical soil transformations. In the case of mercury, the phenomenon of the wide variety of percentage shares in fractional pools in time, should be also evaluated in terms of random scatter of the results, taking into consideration the relatively low concentration of this element in soil (for $Hg_{(0)} = 0.5\ (\pm 0.3)\ mg \cdot kg^{-1}$ TS), and thus the statistical evaluation of the obtained results.

Conclusion

During the four-year agroutilization of the pretreated mixed wastes no significant change in the total mercury content in irrigated and fertilized surface layer of soil was recorded. Analyzing the experimental period, the fractional composition in soil samples handled with pretreated wastes, a gradual decline of the exchangeable fraction was found, whereas the increase in the fraction related to the forms of carbonate and the stability of the fraction concerning hydrated iron and manganese oxides and the fraction of the so-called organic compounds, and the remaining fraction.

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ZMIENNOŚĆ FORM SPECJACYJNYCH RTĘCI W GLEBIE PODDANEJ DZIAŁANIU ŚCIEKÓW Z PRODUKCJI OLEOCHEMICZNEJ

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Abstrakt: Przedstawiono wyniki czteroletnich badań nad zmiennością form specjacyjnych rtęci oznaczanej w glebie poddanej działaniu podczyszczonych ścieków z mało tonażowej produkcji oleochemicznej. Dawki ścieków kierowanych na poletka doświadczalne limitowano stężeniem azotu ogółem, w łącznych porcjach nieprzekraczających granicznej ilości 170 kg · (ha · rok)$^{-1}$. Poletka doświadczalne corocznie były obsiewane roślinnością, w kolejnych latach: owsem, rzepakiem, pszenżytem i gorczycą, które w formie zielonego nawozu były w całej masie wprowadzane do gleb. Analizując w okresie doświadczalnym skład frakcyjny w próbkach gleby traktowanej ściekami podczyszczonymi, stwierdzono sukcesywny spadek zawartości frakcji wymywalnej, natomiast wzrost frakcji związanej z formami węglanowymi oraz stabilność frakcji związanej z uwodnionymi tlenkami żelaza i manganu oraz frakcji tzw. połączeń organicznych i pozostałej.

Słowa kluczowe: skład frakcyjny rtęci w glebie, nawadnianie ściekami, nawożenie ściekami, produkcja oleochemiczna

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METHODS OF LIQUID BIOFUEL PRODUCTION - THE BIODIESEL EXAMPLE*

METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIODIESLA

Abstract: The main problem for present fuel producers is how to cover the demand for new, alternative fuels (biofuels) as a substitute or components of traditional fuels. In this purpose the technologies of biofuels production are still being improved. To show how wide the area of research in this field is, authors of this paper have compared various types of biofuel production methods, pointing out the raw materials needed for their synthesis. Conversion processes, which are used to alternative fuel's production, were also presented. Further in this article authors focus on the more detailed statement and description of today's most popular biodiesel technologies, along with the details of selected parameters and efficiency of installations based on those technologies. This work is a gathering of current knowledge on FAME technology production.

Keywords: biofuels, biodiesel, technology of production

Introduction

The demand for renewable energy sources and alternative fuels is constantly growing. This is a serious argument for potential producers to invest and develops new, more efficient technologies for biofuels production, especially because of the limited amount of fossil fuel.

Liquid biofuels belong to the few groups of compounds with properties and parameters which allow their use in relevant types of internal combustion engines. The main types of biofuels are bioethanol and biodiesel, and their blends with fuels, like bioethanol with gasoline and biodiesel with diesel fuel. Sometimes there could be found a mixture of diesel fuel with ethanol, the oxydiesel or bioxydiesel type [1].

The main types of liquid biofuels and biocomponents are [2, 3]:

- bioethanol - anhydrous ethyl alcohol produced from biomass or biodegradable waste from fermentation or dehydratation process;
- bioesters - methyl esters produced from vegetable oils or animals fats;
- biomethanol - methyl alcohol (CH_3OH), produced from biomass. Biomethanol can be obtained by dry distillation of wood or the Fisher-Tropsch reaction of the gas obtained by gasification of biomass. Unfortunately methanol is toxic and its production process is expensive. In Poland Prof. D. Nazimek from UMCS works on catalytic synthesis of methanol from CO_2 and water, which may hopefully decrease the costs [4, 5];
- bio-ETBE (Ethyl tert-butyl ether) - produced on the basis of bioethanol. Synthesized by isobutylene (from petroleum) and ethanol (from fermentation process) mixing.

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Bio-ETBE is used as a biocomponent in fuels, in accordance with EN 228 standard (up to 15% v/v);

- bio-MTBE (Methyl tetr-butyl ether) - produced on the basis of biomethanol. Obtained in the distillation of wood or isobutylene with methanol reaction. Bio-MTBE is used as a gasoline biocomponent, but its parameters are worse than bio-ETBE. Due to this fact and the greater toxicity of the product justifies much less production of bio-MTBE than bio-ETBE;
- bio-DME - Dimethyl ether (CH_3OCH_3) produced form biomass. It is gaseous fuel for diesel engines, characterized by a high cetane number (over 55). It can be obtained from synthesis gas (gain from biomass gasification), or from dehydratation of methanol. Unfortunately, the use of this fuel is associated with various problems including fuel injection, and so far it is not commonly used as fuel;
- pure vegetable oils (PVO) - which are oils produced in fat processing plants by cold pressing and extraction, as crude oil or refined but not chemically modified;
- biobutanol - produce from biomass and biodegradable waste. It is a mixture of isomeric alcohols like: n-butanol (1-butanol), sec-butanol (2-butanol), isobutanol (2-methyl-1-propanol), tert-butanol (2-methyl-2-propanol). Butanol can be obtained by chemical reactions or using biotechnology. In fermentation process bacteria like *ie Clostridium Acetobutylicum* can be used. This bacterium has the ability to produce butanol from sugar beets, sugarcane, wheat, corn, straw or wood waste. Biobutanol is similar fuel to gasoline (calorific value: butanol - 29 MJ/g, gasoline - 32 MJ/g) and is used in an amount of 8-32% as a gasoline component to increase its octane number.

Industrial methods of transesterification process

Production of biodiesel can be carried out both periodically and continuously. First type approach prevails mostly in small installations, working for one or several groups of farmers. The amount of biodiesel obtained this way is usually less than 20 thousand tons per year, and a single periodic cycle takes from 6 to 24 hours [6]. In order to achieve an adequate mixing of the substrates special reactors with mechanical mixers (axial propeller) are being used in the process. They are filled with vegetable oil and an appropriate amount of catalyst mixture consisting of methanol and a catalyst. Then, for about 1 hour, the reaction mixture is mixing. The solution proposed here is applied by many companies which provide FAME (*fatty acid methyl ester*) installations. The Polish companies are: Promar from Poznan [7], IMIX Biofuel [8], Bio-Tech [9], Hydrapres et al [10]. There are also methods for mixing the raw materials with combined techniques. The company Protechnics [11] *ie* has in its offer installation using the mixing in the pipe, combined with additional mixing by a pump.

Biodiesel production method used by the Henkel company

The main difference between available in the market large biodiesel plants, rely mainly on different techniques of mixing oil with methanol and catalyst. For example Henkel offers a number of static mixers containing special design pads, which cause turbulence flow and intensify mixing.

Fatty acids (vegetable oils) after heating in heat exchanger and mixing with catalyst and methanol, go to flow tubular reactor, in which the reaction mixture is still intensely mixed. Products are decanted in a separator. Esters fraction with unreacted oil goes to the second part of the process. After that glycerine fraction goes to separator. This process goes in two stages, but if it is necessary they could be repeated.

Biodiesel production process used by Lurgi company

The continuous process developed by Lurgi company provides another type of installation. The reaction has two stages but in contrast to previous solution, the mixing process is done by using mechanical stirrers placed directly in transesterification reactor. After that, the reaction mixture goes to separator and subsequently is pumped to second reactor. Products, after second stage of the process (mixture of FAME, glycerine and methanol), are re-routed to separator. Unreacted oil (after separation) is returned to first stage of process. Glycerine, methanol and esters of rapeseed oil are neutralized by phosphoric acid in mixer and then goes to centrifuge. In distillation column glycerine and methanol are separated and then recycled to process. Separated in centrifuge water is stored in tanks. From the washing water could be recovered potassium-phosphorus fertilizer, which the main compound is K_3PO_4.

Multistage technology by Connemann

It is also known as CD technology (*continous deglyceration*), and was developed and patented in 1990 (DE 4209779, US 5,354,878). In 1996 the worldwide production of biodiesel in this technology reached level of 120 000 Mg [12], and the product meets the high requirements (standard DIN EN 14214). Currently production decreased to the one company in Czechowice-Dziedzice [13].

Transesterification process is similar to previous technologies, but by multistage glycerin draining and methanol-catalyst addition, higher yield and purity of the products can be obtained [14]. From 1015 kgs of oil and 109 kgs of methanol they could produce 1000 kg of high quality biodiesel, with the cetane number about 54-58, and only 96 kg of glycerine (99.7% purity) [12].

Esterification of soybean oil technology

The kinetics of transesterification reaction of soybean oil with methanol and NaOH, studied by Noureddini and Zhn [15], results in developing new technology [16].

In this technology substrates are brought through the feeder serially connected to the static mixers with inserts, which provides turbulent flow. Second mixer has got water jacket to allow temperature control of the reaction mixture, which is directed from it into the reactor with a mechanical stirrer. Esterification reaction is then carried out in the tubular flow reactor. So, the reaction starts in the mixer, but continues and ends in tubular flow reactor. Biodiesel and glycerin products after cooling in a heat exchanger can be separated in the disc separator or as described in [14] and [6] in gravitational separator.

Esterification of used fats by LUT Technology

The technological process of LUT (*Lappeenranta University of Technology*) [17] was developed for waste oils (vegetable oils - mainly palm oil, and animal fats with high FFA (*free fatty acids*)) into biodiesel processing. In the first stage of process waste fats with FFA are esterificated in the reactor. Then the substrates are directed to subsequent reactors, in which vegetable oils, methanol and H_2SO_4 (as a catalyst) are being mixed, and two stages transesterification occurs. Glycerin from ester and unreacted fatty acids separators, together with glycerin from biodiesel separators have been placed between the reactors.

In the glycerine fraction methanol, sulphuric(VI) acid and water are diluted. This mixture is heated in heat exchanger and separated by distillation under reduced pressure. Products of distillation are: pure technical glycerine, methanol and water. Methanol could be return into process.

ICHP technology

ICHP is one of the first technology developed by the Institute of Industrial Chemistry (*ICHP*) in Warszawa. Nowaday, after new technology was discribed and patented [18], [19], this name of process has only historical meaning. In this process a catalyst is a sulphuric acid (H_2SO_4). Methanol vapours, overheated in superheater, are directed to vertical, tubular reactor. Stream of compunds goes into reactor from the bottom and with countercurrent to oil. Bubbles are floating upwards causing pneumatic mixing of the components. Two stages of process: esterification and transeterifiaction takes place between 90-120°C. In separator the glycerine fraction is isolated from FAME. Unreacted methanol vapours with water are condensated in the condenser and rectified in rectifying column. Methanol is compressed, overheating and then is returned into reactor [6].

Cvengros-Powazanec method

In this process (proposed by Slovak researchers J. Cvengros and F. Powazanec) seeds are pressed without heating with the efficiency of about 83%. From one ton of seeds approximately 340 kg of oil could be produced. Pressing is carried out in low capacity oil presses at temperatures below 70°C. Two stages transesterification process takes place in 1.3 m^3 reactor at temperature level between 60-70°C, with NaOH (3-6%) as a catalyst. In first stage of process the oil-to-methanol molar ratio is 1 : 3.5, in second 1 : 0.95. After the reaction, residue of methanol is being removed by blowing air and products separated from glycerine phase. Esters are neutralized with phosphoric acid, and free fatty acids with ammonium hydroxide. Soap, free fatty acids and methanol (by adding phosphoric acid) are also being removed from the glycerin phase. After such purification crude glycerin is obtained [20].

Vogel & Noot process

This Austrian company produce methyl esters under the commercial name of "BIO diesel". Installation works in two-stage semi-continuous system, and the catalyst is a 2% potassium hydroxide, which is added as a mixture with methanol. The recovery of methanol is carried out with two phases. Glycerine phases from both stages are being mixed. The phosphoric acid is added in order to separate the free fatty acids and neutralize the excess of KOH. Free fatty acids may be collected as a separate product or returned back to the esterification process. Crude glycerine could be sale or purified. The potassium phosphate, formed from the remnants of the catalyst and phosphoric acid, is used as a component of mineral fertilizers.

Other technologies of FAME production

The IKA POL company has an interesting way of biodiesel production process conducting, which uses ultrasonic reactor. The preheated oil with the catalyst mixture and methanol is transported through a pipeline into the flow cell. The esterification reaction runs there with the help of ultrasonic waves, which cause mixing intensification.

Then in the centrifugal separators the post-reaction mixture is separated to FAME and glycerine. Residence time of the reactants in the installation in this continuous technology takes only about 20 min, the reaction lasts for 5 min, and the time of separation is less than 15 min [14, 21].

The new technology of biodiesel production is used in the systems, which are offered by the Uni-Masz company. Single installation is running in a continuous process, and has a capacity of 1.5 m^3/h. Substrates mixing and transesterification reaction is carried out through a mixing pump, with an additional microwave radiation exposure. Further process including gravitational separation of the products is conducted in a flow tank. Improved quality of produced FAME is obtained by washing esters with liquid extractant derived from vegetable oil processing. The use of microwaves allows better mixing of raw materials and faster separation of the products [22].

Summary

The main technologies of biodiesel production are described in this study. Of course they are not the only possibilities of obtaining alternative energy source. Certainly they are not all the options, furthermore demand for new, cheaper and more efficient technology is way of determines new invention [23]. The collection of these technologies, however, allows a large extent on the systematization of knowledge on this subject and is a good starting point for further analysis in the field of biofuels.

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METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIODIESLA

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Abstrakt: Zapewnienie pokrycia zapotrzebowania na nowe, alternatywne źródła energii, które można z powodzeniem wykorzystywać jako substytut bądź dodatek do paliw tradycyjnych, od jakiegoś czasu stanowi główny cel wielu firm zajmujących się ich produkcją. W tym celu opracowano i w dalszym ciągu udoskonala się coraz więcej technologii wytwarzania paliw zastępczych, zwanych biopaliwami. Aby wskazać, jak szeroki obszar obejmują badania w tym zakresie, w niniejszej pracy porównano ze sobą różne rodzaje biopaliw, wskazując surowce potrzebne do ich produkcji oraz procesy konwersji prowadzące do uzyskania poszczególnych produktów. Mając na uwadze rozmiar zagadnienia, w dalszej części artykułu skupiono się na bardziej szczegółowym zestawieniu i opisie najpopularniejszych obecnie technologii produkcji biodiesla wraz z wyszczególnieniem wybranych parametrów pracy oraz wydajności instalacji opartych na tychże technologiach. Praca przybliża aktualny stan wiedzy z zakresu technologii produkcji FAME.

Słowa kluczowe: biopaliwa, biodiesel, technologie produkcji

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REMOVAL OF VINYL ACETATE FROM WASTE GASES IN THE PILOT-SCALE BIOLOGICAL TRICKLE - BED REACTOR[*]

OCZYSZCZANIE GAZÓW ODLOTOWYCH Z OCTANU WINYLU W PILOTOWEJ INSTALACJI BIOREAKTORA STRUŻKOWEGO

Abstract: The removal of vinyl acetate from air streams in a pilot-scale trickle-bed bioreactor (TBB) inoculated with *Pseudomonas* sp. PCM 2123 strain was studied experimentally. For various gas and liquid flow rates and inlet vinyl acetate concentration ranging from 0.25 to 1.5 $g \cdot m^{-3}$ the efficiency of the process was tested. For all the operating conditions high elimination capacity was obtained.

Keywords: vinyl acetate, air purification, trickle-bed bioreactor

Introduction

Vinyl acetate belongs to a group of compounds known under the common name of Volatile Organic Compounds (VOCs). In normal/standard conditions it is a colourless liquid with a characteristic sweetish odour, forming flammable and explosive mixtures with air. This chemical compound is commonly used in industry to produce polyvinyl acetate which is a component of masses bonding glues, water based paints, foils, inter-layers of chilled glass, paper impregnates and many copolymers [1]. Vinyl acetate was listed by US EPA among the 189 pollutants most noxious for the environment [2].

The emission of vinyl acetate into the atmosphere is significant. According to EPA report from 2002 concerning the emission of pollutants in the organic chemistry industry, the amount of vinyl acetate emitted into the atmosphere was 235,542 Mg per year [3].

This compound has a great influence on the functioning of living organisms. In case of human beings vinyl acetate in the concentration of more than 21.6 ppm irritates breathing tracts. The negative influence of this pollutant on a human body is confirmed by tests; 17 chromosome aberrations and the phenomena of sister chromatid exchanges (SCE), and DNA cross-linking were observed, while incubating in vitro human lymphocytes and leukocytes in the presence of vinyl acetate [4]. The mechanism of metabolism of vinyl acetate in the tissues of mammals was described in the work [5] where the negative influence of the products of vinyl acetate decomposition (acetic aldehyde and acetic acid) on tissues exposed to the action of this compound was emphasized. Clinical testes proved its effect as a carcinogenic factor inducing nose cancer (papillomas and squamous cell carcinomas) among rodents, which gives a good view on the hazard that is posed by the presence of vinyl acetate in the environment. The application of microbiological processes to eliminate vinyl acetate does not increase the risk of uncontrolled genetic modifications in case of micro-organisms since this compound is not mutagen for bacteria [6]. Thanks to it,

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it is possible to use bacteria in the process of biological purification of air from vinyl acetate.

There is very little information about microbiological decomposition of vinyl acetate in literature. They are only the works of Nieder et al [7] who studied the rate of degradation of the compound by an environmental strain marked V2 and works [8-10] where the efficiency of vinyl acetate biodegradation by a group of environmental and laboratory strains was compared, the most effective strain was selected and the kinetics of its growth on a biodegraded substrate was determined.

The basic criterion to choose the technology of air purification should be the concentration of pollutant in the stream of the purified gas and the rate of that stream. Figure 1 shows the ranges of the concentrations of pollution and the gas flow rate in which the use of proper technologies can give measurable effects. As it can be seen, biological methods can be used for very big air streams, however, the concentration of the pollutant cannot exceed 10 g · m^{-3}. Here biological methods are more advantageous in comparison with the other technologies that are used such as catalytic oxidation, combustion, adsorption, absorption or concentrations on membranes [11].

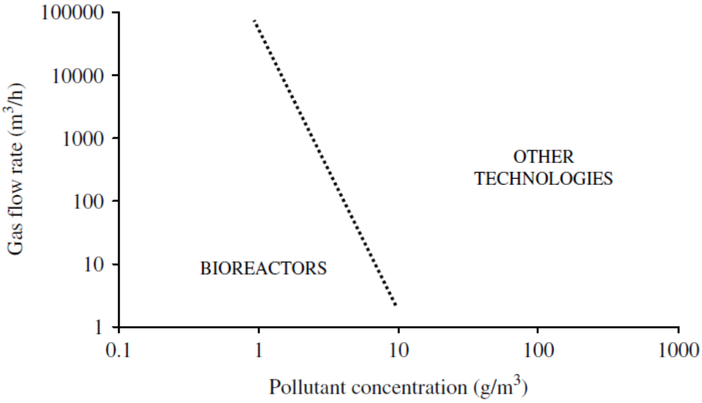

Fig. 1. Ranges of the use of various technologies of eliminating organic pollutants depending on gas flow rate and concentration of pollutants [12]

VOCs biodegradation in trickle-bed reactors is a process carried out in pressure and temperature conditions slightly different from standard conditions, which is its important advantage in comparison with other technologies of waste gases purification. Biotechnological methods require the lowest expenditures connected with VOCs utilization calculated for 1 $m^3 \cdot h^{-1}$ of the polluted air.

In comparison, depending on the used method, expenses are in the range of: $ 13-90 - biotechnological methods, $ 25-155 - adsorption, $ 30-600 - combustion, $ 40-190 - absorption, $30-200 condensation. As it has been mentioned above, chemical and physical methods can be used only at the determined operational conditions at proper ranges of concentration of the pollution [13].

The aim of the study was to check the efficiency of the pilot-scale trickle-bed bioreactor (TBB) installation designed to purify ~200 $m^3 \cdot h^{-1}$ of air polluted by a volatile organic compound. The carried out studies are to provide directions making it possible to scale up bioprocesses and determine the range of changes in operational biodegradation process parameters for which high conversion of the pollutant will be ensured.

Materials and methods

The pilot installation was made up of three basic systems: a system feeding the bioreactor with a given stream of air containing enough volatile organic compound vapour, a system recycling liquid in which the composition of the solution feeding the bioreactor was controlled and adjusted, and the trickle-bed bioreactor system provided with ports to sample liquid and gas, to measure pressure drop etc. The scheme of the installation was shown in Figure 2.

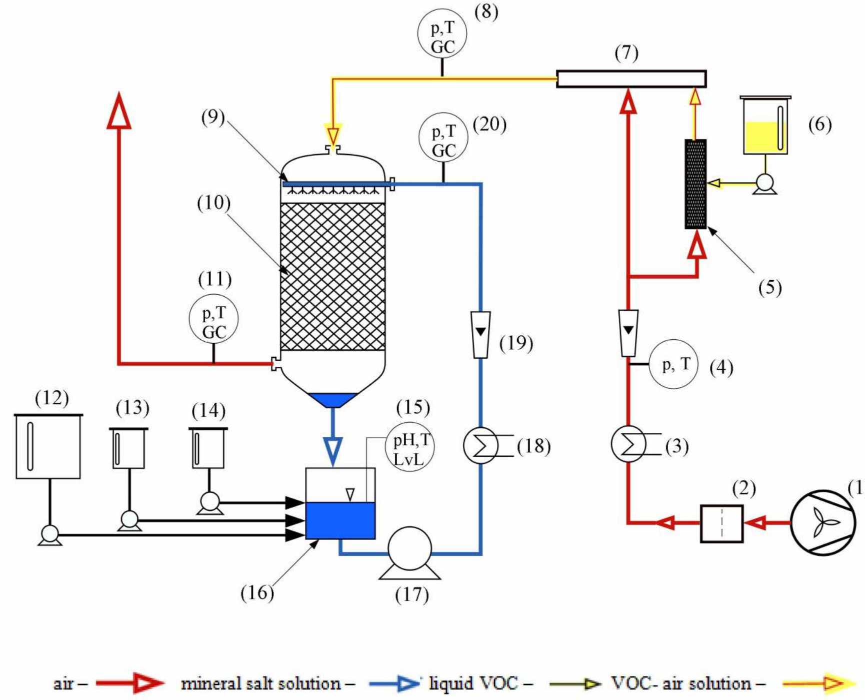

Fig. 2. Schematic diagram of the experimental setup: 1 - compressor, 2 - air filter, 3 - air heater, 4 - gas flow meter, pressure and temperature meter, 5 - VOC evaporation chamber, 6 - VOC container integrated with dosing pump, 7 - gas mixing chamber, 8 - concentration, pressure and temperature measurement in gas inlet, 9 - sprinkler, 10 - packed column, 11 - concentration, pressure and temperature measurement in gas outlet, 12 - mineral salt solution container with dosing pump, 13 - KOH solution container with dosing pump, 14 - KH_2PO_4 solution container with dosing pump, 15 - level, temperature and pH measurement, 16 - solution container, 17 - liquid pump, 18 - liquid heater, 19 - liquid flow meter, 20 - VOC concentration, temperature and pressure measurement

The air and liquid phases flowed concurrently downward through the column packed with polypropylene Ralu Rings ($\varepsilon = 0.94$), covered with a thin layer of microorganisms

(*Pseudomans fluorescens* PCM 2123). During experiments the gas flow rate was changed from 50 to 200 $m^3 \cdot h^{-1}$, liquid flow rate was changed from 5 to 10 $m^3 \cdot h^{-1}$, whereas concentration of vinyl acetate was changed in the range 0.25 to 1.5 $g \cdot m^{-3}$.

All experiments were carried out under steady-state and optimal for used microorganism conditions (pH = 6.9-7.0, $t = 30.0 \pm 0.5$°C).

During experiments the concentration of vinyl acetate and carbon dioxide in the gas phase and concentration of vinyl acetate and intermediate products of biodegradation in the liquid phase, at the inlet and outlet of the bioreactor were controlled every day (gas chromatograph Varian Star 3800 (USA)).

Results and discussion

The performance of the bioreactor was evaluated by the following performance parameters: vinyl acetate (pollutant) load (*PL*), elimination capacity (*EC*) and removal efficiency (*RE*). The definitions of these parameters are set out below:

$$PL = \frac{C_g}{\tau} \tag{1}$$

where:

$$\tau = \frac{V_{bed}}{V_g} \tag{2}$$

$$EC = PL^0 - PL^H \tag{3}$$

$$RE = \frac{\left(C_g^0 - C_g^H\right)}{C_g^0} \tag{4}$$

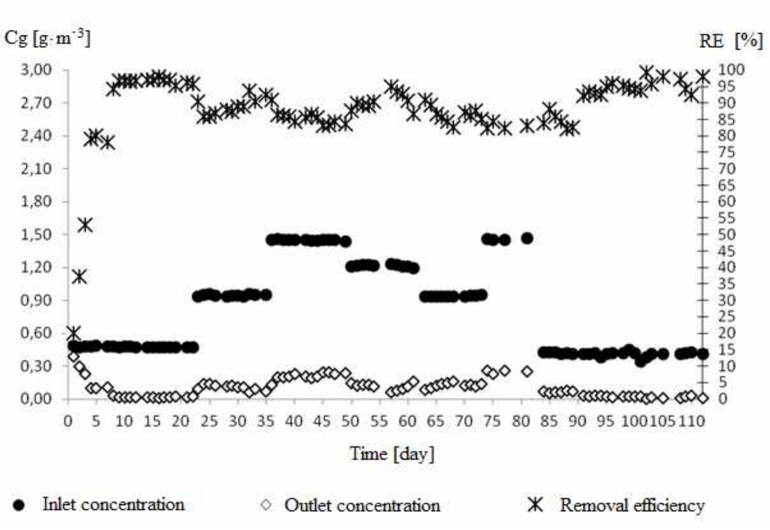

Fig. 3. Inlet and outlet concentrations and removal efficiency of vinyl acetate versus operation time

The pilot-scale trickle-bed bioreactor was operated for five months and no clogging of the column, due to excess growth of biomass on the packing material, was observed. The changes of inlet and outlet concentration of vinyl acetate and removing efficiency during experimental period was shown in Figure 3.

It has to be emphasized that the efficiency of the bioreactor was not lower than 85% even at the highest concentration of the pollutant in the purified gas. Figure 4 shows the results of the experiments in the form of *EC* vs. *PL* dependence. The presented comparison shows that if the inlet pollutant load of the bed (PL^0) does not exceed ~40 g · m^{-3} · h^{-1} then the pollutant conversion is close to 100%. The *EC* value decreases slightly for higher loads of bed with pollutant.

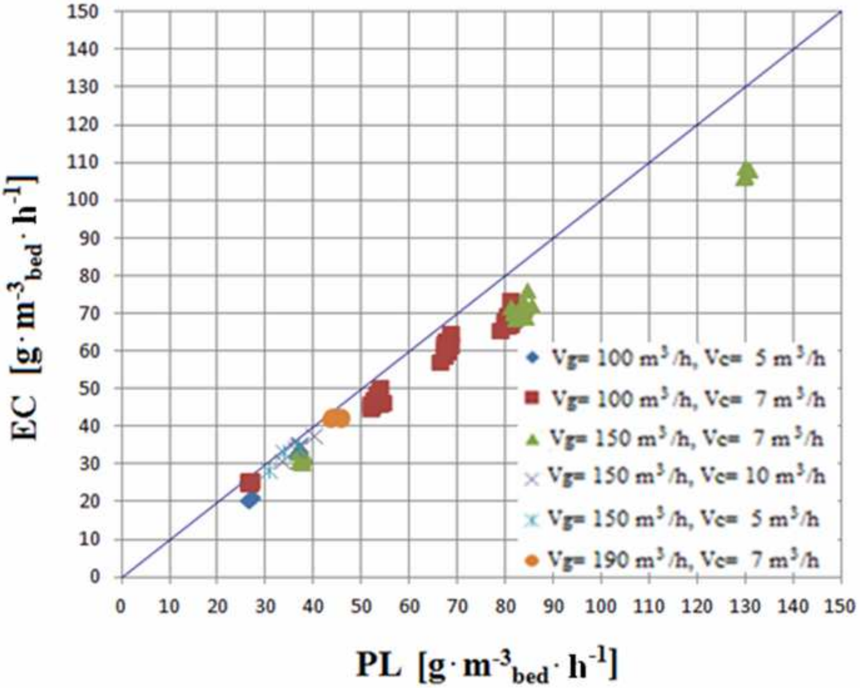

Fig. 4. Measured specific Elimination Capacity *EC* versus specific Pollutant Load *PL*

Conclusions

The experiments showed the significant potential applicability of TBB for the purification of large waste gas streams containing low concentrations of VOCs. More than 98-85% removal efficiency was achieved for influent vinyl acetate concentration ranging from 0.25 to 1.50 g · m^{-3}. The conducted experiments provided a lot of crucial information connected with scaling up of the process from laboratory to pilot-scale and made it possible to work out procedures ensuring the effective and long-term operation of the installation. The analysis of process parameters made it also possible to verify kinetic parameters of biodegradation processes determined in batch experiments.

Symbols

C - substrate concentration [$g \cdot m^{-3}$]
EC - elimination capacity [$g \cdot m^{-3} \cdot h^{-1}$]
PL - pollutant load [$g \cdot m^{3} \cdot h^{-1}$]
RE - removal efficiency [%]
V - volumetric flow rate [$m^{3} \cdot h^{-1}$]
V_{bed} - bed volume [m^{3}]
τ - empty bed residence time [h]

Subscripts

$_g$ - gas
$_c$ - liquid
$_H$ - outlet of reactor
$_0$ - inlet of reactor

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OCZYSZCZANIE GAZÓW ODLOTOWYCH Z OCTANU WINYLU W PILOTOWEJ INSTALACJI BIOREAKTORA STRUŻKOWEGO

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Abstrakt: Przeprowadzono badania usuwania octanu winylu z gazów odlotowych w instalacji pilotowej bioreaktora strużkowego zaszczepionego bakteriami *Pseudomonas sp.* PCM 2123. Badania przeprowadzono dla różnych wartości natężeń przepływu gazu i cieczy oraz przy stężeniach octanu winylu w zakresie od 0,25 do 1,5 $g \cdot m^{-3}$. Dla wszystkich warunków operacyjnych uzyskano wysoką wydajność eliminacji zanieczyszczenia.

Słowa kluczowe: octan winylu, oczyszczanie powietrza, bioreaktor strużkowy