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Artykuły

Proceedings of ECOpole

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Michał KOZIOŁ[1]

POSSIBILITIES OF CO-INCINERATION OF GLYCERIN PHASE WITH FUEL OIL IN BURNER INJECTOR

MOŻLIWOŚCI WSPÓŁSPALANIA FAZY GLICERYNOWEJ Z OLEJEM OPAŁOWYM W PALNIKU INŻEKTOROWYM

Abstract: Existing regulations (the need to achieve National Indicative Targets in the next years) force increased consumption and production of biofuels and biocomponents. In Poland, the production of esters is particularly important. Last year in Poland, the production of esters reached 650 000 Mg. It can be estimated that the production of esters triggered, at the same time, the production of more than 100 000 Mg of glycerol phase. Existing methods of using glycerol fraction usually require to carry out a multi-stage and relatively complex process of its purification. The paper presents the results of the process of co-incineration of glycerin phase with fuel oil. The burner injector was used in the research which allowed to preheat the combusted fuel mixture. As part of the study, the compounds which were burnt included the mass fraction of glycerol phase not exceeding 40%. The study was carried out in a research laboratory allowing for temperature measurements along the flame length. The paper presents the results obtained during the co-incineration of the compounds in comparison with the analogous data obtained during the incineration of fuel oil.

Keywords: glycerin phase, atmospheric burner, co-incineration of glycerin phase with fuel oil

Introduction

The growing global need for energy and the increasing environmental awareness of the societies in developed countries fosters the use of renewable energy. Due to the climatic and geological conditions in Poland, solar and geothermal energy will not constitute a significant percentage of overall energy output. There possibilities of harnessing hydrological sources are also scarce. Wind energy can be feasibly generated only in some areas of Poland, and this type of energy is recently met with increasing resistance. For these reasons, biomass is an important source of renewable energy in Poland that can be tapped in the short term. One of the easiest ways to take advantage of biomass in Poland is its firing or cofiring. The applicable EU regulations stipulate that liquid fuels shall contain an addition of biocomponents. For example: the Polish National Index Target for this year stipulates that among the total amount of fuels introduced to the market there shall be at least 7.1% biocomponents and biofuels (in terms of calorific value). In recent years, the implementation of the applicable regulations resulted in a substantial increase in the production of bioethanol and esters in Poland. In Poland, 5 percent of bioethanol is added to gasoline, and 7 percent esters is added to diesel fuel. There are also fuels on the market with a higher content of biocomponents, e.g.: B20, B80, B100 fuels with ester content of 20, 80 and 100% respectively, and E85 fuel with 85 percent of bioethanol.

Approximately 170 000 Mg of bioethanol and nearly 700 000 Mg of esters were manufactured in 2013 in Poland [1]. Glycerine phase is a by-product in the production of

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the latter. Glycerine phase generation amounts to a dozen to twenty percent of the mass of the manufactured esters. As the amount of manufactured esters grows, the issue of handling the increasing amounts of glycerine phase becomes more and more urgent. It is estimated that in 2014 the manufacture of esters resulted in the generation of approximately 80-130 Gg (80 000-130 000 Mg) of glycerine phase. It is worth noting that much greater production volumes of methyl esters were forecasted several years ago. It was anticipated that the production capacity of esters in Poland would reach the level of 1.5 million Mg, which would result in the generation of 200 000-300 000 Mg of glycerine phase. These plans were not realised in full due to, among others, the discussion on the role of 1st generation biofuels and fuels in a sustainable economy [2-5]. The uncertainties brought forward by this discussion discouraged new investments in the manufacture of biocomponents from agricultural raw materials. The possible outcome of this ongoing discussion involves the growing role of waste materials in the manufacture of biocomponents and biofuels. The reason for this is that fuels made from waste materials are classified as 2nd generation fuels.

The glycerine phase which is a by-product of the manufacture of methyl esters (or, less often: ethyl esters) of fatty acids is a mixture of various substances: glycerine (up to 70%), methanol (ethanol), free fatty acids, water, soaps and a number of other compounds and solid contaminants. The composition of glycerine phase depends on the raw materials used in the manufacture of esters, and the applied technology of production. A variety of raw materials can be used to manufacture esters, e.g.: vegetable oils and animal fats, as well as waste fats of vegetable and animal origin (e.g. used frying oils).

There are several possibilities of managing the glycerine phase [6, 7]. Their significant part is based on obtaining pure glycerine first [8, 9]. Pure glycerine is used in cosmetics, pharmaceutical, food and chemical industries. After separating methanol, the glycerine phase can be used as a fertilizer component or as a feed additive. The glycerine phase can be also a raw material for process gas production (e.g. in gassing and hydrogenation processes). One of the simpler methods of the glycerine phase management is its co-combustion performed in professional power industry facilities [10, 11].

Thus, there are many applications for the glycerine phase or for the glycerine obtained on its basis. In the case of large manufacturers of biocomponents, utilisation of the glycerine phase is easier. The glycerine phase obtained by individual producers of esters in subsequent production cycles is most frequently characterised by stable properties, and thus, its processing can be carried out in accordance with the same selected technology.

In the case of small producers, the situation is different. They produce esters in various technologies. This production is accompanied by relatively small amounts of the glycerine phase produced. Therefore, it is necessary to find a technology that will make it possible to utilise the glycerine phase produced at small producers in an economically effective and environmentally safe manner. Co-combustion of the glycerine phase with fuel oil could be one of such technologies.

Oil-fuelled boilers are commonly used devices. Conducting the process of co-combustion there would allow for using the chemical energy of the glycerine phase.

Further in the paper, selected results of tests intended to determine technical possibilities of the implementation of such a co-combustion process are presented.

Testing methodology

Testing was conducted on a test stand composed of a cylindrical combustion chamber and a universal burner. The combustion chamber was characterised by internal height of 1.7 m and internal diameter of 0.9 m. The combustion chamber was isolated. A number of instrument nozzles are installed in the combustion chamber structure, which enable performing temperature measurements and taking samples for analysis. Figure 1 presents the test stand used.

Fig. 1. Test stand

The universal burner used in testing was a low-power injector burner by Kroll, type KG 20 (Fig. 2). The burner was equipped with a burner tank with adjustable temperature.

In the injector burner, the fuel is sucked in by the compressed air jet (which is also the primary air) from the burner tank. Then, the fuel is sprayed through a special nozzle. MGA 5 VarioPlus analyser with IR sensors was used to measure the concentration of flue gas components.

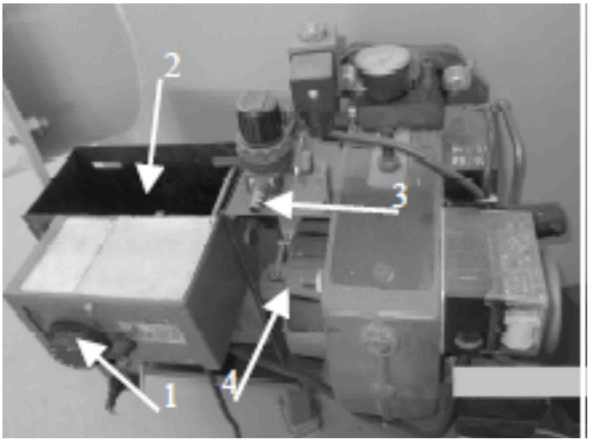

Fig. 2. Burner injector Kroll KG 20. Basic elements of the burner: 1 - adjustable thermostat knob, 2 - burner tank, 3 - primary air supply system, 4 - fan engine

As part of the presented testing, a mixture of light fuel oil and glycerine phase was combusted. Mass fraction of the glycerine phase in the combusted mixture amounted to 20%. Table 1 presents the glycerine phase composition and in Figure 2 it is presented in photographs.

Table 1

Selected fuel parameters of glycerine phase

Item	Unit	Glycerine phase
C	[%]	43.23
H		6.88
N		0.03
S		1.64
Cl		-
O		47.70
Ash		0.14
Water		0.38
Calorific value	[MJ/kg]	17.3

The quantities of primary and secondary air supplied to the process were changeable factors in the conducted testing. The primary air jet was adjusted by changing the air pressure. The adjustment was done with the use of a special control knob placed on the burner head. In the presented testing, the primary air pressure amounted to: 0.08, 0.1, 0.12 and 0.14 MPa. The secondary air jet was adjusted by adjusting the size of the slot supplying the air to the secondary air fan. The secondary air jet was adjusted by setting 4 sizes of the slot. These sizes are hereinafter conventionally referred to as: 1, 2, 3 and 4. Where one is the minimum adjustable value of the slot and 4 is its maximum value.

Test results obtained during the mixture combustion were compared to the test results obtained during the combustion of fuel oil.

Test results

Figures 3 and 4 present exemplary results of tests on the impact of the quantity of preliminary and secondary air supplied on the volume of CO concentrations obtained. CO concentration values were converted into comparable values at 3% O_2 content in flue gas. Figure 3 presents results obtained during the combustion of fuel oil and Figure 4 - during the combustion of the 20% mixture.

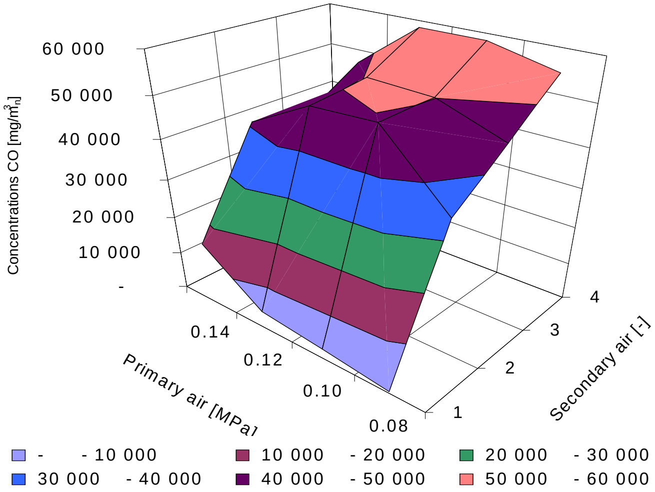

Fig. 3. Impact of primary and secondary air settings on CO concentrations during fuel oil combustion (CO concentrations are converted into 3% O_2 content; m^3_n - normal cubic meters)

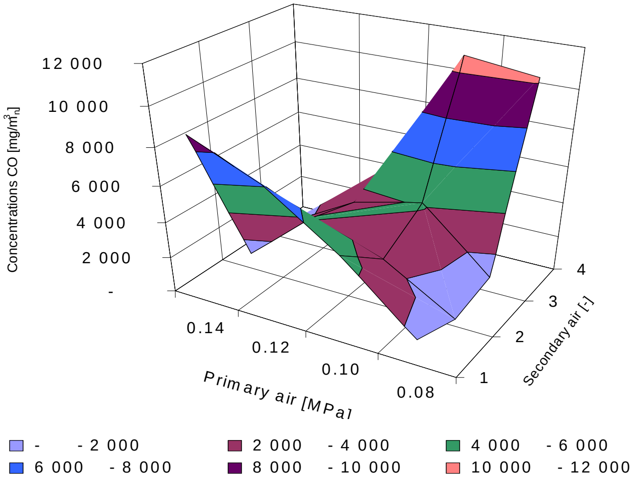

Fig. 4. Impact of primary and secondary air settings on CO concentrations during the combustion of a mixture with 20% of glycerine content (CO concentrations are converted into 3% O_2 content)

As Figure 3 demonstrates, the lowest CO concentration values during oil combustion are obtained when the smallest amounts of primary and secondary air are supplied (i.e. for the setting of 0.08 MPa of primary air and “1” of secondary air).

According to the data presented in Figure 4, the lowest CO concentration values are obtained in the case of two groups of burner settings:

- primary air setting of 0.08 MPa and secondary air of “2” or “3”;
- primary air setting of 0.08 MPa and secondary air of “4”.

Conclusions

Conducted testing proved the possibility of performing the co-combustion process of the glycerine phase with fuel oil in the injector burner. Conducted testing also demonstrated that under ambient temperature of 20°C, the glycerine phase can be smoothly mixed with fuel oil. Pre-heating of the mixture prior to its feeding to the burner is also unnecessary.

During conducted testing, no impact of the glycerine phase content in the combusted fuel on the volume of observed NO_x concentrations was reported. For SO_2 concentrations, a concentration increase was observed resulting from the increased sulphur content in the glycerine phase.

For CO, the adjustment ranges of the primary and secondary air jet volumes were determined, which allow for obtaining the lowest concentration values of this gas during the combustion process.

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MOŻLIWOŚCI WSPÓŁSPALANIA FAZY GLICERYNOWEJ Z OLEJEM OPAŁOWYM W PALNIKU INŻEKTOROWYM

Katedra Technologii i Urządzeń Zagospodarowania Odpadów, Politechnika Śląska, Gliwice

Abstrakt: Obowiązujące regulacje prawne (konieczność osiągnięcia w kolejnych latach Narodowych Celów Wskaźnikowych) wymuszają zwiększone zużycie oraz produkcję biopaliw i biokomponentów. W Polsce szczególnie istotna jest produkcja estrów, których w ubiegłym roku wytworzono ponad 700 000 Mg. Można szacować, że przy produkcji estrów powstało równocześnie ponad 100 000 Mg fazy glicerynowej. Istniejące metody wykorzystania frakcji glicerynowej wymagają najczęściej przeprowadzenia wieloetapowego, stosunkowo skomplikowanego procesu jej oczyszczania. W pracy przedstawiono wyniki badań procesu współspalania fazy glicerynowej w mieszance z olejem opałowym. W badaniach wykorzystano palnik inżektorowy pozwalający na wstępne podgrzanie spalanej mieszanki paliwowej. W ramach prezentowanych badań spalano mieszanki o udziale masowym frakcji glicerynowej nieprzekraczającym 40%. W badaniach wykorzystano stanowisko badawcze umożliwiające pomiary temperatur wzdłuż długości płomienia. W pracy przedstawiono uzyskane w trakcie spalania mieszanek wyniki na tle analogicznych, otrzymanych w trakcie spalania oleju opałowego.

Słowa kluczowe: faza glicerynowa, palnik inżektorowy, współspalanie fazy glicerynowej z olejem opałowym

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Anna KWIECIŃSKA[1], Radosław LAJNERT[1] and Rafał BIGDA[1]

COKE OVEN WASTEWATER - FORMATION, TREATMENT AND UTILIZATION METHODS - A REVIEW

ŚCIEKI KOKSOWNICZE - MIEJSCA POWSTAWANIA, SPOSOBY OCZYSZCZANIA I METODY UTYLIZACJI - PRZEGLĄD LITERATURY

Abstract: Coke making process is strictly connected with formation of coke oven wastewater, highly loaded and contaminated stream, proper treatment and utilization of which requires sophisticated methods and technologies. This wastewater is defined as a mixture of technological streams, which are formed during coke oven gas cleaning and coal-derivatives production, and sanitary wastewater formed at coke oven plant. Due to the composition and specificity of contaminants present in coke oven wastewater, its proper treatment requires the involvement of physical, chemical and biological methods, which are often proceeded with additional polishing. In dependence on its further use (deposition to environment or wet quenching of coke) different types of contaminants are found to be priority substances, removal of which during the stream treatment is especially important. In the article, a literature review on coke production, coke oven wastewater formation, its parameters, applied technologies of treatment and utilization methods is presented. The special attention was given to the applied treatment techniques, which were found to be the key factor in further stream utilization. Additionally, issues related with nowadays used systems were pointed out.

Keywords: coke oven wastewater formation, coke oven wastewater characteristics, coke oven wastewater treatment, coke oven wastewater utilization

Coke production

Coke is produced by the destructive distillation of coal in coke ovens. Specially prepared coal blend comprising of various types of coals of desired coking parameters is heated in an oxygen-free atmosphere (coked) until most volatile components in the coal are removed [1-3]. The remaining material is a carbon mass called coke, and it is used in various processes, among which pig iron production of the most significant one. The branches of coke application are shown in Figure 1.

There are over 560 coke oven plants in the world (Fig. 2). Most of them (ca. 400, each with over 600,000 Mg/y capacity) are located in China. The annual worldwide production of coke in 2015 reached 716 Tg, while only for Asian coke oven plants it was 582 Tg.

Ca. 6% of total world coke production is generated in European Union. In 2015 the production capacity of EU coke producers reached 44 Tg (Fig. 3), among which above 19 Tg were generated in Germany (9.7 Tg) and Poland (9.6 Tg). Domestic market of coke production is based on 9 coke oven plants, among which Zdzieszowice coke oven plant, of annual capacity 4.2 Tg is the biggest plant in Europe, while Przyjazn coke oven plant (in Dabrowa Gornicza) is the youngest European plant [4-7].

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Fig. 1. Branches of coke application

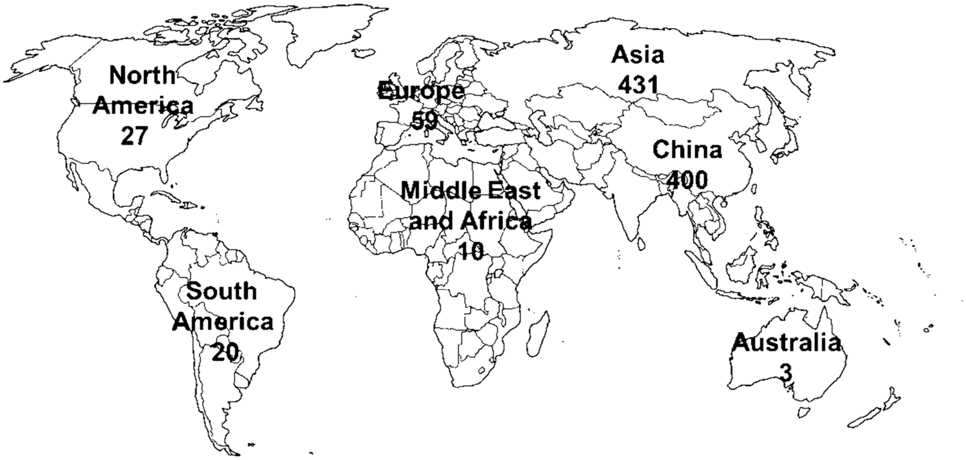

Fig. 2. Number of coke oven plants over the world

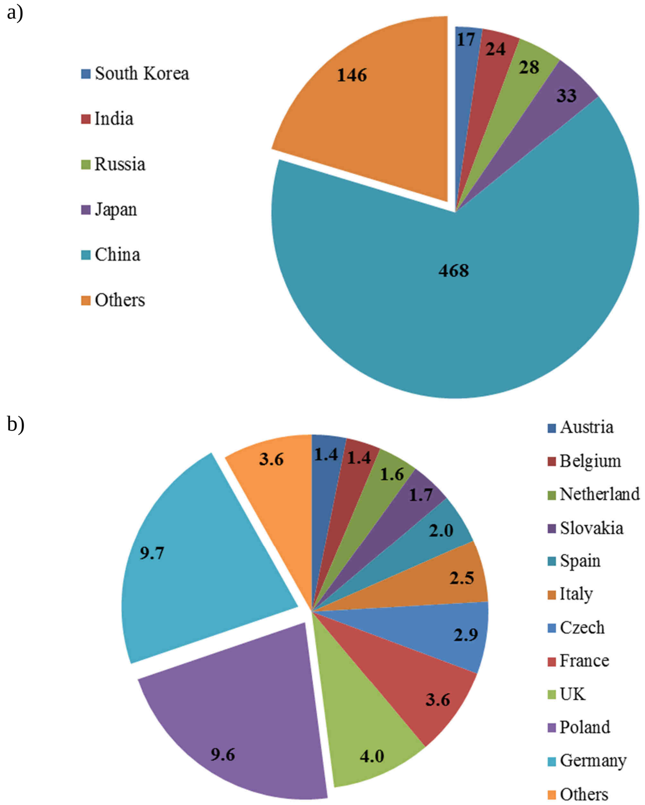

Fig. 3. World (a) and EU (b) production of coke [Tg] in selected countries in 2015

Coke oven plant operation

Coke oven plants are complex technological plants, which comprise of different technological sites, at which coal preparation, coking and coal derivatives recovery and upgrading occurs. The scheme of a coke oven plant is presented in Figure 4.

The coal-to-coke transformation starts from the transfer of heat from the heated brick walls into the coal charge. From about 375 to 475°C, the coal decomposes to form plastic layers near each wall. At about 475 to 600°C, there is a marked evolution of tars and aromatic hydrocarbon compounds, followed by re-solidification of the plastic mass into semi-coke. At 600 to 1100°C, the coke stabilization phase begins. This is characterized by contraction of coke mass, structural development of coke and final hydrogen evolution. During the plastic stage, the plastic layers move from each wall towards the centre of the oven trapping the liberated gas and creating gas pressure build up, which is transferred to the heating wall. Once the plastic layers have met at the centre of the oven, the entire mass has been carbonized. The incandescent coke mass is pushed from the oven and is wet or dry quenched, while the raw coke oven gas is collected and directed to further processing [8, 9]. During the coking process, except for coke, there is a range of other products (coal-derivatives) also obtained, and they are mostly recovered during gas processing [10-12]. The share of particular product in the overall production cycle per 1 Mg of coal can be established at:

- coke - 70-80%
- tar - 2.5-4.5%
- pyrogenetic water - 3-5%
- ammonia - up to 0.4%
- BTX (benzene, toluene, xylene) - up to 1.3%
- clean coke oven gas - 12-18%

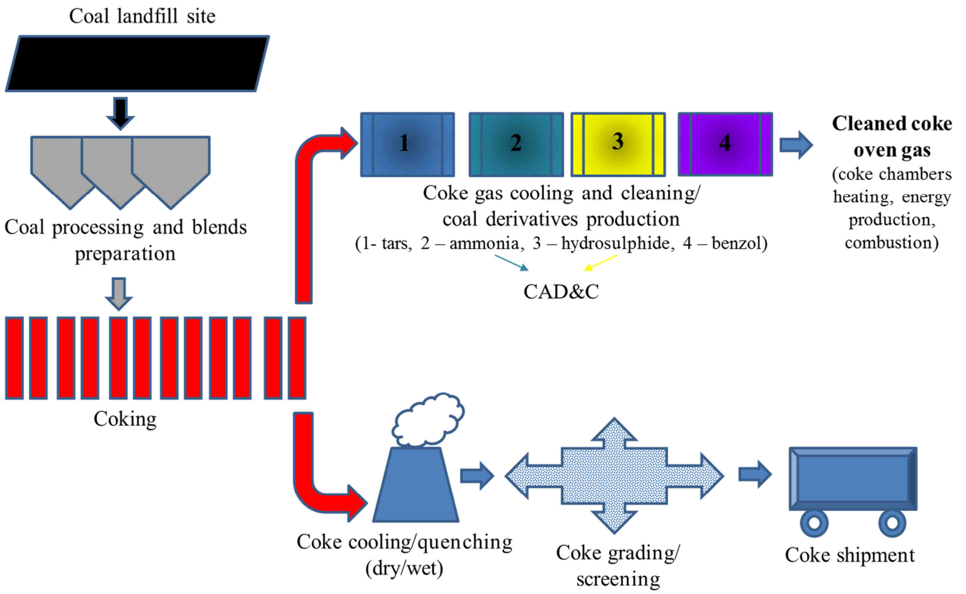

Fig. 4. The scheme of coke oven plant

Coke oven wastewater formation

The processing of coke oven gas and the recovery of coal derivatives results in the formation of highly contaminated liquor which, after separation of tars and ammonia, becomes so called coke oven wastewater. The liquor is formed at coke oven gas cooling stage (gas cooling/condensation unit), at which tars, water vapour and other substances present in the gas condensate or are partially washed out from the gas. The liquor is firstly directed to tars separation unit, at which two major streams are formed: organic stream (tars) and aqueous phase. The latter phase can be involved in further gas treatment for removal of ammonia and hydrogen sulphide by means of scrubbing. However, the amount of initially formed liquid always exceeds the requirement of scrubbing units. In such a case, over amount of liquid is directed to ammonia stripping and the remaining stream is deposited to coke oven plant [13-16]. The formation of coke oven wastewater at a plant is shown in Figure 5.

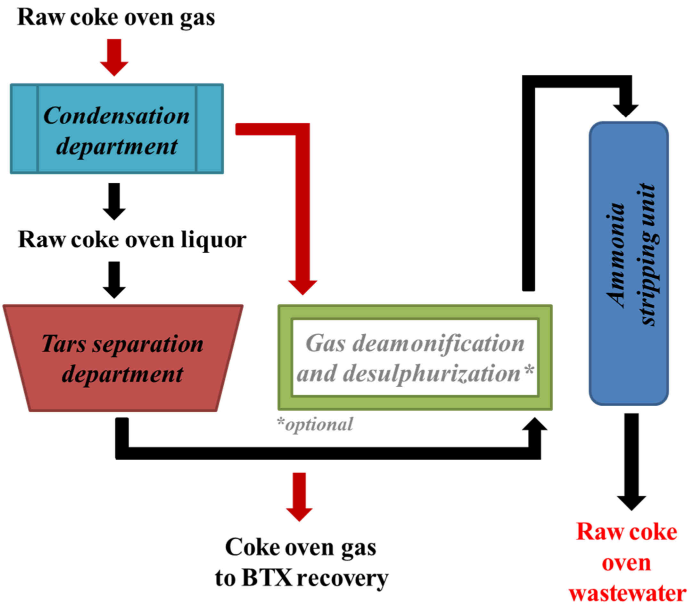

Fig. 5. The formation of coke oven wastewater at a plant

Coke oven wastewater characteristic and treatment

Wastewater produced at coke oven plants, contains toxic xenobiotics, phenols and their derivatives (pyrocatechol, quinone, pyrogallol), as well as ammonia, thiocyanates and cyanides. Typical pollutants concentration may reach up to 1200 mg/dm^3 of phenol and 20 mg/dm^3 of cyanides, respectively [17-19]. A typical composition of coke oven raw wastewaters is shown in Table 1.

Table 1

Typical composition of raw coke oven wastewater

Parameter	**Unit**	**Concentration**
pH	[-]	7-9.5
Specific conductivity	[µS/cm]	5000-12 500
COD	[mg O_2/dm^3]	2400-4200
BOD_5	[mg O_2/dm^3]	500-1500
Tars	[mg/dm^3]	5-150
Sulphides	[mg/dm^3]	10-50
Cyanides	[mg/dm^3]	5-20
Thiocyanates	[mg/dm^3]	50-420
Phenols	[mg/dm^3]	150-1200
Ammonia	[mg/dm^3]	120-790
Chlorides	[mg/dm^3]	2500-3500
Sulphates	[mg/dm^3]	900-1200

Per every Mg of coke 0.6 to 1.6 m^3 of wastewater is generated. It means that ca. 75·10^7 m^3 of coke oven wastewater is annually generated at worldwide coke oven plants (in Europe it is ca. 9.2·10^7 m^3, in Poland ca. 1·10^7 m^3) and it will continue to increase.

The removal of pollutants from coke oven wastewaters is a significant issue due to the environmental impact of these compounds. Especially cyanides and thiocyanates represent an important problem in wastewater treatment plants, due to their toxic properties, including reduction of enzymatic activity of unicellular organisms, such as the typical bacteria inhabiting in the activated sludge. The technological cycle of coke oven wastewater treatment is based on the conventional arrangement, i.e. physical separation of larger solids by means of grids and/or grates, chemical coagulation for removal of suspensions and precipitation of inorganic contaminants and biological nitrification/denitrification systems for ammonia and soluble (DOC) organics elimination (Fig. 6). The purified wastewater, after the treatment process, can be managed by means of its use to wet coke quenching or deposition to the environment [20-22].

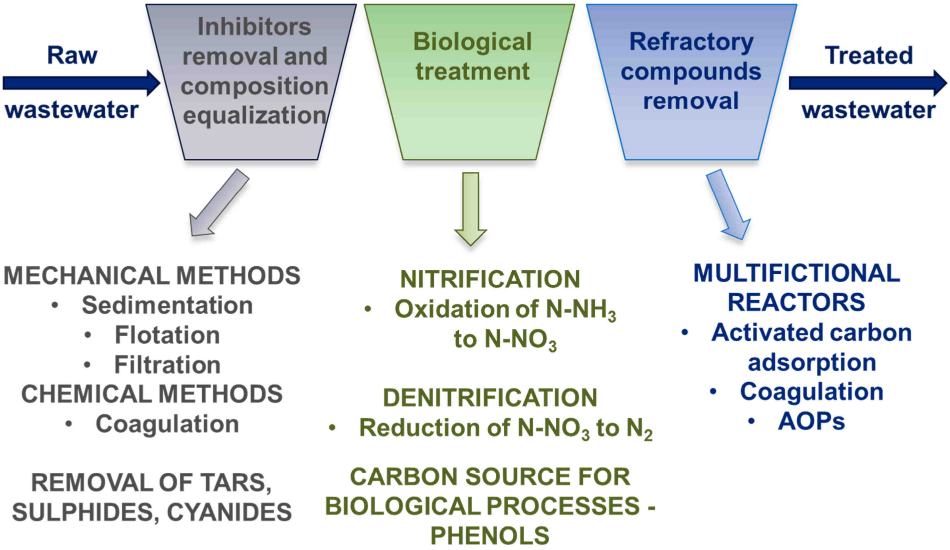

Fig. 6. The arrangement of typical coke oven wastewater treatment plant

Despite the fact, that the coke oven wastewater treatment process is the complex operation it is often not enough sufficient to remove all the contaminants present in the treated stream and to achieve the limits established in various regulations (regulations on quality of wastewater deposited to the environment, industrial wastewater standards, etc.). The most problematic treatment operation is connected with the efficient removal of cyanides. They appear in the raw wastewater as a simple CN$^-$ ions and their removal should be obtained during chemical coagulation. However, the efficiency of traditional process is poor, especially in the case of high load of the stream with dispersed organic contaminants (tars), hence it requires the addition of high amounts of chemicals. The insufficient removal of cyanides during chemical treatment stages is highly undesired, especially considering proceeding biological processes. Cyanides, as well as sulphides, are known to be toxic to activated sludge microorganisms, and their presence in the influent to biological treatment stage results in the inhibition of the process and its improper run. Additionally, standards on cyanides content in coke oven wastewater after treatment are very sharp and the permissible levels are usually established below 0.1 mg/dm^3 for free form of the compound and 5 mg/dm^3 for its complexes [23-25].

Chemical coagulants, which are used for dispersed tars, cyanides and sulphides removal, comprise of metal ion, which is responsible for the coagulation process performance, and inorganic ion support (usually chloride Cl^- or sulphate SO_4^{2-}). If the coke oven wastewater treatment influent contains high amount of tars, cyanides and sulphides, the efficient run of coagulation requires the addition of significant amounts of chemicals. Hence, the excess of inorganic ions, the amount of which is already quite high in the raw stream, is introduced to the wastewater. The high salinity of purified wastewater possesses many disadvantages considering further stream management methods. If the purified wastewater is dedicated to wet quenching of coke, the presence of inorganic ions, especially chlorides, may seriously affect the quality of the final product. On the other hand, the regulations on purified industrial wastewater quality, which is deposited to the environment, limit the maximum content of salts at the level of 1500 mg/dm^3 [26, 27].

The water/wastewater management of coke oven plant do not only face the efficient treatment and utilization of wastewater, but also need to assure huge amount of properly treated water dedicated to various technological purposes (heating/cooling systems, steam generators, wet gas cleaning, etc.). Hence, there exists a high demand for fresh water, which need to be in-taken either from the municipal water network or from natural sources (surface or ground water). Depending on the further destination, the water needs to be softened or completely demineralized, what requires the use of sophisticated treatment techniques and results in generation of additional waste streams (e.g. effluent from washing of ionites). The most favourable solution would be the reclamation of technological grade water from the wastewater stream [28-30].

Summary and conclusions

In the article, the worldwide coke production review, discussion on coke oven gas cleaning and coke oven wastewater formation and treatment techniques has been made. It clearly indicated a list of issues related with the proper treatment and utilization of coke oven wastewater, i.e.:

- to improve the removal of cyanides,
- to enhance the performance of biological treatment stage,
- to decrease the load of harmless substances (e.g. salts),
- to limit the need of introduction of additional unit operation,
- to enable the recovery of technological water from the purified stream,
- to apply relatively simple solutions,
- to propose modifications and supporting methods for existing techniques.

The above notes were used to formulate the main objectives of INNOWATREAT project (The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies), the main goal of which is to develop the novel system for coke oven wastewater treatment based on clean technologies, including enhanced flotation, membrane filtration and electrocoagulation, suitable to be applied at both, future and currently operate coke oven wastewater treatment plant. The project should bring many benefits considering both, cokemaking operations and environmental protection areas.

Acknowledgements

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ŚCIEKI KOKSOWNICZE - MIEJSCA POWSTAWANIA, SPOSOBY OCZYSZCZANIA I METODY UTYLIZACJI - PRZEGLĄD LITERATURY

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Abstrakt: Proces koksowania jest nieodłącznie połączony z powstawaniem silnie zanieczyszczonych ścieków, które wymagają odpowiednich metod oczyszczania i utylizacji. Ścieki te definiuje się jako mieszaninę wód technologicznych powstających w procesie oczyszczania i produkcji produktów węglopochodnych z gazu koksowniczego oraz ścieków sanitarnych powstających na koksowni. Ze względu na skład i specyfikę zanieczyszczeń występujących w ściekach koksowniczych ich oczyszczanie wymaga zastosowania fizycznych, chemicznych oraz biologicznych procesów, po których często stosuje się dodatkowe procesy doczyszczania. W zależności od dalszego wykorzystania (odprowadzenie do środowiska lub uzupełnianie obiegu mokrego gaszenia koksu) różne rodzaje zanieczyszczeń uznaje się jako priorytetowe dla zastosowanego systemu oczyszczania. W niniejszym artykule przedstawiono przegląd literatury dotyczącej formowania, właściwości, oczyszczania i zagospodarowania ścieków koksowniczych ze szczególnym uwzględnieniem stosowanych metod usuwania poszczególnych zanieczyszczeń oraz wskazaniem zagadnień problematycznych obserwowanych w obecnie pracujących oczyszczalniach.

Słowa kluczowe: powstawanie ścieków koksowniczych, oczyszczanie ścieków koksowniczych, charakterystyka ścieków koksowniczych, utylizacja ścieków koksowniczych

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THE SYNTHESIS OF ZEOLITES FROM SEWAGE SLUDGE ASH

SYNTEZA ZEOLITÓW Z POPIOŁÓW Z OSADÓW ŚCIEKOWYCH

Abstract: The chemical composition of sewage sludge ash is similar to the chemical composition of substrates used for the synthesis of zeolites. The study shows the results of sewage sludge ash zeolitization with a fusion method. The research on sewage sludge ash before and after the process of zeolitization included the identification of a phase composition (XRD method) as well as the evaluation of both grain structure change (SEM method) and the cation exchange capacity (a method with the use of ammonium acetate). After zeolitization, sewage sludge ash contained hydroxysodalite, zeolite X and hydroxycancrinite. It was stated that zeolitization caused a positive increase of the cation exchange capacity.

Keywords: sewage sludge ash, zeolitization, hydroxysodalite, hydroxycancrinite, zeolite X, cation exchange capacity

Introduction

Utilization of municipal sewage sludge ash is an important issue in the current situation of the increase of the amount of incinerated sewage sludge [1, 2]. There are known methods of sewage sludge ash utilization in the production of lightweight aggregates [3, 4], bricks [5], mortars [6] and concrete [7]. A wide range of applications of sewage sludge ash in the production of building materials is the consequence of its chemical composition. Main components of sewage sludge ash are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and P_2O_5 [8].

Zeolites are hydrated alumina silicates. The structures of zeolites consists of primary building blocks of inorganic tetrahedrons of silicon and alumina oxides. These atoms are strongly bonded together via oxygen bridges to form well-defined channels and cavities [9]. In the tetrahedral framework of synthetic zeolites other ions can also be found. Synthetic zeolites are obtained mainly under hydrothermal conditions with the use of various silica carriers in the presence of alkaline solutions [10]. For the synthesis of zeolites, coal fly ash [11] and paper sludge ash [12] can be used. The effect of the synthesis of zeolites depends among others on the activation temperature, the crystallization temperature, the crystallization time and the ratio of ash to sodium hydroxide. Besides, the ratio of Si:Al determines the formation of a particular type of zeolite [13, 14]. Due to zeolite properties such as high ion exchange, catalysis, adsorption and hydrothermal stability, they are widely used in environmental engineering, construction industry, refinery industry and agriculture [15-18].

The aim of the study was the verification of the thesis: the source of silica for the synthesis of zeolites can be sewage sludge ash. The research also covered the evaluation of the influence of zeolitization parameters on the ion-exchange properties of products.

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Material and methods

In this study, sewage sludge ash was obtained as a result of sewage sludge combustion in a laboratory furnace. The sewage sludge used in the study was taken from a municipal wastewater treatment plant in Sitkowka-Nowiny near Kielce. The sewage sludge was dried in a laboratory drier at the temperature of 105°C within 24 hours. Then, it was crushed in a mortar to a fraction < 125 µm. The sewage sludge was incinerated at the temperature of 980°C within 11 minutes. After the combustion, the sample remained in the furnace until it cooled down to the temperature of 20°C.

The chemical compositions of sewage sludge and sewage sludge ash were determined by using the X-ray fluorescence spectroscopy. Phase analysis of sewage sludge ash and sewage sludge ash after the zeolitization was performed with X-ray diffraction (XRD). The structure of the synthesized materials was observed by the scanning electron microscopy (SEM). The cation exchange capacity (CEC) was determined by a method with the use of ammonium acetate [19]. The concentration of ammonium in solutions was determined by the ion chromatograph.

Zeolitization of sewage sludge ash

Sewage sludge ash particles in the amount of 10 g were mixed and ground with granular NaOH to obtain a homogeneous mixture. The mixture was heated in an laboratory furnace at the temperature of 550°C for 1 hour. Different ratios of sewage sludge ash to NaOH samples were used to explore the effect of this parameter on zeolitization.

Table 1

Experimental conditions of sewage sludge ash zeolitization

Sample	**SSA:NaOH**	**Activation temperature**	**Crystallization temperature**	
			Time 6 h	**Time 72 h**
	[g/g]	**[°C]**	**[°C]**	**[°C]**
S1	1:1.4	60	60	-
S2	1:1.4	60	90	-
S3	1:1.4	90	60	-
S4	1:1.4	90	90	-
S5	1:1.4	60	-	60
S6	1:1.4	60	-	90
S7	1:1.4	90	-	60
S8	1:1.4	90	-	90
S9	1:1.8	60	60	-
S10	1:1.8	60	90	-
S11	1:1.8	90	60	-
S12	1:1.8	90	90	-
S13	1:1.8	60	-	60
S14	1:1.8	60	-	90
S15	1:1.8	90	-	60
S16	1:1.8	90	-	90

The sintered mixture was ground and mixed with distilled water (the applied concentration 3 N NaOH), followed by an aging process with an agitation in a shaking water bath at given temperatures of 60 and 90°C respectively. Then the mixture was crystallized under static conditions at the given temperature. After the completion of the crystallization, the solid product was washed with distilled water until the pH of the solution reached 10.0, then dried at 105°C for 10 hours. The synthesis conditions for each sample are shown in Table 1.

Results and discussion

Table 2 shows the characteristics of sewage sludge and sewage sludge ash. Sewage sludge ash has a high-silica content because of the SiO_2 to Al_2O_3 ratio of 3.74.

Table 2

Characteristics of sewage sludge and sewage sludge ash

Parameter	Units	Sewage sludge	Sewage sludge ash
pH	-	7.50	-
moisture	[%]	72.60	-
SiO_2	[%]	8.81	26.10
Al_2O_3	[%]	2.11	6.98
Fe_2O_3	[%]	3.74	12.40
CaO	[%]	5.66	18.50
MgO	[%]	1.42	4.56
SO_3	[%]	0.01	0.57
K_2O	[%]	0.58	1.98
Na_2O	[%]	0.16	0.60
P_2O_5	[%]	7.06	25.30
TiO_2	[%]	0.32	0.98
Mn_2O_3	[%]	0.03	0.11
SrO	[%]	0.02	0.06
ZnO	[%]	0.03	0.35
BaO	[%]	0.04	0,12
CuO	[%]	0.02	0.07
TOC	[% m/m]*	33.69	0.03

* a percentage by mass

Sewage sludge ash contains the following phases: amorphous substance - 13.61% m/m (a percentage by mass), quartz - 15.44% m/m, potassium feldspar - 4.96% m/m, whitlockite - 34.19% m/m, hematite - 10.76% m/m, stanfieldite - 13.05% m/m, tridymite - 7.99% m/m.

The XRD diffractograms of samples are presented in Figures 1 and 2. Sample S1 is defined by the absence of zeolites while the obtained phase was exclusively apatite. Samples S2-S4 are characterized by the presence of apatite and hydroxysodalite. They were subjected to a higher temperature of activation and/or crystallization in comparison to samples S1.

Hydroxysodalite is made of a cubic array of β-cages and exhibits a similar structure of sodalite [20]. The pore size of hydoxysodalite is smaller than of the zeolites with an eight membered ring aperture, e.g. NaA zeolite. Such a feature makes them an interesting material for the separation of small molecules like H_2 from liquid mixtures [21]. The structures of hydroxysodalite containing water can be dewatered. However, when the water molecule of the hydroxy-group leaves the sodalite framework at the temperature of above 600-700°C, the structure collapses. This process is irreversible and the resulting powder can no longer adsorb water. Therefore, hydroxysodalite is not thermally stable [22].

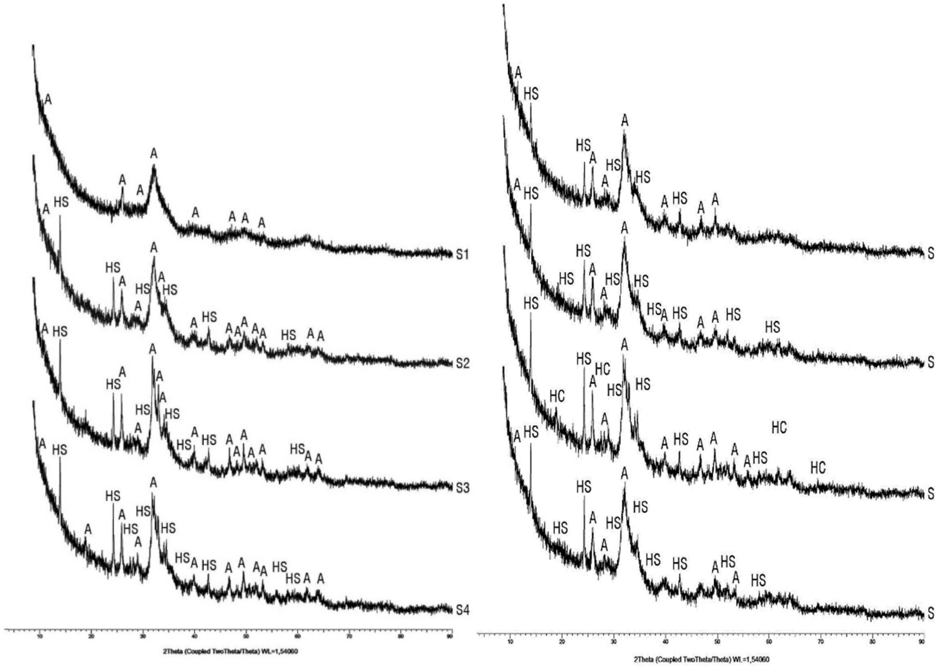

Fig. 1. XRD of sewage sludge ash after zeolitization by 6-hour crystallization

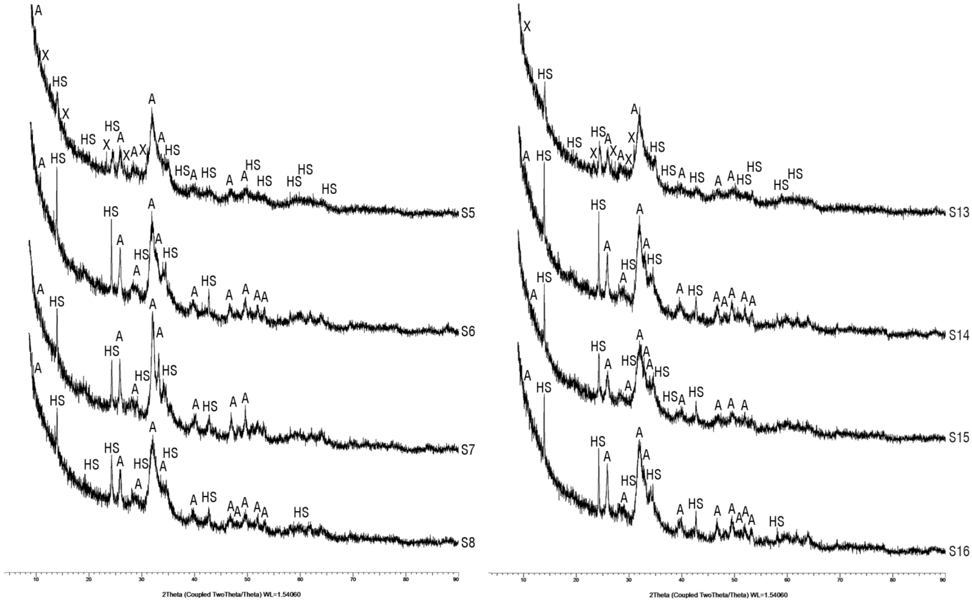

Fig. 2. XRD of sewage sludge ash after zeolitization by 72-hour crystallization

Zeolite X, hydroxysodalite and apatite were present in samples S5, that is in the samples of a 72-hour crystallization time and the SSA:NAOH ratio of 1:1,4. Zeolite X is a member of the faujasite group. Its structure is made up of a framework of 4-, 6- and 12-membered rings of SiO_4 and AlO_4 tetrahedra [23].

Zeolite X is the most difficult to prepare in high purity. This could be due to the thermodynamically metastable characteristics of highly porous faujasite [24]. Furthermore, zeolite X has a large pore size (7.3 Å) and a high CEC (500 meq/100 g) which make this zeolite an interesting molecular sieve and a high-cation exchange material [25].

Samples S6, S7 and S8 are characterized by peaks of hydroxysodalite and apatite, similarly as samples S9, S10, S12, S14, S15 and S16. Whereas samples S11 is defined by the presence of hydroxycancrinite. In samples S13, peaks typical for zeolite X, hydroxysodalite and apatite were identified.

Figure 3 shows SEM of sewage sludge ash. The structure of sewage sludge ash was non-porous.

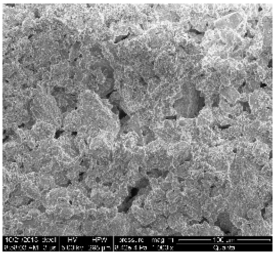

Fig. 3. SEM of sewage sludge ash, magn. 1000x

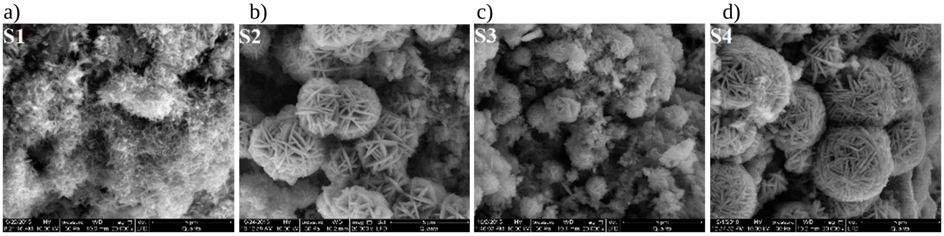

Fig. 4. SEM of sewage sludge ash after zeolitization by 6-hour crystallization and SSA:NaOH ratio of 1.0:1.4, magn. 20,000x

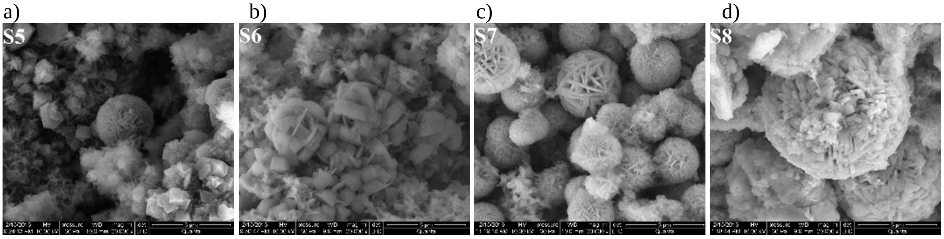

Fig. 5. SEM of sewage sludge ash after zeolitization by 72-hour crystallization and SSA:NaOH ratio of 1.0:1.4, magn. 20,000x

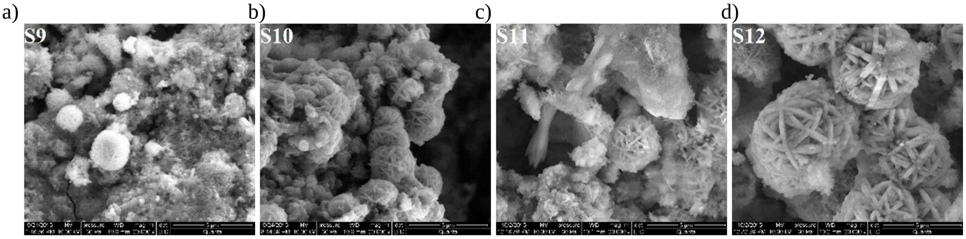

Fig. 6. SEM of sewage sludge ash after zeolitization by 6-hour crystallization and SSA:NaOH ratio of 1.0:1.8, magn. 20,000x

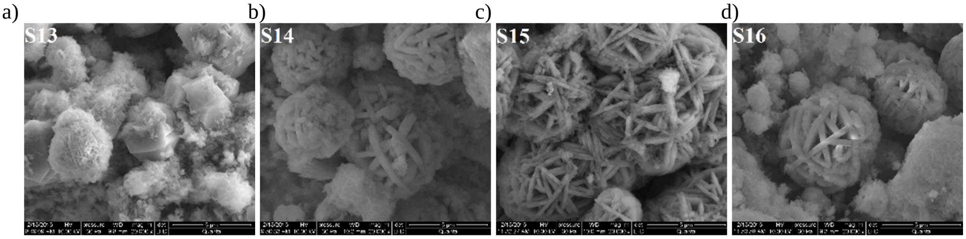

Fig. 7. SEM of sewage sludge ash after zeolitization by 72-hour crystallization and SSA:NaOH ratio of 1.0:1.8, magn. 20,000x

Figures 4-7 show the SEM images of the particles formed in this study. Figures 4b-d and Figures 5-7 present spherical shapes which correspond to hydoxysodalite. Figure 6c illustrates structures of long and sharp shapes characteristic for hydroxycancrinite. Figure 5a and Figure 7a demonstrate the octahedral morphology typical of zeolite X. Generally, the SEM images indicated that hydrothermal reactions during the process of zeolitization significantly changed the structure of samples.

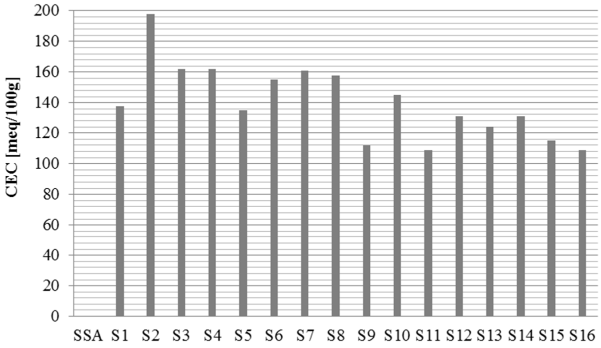

Fig. 8. CEC of sewage sludge ash and samples after zeolitization

The CEC results of sewage sludge ash and sewage sludge ash after zeolitization are presented in Figure 8. The CEC values of samples after zeolitization were within the range of 109.2-197.6 meq/100 g. Thus, the CEC values were higher in comparison to sewage sludge ash which was not subjected to modifications and lower than the values of commercial zeolites. The CEC values of commercial zeolites were within the range of 200-300 meq/100 g or even 900 meq/100 g [26, 27]. Moreover, the CEC values of tested samples did not depend on the parameters of the zeolitization process.

Conclusions

The study demonstrated the possibility of using sewage sludge ash for the synthesis of zeolites with a fusion method. Zeolite X was obtained for the SSA:NaOH ratio of 1:1.4 and 1:1.8. Other optimal parameters of the synthesis of zeolite X were identical for both samples, i.e. the activation and crystallization temperature of 60°C and the crystallization time of 72 hours.

The obtained zeolites can be used for the removal of contaminants from sewage.

The research proved that it is not easy to obtain only one type of zeolite from wastes. On the basis of the obtained test results, further work will be continued in order to improve the quality of the synthesized product.

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SYNTEZA ZEOLITÓW Z POPIOŁÓW Z OSADÓW ŚCIEKOWYCH

Wydział Inżynierii Środowiska, Geomatyki i Energetyki, Politechnika Świętokrzyska w Kielcach

Abstrakt: Skład chemiczny popiołów z osadów ściekowych jest podobny do składu chemicznego substratów stosowanych do syntezy zeolitów. W pracy przedstawiono wyniki zeolityzacji popiołów z osadów ściekowych metodą fuzji. Badania popiołów z osadów ściekowych przed oraz po procesie zeolityzacji obejmowały identyfikację składu fazowego (metoda XRD) oraz ocenę zmiany struktury ziaren (metoda SEM) i pojemności wymiany kationowej (metoda z wykorzystaniem octanu amonu). W popiołach z osadów ściekowych podanych zeolityzacji zidentyfikowano hydroksy sodalit, zeolit X oraz hydroksy kankrynit. Stwierdzono, że zeolityzacja spowodowała korzystny wzrost pojemności wymiany kationowej.

Słowa kluczowe: popiół z osadów ściekowych, zeolityzacja, hydroksy sodalit, hydroksy kankrynit, zeolit X, pojemność wymiany kationowej

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ECOTOXICITY STUDIES OF E-LIQUIDS FOR E-CIGARETTES

BADANIA NAD EKOTOKSYCZNOŚCIĄ E-PŁYNÓW DO E-PAPIEROSÓW

Abstract: E-cigarette has gained popularity as a "healthier" alternative to receiving nicotine, which reduces the side effects of smoking traditional cigarettes. Consequently, the question arose how solutions for filling the electronic cigarettes (e-liquids) impact on the environment. They contain, among others, nicotine, propylene glycol and/or glycerin and flavorings. The aim of this study was to evaluate the impact and toxicity degree of selected e-liquids on microorganisms come from two different aquatic ecosystems. Studies were conducted using 96-well microtiter plates where a medium (peptone from soybean) containing the tetrazolium hydrochloride and selected for testing e-liquids with the nicotine concentration gradient were applied. An inoculum was the water from the Brynica River and an effluent was from a waste water treatment plant. The results were evaluated after two days incubation at 30°C. As a measure of the ecotoxicity degree of tested samples used the value of microbial toxic concentration (*MTC*) which was determined using the MARA® procedure (NCBI, Scotland). All tested e-liquids triggered off an inhibition of microorganism growth only after two or eightfold dilution. It was found that obtained *MTC* values were slightly varied for base components and individual e-liquids.The amount of nicotine in the e-liquids had no influence on the microorganisms growth.To a greater extent, only some flavorings might have had an impact on microorganisms.

Keywords: ecotoxicity, MARA, e-cigarettes, e-liquids, microorganism

Introduction

Electronic cigarettes were designed to provide nicotine vapor without toxic compounds, which are present in tobacco smoke [1] and mimic behavior associated with smoking. They gained popularity as a less harmful alternative to conventional cigarettes.

Electronic cigarettes use heat to transform e-liquids into a vapor inhaled by a user. E-liquids mainly consist of base components - propylene glycol and glycerin, nicotine and flavorings [2]. Propylene glycol and glycerin are mostly combined in a ratio of 4:1 or 7:3, respectively. They can also contain polyethylene glycol (PEG) or diethylene glycol (DEG) as a substitute of base components. The maximum concentration of nicotine permitted currently in Poland is 20 mg/cm^3 [3], but "free-of-nicotine" e-liquids are also available. Other used additives are preservatives (e.g. ethanol, up to 5%) and substances regulating viscosity (e.g. water, ethanol). Generally, e-liquids differ in various flavorings, for example, vanilla, fruity or tobacco flavor and a percentage composition of main ingredients [4]. The appearance on the market of new products such as e-liquids used in e-cigarettes arises the questions how they influence a human health, as well as an environment.

There are many available tests evaluate an ecotoxicity of test agent or substance to microorganisms in different taxonomic groups. Microbiological tests are useful in an assessment of an aquatic environment pollution degree and introduction effects of a specific pollutant in the biosphere. In a case of samples collected from aquatic environment (water or sediments), a presence of a harmful or toxic substance is observed as a vital functions and activity inhibition of test microorganisms. This phenomenon displays

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inter alia as a growth speed (cells or biomass), luminescence bacteria *Photobacterium phosphoreum* (*Vibrio fisheri*) or an activity of enzymes (ATPases, LDH dehydrogenases, nitrate reductase).

An example of bioecotoxicological test is MARA® test (Microbial Assay for Risk Assessment Test). This biotest is mainly a screening test in an assessment of surface waters (fresh, salty and salt water), ground waters, treated and untreated waste waters and leachate from landfills toxicity. As a multispecies toxicity test includes 10 different bacteria in taxonomic terms and yeast. These organisms are placed in a 96-well microtiter plate. In addition, a medium and a dye (2,3,5-triphenyltetrazolium chloride) are added to each well. The changes of the dye from colorless to red are observed only in healthy microorganisms by reduction reaction. Introduction of a toxic substance (in concentration gradient) to each microorganism strain may result in their growth inhibition and display as a lack of characteristic color of the reduced dye. After an incubation microtiter plate is scanned and resulted picture is analyzed using MARA® software.

In our study, we used a modified MARA® procedure [5] to evaluate ecotoxicity of 8 selected e-liquids, propylene glycol and glycerin. As a source of microorganisms, we used water from the Brynica River and an effluent from waste water treatment plant. This new approach enabled to gain preliminary information about influence e-liquids on natural ecosystem using fast and inexpensive method.

Materials and methods

Reagents

Eight kinds of commercially available e-liquids were selected for the study. The main selection criteria were as follows: 1) the products came from different manufacturers, 2) e-liquids had various nicotine concentration and 3) one manufacturer but e-liquids had different additives/flavorings. The characteristics of the e-liquids used in the experiments are presented in Table 1.

Table 1

The characteristics of the investigated e-liquids

Trade name of e-liquid	Manufacturer	Nicotine content [mg/cm^3]	Batch No.	Abbreviation in text
Coffee Gold	Volish, Poland	18	01/2014	VCG
Coffee	Mild, PRC	18	BOGE30032013	MK
Caffe Latte	Liqueen, PRC	18	PI05010014	LCL
German Hazelnut	Liqueen, PRC	18	PI05006014	LGH
Blackcurrant	Liqueen, PRC	11	AI-85/07/2013	LBC
New Zealand Peach	Liqueen, PRC	11	AI-85/04/2013	LNZ
Italian Cherry	Liqueen, PRC	11	AI-85/04/2013	LIC
Ice Mint	Liqueen, PRC	24	130217	LM

Propylene glycol (POCh, Poland, p.a. grade) and glycerin (POCH, Poland, p.a. grade) were used as a reference. Before ecotoxicity determination selected liquids, propylene glycol or glycerin was mixed with redistilled water in the ratio 1:1 (v/v). To estimate the e-liquids ecotoxicities to microorganisms present in the collected water samples, an aqueous medium containing peptone from soybean meal (2% w/v; Becton, Dickinson &

Co. San Jose, CA, US) and 2,3,5-triphenyltetrazolium chloride (TTC; 0.01% w/v, POCh, Poland, p.a. grade) was used.

Test microorganisms

In the research the following test microorganisms were used: unselected microorganisms took from the water stream of heavily polluted the Brynica River (Poland) and microorganisms presented in effluent from waste water treatment plant (WWTP) in Sosnowiec-Zagorze (Poland).

Assessment of toxicity of the investigated samples

To assess the ecotoxicity of investigated samples to microorganisms, the 96-well microtiter plates were used in experiments. Firstly, 0.15 cm^3 of growth medium (2% w/v peptone from soybean with 0.01% w/v TTC) was filtered with a sterile filter (Nalgene Syringe Filter, Sterile SFCA membrane, 0.2 μm, Thermo Scientific) and added to each well in rows A-F.

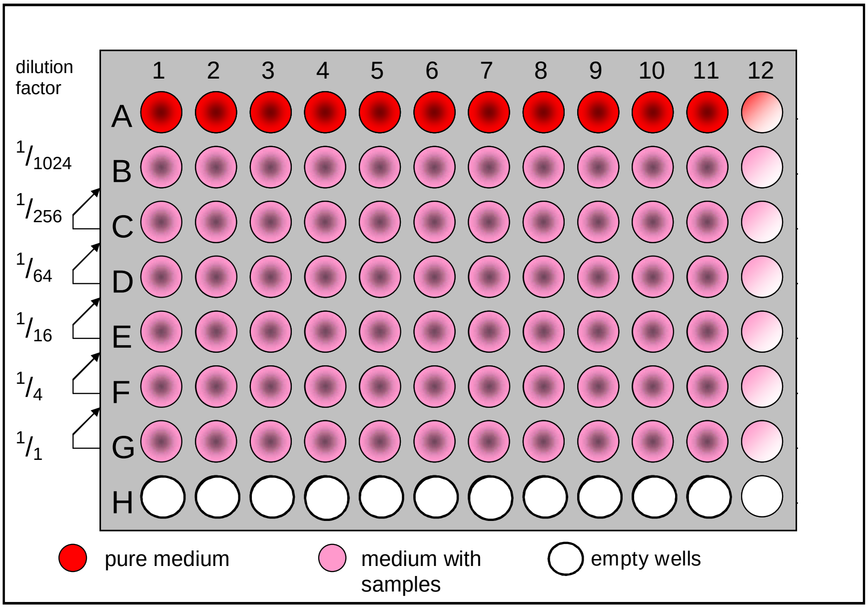

Fig. 1. Procedure of plate preparation

Immediately prior to starting an experiment solid peptone from soybean (2% w/v) and TTC (0.01% w/v) were added to redistilled water solution of selected liquid, propylene glycol or glycerin (samples). Thus prepared samples were also filtered with sterile filter and were added (0.2 cm^3) to each well in a row G. Then, 0.05 cm^3 of the solutions from each well of the row G were transferred to the corresponding wells in a row F. After mixing well contents (medium with sample), 0.05 cm^3 of the solutions from each well in the row F was transferred to wells in a row E. This procedure was repeated to a row B, generating subsequent sample dilutions. To retain a constant volume of the solutions in each well, 0.05 cm^3 of each well content of the row B was collected and discarded. The row A contained 0.15 cm^3 of sterile medium only (positive control). Prepared plates were inoculated with the 0.015 cm^3 of freshly collected water from the Brynica River or effluent from WWTP, except for solutions in the column number 12, which was the cleanliness control. The procedure of plate preparation is presented in Figure 1.

Every sample was repeated 11 times (one plate). Microtiter plates were incubated for 48 h at 30°C. The growth of test microorganisms was observed as a red pellet (*P*) in the wells. The TTC dye changed color (from colorless to red) due to the reduction reaction in viable cells. Thus intensity of pellet color was directly proportional to the growth degree of test microorganisms [6-9].

The minimum sample concentrations inducing visible the growth inhibition of each microorganism expressed as Microbial Toxic Concentration (*MTC*) were determined by the MARA®software (NCIMB Ltd, Scotland) as follows:

$$MTC = C_{min} \cdot d^{\left(P_{tot}/P_0\right)-1}$$

where C_{min} is the lowest concentration in the gradient, *d* is the dilution factor, P_0 is the pellet size in the control well and P_{tot} is the sum of the pellet sizes in all wells that were exposed to the concentration gradient of the samples solutions [10]. The changes on each plate after incubation time were recorded using a scanner (HP Scanjet G4050) with transmitted light. The scans were analyzed using the MARA® software, which calculated the percentage growth and growth inhibition of the microbes in each well relative to the control and the *MTC* values for test microorganisms.

Results and discussion

In this study, we examined the influence of selected e-liquids on unselected microorganisms presented in the Brynica River (Poland) and in the effluent from waste water treatment plant (Sosnowiec-Zagorze, Poland). Additionally, an antimicrobial activity of propylene glycol and glycerin (main ingredients of e-liquids) was investigated. Ecotoxicity degree was determined based on modified MARA procedure and *MTC* value. The highest sample concentration (e-liquid, propylene glycol or glycerin) was 500 g/dm^3. An illustrative test plate is presented in Figure 2.

A plot in Figure 3 shows a corresponding correlation $P_i = f(C_i)$, where P_i is a pellet size in a well with a sample, C_i is a sample concentration. The percentage microbial growth relative to control is marked on the right axis. The denoted EC_{50} value expresses the concentration of investigated e-liquid that causes 50% inhibition of microorganisms growth.

All results of carried out experiments (*MTC* values) are presented in Table 2 and Figure 4.

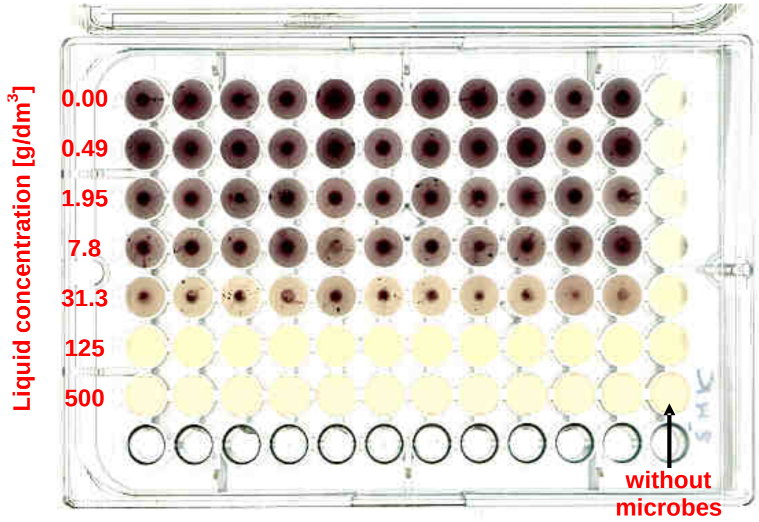

Fig. 2. Scan of the selected plate containing investigated e-liquid (MK) and inoculated with the effluent from WWTP (color intensity is proportional to growth of microorganisms)

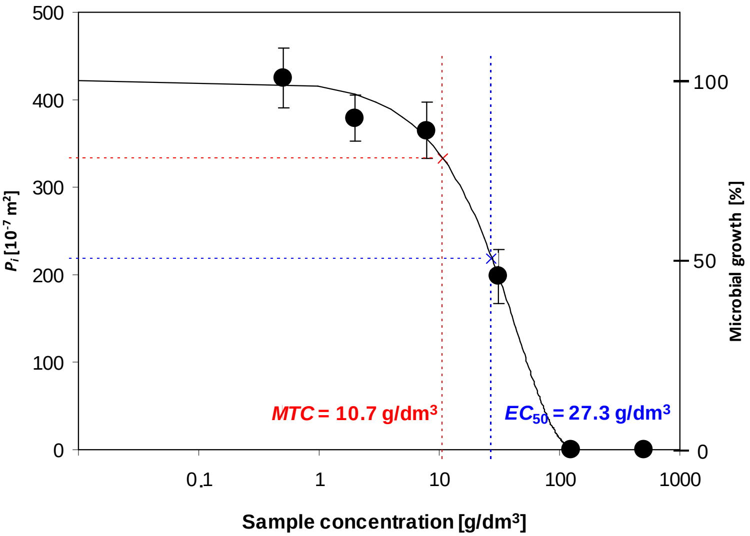

Fig. 3. Effect of the e-liquid concentration (MK) on the pellet size of test plate (left axis) and on percentage microbial growth (right axis) inoculated with the effluent from waste water treatment plant. *MTC* and EC_{50} values are marked on the plot

Table 2

The *MTC* values ± SD [g/dm^3] determined for samples in relation to test microorganisms

Sample	Water from the Brynica River	Effluent from the WWTP
Propylene glycol	31.6 ± 2.7	29.0 ± 5.7
Glycerin	48.8 ± 7.6	20.8 ± 7.4
VCG	37.2 ± 3.3	22.5 ± 6.1
MK*	27.5 ± 2.5	10.7 ± 3.2
LCL	36.4 ± 4.5	20.5 ± 6.9
LGH	34.6 ± 1.2	25.4 ± 3.7
LBC	56.1 ± 8.4	33.1 ± 1.2
LNZ	38.5 ± 4.2	31.7 ± 3.1
LIC	35.1 ± 1.4	32.4 ± 2.0
LM	32.0 ± 6.3	23.4 ± 1.5

* the most ecotoxic e-liquid (mean *MTC* values ± SD determined for this e-liquid were lower than values determined for propylene glycol and glycerin in all experiments)

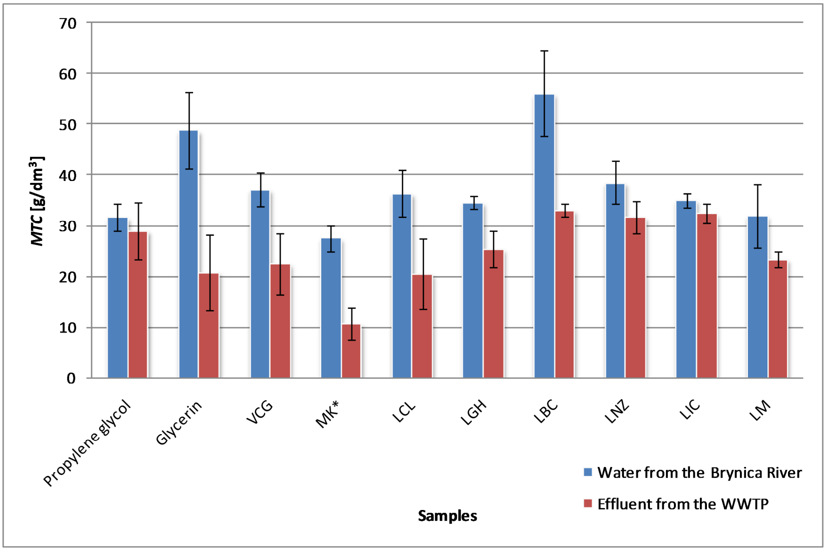

Fig. 4. Ecotoxicity of the investigated e-liquids relative to microorganisms from the inoculum selected for study

Obtained *MTC* values indicate that propylene glycol, glycerin, and selected e-liquids appear to inhibit microbial growth in both tested water samples used at a concentration > 50 g/dm^3. Such high concentrations of the investigated substances and e-liquids should not exhibit negative influence on microorganisms in the natural environment. Slightly higher *MTC* values were noted for the water from the Brynica River. Water from this river can be classified as highly contaminated, mainly industrial pollution, which may indicate its high electrical conductivity [11]. The above data suggest a greater resistance of microorganisms present in this water to the impurities.

The lowest *MTC* value, thus the highest ecotoxicity, was obtained for the coffee flavored e-liquid (MK). Due to the high average *MTC* values for the base components (propylene glycol and glycerin), their effect on growth inhibition of microorganisms can be probably eliminated. In addition, there was no correlation in the increase in nicotine concentration in e-liquid with the decrease of *MTC* values. Based on the above observations, it can be assumed that the greatest ecotoxicity of coffee flavoured e-liquid (MK) may be driven by the presence of flavors.

Conclusions

We found that propylene glycol and glycerin- e-liquid base components as well as selected e-liquids used in electronic cigarettes, inhibit the growth of microorganisms present in water samples, but only in the examined concentrations of > 50 g/dm^3. This ecotoxicity effect may be due to a rheological change of the medium. However, such high concentrations of investigated substances and e-liquids should not exhibit negative influence on microorganisms in the natural environment. Based on analysis of the *MTC* values, e-liquids are more ecotoxic than propylene glycol or glycerin. Furthermore, the ecotoxicity of e-liquids does not depend on the concentration of nicotine in e-liquid. Thus, it can be assumed that the flavors added to e-liquids are responsible for observing inhibition of microbial growth.

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BADANIA NAD EKOTOKSYCZNOŚCIĄ E-PŁYNÓW DO E-PAPIEROSÓW

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Abstrakt: E-papieros zyskał popularność jako „zdrowsza” alternatywa przyjmowania nikotyny, która ogranicza skutki uboczne palenia tradycyjnych papierosów. W związku z tym pojawiło się pytanie, jak wpływają na środowisko roztwory służące do napełniania e-papierosów (e-liquidy). Zawierają one m.in. nikotynę, propanodiol i/lub glicerynę oraz substancje smakowe. Celem pracy była ocena wpływu i stopnia toksyczności wybranych e-liquidów na mikroorganizmy pochodzące z dwóch różnych ekosystemów wodnych. Badania przeprowadzono z użyciem 96-dołkowych płytek mikrotitracyjnych, na których aplikowano pożywkę (pepton sojowy) zawierającą chlorowodorek tetrazoliny i gradient stężeń wytypowanych do badań e-liquidów. Inokulum stanowiła woda z rzeki Brynicy oraz efluent z oczyszczalni ścieków. Wyniki oceniano po inkubacji trwającej dwie doby w temperaturze 30°C. Jako miarę stopnia ekotoksyczności badanych próbek wykorzystano wartość mikrobiologicznego stężenia toksycznego (MTC), wyznaczanego za pomocą programu procedury MARA® (NCBI, Szkocja).Wszystkie badane e-liquidy powodowały inhibicję wzrostu mikroorganizmów jedynie po dwukrotnym lub ośmiokrotnym rozcieńczeniu. Stwierdzono, że uzyskane wartości MTC były zróżnicowane w niewielkim stopniu dla składników bazy i poszczególnych e-liquidów. Ilość nikotyny w e-liquidach nie miała wpływu na wzrost mikroorganizmów. W większym stopniu na mikroorganizmy mogły oddziaływać jedynie niektóre z dodatków smakowych.

Słowa kluczowe: ekotoksyczność, MARA, e-papierosy, e-płyny, mikroorganizmy

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Mateusz MUSZYŃSKI-HUHAJŁO[1] and Kamil JANIAK[1]

ACCURATE OXYGEN TRANSFER EFFICIENCY MEASUREMENTS BY OFF-GAS METHOD - TANK COVERAGE DILEMMA

POMIAR SPRAWNOŚCI TRANSFERU TLENU METODĄ OFF-GAS - PROBLEM STOPNIA POKRYCIA REAKTORA

Abstract: The off-gas method is one of two primary aeration efficiency examination methods. In off-gas method, exhaust air from aeration tank is collected by a floating hood and conveyed to a measurement module. In this part of the installation, gas flow is measured, collected air is dried, stripped of CO_2 and subsequently oxygen concentration is measured. The hood area is usually few square meters or even less and is a very small part of the aeration tank area. The main advantage of the off-gas method is that it offers measurement without disturbances to reactor routine work, which are necessary in the case of alternative, absorption method. Thereby, the off-gas method can be used in any circumstances and is free from uncertainty about the influence of reactor disturbances on the obtained results. However, a question remains about the number of measurement points required to obtain representative results for the whole reactor. According to The Environmental Protection Agency (EPA) guidelines, coverage of 2% of the tank area is sufficient, but this number seems insufficient. This article presents an analysis of the influence of tank coverage on the obtained oxygen transfer efficiency values. The presented analysis is based on real data.

Keywords: wastewater treatment, aeration, oxygen transfer efficiency, off-gas method

Introduction

Oxic biological treatment processes has been key element of modern wastewater treatment for decades and are used in every single activated sludge based wastewater treatment plant (WWTP). Optimization of wastewater aeration is very important as the process plays a vital role advanced nitrogen and phosphorus removal, while being also very energy-intensive. According to research reports [1], aeration process is responsible for around 50% of total electricity consumption in the wastewater treatment plant. Having such significant share in the energy balance of wastewater treatment, aeration process optimization has been the object of scientific research for a long time, especially due to the growing energy prices. Therefore, good understanding of the mechanisms involved in oxygen transfer from gaseous to liquid phase and in the subsequent role of oxygen in biochemical reactions seems vital. One of the basic indicators of aeration process quality is oxygen transfer efficiency (OTE, $\mathrm{g\,O_2{\cdot}Nm^{-3}{\cdot}m_{depth}^{-1}}$) which is the measure of oxygen transfer efficiency in process conditions.

While other measurement methods exist that allow the OTE calculation**,** the off-gas method, which consists in the analysis of the exhaust air from the reactor, proved to be particularly useful. It is the only method which allows taking measurements during regular operation of the aeration tank and hence allows the elimination of interference caused by deviating from normal operating conditions. Unfortunately, despite its obvious

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advantages, the method is not very popular worldwide; the team from Wroclaw University of Science and Technology is the only one in Poland to make use of it. This is probably due to the need to possess specialist measuring apparatus, which is of limited commercial availability. Another important reason is that taking measurements and analyzing the data requires skilled and experienced personnel.

Aim of work

Finding the average value of oxygen transfer efficiency in the aeration tank necessitates taking measurements in an adequate number of points on the aeration tank surface, which will translate into the area of the aeration tank covered with the hood capturing the exhaust air. According to the American Environmental Protection Agency guidelines [2] and to German ATV M 209E 1996 standard [3], coverage of 2% of tank area is sufficient to obtain reliable results that are needed to assess the aeration efficiency in an investigated system. However, some reports [4] indicate that detailed information on the condition of the aeration system can be provided only by measurements that would cover a larger area of the reactor. The influence of the number of measurement points on the accuracy of the results is not known either. This paper presents the analysis of the relationship between the number of measurement points, which corresponds to reactor's area covered by hood during the off-gas test and the quality of the obtained results, based on a measurement series performed with off-gas method in one of Polish municipal WWTPs.

Off-gas method - an outstanding method for the diagnostics of aeration systems

Wastewater aeration systems examinations which are performed with the off-gas method have unique features as compared to other available measurement methods. The measuring apparatus may be situated in practically any location on the reactor surface and this feature allows finding spatial variation of oxygen transfer efficiency (e.g. resulting from progressive biodegradation present in the sewage, as it passes through the plug flow reactor) as well as finding OTE time variation that results from varying wastewater composition (e.g. surfactants) and reactor loading [4-6]. Such information enables optimization of the aeration system by adapting the control system to reduce aeration at those locations where and those times when the process would be less effective, and to increase aeration intensity in more advantageous conditions, thus saving electric energy. As mentioned before, one of the indisputable advantages of the off-gas method is that it allows measurements without the need to interrupt normal operation of the reactor, as is the case with the competing method that consists in oxygen absorption. According to some research [7], flow velocity of the aerated medium has significant impact on the values of oxygen transfer, and this factor is extremely difficult to be included in calculations when a reactor is not operated normally. Another important advantage of the off-gas method is that it allows finding the localization of leaks in the air distribution system, which is situated at the bottom of the reactor, by identifying spots characterized by high exhaust air flow and low oxygen transfer [8].

The off-gas method was developed in 1983 in the United States [9]. The method is based on the fact that the exhaust air from the aeration tank is a good source of information on the oxic processes that occur inside the reactor. The exhaust air from the bioreactor has lower level of oxygen as compared to atmospheric air, because the oxygen is used by activated sludge in biochemical processes, and contains impurities that are the result of those processes, e.g. nitrogen oxides and dinitrogen monoxides, volatile organic compounds etc. It has been shown that information obtained from exhaust air composition may be effectively used to diagnose and control such biological processes as nitrification and to determine the amount of emitted gases that influence the condition of the atmosphere [10-15]. This technique has also been proven as a useful tool in plant energy usage optimization process as it can be used for aeration systems diagnosis [16-19]. In off-gas measurement apparatus, exhaust air is collected in an airtight hood floating on the surface of wastewater. The hood may have an area of up to several square meters. From the hood, the air is sent, via a duct, to a measurement module in which humidity is removed, air flow is measured, and oxygen and carbon dioxide levels are monitored. The module may be further equipped with practically any type of sensors (e.g. nitrogen oxide sensors) or the measured gases may be limited to oxygen only - in such case a CO_2 binding agent must be introduced into the installation directly upstream of the oxygen sensor. Figure 1 shows a schematic diagram of the off-gas method.

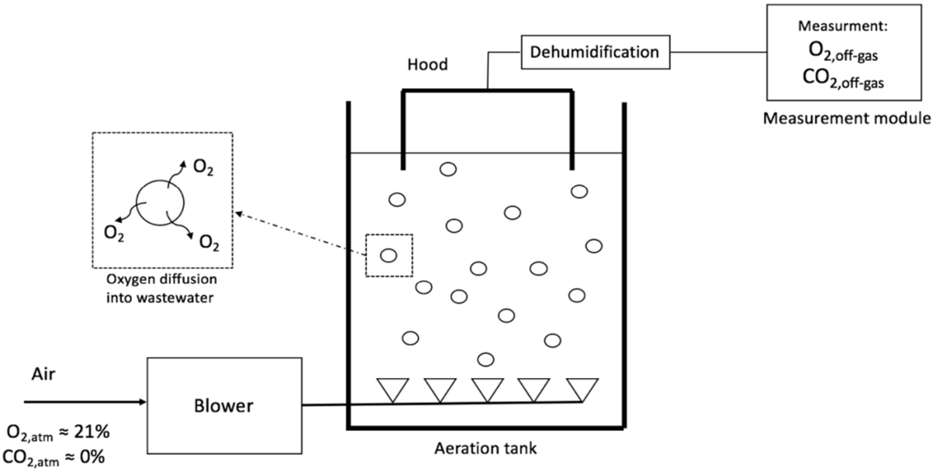

Fig. 1. Schematic diagram of oxygen transfer efficiency measurement using the off-gas method

Materials and methods

Description of the off-gas apparatus

Because solutions for off-gas measurement apparatus are commercially unavailable, the team from Wroclaw University of Science and Technology developed a series of measurement instruments in accordance with the guidelines provided by literature [2, 3]. The presented tests were performed with the third, upgraded development version of the apparatus (both the hood and the measurement module). This version did not contain some design flaws identified in previous measurements that could have some impact on the results. Figure 2 shows the hood and the measurement module used during the tests described in this paper.

The hood used in the apparatus had the area of 2 m^2 and its design allowed it to float on the surface of wastewater. During tests, the hood was fastened with ropes to prevent its movement on the reactor surface. The measurement module comprised a Testo 6641 flowmeter, which monitored the stream of off-gas air flow captured by the hood. The installation further comprised 2 sorption columns in which the analysed air was dried and the CO_2 in it was bound. The last stage comprised an oxygen concentration analyser in the form of an AMI 65/O_2 zirconium probe. Furthermore, Hach LDO® dissolved oxygen probes were located at suitable depths directly below the hood. The measurement error was calculated using total differential method on the basis of the data which were available on the accuracy of the equipment used. Apart from the earlier described parameters, measurement uncertainty in the off-gas method was calculated including measurement uncertainty for sewage depth and temperature. The calculated measurement uncertainty is $0.9\ \mathrm{g\,O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}$ and corresponds to a few percent of the measured value [20].

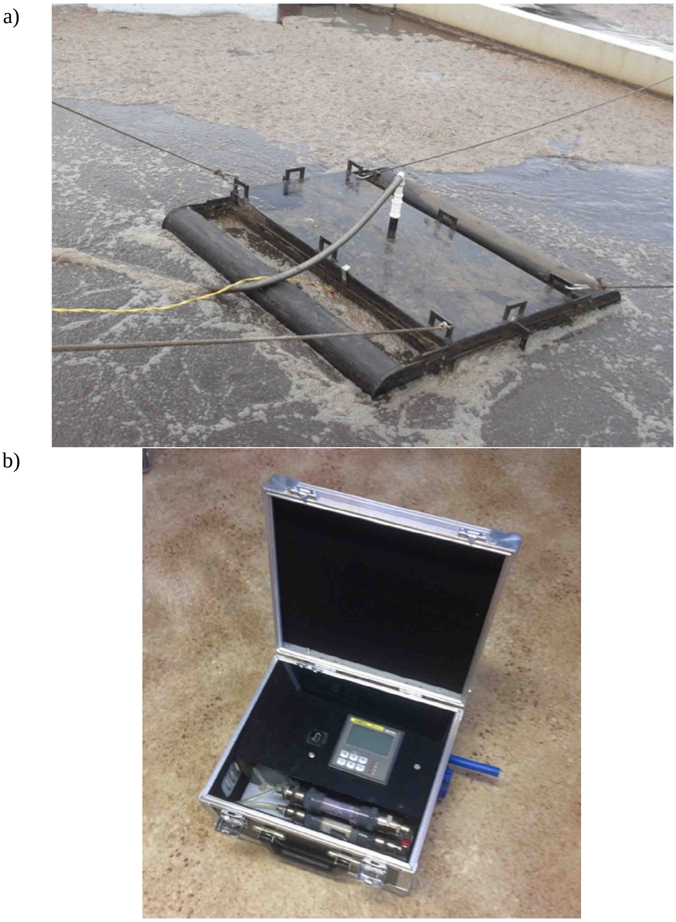

Fig. 2. Measurement hood (a) and measurement module (b) [20]

WWTP description

The tests were performed in one of Polish municipal wastewater treatment plants with population equivalent PE > 100 000. The sewage process line comprises 2 identical technological lines equipped with identical aerated CSTR bioreactors (BR I and BR II). Each chamber's volume is 6905 m^3 and the total area of the diffuser section in the chamber is 564 m^2. The tests were performed during normal, stable operation of the facility.

The measurement methodology

Prior to measurements, a virtual grid is established on the surface of the reactor to facilitate finding the coordinates of the measurement points. In the next step, a number of points (usually between ten and twenty measurements for aeration tanks) are randomly selected that will ensure reliable results for oxygen transfer efficiency measurement, i.e. a minimum of 2% coverage of the tank area. In this case, 24 measurements were performed in Biological Reactor I (BR I) and 33 measurements were performed in BR II, which translates into the coverage of 8.8 and 12.0% of the area of each of the tanks, respectively. Single measurement lasts for about 30 minutes, and after that time the apparatus is moved to the next point, according to the schedule. The data collected using this method allow finding spatial variation of oxygen transfer efficiency for the analyzed reactor. Due to the significant impact of time variation of oxygen transfer efficiency, all results were standardized against the parallel measurements of this variation performed with an identical apparatus with the hood secured in one measurement point.

Data preparation

The results gathered with the off-gas method were used to prepare an MS Excel spreadsheet that allows the user to randomly choose (sample) a selected value number from the set of oxygen transfer efficiency results for each chamber as in Monte Carlo method. The number of the results for each sampling corresponds to the selected percentage of the tank area with the hood area of 2 m^2. The sampling was performed for the numbers of measurement points that correspond to the tank area between 4 points (1.3% of the area) and 20 points (6.7% of the area) with an interval of 2 measurement points. The set of values that was obtained after each sampling served to calculate the average oxygen transfer efficiency in the reactor. This value was then recorded. After 30 sampling rounds were performed, the recorded data served to calculate the average for each variant, which was presented with maximum and minimum values and standard deviation for the created set. Each chamber was also described with a histogram that presented the accuracy of the results with 2% coverage of the tank area.

Results

Biological Reactor I (*BR I*)

Table 1 shows the results obtained from a simulation performed for the set of real measurement results of oxygen transfer efficiency in Biological Reactor I (BR I) that was tested in accordance with the methodology here presented. Figure 3 shows a histogram of average αFSOTE values obtained from 6 randomly selected measurement points (2.0% of the tank area).

Table 1

Simulation results for BR I

BR I						
-	**Number of measurement points**	**Tank coverage area**	**Average avSOTE** $[\mathrm{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$	**Standard deviation**	**Max avSOTE** $[\mathrm{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$	**Min avSOTE** $[\mathrm{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$
Variant	4	1.3%	20.71	1.45	24.60	18.60
	6	2.0%	20.44	1.44	23.20	17.80
	8	2.7%	20.95	0.80	23.20	19.70
	10	3.3%	20.54	0.82	22.60	19.30
	12	4.0%	20.5	0.67	21.90	19.10
	14	4.7%	20.56	0.56	21.30	19.40
	16	5.3%	20.30	0.46	21.20	19.50
	18	6.0%	20.58	0.35	21.10	19.60
	20	6.7%	20.54	0.30	21.00	19.70
Measurement results	24	8.8%	20.50	-	-	-

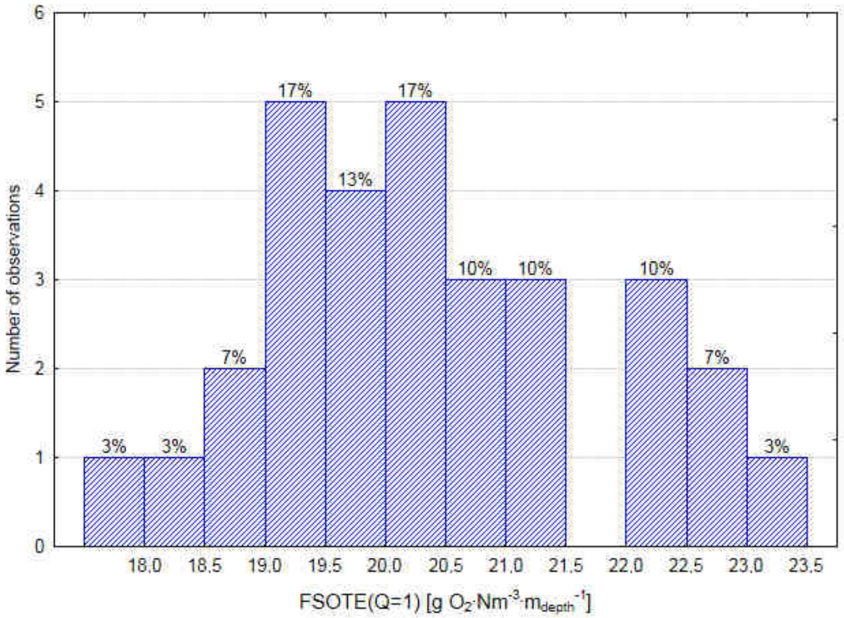

Fig. 3. Histogram of average αFSOTE for BR I with 2% hood coverage of the tank, obtained by randomly selecting measurement points

Biological Reactor II (*BR II*)

Table 2 shows the results obtained from a simulation performed for Biological Reactor II that was tested in accordance with the methodology here presented.

Table 2

Simulation results for BR II

BR II						
-	**Number of measurement points**	**Tank coverage area**	**Average avSOTE** $[\mathbf{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$	**Standard deviation**	**Max avSOTE** $[\mathbf{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$	**Min avSOTE** $[\mathbf{g\ O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}}]$
Variant	4	1.3%	16.71	1.34	19.60	14.50
	6	2.0%	16.71	1.02	18.40	14.60
	8	2.7%	16.89	1.23	19.00	15.00
	10	3.3%	16.66	0.90	18.90	14.90
	12	4.0%	16.96	0.70	18.00	15.60
	14	4.7%	16.66	0.51	17.50	15.20
	16	5.3%	16.87	0.55	18.10	15.60
	18	6.0%	16.92	0.63	18.60	15.90
	20	6.7%	16.89	0.37	17.70	16.20
Measurement results	33	12.0%	16.8	-	-	-

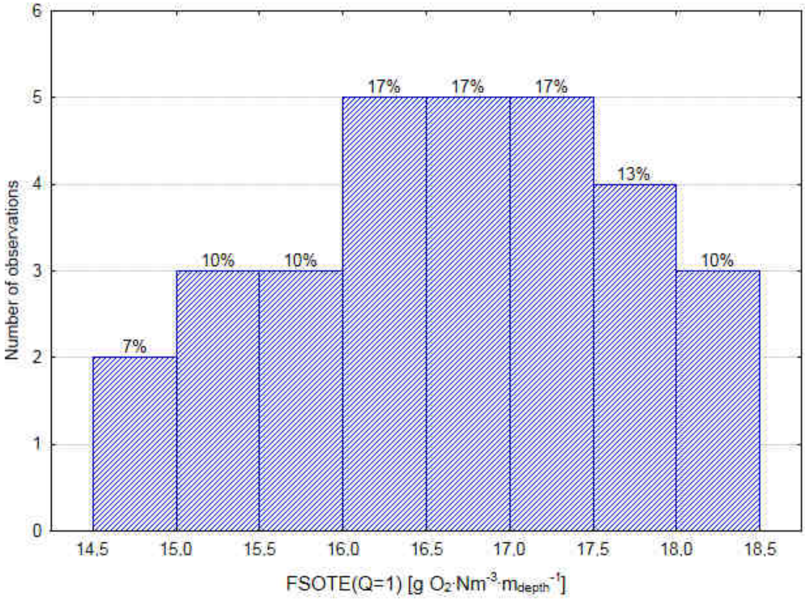

Fig. 4. Histogram of average αFSOTE for BR II with 2% hood coverage of the tank, obtained by randomly selecting the measurement points

Figure 4 shows a histogram of average αFSOTE values obtained from 6 randomly selected measurement points (i.e. 2.0% of the tank area).

Results

The results of the simulation performed for both biological reactors in the analyzed WWTP indicate that covering only 2% of the tank area with the measurement hood may be insufficient. Hood coverage according to the recommendations of EPA and ATV standards was already achieved after measurements performed in just 6 points of the reactor. Such a limited number of measurement points increases the significance of spatial variation in the reactor, thus introducing error to the average oxygen transfer efficiency values for the tested aeration tank.

In the case of BR I, the difference between αFSOTE value for 2% coverage and for 8.8% coverage may reach up to 15% and the number of simulations leading to such differences exceeds 10% of gained results**.** The percentage of the area covered with the hood during tests performed in accordance with the current recommendations entails low probability of obtaining accurate results - about 50% (with ± 1 g $O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}$ error).

Similar results were also observed in the case of simulations performed for the results from OTE measurements in BR II. Maximal discrepancies between the obtained values reached about 15% of the real value. As in the case of BR I in the same WWTP, the spread of values with 2% hood coverage of the tank area allows a conclusion that the currently recommended degree of tank coverage is not sufficient, and leads to low probability of obtaining accurate results at about 64% (with ± 1 g $O_2 \cdot Nm^{-3} \cdot m_{depth}^{-1}$ error).

Conclusions

In Poland, off-gas measurements are a novel method for diagnosing the condition of aeration systems in wastewater treatment. Insufficient number of national publications and a limited number of international ones results in imperfect methodology for both the measurements and the results analysis. The above analysis allows the formulation of the following conclusions:

- the value provided by the measurement methodology described in ATV209E and referred to as the minimum percentage of the tank area covered by the measurement points is insufficient to obtain reliable results of the average oxygen transfer efficiency in the tested aeration tank,
- the minimum coverage area with the measurement hood needs further verification for plug-flow reactors.

The conclusions from the analysis here presented will serve as the basis for an attempt at revising the methodology of oxygen transfer efficiency measurements using the off-gas method and at improving the accuracy of the results.

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POMIAR SPRAWNOŚCI TRANSFERU TLENU METODĄ OFF-GAS - PROBLEM STOPNIA POKRYCIA REAKTORA

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Abstrakt: Pomiary off-gas są jedną z dwóch dostępnych metod określenia stopnia wykorzystania tlenu w systemach napowietrzania oczyszczalni ścieków. Największą zaletą prezentowanej metody jest możliwość prowadzenia pomiarów w warunkach procesowych bez ingerencji w funkcjonowanie układu oczyszczania ścieków. Na podstawie danych zebranych podczas pomiarów wykonanych na jednej z komunalnych oczyszczalni ścieków w Polsce przeprowadzono analizę wpływu ilości punktów pomiarowych na uzyskiwane wartości stopnia wykorzystania tlenu. Analizę przeprowadzono, wykorzystując wyniki uzyskane z pomiarów zapewniających dużo wyższe pokrycie powierzchni reaktora (odpowiednio 12 i 8,8%) względem wytycznych literaturowych mówiących o 2% stopniu pokrycia reaktora.

Słowa kluczowe: oczyszczanie ścieków, napowietrzanie, stopień wykorzystania tlenu, metoda off-gas

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CURRENT STATUS, CHALLENGES AND PROSPECTS OF SEWAGE SLUDGE VALORISATION FOR CLEAN ENERGY IN POLAND

AKTUALNY STAN WIEDZY, WYZWANIA I PERSPEKTYWY WYKORZYSTANIA OSADÓW ŚCIEKOWYCH W PRODUKCJI CZYSTEJ ENERGII W POLSCE

Abstract: The valorisation of sewage sludge (SS) is a practical approach for the production of chemicals, fuels and clean energy. In the past, sewage sludge disposal and management in the European Union (EU) typically involved landfilling, incineration, agricultural application, or bulk storage. With the prohibition of these techniques, novel processes are urgently required to address the growing stockpiles of sewage sludge particularly in nations with high demographics such as Poland. The most promising technologies for SS valorisation are the thermal conversion; pyrolysis, gasification, combustion and co-firing. However, SS valorisation is beset by numerous challenges. Consequently, this paper seeks to examine the current status, challenges and prospects of SS valorisation in Poland. The findings demonstrated that the treatment of municipal and industrial wastewater generates substantial quantities of sewage sludge (SS) each year. Currently, the SS is mostly utilized for agriculture, landfilling and bulk storage. The paper reports that municipal SS is the mostly utilized SS for agriculture, compost production, thermal conversion, bulk storage; whereas industrial SS is used for land reclamation and landfilling. However, the bulk of Polish SS is still not effectively and efficiently utilized. Therefore, the authors proffered prospective technologies such as co-firing and direct utilization of SS for future green electricity production as possible solutions. However, it is pertinent to state that the application of novel SS valorisation technologies will require adapting and adopting low carbon strategies and legal frameworks in the future.

Keywords: sewage sludge valorisation, clean energy, sustainability developement

Introduction

Sewage sludge (SS) is the heterogeneous residue produced from the processing of industrial or municipal waste water effluents in treatment plants [1, 2]. The treatment of SS involves several physical (mechanical), chemical, biological or various combinations [3] resulting in the production of large quantities of solid, semi-solid or liquid residues [4]. Consequently, the effluent sources and the physico-chemical or biochemical composition of treated SS is significantly determined by the selected treatment technique. In view of this, SS potentially consists of harmful inorganic, biodegradable, chemical constituents such as heavy metals, pharmaceuticals, pesticides, hormones and dioxins [5-7]. However, the biological fraction contains nutrient rich organic matter with potential applications in agriculture. Based on its constituents, SS is predominantly disposed, managed or utilized through traditional technologies such as landfilling, incineration, and bulk storage [8].

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Conversely, European Union (EU) regulations prohibit the proliferation of these methods due to their potential threats to human health, safety and environment (HSE) [9]. The protocols are largely targeted at reducing biodegradable wastes landfills, agricultural application, environmental accumulation of chemicals and costs of off-site disposal solutions for sewage sludge. Furthermore, increased population, high living standards and rising processing costs have geometrically increased sewage sludge production in Poland 540 thousand Mg [10]. Additionally, increased pressure on sewage treatment infrastructure has resulted in the search for more cost effective, efficient and environmentally friendly methods for SS disposal and management.

Hence, novel sewage conversion technologies are urgently required to address the current challenges encountered by wastewater treatment plants (WWTPs) in Poland [11]. One of the most promising approach for the valorisation of SS is the use of thermal conversion processes such as pyrolysis, gasification, combustion and co-firing technologies [10, 12]. This has the potential to create a circular economy from SS valorisation in sustainable chemicals, fuels and energy for future applications. However, the transition to the circular economy will require identifying and addressing potential challenges due to socio-economic, environmental and technological factors.

Therefore, the main objective of this paper is identify and examine the current status of SS valorisation for clean energy generation in Poland. It will also present an overview of the various challenges that will potentially hamper the valorisation of SS for clean energy generation. Lastly, the study will outline the future prospects of SS valorisation through various thermal conversion technologies.

Current status of sewage sludge in Poland

The Republic of Poland is a central European nation located east of Germany on the geographical coordinates 52°N 20°E with a total land mass of 312,685 km^2. The land mass comprises 2.71% water and 97.3% land with 3,070 km^2 of territorial boundaries shared with Belarus, Czech Republic, Germany, Lithuania, Russia, Slovakia and Ukraine. The land terrain consists of flat plains and mountains along the borders in the south which account for its temperate climate. The seasonal weather is typically characterized by moderate to severely cold, cloudy winter conditions with regular rainfall whereas summer conditions are mild with periodic showers and thunderstorms.

According to year 2016 estimates, Poland is inhabited by 38.5 million people comprising 96.90% Polish, 1.10% Silesian, 0.20% German, 0.10% Ukrainian, and others 1.70%. The economy of Poland is dominated by the Services sector with 55.60%, Industrial Manufacturing 41.10% and 3.30% Commercial Agriculture. The three sectors jointly account for USD$ 1.005 trillion of Poland’s Gross Domestic Product (GDP, Purchasing Power Parity). Consequently, the per capita income of the average Pole is estimated at USD$ 26,000 which buttresses the nation’s high living standards [13]. According to empirical studies, higher livings standards have significantly influenced the generation of municipal and industrial waste around the globe [14]. Similarly, Hoornweg et al. [15] posit that rising urban population has increased solid waste generation by tenfold around the globe. In addition, global estimates indicate solid waste generation will double from 3.5 million to 6 million Mg/day by 2025 exceeding environmental pollutants and greenhouse gases (GHGs) [15]. In corroboration, Matsunaga et al. [14] assert that rising solid waste generation prompted by rising wealth and population dynamics will increase pressure on current waste management systems. In addition, this will result in significant socio-economic, environmental, technological and geopolitical implications globally.

Consequently, it stands to reason that sewage sludge production in Poland is set rise to 706 thousand Mg (dry matter) in the future [10]. Table 1 presents data on the disposal, management and utilization of the total industrial and municipal sewage sludge produced from over 4,255 waste water treatment plants (WWTP) operating in Poland for the year 2014.

Table 1

Sewage sludge [Mg d.m.] production in Poland for 2014 [16]

Sewage sludge utilization	Industrial SS	Municipal SS	Total SS
Agriculture	20,940	107,222	128,162
Land reclamation	95,034	21,961	116,995
Compost production	1,707	46,330	48,037
Thermal conversion	80,184	84,237	164,421
Landfilling	103,736	31,503	135,239
Bulk storage	17,042	62,192	79,234
Other uses	92,789	202,537	295,326
Accumulated*	6,280,853	226,034	6,506,887
Grand Total	6,692,285	782,016	7,474,301

* Total annual SS accumulated on the WWTP on landfill areas

According to the data in Table 1, the treatment of wastewater in Poland resulted in 7.5 million Mg of municipal and industrial SS. As can be observed the amount of industrial SS (89.54%) is significantly higher than from municipal sources (10.46%). The marked difference may be due to the high volume of waste water generated from industrial manufacturing or service industry processes which account for approximately 96.7% of Poland's GDP. However, the low SS from municipal sources could also be due to the lack of extensive sewerage network, waste management systems or low sewage sludge per capita around municipal areas in the country. Lastly, the enforcement regulations from the government agencies require higher HSE standards in WWTP in the industry. This ultimately results in high volume, specialized treatment of waste water in SS.

Furthermore, Table 1 presents the sectorial utilization of treated SS in Poland. As can be observed, SS in Poland is utilized for agriculture, land reclamation, compost production, thermal conversion, landfilling, bulk storage, and other uses. The data indicates that municipal SS is mostly utilized for agriculture, compost production, thermal conversion, bulk storage, and other uses than industrial SS. However, land reclamation and landfill applications are the most predominant applications of industrial SS. Overall, the data indicates that municipal SS is more widely applied or utilized than industrial SS in Poland. This may be due to strict regulations on industrial SS due to harmful chemical based compounds such as pharmaceuticals and metal compounds [5-7].

Figures 1 illustrates the proportions of SS from municipal and industrial WWTPs utilized for various applications in Poland as deduced from Table 1. The data in Figure 1 indicates that the highest proportion or 29% of municipal SS is reserved (accumulated) on

WWTPs on landfill areas. Conversely, 13% is used as agricultural input for use as fertilizer while 11% is thermally converted for energy or energy related applications. In addition, the use of municipal SS also includes bulk storage (8%), compositing (6%), landfilling (4%), and land reclamation (3%). Lastly, the remainder (26%) of the SS has no clearly defined use. In summary, 71% of all SS produced from municipal WWTP in Poland is valorised for various applications. In contrast, the industrial SS is sparingly utilised for any applications. The data indicates that only 6% of all SS produced is utilised for utilized for agriculture, land reclamation, compost production, thermal conversion, landfilling, or bulk storage. The highest proportion (2%) of the SS is used for landfilling and land reclamation. Agriculture and compost production account for less than 1% in each case. This may be due either strict regulations on its usage or lack of incentive from legislation to valorise the large proportions of industrial SS.

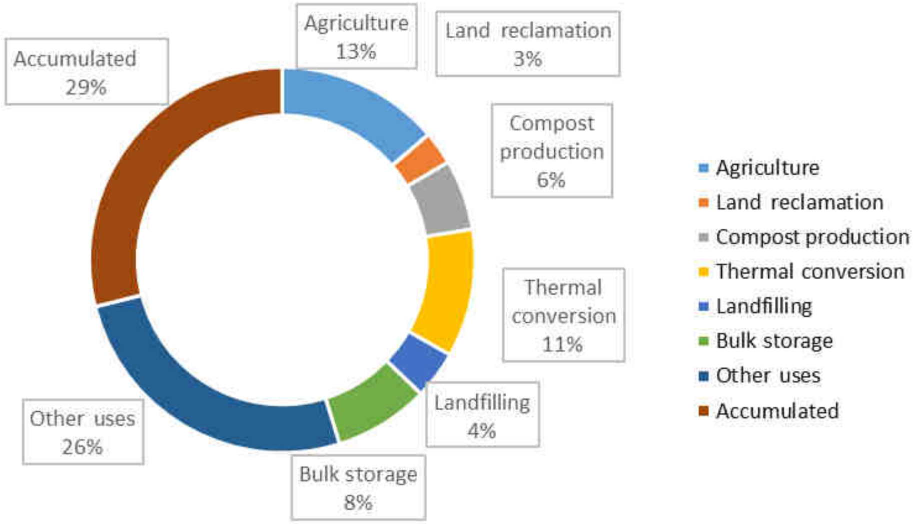

Fig. 1. Sectorial utilization of municipal SS in Poland

In view of this, Poland and the EU have enacted and instituted the legislative framework to not only monitor potential emissions and harmful substances from SS. It is envisage this will stimulate SS valorisation into useful chemicals, fuels and energy in the future. Table 2 presents an overview of the major legislative framework for SS disposal, management and utilization on the continent.

Based on these laws, the Polish government has established modalities to ensure the definition of wastes streams such as SS, recycling, reuse, recovery and safe disposal. Figure 2 presents an illustration of the approach as described in the Waste Framework Directive (WFD) (2008/98/EC) [17].

Table 2

Overview of major legislation on SS Management in the EU [17-29]

Law/Act	**Code**	**Date of enactment**	**National or EU**	**Summary of goals and objectives**
Sewage Sludge Treatment Directive	86/278/EEC [21]	12th June 1986	EU Directive	To determine rules for the use of sewage sludge as a fertiliser or agricultural purposes by farmers. To regulate and set limits for heavy metal concentrations in SS. To prevent adverse effects of SS human health, water and environment.
Urban Waste Water Treatment Directive	91/271/EEC [22]	21st May 1991	EU Directive	To protect the environment from the effects of urban waste water and industrial discharges. To determine guidelines for the collection, treatment and discharge of domestic, and industrial waste water effluents.
Landfill Directive	99/31/EEC [23]	26th April 1999	EU Directive	To prevent or reduce the negative effects of landfilling waste on the environment. To define the different categories of waste for landfills. To define wastes accepted in landfills, establish systems and operating permits. To introduce stringent technical requirements for landfills.
Waste Incineration Directive	2000/76/EC [24]	4th December 2000	EU Directive	To impose strict operating conditions and technical requirements on waste incineration plants and waste co-incineration plants in the European Union. To prevent or reduce pollution of the air, water and soil due to emissions form incineration or co-firing of waste. To set limits for pollutant emissions in air or water.
Implementation Directive on Landfills	2000/738/EC [25]	17th November 2000	EU Directive	To establish questionnaire for Member States to file reports on directive 1999/31/EC on the landfill of waste. To serve as implementation directive for the landfill directive and create modalities for effective implementation by EU Member states.
6th Community Environment Action Programme	EAP [26]	10th September 2002	EU Directive	To define the objectives of EU on the environment. To establish policy guidelines for the implementation of sustainable development strategies. To prioritize the efficient disposal, management and utilization of waste streams among EU Member states.
National Programme for Municipal Waste Water Treatment	NPMWWT [27]	16th December 2003	Polish National Directive	To establish the Polish national legal framework for the implementation of Directive 91/271/EEC of the EU. To create environment for the construction of sewage management systems, sewerage networks, and waste water treatment plants (WWTP).
Waste Framework Directive	2008/98/ECC [28]	12th December 2008	EU Directive	To establish legal framework for the treatment of waste in the EU. To define the basic concepts associated with waste management (WM). To determine principles for WM in the EU. To enact legislation for defining waste streams, responsibilities and penalties for Member States.
National Waste Management Plan 2014	NWMP [29]	31st December 2010	Polish National Directive	To establish a National Programme for waste reduction. To control pollutant emissions in the air, waters and soil. To establish mechanisms for recycling, reuse, landfilling or incineration of waste streams within the safety limits. To ensure implementation of Municipal Waste Water Treatment (NPMWWT) scheme.

Fig. 2. Schematic for Waste Management [17]

The "polluter pays principle" and "extended producer responsibility" described in the Waste Framework Directive requires novel sustainable technologies for waste valorisation. In addition, the directive mandates Member States to implement waste management plans and prevention programmes [17].

Prospects of sewage sludge valorisation

Based on WFD, there is an urgent need to explore technologies for the valorisation of SS in Poland. The use of thermal conversion technologies is considered one of the most effect methods for valorising organic wastes streams [30-34]. The most commonly used techniques are presented in Table 3.

Table 3

Potential routes for thermal valorisation of SS

Conversion technologies	**Process definition, Reaction conditions, and effects**	**Reaction products**	**References**
Pyrolysis	Thermal conversion (400-600°C) of carbonaceous feedstock in oxygen deficient conditions. Process ensures size reduction, increase in calorific value and energy density.	Biochar, activated carbons, bio-oil, biogas	[30-35]
Torrefaction	Mild pyrolysis process (200-300°C) for thermal pretreatment of carbon based feedstock. Process improves grindability, hydrophobicity, calorific value, and energy density	High heating value torrefied fuel, pellets	[36-38]
Hydrothermal carbonisation	Thermochemical process for converting organic feedstock into carbonaceous products under mild temperatures (180-350°C) and pressures (2-10 MPa)	Hydrochars, and aqueous by-product	[39-41]
Gasification	Conversion of feedstocks into clean synthesis gas (Syngas) at temperatures 650-1000°C. The syngas is used for producing chemicals, fuels or clean energy	Synthesis gas (syngas), hydrocarbons, biochar	[12, 42-44]
Combustion	High temperature (1000°C) conversion of feedstocks	Fuel gases for energy production	[45]

Other prospective technologies for SS valorisation include pyro-torrefaction, pyro-gasification, catalytic gasification, chemical looping gasification, vermicomposing, and conversion into plastics and pharmaceuticals. In addition, the large quantities of industrial SS can be directly utilized or co-fired with coal or biomass in existing power plants for energy production [45, 46].

Challenges of sewage sludge valorisation

The challenges of SS valorisation in Poland will be briefly described based on Social-Economic, Environmental and Technological implications. The socio-economic challenges will largely stem from public and government acceptance of product chemicals, fuels and energy produced from SS valorisation. The environmental challenges of SS valorisation may arise from the potential pollutant emissions, greenhouse gases (GHGs) and secondary wastes generated from conversion technologies such as combustion. Lastly, the technical challenges could potentially be due to solids management, low efficiencies of conversion processes, equipment corrosion due to SS components, and reduction of secondary wastes products. In general, the outlined challenges can be potentially addressed by adapting and adopting low carbon strategies augmented by legal frameworks for SS valorisation in the future. Emphasis will need to be focused on the sustainable conversion of industrial SS as this constitutes approximately 90% of the SS stock in Poland.

Conclusions

The main paper examined the current status, prospects and challenges of SS valorisation in Poland. The findings demonstrate that the treatment of wastewater effluent streams from municipal and industrial sources generates significant quantities sewage sludge. Currently, the treated SS is predominantly utilized for agriculture, landfilling and bulk storage. In addition, the analyses revealed that municipal SS is mostly utilized for agriculture, compost production, thermal conversion, bulk storage, whereas industrial SS is used for land reclamation and landfilling. Nonetheless, the bulk of Polish SS is not effectively and efficiently utilized. Therefore, the authors proffered prospective technologies such as co-firing and direct utilization of SS for green electricity production in the future as possible solutions. However, it is pertinent to state that the implementation of novel SS valorisation technologies will require adapting and adopting effective low carbon strategies and legal frameworks in the future.

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AKTUALNY STAN WIEDZY, WYZWANIA I PERSPEKTYWY WYKORZYSTANIA OSADÓW ŚCIEKOWYCH DO PRODUKCJI CZYSTEJ ENERGII W POLSCE

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Abstrakt: Aktualnie zagospodarowanie osadów ściekowych (OŚ) polega m.in. na wykorzystaniu ich jako paliwa do produkcji energii. W przeszłości osady ściekowe w Unii Europejskiej (UE), otrzymane z oczyszczalni ścieków, składowano, spalano w sposób niekontrolowany oraz wykorzystano do użyźniania gleby w rolnictwie. W związku z wprowadzeniem zakazu stosowania ww. sposobów ich utylizacji konieczne było poszukiwanie nowych metod, w szczególności w krajach o wysokiej liczbie ludności, jakim jest na przykład Polska. Jedną z obiecujących metod zagospodarowania osadów ściekowych mogą być takie procesy, jak piroliza, zgazowanie i spalanie, w wyniku których powstaną produkty chrakteryzujące się energetycznymi właściwościami. Jednakże prowadzenie tych procesów wymaga uwzględnienia społecznych, ekonomicznych, środowiskowych i technologicznych czynników. Dodatkowo, regulacje UE w zakresie zagospodarowania osadów ściekowych zakazują termicznego ich przekształcania bez prowadzenia efektywnych procesów wstępnych (tzw. „pre-treatment processes”). W pracy przedstawiono stan bieżący, wyzwania oraz perspektywy wykorzystania osadów ściekowych w procesie produkcji czystej energii.

Słowa kluczowe: waloryzacja osadów ściekowych, czysta energia, zrównoważony rozwój

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THE REMOVAL EFFICIENCY OF DUST DURING SHORT-TERM RAINS - VERIFICATION OF ADDITIONAL FACTORS

SKUTECZNOŚĆ USUWANIA PYŁU PODCZAS OPADÓW KRÓTKOTRWAŁYCH - WERYFIKACJA DODATKOWYCH CZYNNIKÓW

Abstract: This paper reports the results of a comparison of the results of field study concerned with the effectiveness of PM10 scavenging by liquid precipitation in a warm and cold season of the year. The aim of this study involved: - verifying if the value of the removal coefficient (ΔC) is relative to the duration of the phenomena of wet deposition, - verification of a hypothesis that the initial value of PM concentration does not affect the value of ΔC_{PM10}. The registration of the variability of PM concentrations was undertaken over the period of seven years in the conditions of the occurrence of convective and large-scale precipitation and it was performed in a non-urbanized area. The analysis involved 344 cases of observation with the constant time interval of 0.5 h. The measurements of PM10 mass concentration was performed with the aid of a reference method accompanied by concurrent registration of the basic meteorological parameters. It was indicated that the value of the removal coefficient assumes similar values in the cold and warm season for all types of precipitation with the mean intensity of $R > 0.5$ mm h^{-1}. It was additionally noted that the effectiveness of PM10 removing by precipitation with various origin does not statistically vary according to the season. It was indicated that for precipitation with a low intensity, the values of the mass concentration of particulate matter in the ground-level zone could affect the values of the removal coefficient. It was also concluded that the diverse structure of wet deposition with a small intensity plays an important role in the process of the scavenging of solid particulate matter from close-to-ground troposphere.

Keywords*:* precipitation, PM10, scavenging process, background area

Introduction

Below-cloud scavenging plays the role of a principal process which ensures the removal of pollutant from the ground-level zone and takes on a principal role in the maintenance of high environmental qualities of the air at the expense of other components of the natural environment [1]. Therefore, it forms one of the major processes by which a balance is maintained between the inflow and outflow of aerosol particles [2]. Wet below-cloud scavenging includes all phenomena, which lead to the washing out particulate matter together with all forms of precipitation: rain, snow, fog and ice. According to [3], from the point of view of human well-being and quality of the ground-level zone, below-cloud scavenging seems to play a more important role than in-cloud scavenging. This statement is confirmed by the remark that the particulate matter which poses immediate danger to the human health is principally deposed as a result of below-cloud scavenging, while the mechanism which plays a major role in it is associated with the collision of solid particles with rain drops [4]. The process of wet aerosol washout is inherently complex as it is affected by a number of external phenomena, which include: drop size, distribution of particle sizes, chemical composition of water, rainfall intensity

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ambient temperature as well as chemical and physical properties of drops and aerosol and the area of the collision between the aerosol and rainfall drops [5].

The actual effects of the scavenging of the solid particles suspended in the atmosphere which accompanies precipitation is usually determined on the basis of the scavenging coefficient Λ [s^{-1}], and it is considered to be the most important parameter to characterize below-cloud particle washout [6]. For a particle with a given size, scavenging coefficient is the function of the boundary velocity of the droplet and effectiveness of the collisions between rainfall droplets and the particles in the atmospheric aerosol [7]. However, as it was noted, due to the great number of the factors which play a role in the processes occurring below-cloud, the values of scavenging coefficient are characterized by a considerable variability [8].

The aerosol scavenging coefficient can be defined in terms of the bulk particle number, bulk particle mass, or size-resolved particle number and mass concentration. The bulk approach directly measures or models the average precipitation rate and the variation of aerosol mass. Results from a bulk approach can be substantially different from a more detailed one with size spectra included [9, 10]. A size resolved particle and droplet experimental approach requires measurements during the considered events of the size distribution of the aerosol and of the droplets. The adopted methodology of observation (in current article) does not allow to meet the criteria presented above. In the other hand, the effectiveness of PM10 removal by precipitation can also be shown as a simple relationship of percentage change (ΔC) in the concentrations before (C_0) and after (C_t) episodes of rain (to distinguish, the ΔC will be called the removal coefficient instead of the scavenging coefficient).

Experimental studies into below-cloud purification performed in actual conditions focus on various aspects of this process. The processes are researched both on a complex scale, i.e. with details of the effectiveness of solid particle removing by the particular types of precipitation, as well as on a specific scale, when a study can involve the effectiveness of scavenging of particular particle types by the specific types of precipitation. Experimental studies often occur through measurements in the direct vicinity of anthropogenic sources of emissions, both in urban and rural areas [8, 11]. It is reasonable to remark at this point that a vast proportion of the studies was conducted on a local scale, while on the other hand, local emission of pollutants and the structure of rain clouds has a considerable effect on the characteristics of wet deposition [1]. Besides, the variations in the concentration of aerosols in the troposphere after incidences of precipitation can occur in the adjacent as well as remote areas [7].

The variation in the concentration of aerosols in two successive time intervals in the actual conditions is relative to a number of phenomena, such as turbulence in the boundary layer, chemical processes in the liquid phase as well as potential emission and transport of pollutants from the more remote areas [12]. One could risk putting a question at this point: does the lack of a uniform value of the removal coefficient result from the sole effect of the above mentioned parameters? Could it be that the variability in the value of ΔC is due to other, more ordinary reasons?

The studies into the effectiveness of removing coarse particles in the processes of wet deposition have a primarily theoretical inclination (that is they involve numerical studies), in which weather conditions specific for a particular area and the season are not considered.

An insight into the existing literature also yields that the effect of the concentration of aerosols in the air directly before the incidence of a rainfall has not been sufficiently recognized and researched as a factor which affects the value of percentage change in the concentrations before and after episodes of rain. Besides PM10 is still one of the most important air quality indexes. Hence, a decision was made to compare the effectiveness of removing PM10 by the liquid precipitation in the cold and warm season of the year. In addition, an attempt was made to estimate the effect of the initial concentration of PM10 on the value of ΔC.

The principal objective of the research involved verification of hypotheses regarding the following:

- for specific intensity ranges and types of liquid precipitation, the value of removal coefficient ΔC_{PM10} is the same in the cold and warm season (I),
- for specific ranges of precipitation intensity with various origin, the effectiveness of particles removing is the same in the cold and warm season (II),
- for specific ranges of precipitation intensity, the initial value of the concentration does not affect the value of ΔC_{PM10} (III).

Materials and methods

The testing was performed over a period of 7 successive years (2007-2013). In order to minimize the effect of anthropogenic sources, the concentration of PM10 was measured in an undeveloped area, i.e. in the vicinity of a village (Kotorz Maly, Poland, 50°43’37”N; 18°03’22”E, 1,025 inhabitants). The measurement point was located in an open, yet shielded meadow area protected by the surrounding wood - 11 km from the border of a provincial town (Opole, 122,000 inhabitants) and 2 km from the nearest compact rural building development. The measurement campaign involved the observation of the PM10 concentration resulting from the occurrence of two types of precipitation (frontal and convective ones) with different intensity R.

The procedure by which the measurement of the concentration of PM10 was performed was in conformity with the European standard [13]. The aspiration of the PM10 in the air was carried out by a MicroPNS HVS16 (UMWELTTECHNIK MCZ GmbH®) sequential dust sampler. The aspiration headers were installed 2 m above ground level. The flow rate was 68 $m^3\ h^{-1}$. The PM separators applied Whatman GF/A fibreglass air filters with a diameter of 150 mm. The aspiration at a constant time interval of 0.5 h was conducted directly before and during the occurrence of precipitation. The expanded mass concentration measurement uncertainty (U) did not exceed 3.2%. The time interval guaranteed the PM collection to a degree that was sufficient to determine the mass of the captured particulate matter, even in conditions when its concentration in the air was low. The initial testing (n = 25, time interval of registration - 10 seconds, time of a single registration - 1800 seconds) using a DustTrak 8520 Aerosol Monitor - TSI®, was conducted in variable weather conditions; however, with the exception of rain, it did not yield considerable differences in the results of PM10 concentration over 10 and 1800 seconds in the investigated area.

To determine the meteorological conditions, a portable weather station (DAVIS®) was used, which is widely used for registration of weather conditions in field measurements

[14]. This weather station was installed 12 m from the PM sampler. The sensors, which determined relative humidity (*RH*), temperature (*T*), atmospheric pressure (*P*), wind speed (*Ws*), wind direction (*Wd*) and rainfall (*R*), similarly to the case of the dust sampler aspiration header, were installed at a height of 2 m above the ground.

The removal coefficient of the particulate matter was determined with the relation (1):

$$\Delta C = \frac{C_t - C_0}{C_0} \cdot 100\% \tag{1}$$

The proposed solution has a primarily practical character and constitutes an attempt to offer a way of approaching the effect of scavenging of particulate matter suspended in the ground-level zone.

As the scavenging coefficient Λ, the removal coefficient ΔC is relative to the aerodynamic diameter of the PM; however, due to the applied measurement methodology, the entire fraction of PM with the diameter below 10 μm was identified. The values of the removal coefficient were derived on the basis of 30-minute mean mass concentrations of PM10.

All statistical operations were undertaken by means of the STATISTICA 13.1® program.

Results and discussion

Meteorological parameters

The measurement campaign conducted over 7 years yielded the results of 344 cases of a potential change in the mass concentration of PM10 accompanying the occurrence of liquid precipitation. A descriptive characteristic of meteorological parameters which characterize the conditions of the observations is found in Table 1. In total, around 46% of observations involved convective precipitation (including 25 cases of observations of variations in PM10 mass concentrations accompanying storms). During the cold season (November to April), the analysis involved the observations regarding 20 instances of convective precipitation and 98 large-scale ones. The majority of observations was taken during the warm season (May to October), i.e. 140 for occurrences of convective precipitation and 86 for large-scale ones. The highest number of cases (around 48%) corresponded to light precipitation types with the intensity $R \leq 0.5$ mm h^{-1}. However, light precipitation was not observed for instances of storms. Around 70% cases of the occurrence do light precipitation were registered during the warm season. The mean precipitation, in the range from 0.6 to 2 mm h^{-1} (with a total number of 108), was registered 47 times during the cool season (including 13 instances of convective precipitation). In addition, 42 cases (including 26 in the cold season) involved rainfall intensity in the range from 2.1 to 5 mm h^{-1}, where the proportion of large-scale rainfall amounted to 22%. Over 93% cases of heavy precipitation (> 5 mm h^{-1}) occurred in the form of convective precipitation in the warm season. This type of precipitation was most common during storms (i.e. in 16 out of 29 instances) and incidentally during large-scale precipitation - in around 7% of cases.

During the duration of the observations, the relative humidity was characterized with small variability and its value was comparable during all instances of precipitation. In regard to the observed convective precipitation, small variability in the ambient air temperature was additionally observed. The greatest variability in terms of this parameter was noted for large-scale precipitation and could be mainly associated with cold fronts. Beside the intensity of hydrometeors, high variability was noted for the velocity of horizontal air masses. Nevertheless, during the measurement campaign, 21% of instances of precipitation were not accompanied by wind. The horizontal movement of air masses were registered in the north (47%) and south direction (31%), i.e. from the areas with high quality of the environment and low air pollution [15]. Only in 13% of cases (i.e. with wind in the west and north-west), the incoming air masses originated from areas with high anthropogenic pollutions levels i.e. from the area of Opole city with severe PM10 pollution as well as from the surrounding areas of rural development.

Table 1

Meteorological parameters characterizing the conditions during the observations

Type of precipitation period	**Descriptive statistics**	T **[°C]**	RH **[%]**	R **[mm h^{-1}]**	Ws **[km s^{-1}]**	**PM10 C_0 [µg m^{-3}]**
Convective Cold season	avg	14.1	0.85	1.1	3.2	18.9
	med	13.6	0.89	0.9	1.9	19.0
	SD	3.7	0.09	0.93	3.13	10.7
	min	8.5	0.66	0.2	0.2	5.10
	max	18.4	0.94	4.5	11.7	42.0
Convective Warm season	avg	17.7	0.79	3.0	3.5	18.6
	med	15.3	0.81	1.3	2.7	19.0
	SD	4.41	0.12	4.75	3.32	8.01
	min	12.8	0.69	0.2	0	3.40
	max	28.4	0.95	37.0	16.8	48.0
Frontal (large scale) Cold season	avg	7.6	0.83	0.6	4.1	20.9
	med	7.7	0.86	0.4	2.2	21.0
	SD	3.4	0.10	1.27	4.93	7.79
	min	0.0	0.73	0.2	0	3.00
	max	14.7	0.99	13.0	24.0	63.0
Frontal (large scale) Warm season	avg	13.5	0.85	0.9	4.2	19.0
	med	13.3	0.88	0.5	2.5	18.0
	SD	3.74	0.09	0.83	5.87	8.56
	min	6.1	0.69	0.2	0	4.90
	max	27.2	0.94	5.1	27.3	59.0

Removal coefficient in cold and warm season

An initial analysis with the application of the Kolmogorov-Smirnov test indicates that the registered values of the specific meteorological parameters and the calculated values of the removal coefficient (ΔC) are not characterized with normal distribution. Consequently, all statistical analyses which were used to verify the initial hypotheses had to apply non-parametrical tests.

The analysis of all collected results, not accounting for the identified types of liquid precipitation and times of its occurrence confirms the general approach that the removal coefficient is considerably correlated with intensity of precipitation. On the basis of the Guilford scale [16], one can note that the results of the observations indicate a considerable degree of correlation between ΔC and R (Spearman correlation coefficient $rho = -0.85$). The value keeps its relevance level at *p-value* < 0.01. The calculated determination coefficient makes it possible to risk a statement that the rainfall intensity is responsible for explaining around 73% of the variability in the value of Δ*C*. The results of the variability in PM10 mass concentration and calculations indicate that within the range of the precipitation *R*: 0.2-37.0 mm h^{-1}, the value of Δ*C* is found in the range from 0.00 to –93.0% with a median equal to –12.0% for R_{MED} = 0.6 mm h^{-1}. Absence of positive values of Δ*C* means, that after short-term rainfall episodes no increase in PM10 mass concentration has been observed.

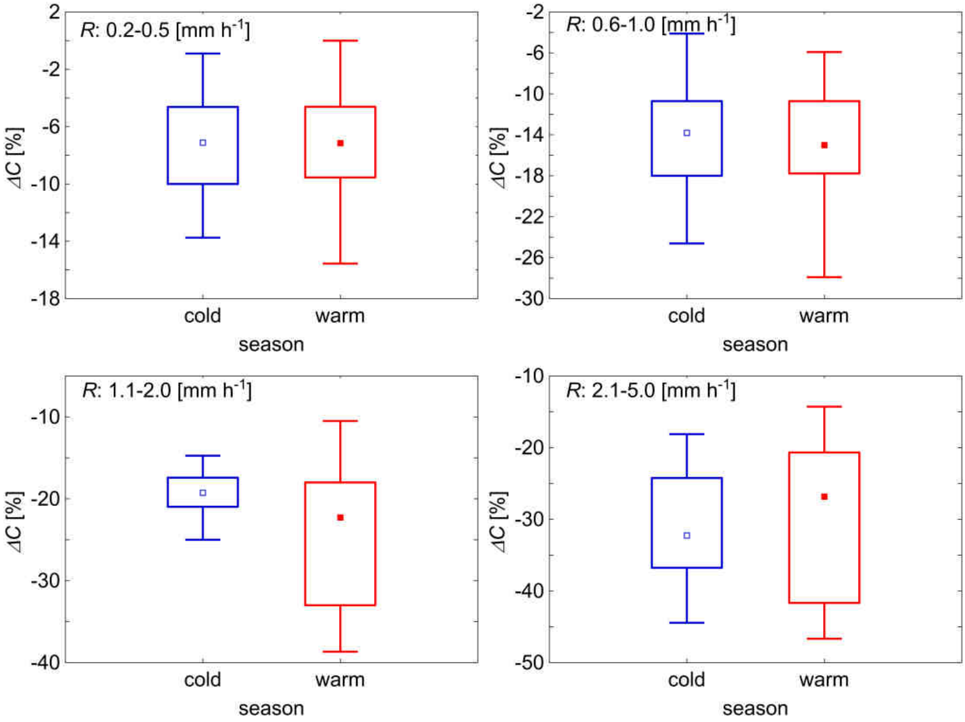

Fig. 1. Removal coefficients determined in cold and warm season as a function of rainfall intensity

Figure 1 contains box charts which illustrate the variability of the value of Δ*C* in the function of four adopted ranges of rainfall intensity for the investigated observation periods. Graphical interpretation seems to confirm the earlier statement regarding the principal reason which affects the intensity of wet deposition is associated with the effectiveness of scavenging. At the same time, it is noticeable that for the particular ranges of *R*, the variability in Δ*C* is slightly higher for the warm season. Such a condition could be attributed to the instability of quantitative parameter associated with particulate matter emission from the local natural sources occurring in the investigated area, whose activity is predominant in the warm season. The results of statistical analysis summarized in Table 2 with the use of non-parametric Mann-Whitney test indicate statistically relevant differences between the effectiveness of scavenging in the cold and warm season; however, they are only noted for precipitation with the lowest intensity. At the same time, *p-value* is affected by the results gained for R = 0.2 and 0.4 mm h^{-1}, for which, under the adopted relevance level α, the value of the test probability was lower than 0.01. One can also note that the results of the removal coefficient were slightly lower during the cold season. Apparently, this fact could also be attributed to the local atmospheric dispersion and limited transport of particles from the areas with higher pollution due to occurrence of precipitation. Consequently, this affects the level of PM10 concentration during the occurrence of the phenomenon of wet deposition. The high values of the test probability gained for the rainfall intensities of 0.6-1.0, 1.1-2.0 and 2.1-5.0 mm h^{-1} indicate that the value of median ΔC could be noted for the particular seasons. The results of statistical analysis presented in the last two columns of Table 2 contains a summary of adopted ranges of precipitation with the same origin (i.e. convective and large-scale types) and indicates very similar results, which could suggest that the type of precipitation does not affect the value of ΔC for the same intensity of wet deposition. However, it is worth noting at this point that the differences in the value of removal coefficient between the examined seasons occur solely for the case of precipitation with the smallest registered intensity. It seems that this result is affected by the structure of the wet deposition, which for the case of large-scale precipitation usually takes the form of very densely packed raindrops with a small size. Such a form of precipitation is likely to wash out pollutions from the troposphere with considerable effectiveness and this process is rather effective regardless of its duration. For the case of convective rainfall with a low intensity, the difference in the effectiveness of scavenging is more discernible. This state could also be attributed to the structure of precipitation (drops with a high speed and small drop density and lower effectiveness of collisions with solid particles) as well as to the conditions of the convective and transport of pollution mass due to advection (lower values of ΔC in the warm season, i.e. during the period with the more intense dissipation of solid particles due to bottom-up currents). The results indicate that the test hypothesis is true for all types of liquid precipitation with intermediate intensity, i.e. for $R > 0.5$ mm h^{-1}.

Table 2

The results of Mann-Whitney test. *p-value* for two different seasons (cold and warm). Critical *p-value*: 0.05

Precipitation intensity *R* [mm h^{-1}]	**Mixed convective and frontal rainfall**	**Convective rainfall**	**Frontal rainfall**
0.2	0.006	0.004	0.024
0.4	< 0.001	< 0.001	**0.183**
0.5	**0.349**	**0.381**	**0.293**
0.2-0.5	0.039	**0.158**	**0.051**
0.6-1.0	**0.426**	**0.674**	**0.797**
1.1-2.0	**0.074**	**0.525**	**0.124**
2.1-5.0	**0.687**	to less data to compare	**0.967**

Bold values showed realization of condition of Mann-Whitney test

Figure 2 presents the ranges of the removal coefficient derived for the cold and warm season with its classification according to the distinction between convective and large-scale precipitation types. The value of removal coefficient is likely to decrease along with the increase of the intensity of both convective and frontal rains. The graphical illustration suggests differences in the values of the removal coefficient obtained for particular precipitation types. However, the analysis performed with the aid of the Kruskal-Wallis (ANOVA) test rejects this statement completely. For the case of light rainfall (for n = 177), the value of the Kruskal-Wallis test - H was equal to 6.279, and the relevance level *p-value* was equal to 0.098. For rainfall intensity in the range R = 0.6-1.0 mm h^{-1}, for the total number of observations n = 64 and R = 1.1-2.0 mm h^{-1} for n = 40, the value of H was gained at the level of 1.736 and 3.136 with the corresponding *p-values* of 0.629 and 0.371, respectively. The low values gained in the test accompanied by high relevance levels make viable the hypothesis that for the identified ranges of rainfall intensity with various origin, the effectiveness of PM10 removing from the boundary layer does not vary statistically for the warm and cold season.

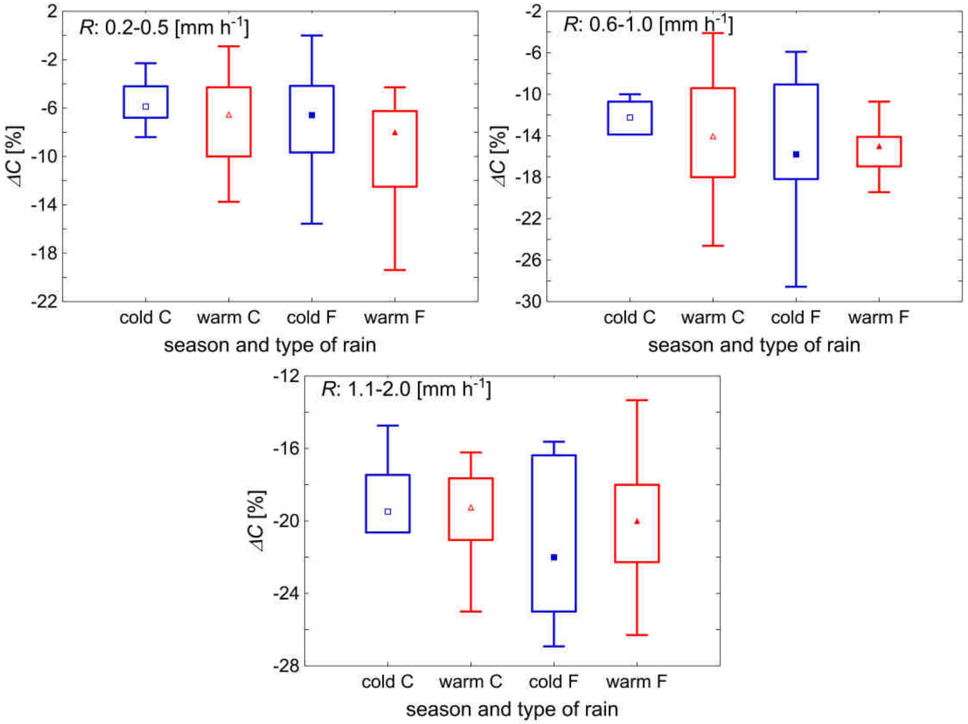

Fig. 2. Removal coefficients determined in cold and warm season as a function of rainfall intensity of two different types of precipitation (C - convective, F - frontal)

Effect of the initial concentration C_0 on the value of removal coefficient ΔC

Figure 3 illustrates the scatter of the calculated values of removal coefficient depending on the initial concentration obtained directly before the episodes of rainfall. Table 3 presents the results of the Spearman correlation between initial concentration and ΔC undertaken separately for mixed convective and large-scale precipitation types. On the basis of data in Figure 3 one can see that for mixed convective and frontal rains, along with the increase in their intensity, the correlation (ΔC – C_0) tends to disappear. Nevertheless, the results confirmed by statistical analysis indicate that for rainfall with a low intensity, the relation tends to be moderate and the value of the correlation coefficient is significant.

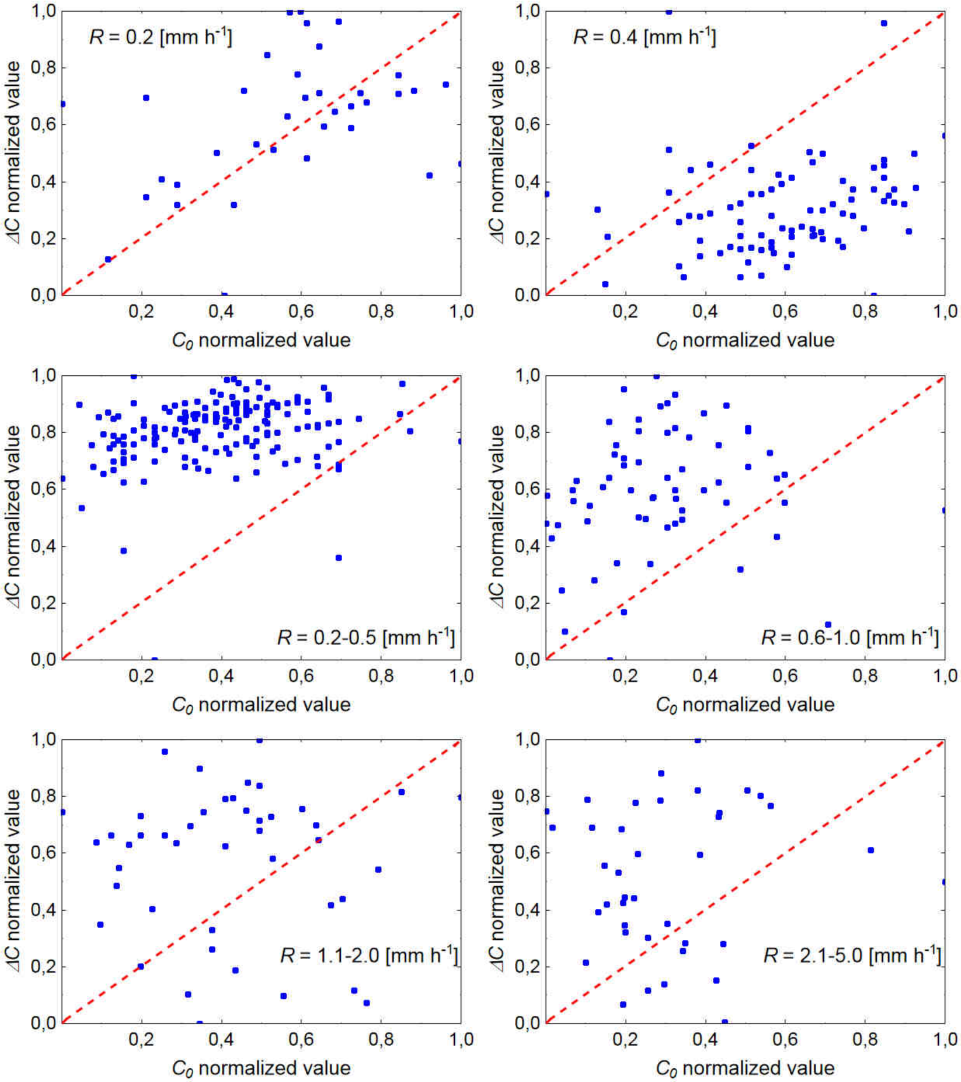

Fig. 3. Removal coefficient as a function of the initial mass concentration of PM10 for different ranges of precipitation intensity

In addition, one can note that convective rainfalls indicate a higher positive correlation ($\Delta C - C_0$) and this relation, although not always considerable, tends to keep its relevance for all investigated rainfall intensity ranges. For the case of convective rainfall with the low intensity, rain does not usually take the form of a standard drizzle, but the drops which are elongated and, thus, their ability to wash out pollutants is limited. Hence, the correlation between ΔC and C_0 is in this case very clear. For the case of large-scale rainfall, which is characterized with the smaller intensity of dynamic changes in time, the value of the initial concentration does not affect the effectiveness of scavenging during the liquid deposition with the intensity $R > 0.5$ mm h^{-1}.

Table 3

Spearman correlation ΔC - C_0 results

Precipitation intensity R [mm h^{-1}]	**Mixed convective and frontal rainfall**	**Convective rainfall**	**Frontal rainfall**
0.2	-0.659^{*}	-0.618^{*}	-0.539^{*}
0.4	-0.568^{*}	-0.338^{**}	-0.474^{*}
0.5	-0.394^{*}	-0.339^{**}	–0.325
0.2-0.5	-0.518^{*}	-0.604^{*}	-0.324^{*}
0.6-1.0	–0.228	-0.391^{**}	–0.105
1.1-2.0	–0.040	-0.348^{**}	–0.023
2.1-5.0	0.121	to less data to compare	0.098

* - significant at $p < 0.01$, ** - significant at $p < 0.05$

As reported in the studies by Aikawa and Hiraki [17] conducted for a constant rainfall intensity, the value of the scavenging coefficient assumes highest values during the initial phase of the wet deposition process. The results gained in this study do not seem to confirm this statement, as they are limited to only the first 30 minutes of the duration of precipitation, and therefore, extensive comparison is not possible on its basis (also due to different base for coefficient calculations). On the other hand, the results gained in the study indicate, that for the rainfall with a constant and low intensity, higher levels of initial mass concentration of PM10 could lead to the reduction in the value of ΔC (to better scavenging). This conclusion could to a certain degree explain the lack of conformity of the results gained by various researchers for precipitation with the same characteristics and duration of rainfall, which however, vary in terms of location and level of the immission of particulate matter suspended in the lower layers of the troposphere.

Finally, it is possible to remark that the initial hypothesis stating that for the particular ranges of rainfall intensity, the initial value of the mass concentration does not affect the value of ΔC_{PM10} could be considered to be true for large-scale precipitation with intermediate intensity. At the same time, it would be false to think that the same statement is also relevant for all registered precipitation types, without their distinction according to an origin as the results are considerably affected by the results for frontal precipitation.

Conclusions

The conducted field studies indicate that for the examined intensity range of large-scale (frontal) and convective rains, the medians of PM10 removal coefficient do not assume values which are statistically different depending on the thermal conditions which define the warm and cold season during the occurrence of wet deposition with intermediate intensity. The effectiveness of PM10 removing by precipitation with various origin (convective vs. frontal rains) does not differ statistically for the warm and cold seasons.

Nevertheless, the results could indicate that the distinct structure of the analysed forms of wet deposition, in particular for the case of their low intensity plays a major role in the process of scavenging particulate matter and could justify the evident variability in the value of ΔC. The results of field studies indicate that the initial value of dust mass concentration in the air could affect the value of ΔC_{PM10} to a limited degree during the phenomenon of wet deposition, while slightly reducing the effectiveness of removing particulate matter by light rains.

The scope of the realized research was local, nevertheless, the results could be considered to be representative for areas located remote from direct sources of enriching atmosphere with pollutant of anthropogenic origin. Generally, these results could be deemed as representative for the moderate climate. In addition, the considerable volume of observations undertaken in the conditions of the occurrence of wet deposition could contribute as complementary to the existing state of knowledge regarding effectiveness of PM10 scavenging.

The results and analysis of the conducted experiments could prove to be useful for clarifying and enabling better understanding of existing discrepancies regarding the value of scavenging particulate matter reported in the research which deals with this subject matter.

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SKUTECZNOŚĆ USUWANIA PYŁU PODCZAS OPADÓW KRÓTKOTRWAŁYCH - WERYFIKACJA DODATKOWYCH CZYNNIKÓW

Katedra Techniki Cieplnej i Aparatury Przemysłowej, Politechnika Opolska

Abstrakt: Artykuł prezentuje porównanie rezultatów badań polowych nad efektywnością wymywania PM10 przez opady ciekłe występujące w chłodnym i ciepłym okresie roku. Celami artykułu było: - sprawdzenie, czy wartość współczynnika usuwania (ΔC) zależy od okresu występowania zjawiska mokrej depozycji, - weryfikacja hipotezy, iż początkowa wartość koncentracji nie wpływa na wartość ΔC_{PM10}. Siedmioletnie rejestracje zmian stężenia pyłu w warunkach występowania opadów konwekcyjnych i wielkoskalowych przeprowadzono na obszarze niezurbanizowanym. Analizie poddano 344 przypadki obserwacji o stałej rozdzielczości czasowej 0,5 h. Pomiary stężenia PM_{10} prowadzono z użyciem metody referencyjnej przy jednoczesnej rejestracji podstawowych parametrów meteorologicznych. Wykazano, że współczynnik usuwania ΔC_{PM10} przyjmuje podobne wartości w sezonie chłodnym i ciepłym dla wszystkich form opadów ciekłych o średnim natężeniu $R > 0,5$ mm h^{-1}. Stwierdzono, że efektywność wymywania PM10 przez opady o różnej genezie nie różni się statystycznie dla sezonu chłodnego i ciepłego. Pokazano, że dla opadów o niskiej intensywności wartość koncentracji pyłu w troposferze przyziemnej przed opadem może wpływać na wartość współczynnika usuwania. Wykazano, że odmienna struktura form mokrej depozycji o niskiej intensywności odgrywa istotną rolę w procesie wymywania cząstek stałych z atmosfery przyziemnej.

Słowa kluczowe: opad atmosferyczny, PM10, proces wymywania, obszar niezurbanizowany

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Terese RAUCKYTE-ŻAK[1]

ASSESSMENT OF SLUDGES FROM RAIL FREIGHT CAR WASH WASTEWATERS. THE PRIMARY SLUDGES

OCENA OSADÓW Z OCZYSZCZANIA ŚCIEKÓW Z MYJNI KOLEJOWYCH WAGONÓW TOWAROWYCH. OSADY WSTĘPNE

Abstract: This article presents the assessment results concerning sludges after sedimentation generated under full scale technical conditions on the system for pretreatment of sludges formed as a result of water washing of usable areas of railway freight transport of category: G, H and T in accordance with the International Union of Railways classification. The sludges were separated in a storage and average tank, being the first processing node of sludge pretreatment system to which the raw wastewaters were discharged. Due to significant diversification of the pollutants load, the sludges were characterised by significant inhomogeneity. The article presents the results of leaching procedure (TCLP) carried out for selected samples and the risk assessment using RAC code performed on the basis of the analysis of fractional composition of selected heavy metals such as: Cu, Ni, Pb and Zn. It was found out that gravitationally post-sedimentary sludges, generated during randomly selected three operational months of the installation, indicated a low risk (LR) in relation to Cu and a moderate one (MR) regarding Ni, Pb and Zn. In accordance with TCLP criteria, primary sludge - being the effect of raw sewage retention and sedimentation of its dispersed solids was classified as a non-toxic waste.

Keywords: wastewaters from railway freight car wash, post-sedimentary sludges, TCLP test, fractional composition of heavy metals in sediments, risk assessment code (RAC)

Introduction

The use of railway rolling stock of commodity type is inseparably connected with car surface cleaning and generating wastewaters and sludges formed in the processes of their physico-chemical treatment [1-10]. The composition, diversity and the amount of the pollutants load in wastewaters generated in freight car wash is a function of the composition of transported commodities [1-10]. In a specific development, the recorded load levels of individual pollutions depend on i.a.: a physical state and chemical composition, solid dispersion, humidity, heterophase state, methods of packaging and sealing of packages as well as repeatability of the transported commodities categories in long-term quantification [11, 12]. The composition and the amount of the pollutants load in wastewaters may also be a result of incidental cases of mechanical damage of protective packages for transported commodities during their shipment or transportation [12]. In the processes of wastewater pretreatment, post-processing sludges are generated. The sludges are characterised by specific and variable physico-rheological features and chemical composition that has to be disposed ultimately [13].

The aim of this study was to assess the risk on the basis of the analysis of fractional composition of selected heavy metals and leaching tests (TCLP) concerning settled primary

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sludges separated at the first step of raw effluents pretreatment after their retention and sedimentation of dispersed solid fractions, generated as the result of surface cleaning of railway cars of classes G, H and T, according to the International Union of Railways classification [14].

Experimental part

Basic characteristics of the source of primary sludges generation and sampling

The post-sedimentary sludges were sampled from the first processing volume of physico-chemical wastewater treatment plant with daily capacity up to 50 m^3/day [15]. It was designed for water cleaning of rail freight cars of class E, F, G, H, K, L, R and T according to the International Union of Railways classification [14]. Raw effluents from washing surfaces of transport rolling stock were directed to flow gravitationally to the first retention-averaging tank. There the treated wastewaters were kept for at least 90 minutes to separate the sludges after sedimentation. Periodically accumulated sludges were pumped onto a unit of its gravity drainage that consisted of open sack filters. Sample groups of sludges dewatered separately each month were marked with: A, B and C indices. Specimens for analyses were collected after 7 days of final dewatering, counting from the moment that the last batch of raw sludges onto the filter unit. The filtrate pH recorded from the start of filtration and within seven days of final gravity filtering, counting from the moment of introducing the last batch of raw sludge onto the filter unit, formed as follows: a) A pH 6.4 ±0.5, b) B pH 7.2 ±0.5, c) C pH 7.3 ±0.6.

Collected sludge specimens were subject to 5-stage sequential extraction procedure in accordance with Tessier's methodology [16] and TCLP (Toxicological Characteristic Leaching Procedure) [17], then concentrations of selected heavy metals were determined.

TCLP leaching tests procedure

The assessment of gravitationally sampled dewatered sludges was made in compliance with TCLP methods in accordance with the USEPA Method 1311 [17] determining leachable forms of metals such as Cu, Ni, Pb and Zn, because only those metals were found in the raw sewage flown. The final determinations in the extracts were made using the Jobin Yvon EMISSION JY 38S ICP-OES emission spectrometer and the standard for the determination of metals PN-EN ISO 11885:2009E [18]. The proceedings used in the TCLP leaching procedure included the following stages:

a) sampling of sludge of particles size < 9.5 mm, homogenising and sieving;

b) the reaction of sludge was checked: 96.5 cm^3 of distilled water was added up to 5.0 g of “non-anhydrous” sample and mixed for 5 minutes and then pH was measured. When pH < 5.0, the extraction solution L no. 1 was used, and when pH > 5.0 then 3.5 cm^3 of 1 M HCl was added. Then, the covered content was heated up to 50°C for 10 minutes. After cooling to room temperature, pH was measured to determine a type of extraction solution L. If pH < 5.0 extraction solution L no. 1 was applied. If pH > 5.0, extraction solution L no. 2 was used (extraction solution L no. 1 was a mixture of the following composition: 11.4 cm^3 HOAc + 128.6 cm^3 1 M NaOH and topped up with distilled water to 2.0 dm^3, and its final reaction was at the level of the pH = 4.93±0.05. Extraction solution L no. 2 was prepared by diluting 11.4 cm^3 HOAc with distilled water up to 2.0 dm^3 due to which its final reaction was at the level of pH = 2.88±0.05);

c) preparing the composition for extraction - for the determination of components: 100.0 g of "non-anhydrous" of sludge samples (S) in duplicates, to which suitable extraction solution (L) as described in point (b) was added in relation of the liquid to solid sludge (S), respectively (L/S) = 20:1 were used;
d) shaking during 18.0±2.0 hours at room temperature;
e) separating the phases by filtering;
f) the analysis of metals concentration in the filtrate with pH < 2 (acidifying with HNO_3).

In the event of noticing the incidentally high concentrations of metals in the influencing raw sewage, for the relevant batch of settled sludge from such a stream of the effluents, an additional leaching procedure was run and its results are presented in the list of results.

The analysis of fractional composition of selected metals according to Tessier's procedure

Gravitationally settled deposits were submitted to sequential extraction consisting in determining five fractions in accordance with Tessier's basic procedure specified in item [16]. 100.0 g of "non-anhydrous" sludge in two replications was used for the extraction. The conditions of sequential extraction are set in Table 1.

Table 1

The proceedings in the sequential extraction was adopted on the basis of position [16]

Fractions	Quantities of used reagents for the sample of 100.0 g	Details of the proceedings
(F1) Exchangeable	● 800 cm^3 1 M $CaCl_2$ (pH 7)	● shaking 1.0 h at room temperature
(F2) Carbonate	● 800 cm^3 1 M CH_3COONH_4 (pH 7) (acidification with 25% CH_3COOH [a])	● shaking 5.0 h at room temperature
(F3) Fe-Mn oxides bound	● 2000 cm^3 0.04 M $NH_2OH•HCl$ in 25% CH_3COOH [a] (v/v) (pH 2)	● shaking 5.0 h at 96°C
(F4) Organic	● 300 cm^3 0.02 M HNO_3 and 500 cm^3 30% H_2O_2 [b] (pH 2), ● 500 cm^3 3 M CH_3COONH_4 in 20% HNO_3 (v/v) (pH 2)	● shaking 3.0 h at 85°C ● shaking 0.5 h at room temperature
(F5) Residual	● a mixture of aqueous solutions of HNO_3 and H_2O_2 was added twice within an hour (a mixture of pH 2 was prepared from 300 cm^3 HNO_3 [c] and 500 cm^3 30% H_2O_2 [b]), ● 500 cm^3 30% H_2O_2 [b] was added	● shaking during 1.0 h at boiling point up to a moment of the emission of white vapours, ● shaking during 0.5 h at boiling point

densities of chemical reagents used were as follows: [a] 25% CH_3COOH (ρ = 1.0320 g/cm^3), [b] 30% H_2O_2 (ρ = 1.1110 g/cm^3), [c] 65% HNO_3 (ρ = 1.4020 g/cm^3)

Results and discussion

Both fractions: the exchange one (F1) and the carbonate (F2) one, are considered to be loosely associated with matrices of sludge, and sensitive even to minor changes of environmental conditions, i.a. changes in pH or ionic strength [19]. In most known methods of sequential extraction, fraction F1 is obtained using mild extraction solvents such as mild solutions of acids or salts.

Table 2

The content [%] of metals in various fractions of 5-stage sequential extraction carried out in compliance with Tessier's methodology for gravitationally dewatered post-sedimentary primary sludge from wastewater treatment generated in rail freight car wash [a)]

Metals	**Sample (pH)**	**F1**	**F2**	**F3**	**F4**	**F5**
Zn	B1 (7.2)	3.1	9.6	9.7	25.5	52.1
	B2 (7.1)	17.7	10.3	14.9	21.0	36.1
	B3 (7.3)	2.9	9.9	9.6	25.8	52.4
	A1 (6.4)	6.2	6.8	10.3	26.1	50.6
	A2 (6.5)	5.8	27.0	29.8	27.1	10.3
	A3 (6.4)	17.1	5.8	10.1	26.6	50.4
	C1 (7.2)	5.8	5.2	9.6	22.3	57.1
	C2 (7.3)	5.9	14.9	9.3	28.0	41.9
	C3 (7.3)	5.2	5.1	10.1	21.9	56.7
Pb	B1 (7.2)	4.7	2.5	0.9	7.7	84.2
	B2 (7.1)	5.1	7.6	1.1	7.9	78.3
	B3 (7.3)	5.5	7.3	1.6	7.4	78.2
	A1 (6.4)	2.8	9.1	1.6	7.4	79.1
	A2 (6.5)	2.5	9.3	1.3	7.7	79.2
	A3 (6.4)	3.1	9.7	1.1	7.2	78.9
	C1 (7.2)	8.5	3.8	0.8	7.6	79.3
	C2 (7.3)	4.5	3.1	1.5	7.8	83.1
	C3 (7.3)	8.2	4.9	1.2	7.9	77.8
Cu	B1 (7.2)	5.8	0.2	1.9	67.6	24.4
	B2 (7.1)	5.5	0.5	2.1	67.8	24.1
	B3 (7.3)	4.0	1.9	2.3	68.5	23.3
	A1 (6.4)	9.8	2.3	47.9	28.1	11.9
	A2 (6.5)	2.8	3.1	2.2	68.2	23.7
	A3 (6.4)	3.3	2.9	2.1	62.6	29.1
	C1 (7.2)	3.9	2.2	1.8	67.7	24.4
	C2 (7.3)	3.6	2.5	1.9	67.8	24.2
	C3 (7.3)	3.8	2.3	1.8	67.7	24.4
Ni	B1 (7.2)	6.8	9.3	16.8	35.6	31.5
	B2 (7.1)	16.6	9.8	6.6	35.3	31.7
	B3 (7.3)	6.3	9.8	16.9	30.0	37.0
	A1 (6.4)	6.1	10.2	7.4	39.8	36.5
	A2 (6.5)	6.3	10.6	7.5	36.2	39.4
	A3 (6.4)	7.8	9.8	7.1	35.1	40.2
	C1 (7.2)	4.2	12.6	5.9	34.7	42.6
	C2 (7.3)	4.3	12.5	5.7	35.2	42.3
	C3 (7.3)	9.9	10.2	19.7	38.1	22.1

[a)] the raw wastewater was generated as a result of water cleaning of usable surface of transport railway rolling stock, mainly of: G, H and T classes according to the International Union of Railways classification [14]

The forms of metals associated with reducible fraction (F3) are considered as thermodynamically labile and available under anaerobic or anoxic conditions [19]. Therefore, fractions F1-F3 are considered as the pools of metals from direct effects and involving a direct toxicity. In oxidizing conditions that are obtained for the determination of fraction F4, metals which are connected with organic matter and metals that react with sulphides may be released or converted from the forms of preferred for fractions F1-F3. Fraction F4 is also identified as a pool of speciation forms of potential effect and potential toxicity. But the residual fraction F5 is regarded as chemically stable and durable because it contains mainly primary and secondary mineral forms and the metals are firmly bonded in their structures with predominant participation of crystallized forms as well. Currently, it is usually assumed that metals from residual fraction are not easily released to different components of the environment and do not represent any potential toxic risk for the biosphere [20]. Table 2 shows the data obtained from the 5-stage sequential extraction (according to Tessier's methodology) for settled dewatered post-sedimentary sludges collected at monthly intervals within the period of 3 months of the operation of the physico-chemical treatment plant for sewage generated from water cleaning of usable surfaces of railway transport rolling stock, mainly of classes: G, H and T according to the International Union of Railways classification [14]. Samples for the research were collected after seven days of gravity settling of sludges on the sets of open sack filters, counting from the moment of pressing the last volume of post-sedimentary sludge. Differences in pH of filtrates recorded every day in the time of sludges dewatering are given in part of basic characteristics of the source of primary sludges generation and sampling of this stage of the work.

An interesting and useful criterion for assessing the waste is the risk assessment code (RAC). RAC classification for 5-stage sequential Tessier's extraction was introduced by Perin et al. [21], whereas Sundaray et al. introduced this classification for standardized 3-stage sequential extraction BCR [19]. RAC methodological guidelines are used to determine the risk with reference to each metal contained in the waste. The risk assessment code is determined on the basis of the percentage of total heavy metals content in the exchangeable fraction and the one associated with carbonates. In the exchangeable fractions, metals are associated with a solid phase of the waste by different kind of weak bonds. Therefore, the higher the percentage of metal in these fractions, the greater the likelihood of its release from the solid phase of the waste to the adjacent water phase having direct physical contact with it. In accordance with RAC classification, if a sum of two fractions F1+F2 (in 5-stage extraction) or if the content of F1 (in BCR extraction) is less than 1%, then the sludge does not constitute a threat (NR) carrying the risk (I) for the aquatic environment by the individual metal. When the total percentage of metal in the fraction F1 or in the sum of the fractions F1+F2 is, respectively: 1-10, 11-30, 31-50%, and more than 50%, it means, respectively: low (LR) risk (II), moderate (MR) risk (III), high (HR) risk (IV) and very high (VHR) risk (V). It is suggested that basing on the criterion defined in such way, you can estimate the easiness of introducing the metal into the food chain [21-25].

Analysing fractional composition of heavy metals in the post-sedimentary primary sludge, you can notice (Table 2 and Fig. 1) that in case of Zn, the labile fractions, including exchangeable, carbonate, reduction and organic ones, are quantitatively similar to the contents of a stable residual fraction F5, the share of which varies between 40 to 50%. It can be assumed that the analytically evaluated primary deposits are characterised by a moderate risk (MR 11-30%) for aquatic environment due to the recorded concentration level of mobile forms of Ni, Zn and Pb (the exceptions are two sludge samples with reference to lead: B1 and C2, of low risk (LR)). The nature of low risk (LR 1-10%) is characteristic of “non-anhydrous" samples of sludge in relation to Cu, with the exception of sample A1 of moderate character. Moderate risk (MR) and moderate likelihood of introducing metals into the food chain concerns 70% (25 of 36) of the analysed samples of sludge and a low risk: 30% (11 analysed samples of 36 in total). The sludge samples of slightly acidic pH 6.4 indicate the moderate nature of risk for the aquatic environment concerning Ni, Pb and Zn and low nature of risk in relation to Cu. This can be interpreted by higher availability of mobile metals forms in more acidic pH, which results in a higher level of their extraction.

To assess the potential toxicity of individual metals, it is worth considering the test results for samples with pH = 6.4 which is the nearest to pH found in TCLP method. The concentrations of mobile metals forms released in the exchangeable and carbonate fractions are comparable with the concentrations determined in accordance with TCLP procedure with acidic values of pH. According to a broad group of authors, to estimate the potential risk of toxicological wastewaters or sludges, the number of metals bond in mobile fractions, i.e. the sum of exchangeable fraction and carbonate one, instead of the total contents of metals [21, 26-30] are taken into account.

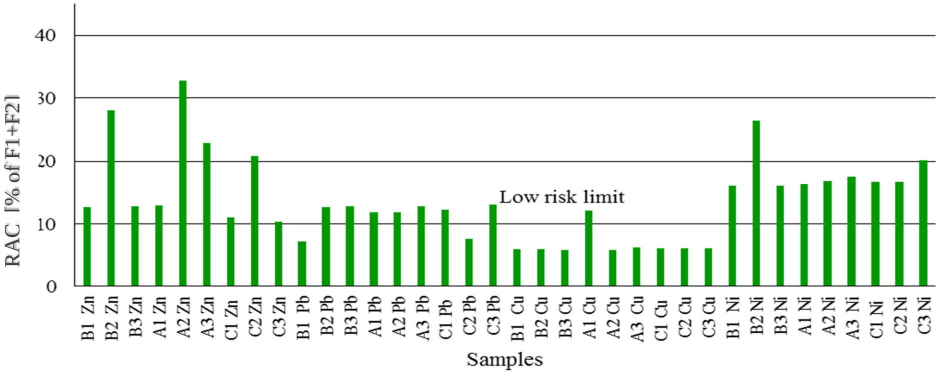

Fig. 1. Comparison of the risk assessment code (RAC) determined in relation to Cu, Ni, Pb and Zn for the gravitationally dewatered samples of post-sedimentary primary sludge from the first stage treatment of wastewaters generated as a result of water cleaning of rail freight cars, mainly of: G, H and T classes; where: indexes A-C indicate the groups of sludge samples taken in consecutive months from the sludge dewatering stage with simultaneous registration of pH values and pH of filtrates were at the level, respectively for: A - 6.4 ±0.5, B - 7.2 ±0.5 and C - 7.3 ±0.6

Exemplary results of leaching Cu, Ni, Pb and Zn from gravitationally dewatered post-sedimentary primary sludge, obtained after the application of TCLP procedure, is set in Table 3. The highest concentrations of all metals were leached for sediments with pH 6.4 that were, respectively for Pb and Zn, at levels: 0.041-0.13 and 0.54-0.99 mg/dm^3, whereas in case of Cu and Ni at the same pH of leaching, the concentration limits were the following: 0.05-0.93 and 0.60-0.67 mg/dm^3.

In accordance with US EPA, the leaching limit value has been defined only for lead, on the basis of which a nature of waste toxicity is determined. For this metal, the concentration limit is set at the level of 5 mg/dm^3 [17]. In case of post-sedimentary deposits from the first stage of wastewater treatment, an incidental value of leached lead concentration at the level of 6 mg/dm^3 was determined in a separated "non-anhydrous" additional sample during the last month of this research. The additional procedure was applied due to the found out incidentally increased concentration of this metal in the raw sewage which was at the level of 1.06 mg/dm^3. Considering a final value of Pb concentration from the TLCP test for assessment, it was assumed that the incidental cases of unusual short-term concentrations for random sampling test specimens cannot be taken into account for assessing the final value of leachability of representative samples for the whole mass of the waste. Therefore, in previous months (groups of samples marked with indices A and B), no concentrations of leached Pb above the assumed criterion threshold values were found and Pb concentrations in the influent raw sewages were recorded at definitely lower levels.

Table 3

Recorded concentrations of leachable pools of metals [mg/dm^3] after applying TCLP procedure for "non-anhydrous" samples of gravitationally dewatered post-sedimentary primary sludge of the wastewater generated in the installation of rail freight cars wash

Samples (pH)	**TCLP [mg/dm^3]**			
	Zn	**Pb**	**Cu**	**Ni**
B1 (7.2)	0.33	ND	0.109	0.041
B2 (7.1)	0.53	0.029	0.18	0.061
B3 (7.3)	0.062	0.008	0.095	0.047
A1 (6.4)	0.54	0.041	0.1	0.6
A2 (6.5)	0.76	0.089	0.05	0.61
A3 (6.4)	0.99	0.13	0.93	0.67
C1 (7.2)	0.71	0.082	0.076	0.049
C2 (7.3)	0.061	ND	0.107	0.053
C3 (7.3)	0.58	0.17 (6.0) [a]	0.006	0.067

[a] This incidental value was determined for a sample of gravitationally dewatered sludge from isolated batch of raw wastewaters, in which Pb concentration was determined at the incidentally high level of 1.06 mg/dm^3

The post-sedimentary primary sludges from the first stage wastewater treatment may be classified as non-toxic, as the limit value of 5 mg/dm^3 of leached lead was not exceeded. Therefore, in accordance with the adopted criterion, the primary sludge may be qualified as non-toxic for the environment, taking into account the range of TCLP assessment proposed by the US EPA [17].

Conclusions

Gravitationally dewatered post-sedimentary sludges generated as a result of the pretreatment of effluents from water cleaning of usable surfaces of railway transport rolling stock transport are in particular characterised by:

a) irregularity of leached quantities in accordance with the TCLP test procedure concerning such metals as: the Cu, Ni, Pb and Zn and a variable fraction of these metals pools determined as a result of conducting a sequential extraction procedure in accordance with the methods set out by Tessier,

b) low-risk (LR) regarding Cu,

c) moderate risk (MR) in case of Zn, Pb and Ni.

Analysed deposits may be classified as non-toxic waste with reference to Pb and Zn, Cu, Ni (which are unlimited) in accordance with the TCLP criteria of USEPA.

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OCENA OSADÓW Z OCZYSZCZANIA ŚCIEKÓW Z MYJNI KOLEJOWYCH WAGONÓW. OSADY WSTĘPNE

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Abstrakt: Przedstawiono wyniki oceny osadów posedymentacyjnych generowanych w warunkach pełnej skali technologicznej na instalacji do podczyszczania ścieków powstających w wyniku stosowania wodnego oczyszczania powierzchni użytkowej kolejowych środków transportu towarowego, głównie klas G, H i T według typologii International Union of Railways. Osady wydzielano w zbiorniku magazynująco-uśredniającym, będącym pierwszym węzłem procesowym instalacji podczyszczania, do której napływały ścieki surowe. Z uwagi na znaczące zróżnicowanie ładunku zanieczyszczeń kierowanych do tej objętości również osady charakteryzowały się istotną niejednorodnością. Zaprezentowano wyniki z przeprowodzonej procedury wymywalności TCLP dla wytypowanych próbek oraz przedstawiono ocenę ryzyka, stosując kod RAC na podstawie analizy składu frakcyjnego wytypowanych metali ciężkich, takich jak Cu, Ni, Pb i Zn. Stwierdzono, że odwodnione grawitacyjnie osady posedymentacyjne, generowane w okresie losowo wytypowanych trzech miesięcy eksploatacji instalacji, wykazują niskie ryzyko (LR) względem Cu oraz umiarkowane (MR) wzgledem Ni, Pb i Zn. Zgodnie z kryteriami TCLP, osad wstępny, będący efektem przetrzymania surowych ścieków i sedymentacji z nich frakcji zdyspergowanych, sklasyfikowano jako odpad nietoksyczny.

Słowa kluczowe: ścieki z myjni wagonów towarowych, osady posedymentacyjne, test TCLP, skład frakcyjny metali ciężkich w osadach, kod oceny ryzyka (RAC)

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WASTEWATERS TREATMENT FROM RAIL FREIGHT CAR WASH. ASSESSMENT OF PHYSICOCHEMICAL TREATED SLUDGES

OCZYSZCZANIE ŚCIEKÓW Z MYJNI WAGONÓW TOWAROWYCH. OCENA OSADÓW PO FIZYKOCHEMICZNYM OCZYSZCZANIU

Abstract: The process of physico-chemical pretreatment of wastewaters produced in the rail freight car wash was carried out under flow conditions in two-chamber reactor of accelator type with a final fine purification on multi-layer gravel filter. The post-processing sludge were generated as a result of the use of coagulation and flocculation and, to a minimum degree, from washings formed due to a periodic backwash of gravel filters. This article presents the results concerning assessment of gravitationally dewatered post-coagulation sludge and sludge from backwashing of gravel filters, released after sedimentation, and dewatered mixture of these two types of sludge. These all precipitates were subject to leaching with the use of TCLP procedure and risk assessment based on the analysis of fractional composition of selected heavy metals. It was found that sludge from wastewater treatment after the use of the two-stage acid-alkaline (PIX® 116 - SAX® 18) or alkaline-acid coagulation (SAX® 18 - PAX® 18) with a final flocculation and phase separation in a flow type accelator are characterised by a distinctly lower leachability levels of heavy metals than in case of post-sedimentary primary sludge and they manifest low risk considering Cu, Ni, Pb and Zn determined by the adopted level of risk assessment code (RAC). According to the criteria adopted for TCLP classification, the analysed sludge are neither toxic nor hazardous waste.

Keywords: treatment of wastewaters from railway freight car wash, sludge after coagulation, sludge from gravel filter backwashing, TCLP test, fractional composition of metals in sludge, risk assessment code (RAC)

Introduction

Water cleaning of usable surfaces of rail freight cars of class E, F, G, H, K, L, R and T in accordance with the International Union of Railways classification creates significant quantities of wastewaters that are predominantly loaded with the specific and rarely repeatable levels of pollutants [1]. The low-loaded wastewaters, with a rational use of water, may be effectively pretreated with physico-chemical methods and returned to be reused in the cleaning processes of railway transport rolling stock [2, 3]. The size and composition of the pollutants load depend, among other things, on physical state and chemical composition of residues after transported goods and their fineness, sealing of different types of packaging used to secure the transported goods etc. [4, 5]. In raw sewage, there can also be microbiological, mycological contamination and other forms of biologically active organisms [6-9]. Moreover, incidentally or periodically heavy metals in various speciation forms may become a significant load in contamination pools generated in effluents [10].

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Bio-activity and eco-toxicity of heavy metals primarily depend on their fractional speciation [11-13]. Sequential extraction is a group of known and widely used methods to determine fractions of metals in different environmental components and other matrices containing these contaminants. A method that uses Tessier's procedure, enables an interesting risk estimation of speciation forms by dividing them into five different fractions on the basis of a criterion linked to their leachability with the use of various solvents revealing different activity and ionic strength. For example, the pools of metal marked and classified as exchangeable and carbonate forms are easily released under acidic environmental conditions. This fact causes a considerable interest in search for different forms of relationships between the results obtained by TCLP methods and sequential extraction for different matrices, e.g.: soil ones [14], ashes from the incineration of medical wastes [15], residues from the incineration of municipal solid wastes [16], residues from metallurgical leaching of zinc [17] or waste paints from protective covering of bridge structures [18].

The aim of this study was to assess the risk on the basis of the analysis of fractional composition of selected heavy metals and (TCLP) leaching tests concerning mixed post-processing sludge (after-coagulation ones, from backwashing of gravel filters) generated as the result of physico-chemical pretreatment of water used for surface cleaning of railway cars of classes G, H and T for the post part, according to the International Union of Railways classification [1]. The research focused on the analysis of fractional composition of such heavy metals as Cu, Ni, Pb and Zn, because their presence was found in the influent raw wastewaters during the randomly selected three months of operation of the wastewaters pretreatment plant. The results obtained using TCLP method with values assigned to the risk assessment code (RAC) were also compared in this paper.

Experimental part

Basic technical characteristics of physico-chemical pretreatment installation

The post-processing sludge used for the analyses were sampled from the physico-chemical wastewater pretreatment plant with daily capacity up to 50 m^3/day [19]. It was designed for water cleaning of rail freight cars of class E, F, G, H, K, L, R and T in accordance with the International Union of Railways classification [1]. Raw sewage originating from washing the surface of the railway rolling stock of freight type were gravitationally drained to a retention-averaging tank, to its sedimentary-settling section, where they were kept, the result of which were post-processing primary sludge assessed in the first part of this study. Then, the sludge was directed to the flow installation for physico-chemical pretreatment of accelator type, where post-coagulation sludge (SC) were generated as a result of metering the 1st-stage coagulant and then the 2nd-stage coagulant; the sludge were accumulated gravitationally in sediment pockets of sedimentary zone of the accelator. This part presents the results for sludge generated after applying the associated acid-alkaline coagulation with the use of a system coagulants of Kemira Kemipol Sp. z o.o. class [20], respectively: PIX® 116 - SAX® 18 (acidic ferric coagulant - alkaline aluminium coagulant) or alkaline-acidic ones, respectively: SAX® 18 - PAX® 18 (alkaline aluminium coagulant - acidic ferric coagulant) (Table 1). Thickening of dispersed precipitated fractions was carried out by means of 0.3% flocculant solution (aqueous solution of FLOPAM™ FO

4800 SNF Floerger S.A.S. ZAC de Milieux). After the sedimentation phase, cleared pretreated sewage was directed onto the process unit of open, multilayer gravel gravity filter, on which periodic backwashing was conducted, resulting in generation of backwash sludge marked with index SG (Table 1). The mentioned above streams of post-processing sludge were periodically transported using sludge pumps onto the drainage system equipped with open gravity bag filters, where a concentration of solid fractions was performed under conditions of gravitatively forced filtration. The application of such a method of filtration enabled to isolate individual types of sludge after coagulation on separated units of their gravity drainage. The separated sludge were marked with indexes in further parts of this text as follows:

a) post-coagulation sludge obtained using system PIX$^{®}$ 116 - SAX$^{®}$ 18 ($SC_{(PIX® 116 - SAX® 18)}$),
b) post-coagulation sludge obtained using system SAX$^{®}$ 18 - PAX$^{®}$ 18 ($SC_{(SAX® 18 - PAX® 18)}$),
c) sludge from backwashing the gravel filter (SG),
d) mixed sludge (MS) containing post-coagulation sludge and gravel filter backwash sludge.

Short characteristics of the place of post-processing deposits generation and sampling

Post-coagulation sludge of classes $SC_{(PIX® 116 - SAX® 18)}$, $SC_{(SAX® 18 - PAX® 18)}$ and mixed ones (MS) originating from coagulation systems PIX$^{®}$ 116 - SAX$^{®}$ 18 and SAX$^{®}$ 18 - PAX$^{®}$ 18 with the participation of sludge from gravel filter backwash (SG) without specifying the percentage fraction of them, accumulating in precipitate pockets of sedimentary-depositional zone of the accelator were periodically transported using a sludge pump onto the unit of gravity drainage of them, consisting of open bag filters. Such technical solution of the filtration enabled to particular types of sludge to be dewatered. After seven-day period of gravity drainage (counting from the moment that the last batch of sludge was input onto the filtration unit), samples for further analyses were collected and the results obtained are summarized in Table 1. The pH of the individual filtrates also measured during the final, seven-day drainage was registered at a stable level and was the following for the individual types of sludge:

a) SC1 and SC2 (from coagulation with system PIX$^{®}$ 116 - SAX$^{®}$ 18) $pH_{SC1} = 7.7 \pm 0.3$ and $pH_{SC2} = 8.2 \pm 0.2$,
b) SC3 (from coagulation with system SAX$^{®}$ 18 - PAX$^{®}$ 18) $pH_{SC3} = 8.4 \pm 0.3$,
c) SG1 (post-filtering sludge from filter backwash SC1) $pH_{SG1} = 7.9 \pm 0.1$,
d) SG2 (post-filtering sludge from filter backwash SC2) $pH_{SG2} = 8.3 \pm 0.1$,
e) SG3 (post-filtering sludge from filter backwash SC3) $pH_{SG3} = 8.5 \pm 0.1$,
f) SM1, SM2 and SM3 (mixed post-coagulation and post-filtration sludge) $pH_{SM1} = 8.8 \pm 0.1$, $pH_{SM2} = 8.2 \pm 0.2$ and $pH_{SM3} = 8.4 \pm 0.1$.

TCLP leaching tests procedure

The assessment of wastes generated after the process of their gravity drainage was performed by determining leachable forms of metals (Cu, Ni, Pb and Zn) in accordance with the TCLP methods (Toxicological Characteristic Leaching Procedure) in compliance with US EPA procedure, Method 1311 [21], for 100.0 g of “non-anhydrous” sludge in two replications with the use of Jobin Yvon EMISSION JY 38S emission spectrometer ICP-OES and standard ISO 11885:2007 [22] for the determination of metals in the filtered extracts.

The analysis of fractional composition of selected metals according to Tessier's procedure

Post-processing sludge, including the ones after coagulation (SC1-SC3), form the backwash of gravel filter (SG1-SG3) and mixed sludge (MS1-MS3) were subject to sequential extraction consisting in determining five fractions in accordance with basic Tessier's procedure specified in detailed description in [23] and in the first part of this study. 100.0 g of the sludge of the "non-anhydrous” sample in two replications was applied for the extraction.

Results and discussion

In recent decades, there have been developed different methods of a simple one- and multi-stage sequential extraction [23, 24]. The use of sequential extraction in accordance with the proposal of Tessier et al. [23] provides the possibility to obtain information concerning potential mobility and bioavailability of heavy metals in a hypothetical environment. The data obtained from the use of fractionation procedures, provide i.a. the information on speciation of heavy metals and their origin, occurrence, bioavailability, mobility and a possible pool for migration [25, 26]. Table 1 shows the results of 5-stage sequential extraction (acc. to Tessier), which were obtained for the samples of post-processing sludge: after coagulation (SC1-SC3) and after backwashing of gravel filter (SG1-SG3) and the mixed sludge (SM1-SM3). The sludge were generated on the full scale installation in the randomly selected time period of three months of continuous operation and the application of associated acid-alkaline coagulation using the PIX® 116 - SAX® 18 system or of alkaline-acid coagulation using the SAX® 18 - PAX® 18 system. The determined fractional composition of the analysed metals in sludge indicates an evident qualitative growth in fractional stability of post-processing sludge with reference to fractional composition determined in raw sludge separated as the result of sedimentation (characterised in the first part of this study). The use of associated coagulation especially affects the increase in a quantitative share of residual fraction F5 for nickel and lead. Those post-processing sludge may be classified as not posing risk considering Pb for samples after coagulation (SC) and mixed (SM) sludge. Sludge samples from backwashing gravel filter (SG) for lead are characterised by a high content of residual fraction (approx. 62%) and a relatively considerable content (1-5.1%) of mobile - carbonate fraction F2 which affects the qualification of sludge in the category presenting low risk to the environment. Other analysed samples feature a low risk considering Cu, Ni and Zn. A dominant speciation fraction in the tested post-processing sludge was residual F5 for Cu, Ni, Pb and Zn. In terms of chemical composition and structure, you can interpret the size of the F5 pool as a permanently composed mixture (mainly preferred in terms of pH) of sparingly soluble hydroxide pools of the following type: $Cu(OH)_{2(s)}$, $Ni(OH)_{2(s)}$, $Pb(OH)_{2(s)}$ and $Zn(OH)_{2(s)}$ in quantitatively dominant vicinity of solid conglomerates generated as a result of precipitation of iron and aluminum forms.

Table 1

Example of fractional composition [%] of selected heavy metals, determined according to Tessier's procedure in the following dewatered sludge: sludge after coagulation (SC), sludge from backwashing of gravel filter (SG) and mixed sludge (SM) generated as a result of the physico-chemical treatment of wastewaters from the rail freight car wash, and the risk assessment code (RAC) adopted for the individual types of sludge a-c)

Metals	**Sample (kind of sludges) d)**	**F1**	**F2**	**F3**	**F4**	**F5**	**∑F1+F2**	**RAC e)**
Zn	SC1$_{(PIX® 116 - SAX® 18)}$	1.3	0.8	9.1	19.5	69.3	2.1	LR
	SC2$_{(PIX® 116 - SAX® 18)}$	1.2	0.8	12.3	22.4	63.3	2.0	LR
	SC3$_{(SAX® 18 - PAX® 18)}$	0.6	0.6	15.2	16.3	67.3	1.2	LR
	SG1$_{(PIX® 116 - SAX® 18)}$		1.3	18.1	9.1	71.5	1.3	LR
	SG2$_{(PIX® 116 - SAX® 18)}$	0.3	0.9	15.5	11.2	72.1	1.2	LR
	SG3$_{(SAX® 18 - PAX® 18)}$		1.1	19.2	10.3	69.4	1.1	LR
	SM1		1.4	13.6	14.1	70.9	1.4	LR
	SM2		1.1	11.4	18.8	68.7	1.1	LR
	SM3	1.2		12.5	14.1	72.2	1.2	LR
Pb	SC1$_{(PIX® 116 - SAX® 18)}$		5.1$^{c)}$	2.5	29.5	62.9	5.1	LR
	SC2$_{(PIX® 116 - SAX® 18)}$		3.2	2.1	36.6	58.1	3.2	LR
	SC3$_{(SAX® 18 - PAX® 18)}$		1.3	2.3	34.3	62.1	1.0	LR
	SG1$_{(PIX® 116 - SAX® 18)}$			7.4	28.5	64.1		NR
	SG2$_{(PIX® 116 - SAX® 18)}$			9.2	29.1	61.7		NR
	SG3$_{(SAX® 18 - PAX® 18)}$			8.5	28.3	63.2		NR
	SM1				38.3	61.7		NR
	SM2				37.6	62.4		NR
	SM3				39.1	60.9		NR
Cu	SC1$_{(PIX® 116 - SAX® 18)}$		1.4		13.1	85.5	1.4	LR
	SC2$_{(PIX® 116 - SAX® 18)}$		0.9		13.2	85.9	0.9	NR
	SC3$_{(SAX® 18 - PAX® 18)}$	0.8			8.1	91.1	0.8	NR
	SG1$_{(PIX® 116 - SAX® 18)}$		1.2		16.7	82.1	1.2	LR
	SG2$_{(PIX® 116 - SAX® 18)}$		1.1		17.2	81.7	1.1	LR
	SG3$_{(SAX® 18 - PAX® 18)}$				19.6	80.4		NR
	SM1		0.5		15.1	84.4	0.5	NR
	SM2		0.8		13.7	85.5	0.8	NR
	SM3				11.8	88.2		NR
Ni	SC1$_{(PIX® 116 - SAX® 18)}$		1.3	7.4	12.1	79.2	1.3	LR
	SC2$_{(PIX® 116 - SAX® 18)}$	1.1		8.1	14.1	76.7	1.1	LR
	SC3$_{(SAX® 18 - PAX® 18)}$		1.1	6.9	12.9	79.1	1.1	LR
	SG1$_{(PIX® 116 - SAX® 18)}$		1.7	7.5	14.1	76.7	1.7	LR
	SG2$_{(PIX® 116 - SAX® 18)}$			6.5	16.3	77.2		NR
	SG3$_{(SAX® 18 - PAX® 18)}$		1.1	7.7	15.1	76.1	1.1	LR
	SM1	0.9		7.8	11.1	80.2	0.9	NR
	SM2		1.4	7.1	12.4	79.1	1.4	LR
	SM3		1.1	7.3	13.2	78.2	1.1	LR

a) the process of coagulation in the accelator was conducted with the control of the reagent uniform mixing using pH-meters process at the inlet (pH1) and outlet (pH2) of tube reactor installed at the upstream of the flow chamber of high speed mixing of the accelator, setting the dose of coagulant PIX® 116 in metering mode “up to pH” with reference to the algorithm of pH-meter readouts (pH1), and the dose of alkaline coagulant SAX® 18 according to the dose of coagulant PIX® 116 in preset relations while meeting the conversion relationship of pH, respectively: $pH_{(PIX\ 116)} = 1.2 \cdot pH_{(SAX\ 18)}$, but with keeping the preset value of upper limit after neutralization at pH = 8.8

b) analogous to the one given in a) metering procedure was adopted for coagulation system SAX® 18 - PAX® 18

c) retention time of wastewaters treated by sedimentation (total flow time) in processing chambers of slow and fast mixing of the accelator, established for the procedures of this series of experiments at the level of 90-95 minutes

d) adopted indices SC1-SC3, SG1-SG3 and SM1-SM3 mean, respectively, sludges after coagulation (after coagulation using the following systems: PIX® 116 - SAX® 18 or SAX® 18 - PAX® 18), from the backwash of gravel filter, and mixed sludge

e) adopted indices mean, respectively: NR - no risk and LR - low risk (Table 2)

These structures can be presented by the simplified stoichiometric notation (e.g.: $x_{(1)}Fe(OH)_{3(s)}\bullet y_{(1)}Al(OH)_{3(s)}\bullet z_{(1)}H_2O$), or alumino-ferric (e.g.: $x_{(2)}Al(OH)_{3(s)}\bullet y_{(2)}Fe(OH)_{3(s)}\bullet z_{(2)}H_2O$), where: the value of coefficients $x_{(1)}$, $x_{(2)}$, $y_{(1)}$ and $y_{(2)}$ depends on a dose of coagulants and a final pH value of the post-processing sludge, $z_{(1)}$, $z_{(2)}$ - the number of bounded water molecules (e.g. constitutional and/or crystallisation water and/or water in other forms) [27].

Speciation forms determined by fractional analysis are essential to estimate the potential mobility and toxicity of heavy metals identified in the tested post-processing sludge. Depending on the further proceedings, wastes may involve even the risk of releasing the metals into the environment by a spontaneous run of natural or anthropogenic processes [28]. The quantitative distribution in different fractional pools, determined with the use of sequential extraction in accordance with Tessier's or BCR procedures, provides an estimate for their availability which, in turn, affects the risk associated with the potential migration of metals into the aquatic environment from the post-processing wastes under discussion. Historically, the RAC classification for 5-stage sequential Tessier's extraction was introduced by Perin et al. [29], whereas Sundaray et al. introduced this classification for standardized 3-stage BCR sequential extraction [13], which is presented in Table 2 in a form of indices.

Table 2

Scale according to risk assessment code criteria (RAC)

Risk category	Risk level (adopted index)	% of metal in fraction F1 [a)] or the sum of fraction F1+F2 [b)]
I	No risk (NR)	< 1
II	Low risk (LR)	1-10
III	Medium risk (MR)	11-30
IV	High risk (HR)	31-50
V	Very high risk (VHR)	> 50

[a)] soluble in acid/exchangeable in BCR procedure [13]; [b)] in Tessier's procedure [29].

Table 3

Exemplary concentrations of the leachable metals on the basis of TCLP procedure for sludge after coagulation (SC1-SC3), sludge from the backwash of gravel filter (SG1-SG3) and mixed sludge (SM1-SM3) generated as a result of physico-chemical treatment of wastewaters from the rail freight car wash

Samples (kind of sludge)	TCLP test results [mg/dm^3] [a)]			
	Zn	Pb	Cu	Ni
SC1(PIX® 116 - SAX® 18)	0.31	0.065	0.1	0.017
SC2(PIX® 116 - SAX® 18)	0.25	0.03	0.067	0.038
SC3(SAX® 18 - PAX® 18)	0.062	0.008	0.059	0.013
SG1(PIX® 116 - SAX® 18)	0.43	ND	0.11	0.089
SG2(PIX® 116 - SAX® 18)	0.15	ND	0.1	ND
SG3(SAX® 18 - PAX® 18)	0.17	ND	ND	0.081
SM1	0.23	ND	0.054	0.008
SM2	0.55	0.01	0.079	0.036
SM3	0.25	ND	ND	0.009

[a)] ND - below the method determination threshold for Zn, Pb, Cu and Ni at the level of 7 μg/dm^3

However, the risk assessment code (RAC) shows the potential of possible availability to migrate on the basis of the percentage of the metal content in the exchangeable and carbonate fractions [29]. These fractions are considered to be weakly bounded chemically that they are able to migrate into aqueous phase, and in this way they may constitute a pool that is directly available for biocenoses of aquatic ecosystems [30, 31]. Therefore, the RAC can be treated as an analytical scale which can be used to evaluate the potential mobility and at the same time the potential risk based on the estimated percentage of metal associated with both exchangeable and carbonate fractions, determined quantitatively for the sediments [24, 25, 32, 33]. According to RAC criteria, deposits may be classified as not posing or posing a threat to a hypothetical ecosystem [25, 28, 30].

In order to assess the potential toxicological risk of the wastes or sludge caused by the presence of heavy metals, the quantity of metals bonded in mobile fractions, i.e. the total of exchangeable and carbonate fraction are taken into account more frequently than the total contents of metals, which for the presented waste are listed in Table 3 [17, 29, 35-38].

The limit leachability value for Pb in accordance with US EPA was determined at the level of 5.0 mg/dm^3 and on this basis the nature of the waste toxicity is determined (for Cu, Ni and Zn, no limit values were determined). In all samples of the analysed groups of sludge: SC1-SC3, SG1-SG3 and SM1-SM3 no exceedance of limit value for leachable Pb, determining toxicity in accordance with US EPA criteria, was analytically found. It is an argument for the effective physico-chemical treatment of wastewaters and obtaining post-processing sludge with a low leachability level and it also suggests to consider the further practical use of dewatered sludge. The listed results include the assessment of post-processing sludge generated over a short, three-month period of operation of the installation for physico-chemical pretreatment of wastewaters and they are a part of a certain level of values recorded in real conditions. In that period, the pretreated wastewaters were generated as a result of water cleaning of usable surfaces of transport railway rolling stock, mainly of classes: G, H and T according to the International Union of Railways classification [1]. Therefore, the results obtained might be the derivatives of the composition of residues left by the transported commodities for a category referred to by the International Union of Railways classification, only from this operational period of the rail freight car wash. Therefore, the presented here results should be treated as an approximation of the inadequately described in literature problem of assessment of post-processing sludges generated as a result of physico-chemical treatment of effluents from water cleaning of the surfaces of freight type railway rolling stock.

Conclusions

Post-processing sludge generated from physico-chemical pretreatment of wastewaters from the water cleaning of freight railway rolling stock surfaces are particularly characterised by:

a) comparable values of the results obtained in case of TCLP leaching procedure and comparable fractional composition of the selected heavy metals;
b) prevailing content of stable residual fraction determined in accordance with Tessier's procedure for each type of sludge;
c) non-toxic nature according to the criteria obtained from TCLP procedure.

Mixed streams of post-processing sludge (MS) might be classified in accordance with the risk assessment code, as not posing any risk considering Cu and Pb, and as carrying low risk for aquatic ecosystems considering Ni and Zn.

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OCZYSZCZANIE ŚCIEKÓW Z MYJNI WAGONÓW TOWAROWYCH. OCENA OSADÓW PO FIZYKOCHEMICZNYM OCZYSZCZANIU

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Abstrakt: Proces fizykochemicznego podczyszczania ścieków wytwarzanych na myjni kolejowych wagonów towarowych był prowadzony w warunkach przepływowych na dwukomorowym reaktorze typu akcelator z końcowym doczyszczaniem na wielowarstwowym filtrze żwirowym. Osady poprocesowe były generowane w wyniku zastosowania koagulacji i flokulacji oraz w minimalnym stopniu z wód popłucznych w wyniku stosowania okresowego, wstecznego płukania filtrów żwirowych. Przedstawiono wyniki oceny odwodnionych grawitacyjnie osadów pokoagulacyjnych i osadów z wstecznego płukania filtów żwirowych wydzielanych na drodze sedymentacji oraz odwodnionej mieszaniny tych dwóch rodzajów osadów. Przedmiotowe osady poddano ługowaniu za pomocą procedury TCLP oraz ocenie ryzyka na podstawie analizy składu frakcyjnego wytypowanych metali ciężkich. Stwierdzono, że osady pochodące z procesu oczyszczania po zastosowaniu dwustopniowej koagulacji kwaśno-alkalicznej (PIX® 116 - SAX® 18) lub alkaliczno-kwaśnej (SAX® 18 - PAX® 18) z końcową flokulacją i separacją faz na układzie przepływowym typu akcelator charakteryzują się zdecydowanie niższymi poziomami wymywalności metali ciężkich niż wstępne osady posedymentacyjne oraz wykazują niskie ryzyko względem Cu, Ni, Pb i Zn określone przyjętym poziomem kodu oceny ryzyka (RAC). Według kryteriów przyjętych dla klasyfikacji TCLP, analizowane osady nie są odpadami toksycznymi i niebezpiecznymi.

Słowa kluczowe: oczyszczanie ścieków z myjni wagonów towarowych, osady pokoagulacyjne, osady z wstecznego płukania filtrów żwirowych, test TCLP, skład frakcyjny metali zawartych w osadach, kod oceny ryzyka (RAC)

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ASSESSMENT OF HEAVY METAL CONTENT IN THE SOILS OF INDUSTRIAL SITES IN SKARZYSKO-KAMIENNA AND KIELCE

OCENA KONCENTRACJI METALI CIĘŻKICH W GLEBACH UŻYTKÓW PRZEMYSŁOWYCH NA PRZYKŁADZIE KIELC I SKARŻYSKA-KAMIENNEJ

Abstract: This article presents the results of the analysis of selected heavy metal concentrations in the urban soils of Skarzysko-Kamienna and Kielce. The studies were conducted on industrial soils. In the collected soil samples, the total content of Cu, Zn, and Pb - after mineralisation in *aqua regia* - was determined by the flame atomic absorption spectrometry (FAAS) method. A pH, in turn, was determined by the potentiometric method. The soils of Skarzysko-Kamienna were characterised by the following concentrations of heavy metals: Cu - 2.0-261 mg/kg d.m.; Zn - 9.0-352 mg/kgd.m.; Pb - 2.0-1600 mg/kg d.m. The concentrations of heavy metals in the soils of Kielce were oscillating as follows: Cu: 2.40-134.2 mg/kg d.m., Zn: 17.2-1646 mg/kg d.m, Pb: 10.4-1428 mg/kg d.m. The elevated concentrations were reported for all analysed heavy metals in accordance with the values of geochemical background determined for each chemical element. The obtained results indicated moderate values of geoaccumulation indices I_{geo}. The soils of both cities were characterised by either slightly acidic or slightly alkaline pH. However, the values observed for the soils of Skarzysko-Kamienna were lower than those noted for the soils of Kielce.

Keywords: urban soils, Kielce, Skarzysko-Kamienna, copper, zinc, lead, geoaccumulation index I_{geo}, pH

Introduction

Urban soils, due to multiple transformations of the natural environment caused by urbanisation, highly-developed transportation networks and numerous existing branches of industry, are particularly vulnerable to contamination with heavy metals [1-3]. The presence of many contamination factors concentrated in a small area has a long-term impact on the natural environment. Therefore, many urban areas are excessively enriched in heavy metals. Heavy metals are classified as persistent and toxic inorganic contaminants which, depending on environmental factors, are able to migrate within the water-soil environment and are taken up by plants. This poses a real threat of their accumulation in the subsequent levels of trophic chain [4-6]. The aim of this article is to assess a degree of contamination of the industrial soils of Kielce and Skarzysko-Kamienna with selected heavy metals. The studies presented in the article are preliminary and may contribute to further multi-stage works on the identification of soil environment in both these cities.

Study area and methods

The studies were conducted on the industrial soils of Kielce and Skarzysko-Kamienna (Swiętokrzyskie Province, Poland). Kielce is the capital of the Province and has a total area of 110 km^2. Development of the city was mainly connected with industries operating in

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these areas in the past, which were based on exploitation of mineral resources, such as: iron, copper and lead ores, as well as sandstones. Also Skarzysko-Kamienna is a city of chiefly industrial origins. In these areas, the Staropolski Industrial District was being developed. Nowadays, the city is the capital of the County, covers an area of 64 km^2, and is developing, just like Kielce, in the field of trade and services.

The studies were conducted in the areas performing industrial functions. According to the size of the cities, 34 soil samples were collected from the surface layers of urban soils (depth up to 20 cm) - 24 soil samples in Kielce and 10 soil samples in Skarzysko-Kamienna (Figs. 1 and 2). Each soil sample consisted of soil material collected from a 100 x 100 cm plot with 10 punctures of Egner's sampling stick.

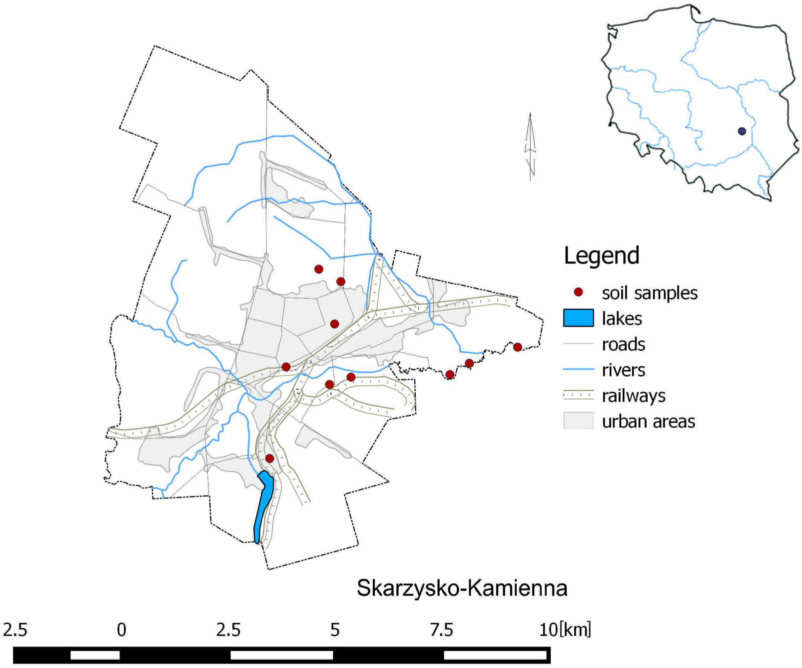

Fig. 1. Location of soil sample collection in the areas of Skarzysko-Kamienna

In the soil samples, such physicochemical properties were determined, as: the total content of Pb, Cu and Zn, after mineralisation in *aqua regia*, by the flame atomic absorption spectrometry (FAAS) method with an atomic absorption spectrometer, as well as pH$_{KCl}$ by the potentiometric method.

In order to assess the enrichment in heavy metals, the geoaccumulation index I_{geo} was calculated [7]

$$I_{geo} = \log_2(C_n/1.5B_n)$$

where: C_n - content of a given heavy metal in the soil, B_n - geochemical background for a given heavy metal, 1.5 - the natural variations of the content of a particular heavy metal in the environment resulting from differences in a geological structure.

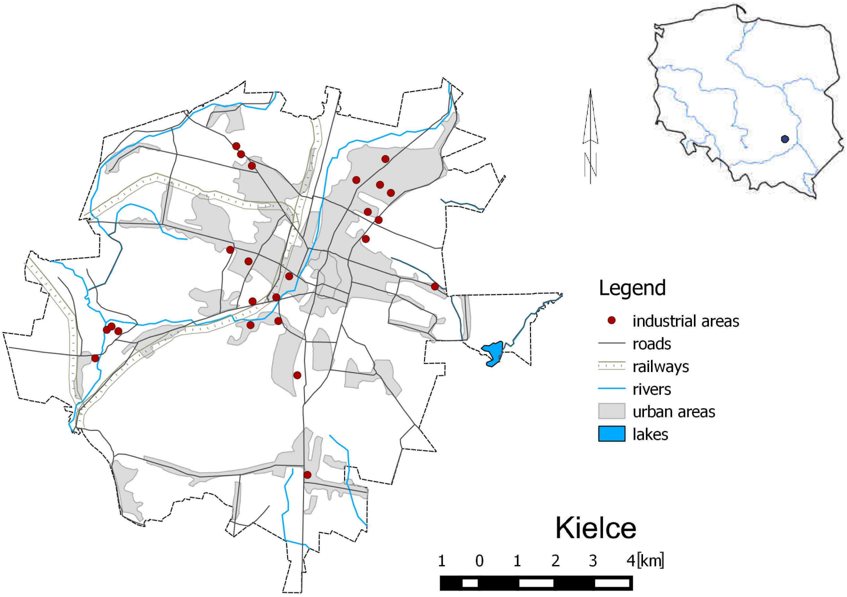

Fig. 2. Location of soil sample collection in the areas of Kielce

Moreover, the obtained results were further analysed according to the geochemical background values determined for the areas of Kielce and Skarzysko-Kamienna [8].

Study results

Table 1 presents the content of heavy metals and pH values determined for the analysed soils.

In the industrial soils of Kielce, the mean pH value was oscillating at the level of 7.04 with a standard deviation equal to 0.76. These soils were characterised by either neutral or slightly alkaline pH; only 12.5% of soil samples had slightly acidic pH. Significantly lower pH value was reported for the industrial soils of Skarzysko-Kamienna - it was oscillating at the level of 6.40 with a standard deviation equal to 0.49. These soils had either slightly acidic (60%) or neutral pH (Fig. 3).

Urban areas (mainly in central parts of cities) are usually characterised by higher pH values which result from dust falls due to local transportation and industry [9]. Naturally, the soils of Kielce are slightly acidic, while the soils of Skarzysko-Kamienna are acidic. The studies conducted on urban soils indicate that they have elevated pH values.

Heavy metal concentrations in soils result from many factors and depend mainly on the geological structure of lands, types of land uses, as well as impact of human activities. The main factors influencing the concentrations of heavy metals in urban areas are: progressing urbanisation, types of industries, density of transportation routes, as well as traffic intensity. Anthropogenic pressure has a long-lasting character and may have a local or point range. Heavy metals are non-biodegradable; therefore, they accumulate themselves in the soil environment and, if pH values are low, may occur as migrating forms and thus migrate within the water-soil environment [10].

Table 1

Content of heavy metals and pH values in the analysed urban soils of Kielce and Skarzysko-Kamienna

Soil sample No.	**Pb**	**Cu**	**Zn**	**pH**
	[mg/kg d.m.]			-
Kielce				
1	36.4	12.20	72.7	6.42
2	56.78	12.90	65.4	7.85
3	25.8	9.70	67.0	7.54
4	18.9	6.00	42.4	6.57
5	27.9	12.40	120.1	6.54
6	120.3	41.00	210.3	6.62
7	39.13	8.60	57.5	6.97
8	156.8	38.70	240.45	7.88
9	120.1~~1~~	9.70	238	7.69
10	10.4	4.40	22.2	7.18
11	57.8	6.70	96.3	7.97
12	25.6	7.80	55.5	7.93
13	33.6	6.90	90.6	7.68
14	101.1	13.40	46.7	6.03
15	45.3	12.50	60.78	6.80
16	36.5	15.20	68.5	7.90
17	26.4	13.60	78.3	7.05
18	112.0	13.60	100.8	6.05
19	49.8	20.11	150.7	5.66
20	67.9	17.10	140.11	7.77
21	12.5	2.40	24.4	5.99
22	44.7	10.07	17.16	6.55
23	1428	134.2	639.5	7.11
24	47.5	14.8	1646	8.33
Skarzysko-Kamienna				
1	10	7.0	17.1	6.49
2	4.0	2.0	9.0	6.25
3	35	14	67.3	6.83
4	14	11	43.2	6.62
5	10	4.0	22.5	6.96
6	37	11	76.3	5.37
7	64	261	143	6.42
8	35	31	352	6.40
9	2.0	3.0	17.1	5.94
10	1600	215	304	6.97

The analysed soils of Kielce and Skarzysko-Kamienna had differentiated concentrations of selected heavy metals (Table 1, Fig. 3). The total content of copper in the soils of Kielce was oscillating at the level of 2.40-134 mg/kg d.m.; while in Skarzysko-Kamienna, these values were ranging from 2 to 261 mg/kg d.m. The soils of Kielce were characterised by higher concentrations of zinc for which high extreme values and high mean value were noted. In the case of Skarzysko-Kamienna, these values were significantly lower and were oscillating at the level of 9.0-352 mg/kg d.m. Lead, in turn, had similar ranges of values in both cities. However, the values reported for Skarzysko-Kamienna were highly differentiated as shown by the coefficient of variation (Table 2).

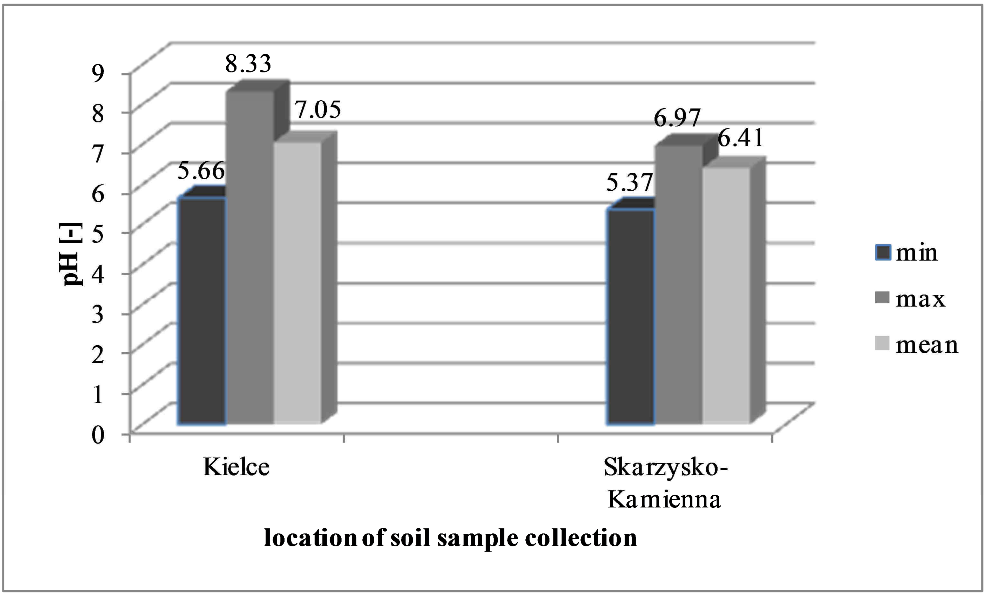

Fig. 3. Ranges in pH values in the industrial soils of Kielce and Skarzysko-Kamienna

Table 2

Statistical parameters of heavy metal concentrations in the soils of Kielce and Skarzysko-Kamienna [mg/kg d.m.]

Statistical parameters	**Cu**		**Zn**		**Pb**	
	Kielce	**Skarzysko-Kamienna**	**Kielce**	**Skarzysko-Kamienna**	**Kielce**	**Skarzysko-Kamienna**
Minimum	2.4	2	17.16	9	10.4	2
Maximum	134.2	261	1646	352	1428	1600
Mean	14.8	14.78	92.93	53.74	50.65	23.5
Coefficient of variation	1.55	173	1.85	118	2.51	275
Geochemical background [8]	3-9	5-9	35-64	35-64	25-128	13-25
Number of soil samples exceeding geochemical background [%]	70.8	60.0	66.7	50	8.3	50
Mean for pure soils [11]	24		100		44	

The degree of soil contamination with heavy metals was determined according to the geoaccumulation indices I_{geo}. The method, elaborated by Muller (1969) [7], is based on the comparison of heavy metal content in soils before and after being contaminated, with respect to a seven-point grading scale (Table 3).

Table 3

Degree of soil contamination according to the geoaccumulation index I_{geo}

I_{geo} **scale**	I_{geo} **value**	**Contamination degree**
0	$I_{geo} < 0$	non-existent
1	$0 < I_{geo} \leq 1$	weak
2	$1 < I_{geo} \leq 2$	weak - moderate
3	$2 < I_{geo} \leq 3$	moderate
4	$3 < I_{geo} \leq 4$	strong
5	$4 < I_{geo} \leq 5$	strong - extreme
6	$5 < I_{geo} \leq 10$	extreme

Table 4

Calculated values of the geoaccumulation index I_{geo}

City	I_{geo} **range**		
	Cu	**Zn**	**Pb**
Kielce	< 0-2	< 0-2	< 0-2
Skarzysko-Kamienna	< 0-2	< 0-1	< 0-2

The calculated geoaccumulation indices I_{geo} demonstrated various origins of determined heavy metals in the analysed soils. In general, no values indicating heavy contamination were recorded.

Conclusions

The studies show that the urban soils are characterised by differing values of the analysed heavy metals, i.e. Cu, Pb and Zn. They also indicate that heavy metal concentrations depend on urban spatial development, and their extreme values are connected with point sources of contamination. Moreover, the concentrations of heavy metals are determined by the character of city and level of its development, but not necessarily its size. Contamination emission has, in turn, an impact on the soil pH values - urban soils are characterised by higher pH values resulting from alkaline dust falls due to local industry and transportation.

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OCENA KONCENTRACJI METALI CIĘŻKICH W GLEBACH UŻYTKÓW PRZEMYSŁOWYCH NA PRZYKŁADZIE KIELC I SKARŻYSKA-KAMIENNEJ

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Abstrakt: Przedstawiono wyniki badań zawartości wybranych metali ciężkich w glebach miejskich Kielc oraz Skarżyska-Kamiennej. Badania prowadzono na glebach o przeznaczeniu przemysłowym. W pobranym materiale glebowym wykonano oznaczenie Cu, Zn oraz Pb metodą atomowej spektrometrii absorpcyjnej ASA po mineralizacji w wodzie królewskiej oraz badania wartości odczynu metodą potencjonometryczną. Gleby Skarżyska-Kamiennej cechują się zawartością metali ciężkich na poziomie Cu: 2,0-261 mg/kg s.m., Zn: 9,0-352 mg/kg s.m, Pb: 2,0-1600 mg/kg s.m. W badanych glebach Kielc zawartość metali oscylowała na poziomie: Cu: 2,40-134,2 mg/kg s.m., Zn: 17,2-1646 mg/kg s.m, Pb: 10,4-1428 mg/kg s.m. Stwierdzono podwyższoną zawartość analizowanych metali w odniesieniu do wartości tła geochemicznego wyznaczonego dla każdego z pierwiastków. Badania wskazują na umiarkowane wartości wskaźników geoakumulacji I_{geo}. Gleby obu miast charakteryzowały się odczynem od lekko kwaśnego do lekko alkalicznego. Jednak wartości, jakie zostały zanotowane dla gleb Skarżyska-Kamiennej, były niższe niż te dla gleb Kielc.

Słowa kluczowe: gleby miejskie, Kielce, Skarżysko-Kamienna, miedź, cynk, ołów, indeks geoakumulacji I_{geo}, pH

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PROPERTIES OF THE WASTE PRODUCTS FROM THE HEAVY METAL CONTAMINATED ENERGY CROPS GASIFICATION PROCESS

WŁAŚCIWOŚCI PRODUKTÓW ODPADOWYCH ZE ZGAZOWANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: The phytoremediation ability of the energy crops is widely known. Unfortunately, the possibility of the effective, safe and ecological way for treatment such contaminated plants is still unresolved. It is postulated that one of such methods can be gasification - conversion process of organic matter into a combustible gas mixture. This process is associated with the formation of solid and liquid waste products. The paper presents the results of basic physico-chemical properties of solid (ash) and liquid (tar) waste products formed during the heavy metal contaminated energy crops gasification. Plant cultivation was carried out with the modification: 1) N, P, K fertilizer application and 2) inoculum made from specially selected microbial cultures application. The gasification process was carried out in a laboratory fixed bed reactor. Three types of energy crops were used: *Miscanthu*s x *giganteus, Sida hermaphrodita, Spartina pectinata*. The experimental plots were established on heavy metal contaminated arable land located in Bytom (southern part of Poland, Silesian Voivodship). The influence of the type of additives on the liquid and solid waste products quality was analyzed. The results show that the addition of fertilizer (N, P, K) to soil couses that zinc content in ash is higher in comparison to control samples (biomass cultivated on soil without fertilization). The opposite situation is observed for lead. The application of the inoculum promotes the migration of lead into solid. In both cases, the cadmium content in ash is lower than detection limits. In the case of tars, there is no significant impact of the additive application on the heavy tars content.

Keywords: energy crops gasification, heavy metals, tars, ash

Introduction

Energy crops are in the area of interest because of multiple ways of advantageous utilization. They can be used for biofuels (solid, liquid and gaseous) and biocomponents production. Examples of commonly used plants are *Salix* L., *Miscanthus* x *giganteus*, *Spartina pectinata*, *Panicum virgatum*, *Sida hermaphrodita*, *Rosa multiflora* [1].

In Poland, agro-biomass is not widely used, which becomes a reason for underdeveloped cultivation techniques, lack of methods of preventing crop diseases and other detrimental external factors. That has a great impact on the volume of production and the quality of fuel. Other factors that affect an agro-fuel production are soil fertility, quality of agricultural treatment and field preparation (e.g. number of weeds). However, the current state of the Polish agro-energy sector gives number of opportunities for relatively easy and quick progression.

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Energy crops utilization can be useful in more than one field. Phytoremediation is one of the techniques used for remediation of contaminated areas. Soil contamination can be found close to landfills, heavy-metal/oil industry areas. There are energy crops which can be grown on contaminated areas and have a potential to accumulate contaminants. The reasonable method of contaminated biomass utilization is gasification [2].

Gasification is a thermo-chemical conversion of solid feedstock into a gaseous fuel. Because of the low amount of the oxidizer used in the process and the reducing atmosphere, gasification prevents sulphur and nitrogen oxides emission, also it is possible to accumulate part of the contaminants in the solid residues. Gasification is a way to utilize contaminated biomass while useful syngas is produced. Syngases are mostly low-calorific gases (depends on the feedstock and gasification agent) that can be used in power boilers, industrial furnaces, gas turbines or piston engines [3]. Biomass gasification gases, as a fuel that might be received from local energy sources shows a great potential as fuel for CHP plants [4, 5]. Combined heat and electricity generation in distributed energy systems with internal combustion piston engines is a good option for local communities due to a relatively low investment cost and the high efficiency of electricity production. What is more, the market of commercial solutions for low-calorific value gases (e.g. biogas, syngas) is constantly growing [6].

Werle shows [7] that it is possible to obtain a combustible gas from the gasification of sewage sludge at a relatively high process efficiency and low environmental impact. However, it was found, that still unsolved problem is solid and liquid waste products generated during the process [8]. These products can be the source of a variety of toxic organic [9] and inorganic [10] substances. In this study the results of basic physico-chemical properties of solid (ash) and liquid (tar) waste products formed during the heavy metal contaminated energy crops fixed bed gasification process.

Feedstock and apparatus

In order to study the three plants were selected: Miscanthus (*Miscanthus* x *giganteus*), Virginia mallow (*Sida hermaphrodita*) and Cordgrass (*Spartina pectinata*). The field experimental options include:

- 3 control plots (no additives),
- 3 plots with standard NPK fertilization, specific for each of the species - two weeks before planting ammonium sulphate and Polifoska (Grupa Azoty Zaklady Chemiczne "Police" S.A., Poland) were applied,
- 3 plots with commercially available microbial inoculum solution (EmFarma Plus, ProBiotics Magdalena Gorska, Poland) - inoculum was applied on rhizomes before planting and on the leaves as aerosol in the middle of each month of the growing season.

The test site is located in Poland in the Upper Silesian Industrial Region, on the outskirts of Bytom - an industrial city about 15 km from Katowice, in the proximity of a shutdown large lead/zinc/cadmium works consisting of the ore mining, enriching and smelting facilities. This metallurgical complex was in operation for more than 100 years and contributed significantly to the contamination of the local soils. During the last 30 years the area was used for agricultural purposes. Recently the land has been used for grain crop farming, especially for wheat production. Soil contamination with lead, cadmium and zinc in this area exceeds permissible limits for agricultural soil in Poland. The feedstock samples is presented in Figure 1.

Fig. 1. Samples of gasified energy crops

Proximate analysis of the studied plants are presented in Table 1 and the proximate analysis in Table 2. The heavy metal concentration of the analysed feedstock is presented in Table 3.

Table 1

Ultimate analysis of the analysed feedstock

Plants	**Carbon**	**Hydrogen**	**Nitrogen**	**Oxygen**	**Sulphur**
	[% d.m.]				
SH	46.2 ±2.3	6.69 ±0.33	0.430 ±0.020	46.5 ±2.3	0.200 ±0.001
SH_{NPK}	46.4 ±2.3	7.22 ±0.36	0.380 ±0.019	45.8 ±2.3	0.200 ±0.001
SH_{EFP}	47.0 ±2.4	7.06 ±0.35	0.300 ±0.016	45.4 ±2.3	0.200 ±0.001
MG	46.9 ±2.4	7.32 ±0.37	1.380 ±0.069	44.2 ±2.2	0.200 ±0.001
MG_{NPK}	45.5 ±2.3	6.88 ±0.34	1.130 ±0.056	46.3 ±2.3	0.200 ±0.001
MG_{EFP}	46.5 ±2.3	7.13 ±0.36	1.490 ±0.074	44.7 ±2.2	0.200 ±0.001
SP	46.7 ±2.3	6.33 ±0.32	0.320 ±0.016	46.5 ±2.3	0.200 ±0.001
$P_{NP}S_{K}$	46.3 ±2.3	6.77 ±0.34	0.380 ±0.019	46.4 ±2.3	0.200 ±0.001
SP_{EFP}	47.0 ±2.3	7.07 ±0.35	0.590 ±0.029	45.1 ±2.3	0.200 ±0.001

Legend: MG - *Miscanthus* x *giganteus* - control, MG_{NPK} - *Miscanthus* x *giganteus* - nutrients NPK, MG_{EFP} - *Miscanthus* x *giganteus* - Em Farma Plus, SH - *Sida hermaphrodita* - control, SH_{NPK} - *Sida hermaphrodita* - nutrients NPK, SH_{EFP} - *Sida hermaphrodita* - Em Farma Plus, SP - *Spartina pectinata* - control, SP_{NPK} - *Spartina pectinata* - nutrients NPK, SP_{EFP} - *Spartina pectinata* - Em Farma Plus

Table 2

Ultimate analysis of the analysed feedstock

Plants	**Moisture**	**Volatiles**	**Ash**
	[% d.m.]		
SH	9.8 ±0.5	75.8 ±3.8	2.7 ±0.1
SH_{NPK}	9.1 ±0.5	76.9 ±3.8	2.4 ±0.1
SH_{EFP}	9.4 ±0.5	76.6 ±3.8	4.8 ±0.2
MG	8.6 ±0.4	74.9 ±3.8	5.5 ±0.3
MG_{NPK}	8.3 ±0.4	76.5 ±3.8	4.2 ±0.2
MG_{EFP}	8.2 ±0.4	75.3 ±3.8	4.9 ±0.3
SP	8.3 ±0.4	77.9 ±3.9	3.7 ±0.2
$P_{NP}S_{K}$	8.4 ±0.4	77.5 ±3.9	3.4 ±0.2
SP_{EFP}	9.5 ±0.5	75.7 ±3.8	3.4 ±0.2

Table 3

Heavy metal concentration in analysed feedstock

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	N/A*	6.1 ±0.3	747 ±37
SH_{NPK}	N/A*	4.0 ±0.2	1024 ±51
SH_{EFP}	47.1 ±2.4	4.0 ±0.2	543 ±27
MG	232 ±12	5.1 ±0.3	571 ±29
MG_{NPK}	162.0 ±8.1	3.9 ±0.2	630 ±32
MG_{EFP}	192.8 ±9.6	4.6 ±0.2	638 ±32
SP	111.3 ±5.7	0.9 ±0.05	287 ±14
SP_{NPK}	111.6 ±5.7	1.0 ±0.1	295 ±15
SP_{EFP}	115.2 ±5.7	1.1 ±0.1	367 ±18

*N/A - not available

The heavy metal content in solid biofuels is regulated in EU by the European Standard [11]. According to this document, the limits established for heavy metal content in solid biofuels are as presented in Table 4.

Table 4

Heavy metal content in solid biofuels according to [11]

Heavy metal [mg/kg d.m.]	Limit
Lead	≤ 10
Cadmium	≤ 2.0
Zinc	≤ 100

Comparing the results from the lab tests for biomass samples with the limits from the table above, results the following conclusions:

- the lead and the zinc content in all biomass samples exceeds the limits established in the standard,
- the cadmium content in majority of biomass samples exceeds the limits established in the standard.

The experimental study was conducted using laboratory-scale fixed-bed gasification facility [12]. The scheme of the installation is shown in Figure 2.

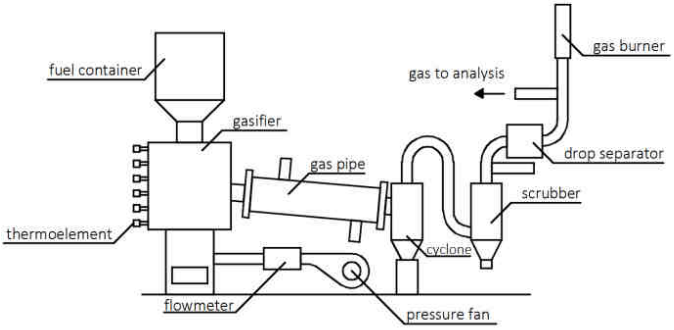

Fig. 2. Scheme of the gasification installation

The main part of the system is a fixed-bed gasifier with the maximum weight of the feedstock of 5 kg. The gasified material was fed into the reactor form the fuel container above. Gasification agent (air) was fed from the bottom by pressure fan. Air flowmeter allows to set the desirable air excess ratio in the gasifier. Produced gas passes basic gas cleaning equipment and the sample to analysis is taken. The internal temperature profile in the reactor is measured by six thermoelements located along the vertical axis of the reactor.

There are four main zones in the reactor: drying zone (water is evaporated), pyrolysis zone (thermal decomposition to volatiles and solid char), reduction zone (where main combustible gas components are produced) and combustion zone (where part of the biomass is combusted to generate heat for endothermic reactions).

Gasification process was carried out for six air excess ratios: 0.12, 0.14, 0.16, 0.18, 0.23, 0.27. The gas composition was measured. The results of this aspect was presented earlier [2].

Additionally, after each gasification tests completed, ash and tar samples were collected in order to performed analyses on heavy metals content. In the Figure 3, example of the tar samples is presented.

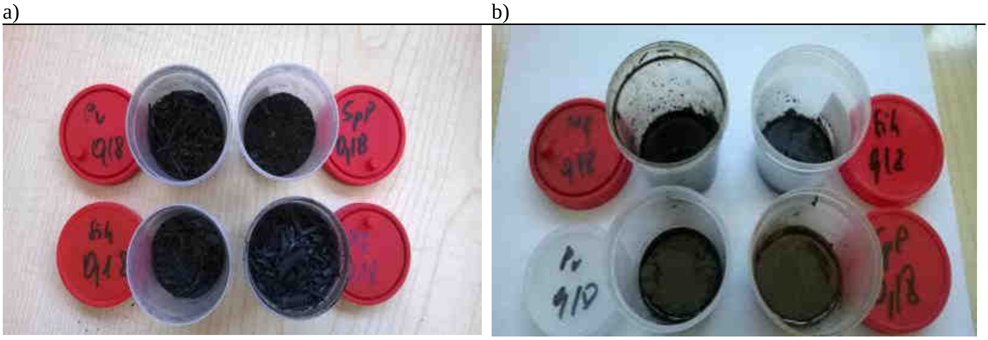

Fig. 3. Analysed samples: a) ash, b) tar

Results of experimental investigation

The key findings demonstrate that gasification process of heavy metal contaminated biomass is characterized by a lower emission of gaseous pollutants into the atmosphere compared to combustion as most of the heavy metals from biomass are moved into solid products. Heavy metal content in tars was much lower in comparison to ash. Taking into consideration the results of the composition the ashes, their potential land application should be carefully analysed. In Tables 5 and 6 the heavy metal concentration in the ash and tar samples is presented.

Analyzing the content of metals in the ashes after gasification, we can see that the maximum content of lead is for MG - 1342 mg/kg while SH_{NPK} has the minimum value - 81 mg/kg. The cadmium concentration is less than < 0.6 mg/kg for all ash samples. For zinc, the maximum content was found for SH_{NPK} - 5805 mg/kg and the minimum content was found for SP_{EFP} - 1918.0 mg/kg.

Table 5

Heavy metal content in ash samples

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	171.0 ±8.6	< 0.6 ±0.03	2471 ±124
SH_{NPK}	81.0↓ ±4.0	< 0.6 ±0.03	5805↑ ±290
SH_{EFP}	296 ±15	< 0.6 ±0.03	2370 ±118
MG	1342↑ ±67	< 0.6 ±0.03	3308 ±165
MG_{NPK}	947 ±47	< 0.6 ±0.03	3603 ±180
MG_{EFP}	1164 ±58	< 0.6 ±0.03	2909 ±145
SP	599 ±30	< 0.6 ±0.03	2511 ±126
SP_{NPK}	584 ±29	< 0.6 ±0.03	3003 ±150
SP_{EFP}	477 ±24	< 0.6 ±0.03	1918↓ ±96

In case of tar analysis, the content of metals in the ashes after gasification, we can see that the maximum content of lead is for SP sample (91.1 mg/kg), while for MG_{NPK} the lead content is the lowest (12.4 mg/kg). The maximum value of cadmium concentration was registered for MG_{EFP} (5.17 mg/kg), while the minimum values (< 0.6 mg/kg) were found for SH_{EFP}, MG and MG_{NPK} samples. For zinc, the maximum content was found for SP - 225 mg/kg and the minimum content was 19.2 mg/kg for MG_{NPK}.

Analyzing results presented in both tables it should be concluded that most of the heavy metals contained in the feedstock are transferred to solid products, not to liquid phase.

In the case of Poland the first option is regulated in Poland by Decision of Polish Ministry of Agriculture and Rural Development [13]. The maximum level of heavy metals in the fertilizers is 5 mg/kg d.m. for cadmium and 140 mg/kg d.m. for lead. Analyzing the content of lead in the ashes these requirements have been fulfilled only for ashes after SH_{NPK} gasification.

Table 6

Heavy metal content in tar samples

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	46.0 ±2.3	2.9 ±0.2	100.0 ±5.0
SH_{NPK}	80.0 ±4.0	3.6 ±0.2	184.0 ±9.2
SH_{EFP}	34.2 ±1.7	0.60 ±0.03	138.0 ±6.9
MG	51.2 ±2.6	0.60 ±0.03	39.6 ±2.0
MG_{NPK}	12.4↓ ±0.6	0.60 ±0.03	19.2↓ ±1.0
MG_{EFP}	64.4 ±3.2	5.2 ±0.3	221 ±11
SP	91.1↑ ±4.6	3.9 ±0.2	225↑ ±11
SP_{NPK}	71.7 ±3.6	1.6 ±0.1	174.0 ±8.7
SP_{EFP}	61.5 ±3.1	3.8 ±0.2	177.0 ±8.9

The other option considered is to use ashes after gasification as an amendment improving soil quality at post-industrial areas. However there is no direct regulation for using ashes for improving post-industrial soil quality. But in the case of Poland the quality of the ashes (especially heavy metal content) can be assessed using Decision of the Ministry of the Environment on Sewage Sludge [14]. The maximum permissible levels of metals in sewage sludge used for non-agricultural land reclamation are 25 mg/kg d.m. for cadmium, 1000 mg/kg d.m. for lead and 3000 mg/kg d.m. for zinc. Majority of the tested ashes after gasification process met the standards.

Conclusions

Based on the investigation following general conclusion can be drawn:

- Phytoremediation is one of the techniques used for remediation of contaminated areas.
- The group of energy crops has taken into consideration include native and foreign species such as perennial dicotyledonous plants (*Sida hermaphrodita*) and perennial grass species (*Miscanthu*s x *giganteus*, and *Spartina pectinata*).
- Gasification has many more advantages than the classic combustion. It is characterized by a lower emission of gaseous pollutants into the atmosphere. Heavy metals from the biomass are moved to the solid (not liquid) phase. Concentration of heavy metals may be reduced after recovery of heavy metals from solid products, which will help to protect the environment.
- Heavy metal content in tars was much lower in comparison to ash.
- Analyzing the possibility of the use ash as a fertilizer it should be emphasize that only ashes after SH_{NPK} gasification have been fulfilled the requirements.
- Majority of the tested ashes after gasification process met the standards as an amendment improving soil quality at post-industrial areas.

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WŁAŚCIWOŚCI PRODUKTÓW ODPADOWYCH ZE ZGAZOWANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

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Abstrakt: Zdolność fitoremediacyjna roślin energetycznych jest powszechnie znana. Wciąż jednak niedostatecznie rozpoznanym problemem jest możliwość efektywnego, bezpiecznego i ekologicznego wykorzystania energetycznego takich zanieczyszczonych roślin. Postuluje się, że jednym z takich sposobów może być zgazowanie, polegające na przekształcaniu substancji organicznej w palną mieszaninę gazów. Niestety proces ten wiąże się z powstawaniem stałych i ciekłych produktów odpadowych. W pracy przedstawiono rezultaty badań podstawowych właściwości fizyczno-chemicznych stałych (popiół) i ciekłych (smoły) produktów odpadowych pochodzących z procesu zgazowania roślin energetycznych uprawianych na terenie zdegradowanym ekologicznie. Uprawa roślin prowadzona była z zastosowaniem modyfikacji polegających na dodawaniu do gleby nawozów (N, P, K) oraz aplikowania szczepionki, będącej preparatem złożonym ze specjalnie dobranych kultur mikroorganizmów. Proces zgazowania prowadzono w laboratoryjnym reaktorze ze złożem stałym. Wykorzystano trzy rodzaje roślin energetycznych: miskanta olbrzymiego, ślazowca pensylwańskiego i spartynę grzebieniastą. Rośliny pozyskano z gruntów ornych zanieczyszczonych metalami ciężkimi zlokalizowanych w okolicach Bytomia na Górnym Śląsku. Zbadano wpływ rodzaju dodatku do gleby na jakość powstałego odpadu. Wyniki pokazują, że dodatek nawozu (N, P, K) do gleby powoduje, że w fazie stałej po procesie zgazowania jest wyższa zawartość cynku w porównaniu z próbą kontrolną. Odwrotna sytuacja obserwowana jest w przypadku ołowiu. Aplikacja szczepionki sprzyja z kolei wiązaniu ołowiu, a utrudnia wiązanie cynku. W obu przypadkach zawartość kadmu w popiele jest poza granicą oznaczalności. W przypadku smół nie można stwierdzić istotnego wpływu rodzaju dodatku do gleby na zawartość metali ciężkich.

Słowa kluczowe: zgazowanie roślin energetycznych, metale ciężkie, smoły, popiół

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THE NUMBER OF KERATINOLYTIC MICROORGANISMS IN FEATHERS AFTER SLAUGHTER POULTRY

LICZEBNOŚĆ MIKROORGANIZMÓW KERATYNOLITYCZNYCH W PIÓRACH PO UBOJU DROBIU

Abstract: Due to demand, the industry is rapidly growing, and poultry farms and slaughterhouses increase in operation size. All kind of waste, also feather waste, must be properly managed and disposed of. However, this is not a simple process, since feathers contain keratin which is resistant to biodegradation. Therefore, the obtaining microorganisms capable of degrading this protein is indicated. The number of microorganisms in research samples has importance in the isolation of strains which are characterized by the desired properties such as high enzymatic activity. The aim of the research was to determine the colony size of microorganisms showing high keratinolytic activity to degrade chicken, duck, goose and turkey feather waste. Samples of bacteria were harvested at various times in the period from March 2015 to January 2016 in poultry slaughterhouses located in the Lubuskie and West-Pomeranian provinces. Microorganisms were grown in Mandel's and Omelianski's mineral media, with addition of keratin. The presence of keratinolytic microorganisms was confirmed in all feather samples, though colony sizes varied. Turkey feather waste was the most populated by keratinolytic microorganisms ($5.8 \cdot 10^8$ CFU$\cdot$g^{-1} d.m.), followed by duck feather ($4.7 \cdot 10^8$ CFU$\cdot$g^{-1} d.m.). The colony size was smaller in case of goose feather ($2.8 \cdot 10^7$ CFU$\cdot$g^{-1} d.m.), and definitely the smallest for chicken feather. Since the Mandel's medium was more favourable for the cultivation of keratinolytic microorganisms, larger colonies were isolated from this substrate than from the Omelianski's medium. What is noteworthy is that only in the case of chicken feather waste, the size of keratinolytic microorganism colonies grown on both substrates was similar, and did not exceed 10^6 CFU$\cdot$g^{-1} d.m. Contrary to what was expected, in the research samples bigger population of the said microorganisms was identified in the autumn and winter season.

Keywords: feathers, keratin, microorganisms, poultry industry

Introduction

More and more dynamically developing poultry industry is struggling with problems of a significant waste amount formation. Poultry facilities are facing a big challenge of a proper management of this material type, including keratin protein [1]. This is primarily due to the large technological difficulties resulting from the keratin structure, that is a part of this waste type, along with large financial outlays [2]. A major problem is the slow and difficult biodegradation of feathers resulting from their resistance to proteolytic enzymes and water insolubility [3-5]. Feathers are populated by microorganisms among which those able to degrade keratin, are found [6-9]. This is possible due to the production of appropriate proteolytic enzymes [10, 11].

Therefore, it is necessary to recognize the nature of microflora inhabiting feathers to select and isolate the active strains of microorganisms that may form the basis of a vaccine that would allow management of the waste containing protein material. Such

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bio-preparation would be useful to optimize that type of a substrate used in methane fermentation processes in the bio-gas plant or composting facility [12, 13].

The aim of the study was to determine the number of microorganisms capable of degrading the keratin in different types of feathers from poultry slaughterhouse in Poland.

Materials and methods

The study was conducted using chicken, duck, turkey, and goose feathers taken from different poultry processing plants in the Lubuskie and West-Pomeranian provinces. Chicken feathers were collected 4 times (I - 5 March 2015, II - 21 May 2015, III - 25 June 2015, IV - 14 January 2016), duck's 3 times (I - 11 May 2015, II - 20 June 2015, III - 23 November 2015), turkey's 2 times (I - 11 May 2015, II - 23 November 2015), and goose's once (20 June 2015). Microbiological assays were performed by means of plating dilutions. To isolate the keratinolytic microorganisms with different requirements in relation to the culture medium, two modified mineral substrates were applied Mandel's (MAN) and Omelianski's (OM) [14, 15], to which powdered keratin was added. The cultures of microorganisms were performed at 23-25°C for a period of 7-14 days. Assays were carried out in three replicates. Results were converted and reported in colony forming units (CFU) per one gram of dry mass.

Statistical analysis was performed using Statistica 12 software. The t-test was used for the comparison of the mean keratinolytic microorganisms number on the Mandel's and Omelianski's substrate for any kind of research material.

Results and discussions

Analysis of the results on microorganisms capable of degrading keratin and inhabiting the protein waste in the form of feathers, revealed variable number in the test feathers grown on two different mineral substrates (Fig. 1).

The highest mean number of keratinolytic microorganisms was found in turkey feathers ($5.8 \cdot 10^8$ CFU$\cdot$g^{-1} d.m.). Predominating group of microorganisms appeared to be those grown on Mandel's substrate ($7.5 \cdot 10^8$ CFU$\cdot$g^{-1} d.m.), that were more numerous by 46% than those grown on Omelianski's substrate. In autumn, population of microorganisms was the highest and on both substrates amounted to $8.6 \cdot 10^8$ CFU$\cdot$ g^{-1} d.m.

Smaller numbers of keratinolytic microorganisms inhabited duck feathers. The average number of microorganisms on the Mandel's substrate was at the level of $6 \cdot 10^8$ CFU$\cdot$g^{-1}, while on Omelianski's substrate, they made up by over 40% less. Like for turkey feathers, in this case of both substrates, the most numerous keratinolytic microorganisms were found in the autumn measurement ($1.0 \cdot 10^9$ CFU$\cdot$g^{-1} d.m.).

Smaller numbers of microorganisms capable of degrading the structural protein were recorded in goose feathers, in which the average population was $2.8 \cdot 10^7$ CFU$\cdot$g^{-1} d.m. More microorganisms were observed on Mandel's substrate (by 54%) than on Omelianski's substrate ($1.8 \cdot 10^7$ CFU$\cdot$g^{-1} d.m.) (data were not presented on figures).

The lowest keratynolytic microorganisms populations were observed in chicken feathers. In this case, the number of these microorganisms dominated in winter ($2.4 \cdot 10^6$ CFU$\cdot$g^{-1} d.m.). For all measurement dates, average number of basic microorganism group, both on Mandel's and Omielianski's substrate, was at similar levels of $1.0 \cdot 10^6$ CFU$\cdot$g^{-1} d.m.

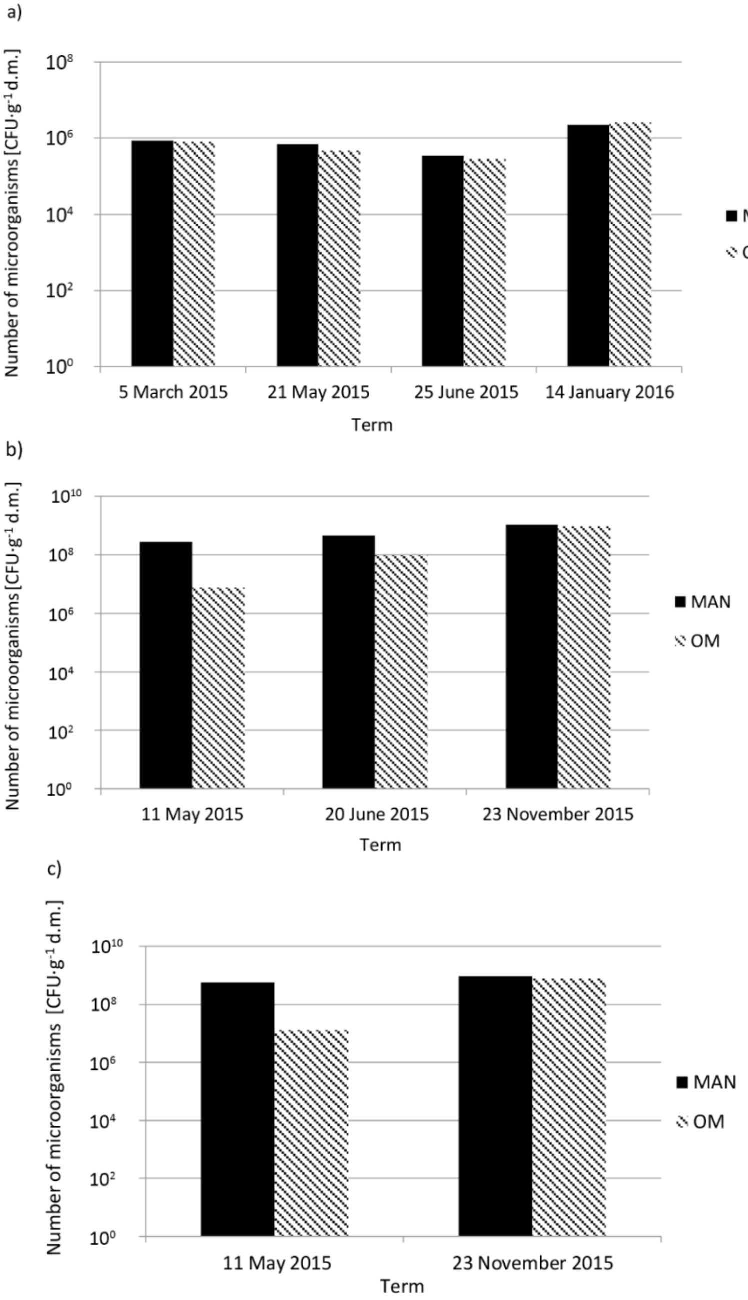
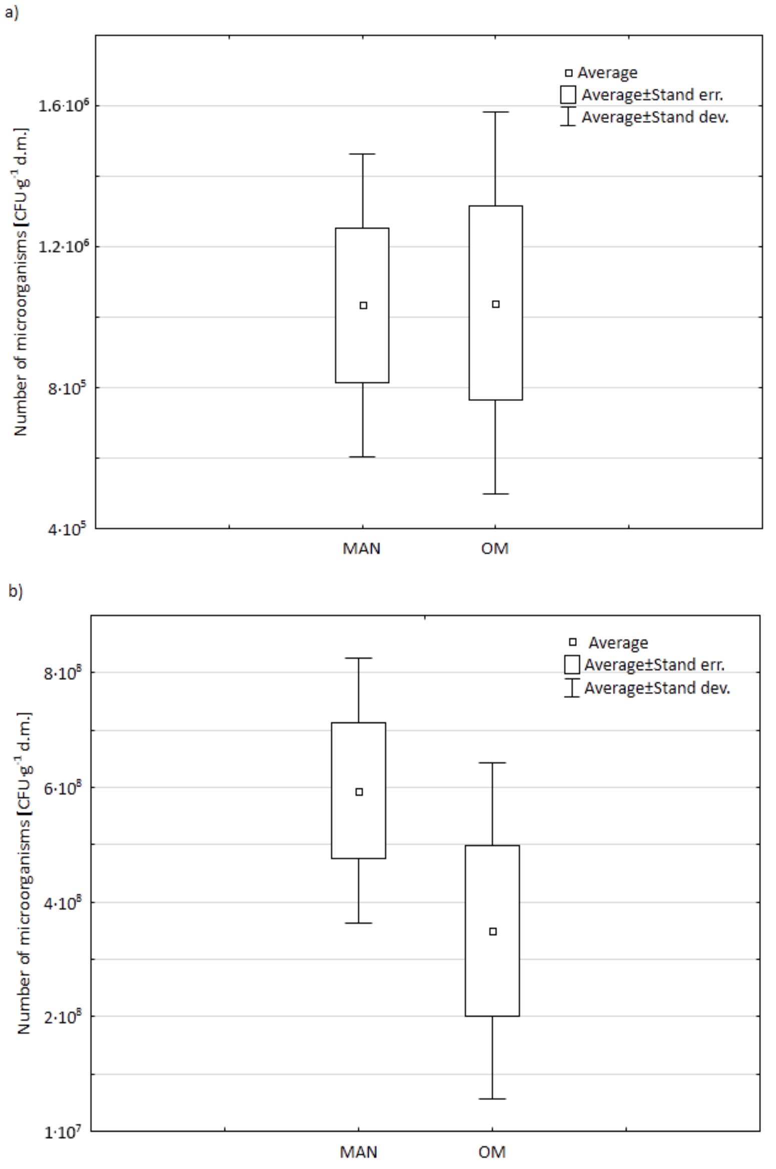


Fig. 1. The number of keratinolytic microorganisms in analyzed term: a) chicken feathers, b) duck feathers, c) turkey feathers, MAN - Mandel's medium, OM - Omelianski's medium

In the analyzed samples, keratinolytic microorganisms most frequently colonized turkey feathers, by 18% less duck feather, and by 94% goose feathers. A small percentage of the population of keratin-decomposing microorganisms were found in chicken feathers (Fig. 2).



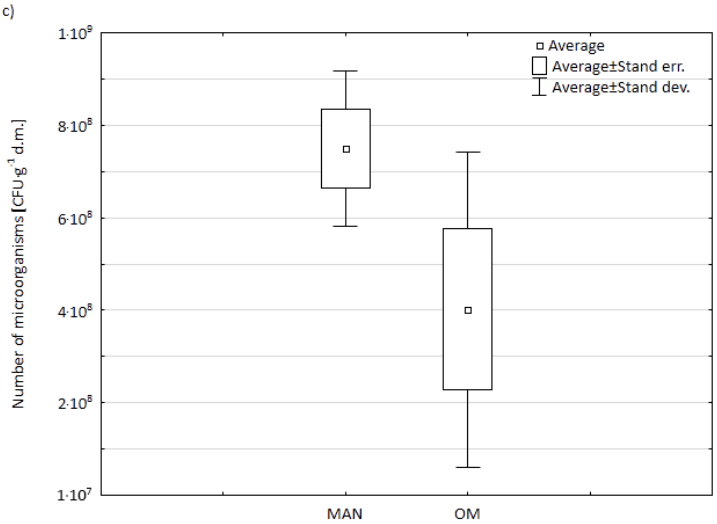


Fig. 2. The number of keratinolytic microorganisms on various medium: a) chicken feathers, b) duck feathers, c) turkey feathers, MAN - Mandel's medium, OM - Omelianski's medium

The number of microorganisms can be affected by technology applied in the processing facility, the poultry species, and hygiene conditions in livestock farms [16, 17]. Microorganisms frequently occurred on mineral substrates, for which keratin as a component, was a source of carbon and energy. The ability of environmental microorganisms to produce keratinase and to use keratin as a carbon source was confirmed on an example of *Bacillus subtilis* bacteria [18, 19]. Isolated microorganisms were characterized by different growth rate, which can be attributed to their generic or species differences. The ability of keratin degradation is often a feature of thermophilic microorganisms, which [20] associated with the need to supply large amounts of energy to effectively degradation of the substrate. On average for all of the analyzed samples, 45% less keratinolytic microorganisms was grown on Omelianski's than on Mandel's substrate ($3.5 \cdot 10^8$ CFU·g^{-1} d.m.). Smaller number on Omelianski's substrate confirms that it is the substrate much poorer in nutrients. These differences demonstrate the need to ensure appropriate conditions for growing microorganisms that can be used in biodegradable waste from, among others, the poultry industry.

Conclusions

1. Analyzed types of feathers were numerously colonized by keratinolytic microorganisms. The poultry species, slaughterhouse type, and date of sampling had a great impact on this fact.
2. Turkey feathers were the most often inhabited by microorganisms capable of degrading keratin, then duck and goose feathers, while the lowest numbers were found in chicken feathers.

3. Mandel’s rather than Omelianski’s appeared to be the preferred mineral substrate with keratin as the sole carbon source.
4. Keratinolytic microorganisms colonized feathers of different poultry kinds more in autumn and winter than in other periods.

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LICZEBNOŚĆ MIKROORGANIZMÓW KERATYNOLITYCZNYCH W PIÓRACH PO UBOJU DROBIU

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Abstrakt: Stale powiększająca się koncentracja produkcji mięsa drobiowego powoduje powstawanie ogromnych ilości produktów odpadowych. Jak każdy materiał odpadowy, również pierze musi zostać odpowiednio zagospodarowane. Nie jest to jednak prosty mechanizm, gdyż w skład piór wchodzi odporna na degradację keratyna. Z tego też względu wskazane jest poszukiwanie drobnoustrojów zdolnych do degradacji tego białka. Liczebność drobnoustrojów w badanych próbach ma istotne znaczenie w izolacji szczepów cechujących się pożądanymi właściwościami, tj. wysoką aktywnością enzymatyczną. Celem badań było określenie liczebności drobnoustrojów zdolnych do rozkładu keratyny w piórach kurzych, kaczych, gęsich oraz indyczych pozyskanych w wyniku uboju. Zostały one pobrane w różnych terminach badawczych w okresie od marca 2015 do stycznia 2016 roku, w ubojniach drobiu zlokalizowanych w województwach lubuskim i zachodniopomorskim. Hodowle prowadzono w oparciu o mineralne podłoża Mandela i Omeliańskiego, uzupełnione o keratynę. We wszystkich analizowanych piórach stwierdzono występowanie drobnoustrojów keratynolitycznych. Były one w różnym stopniu zasiedlone przez te mikroorganizmy. Pióra indycze były najliczniej reprezentowane przez mikroorganizmy zdolne do rozkładu keratyny ($5{,}8 \cdot 10^8$ jtk$\cdot$g^{-1} s.m.), następnie pióra kacze ($4{,}7 \cdot 10^8$ jtk$\cdot$g^{-1} s.m.). Mniejsze liczebności stwierdzono w piórach gęsich ($2{,}8 \cdot 10^7$ jtk$\cdot$g^{-1} s.m.), z kolei najmniejsze w piórach kurzych. Ze względu na lepsze dostosowanie składu pożywki Mandela do potrzeb keratynolitycznych udało się wyizolować na tym podłożu większą ich liczebność w porównaniu do podłoża Omeliańskiego. Jedynie w przypadku piór kurzych liczebność drobnoustrojów keratynolicznych na obu podłożach była zbliżona i nie przekraczała 10^6 jtk$\cdot$g^{-1} s.m. Wbrew oczekiwaniom w badanych materiałach w okresie jesienno-zimowym stwierdzono większą liczebność analizowanej grupy drobnoustrojów.

Słowa kluczowe: pióra, keratyna, mikroorganizmy, przemysł drobiarski