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SPIS TREŚCI

VARIA

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Elwira TOMCZAK[1*] and Anna DOMINIAK[2]

LIVING ORGANISMS IN WATER QUALITY BIOMONITORING SYSTEM

ORGANIZMY ŻYWE W SYSTEMIE BIOMONITORINGU JAKOŚCI WODY

Abstract: The typical living organisms used for biological monitoring of surface waters and their use in applications are presented in the paper. The main focus is on the characterisation and use of freshwater mussels. The paper discusses the role of biomonitoring in surface water supply systems. Three-stage biomonitoring system which has been functioning for 20 years in Water and Wastewater Company (ZWiK Sp. z o.o.) in Lodz is presented as an example. The system employs living organisms such as mussels, perch and luminescent bacteria.

Keywords: bioindicators, water quality biomonitoring, mussels

Introduction

Bioindication is used to assess the quality of lake and river surface water, groundwater and, more and more often, treated water. The degree of water contamination is determined using short-term cultures (bioassays) or through long-term observation, *ie* continuous recording of the condition of aquatic organisms (biomonitoring). Behavioural changes observed in bioindicators are a sign of stress resulting from adverse or harmful effect of external factors.

Bioindication allows for detection of total toxicity of all hazardous substances, which is particularly important for substances with synergistic toxic effect. It is thus a measure for evaluation of total toxicity of the controlled system and a valuable addition to periodic laboratory tests of water.

The usefulness of species or groups of species whose behaviour may serve as a biological indicator of the change in the quality of ecosystems and environment is

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being analysed [1]. Response of indicator organisms may differ in terms of sensitivity, from behavioural and physiological changes to morphological changes and mortality. The paper [2] discusses the role of bioindication in water quality analysis, aquatic indicator organisms useful in bioindication, active and passive bioindication approaches and measures of restoration of water resources. The organisms most frequently used as bioindicators include crustaceans (including bivalves), fish, protozoa and algae [3–5]. Numerous publications [6–12] provide information on sorption properties of marine and freshwater algae. They discuss kinetics and sorption equilibrium of heavy metals in algae-solution system, influence of abiotic factors on the process of sorption and desorption of analytes from biomass. The results of laboratory tests conducted on different species and types of algae to assess their usefulness as natural sorbents are provided. Studies conducted on algae take into consideration, among others, their chemical composition, biology, taxonomy, physiography and their application for the assessment of water pollution with heavy metals, pesticides and radionuclides. In another study [13] water quality was assessed in five oxbow lakes of Lyna. Apart from physico-chemical indicators, typical biological indicators were used. Water quality was assessed based on the assumption that healthy aqueous ecosystem is inhabited by abundant invertebrate communities. Several groups of invertebrates were analysed. Dietera, Oligochaeta and Gastropoda larvae were shown to be the most abundant. The structure of invertebrate communities is not only a source of information on water quality but it may also help to develop measures for the protection of water resources. Biomonitoring plays a particularly important role in surface water intake systems. Surface waters are characterised by high variability of quality and chemical composition related to, among others, surface runoff, discharge of untreated wastewater, inflow of leachates from landfills, contamination from industrial accidents, increased use of chemicals in agriculture and internal factors such as algal bloom. Furthermore, despite establishment of safeguard zones, surface waters may become contaminated as a result of ecological disasters or terrorist attacks.

The criteria for selection of organisms to be used in biomonitoring of water in water supply systems (and for other purposes) are strict: such organisms must react quickly and reliably to environmental changes, responses should be unambiguous and easily interpretable, their maintenance in laboratory conditions should be easy, living conditions and habits should allow automated and continuous monitoring of their behaviour. There are two approaches that may be adopted in biomonitoring. One approach involves working with the selected groups of living organisms which satisfy the above criteria and the other is observing the behaviour of typical groups of organisms in their natural habitats in ecosystem, as mentioned before. The former approach is usually applied in laboratory conditions, particularly in inspection of the quality of drinking water.

Taking into consideration the criteria applicable to specific groups of organisms useful in biomonitoring, the paper discusses freshwater mussels used most frequently as bioindicators of negative changes in their living environment (both in laboratory and natural conditions). Other organisms which may serve as bioindicators are discussed. The paper presents three-stage water quality control system at Water and Wastewater

Company [Zaklady Wodociągow i Kanalizacji – ZWiK Sp. z o.o.] in Lodz as an example of biomonitoring used for the surveillance of the quality of drinking water with the use of mussels and other organisms.

Characterisation and use of bivalves in biomonitoring

Bivalves (*Bivalvia*) belong to a class encompassing 8000 species, the majority of which lead a fairly sedentary life, moving to other sites only when they are in danger [14]. 38 species of gastropods and 6 species of bivalves are protected pursuant to the Polish law (Regulation of the Minister of Environment as of 28th September 2004 on the species of wild animals under protection; Journal of Laws No. 20). These are only benthos aquatic animals (known already in the Cambrian) of laterally compressed bodies enclosed by a shell consisting of two valves. Bivalve body is bilaterally symmetrical, usually elongated, laterally compressed and enclosed between two, usually symmetrical, halves of shell. Both halves (right and left) are joined together at the top with a conchiolin ligament. In some species it is an arrangement of calcareous plates and various type of teeth that form the hinge. Hinge plates are an important element in bivalve structure as they prevent the shell from becoming disarticulated when the shell opens and closes. Bivalves vary greatly in size and weight from several millimetres of freshwater *Pisidium* up to 250 kg of the giant clam (*Tridacna gigas*). Bivalve shell is composed of three layers: the outermost layer made of conchiolin, middle layer made of calcite and the innermost layer made of nacre. Nacreous layer is composed of tiny aragonite platelets [15]. 34 species of bivalves have been observed in Poland's inland waters and 9 species have been observed in the Baltic Sea. Bivalves feed mainly on detritus, algae, protozoa and bacteria. They are excellent filters. Within one hour an individual is able to filter as much as 1.5 litre of water. Freshwater mussels have strong sense of touch. Numerous sensory receptors are located on labial palps, foot surface and along the edges of the siphons. Bivalves protect themselves against hostile environment. The following may be interpreted as a potential threat: change of water temperature, sudden water flow or increased concentration of pollution. Upon the inflow of substances which are harmful to their metabolism they close the valves and siphons abruptly thereby reducing their physiological activity. They are also very sensitive to increased concentrations of coarse-grained suspensions in water. They have an excellent chemical sense, which makes them even more sensitive to the presence of chemical substances in water. This feature has been used for bioindication purposes in water bodies. The crustacean *Balanus improvisus* and the mussel *Mytilus trossulus* were used as biomonitors of the trace metals Cu, Zn, Cd, Fe, Pb, Mn and Ni at five selected sites of the Gdansk Bay [16]. Biomonitoring run as a pilot of the future programme was to establish local contamination of water with metals the loads of which might vary according to what flows into the bay with waters of the Vistula river. The study showed correlations between accumulated concentrations of metals in the two bioindicators. Similar study was described in the paper [17]. Native and caged mussels were used for the monitoring of biological pollution in the Basque coast. After 3 weeks the mussels were collected from each site and analysed (from molecular to organism level) to determine chemical contaminant concentrations (metals, PAHs, PCBs, phthalates and nonylphenol). The authors concluded that the use of native mussels is an appropriate and cost-effective approach to monitoring the effects of pollution as it allows for adaptation to the changing site conditions. On the other hand, caged mussels remain particularly useful to determine the effects of large and transient pollution as they provide a highly sensitive and rapid response. Since 1983, the Ontario Ministry of the Environment has run its comprehensive 26-year Niagara River biomonitoring program using mussels (*Elliptio complanata*) [18, 19]. The objective of the program was to determine the presence and fluctuation of pollution at selected sites: several sites in Canada and five in the USA. Over the years no significant contamination was detected and in some cases pollution concentrations in tissues of the analysed mussels were found to have decreased. Optimistic results concerning the decreased concentrations of hexachlorobenzene, chlorobenzene, pesticides and industrial chemicals were reported.

Biomonitoring System at ZWiK Sp. z o.o. in Lodz

Mussels as bioindicators

Mussels may be useful also outside their natural environment. Placed in flow-through aquariums they form an important element of water quality control system in water supply company. The Lodz's water supply company introduced its first bioindicator system in mid-1990s. At that time perch fry was used to determine the quality of surface water drawn from Sulejowski Reservoir. Later on, mussels were introduced for biomonitoring at that intake. The same bioindication system was implemented at another Lodz's surface intake, *ie* the Pilica intake in Tomaszów Mazowiecki. The originator and founder of the entire biomonitoring system at Water and Wastewater Company (ZWiK Sp. z o.o.) in Lodz was its Chief Technology Officer – Bogumił Rzerzycha.

At present, biomonitoring at ZWiK Sp. z o.o. in Lodz is based on a comprehensive water quality system located throughout entire water supply network providing water to points of consumption in Lodz, Tomaszów Mazowiecki, Rokiciny and villages along the road connecting Tomaszów Mazowiecki and Lodz. Perch (*Perca fluviatilis*) and bivalves – swollen river mussels (*Unio tumidus*) are used as indicator species. Such bioindicator systems were installed: at surface water intakes and groundwater wells, after each water treatment stages and at outlets of the treatment plant. Furthermore, in 2011, rapid toxicity tests employing bioluminescent bacteria (*Vibrio fischeri*) were put into place [20].

SYMBIO system employing mussels comprises three elements (Fig. 1):

– Flow-through aquarium – to which the tested water is fed. 8 specimens attached to plastic plates are placed inside. The occurrence of harmful substance in water induces stress in mussels and they respond by immediate closure of shell;

– System controller – receiving signals from the probes. System controller analyses data, converts it into digital format and triggers the alarm system in case of water pollution. The controller also sends the processed data to a higher level system – a PC;

– PC – it provides data visualisation, stores data and generates reports. An alarm message is displayed on the monitor screen and a sound is emitted through PC's loudspeakers.

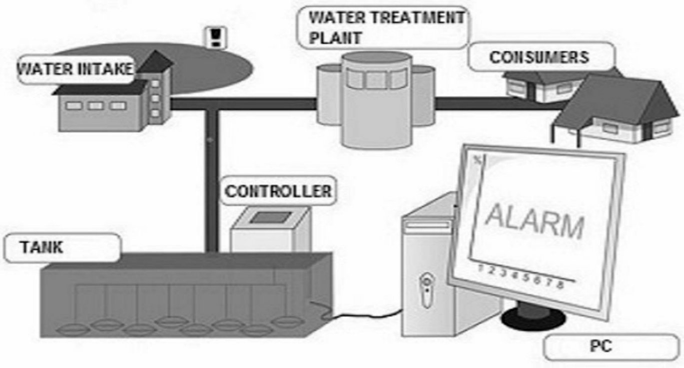

Fig. 1. Water quality monitoring using mussels

Bioindicators used to control water quality at ZWiK Sp. z o.o. in Lodz comply with the requirements for indicator species. Mussels – swollen river mussels are collected from lakes in the vicinity of Poznań selected as water bodies subject to minimal anthropogenic pressures, *ie* without direct point sources of pollution or runoff from agricultural catchment. Size, age and condition of mussels are taken into consideration during selection of specimens. Similarly sized mussels (with larger specimens being preferred) that do not differ much in terms of morphology from other population specimens are selected. The mussels are then transported in lake water in a special, thermally insulated container. Acclimatisation is required to minimize mussel stress resulting from change in environmental conditions. The selected specimens spend two weeks in special aquariums with temperature gradually adjusted to that of the target tank. The target tank which contains 8 mussels at a time is made of stainless steel (Photo 1). Mussels are placed in the tank for 3 months. This period is optimal for their functioning in the system as they do not require additional feeding. After 3 months, the mussels are replaced with other specimens, and the ones that were taken out of the aquarium are returned to their natural environment. The tank is designed to eliminate or minimise external factors that may adversely affect mussel activity. It provides darkness and isolation from noise, it also cushions ground vibrations. Installed in the tank is an air-operated filter that ensures proper oxygen saturation of water. Measuring probes connected to a magnet are attached to the shell of each mussel and record their activity (Photo 2). Mussels at different activity levels (different state of opening/closure of the shell) are selected for the tank. Integrated with the tank is a system controller that processes the data and sends them to the PC. PC software provides data visualisation and data storage as well as report generation and storage. This allows for up-to-date evaluation of system operation and following the history of mussel activity.

Data represented as bar graphs shows current degree of valve opening for each mussel in percent (sampling is done every 1s). Line graphs allow for following the

Photo 1. Aquarium with mussels

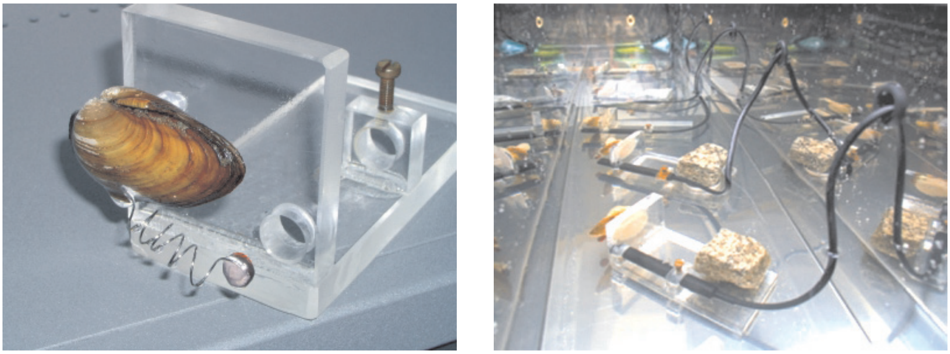

Photo 2. Mussels with measurement probes

history of mussel activity. Under natural conditions, the biorhythm of each mussel comprises cyclical periods of increased and decreased activity. During its decreased activity the valves may be partly or entirely closed for a period of several up to a dozen or so hours. Closure of the valves to only a few percent or its gradual closure may not be a sign of stress. Only a sudden, and what is important, simultaneous closure observed in a group of mussels may be considered a reaction to stress.

Upon a sudden change of water quality, mussels abruptly close their valves and the system generates the alarm. An alarm message is displayed on the computer screen, a sound is emitted through the PC's loudspeakers and a signalling lamp is lit.

Perch fry as a bioindicator

The other biological indicator species is perch (*Perca fluviatilis*). Aquariums with the fish and the tanks containing the mussels are installed in parallel arrangement. Perch, similarly to mussels, are collected at proper age (1–2 years), in proper condition and with the desired set of behavioural characteristics (no or poorly developed predatory features). The specimens are collected and replaced by an ichthyologist. The necessary reserves of fish for emergency replacement are located throughout ZWiK Sp. z o.o.'s sites in Lodz. Replacement dates are suited to natural biological cycle of perch (size, condition, habitat, population in water bodies): spring (March–April) – date depends on disappearance of ice cover; summer (June–July) – when perch reach the length of at least 4 cm; autumn (October–November) – before drop of temperature of surface water below 4 ^{o}C and icing. When no longer used as biomonitors, the fish are returned to natural habitat by the ichthyologist responsible for fish replacement. Observation of perch is done on a systematic basis by the employees of ZWiK Sp. z o.o. in Lodz. The alarm generated by mussel activity monitoring system and observation of intoxication of fish will result in implementation of actions indicated in the instruction prepared for this purpose.

Ecotoxicological tests

Apart from the internationally used methods employing crustaceans and fish (due to their vital role in the food chain), ecotoxicological bioassays with living organisms at different level of organisation and development, such as bacteria, are receiving increased use. Luminescent bacteria (*Vibrio fischeri*) are the third species used by Lodz's ZWiK biomonitoring system. Under normal conditions a great part of the bacteria's metabolism is dedicated to emitting light (luminescence). Bioluminescence occurs as a result of chemical reactions, oxygenation of luciferin in the presence of oxygen and enzymes. Luminescent bacteria emit visible light as a part of their normal metabolic processes. Any change in these processes through exposure to factors affecting metabolism results in decreased luminescence intensity. DeltaTox analyser measures the amount of light emitted by bacteria. Change in luminescence intensity occurs very rapidly, results may be available after 5–15 minutes of incubation of the bacteria-containing sample. Although it is a popular rapid solution, it may not be used as a sole indicator for water quality [21]. The paper [22] presents a group of specific tests called Toxkits which employ cryptobiotic stages of the test organisms. Cysts, resting eggs of crustaceans or algal cells, stored in special protective tubes, are dormant and have a shelf-life of up to several months. The most popular toxkits include: Microtox (with luminescent bacteria *Vibrio fischeri*); Spirotox, Protoxkit (using protozoa); Rotoxkit F (with rotifier *Brachionus calyciflorus*); Daphtoxikit F, Thamnotoxkit (using crustaceans).

Summary and conclusions

Bioindicators are any animal or plant species having a narrow range of tolerance for variation in environmental conditions (so-called stenotopic species). They are usually used to assess the degree of environmental degradation or determine changes occurring in a biocenosis or an ecosystem. Bioindicators may include organisms at various levels of organisation and development. Different species of mussels, gastropods and algae are among the most widely used. The requirement for early detection of water quality changes, including toxicity, necessitated the introduction of ecotoxicological tests to analytical science as they provide practically immediate responses based on reactions of simple organisms such as bacteria or protozoa. Responses of living organisms to unfavourable habitat conditions are used mainly for surveillance of water quality in rivers, freshwater and saltwater bodies and water supply networks. The three-stage biomonitoring system used at ZWiK Sp. z o.o. in Lodz comprising a flow-through aquarium with mussels, an aquarium with perch and ecotoxicological tests provides continuous surveillance of water quality both at production and distribution stages ensuring safety of water consumers. It is also a valuable addition to chemical analyses run periodically by water control laboratories.

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ORGANIZMY ŻYWE W SYSTEMIE BIOMONITORINGU JAKOŚCI WODY

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Abstrakt: Przedstawiono typowe organizmy żywe służące do biomonitoringu wód powierzchniowych oraz ich wykorzystanie w prezentowanych w pracy aplikacjach. Główną uwagę poświęcono charakterystyce i wykorzystaniu małży słodkowodnych. Uwzględniono rolę jaką odgrywa biomonitoring w wodociągowych systemach ujmowania wód powierzchniowych. Za przykład posłużył trójstopniowy system biomonitoringu funkcjonujący od 20 lat w Zakładzie Wodociągów i Kanalizacji Sp. z o.o. w Łodzi, wykorzystujący małże, narybek okonia i bakterie luminescencyjne.

Słowa kluczowe: bioindykatory, biomonitoring jakości wody, małże

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SANITARY EVALUATION OF THE WATER FROM WATER INTAKE POINTS SITUATED IN GORZOW WIELKOPOLSKI AND NEIGHBOURING LOCALITIES

OCENA SANITARNA WODY POCHODZĄCEJ Z UJĘĆ WODNYCH NA TERENIE GORZOWA WIELKOPOLSKIEGO ORAZ OKOLIC

Abstract: Water is an essential component necessary for sustaining life. Nevertheless, it may pose a serious threat to human life resulting from possible occurrence of pathogenic and potentially pathogenic microorganisms. Therefore, monitoring and continuous microbial surveillance of the water intended for consumption is extremely important. The requirements referring to qualitative parameters which should be met by water are set out in the Regulation of the Minister of Health of 29 March 2007, as amended on 20 April 2010, and the EU directives. The quality of water being supplied to consumers depends on many factors, among other on the type of water intake (surface water or groundwater), efficiency of water treatment and disinfection, and technical condition of the water supply network.

The analysis of the sanitary condition of drinking water has been conducted form water intakes in the city of Gorzow Wielkopolski, *ie* Centralny Kosynierow Gdynskich intake, Klodawa intake and Siedlice intake, and in neighbouring localities, *ie*. Maszewo and Marwice. The research material was raw and treated water samples. The population size of *Faecal streptococci*, coliform bacteria, including *E. coli*, and total mesophilic and psychrophilic bacteria counts was determined. The analysis of the sanitary condition of drinking water has been conducted.

The number of coliform bacteria, including *E. coli*, and streptococci was determined by the method of membrane filters, whereas total mesophilic and psychrophilic bacteria counts using the plate method under incubation conditions conforming to the standards.

The presence of mesophilic and psychrophilic bacteria was observed in all examined water intake points. Differences in their counts over the whole year being significant. In three research points, *ie* Centralny Kosynierow Gdynskich intake, Maszewo intake and Marwice intake, psychrophilic bacteria count was exceeded (100 CFU $\cdot$ cm^{-3}). In the case of pathogenic bacteria, their occurrence was occasionally observed in the drinking water intake points. The water treatment processes applied and, as the final result, water sanitary assessment according to the existing standards and the provision stipulated allow it to be collected for consumption purposes and do not pose the threat to human health and life.

Keywords: drinking water, bacteria, *E. coli*, *E. faecalis*, water contamination

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Introduction

Seas and oceans cover about 75 % of the Earth's surface. The volume of this water is estimated at about $2 \cdot 10^{18}$ m^3, of which the most is saltwater, while barely 0.025 %, *ie* 500 000 km^3 is freshwater. This is the freshwater to which surface water and ground water, being a reservoir of drinking water, are classified [1]. Excessive and non-scientific chemicalisation in agriculture, illegal and uncontrolled domestic and industrial wastewater discharge, landfill leachate or discharge of slurry and liquid excrement in the close vicinity of water intake protection zone are not indifferent to the quality of water. These different manifestations of human activity lead both to anthropogenic and microbial contamination. Pathogenic and potentially pathogenic microbes are being introduced into water bodies [2–4]. These micro-organisms may then pass over into water supply network, also with treated water (water disinfection at water treatment plant not effective enough) as a result of fault or mechanical damage during operation, or from soil pollution during water supply network repair works [5–6]. Water supply network creates good conditions for their development and survival. Organic and inorganic compounds contained in the water from water intake, pipeline corrosion products as well as biofilm and internal pipeline sediments, being a habitat for microbial biomass, constitute nutrients for them [7–8]. Therefore, the application of effective water purification processes and the use of chemical reagents, as well as the preservation of adequate technical condition of water supply network, is so important to ensure clean and safe water, not threatening consumer's health or life [9–11].

The water intended for consumption has to meet requirements being set to it at water intake point by consumers. For this reason, permanent residents of human and animal intestinal flora, *ie* coliform bacteria (*Escherichia coli*), *Faecal streptococci* (with a typical species *Enterococcus faecalis*) and *Clostridium perfringens*, are considered useful sanitary indicators for drinking water quality control [12–14]. According to the standards the presence of these biological indicators should not be proven per each sampled 100 cm^3 of water [15–16]. The water intended for human consumption is also analysed in terms of the total number of bacteria being present in it, *ie* psychrophilic and mesophilic bacteria. Psychrophiles include heterotrophic bacteria which are adapted to live in cold environment. Their optimum temperature does not exceed 15 ^{o}C, whereas the maximum one 20 ^{o}C. The occurrence of psychrophilic bacteria in tap water is evidence of the presence of nutrients and allows assessment of the efficiency of water treatment processes (coagulation, filtration and disinfection) [17–18]. Mesophiles comprise the bacteria developing at moderate temperature, the optimum of which is in the range of 25–40 ^{o}C. They include pathogenic bacteria, the thermal optimum of which is a temperature of human body. The presence of mesophilic bacteria in water is indication of its pollution with wastewater and, consequently, of the possibility of water contamination with pathogenic bacteria, too [19].

The objective of this study was to analyse and assess bacteriologically the freshwater and treated water collected from water intakes in the city of Gorzow Wielkopolski and neighbouring localities.

Material and methods

The object of microbiological analysis was the samples of freshwater and treated water collected from the groundwater intakes supplying the city of Gorzow Wielkopolski, *ie* Centralny Kosynierow Gdynskich intake, Siedlice intake and Klodawa intake. These water intakes and the water supply network are operated by Przedsiebiorstwo Wodociagow i Kanalizacji (Water and Sewage Service Co. Ltd) in the aforesaid city. The Centralny Kosynierow Gdynskich intake is the oldest and the only water intake situated entirely in the city and supplies water to about 15 % of the city. The Siedlice intake is situated along the left side of the Warta River and supplies water to about 59 % of the city. The Klodawa intake is located about 5 km to the north of the centre of Gorzow Wlkp., outside the city limits. It supplies water to about 26 % of the city [20]. The research material came also from neighbouring localities. *ie* Maszewo and Marwice. Maszewo is a rural borough situated in the western part of the Lubuskie Province, whereas Marwice is a village situated about 10 km to the north-west of Gorzow Wielkopolski. At all waterworks there are water purification plants where the water undergoes aeration, filtration and disinfection. In the Central Waterworks and Siedlce Waterworks the aeration takes place with the use of open systems at aeration towers and then the water flows through open high-rate filters. In Klodawa Waterworks, Maszewo Waterworks and Marwice Waterworks the aeration takes place in a closed pressure aerator and then the water flows through closed pressure high-rate filters. Both closed and open filters are filled with high-silica sand. After the filtration the water is subject to disinfection: in Central Waterworks, Siedlce Waterworks and Klodawa Waterworks they apply chlorine dioxide manufactured from hydrochloric acid and chlorite directly at the water purification plant. In Marwice Waterworks and Maszewo Waterworks sodium hypochlorite is used.

The collection of water samples for analyses was conducted from January to December 2012, several times depending on the research point. Freshwater samples from three water intakes, *ie* Centralny Kosynierow Gdynskich intake, Siedlice intake and Klodawa intake, were collected three times a month, whereas those of treated water five a week. Freshwater samples from two water intakes, *ie* Maszewo intake and Marwice intake, were collected two times a month, whereas those of treated water, on average, four time a month.

The number of coliform bacteria, including *E. coli*, was determined on Endo Les medium (Merck & Co., Inc.), using the method of membrane filtration. Water samples, 100 cm^3 each, were filtered through paper discs, with pore size of 47 µm, and then incubated at 36 ^{o}C for 24 h [16]. *Faecal streptococci* were determined on Slanetz-Bartley medium (Merck & Co., Inc.), also using the method of membrane filtration. Water samples, 100 cm^3 each, were filtered through paper discs with pore size of 47 µm, which were then incubated at 36 ^{o}C for 24–48 h [15]. Total bacterial count was determined on nutrient agar medium (Merck & Co., Inc.) by the plate method. Water samples, 1 cm^3 each, were transferred onto Petri dishes and flooded with liquid agar medium. After the agar hardened, Petri dishes were incubated at 36 ^{o}C for 48 h (mesophilic bacteria) and at 22 ^{o}C for 72 h (psychrophilic bacteria). After incubation, bacterial colonies that developed on Petri dishes were counted. The readings were converted to colony forming units per a specific water unit [19].

The research results were analysed statistically using Statistica 10.0 software package. The variance analysis (ANOVA) with the use of Duncan's test has been conducted.

Results and discussion

The research results showed the presence of psychrophilic and mesophilic bacteria in the treated water being collected from water intake points under examination. The highest average annual number of psychrophiles, 61 CFU · cm^{-3}, was found in the Centralny Kosynierow Gdynskich intake (Fig. 1). In this water intake point, an increase in the number of theses bacteria was recorded in spring and summer when it exceeded the standard limit value, *ie* 100 CFU · cm^{-3}. In autumn and winter seasons the increased values of this type of bacteria have not been observed. Relatively high number of psychrophilic bacteria in water was also observed in the Maszewo intake, where in autumn their acceptable number has been exceeded (Fig. 4). Relatively high number of psychrophilic bacteria in water was also observed in the Maszewo intake, where The least average annual number of the bacteria mentioned above was recorded in the Klodawa, Siedlice and Marwice intakes, where they numbers were similar. In case of the test points mentioned above, the quantity of psychrophiles was not exceeded (Fig. 2, 3, 5). The analysis of variance performed showed significant differences in the number of psychrophilic bacteria between respective water intake points. Significant difference number of psychrophilic bacteria in the Centralny Kosynierow Gdynskich intake than in other water intake points being examined may result from the technical condition of water supply network, connections and water system. The Centralny Kosynierow Gdynskich water intake point is the oldest one in Gorzow Wielkopolski, where old

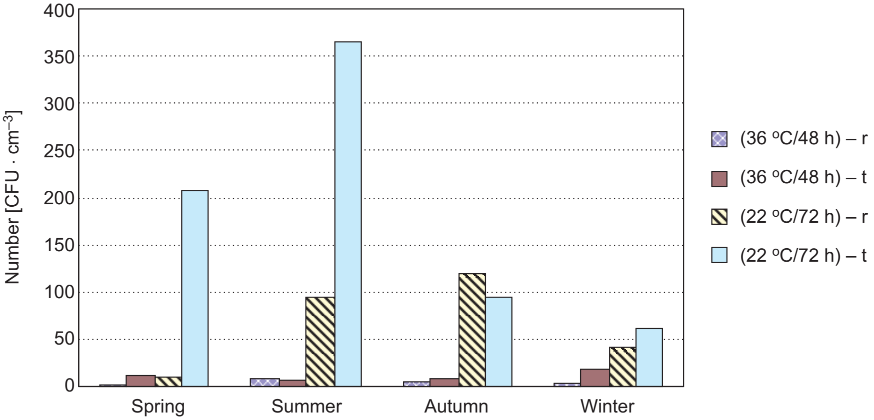

Fig. 1. The number of bacteria in the raw and treated water sampled from the Centralny Kosynierow Gdynskich water intake depending on the season of the year; incubated at 36 °C for 48 h – mesophilic bacteria, incubated at 22 °C for 72 h – psychrophilic bacteria; r – raw water, t – treated water

water systems continue to be operated. Multi-annual operation of the water supply network and water system, made of steel and cast-iron elements, could induce deposition of chemical and biological sediments on the internal surfaces of pipelines. Higher number of psychrophilic bacteria in the spring and summer season in the water intake being discussed above than the values being observed in other months may be evidence of not very effective disinfection at water treatment plant, as well as of a higher temperature creating better conditions for their development, which is also confirmed by Libudzisz and Kowal [17]. It can be assumed that the spring and summer season, when higher temperatures occur, also affected an increase in the temperature of water in water supply network, which, as a consequence, induced a lower efficiency of

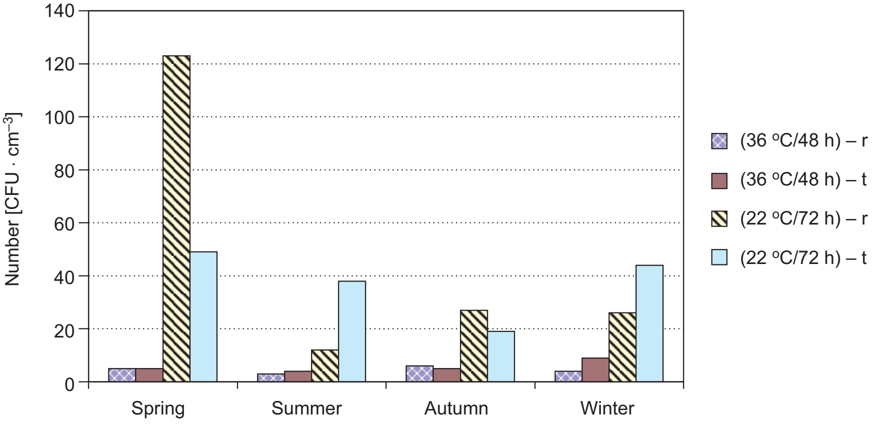

Fig. 2. The number of bacteria in the raw and treated water sampled from the Klodawa water intake depending on the season of the year; incubated at 36 °C for 48 h – mesophilic bacteria, incubated at 22 °C for 72 h – psychrophilic bacterii; r – raw water, t – treated water

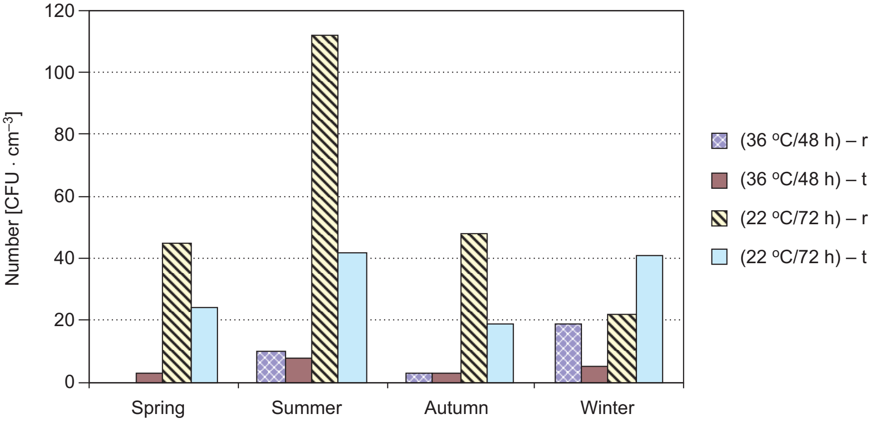

Fig. 3. The number of bacteria in the raw and treated water sampled from the Siedlice water intake depending on the season of the year; incubated at 36 °C for 48 h – mesophilic bacteria, incubated at 22 °C for 72 h – psychrophilic bacteria; r – raw water, t – treated water

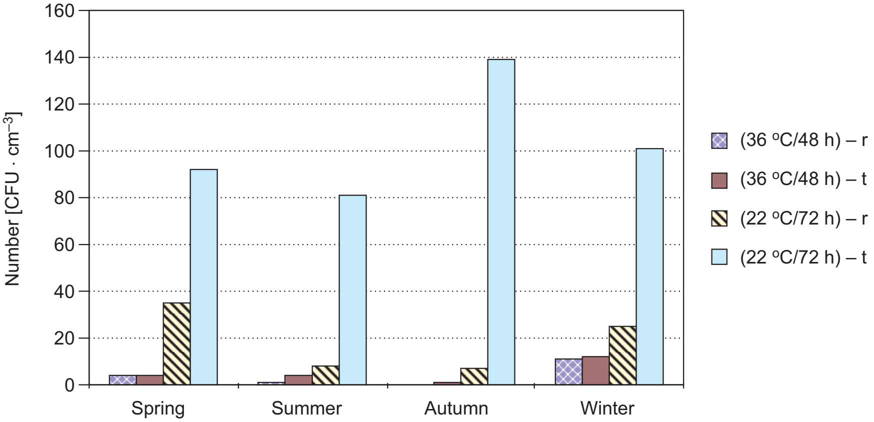

Fig. 4. The number of bacteria in the raw and treated water sampled from the Maszewo water intake depending on the season of the year; incubated at 36 °C for 48 h – mesophilic bacteria, incubated at 22 °C for 72 h – psychrophilic bacteria; r – raw water, t – treated water

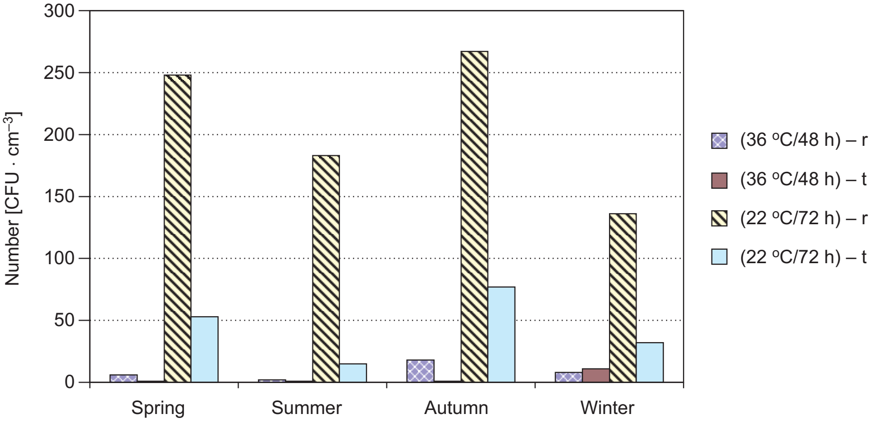

Fig. 5. The number of bacteria in the raw and treated water sampled from the Marwice water intake depending on the season of the year; incubated at 36 °C for 48 h – mesophilic bacteria, incubated at 22 °C for 72 h – psychrophilic bacteria; r – raw water, t – treated water

disinfectants and caused development of bacteria. Cycon and Wiera [21] report that this is summer and early autumn months when normal values for development of micro-organisms in water are exceeded the most, which is induced by more favourable conditions for their growth and development.

The number of mesophilic bacteria in treated water was within normal limits, irrespective of the water intake point being examined, and differences between them were not significant. In all water intake points under examination, the allowable number of these bacteria, *ie* 50 CFU · cm^{-3}, was not exceeded.

The water purification being performed at the water treatment plants of this waterworks did not ensure complete elimination of psychrophilic and mesophilic bacteria, as suggested by their presence in tap water. This is in agreement with the study by Zacheus et al [22], who showed that biofilm developed on polyvinyl chloride, polyethylene and stainless steel within three weeks, despite water purification by coagulation, sedimentation, filtration on sand filters and ozonisation. Although psychrophilic bacteria were found to be present in the treated water collected from all water intake points being examined, it is possible to state that they are not a threat to the health of consumers. Grabinska-Loniewska and Sinski [5] report that psychrophilic bacteria are generally considered harmless to humans. Similarly, Smylla [24] reports that psychrophiles do not seriously endanger water consumers because they do not develop at human body temperature, as is the case of mesophilic bacteria.

Because freshwater samples for analyses were collected from the test points with different frequency, *ie* 3 times a month in the Centralny Kosynierow Gdynskich, Klodawa and Siedlice intakes and 2 times a month in the Maszewo and Marwice intakes, this did not allow its quality to be clearly assessed and compared bacteriologically. It is only possible to suppose that, from among the water intake points being examined, low quality of freshwater was observed in the Marwice intake. In this water intake point, the number of psychrophilic bacteria was exceeded three times. Their quantity in water throughout the whole year as higher than in other test points (Fig. 5). This might have resulted from the application of natural fertilizers in the direct neighborhood of the water intake because this area is typically agricultural one. Also poorly developed sewerage network, or even its lack in some parts of the village, could have a significant effect. The process of water treatment applied contributed to a significant improvement of the quality of drinking water.

Indicator bacteria in water were found occasionally. At some water intakes single units of the bacteria have been observed (Table 1).

Table 1

Presence of indicator bacteria in the water collected in test points (100 cm^3) in the city of Gorzow Wlkp. and around it

Location of sampling points	Sampling period	Coliform bacteria, including *E. coli*	*Faecal streptococci*
Centralny Kosynierow Gdynskich Waterworks	June August	 +	+
Kłodawa Waterworks	July September	+ +	
Siedlice Waterworks	January August	 +	+
Maszewo Waterworks	July August	 +	+

"+" – single bacterial units

According to the standards, however, the presence of coliform bacteria in such a quantity within one year did not endanger the human health and was acceptable. The regulations allow the occurrence of single *coli* bacteria in test samples provided that they are not observed in the succeeding test [24–25]. Szumilas et al [26] confirm that a substantial quantity of indicator and pathogenic bacteria is eliminated during water purification processes, in which the extent of their reduction exceeds 99 %.

Conclusions

1. The research results showed the presence of psychrophilic and mesophilic bacteria in the treated water being collected from water intake points under examination. Their quantity was within the normal values throughout the whole year, despite being occasionally exceeded.
2. The highest number of psychrophilic bacteria in treated water was recorded in the Centralny Kosynierow Gdynskich intake, where allowable quantities for these bacteria were exceeded three times.
3. Pathogenic bacteria were rarely observed in the water being examined.
4. Most often, water disinfection process showed effective elimination of bacteria at the water treatment station being part of the waterworks under examination. However, the processes being applied at some water intake points did not have a 100 % effect in the elimination of micro-organisms from water.
5. The best water quality in sanitary respect after water treatment was observed in the water intake points in Siedlice, Klodawa and Marwice. A slight deterioration of the water quality is associated with the greater presence of micro-organisms being observed in two test points, *ie* Maszewo intake and Centralny Kosynierow Gdynskich intake.

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OCENA SANITARNA WODY POCHODZĄCEJ Z UJĘĆ WODNYCH NA TERENIE GORZOWA WIELKOPOLSKIEGO ORAZ OKOLIC

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Abstrakt: Woda jest podstawowym składnikiem niezbędnym do utrzymania życia. Jednakże, może ona stworzyć poważne zagrożenie dla zdrowia człowieka wynikające z możliwości wystąpienia mikroorganizmów chorobotwórczych i potencjalnie chorobotwórczych. W związku z tym, niezwykle istotna jest kontrola oraz stały nadzór mikrobiologiczny nad wodą przeznaczoną do spożycia. Wytyczne co do parametrów jakościowych, jakim powinna odpowiadać, zawarte są w Rozporządzeniu Ministra Zdrowia z dnia 29 marca 2007 r. wraz ze zmianą z dnia 20 kwietnia 2010 r. oraz Dyrektywach Unii Europejskiej. Jakość wody dostarczanej konsumentom zależy od wielu czynników m.in.: rodzaju ujęcia (woda powierzchniowa lub podziemna), skuteczności procesów uzdatniania i dezynfekcji oraz stanu technicznego sieci wodociągowej.

Przeprowadzono analizę stanu sanitarnego wody pitnej pochodzącej z ujęć wodnych zaopatrujących miasto Gorzów Wielkopolski, tj. ujęcie Centralne Kosynierów Gdyńskich, Kłodawa, Siedlice oraz sąsiadujące miejscowości, tj. Maszewo i Marwice.

Materiałem badawczym były próbki wody surowej i uzdatnionej. Określono liczebność paciorkowców kałowych, bakterii z grupy *coli*, w tym *E. coli* oraz ogólnej liczebności bakterii mezofilnych i psychrofilnych. Liczebność bakterii z grupy *coli*, w tym *E. coli* oraz paciorkowców kałowych oznaczono metodą filtrów membranowych, zaś ogólną liczebność bakterii mezofilnych i psychrofilnych metodą płytkową w warunkach inkubacji zgodnych z normami.

We wszystkich badanych punktach stwierdzono obecność bakterii mezofilnych i psychrofilnych. Różnice w ich liczebności na przestrzeni całego roku były istotne. W punktach badawczych, tj. Centralne Kosynierów Gdyńskich, Maszewo oraz Marwice odnotowano przekroczenie norm ilości psychrofilii 100 j.t.k. · $\mathrm{cm^{-3}}$. Obecność bakterii chorobotwórczych w badanych próbkach wody pitnej wykryto sporadycznie. Zastosowane procesy uzdatniania i w efekcie końcowym ocena sanitarna wody według obowiązujących norm i zawartej klauzuli pozwalają na jej pobór do spożycia i nie stanowią zagrożenia dla zdrowia i życia ludzi.

Słowa kluczowe: woda pitna, bakteria, *E. coli*, *E. faecalis*, zanieczyszczenie wody

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Joanna WYCZARSKA-KOKOT[1]

COMPARISON OF CHLORAMINE CONCENTRATION IN SWIMMING POOL WATER DEPENDING ON SWIMMING POOL INTENDED USE

PORÓWNANIE STĘŻEŃ CHLORAMIN W WODZIE BASENOWEJ W ZALEŻNOŚCI OD FUNKCJI BASENU

Abstract: Swimming pool water is a mixture of supplementary water added to a closed pool circuit (usually from water supply system) and water from a pool basin, constantly purified and disinfected because of its pollution caused by bathing people. In public swimming pools, in accordance with hygiene guidelines, disinfection by chlorine compounds is required. The most commonly used is sodium hypochlorite disinfectant. The disinfectant properties of chlorine are related to its ability to oxidize organic and inorganic compounds, and the result of water chlorination is the formation of disinfection by-products (DBP). Among the most troublesome DBPs for bathers and service facility of the swimming-pool are chloramines. Chloramines are responsible for the so-called syndrome of swimmers irritation, dry skin, irritation of the mucous membranes of the nose, throat and eyes. They give the pool water and the air in the pool hall a characteristic odor and have mutagenic properties. Therefore, analyzing chloramines concentrations and taking actions, in the field of pool water treatment, in order to reduce them are very important. The primary purpose of this paper is to present the distribution of chloramines concentrations (monochloramine and dichloramine) in the pool water, depending on the pool intended use (school training pool, sports pool, pool for children to play, pool with hydromassage and water tunnel). The analysis of the results of research takes into account the swimming pool water treatment systems, exploitation parameters and the number of people bathing. The comparison of parameters (physical, chemical and bacteriological) defining the quality of the pool water, with particular emphasis on the chloramines concentrations, allows to assess the efficiency of the treatment system and the usefulness of the water to swim and bathe in relation to DIN 19643 standards.

Keywords: swimming pool water, chloramines, disinfection

Introduction

Over the past 30 years there has been a continuous growth in the number of swimming pools and recreational pools.

In terms of the number of swimming pools, the European Union is in second place (approx. 4.5 million swimming pools). Almost half of these pools are new

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facilities, created as a result of growing health awareness and increasing recreational needs.

Swimming pool water is a mixture of supplementary water added to a closed pool circuit (usually from water supply system, meeting the requirements for drinking water) and water from a pool basin, constantly purified and disinfected because of its pollution caused by bathing people. The bathers bring into the water unwanted "biological matter" (*eg* epidermis particles, sweat, urine, feces) and micro-organisms. Each of the bathers may enter into the pool water even a billion bacteria, including pathogens that find it a suitable environment for development. With many people in the pool, the infection can be spread very rapidly.

In public swimming pools, in accordance with hygiene guidelines, disinfection by chlorine compounds is required [1–3]. The most commonly used is sodium hypochlorite disinfectant. The disinfectant properties of chlorine are related to its ability to oxidize organic and inorganic compounds, and the result of water chlorination is the formation of disinfection by-products (DBP). Among the most troublesome DBPs for bathers and service facility of the swimming-pool are chloramines. Chloramines are responsible for the so-called syndrome of swimmers irritation, dry skin, irritation of the mucous membranes of the nose, throat and eyes. They give the pool water and the air in the pool hall a characteristic odor and have mutagenic properties [4–9]. Therefore, analyzing chloramines concentrations and taking actions, in the field of pool water treatment, in order to reduce them are very important [10–15].

According to DIN 19643, chlorine concentration in water samples taken from a pool basin should not exceed 0.2 $mgCl_2/dm^3$. Practice, supported by numerous studies, shows that the pools in which the water is purified with the classic treatment method (pre-filtration + coagulation and filtration + disinfection by NaOCl + pH correction), maintaining such low concentrations of chlorine and keeping the recommended concentration of free chlorine at 0.3–0.6 $mgCl_2/dm^3$ is very difficult or even impossible [15, 16].

Chloramines are compounds formed during water disinfection with chlorine, containing: ammonia (NH_3), ammonia nitrogen ($N\text{-}NH_4$) or organic nitrogen compounds. One swimmer, after approx. 2 hours, can enter into the water from 20 to 80 cm^3 of urine and 0.1–1 dm^3 of sweat [17]. Both urine and sweat contain significant amounts of nitrogen which react with chlorine disinfectant and form undesirable disinfection products, including chloramines.

Depending on the proportion of chlorine to ammonia nitrogen, a pH value of water, alkalinity and temperature, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) as well as halogenated organic nitrogen compounds may be formed [18]. The formation of monochloramine and dichloramine is possible due to the specific quality of the swimming pool water (a degree of urine and sweat contamination, and a pH in the range of 7.0–7.6).

The aim of this study was to present the distribution of chloramines concentrations (monochloramine and dichloramine) in the pool water, depending on the pool intended use (sports pool, pool for children to play, pool with hydromassage and water tunnel). The pool facility selected for analysis is characterized by high number of bathers (approximately 650 people a day). The analyzed facility includes: sports pool (SP),

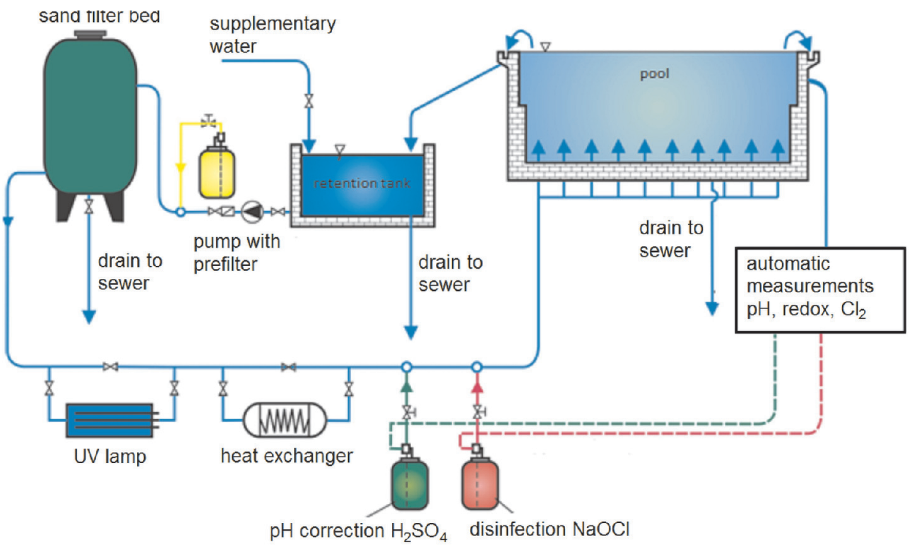

Fig. 1. Pool water treatment system in tested swimming pools

recreational pool (RP), 2 baths with hydromassage jets filled with fresh water (BF), 2 baths with hydromassage jets filled with salt water (BS) and the water tunnel (WT). The facility has five water treatment circuits, each for a different kind of pool. They are closed circuits with active overflow and retention tanks. The swimming pools are equipped with a vertical water flow system with nozzles placed at their bottoms. Figure 1 presents how the water treatment is performed: pre-filtration (to catch fibers and hairs) + coagulation and filtration (in pressure filters with multi-layered bed of sand and anthracite; coagulant: 5 % aluminum sulphate) + UV irradiation (low pressure lamps) + disinfection (sodium hypochlorite produced *in situ* in the membrane electrolysis process) + pH adjustment of water (50 % sulphuric acid).

Table 1

Characteristic parameters of tested swimming pools

Parameter	Unit	SP	RP	BF	BS	WT
Dimensions of the pool basin	m	25 × 12.5	12.5 × 6.0	Φ 2.3	Φ 2.3	—
Capacity of the pool basin	m^3	562	82	1.5	1.5	—
Circiut efficiency	m^3/h	152.6	152.6	46	30	46
Number of filters	—	2	2	1	1	1
Filter diameter	mm	1800	1800	1450	1450	1450
Filtration surface	m^2	2.54	2.54	1.54	1.54	1.54
The height of the filter layer	mm	1350		1250		
Type of filter bed	multilayer sand – anthracite					
Treatment system	pre-filtration, coagulation, filtration, heating pool water, disinfection using low-pressure UV lamps and sodium hypochlorite, pH correction					
Capacity of retention tank	m^3	37.4	17.4	7.48	14.34	36.2

The basic technical and technological parameters of tested swimming pools are summarized in Table 1.

Methods and results of research

In the period of time from 14.03.2014 to 22.04.2014, 8 water samples were collected from each of the tested pools and their physical and chemical parameters were determined with the use of a DR5000 UV/VIS spectrophotometer and in accordance with DIN 19643 (Table 2). The findings were compared with the requirements of DIN 19643, the sanitary and hygienic guidelines and recommendations of the Public Hygiene Institute of the National Institute of Public Health – National Institute of Hygiene (PHI NIPH-NIH) [1–3]. The water pH value, temperature, redox potential and the concentration of free chlorine were read directly from the control and measurement DINOTEC SCL compact DSC device.

Also were determined the bacteriological parameters (Table 3). It was done with the use of methods consistent with PN-EN ISO 9308-1:2004 (*Escherichia coli*), PN-EN ISO 622: 2004 (total number of bacteria at 36 ^{o}C after 48 h) and the National Institute of Hygiene (NIH) guidelines (coagulase-positive staphylococci).

Analysis of research results

On the basis of physical, chemical and bacteriological analysis of the water samples taken from the pools SP, RP, BF, BS and WT, the quality of the swimming pool water was compared with particular attention to the level of and changes in the concentration of chloramines (monochloramine, dichloramine) depending on the swimming pool intended use and the corresponding concentration of free chlorine.

The results of the pool water quality parameters, with the exception of chloramines, corresponded to the requirements of DIN 19643 and the guidelines of the Public Hygiene Institute of the National Institute of Public Health – National Institute of Hygiene (PHI NIPH-NIH) [1–3].

According to DIN 19643, chloramines concentration in water samples taken from the swimming pools should not exceed 0.2 $mgCl_2/dm^3$.

The limit value of chloramines in the SP pool was exceeded on average by 135 % (all samples exceeded the limit), in the RP on average by 25 % (6 out of 8 samples exceeded the limit), in the BF on average by 190 % (all samples exceeded the limit), in the BS on average by 95 % (all samples exceeded the limit) and in the WT on average by 10 % (5 out of 8 samples exceeded the limit).

The usage patterns of the pool basin, dictated by its intended use, operating parameters and the concentration of free chlorine had an influence on chloramines concentration in the water. In the sports pool (SP) – typical swimming pool, for which the time of full water exchange was 3.6 hours and the concentration of free chlorine was in the range of 0.31–0.52 $mgCl_2/dm^3$, the average content of chloramines was 0.47 $mgCl_2/dm^3$ and the percentage of monochloramine (39.9 %) was lower than dichloramine (60.1 %). In the recreational pool (RP), for which the time of full water

Table 2

Values of physical and chemical parameters of water from tested swimming pools

No.	Parameter	Unit	SP			RP			BF			BS			WT		
			Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.
1	Ammonia nitrogen	mgN-NH$_4$/dm^3	0.16	0.26	0.35	0.06	0.14	0.36	0.04	0.13	0.44	0.09	0.16	0.24	0.04	0.11	0.4
2	Nitrate nitrogen	mgN-NO$_3$/dm^3	10	18	26	10	27	37	10	22	37	10	22	34	13	21	33
3	Chlorine free	mgCl$_2$/dm^3	0.31	0.36	0.52	0.33	0.36	0.39	0.40	0.64	0.75	0.47	0.59	0.70	0.62	0.84	1.16
4	Chlorine total	mgCl$_2$/dm^3	0.74	0.83	0.93	0.54	0.61	0.76	0.92	1.22	1.49	0.84	0.98	1.16	0.83	1.06	1.47
5	Chlorine combined	mgCl$_2$/dm^3	0.22	0.47	0.60	0.15	0.25	0.43	0.36	0.58	0.79	0.33	0.39	0.49	0.12	0.22	0.31
6	Monochloramine	mgCl$_2$/dm^3	0.09	0.18	0.33	0.14	0.18	0.33	0.09	0.13	0.17	0.05	0.12	0.17	0.09	0.10	0.12
7	Dichloramine	mgCl$_2$/dm^3	0.08	0.29	0.44	0.01	0.07	0.1	0.23	0.43	0.70	0.20	0.29	0.37	0.10	0.13	0.17
8	Chlorides	mgCl$^-$/dm^3	113.0	126.6	144.0	216.0	228.6	247.5	68.5	218.1	270.0	1351.0	1427.8	1542.5	35.0	39.4	49.0
9	Phosphates	mgPO$_4^{-3}$/dm^3	0.11	0.19	0.33	0.30	0.35	0.41	0.04	0.19	0.31	0.04	0.18	0.30	0.02	0.22	0.39
10	Aluminum	mgAl^{+3}/dm^3	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.00	0.00	0.00
11	Acidity total	mval/dm^3	0.10	0.21	0.50	0.10	0.13	0.20	0.10	0.16	0.25	0.05	0.12	0.20	0.05	0.13	0.20
12	Turbidity	NTU	0.19	0.44	0.92	0.33	0.66	1.11	0.26	0.56	0.74	0.28	0.51	0.74	0.20	0.30	0.58
13	pH	—	7.24	7.32	7.60	7.19	7.30	7.60	7.18	7.33	7.73	7.22	7.27	7.33	6.80	7.07	7.30
14	Hardness total	mgCaCO$_3$/dm^3	103.4	112.7	123.2	125	139.7	158.9	132.1	147.5	175.0	137.5	156.5	173.2	114.3	134.0	151.8
15	Chemical oxygen demand (KMnO$_4$)	mgO$_2$/dm^3	2.60	3.86	5.05	3.00	4.54	6.10	2.10	4.11	5.70	6.35	7.89	9.40	1.30	2.74	6.60
16	Alkalinity total	mval/dm^3	0.3	0.46	0.55	0.3	0.4	0.55	0.25	0.36	0.5	0.2	0.36	0.55	0.3	0.44	0.80
17	Redox	mV	768	790	804	720	750	772	774	793	807	760	794	818	763	790	804

Table 3

Values of bacteriological parameters of water from tested swimming pools

Indicator	Unit	SP		RP		BF				BS				WT	
		March	April	March	April	March		April		March		April		March	April
						1	2	1	2	1	2	1	2		
Escherichia coli	CFU/ 100 cm^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total number of bacteria at 36 ± 2 °C/48 h	CFU/ 100 cm^3	1		0	0	0	0	0	2	0	1	1	1	0	0
Coagulase positive staphylococci	CFU/ 100 cm^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0

exchange was only 0.5 hours and the concentration of free chlorine was in the range of 0.33–0.39 mgCl$_2$/dm^3, the average content of chloramines was 0.25 mgCl$_2$/dm^3 and the percentage of monochloramine (74.3 %) was higher than dichloramine (25.7 %). In baths with fresh and salt water for which the time of full water exchange was approx. 15 minutes, and free chlorine concentration was in the range of 0.40–0.75 mgCl$_2$/dm^3, the percentage of monochloramine (26.0–28.7 %) was significantly lower than dichloramine (71.3–74.0 %) and the average content of chloramines in the BF was 0.58 mgCl$_2$/dm^3, and in BS was 0.39 mgCl$_2$/dm^3. In the water tunnel (WT) in which, due to its specific purpose (massage by water jets), the water was continuously exchanged and the concentration of free chlorine was in the range of 0.62–1.16 mgCl$_2$/dm^3, the average content of chloramines was: 0.22 mgCl$_2$/dm^3, and the percentage of monochloramine (44.1 %) was lower than dichloramine (55.9 %).

The distributions of free chlorine and chloramines concentrations in the tested pools are shown in Fig. 2 and Fig. 3. The percentage of monochloramine and dichloramine in the total content of chloramines, in the following days of research, are shown in Fig. 4.

The type of formed chloramines depends not only on pH, but also on the dose of chlorine. At a weight ratio of $Cl_2/N\text{-}NH_4 < 3/1$ monochloramine is formed and at values $Cl_2/N\text{-}NH_4 > 3/1$ dichloramine is formed [18].

For water in swimming pools, it is difficult to determine a fixed dose of chlorine, primarily due to the fact that the number of bathers is not constant.

The water in sports pools for swimmers (with large capacities and minimum required surface area per person of 4.5 m^2) and in recreational swimming pools for non-swimmers (with a much smaller capacity compared to sports-type pools and the minimum required surface area per person of 2.7 m^2) is disinfected with a dose of chlorine compound so that the content of free chlorine is in the range of 0.3–0.6

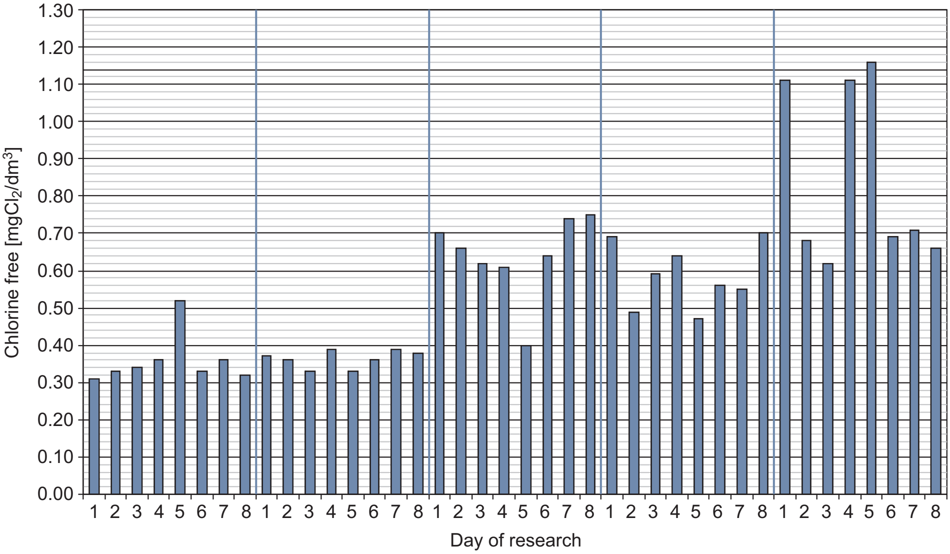

Fig. 2. Distribution of the free chlorine content

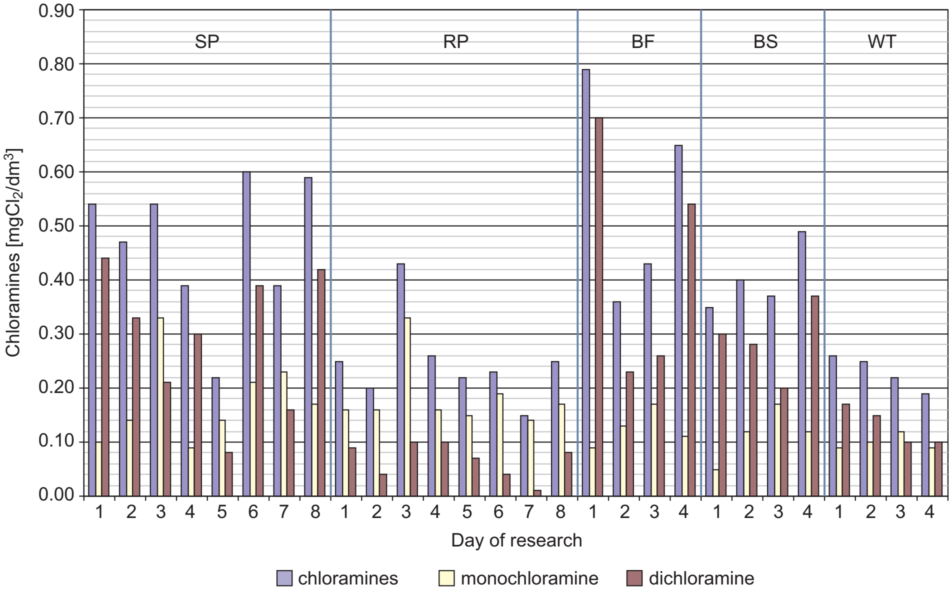

Fig. 3. Distribution of the chloramines content in tested swimming pools

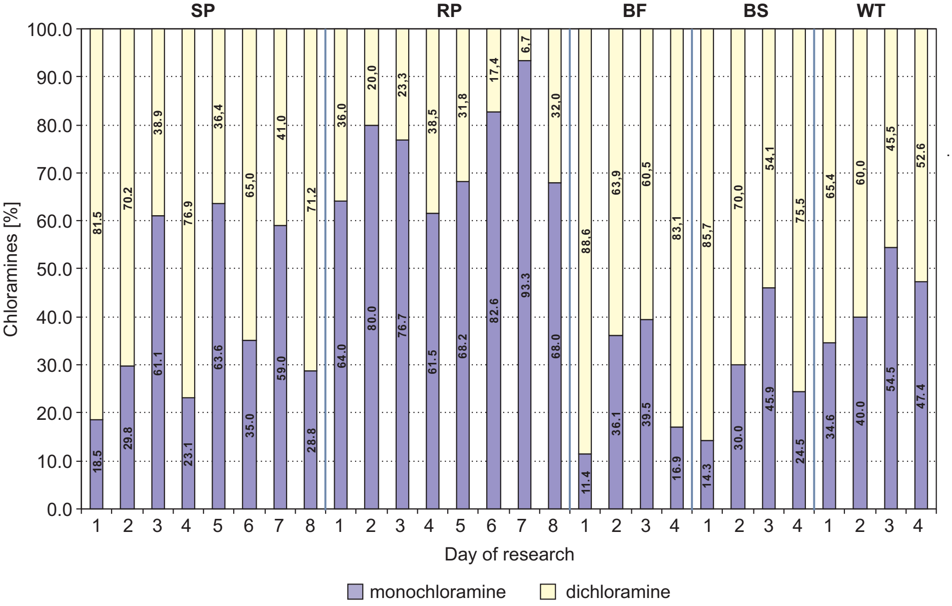

Fig. 4. Percentage of mono- and di-chloramine in the total content of chloramines

$mgCl_2/dm^3$. The water in baths with hydromassage or the one used by “water jet massagers” is disinfected with a dose of chlorine compound to achieve the content of free chlorine in the range of 0.6–1.2 $mgCl_2/dm^3$. Considering the very small volume of water and the surface area taken by a person using the pool with hydromassage, such levels were determined in order to protect the water from bacteriological contamination (Fig. 2).

In the water from RP weight ratio of $Cl_2/N\text{-}NH_4 < 3/1$ and in the water from BF, BS and WT weight ratio of $Cl_2/N\text{-}NH_4 > 3/1$ results in a quantitative relation of monochloramine and dichloramine that is consistent with previous research [18]. In the case of RP, it is a predominance of monochloramine and, in the case of the BF, BS and WT, of dichloramine (Fig. 3 and Fig. 4).

In the water from SP the average weight ratio of $Cl_2/N\text{-}NH_4$ was 1.4 and the predominance of monochloramine was noted in 3 out of 8 water samples tested (Fig. 3 and Fig. 4).

Summary and conclusions

Providing swimming pool water that meets the sanitary and hygienic requirements, attending to safety and public health, in particular protecting against pathogens, obtaining water that is free from disinfection by-products (DBP), providing comfortable stay in the pool (no characteristic “chloral” smell in the hall pool) and the use of water treatment system adapted to the type and intended use of a pool, is of key value for any properly operated swimming pool facility.

In the swimming pool facilities that integrate sport (SP) with recreation (RP, BF, BS and WT) for both adults and small children, the contents of chloramines in the water should be under greater control.

The swimming pool water quality was compared on the basis of physical, chemical and bacteriological analyses of water samples taken from the examined swimming pools. Particular attention was directed to the content of chloramines (including mono- and di-chloramine) in reference to the free chlorine content, the pool intended use and DIN 19643.

It was found that the intended use of the pool – always associated with attendance factor, the surface of the water, the capacity of the pool and the intensity of its use – has an important impact on the content of chloramines in the water.

On the basis of the performed studies, the following conclusions were formulated:

– The comparison of the content of chloramines in tested swimming pool water showed that the used disinfection system (UV irradiation of circulating water flow + NaOCl dosing), the same for all the analyzed pools, does not guarantee the maintenance of chloramines at concentrations ≤ 0.2 $mgCl_2/dm^3$.

– The lowest concentration of chloramines (0.12–0.31 $mgCl_2/dm^3$) was found in the water from WT, where the contact of the bathers with water was the shortest (about 1 min), and the highest in the BF (0.36–0.79 $mgCl_2/dm^3$), and BS (0.33–0.49 $mgCl_2/dm^3$), where the bathers use relatively small volumes of water in a relatively short period of time, approx. 10–15 minutes.

– A wide variation in the content of chloramines was observed in pools SP and RP. In the sports pool with a large capacity (562 m^3) and time of the exchange of water at approx. 3.6 hours, an average content of chloramines was 0.47 $mgCl_2/dm^3$. In the recreational pool with a small capacity (86.6 m^3) and time of the exchange of water at approx. 0.5 hours, an average content of chloramines was 0.25 $mgCl_2/dm^3$.

– Varied doses of sodium hypochlorite (Fig. 2) did not significantly reduce chloramines. For example, in pools BF and BS, despite high concentrations of free chlorine (0.40–0.75 $mgCl_2/dm^3$), in all the samples the content of chloramines was far above 0.2 $mgCl_2/dm^3$.

– In 28 samples of pool water concentrations of mono- and di-chloramine were analyzed. 12 samples showed higher concentrations of monochloramine and 16 samples higher concentrations of dichloramine. In the case of BF and BS, much higher concentrations of dichloramine than monochloramine was observed.

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PORÓWNANIE STĘŻEŃ CHLORAMIN W WODZIE BASENOWEJ W ZALEŻNOŚCI OD FUNKCJI BASENU

Instytut Inżynierii Wody i Ścieków
Politechnika Śląska w Gliwicach

Abstrakt: Woda basenowa to mieszanina wody uzupełniającej zamknięty obieg basenowy (najczęściej woda z sieci wodociągowej) oraz wody z niecki basenowej, podlegającej ciągłemu procesowi oczyszczania i dezynfekcji z powodu jej zanieczyszczania przez osoby kąpiące się. W basenach publicznych, zgodnie z obowiązującymi wytycznymi sanitarno-higienicznymi, wymagana jest dezynfekcja związkami chloru. Najczęściej stosowanym dezynfektantem jest podchloryn sodu. Właściwości dezynfekcyjne chloru związane są z jego zdolnością do utleniania związków organicznych i nieorganicznych, a wynikiem chlorowania wody jest powstawanie ubocznych produktów dezynfekcji (DBP). Spośród DBP najbardziej uciążliwymi dla osób kąpiących się i dla obsługi obiektu basenowego są chloraminy. Chloraminy odpowiedzialne są za tzw. zespół podrażnienia u pływaków, suchość skóry, podrażnienia śluzówki nosa, gardła i oczu, nadają wodzie basenowej i powietrzu w hali basenowej charakterystyczny nieprzyjemny zapach i mają właściwości mutagenne. W związku z powyższym analiza stężeń chloramin oraz podejmowanie działań z zakresu technologii wody basenowej, umożliwiających ich zmniejszenie są bardzo ważne. Podstawowym celem badań jest przedstawienie rozkładu stężeń chloramin (monochloraminy i dichloraminy) w wodzie basenowej w zależności od funkcji basenu (szkolny basen do nauki pływania, basen sportowy, basen do zabaw dla dzieci, basen z hydromasażem i tunel wodny). Analiza wyników badań uwzględnia układ oczyszczania wody basenowej, parametry eksploatacyjne oraz obciążenie niecek basenowych. Porównanie parametrów (fizyczno-chemicznych i bakteriologicznych) określających jakość wody basenowej, ze szczególnym uwzględnieniem stężeń chloramin, pozwoliło ocenić sprawność systemu jej oczyszczania i przydatność wody do kąpieli w odniesieniu do normy DIN 19643.

Słowa kluczowe: woda basenowa, chloraminy, dezynfekcja

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Jarosław MUCHA[1]

CHARACTERISTICS OF GREY WATER FILTRATION ON POLYPROPYLENE FILTERS

CHARAKTERYSTYKA FILTRACJI WODY SZAREJ NA FILTRACH POLIPROPYLENOWYCH

Abstract: In the paper the main characteristics of filtration process of grey water (obtained from the laundry) on polypropylene filter of various size of pores (5 μm and 20 μm) has been presented. In was found well applicability of Ruth's equation for filtration process of grey water in constant pressure. It means that in presented studies process is due to the first stage of formation of so called wet filtration cake. Parameters of Ruth's equation were determined. On their flow resistance involved in the filtration process: resistant of the filter medium $R_f = 1.94 \cdot 10^{11}$ m^{-1} (filter FCPS 5) and $R_f = 1.89 \cdot 10^{11}$ m^{-1} (filter FCPS 20) and the average specific cake resistance α_0 for FCPS 5 = $4.84 \cdot 10^{12}$ m^{-2} and α_0 for FCPS 20 = $4.35 \cdot 10^{13}$ m^{-2} were calculated. Because both filters are made from polypropylene their resistances R_f have similar values. However α_0 of both filters differs by an order of magnitude. Filtration times are equal to 42.3 min and 22.1 min respectively. Efficiency of both filters versus time of filtration were presented on the figures. It was proved higher life time of the FCPS 20 filter.

Keywords: grey water, constant pressure filtration, Ruth's equation

Introduction

Water is the source of life on Earth, indispensable in the growth of organisms that can not live without it. Bathing, garden irrigation, flushing toilets, washing the vehicles or washing the dishes are a group of human activities, which are carried out every day with water. With an increasing number people on Earth the demand for water also increases. Freshwater resources on Earth are limited and already seriously affected. Countries, which, due to their geographical location previously faced a problems of water deficit at the present time are facing a serious problem of water lack. Also in Poland there is a water deficit. Today water resources per capita in our country are two times lower than in Western Europe. This situation obliges to the implementation of actions to reduce water consumption. In the times when humanitarian organizations build wells in poor countries that their people can drink clean water, it is incomprehensible to waste potable water, *ie* for toilet flushing.

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Therefore in many countries, a technology for domestic grey water recycling is being developed. Water generated during bathing or laundry called "gray water" can be treated on site and re-used for flushing toilets and for other purposes such as washing cars, washing driveways, watering lawns, etc. [1]. For high efficiency re-use of domestic gray water, special dual plumbing systems are necessary [2–5]. The benefits of using such systems are enormous. First of all they can give a big savings of potable water, which has a positive impact on the environment. Furthermore, use of dual plumbing system is a source of savings for households as it decreases consumption of tap water. Flushing toilets using gray water can conduct to 30 % savings. If the gray water recycling is connected also with rainwater recycling *ie* for irrigation of lawns, the savings can be even greater. In addition, the concept of using gray water for laundry may increase savings significantly.

Technology of gray water recycling is not very popular in Poland, but in the near future re-use of water may become necessary in every household. There is no doubt it brings enormous benefits therefore it should be promoted and regulated by law as soon as possible.

The aim of this study was to determine the basic characteristics of the gray water filtration on popular polypropylene filter cartridges. The filters with two different pore sizes were tested (5 and 20 microns). The flow resistance and overall filtration performance were determined. Wastewater from laundry of heavily soiled work clothes has been used.

Theoretical principles of surface filtration

Filtration is a process of solid-liquid separation [6] on porous filtration barrier by keeping the solids and passing the fluid. Liquid produced after filtration process is called filtrate. Filtration is the primary method of purifying water used by nature for millions of years. Layers of very clean groundwater were formed by rainwater filtration by various layers of soils. Filtration process in environmental engineering is used for water purification, urban and industrial wastewater treatment, as well as gray water treatment. These methods are based on the mechanisms that occur in the nature, however, they are conducted at much higher speed.

The use of filtration barriers with very small size pores (from 10–4 to 10–1 microns) can even separate solute from the solvent. This is done in the process of ultrafiltration or reverse osmosis. These processes, known as membrane processes are still very expensive.

Depending on the concentration of solids or the suspension in the filtrate we can distinguish cleansing filtration (solids concentration <0.1 %) and the separating filtration (solids concentration >1 %). During cleansing filtration the filtrate is obtained, during the separating filtration valuable sludge and also filtrate are obtained.

Special filtration barrier is the basic element of the filter. This could be the fabric filters, sand filters, porous masses, plastics or even its own sludge filter (so-called filter cake). The nature of filtration process depends on the type of filter cartridge:

– Volume filtration – filtration occurs through the piled layers of sand, slag, gravel, etc. Such filters are used for potable water and waste water clarification. In an event of discoloration of filtered medium, the diatomite, activated carbon or bleaching soil can be used;

– Surface filtration – a porous mass, plastics, fabric filters or filter cake is being used.

Filters used in the surface filtration begin to work properly as soon as the filter cake made from the corresponding layer of the sludge is being created. The thickness of the filter cake, which depends on the form of solids reduces the filtration velocity. When we are dealing with compressible sludge, filter cake is formed very quickly. Due to the low permeability of such cake, the filtration speed decreases rapidly. In such cases the filtration support like diatomite, bleaching soil, glass wool, wood chips or activated carbon is necessary.

Filtration's rate

The ideal conditions for filtration [7] is assumed to be the laminar flow of liquid through a filter layer, which is made of a layer of inelastic and incompressible grains. Grains should have perfectly smooth and spherical surfaces. The filter barrier should be inelastic and incompressible, having perfectly formed, uniform cylindrical pores. For such conditions the Darcy's equation is correct:

$$W = \frac{dV}{d\Theta \cdot S} = \frac{\Delta P}{\mu\,(R_{0S} + R_f)} \tag{1}$$

where: W – filtration rate, per unit area of the filter [m^3/m^2s];
ΔP – pressure difference [N/m^2] (filtration pressure);
V – volume of filtrate [m^3];
Θ – time [s];
μ – dynamic viscosity of liquid [$N \cdot s/m^2$];
R_{0S} – sludge resistance [1/m];
R – filter barrier resistance [1/m];
S – filtration surface area [m^2].

The resistance of a filter cake layer (which is in fact a layer of sediment) is proportional to the thickness of cake L and resistivity α. Volume resistivity α_0 is a resistance of unit volume of sludge [7].

Assuming that the thickness L of the forming sludge is proportional to the volumetric concentration w_0 of the solid in the filtered suspension we obtain the formula for the sludge resistance:

$$R_{0S} = \alpha_0 \cdot L = \alpha_0 \cdot w_0 \cdot \frac{V}{S} \tag{2}$$

where: w_0 = V_0/V;
V_0 – wet volume of sludge = $S \cdot L$;
V – volume of filtrate.

Substituting R_{0S} into equation (1) we get the general equation of filtration:

$$\frac{dV}{d\Theta \cdot S} = \frac{\Delta P}{\mu \cdot \left(\alpha_0 \cdot w_0 \cdot \frac{V}{S} + R_f \right)} \tag{3}$$

This equation relates the one-dimensional filtration (S = const.) where the sludge builds up in only one direction – on a flat surface. In real conditions, the filtration pressure is measured (usually equal to the pressure difference between the one produced by the pump and the atmospheric pressure). It is possible distinguish the filtration under constant pressure or the filtration at constant rate. It is also possible consider complex option of filtration when both parameters are variable.

Filtration under constant pressure, Δp = const.

After the integration of equation (3) in the range of 0 to Θ, and from 0 to V the filtration equation is as follows:

$$V^2 + 2V \cdot \frac{R_f \cdot S}{\alpha_0 \cdot w_0} = 2 \cdot \frac{\Delta P \cdot S^2}{\mu \cdot \alpha_0 \cdot w_0} \cdot \Theta \tag{4}$$

where: V – volume of filtrate [m^3]
S – filtration surface area [m^2];
α_0 – volume resistivity of incompressible sludge [1/m^2];
w_0 – the ratio of the sludge volume versus the filtrate volume [m^3/m^3];
Θ – filtration time [s].

According to the filtration conditions, the values of coefficients occurring at V and Θ are constants. It is assumed that:

$$\frac{R_f \cdot S}{\alpha_0 \cdot w_0} = C \ [\mathrm{m^3}] \ \text{and} \ \frac{2 \cdot \Delta P \cdot S^2}{\mu \cdot \alpha_0 \cdot w_0} = K \ [\mathrm{m^6/s}] \tag{5}$$

where: constants C and K describes the filtration processes through the barrier and the sludge; C – filtration constant which characterizes hydraulic resistance of the filtration barrier. It means the volume of filtrate which should occur for sludge resistance equal to the one of the real filtration barrier, K – filtration constant taking into account the conditions of the filtering process and physicochemical properties of sludge and liquid.

Substituting these values into equation (4) one can obtain the following equation:

$$V^2 + 2 \cdot V \cdot C = K \cdot \Theta \tag{6}$$

This is the Ruth's equation [8, 9] and the C and K are called Ruth's coefficients. After differentiating equation (6) with respect to the filtration time, we obtain an equation describing the rate of filtration is obtained:

$$\frac{dV}{d\Theta} = \frac{K}{2\cdot(V+C)} \tag{7}$$

The inverse of this equation is the following correlation:

$$\frac{d\Theta}{dV} = \frac{2\cdot V}{K} + \frac{2\cdot C}{K} \tag{8}$$

The illustration of this equation is a line in $d\Theta/dV$ coordinate system (if the coordinates are not too far apart from each other, and if their values are not close to zero). The time needed to filtrate can be expressed as: $t_p = C^2/K$.

Mechanical separation process consists of two consecutive phases:

– The phase of free filtration at constant pressure when the filter cake is formed,

– The phase of cake solidification under constant pressure. During this phase, the water bind with the previously formed cake is removed by the filter as a result of volume change caused by the mechanical stress.

Before the increasing filter cake reaches the plane of outlet, the filtration rate can be expressed by the equation (8). If the filtration cake will fill the space between the membrane and the plane of the outlet filter, the filtration surface is reduced and the above equation has to be modified [10, 11].

Experimental

Research methodology and apparatus

Analysis of gray water filtration was carried out at the appropriate test rig. The device consisting of Aquafilter® FHPR-3 body and the appropriate filter cartridge has been used. There were two manometers on the input and output of the system. The diagram of the test rig is shown on Fig. 1.

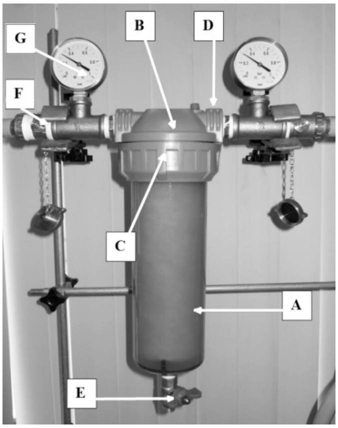

Fig. 1. Test apparatus, the filter body with cartridge is installed on a tripod: A – body, B – head, C – retaining ring, D – vent, E – drain valve, F – valve, G – manometer

Filter consisted of transparent body, polypropylene mounting ring and the polypropylene head with brass 3/4 inch thread. The vent which was placed on the filter's head was the additional element of the filter. It was used to remove the accumulated air from the interior of the cartridge. The body had a drain valve to remove contaminants from the filter's cartridge. The Aquafilter® filter cartridges FCPS 5 (5 microns) and FCPS 20 (20 microns) were placed inside the filter's body. Wastewater was pumped into the filter by the submersible pump with a lift height $H_{\max} = 5$ m and a pump efficiency $Q_{\max} = 6.5$ m^3/h Filters were mounted on a suitable stand. Filtration was carried out at a constant pressure.

The source and basic quality parameters of grey water

To carry out the experiments the gray water produced during laundry of heavily soiled clothing in domestic washing machine was used. Single input of clothing weighed about 3 kg. In all cases of grey water preparation the wash cycle included washing at 40 $^{\circ}$C and three rinses. The color scheme of the laundry (dark colors) and the amount of the same detergent has been retained (150 cm^3). Work cycle of the washing machine lasted about two hours. At this time the 50 liters of gray water has been obtained. The washing was performed on the same day as experiments to eliminate decaying of the grey water. The quality of 6 grey water samples of has been examined. Sample start gray water quality parameters were as follows: pH 9.53; suspension 707 mg/dm^3; turbidity 996 NTU; COD 4480 mgO$_2$/dm^3; BOD$_5$ 430 mgO$_2$/dm^3; TOC 558 mgC/dm^3. The experiments was carried out for two different filter cartridges: FCPS 20 microns and FCPS 5 microns.

Results and discussion

The purpose of this experiment was test the impact of filter clogging on the amount of obtained filtrate. The principles of the filtration theory and the Ruth's equation were used for analysis of the experimental results.

The following experiments have been conducted:

– The filtrate volume at equal time intervals (every 4 min) has been determined;

– The time to obtain a constant volume of filtrate (2 litres) has been determined;

– The pressures on input and output of the filter have been observed.

Filtration through FCPS 5 filter

On the basis of experimental data the graph describing volume of filtrate versus filtration time has been prepared (Fig. 2). The curve fits well to Ruth's equation (6), it shows that the filtration time is proportional to the square of the resulting filtrate's volume. Flattening of the filtration curve during the time is caused by increasing filter cake and thus grows of the flow resistance. Consequently filter clogging occurs (which can be observed on the graph) just after 25 minutes of the experiment. On the basis of the Ruth's curve it is possible to predict the efficiency of the filters and the need for filter flushing or replacement.

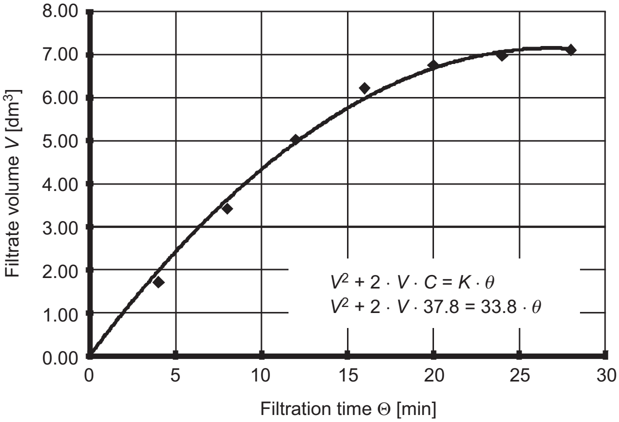

Fig. 2. The filtrate volume V versus the time of filtration (filter FCPS 5), ◆ – experimental points, the theoretical curve according to equation (5)

Observing the gray water filtration through the FCPS 5 filter cartridge was found that the filter blocked quickly.

In order to determine the Ruth's K and C coefficients, the filtration curve (equation (6)) shown in Fig. 3 was presented in the form of dQ/dV versus V (equation (8)).

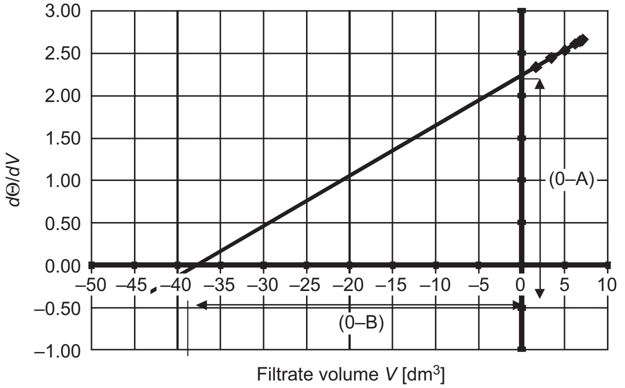

Fig. 3. Dependence of inverse filtration rate dQ/dV on the volume of filtrate V (FCPS 5)

Section 0–A corresponds to the $2C/K$ and the section |0–B| corresponds to |C| value. They are equal to: $|0,A| = 2.24 = 2C/K$; $|0,B| = |-37.8| = C$. On the basis of these data coefficients: $K = 33.8$ [dm^6/min], $C = 37.8$ [dm^3] and the filtration time $t_p = C^2/K$ [min] = 42.3 min has been calculated.

Filtration through FCPS 20 filter

Using the filter with bigger pores (FCPS 20) the duration of filtration process without blocking flow was explained. The time intervals between the measurements have not been changed the graphs showing the filtrate volume versus the filtration time and *dQ*/*dV* versus *V* have been prepared (Fig. 4 and 5).

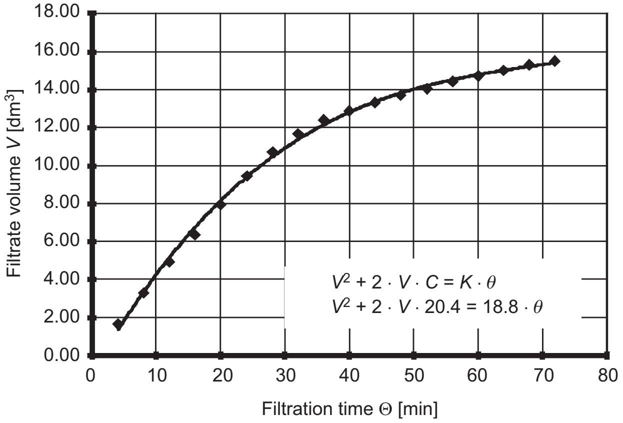

Fig. 4. The filtrate volume *V* versus the time of filtration (filter FCPS 20), ♦ – experimental points, the theoretical curve according to equation (5)

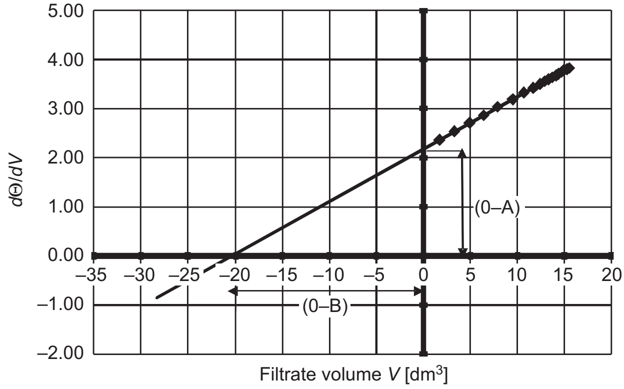

Fig. 5. Dependence of inverse filtration rate *dQ*/*dV* on the volume of filtrate *V* (FCPS 20)

Similar than before: |0,A| = 2.18 = $2C/K$; |0,B| = |–20.4| = C has been determined. On their basis determined: $K = 18.8$ [dm^6/min]; $C = 20.4$ [dm^3] and the filtration time $t_p = C^2/K$ [min] = 22.1 min.

Filtration resistance

On the basis of calculated Ruth's K and C constants the following filtration properties has been calculated: α_0 – volume resistivity of the sludge and R_f – filter barrier resistance. For the calculations the following data has been assumed:

– Filtrations pressure $\Delta p = 0.35$ bar $= 0.35 \cdot 10^5$ Pa;

– Surface area of filters $S = 0.0471$ m^2;

– Dynamic viscosity of grey water $\mu = 11.4 \cdot 10^{-4}$ Pa · s;

– The volumetric concentration of the solid w_0 estimated based on the thickness of the filter cake sludge: $w_0 = 0.05$ (for FCPS 5 filter) and $w_0 = 0.01$ (for FCPS 20 filter);

– Constant $K = 33.8$ dm^6/min (FCPS 5 filter);

– Constant $K = 18.8$ dm^6/min (FCPS 20 filter);

– Constant $C = 37.8$ dm^3 (FCPS 5 filter);

– Constant $C = 20.4$ dm^3 (FCPS 20 filter).

Volume resistivity of the sludge:

$$\alpha_0 = \frac{2 \cdot \Delta p \cdot S^2}{\mu \cdot K \cdot w_0} \tag{9}$$

Filter barrier resistance:

$$R_f = \frac{C \cdot \alpha_0 \cdot w_0}{S} = \frac{2 \cdot \Delta p \cdot C}{\mu \cdot K} \tag{10}$$

For FCPS 5 filter: $\alpha_0 = 4.84 \cdot 10^{12}$ m^{-2}; $R_f = 1.94 \cdot 10^{11}$ m^{-1}.
For FCPS 20 filter: $\alpha_0 = 4.35 \cdot 10^{13}$ m^{-2}; $R_f = 1.89 \cdot 10^{11}$ m^{-1}.

The calculations shows that the barrier resistance of the filter with smaller pores R_f (FCPS 5) is slightly larger than than R_f of filter with bigger pores (FCPS 20). Difference in the values of the barrier resistance R_f is small, since both filters are made from the same hydrophobic material – polypropylene. However, volume resistivities of the sludge α_0 differs by the order of magnitude.

Filter's efficiency

The filter's efficiency defined as the ratio of $[dV/d\Theta]_t$ to $[dV/d\Theta]_{t=0}$ versus filtration's time is presented on Fig. 6 and 7.

The presented graphs show that the use of FCPS 20 filter is more beneficial than the FCPS 5 filter, due to the fact that for longer time filtration process it retains good efficiency.

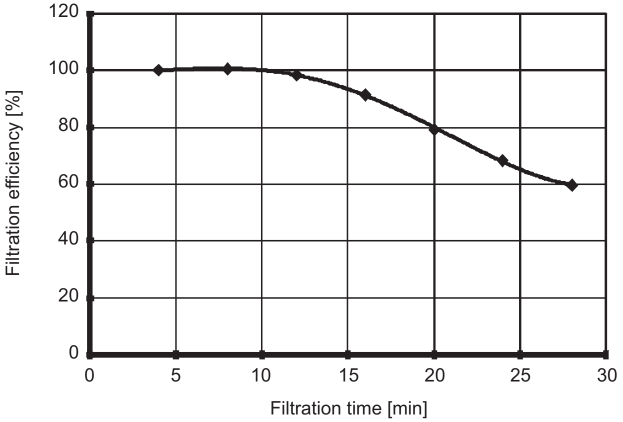

Fig. 6. Efficiency of filtration versus time on the filter FCPS 5

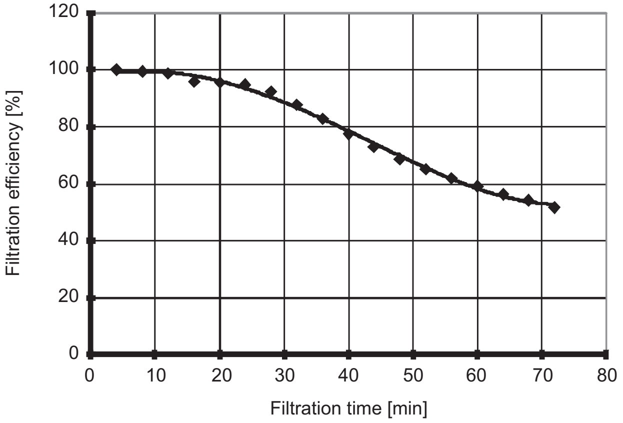

Fig. 7. Efficiency of filtration versus time on the filter FCPS 20

Conclusions

The applicability of the Ruth's equation for gray water filtration process (in undertaken scope of research) indicates on the first phase of the process: forming the wet filter cake [10].

The filter with smaller pores – FCPS 5 shows both a higher resistance of filter barrier (constant *C*) and higher filter constant *K*, related to the sludge properties, than the filter with larger pores FCPS 20.

Values of C constants equals 33.8 [dm^3] for FCPS 5 filter and 18.8 [dm^3] for FCPS 20 filter but the values of *K* constants equals 37.8 [dm^6/min] and 20.4 [dm^6/min] respectively.

According to the *K* and *C* constants filtration's time $t_p = C^2/K$ has been calculated. Its values equals 42.3 min for FCPS 5 filter and 22.1 min for FCPS 20 filter.

On the basis of gray water properties, filter properties and K and C constants, using the equations 8 and 9 the sludge resistivity and resistance of the filtration barrier were determined.

For the FCPS5 filter these values equals: $\alpha_0 = 4.84 \cdot 10^{12}$ m^{-2}; $R_f = 1.94 \cdot 10^{11}$ m^{-1}, for the FCPS 20 filter: $\alpha_0 = 4.35 \cdot 10^{13}$ m^{-2}; $R_f = 1.89 \cdot 10^{11}$ m^{-1}.

The measured efficiency of the filters also confirms better parameters of FCPS 20 filter (Figs. 6 and 7).

In order to fully compare the properties of both filters, the physico-chemical properties of the filtrate has been analyzed which is discussed in a separate publication [12].

On a basis of literature review carried out in the work [11, 13] was found that the physical processes conducted alone are not sufficient to ensure proper reduction of organic compounds and chemicals (including surfactants) contained in the gray water.

The combination of biological, chemical and physical filtration processes is the best method for the proper gray water recycling [14–19].

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CHARAKTERYSTYKA FILTRACJI WODY SZAREJ NA FILTRACH POLIPROPYLENOWYCH

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Politechnika Łódzka

Abstrakt: W pracy przedstawiono podstawową charakterystykę procesu filtracji wody szarej (otrzymanej z prania) na polipropylenowych wkładach filtracyjnych o różnym mikronażu (5 µm, 20 µm). Stwierdzono stosowalność równanie Rutha do procesu filtracji wody szarej, co świadczy o tym, że w podjętych badaniach przebieg procesu dotyczył pierwszej fazy – tzw. formowania mokrego placka filtracyjnego. Wyznaczono parametry równania Rutha oraz na ich podstawie obliczono wartości oporów przegród filtracyjnych oraz objętościowych oporów właściwych osadu. Filtr o mniejszym mikronażu (FCPS 5) wykazywał nieco większy opór przegrody filtracyjnej ($R_f = 1{,}94 \cdot 10^{11}$ m^{-1}) niż filtra o mikronażu wyższym FCPS 20 ($R_f = 1{,}89 \cdot 10^{11}$ m^{-1}). Niewielkie różnice w wartościach oporów wynikają z charakterystyki obydwu filtrów. Obydwa zbudowane są ze spienionego polipropylenu. Natomiast wartości obliczonych objętościowych oporów właściwych osadu różniły się o rząd wielkości α_0 dla filtra FCPS 5: $4{,}84 \cdot 10^{12}$ m^{-2} i α_0 dla FCPS 20: $4{,}35 \cdot 1013$ m^{-2}. Czasy filtracji wynosiły odpowiednio 42,3 min oraz 22,1 min. Oceniono również wydajność filtracji na obydwu wkładach filtracyjnych i przedstawiono je na wykresach w funkcji czasu, z których wynika dłuższa żywotność filtra FCPS 20.

Słowa kluczowe: szara woda, filtracja pod stałym ciśnieniem, równanie Rutha

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GRANULOMETRIC ANALYSIS TO ESTIMATE INFLUENCE OF ANIONIC SURFACTANT ON ACTIVATED SLUDGE STRUCTURE

ZASTOSOWANIE ANALIZY GRANULOMETRYCZNEJ DO OKREŚLENIA WPŁYWU SURFAKTANTU NA STRUKTURĘ OSADU CZYNNEGO

Abstract: The work concerns the evaluation of the possibility of using laser diffraction analyzer to determine changes in the distribution of sludge floc size in the presence of anionic surfactant. As a model of surfactant linear alkylbenzene sulphonate (LAS) was used. Different concentrations: 10, 100 and 200 mg/dm^3 of LAS was applied. The granulometric analysis showed that the pure activated sludge was composed of particles with a size of 1 μm to 2 mm. The largest and fastest changes in the distribution of sludge floc size after the addition of a surfactant at a concentration of 100 mg/dm^3 were observed. The flocs with a diameter above 0.8 mm disappear and the average diameter over volume of particles decrease from 0.29 to 0.19 mm. Doubling the dose of surfactant causes the flocs aggregation. The sludge flocs capability for break-up and aggregation is not proportional to the concentration of LAS. Addition of LAS to the sludge results in decrease of the sludge volume index. This study showed that granulometric measurement may help to estimate an impact of chemical substances contained in wastewater on activated sludge.

Keywords: laser diffraction method, activated sludge, floc size distribution, anionic surfactant

Introduction

Ability to assess the size of activated sludge flocs is one of the important and useful elements of the biological wastewater treatment process analysis. Knowledge of the floc

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size can indicate possible malfunction of wastewater plant. There is a number of technological parameters that influence size of activated sludge flocs such as sludge age, loading as well as aeration method. In well functioning activated sludge bacteria are present mostly in the form of large and medium size flocs. The morphology of activated sludge is also influenced by the composition of the influent of wastewater, particularly the presence of toxins that can cause the formation of small and incoherent flocs [1, 2]. High concentrations of surfactants in surface waters have a negative impact on the environment: hinder the penetration of oxygen into natural waters therefore limiting the development of living organisms and inhibiting self-purification processes [3, 4], are very susceptible to adsorption on sediments [5, 6] and bioaccumulate in living organisms. The presence of synthetic surfactants in the wastewater flowing into the mechanical-biological treatment plants can contribute to serious disturbances in the biological wastewater purification processes [2].

Anionic surfactants concentrations in municipal wastewater generally do not exceed 25 mg/dm^3, but even at such low concentrations can have negative effects on biological wastewater treatment, due to the morphological changes of activated sludge [7]. Concentrations of anionic SPC in industrial wastewater reach values of 300 mg/dm^3 [8, 9]. Such high concentrations of surfactant inhibit the nitrification process [10] changes the structure of activated sludge and its enzymatic activity [2], and thus affect the performance of wastewater treatment.

For the determination of flocs size, microscopic analysis is mostly used. In the works based on digital technology a number of microscopic images of activated sludge has been analyzed [7, 11]. The basic parameter in image analysis is the mean projected area of floc. This technique also allows the assessment of floc morphological features, floc size and the designation of the floc circularity index. Despite numerous advantages, this technique is time consuming, obtaining a representative sample requires a large number of measurements, and microscopic image interpretation can be very difficult. In the case where the object of interest are only particle size rather than their morphological features, measurement technique based on the laser light diffraction, can be used [12–14]. This method allows to obtain analytical results in a very short time.

The operation principle of diffraction analyzer is based on laser light diffraction phenomenon, also called low angle laser light scattering (LALLS) [15]. The laser light is scattered by the suspended particles, and the angle of refraction is inversely proportional to particle size. Although the size of floc measured by this method is not a real value, but may be treated as a parameter describing the examined sample of sludge [13]. Determination of the size of sludge flocs occurs indirectly by calculating its volume. This reduces the error associated with the ambiguity of this assessment, which dimension is measured. By Wilen et al [16] and Bushell [17], this method is valid in the case of particles characterized by small values of particle refractive index and a loose structure.

In considering the spherical particles and for small angles of refraction, this phenomenon can be described by analogy to the diffraction of light through the slit. The split light intensity I (θ) describes the following relationship:

$$I(\theta) = \frac{1}{\theta} \int_0^\infty r^2 n(r) J_1^2 (k \cdot r \cdot \theta) dr \tag{1}$$

where: θ – angle of refraction of light on particles,
r – equivalent particle diameter,
$n(r)$ – particle size distribution,
$k = 2\pi/\lambda$, λ – laser's wave length,
J_1 – Bessels function of the first kind.

Measurement of the intensity of light split by multiple-element type detectors allows, after the transformation of equation (1), to determine particle distribution function $n(r)$. Mathematical description of this phenomenon are provided by McCave and Syvitski [18]. More information on the principles of diffraction analyzer can be found, among various papers, in the publication of De Boer et al [19].

In this work the laser diffraction analyzer was used to determine the granulometric composition of activated sludge from SBR reactor of wastewater treatment plant (WWTP) and to determine what changes occur and are influenced by the presence of an anionic surfactant. Study was carried out for different concentrations of LAS, typical of both, municipal and industrial, wastewater

Materials and methods

Materials

– The activated sludge used in experiments was taken from municipal wastewater treatment plant in Swarzewo. The biological unit of this treatment plant is anaerobic/aerobic sequencing bath reactor (SBR) with biological nutrients removal. The plant treats about 10.000 m^3 of wastewater daily (97 % domestic sewage). The composition of wastewater is generally constant with mean anionic surfactant concentration about 7 mg/dm^3. Suspended solids of the sludge samples were 5.6 g of dry mass per liter.

– The activated sludge for experiments was taken directly from the aeration chamber of SBR during the sedimentation phase, collected in 5 dm^3 containers and immediately transported from WWTP to laboratory.

– The control sample ("background") for all experimental series was oxygenated activated sludge without surfactant.

– In each series of measurements to 1 dm^3 of activated sludge, surfactant at concentrations of: 10 mg/dm^3 ($Serie_{LAS10}$), 100 mg/dm^3 ($Serie_{LAS100}$) or 200 mg/dm^3 ($Serie_{LAS200}$) was added. This corresponds to surfactant loads of: 1.8 mg/g d.m, 17.9 mg/g d.m. and 35.7 mg/g d.m. respectively, for the abovementioned series. LAS concentration range was chosen based on previous studies [20].

– Linear sodium dodecylbenzene sulphonate (LAS) from Sigma Chemical company Ltd has been used as an anionic surfactant.

– Before the granulometric measurement, for each series of test, the sludge sample was diluted (1/5).

Methods

In order to determine the effect of LAS to size change of the activated sludge flocs, its granulometric composition has been studied. Effect of surfactant addition to floc size change was measured over time, *ie* 5, 15, 30 and 45 minutes after the start of testing. Each measurement was conducted as a series of 15 replications.

The measurements were performed using laser diffractometer Mastersizer 2000 (Malvern Instruments Ltd), with unit Hydro 2000MU (integrated stirrer and pump). Particle size range measured by the instrument, through the use of red and blue laser beams, is in the range from 0.0002 mm to 2.0 mm. Analysis of the results is based on Mie theory and Fraunhofer theory [19]. The results of sludge flocs size analysis are presented as histograms, which allowed to evaluate the distribution of "grain" of the analyzed activated sludge.

The Mastersizer software generates a basic floc size distribution parameters (D[4,3], d(0.1); d(0.5); d(0.9)) In order to describe the mean particle size, the volume-weighted average diameter, D[4,3] was used. This parameter is calculated as:

$$\mathrm{D}[4,3]=\frac{\sum_{i=1}^{n} d_i^4}{\sum_{i=1}^{n} d_i^3} \qquad (2)$$

where: d_i – the diameter of the particle with size i.

The influence of the steering on the fragmentation of sludge flocs was examined for the "background" sample. The 1 dm^3 of diluted activated sludge, without surfactant, at temperature 20 ^{o}C, was stirred for 5 min at a speed of pump 900 RPM. This velocity ensured good mixing of sludge without floc breakdown. No changes in particle of sludge distribution was noted. All other measurements were carried out at the same conditions

For each test series ("background", Serie$_{\mathrm{LAS10}}$, Serie$_{\mathrm{LAS100}}$ and Serie$_{\mathrm{LAS200}}$) sludge volume index (SVI) was measured according to standard methods [21] in a 1 dm^3 settling cylinder. SVI is the volume of 1 g of the total suspended solids after 30 min of settling. This parameter is correlated with compressibility of sludge.

Results and discussion

After the addition of LAS at concentrations of 10, 100 and 200 mg/dm^3 for each sample of activated sludge differences in the composition and size of the flocs were identified. These differences depended on the concentration of added surfactant. A wide range of particle sizes is defined as the percentage of particles (v) of diameter (d_i) represented by a distribution function $F(d_i)$ (Fig. 1–4). Studies have shown that activated sludge flocs taken from the SBR reactor (forming the background for further research), significantly differed in size. The sludge consisted of both, a particle size of about 1 μm and larger with substitute diameter equal to 2 mm. Granulometric analysis also showed that the flocs exceeding 0.25 mm accounted for half of all flocs in the sample volume. The distribution of large flocs size in the range from 0.7 mm to 2 mm was only about 6.0 % of all particles volume. No change in the sludge flocs size over time was observed for activated sludge without the surfactant addition, indicating good reproducibility of the test method used.

After the addition of LAS at a concentration of 10.0 mg/dm^3 (Serie$_{\mathrm{LAS10}}$) data analysis showed a significant curves reversal trend $F(d_i)$ in the direction of the smaller size of the activated sludge floc. The reason for this phenomenon was the slow and steady fractionation of sludge flocs taking effect during 30 minutes. Already after 5 min of adding the surfactant particles with sizes larger than 0.2 mm began to undergo fractionation. In addition, no flocs with size greater than 1.0 mm were identified (Fig. 1).

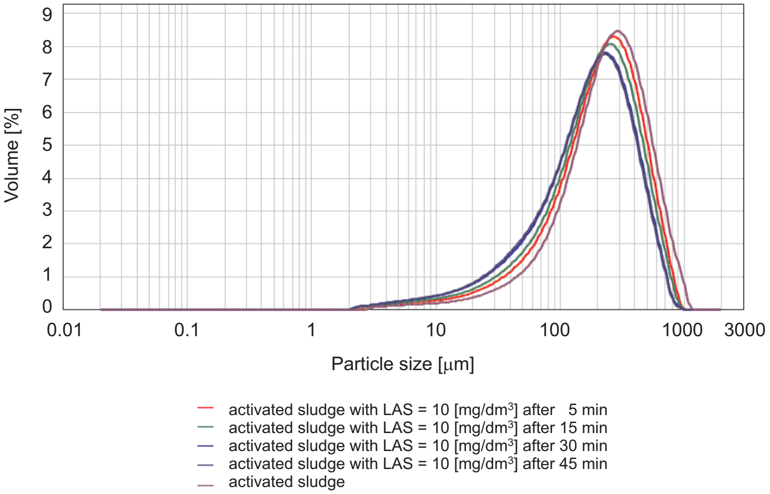

Fig. 1. Particle size distribution of activated sludge for background and Serie$_{\mathrm{LAS10}}$ after 5, 15, 30 and 45 minutes

After a longer time (30 minutes after the start of the tests) the floc size decrease rate observed in the sludge slowed down. After 45 minutes the percentage of floc size in the range from 0.7 mm to 2 mm compared with activated sludge forming the background, was almost six times lower and was only 1.0 %. While the share of floc with a size to 0.25 mm increased and was 67 % of all particles in the sample.

The significant and rapid fractionation of sludge flocs was observed after the addition of a surfactant with ten times higher concentrations (Serie$_{\mathrm{LAS100}}$). In contrast to the Serie$_{\mathrm{LAS10}}$ floc fractionation did not occur gradually but stabilized after 5 minutes of the surfactant impact (Fig. 2).

The percentage of particles larger than 0.7 mm decreased from 6 % to 0.5 % and the percentage of the particles with a diameter of 0.25 mm increased from 50 % to 73 %. The percentage of the average-size flocs, with the best properties of the sedimentation

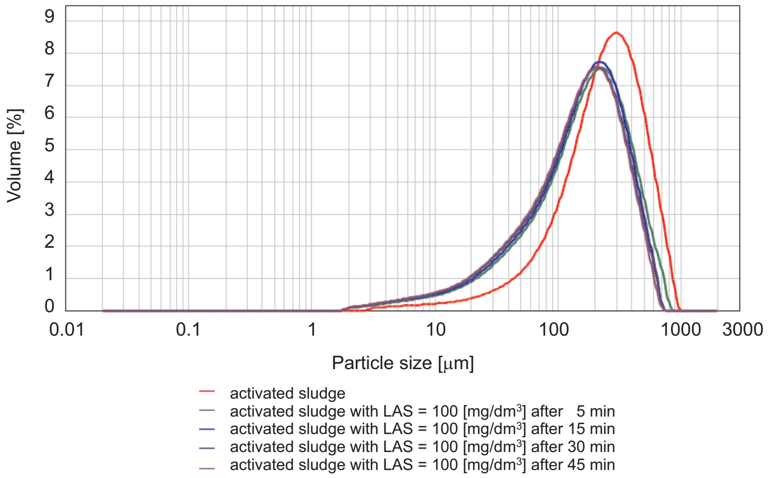

Fig. 2. Particle size distribution of activated sludge for background and Serie$_{LAS100}$ after 5, 15, 30 and 45 minutes

ability, was reduced by only 4.5 %, compared to their content in the sludge without surfactant.

Further doubling of the surfactant dose (Serie$_{LAS200}$) does not result in sludge breakage. After the addition of LAS at a concentration of 200 mg/dm^3 quite different results were observed. With such a large dose of LAS curve $F(d_i)$ "moved", after 5 minutes, in the direction of larger size flocs and were created flocs reaching the size of 2.8 mm, thus resulting in size increase beyond the size attained by activated sludge flocs without surfactant (Fig. 3). The reason for this phenomenon was probably due to the

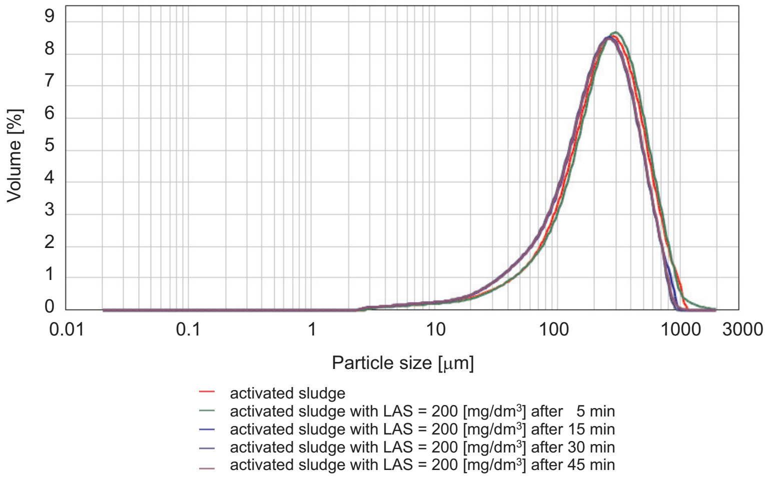

Fig. 3. Particle size distribution of activated sludge for background and Serie$_{LAS200}$ after 5, 15, 30 and 45 minutes

sludge flocs combining into larger aggregates. Over time, part of large aggregates underwent break-up, therefore number of small floc size 0.02–0.2 mm slightly increased and this kind of particle distribution was observed in measurements at 30 and 45 min.

The results of the study showed that for all the concentrations of added surfactant, the size distribution of the activated sludge flocs after 30 min is stable. Figure 4 shows the distribution function $F(d_i)$ for activated sludge (background) and all test series after stabilization of the changes taking place under the influence of surfactant. The displacement of the curve $F(d_i)$ in the direction of the smaller particle size was observed. Dominant particle size decreased from 0.3 mm for "background" to about 0.2 mm for Serie$_{LAS100}$.

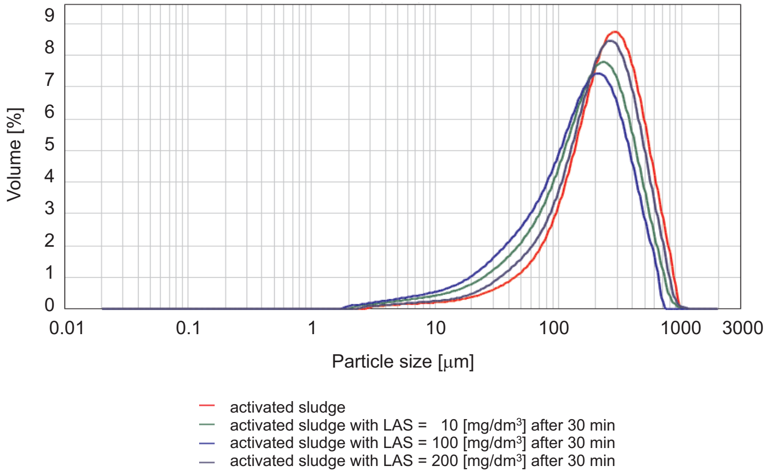

Fig. 4. Particle size distribution of activated sludge for background and series of sludge with LAS, after 30 minutes

Detailed values of volume-weighted average diameter and diameter deciles, obtained after 30 min of measurement are presented in Table 1.

Table 1

Deciles and median for values obtained for background and series of sludge with surfactant after 30min of measurement

Serie	Parametr [μm]			
	D[4,3]	d(0.1)	d(0.5)	d(0.9)
"Background"	293.84	72.35	248.52	579.88
Serie$_{LAS10}$	215.92	40.06	184.28	438.83
Serie$_{LAS100}$	189.78	31.14	159.81	394.02
Serie$_{LAS200}$	250.06	57.27	217.69	490.26

Important role in the binding of microorganisms in compact aggregates are extracellular polymeric substances (EPS), which are a kind of a matrix in which microorganisms are embedded [22, 23]. EPS matrix is not uniform, it can be divided into two fractions which differ greatly in composition and properties. The tightly bound EPS (TB-EPS) is strongly associated with the fraction of microorganisms, containing significant quantities of trivalent and divalent metal ions (Fe^{3+}, Al^{3+}), and is responsible for maintaining a compact structure of floc. This bond is formed by the influence of the negatively charged surface of the TB-EPS of positively charged cations. The loosely bound EPS (LB-EPS), is a fraction of the surrounding floc, more from mobile EPS TB [24]. Significant amounts of this fraction can weaken the bond between the microbial cells and contribute to the deterioration of floc cohesion [25]. Surfactants, due to their properties may lead to biopolymers leaching from the EPS matrix to the supernatant [26]. Used in the studies anionic surfactant LAS, due to its electric charge can also interact with the cations present in the TB-EPS, weakening the structure of the flocs. The presence of a net negative surface charge on floc surfaces may create repulsive electrostatic interactions. These processes may be the cause of the observed, in granulometric analysis, increase of floc fractionation.

Floc aggregation observed in the case of LAS concentration of 200 mg/dm^3 indicates different effects of LAS at so high concentrations. It is known that floc aggregation increases with the content of proteins and nucleic acids in the EPS [23, 27]. Such a high LAS load can lead to cell lysis, which facilitates the release of biopolymers from bacterial cells (disintegration of part of bacterial cells).

It has been reported that there is no simple relationship between the floc size and its compressibility [12, 23]. A comparison between SVI and floc size measurements is presented in Fig. 5.

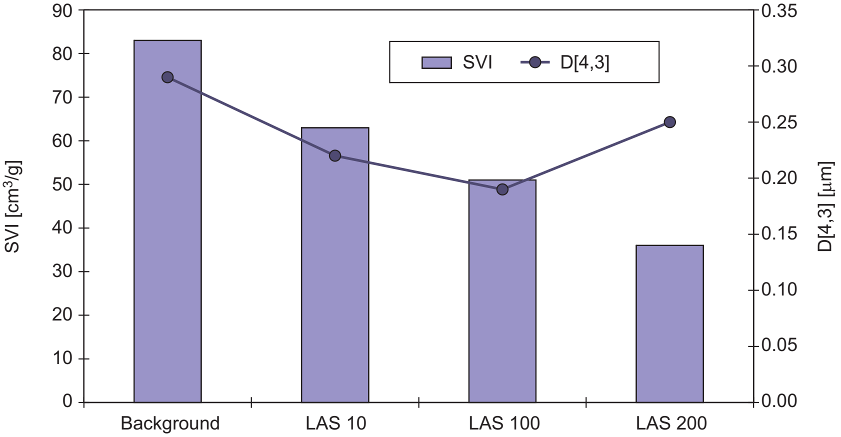

Fig. 5. SVI and D[4,3] evolution with increase of LAS concentration

For all series the sludge volume index value decreases with increase of LAS concentration. This trend is not disturbed even by the increase of floc size resulting with their aggregation (Serie$_{LAS200}$). The reason for this phenomenon may be an increase (in the presence of surfactant) in sphericity and smoothness of the floc borderline, described in the work of [2, 7]. Due to their round morphology flocs could compact efficiently, giving a low SVI [23]

An important factor for sedimentation is the presence of dispersed gas bubbles in the intensive aerated activated sludge, which may contribute to the floating of the sludge. The floc sedimentation may be hindered by air bubbles. Gas bubbles contained in the liquid with surfactant are not stabilized. Since gas density is less than the density of the liquid, the buoyancy force causes the escape of gas bubbles from the liquid in the de-aeration process. In an aqueous solution of a surfactant gas bubbles are stabilized through the creation of a thin layer of adsorption of surfactant molecules at the border of the liquid-phase air. As a result, the thermodynamic description of the interface of the follicle is changed and therefore it's interaction with the liquid and sludge [28]. Lowering the surface tension of a mixture of water and aerated activated sludge reduces air bubbles, has an effect on the speed of lifting, the contact time of the phases, and the interfacial surface area [29, 30]. Moreover, LAS substantially adsorbs on the surface of the floc [31], changing the interfacial surface and its interaction with the liquid. The result of these changes may be an increase in sedimentation rate and better compressibility of the floc in the sludge with a surfactant.

Summary and conclusions

Laser diffraction method is a modern method that can be used to determine the particle size distribution of activated sludge, as well as track the changes taking place in the sludge due to the changing conditions of wastewater treatment. It allows provisionally estimate an impacts of chemical substances contained in waste water on activated sludge. On the basis of studies of activated sludge subjected to the impact of anionic surfactant can be concluded as follows:

– LAS concentrations less than 200 mg/dm^3 cause fragmentation of sludge flocs. Surfactant concentrations higher than this value leads to their aggregation.

– The largest and fastest changes in the distribution of sludge floc size were observed after the addition of a surfactant at a concentration of 100 mg/dm^3

– The method allows to estimate the time after which added chemical compound affects the sludge floc size. It also allows you to assess whether it is a one-time change, or act in time.

– The compressibility of investigated samples of sludge is the result of many factors and it is difficult to clearly determine which factors are decisive. These result (after the addition of LAS to the environment) in decreasing of the volume-weight index of activated sludge in the presence of surfactant. This disproportion deepens with increasing surfactant concentration

It should also be noted that the granulometric size distribution is only a tool for determining the particle size. Changes in floc sizes is not a reliable indicator of the sludge condition, or its enzymatic activity. Further complementary research must be done in order to determine the impact of LAS on activated sludge and its wastewater functions.

It would be desirable to examine in the future whether, at a constant flow of wastewater with LAS, the fragmentation of the floc sludge changes its characteristics permanently, or the elimination of LAS allows the sludge to return to the original characteristics.

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ZASTOSOWANIE ANALIZY GRANULOMETRYCZNEJ DO OKREŚLENIA WPŁYWU SURFAKTANTU NA STRUKTURĘ OSADU CZYNNEGO

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Abstrakt: Praca dotyczy oceny możliwości wykorzystania analizatora dyfrakcji laserowej do określenia zmian w dystrybucji rozmiarów kłaczków osadu czynnego w obecności surfaktantu anionowego. Jako model surfaktantu, zastosowano liniowy alkilobenzenosulfonian sodu (LAS). W przeprowadzonych badaniach użyto różnych stężeń wyjściowych surfaktantu: 10, 100 i 200 mg/dm^3. Analiza granulometryczna osadu wykazała, że rozmiar cząstek osadu mieści się w zakresie od 1 µm do 2 mm. Największe i najszybsze zmiany w rozkładzie wielkości kłaczków osadu zaobserwowano po dodaniu surfaktantu o stężeniu 100 mg/dm^3. Zanikły kłaczki o średnicy powyżej 0,8 mm, a średnia średnica kłaczków zmalała z 0,29 do 0,19 mm. Podwojenie dawki surfaktantu powoduje agregację kłaczków. Stopień rozdrobnienia bądź aglomeracji kłaczków pod wpływem LAS nie jest wprost proporcjonalny do stężenia surfaktantu. Dodatek LAS do osadu czynnego skutkuje spadkiem indeksu wagowo-objętościowego Przeprowadzone badania wykazały, że analiza granulometryczna może być stosowana jako metoda ułatwiająca oszacowanie wpływu związków chemicznych zawartych w ściekach na osad czynny.

Słowa kluczowe: metoda dyfrakcji laserowej, osad czynny, rozkład rozmiaru kłaczków, surfaktant

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and Magdalena KOSEL[1]

PRELIMINARY TESTS OF SORPTION PROPERTIES OF THERMALLY TRANSFORMED ACTIVATED SLUDGE

WSTĘPNE BADANIA WŁAŚCIWOŚCI SORPCYJNYCH TERMICZNIE PRZEKSZTAŁCONEGO OSADU CZYNNEGO

Abstract: Study was conducted in order to check sorption properties of activated sludge which has undergone thermal transformation. For this purpose, anaerobically digested and dewatered activated sludge was dried at 105 °C to constant weight. Next this sludge was milled to a particle with a diameter of 0.5–1.0 mm and subjected to thermal activation in a muffle furnace at 600 °C. In this way obtained a powder activated carbon based on activated sludge (so called SAC – "sludge-based activated carbon"). Studies of static sorption of two dyes (Lissamine Scarlet 4R and Rhodamine B) were conducted for activated carbon prepared as described above. The reaction pH was 2.5 and 7.0 respectively for the dye Lissamine Scarlet 4R and Rhodamine B. During the tests for both dyes a sorption kinetics (for two different values of the ratio of dye weight and SAC weight) were made. Then, for a predetermined time sorption (selected based on the results of the kinetics) sorption isotherms were made for both dyes. Studies have shown that the dye Rhodamine B was well sorbed by activated carbon produced from activated sludge. In the case of Rhodamine B in order to achieve an effective level of removal of that dye it was required only 0.5 hours of contact time. However, in the case of Lissamine Scarlet 4R it required a much longer contact time. That was required two hours of contact time to achieve a relatively high reduction of concentration of this dye. Also, the results obtained during determining the sorption isotherms of these two dyes, have confirmed that conclusion. The adsorbed charge of Rhodamine B per gram of SAC was significantly higher than the adsorbed charge of the second dye. These differences may have been due to the size of the pores of generated SAC. On the basis of sorption of these two dyes can be supposed, that the SAC was characterized by a pore smaller than the size of molecules of Lissamine Scarlet 4R. Therefore, the sorption process of that dye was limited. In contrast, molecules of Rhodamine B, which are smaller than the molecules of Lissamine Scarlet 4R, were much better adsorbed by the SAC. Additionally, it can be supposed that the surface charge of the generated SAC was negative, because the cationic dye (Rhodamine B) was better adsorbed by this sorbent.

Keywords: activated sludge, activated carbon, dyes, sorption isotherm, sorption kinetics

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Introduction

The process of sorption at the liquid-solid system can be defined as the occurrence of compacting of the substance in the surface layer of solid, or within the pores of a solid. Sorbed substance is called ‘sorbate’, while the solid which adsorbed other substances on its surface is called ‘sorbent’. Thus, near the surface of the sorbent increases the concentration of the substance in comparison with its concentration occurring within the solution. Depending on the type of interaction between the solid’s molecules and the substance’s molecules sorption can be divided into physical and chemical. In the case of physical sorption the bonding forces between adsorbed substance and solid are van der Waals interactions. This process is reversible and generally sorption is a multilayer. Moreover, the process is exothermic with evolution of a small amount of heat (comparable to heat of condensation), and when the temperature increases the desorption process occurs (adsorbed substance is released). However, in the case of the chemical sorption the bonding forces between sorbate and sorbent are chemical interactions. Typically, the forces responsible for the chemisorption are covalent forces. Chemisorption is usually an irreversible process and the sorbate molecule is bound to the sorbent as a single layer (monolayer sorption) [1–3].

Sorption rate mainly depends on the rate of diffusion of removal substance in liquid and then in the pores of sorbent. The first step is the diffusion of substances from the interior of the solution near the solid (sorbate). In the second stage diffusion occurs in the boundary layer near the surface of a solid. The third step includes the diffusion of a substance inside the pores of the adsorbent. Finally, it comes to locating a substance in an active points of sorbent [2, 3].

The process of sorption of contaminants from solution onto a solid surface is used in water treatment, treatment of industrial wastewater as well as in the water renovation. Sorption process is used to remove from liquids (water or wastewater) specific, dangerous, toxic or valuable substances (which for example can be reused). In the case of treating water sorption is mainly used for removal of hazardous substances, soluble organic compounds both natural or anthropogenic origin. Moreover, there can also be removed free chlorine and chloramines, viruses, and partially some inorganic compounds (*eg* heavy metals) from water. In the case of renovation of the water (*ie* the third stage of wastewater treatment) sorption is used for removing of refractive organic compounds, heavy metals, as well as phenols, ammonia nitrogen, detergents and pesticides. In the case of industrial wastewater treatment adsorption is often applied for recovery of valuable substances which may be reused in the production process. Furthermore, sorption is also used for removal of dyes from wastewater [2, 4–10].

Because of the wide variety of applications the sorption process in water and wastewater treatment there can be used many different types of sorbents. However sorbents are divided into two main groups: natural and synthetic ones. However, regardless of the type of sorbent, it should characterized by a high surface area and porosity, selectivity for removal of contamination, mechanical strength as well as being safe for the environment (not emit toxic or harmful substances in its application). The most commonly used sorbents are activated carbons, silica gel, activated alumina, zeolites, and natural clays rocks. Activated carbon can be produced from many different materials (such as peat, lignite and coal, anthracite, wood material, material of animal origin – *eg* from the bones, etc.). In the case of zeolite, otherwise known as molecular sieves, they are crystalline aluminosilicates of alkali metals or alkaline earth, which include spatially arranged tetrahedrons of SiO_4 and AlO_4 [11].

For the preparation of activated carbon it may also be used organic waste materials such as palm kernel shell, cashew nut shell, bamboo waste, municipal solid wastes, waste rubber tires as well as wastewater sludge. The last of listed materials can be processed in different ways in order to obtain activated carbon. The first step is always a process of dewatering and drying, and then grinding. Then, sludge is subjected to combustion, wherein there may be different pyrolysis conditions. The pyrolysis process may be conducted over a wide temperature range from 450 ^{o}C to 850 ^{o}C even. In addition, sludge combustion can be realized in different atmospheres. There can be used nitrogen, air, steam, and carbon dioxide. For example SAC can be prepared using raw sewage sludge from paper mill. Li et al [12] generate the SAC by carbonization of raw sludge at 300 ^{o}C for 60 min and then by activation at 850 ^{o}C for 40 minutes in steam atmosphere. They used that SAC for dye sorption from aqueous solutions. Furthermore, in order to produce activated carbon from wastewater sludge, chemical activation can be applied. For this purpose, the strong mineral acids (H_2SO_4, HCl, H_3PO_4) and $ZnCl_2$ and KOH are used. Chemical activation is conducted either before the process of pyrolysis or after burning the sledge. Chen et al [13] activated the anaerobically digested sludge using $ZnCl_2$ and thereafter they conducted a pyrolysis process of that sludge at 500 ^{o}C under nitrogen atmosphere. Moreover, to form a sludge-based activated carbon may be used raw sludge (not undergone digestion process) and stabilized sludge (both in aerobic and anaerobic way) [7, 9, 10, 12–20].

Sludge based activated carbon may be used for removing different kinds of substances. There can be remove dyes, phenols, 4-chlorophenol, nitrobenzene and many other organic compounds [13, 15, 16, 21, 22].

The aim of the research described in this paper was to examine the sorption capacity in relative to the two dyes of thermally transformed anaerobically digested sewage sludge.

Experimental

During the tests anaerobically stabilized and dewatered sludge (mixture of excess and raw sludge) was used. The sludge was dried in 105 ^{o}C to constant weight, ground in a laboratory mill and combusted in a muffle furnace. The combustion process was divided into two phases – the first sludge was calcined in 300 ^{o}C for 45 minutes. Next the temperature raised up to 600 ^{o}C and the combustion was continued for a further 45 minutes. Sorption process was carried out for such a transformed sludge.

Sorption studies (both kinetic and isotherm) were carried out in a static system. Activated carbon (based on the sewage sludge), in an amount of 0.1 g, was introduced into a closed Erlenmeyer flasks with a capacity of 50 cm^3. To the flask was added

50 cm^3 a solution of the dye (Rhodamine B or Lissamine Scarlet 4R) of a suitable concentration. The flasks were placed on a laboratory shaker to ensure constant stirring contents of the flasks.

During the studies two different dyes were used to check the sorption properties of SAC. Namely Lissamine Scarlet 4R and Rhodamine B were examined. The chemical structure of both dyes is shown on Fig. 1 [23, 24]. Rhodamine B is a cationic dye and according to nomenclature of Colour Index is called Basic Violet 10 number C.I. 45170. In contrast Lissamine Scarlet 4R is anionic dye, and according to nomenclature of Colour Index is called Acid Red 18 number C.I. 16255.

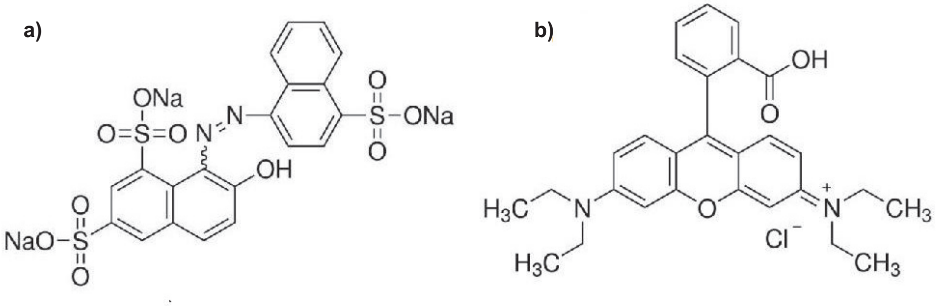

Fig. 1. Chemical structures of examined dyes: a) Lissamine Scarlet 4R; b) Rhodamine B

The tests were only a preliminary experiments in aimed to check, if generated sludge-based activated carbon has any sorption properties. Therefore, the pH value used in this study was the same as is used in determining the specific surface area of the activated sludge (using Rhodamine B and Lissamine Scarlet 4R) [25].

It is required different value of pH for both dyes when specific surface area of activated sludge is measured. It is connected with chemical structures of those dyes and the value of electric charge of dye and electric charge of surface of sorbent. The surface of flocs of activated sludge are characterized by negative electric charge. In contrast Lissamine Scarlet 4R is anionic dye. Therefore it is necessary to change the electric charge of floc surface. That is achieved by reducing pH value of the solution to 2.5.

In the case of Rhodamine B, decreasing of pH value is not required, because it is cationic dye. For that reason there should not be electrical repulsive forces between dye molecules and surface of SAC.

In the case of Lissamine Scarlet 4R the pH of reaction was 2.5, while in the case of Rhodamine B the pH value was equaled to 7.0 [25].

In the first stage of research sorption kinetics studies were performed. There were examined two different initial concentrations of both dyes. The final dye concentration was measured after different times of their contact with the sludge-based activated carbon (Table 1). The concentration of the dye was determined photometrically on the basis of the calibration curve. In the second stage, based on the results of sorption kinetics, sorption isotherm were determined for both dyes.

Table 1

Parameters of sorption kinetics

Kind of dye	Initial concentration of dye [mg/dm^3]	Weight of SAC [g/dm^3]	Reaction time [h]
Lissamine Scarlet R4	50	2	0.5 1.0 1.5 2.0 2.5 3.0 4.0
	700		
Rhodamine B	50		
	700		

Results and discussion

Kinetics

Research has shown that the shape of sorption kinetics depends of kind of dye. In the case of Rhodamine B after half an hour of reaction time, concentration of the dye after the process has reached a constant low level. The degree of reduction of Rhodamine B was in range 82.8–84.7 % and in range 84.1–85.5 % when the initial concentration of dye was respectively 50 and 700 mg/dm^3 (Fig. 2 and Fig. 3).

However, in the case of the second dye (Lissamine Scarlet 4R) there has been no such a high efficiency of removal of that dye. The decrease of concentration of Lissamine Scarlet 4R after adsorption process was only equaled to 26.7 % and 15.8 % when the initial concentration was respectively 50 and 700 mg/dm^3 (Fig. 4 and Fig. 5). In addition, when Lissamine Scarlet 4R was using there was required much longer contact time to achieve a constant degree of adsorption of dye on the SAC. Namely, when the initial concentration was 50 mg/dm^3 the greatest degree of reduction of dye concentration achieved after 3 h of reaction. However, for the initial concentration

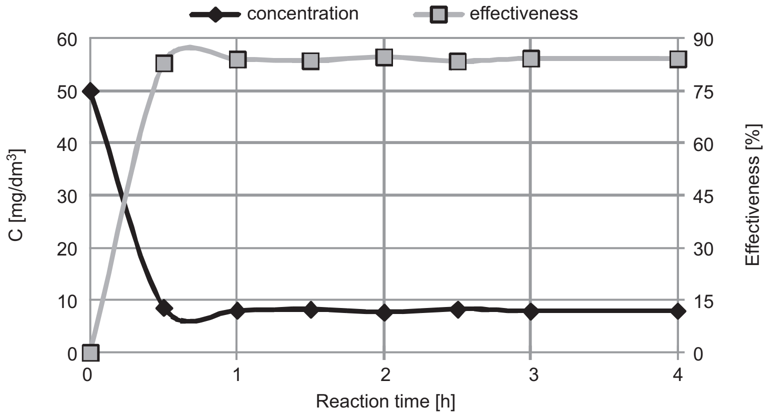

Fig. 2. Sorption kinetics of Rhodamine B – initial concentration 50 mg/dm^3

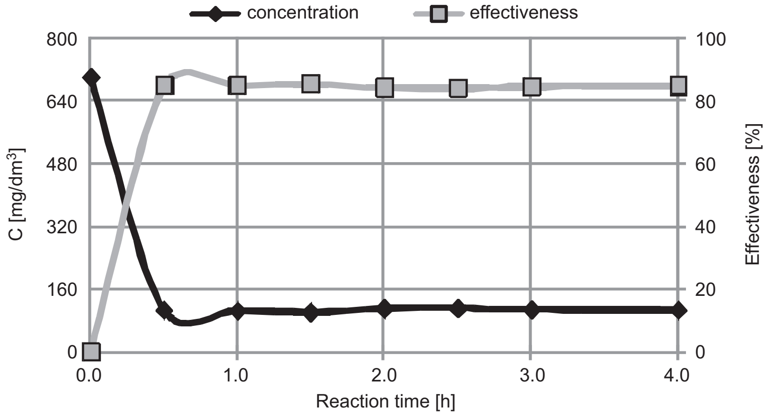

Fig. 3. Sorption kinetics of Rhodamine B – initial concentration 700 mg/dm^3

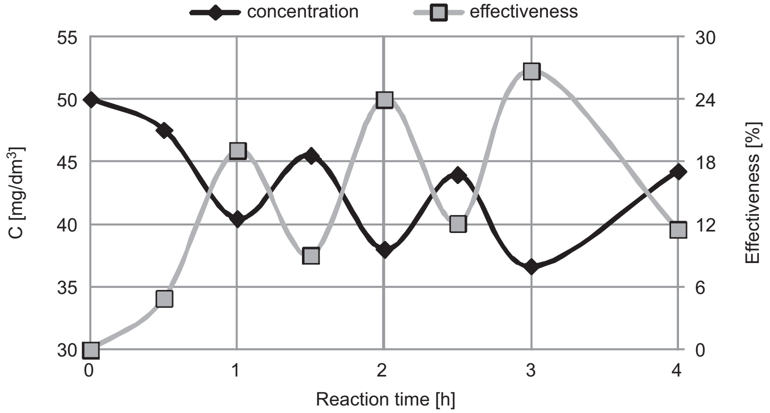

Fig. 4. Sorption kinetics of Lissamine Scarlet 4R – initial concentration 50 mg/dm^3

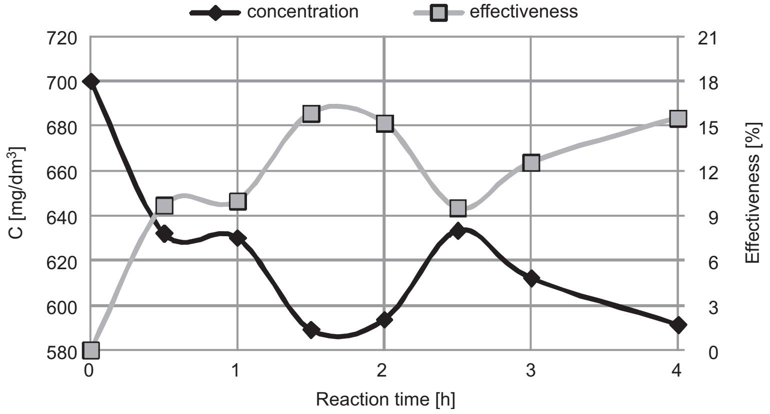

Fig. 5. Sorption kinetics of Lissamine Scarlet 4R – initial concentration 700 mg/dm^3

equaled 700 mg/dm^3 the lowest dye content was observed after 1.5 and 2 hours of reaction. Moreover, in the case of Lissamine Scarlet 4R observed large variations in the dye concentration in subsequent times of measurement. The reason of that phenomenon may be due to the small SAC sorption properties (generated during the studies) in relation to this dye. This could result in desorption of previously adsorbed molecules of Lissamine Scarlet 4R. Then reported an increase of its concentration after sorption process in comparison with concentration equaled in the previous measurement point. That phenomenon was mainly observed in the case of initial concentration equaled 50 mg/dm^3 (Fig. 4). In the case of higher content of Lissamine Scarlet 4R, that variations of effectiveness was not so large, however it also occurred. It is possible that, the bonded forces between SAC and dye were not enough strengths to immobilize molecules of the dye on surface of SAC.

Sorption isotherm

On the basis of studies of the kinetics, the contact time for both dyes were determined. In case of Rhodamine B, the required contact time was 0.5 hour. While in the case of Lissamine Scarlet 4R it was obtained, that the most favorable time was 2 hours. For such a chosen reaction times the sorption isotherm studies of both dyes were determined.

Studies have shown that produced sludge-based activated carbon had much better sorption properties in relation to Rhodamine B. The amount of adsorbed charge of Rhodamine B by SAC reached a much higher values in comparison with Lissamine Scarlet 4R. In the case of Rhodamine B adsorbed charge of dye was even equaled to 727 mg/g_{SAC}. When Lissamine Scarlet 4R was examined the charge of adsorbed dye was only 174.6 mg/g_{SAC}.

That shape of curve of isotherm characterizes a kind of sorption – whether it occurs single-layer or multi-layer sorption. According to the literature there are few different kind of shapes of isotherm curve depending on kind of sorption. That various shapes of isotherm curves shows Fig. 6. In the case of Fig. 6a the curve shows a single-layer

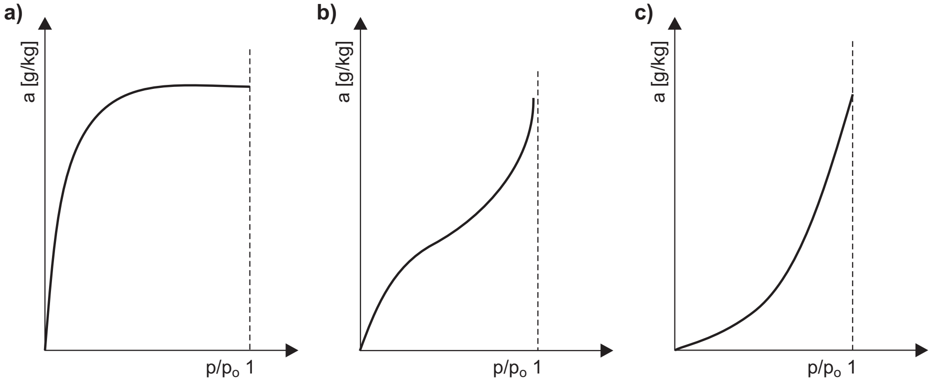

Fig. 6. Shapes of isotherm curve: a) single-layer sorption, b) and c) multi-layer sorption

sorption. Other curves show a multi-layer ones. The single-layer is described be isotherm of Freundlich and Langmuir. In contrast the multi-layer sorption is described by isotherm of BET.

On the basis of the shape of the sorption isotherm of both dyes can be concluded that there occurs the multi-layer sorption (Fig. 7 and Fig. 8). In both dyes during the first stage can be observed gradual increase of value of adsorbed charge with increasing equilibrium concentration of dye. Then in the second stage it can be seen parallel section to the abscissa (so called 'Plateau') on the curve of isotherm. It is then while the first layer of surface of sorbent was filling by dye molecules. Therefore, despite the increase of concentration of the dye was not followed by an increase of the adsorbed charge by SAC. Only a relatively large excess of the dye led to further adsorption of dye molecules in the second layer. It is connected to the coverage of all active spaces on the first layer of surface of SAC by molecules of dye. However in the case of Rhodamine B this parallel section of curve line occurred when the charge of adsorbed dye was about

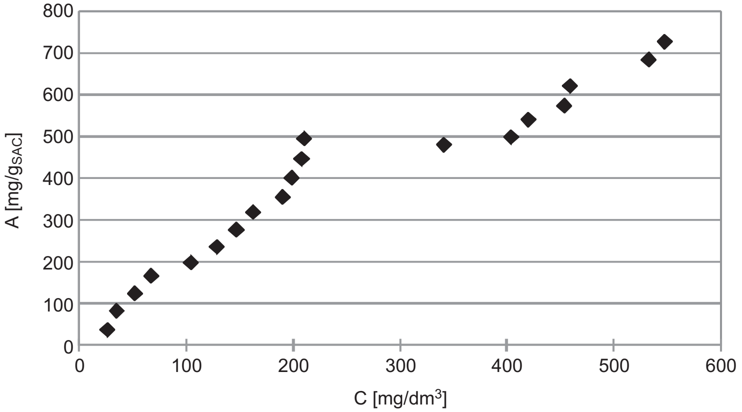

Fig. 7. Sorption isotherm of Rhodamine B

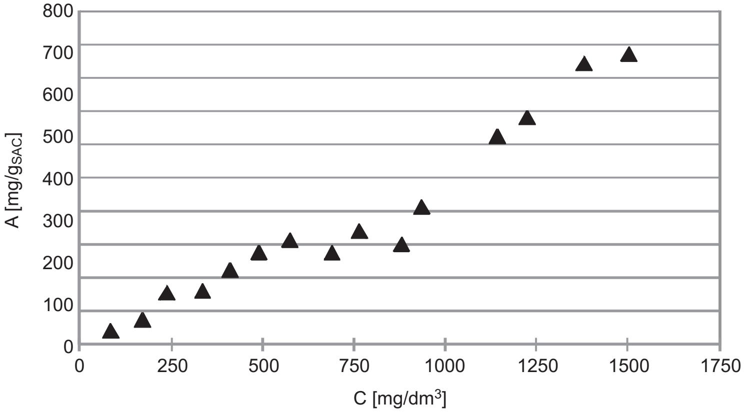

Fig. 8. Sorption isotherm of Lissamine Scarlet 4R

500 mg/g_{SAC}. In the case of Lissamine Scarlet 4R it occurred for much lower value of adsorbed charge of dye – about 60 mg/g_{SAC}. It means that generated SAC had adsorbed much more amount of Rhodamine B then Lissamine Scarlet 4R.

This difference may be due to the particle size of molecules of both dyes. The molecule size is directly related with the surface coverage by single molecule. In the case of Rhodamine B coverage surface of single molecule equals 160 Å^2. While Lissamine Scarlet 4R is characterized by larger particles, and the coverage surface of single molecule reaches a value of 196 Å^2. It can therefore be assumed that the pore size of the generated SAC is smaller than the particle size of Lissamine Scarlet 4R molecules. Such a size of pores of SAC could have limited the adsorption of that dye. It is possible that molecules of Lissamine Scarlet 4R did not penetrate the pores of SAC and molecules of that dye were adsorbed only near the surface of SAC. Moreover for this reason the bonded forces between dye and sorbent were not strong enough to immobilize the molecules of Lissamine Scarlet 4R effectively and desorption occurred while establishing kinetics of sorption of that dye.

Conclusions

The study showed that the wastewater sludge may be use as a material from which an activated carbon can be produced. Subjecting the sewage sludge only into thermal transformation allowed to generate a sorbent capable to adsorb Rhodamine B. Based on the results obtained during kinetics of sorption of that dye it can be observed that it was required only 0.5 hour to obtain high efficiency of removal of Rhodamine B. Moreover, after half an hour of contact of SAC and dye the stable value of concentration occurred. In contrast performed studies have shown that the much longer contact time was required to achieve the highest efficiency of sorption of Lissamine Scarlet 4R on SAC. After about 2 hours of reaction observed a relatively high effectiveness of dye removal was observed. However the efficiency degree was not stable and sorption and desorption process occurred alternately in the following measurement points. It manifested by an alternating decrease and increase of dye concentration after sorption process.

The results of isotherm sorption also showed the difference of sorption properties of generated SAC according to examined two dyes. Much higher amount of Rhodamine B was sorbed by SAC in comparison with Lissamine Scarlet 4R. However in case of both dyes occurred a multi-layer sorption. The shape of curve of isotherm sorption shows it. It can be observed the section of parallel line to abscissa. Beyond this section it can be observed an increase in value of adsorbed charge with increase value of equilibrium concentration of dye. Therefore for both dyes it can be concluded that physical sorption occurred. It is known that multilayer sorption occurs when forces bonded molecules and solid surface are van der Waals interactions. This forces can interact The impact of these forces is greater than the size of single molecules sorbed on the surface. Therefore, it is possible the formation of subsequent layers of molecules of substance on the surface of the sorbent.

Differences between sorption effectiveness of both dyes could have been connected with size of their molecules. Rhodamine B has smaller molecules then molecules of Lissamine Scarlet 4R. It is possible that pore size of SAC was relatively small and this could have limited the sorption of Lissamine Scarlet 4R. Moreover that dye has anionic character while Rhodamine B has cationic one. It could be possible that generated SAC has an negative charge of surface. Maybe pH 2.5 was not enough low to change anionic charge of Lissamine Scarlet 4R what affected the sorption efficiency of that dye.

However, that were preliminary studies when used pH of the reaction was such as is used in determining the specific surface area of the activated sludge using these two dyes. Therefore, it may be that in the case of using a different pH in the case of Lissamine Scarlet 4R, the efficiency of its sorption will increase. This implies the need for further research aimed at verifying a wider range of properties of the produced SAC.

Acknowledgements

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WSTĘPNE BADANIA WŁAŚCIWOŚCI SORPCYJNYCH TERMICZNIE PRZEKSZTAŁCONEGO OSADU CZYNNEGO

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Abstrakt: Przeprowadzono badania mające na celu ocenę właściwości sorpcyjnych osadu czynnego, który został poddany termicznej obróbce. W tym celu ustabilizowany beztlenowo i odwodniony osad czynny wysuszono w 105 ^{o}C do stałej masy. Następnie osad ten zmielono do ziaren o średnicy 0,5–1,0 mm i poddano termicznej aktywacji w piecu muflowym w 600 ^{o}C uzyskując w ten sposób pylisty węgiel aktywny bazujący na osadzie czynnym (tzw. SAC – czyli "sludge-based activated carbon"). Dla tak spreparowanego węgla aktywnego przeprowadzono badania procesu sorpcji statycznej względem barwników: Lissamine Scarlet 4R i Rodamina B. W badaniach pH reakcji wynosiło 2,5 oraz 7,0 odpowiednio dla barwnika Lissamine Scarlet 4R i Rodaminy B. w pierwszym etapie wykonano kinetykę sorpcji obu barwników dla dwóch różnych wartości stosunku masy barwnika przypadającego na masę SAC. Następnie dla ustalonego czasu sorpcji (wybranego na podstawie wyników przeprowadzonej kinetyki) wykonano izotermę sorpcji obu barwników. Badania wykazały dobre właściwości sorpcyjne wytworzonego z osadu węgla aktywnego względem barwnika Rodamina B. W przypadku Rodaminy B w celu uzyskania efektywnego stopnia usunięcia tego barwnika wymagany był jedynie pół godzinny czas kontaktu. Natomiast w przypadku Lissaminy Scarlet 4R wymagany był znacznie dłuższy czas kontaktu. Potrzeba było aż 2 godzin kontaktu by uzyskać stosunkowo wysoki stopień redukcji stężenia tego barwnika. Również wyniki otrzymane w trakcie wyznaczania izotermy sorpcji obu barwników potwierdziły te wnioski. Wartość zabsorbowanego ładunku Rodaminy B przez gram SAC była znacznie większa niż w przypadku drugiego badanego barwnika. Różnice te mogły wynikać z wielkości porów wytworzonego SAC. Na podstawie badań sorpcji tych dwóch barwników można podejrzewać, że wytworzony SAC charakteryzował się wielkością porów mniejszą od wielkości cząsteczek Lissaminy Scarlet 4R. Z tego też względu sorpcja tego barwnika była utrudniona. Natomiast cząsteczki Rodaminy B, które są mniejsze od cząsteczek Lissaminy Scarlet 4R, były w znacznie większym stopniu zatrzymywane przez SAC. Ponadto można podejrzewać, że ładunek powierzchniowy wygenerowanego SAC miał wartość ujemną, dlatego kationowy barwnik (Rodamina B) była lepiej sorbowana przez ten sorbent.

Słowa kluczowe: osad czynny, węgiel aktywny, barwniki, izoterma sorpcji, kinetyka sorpcji

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CONTENT OF LEAD IN MAIZE AND SOIL FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ OŁOWIU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The research was conducted to determine the influence of fertilization with waste organic materials on the content and uptake of lead by maize as well as on the total content of lead in soil. The three-year field experiment comprised 7 treatments: a non-fertilized soil (control treatment) as well as a soil fertilized with mineral fertilizers, cattle manure, green waste compost, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. Maize cultivated for silage was the test plant. The lead content in the above-ground parts of plants and in the soil was determined using ICP-AES method. During the research, no lead pollution of the soil or the above-ground parts of the maize was found. No statistically significant effect of fertilization on the lead content in the maize was found or the fertilized plants contained considerably less of the element than the control plants. The lowest weighted mean content of lead was found in the maize fertilized with the green waste compost, sewage sludge as well as with the compost from sludge and straw. Soil with the lowest lead content was the soil of the treatment fertilized with organic materials. The soil fertilized with the green waste compost (all the years), sewage sludge (2nd year) as well as with the mixture of sludge and ash (1st and 2nd year) contained significantly more lead than the soil fertilized with mineral fertilizers.

Keywords: waste organic materials, sewage sludge, compost, lead, maize, soil

Introduction

One of the ways of lead penetrating into animal and human organisms is through food. Lead, like other heavy metals, accumulates in successive links of the “soil-plant-

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-animal-human" food chain. Introducing high doses of lead to soil translates into an increased risk of accumulating this element in plant, animal and human organisms.

According to the current state of knowledge, lead is not an element which has physiological functions in living organisms, whereas its harmful effect is well known. Lead shows genotoxic effect (by inhibiting the processes of DNA repair and generating free radicals) as well as neurotoxic and teratogenic effects [1–3, based on different sources]. It also impairs the effect of the vascular and immunological systems [2, based on different sources]. Having an impact on the human organism, lead is particularly dangerous for small children. In plants, excessive exposition to this element inhibits total chlorophyll level and disturbs the photosynthesis, nitrogen transformation (hampering the activity of nitrate reductase), and cell division processes as well as disturbs water management [4, 5 based on different sources]. Kurtyka et al [6] found that exposition to lead leads to diminishing growth of maize coleoptile segments.

The aim of the research was to determine the influence of fertilization with waste organic materials on the content and uptake of lead by maize as well as on the total lead content in soil.

Material and methods

The three-year field experiment was set up in 2008 at an experimental station of the University of Agriculture in Krakow, located in Krakow-Mydlniki. The experiment was conducted on brown soil typical proper, with graining of light soil. It was an acid soil (pH_{KCl} = 5.40), with a very high content of available phosphorus and potassium (94.9 mgP and 219.2 mgK $\cdot$ kg^{-1} d.m.). The soil contained 9.88 gC_{org} $\cdot$ kg^{-1} d.m., 1.07 gN_{total} $\cdot$ kg^{-1} d.m. and 26.5 mgPb $\cdot$ kg^{-1} d.m. The content of trace elements in the soil did not exceed the limit values established for agricultural use of sewage sludge, neither did the pH_{H2O} value of the soil make fertilization with sewage sludge impossible [7].

The experiment comprised of 7 objects: a non-fertilized soil (control) as well as a soil fertilized with mineral fertilizers, cattle manure, green waste compost (the waste came mainly from the maintenance of urban green areas), municipal sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and ash. Each treatment was carried out in 4 replications. Pioneer 'PR 39F58' maize, cultivated for silage and harvested at the wax maturity stage of the grain, was the test plant in all years of the research. In the first year, 160 kgN, 168 kgP_2O_5 (that is 73 kgP) and 140 kgK_2O (that is 116 kgK) per ha were introduced to the soil of fertilized treatments (except the control). To the soil fertilized with the manure and organic materials the whole nitrogen dose was introduced in that fertilizer and those materials. Mineral fertilizers: ammonium nitrate (34 % N), enriched superphosphate (40 % P_2O_5) and potassium chloride (60 % K_2O) were used in order to introduce nutrients to the soil fertilized with mineral fertilizers as well as to even up the doses of phosphorus and potassium in the soil of the remaining fertilized treatments. These fertilizers were also used to conduct fertilization in the second and third year of the experiment, introducing 100 kgN, 30 kgP_2O_5 (13 kgP) and 110 kgK_2O (91 kgK) per ha to the soil each year. Accurate data regarding conditions of conducting the experiment are included in the papers of Tabak and Filipek-Mazur [8, 9].

The content of trace elements in the organic materials used for fertilization did not exceded the limit values established for agricultural use of sewage sludge [7]. Table 1 shows the lead content in the manure and in the organic materials used in fertilization as well as doses of lead introduced to the soil.

Table 1

Lead content in manure and in waste-derived organic materials as well as doses of lead introduced to soil with manure and materials

Material	Content [mgPb · kg^{-1} d.m.]	Dose [gPb · ha^{-1}]
Manure	5.59	31
Green waste compost	61.33	680
Sewage sludge	73.50	582
Compost from sewage sludge and straw	59.50	389
Mixture of sewage sludge and ash	38.73	428

The manure was a material which had a significantly different lead content than the other materials. It contained the least of this element (5.59 mgPb · kg^{-1} d.m.), and as a result the dose of the element introduced with the manure to the soil was also the lowest. The other materials contained between 38.7 mg and 73.5 mgPb · kg^{-1} d.m. The content of this element in the organic materials increased in the following order: mixture of sludge and ash < compost from sludge and straw ≈ green waste compost < sewage sludge. Along with the organic materials, between 389 g and 680 g Pb · ha^{-1} was introduced to the soil; the highest dose was introduced with the green waste compost and with the sewage sludge.

After harvest, the plant material was dried at 70 °C in a hot air dryer, milled and mineralized in a muffle furnace (8 hours, 450 °C). The residue was evaporated with hydrochloric acid solution, and then diluted in nitric(V) acid solution [10]. The total lead content in the air-dry soil sieved through a sieve with a mesh size of 1 mm was determined after incineration in a furnace (8 hours, 450 °C), evaporation with a mixture of concentrated nitric(V) and chloric(VII) acids, and dilution of the residue in hydrochloric acid solution [10]. The lead content in the above-ground parts of the maize and in the soil was determined with inductively coupled plasma atomic emission spectrometry (ICP-AES) on JY 238 Ultrace apparatus [Jobin Yvon].

Statistica software, version 10 (StatSoft, Inc.), was used for statistical elaboration of the results. A univariate analysis of variation was carried out, and the significance of differences between the mean values was estimated using the Duncan test ($\alpha \le 0.05$).

Results and discussion

Depending on the year of the research and on the treatment in the experiment, between 0.34 and 1.12 mgPb · kg^{-1} d.m. was determined in the above-ground parts of the maize (Table 2). This means that there was no lead pollution of the above-ground parts of the maize, since the permissible lead content in plants intended for feed amounts to 10 mg · kg^{-1} d.m. [11].

Table 2

Lead content in above-ground parts of maize [mgPb · kg^{-1} d.m. ±SD]

Fertilization treatment	1st year	2nd year	3rd year	Weighted mean content
No fertilization	$0.87^{d*} \pm 0.06$	$1.12^{b} \pm 0.13$	$0.39^{ab} \pm 0.10$	0.80
Mineral fertilizers	$0.80^{cd} \pm 0.04$	$0.96^{b} \pm 0.24$	$0.45^{ab} \pm 0.11$	0.77
Manure	$0.77^{bcd} \pm 0.09$	$1.01^{b} \pm 0.02$	$0.50^{b} \pm 0.14$	0.79
Green waste compost	$0.60^{a} \pm 0.02$	$1.01^{b} \pm 0.06$	$0.40^{ab} \pm 0.08$	0.68
Sewage sludge	$0.62^{a} \pm 0.13$	$0.74^{a} \pm 0.07$	$0.45^{ab} \pm 0.04$	0.62
Compost from sewage sludge and straw	$0.67^{ab} \pm 0.09$	$0.92^{ab} \pm 0.02$	$0.34^{a} \pm 0.07$	0.66
Mixture of sewage sludge and ash	$0.70^{abc} \pm 0.10$	$1.06^{b} \pm 0.16$	$0.40^{ab} \pm 0.02$	0.74

* Mean values in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Duncan test.

Maize accumulates uptaken trace elements mainly in roots [4, 12], hence the low lead content in the above-ground parts. For example, the obtained by Sekara et al [12] ratio value of the lead content in the above-ground parts of maize to the lead content in roots was 0.21. Bi et al [13] state that lead located in maize leaves and grains comes mainly from foliar uptake of atmospheric Pb, whereas lead taken up by plant from soil is accumulated mainly in stalk and root tissues.

In all years of the research, the fertilized plants contained statistically significantly less lead than the control plants or the differences in the lead content in the biomass were not statistically significant. In the 1st year of the experiment, the lead content in the maize fertilized with materials derived from waste was 20–31 % lower than in the non-fertilized plants. In the following year, the plants fertilized with sewage sludge again contained significantly less (by 34 %) of the element than the control plants. In the third year of the experiment, all the plants contained significantly less lead than the plants harvested in the two previous years. At the same time, the applied fertilization did not lead to statistically significant changes in the content of the element in the yield when compared to the content determined in the control plants. The weighted mean content of lead in the fertilized plants was by 1–22 % lower than the content in the plants cultivated on non-fertilized soil. The lowest mean lead content (0.62 mg · kg^{-1} d.m.) was found in the plants harvested from the treatment with sewage sludge fertilization.

In the authors' own research, no increase in the lead content in the plants as a result of fertilization with organic materials derived from waste was found. Labetowicz et al [14] showed, however, that soil fertilization with compost generated from unsegregated municipal waste results in an increase in lead content in plants (fodder beet roots and leaves, barley grains and straw as well as grass). Similarly to the authors' own research, Akdeniz et al [15] did not show a statistically significant effect of fertilization with sewage sludge on lead contents in sorghum leaves and grains. Jamali et al [16] as well as Singh and Agrawal [17, 18] obtained different results. They found an increase in content lead in wheat grain, chard leaves and roots as well as in bean seeds. In one part of the research, however, the authors used a large addition of sewage sludge, amounting to 20–40 % of the soil mass [16, 17].

The amount of the element collected with the plant yield was calculated as a product of the content of that element in the yield and the amount of that yield. In the authors' own research, despite a relatively high lead content in the control plants, the lead uptake from the fertilized soil was generally higher than from the soil of the control treatment (as a result of low yield from the non-fertilized plants [9]), as shown in Fig. 1.

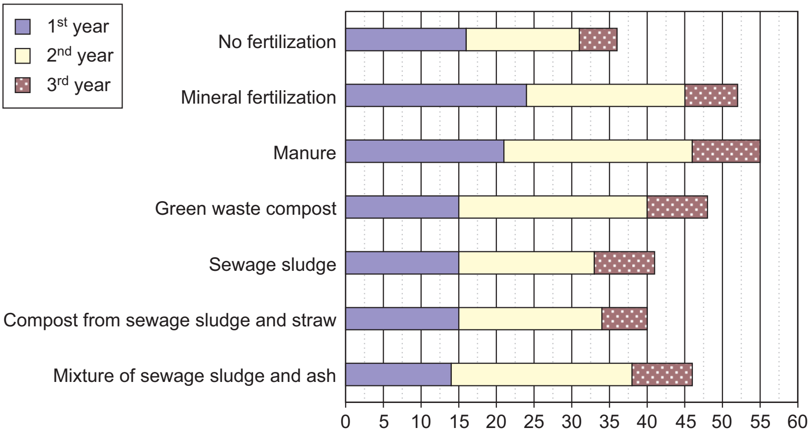

Fig. 1. Amount of lead taken up by maize [gPb · ha^{-1}]

The non-fertilized plants took up in total 36.6 g lead from 1 ha of soil. The total uptake of the element from the fertilized soil was between 109 and 148 % of the uptake from the control soil.

The lead content in the soil from the experimental field was between 22.9 and 29.3 mg · kg^{-1} d.m. (Table 3). As specified by Kabata-Pendias et al [16], natural lead content in medium soil (which was examined in the authors' own experiment) is up to 40–60 mg · kg^{-1} d.m., depending on soil pH values. The soil from the experimental field contained less lead, so it was not polluted with this element. The lead content in the studied soil also did not exceed the permissible content in soils of agricultural lands, established in the regulation on soil and earth quality standards [20] amounting to 100 mg · kg^{-1} d.m. In addition, the lead content in the soil was lower than 60 mg · kg^{-1} d.m., which is the permissible content established for fertilizing use of sewage sludge [7].

The lowest lead content was found in the soil fertilized with mineral fertilizers. In the 1st year of the research, the soil fertilized with the green waste compost and with a mixture of sewage sludge and hard coal ash contained significantly more of the element (by 23–28 % more). In the following year, soil of the four treatments was characterized by a significantly higher lead content than the soil fertilized with mineral fertilizers – it applied to the non-fertilized soil as well as the soil fertilized with the mixture of sludge and ash, the green waste compost and sewage sludge (16–24 % more lead).

Table 3

Content of total forms of lead in soil [mgPb · kg^{-1} d.m. ±SD]

Fertilization treatment	1st year	2nd year	3rd year
No fertilization	$26.5^{ab*} \pm 3.3$	$27.1^{b} \pm 1.9$	$27.0^{ab} \pm 2.9$
Mineral fertilizers	$22.9^{a} \pm 0.6$	$23.2^{a} \pm 2.4$	$24.8^{a} \pm 2.3$
Manure	$25.6^{ab} \pm 2.4$	$25.6^{ab} \pm 1.9$	$27.8^{ab} \pm 0.1$
Green waste compost	$29.3^{b} \pm 5.1$	$28.1^{b} \pm 4.1$	$29.2^{b} \pm 3.5$
Sewage sludge	$27.1^{ab} \pm 3.0$	$28.8^{b} \pm 1.3$	$28.0^{ab} \pm 2.4$
Compost from sewage sludge and straw	$26.5^{ab} \pm 1.8$	$25.8^{ab} \pm 1.1$	$26.6^{ab} \pm 1.2$
Mixture of sewage sludge and ash	$28.2^{b} \pm 1.0$	$27.0^{b} \pm 1.3$	$28.2^{ab} \pm 0.7$

* See Table 2.

In the authors' own research, the non-fertilized soil did not differ significantly in the lead content from the fertilized soil. However, Jamali et al [16], Singh and Agrawal [17] as well as Weber et al [21] point out to a possibility to increase total content of lead in soil as a result of fertilization with sewage sludge and compost from municipal sewage coming from a heavily industrialized area. Otherwise, Antonkiewicz [22] did not find a statistically significant effect of using mixtures of sewage sludge and fly ash on the lead content in soil.

As highlighted above, in the authors' own research no soil or plant pollution with lead as a result of using the green waste compost, sewage sludge or sludge-containing materials was detected. Application of relatively small doses of those materials was one of the causes. The risk of environmental pollution with heavy metals increases if applied doses of these materials are higher and because of those doses of individual heavy metals introduced to soil are also high. Availability of elements in soil and sludge, dependent on their form of occurrence [23], is also important.

Conclusions

1. During the three-year field research, fertilization with mineral fertilizers, manure and waste-derived organic materials, no pollution of the soil or the above-ground parts of maize with lead was found.

2. When comparing to the lead content determined in the non-fertilized plants, no statistically significant effect of fertilization on the lead content in the maize was found or the fertilized plants contained considerably less of the element than the control plants. The fertilized plants had a lower mean content of lead than the non-fertilized ones.

3. The lowest lead content was found in the soil fertilized with mineral fertilizers. The soil fertilized with compost from green waste (all the years), sewage sludge (2nd year) as well as with a mixture of sludge and ash (1st and 2nd year) contained significantly more lead than the soil fertilized with mineral fertilizers.

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ZAWARTOŚĆ OŁOWIU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

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Abstrakt: Celem badań było określenie wpływu nawożenia materiałami organicznymi pochodzenia odpadowego na zawartość i pobranie ołowiu przez kukurydzę oraz na ogólną zawartość ołowiu w glebie. Trzyletnie doświadczenie polowe obejmowało 7 obiektów: glebę nienawożoną (kontrola) oraz glebę nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową była kukurydza uprawiana na kiszonkę. Zawartość ołowiu w częściach nadziemnych roślin i glebie oznaczono metodą ICP-AES.

W trakcie prowadzenia badań nie stwierdzono zanieczyszczenia gleby i części nadziemnych kukurydzy ołowiem. Nie wykazano istotnego statystycznie wpływu nawożenia na zawartość ołowiu w kukurydzy lub rośliny nawożone zawierały istotnie mniej pierwiastka niż rośliny z obiektu kontrolnego. Najmniejszą średnią ważoną zawartość ołowiu stwierdzono w kukurydzy nawożonej kompostem z odpadów zielonych, osadem ściekowym oraz kompostem z osadu i słomy. Gleba nawożona nawozami mineralnymi zawierała najmniej ołowiu. Gleba nawożona kompostem z odpadów zielonych (wszystkie lata), osadem ściekowym (II rok) oraz mieszaniną osadu i popiołu (I i II rok) zawierała istotnie więcej ołowiu niż gleba nawożona nawozami mineralnymi.

Słowa kluczowe: odpadowe materiały organiczne, osad ściekowy, kompost, ołów, kukurydza, gleba

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HEAVY METALS CONTENT AND BIOCHEMICAL INDICATORS IN BIRCH LEAVES FROM POLLUTED AND CLEAN AREAS

ZAWARTOŚĆ METALI CIĘŻKICH ORAZ WSKAŹNIKI BIOCHEMICZNE W LIŚCIACH BRZOZY Z TERENÓW ZANIECZYSZCZONYCH I CZYSTYCH

Abstract: There were conducted studies concerning accumulation of heavy metals (Fe, Zn, Cd and Pb) in *Betula pendula* Roth. leaves, in surface soil within cities of Silesian and Małopolska District. Additionally, there was studied guaiacol peroxidase activity and content of -SH groups.

Concentrations of heavy metals in birch leaves in most cases did not exceed permissible values. There was noticed an increased Zn content (above 100 mg/kg d.m.) in *Betula pendula* Roth. leaves on the all studied stands of Silesia. Accumulation of Fe, Zn, Cd and Pb in soils of the Silesian cities often exceeded the permissible level. The conducted studies showed that there is a positive correlation between Zn accumulation in white birch leaves and its accumulation in surface soil. There were not noticed significant differences in content of non-protein -SH groups and guaiacol peroxidase activity in *Betula pendula* ROTH. leaves coming from Silesia and Małopolska District.

Keywords: *Betula pendula* Roth., heavy metals, guaiacol peroxidase, -SH groups

Introduction

Because of the increasing population and industrialization plants are affected by a wide array of substances, inter alia heavy metals, that contaminate air, water and soil [1].

Biological material such as lichens, tree bark, tree rings and leaves of higher plants had been used to detect the deposition, accumulation and distribution of metals [2]. Higher plants are usually not as suitable biomonitors as lichens and mosses are often missing, higher plants can act as biomonitors. In industrial and urban areas higher plants

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can give better quantifications for pollutant concentrations and atmospheric deposition than non-biological samples [3]. Foliage analysis has been used as a valid indicator of air pollution and in order to identify and possible polluted areas classification according to their pollution level [2].

Defending against heavy metal contamination plants developed defense mechanisms which allow them to grow and expansion in the contaminated environment. Within the confines of heavy metal tolerance plants separate toxic compounds in vacuole (sequestation), there are induced antioxidant enzymes *eg* superoxide dismutase, catalase and peroxidase [4], plants also release compounds complexing metals such as phytosiderophores, organic acids, free amino acids, peptides such as glutathione, phytohelatins and metallothioneins [5, 6]. Ecophsiological changes in the urban trees may be used as heavy metal stress biomarkers [1]. Activities of antioxidant enzymes in trees have been reported in the literature and used as in indicator in pollutions monitoring [7]. Similarly non protein compounds rich in -SH groups which are important factors determining plant tolerance to heavy metals ions [8].

Betula pendula Roth. is a common species found in urban parks in many cities in Poland. Also silver birch has proved to be a good bioindicator of heavy metals in contaminated environments of both natural and anthropogenic origin [9].

The aim of this work was evaluation of the heavy metals concentration in *Betula pendula* Roth. leaves and in soil in polluted area in Silesia in comparison to a potentially unpolluted area of Małopolska. Looking for indicators of stress caused by heavy metals we studied the activities of guaiacol peroxidase and non-protein -SH groups content.

Materials and methods

Material (*Betula pendula* Roth. leaves and soil) were collected in June and July 2008 from the eight parks localized on: Silesian area (Silesian Park of Culture and Recreation in Chorzow, urban park in Szopienice, Bytkowski Forest, Alfred's Park) recognized as a polluted area and from Malopolska District (urban park in Jaszowice, urban park in Brzeszcze, urban park in Bobrek and ethnographic park in Wygielzow) which was recognized as an area potentially free from heavy metal pollution.

Soil sampling

Soil Samples were taken from the two depths: 0–10 cm and 10–20 cm. The soil samples were air-dried and sieved through a 1 mm sieve. Metals were extracted with 10 % HNO_3 [10]. The concentration of metals (Zn, Cd, Pb and Fe) was measured with flame absorption spectrometry (Unicam 939 Solar). The quality of the analytical procedures was controlled using reference material (Certified Reference Material CTA-OTL-1 Oriental Tobacco Leaves).

Plants samples

Leaves of *Betula pendula* Roth. were collected randomly from ten trees in each of the parks.

Leaves were washed in tap and distilled water, dried at 105 ^{o}C to a constant mass and grounded to a fine powder, then dry mineralized at 450 ^{o}C and dissolved in 10 % HNO_3. After filtration the metal (Zn, Cd, Pb and Fe) contents was determined by the flame Atomic Absorption Spectrometry [10]. The quality of the analytical procedures was controlled using reference material (Certified Reference Material CTA-OTL-1 Oriental Tobacco Leaves).

To measure the contents of -SH groups, the plant material was homogenized in a 5 vol/g mixture containing 2 % 5-sulphosalicylic acid, 1 mM EDTA and 0.15 % sodium ascorbate. The extract was centrifuged at 20 000 × g for 10 min. The absorbance at 415 nm was read 1 min after addition DTNB (5,5'-dithio-bis(2-nitrobenzoic acid). The number of non-protein -SH groups was calculated from the standard curve prepared using L-cysteine and expressed as nmol -SH g^{-1} fresh mass [11].

Guaiacol peroxidase POD activity was measured according to Fang and Kao [12]. Leaf tissues were homogenized with 100 mM sodium phosphate buffer (pH 6.8) in a chilled pestle and mortar. The homogenate was centrifuged at 12000 × g for 20 minutes. The POD activity was measured in a reaction mixture that contained enzyme extract, phosphate buffer (pH 5.8), H_2O_2 and guaiacol. The increase in absorbance was recorded in the spectrophotometer at 470 nm and a unit of peroxidase activity was expressed as a change in absorbance per minute and per gram fresh mass of tissue.

Statistical analysis

The data were processed using software Statistica to compute significant statistical differences between samples ($p < 0.05$) according to Tuckey's multiple range test and to compute Pearson correlation coefficients.

Results and discussion

Contents of the studied heavy metals in soil from levels of 0–10 cm and 10–20 cm and in *Betula pendula* Roth. leaves are presented in the Table 1 and 2.

On the all studied sites localized in Silesia there was noticed an outpass of permissible values given by Kabata-Pendias and Pendias [13] for the studied elements. Heavy metal content in the parks of Malopolska was within limits recognized as normal values.

Pb content in soil closely depends on mineralogical and granulometric composition and derivation of soil bedrocks but simultaneously occurrence of this element in soil surface is, first of all, connected with anthropogenic factors. Pb content in unpolluted soils should amount to 20 mg/kg, however Gambus and Gorlach [14] increase this range to 25 mg/kg, giving also Pb content for the polluted soils within 4560 mg/kg. Permissible Pb concentration in soil is 100 μg/g [13]. Lukasik et al [15] in studies on

Table 1

The concentrations of heavy metals in fractions of the soils extracted with HNO_3 [$mg \cdot kg^{-1}$ air-dry mass], average ±SD

Metal / Site	Fe [mg/kg]		Zn [mg/kg]		Cd [mg/kg]		Pb [mg/kg]	
	0–10 cm	10–20 cm	0–10 cm	10–20 cm	0–10 cm	10–20 cm	0–10 cm	10–20 cm
SPCR	3031.7 ± 134.6^{a}	2010 ± 152.3^{a}	1526.7 ± 66.1^{a}	1171.3 ± 112.4^{a}	15.7 ± 0.2^{a}	14.59 ± 0.1^{a}	619.9 ± 46.8^{a}	387.03 ± 8.5^{a}
Park in Szopienice	2341 ± 124.5^{b}	954.4 ± 52.5^{b}	1804.7 ± 74.3^{b}	714.4 ± 58.4^{b}	18.6 ± 0.7^{b}	8.2 ± 0.3^{b}	420.5 ± 23.7^{b}	209.9 ± 7.7^{b}
Bytkowski Forest	3550 ± 18.4^{c}	3779.3 ± 76.0^{c}	1926.0 ± 13.7^{c}	2181 ± 50.6^{c}	29.6 ± 1.6^{c}	43.2 ± 0.6^{c}	991.8 ± 50.1^{c}	1145.3 ± 72.9^{c}
Alfred's Park	3345 ± 135.5^{c}	3137.5 ± 91.2^{d}	1737.7 ± 29.1^{b}	1343.5 ± 51.6^{a}	14.3 ± 0.06^{a}	12.5 ± 0.3^{d}	437.1 ± 0.07^{d}	393.2 ± 0.3^{d}
Park in Jawiszowice	906.6 ± 71.0^{d}	1056.7 ± 120.1^{bc}	65.2 ± 2.6^{d}	47.1 ± 4.5^{d}	0.76 ± 0.02^{d}	0.5 ± 0.02^{e}	23.9 ± 0.2^{e}	20.9 ± 0.4^{e}
Park in Brzeszcze	992.2 ± 66.2^{d}	1214.3 ± 164.0^{be}	78.4 ± 0.7^{d}	157.1 ± 13.4^{e}	0.82 ± 0.02^{d}	1.98 ± 0.4^{g}	41.9 ± 1.3^{f}	103 ± 2.9^{f}
Park in Bobrek	1829.5 ± 243.9^{e}	2687 ± 136.8^{f}	55.5 ± 7.1^{d}	69.7 ± 4.2^{f}	1.3 ± 0.1^{d}	1.4 ± 0.07^{g}	46.7 ± 1.4^{f}	52.6 ± 1.4^{g}
Park in Wygielzow	696.2 ± 69.5^{f}	388.8 ± 47.0^{g}	94.2 ± 2.2^{e}	32.2 ± 11.5^{d}	2.4 ± 0.5^{d}	1.18 ± 0.07^{g}	83.7 ± 1.9^{g}	36.97 ± 0.9^{h}

* a, b – values with the same letter in one column are statistically the same for $p < 0.05$.

the area of Piekary Slaskie find 4–25-fold outpass of permissible standards. In surface soil there was noticed accumulation on the level of 1506,2 mg/kg. Nadgórska-Socha et al [16] in the vicinity of the Nonferrous Smelting Plant "Szopienice" noticed values reaching up to 1350 mg/kg. Kabata-Pendias, Pendias [13] state that in Upper Silesia Pb concentration can reach from 6000 to 8000 mg/kg of soil.

Table 2

The concentrations of heavy metals in the leaves of *Betula pendula* Roth. [mg · kg^{-1} dry mass]

Metal / Site	Fe		Zn		Cd		Pb	
	Average	SD	Average	SD	Average	SD	Average	SD
SPCR	20.8a	0.7	178.3c	0.8	0.8bc	0.1	3.4d	0.3
Park in Szopienice	84.1d	4.3	177.7c	1.0	1.2d	0.2	9.5e	0.5
Bytkowski Forest	31.4b	5.4	171.5d	4.3	0.6ab	0.2	6.5f	1.4
Alfred's Park	60.1c	3.9	166.8d	1.2	0.3a	0.1	9.1e	0.4
Park in Jawiszowice	39.8b	3.4	139.2a	2.7	0.4a	0.03	1.2a	0.1
Park in Brzeszcze	44.0bc	13.3	116.3b	0.4	0.2a	0.01	2.2b	0.1
Park in Bobrek	33.2b	6.2	131.2a	7.0	0.9cd	0.2	2.3b	0.1
Park in Wygielzow	30.8b	0.3	134.2a	0.3	0.5ab	0.004	1.8b	0.2

* a, b – values with the same letter in one column are statistically the same for $p < 0.05$.

To the most Cd polluted soils belong soils of southern Poland, especially Silesia and Malopolska Districts. From monitoring studies of Terelak et al [17] it results that soils of higher than natural Cd content make up 67.3 % in Silesia and 45.3 % in Malopolska. The range of mean Cd contents in world soils is within 0.2–1.05 mg/kg, for Poland it amounts to 0.2 mg/kg [13]. In soils of Silesian parks the stated Cd concentrations were higher than the permissible one (4 mg/kg) [13]. Many authors show that on polluted areas Cd content can strongly exceed the norms. Relatively high Cd content was reported by Nadgórska-Socha et al [16] in the closest vicinity of Nonferrous Smelting Plant "Szopienice", the zinc wastes heap and a former galmey site were Cd content was within 43.3–123 mg/kg.

Mean Zn concentration in soils of different world countries is within 30–120 μg/g. Permissible Zn content in soil is 300 mg/kg [13]. Lukasik et al [15] in 5 parks on the area of Piekary Slaskie noticed in surface soil 0–5 cm Zn content of 4937 mg/kg, 10–20 cm 4053.2 mg/kg. In Krakow region the mean Zn concentration in the studied surface soils was 104.2 mg/kg, varying in the range of 36.1–732.0 mg/kg [14].

Fe content in natural soil solutions amounts to 470 mg/kg on average [13]. In soils samples collected from the eight parks higher than natural content of Fe was found. The Fe concentrations obtained in this study are higher than the ones obtained by Jankiewicz and Adamczyk [18] in the soil samples collected in the area of the city of Lodz.

The order of concentration Zn > Fe > Pb > Cd was found in leaves of *Betula pendula* Roth. on the investigated areas.

In case of Cd, Pb and Fe obtained concentrations in birch leaves did not exceed values recognized as toxic ones (respectively for Cd 5–30 mg/kg d.m., for Pb 30–300 mg/kg d.m. and Fe 200–400 mg/kg d.m.). Only Zn content was within the range recognized as a toxic one (100–400 mg/kg d.m.) [13].

In case of Pb obtained values were considerably lower than concentrations noticed by Łukasik et al [15] in *Acer pseudoplatanus* L. leaves (13–51 mg/kg d.m.) and *Robinia pseudoacacia* L. (38–53 mg/kg d.m.) growing in urban parks in Piekary Slaskie. Comparable values to the ones obtained in parks of Malopolska were noticed by Nadgorska-Socha et al [2] where in *Philadelphus coronarius* L leaves from urban parks of Cracow and Zagaje Stradowskie Pb content was within 2.39–3.14 mg/kg d.m.

Cd is not an element which plants need for their development, however it is extremely easily collected by root system and leaves, in general, proportionally to concentration in the environment [13]. Cd values not exceeding toxic values and lower than the ones in the present study were noticed by Nadgorska-Socha et al [2] in *Philadelphus coronarius* L. leaves collected from urban parks of Malopolska.

Birch is not mentioned in literature as a hyperaccumulator, however it shows exceptional relationship with Zn, much bigger than other tree species [19]. Steinnes et al [20] determined Zn content in *Betula pubescens* Ehr. leaves from Kola peninsula as 210 mg/kg d.m. on average. Hrdlicka et al [21] notice Zn content in *Betula pendula* ROTH leaves growing in little polluted environment in Rudawy amounting to 189 mg/kg d.m on average, and in the vicinity of a nonferrous smelting plant in Bukowno near Olkusz – amounting to 750–930 mg/kg.

In comparison to results of other authors Zn accumulation in *Betula pendula* Roth. leaves on the studied sites is not high. Higher Zn concentrations in *Betula pendula* Roth. leaves in noted Lukasik et al [15] in *Acer pseudoplatanus* L. and *Robinia pseudoacacia* L. leaves in parks on the area of Ruda Slaska where Zn concentration was within 141–342 mg/kg d.m.

Fe content in plants changes considerably in vegetative period to a different extend in individual plant organs, the most often it is between 10–400 μg/g d.m. Petrova [22] on the area of the town of Plovdiv, in *Betula pendula* Roth. Leaves, noticed Fe content from 89.3 mg/kg to 248.8 mg/kg.

In the study there was not noticed an increase of guaiacol peroxidase activity (Fig. 2) or an increase of number of non-protein SH groups (Fig. 1) on areas of a high degree of heavy metal pollution in relation to areas recognized as potentially free from pollution. The both indicators were on the similar level, regardless of a study site which the studied birch leaves came from.

Guaiacol peroxidase belongs to a big group of peroxidases taking part in the system of antioxidant defense of a plant cell [23]. Peroxidase activity is often used as a potential indicator of metal toxicity [24] However, as in this study also Pongrac et al [25] reported no change in GPX activity in *Thalspsi praecox* and *T. caerulescens* in the presence of Cd and Zn, similar results obtained Gratao et al [26] in leaves, roots and fruits of tomato grown in conditions of cadmium contamination. Baycu et al [1], examining the activity of POD in the leaves of Acer and Alianthus growing in urban

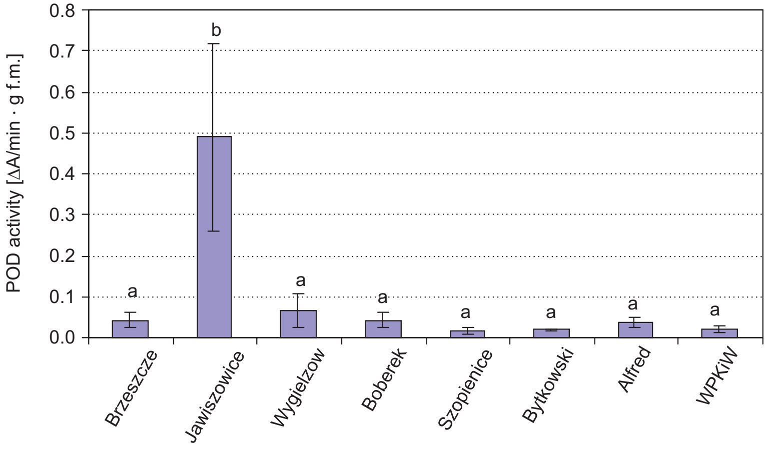

Fig. 1. Mean POD activity in leaves of *Betula pendula* Roth. Values with the same letter are statistically the same for $p < 0.05$

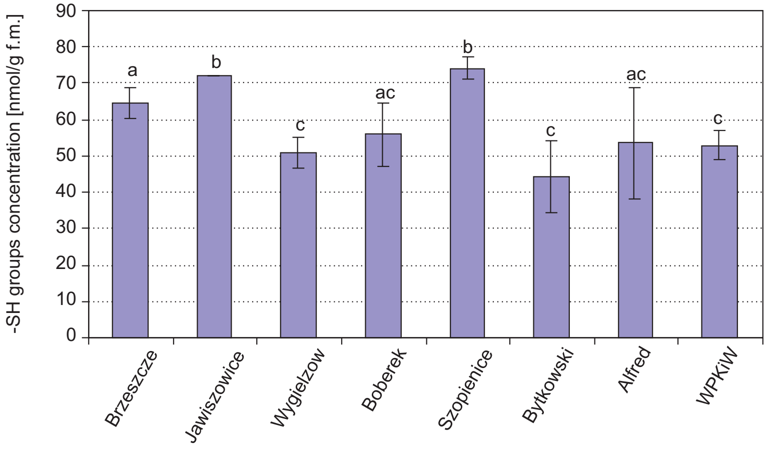

Fig. 2. Mean -SH groups concentration in leaves of *Betula pendula* Roth. Values with the same letter are statistically the same for $p < 0.05$

parks in Turkey, said both increase and decrease in peroxidase activity compared to control.

Many authors *eg* [8, 26,] reported an increase in number of non-protein-SH groups in response to elevated trace metal content which was not observed in the present study. Perhaps it was due to a small accumulation of metals studied in *Betula pendula* Roth. leaves or increased resistance of this species on these metals and the problem requires further study.

Conculsions

The obtained heavy metals concentrations in *Betula pendula* Roth. leaves did not exceed the levels considered as toxic for plants and because of this in the study we haven't observed the growth of non -SH groups level and peroxidase activity at contaminated sites. The environmental studies of ecophysiological parameters seem to be an essential in bioindication and also necessary for confirmation obtained results in controlled conditions and should be continued.

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ZAWARTOŚĆ METALI CIĘŻKICH ORAZ WSKAŹNIKI BIOCHEMICZNE W LIŚCIACH BRZOZY Z TERENÓW ZANIECZYSZCZONYCH I CZYSTYCH

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Abstrakt: Przeprowadzono badania dotyczące kumulacji metali ciężkich (Fe, Zn, Cd, Pb) w liściach brzozy brodawkowatej i w wierzchniej warstwie gleby na terenie miast Slaska oraz Małopolski. Dodatkowo w liściach *Betula pendula* Roth. badano aktywność peroksydazy gwajakolowej i zawartość niebiałkowych grup -SH.

Koncentracje metali ciężkich w liściach brzozy w większości przypadków nie przekraczały wartości dopuszczalnych. Odnotowano podwyższoną zawartość Zn (powyżej 100 mg/kg s.m.) w liściach *Betula pendula* Roth. na wszystkich badanych terenach Śląska. Kumulacja Fe, Zn, Cd, Pb w glebach miast Śląska często wielokrotnie przekraczała poziom dopuszczalny. Przeprowadzone badania wykazały, że istnieje dodatnia korelacja pomiędzy kumulacją Zn w liściach brzozy brodawkowatej a jego kumulacją w wierzchniej warstwie gleby. Nie odnotowano wyraźnych różnic w zawartości niebiałkowych grup -SH i aktywności peroksydazy gwajakolowej w liściach *Betula pendula* Roth. pochodzących ze Śląska i Małopolski.

Słowa kluczowe: *Betula pendula* Roth., metale ciężkie, peroksydaza gwajakolowa, grupy -SH

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CHANGES IN ACTIVITY OF ACID HYDROLASES IN TISSUES OF WILD PHEASANTS INDUCED BY HEAVY METALS

ZMIANY AKTYWNOŚCI KWAŚNYCH HYDROLAZ W TKANKACH DZIKICH BAŻANTÓW WYWOŁANE PRZEZ METALE CIĘŻKIE

Abstract: The aim of the study was to determinate the activity of chosen acid hydrolases in tissues of pheasants (*Phasianus colchicus* L.) and first attempts to use these enzymes as biomarkers of the effect of birds exposure to heavy metals in the environment. The samples of liver, kidneys and testes were collected from wild pheasants shot in the Podkarapacie region in contaminated (n = 5) and clear (n = 5) areas. Tissues were examined for the cadmium and lead concentrations by AAS method, as well as the activity of five hydrolases.

The major site of cadmium accumulation were kidneys, the levels of Cd found in liver and testes were by 5-fold and 30-fold lower ($P < 0.05$), respectively. Similarly, Pb concentrations observed in the liver and testes were lower than in kidney, by 1.5-fold and 6-fold, respectively. The presence of four glycosidases and arylsulphatase in all examined tissues was demonstrated and N-acetyl-β-D-glucosaminiadase (NAG) was identified as the most active enzyme in all studied tissues. Significant differences ($P < 0.05$) were observed only in the level of NAG activity in liver of pheasants inhabiting the contaminated area as compared to the birds from the clear region (control group). We conclude that the determination of NAG in birds organs can be used as biomarker of environmental exposure to cadmium.

Keywords: pheasant, heavy metals, biomarker, acid hydrolases

Introduction

Increasing pollution and environmental degradation are difficult to avoid because of the intense, constant development of many industries and the energy sector [1]. The presence of heavy metals cannot be found in the heavily industrialized regions only, but

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also in natural and agricultural ecosystems. Among the pollutants prominent place is occupied by heavy metals such as lead, cadmium and mercury.

Determination of environmental metals does not reflect the level of their impact on health and biochemical changes in the body of animals or people (the effects of exposure) [2]. Therefore, in recent years there has been a growing interest in using bioindicators for monitoring environmental pollution with heavy and toxic metals and their toxic effect for living organism [3, 4]. In this respect, pheasant play a valuable role in environmental monitoring of their vulnerability to human exploitation, sensitivity to habitat degradation, and central position in the food web [5].

The kidneys and liver are the organs affected by accumulation of toxic heavy metals in the body of animals and humans. Heavy metals originating from the air, food or water, can change the distribution of lysosomal enzymes in an intra-and extracellular fluids [4, 6–8]. Simultaneous administration of cadmium and lead caused enhancement of degenerative changes in proximal tubule cells [6, 9]. These observations suggest that the combined administration of metals causes renal damage that appears to be additive [9]. Therefore, an important issue is the search for enzymatic markers of early warning against the effects of exposure to the toxic heavy metals.

N-acetyl-β-D-glucosaminidase (NAG), one of the lysosomal enzyme, is also present in small amounts in the microsomal fraction of kidney tubule cells which activity is increased by cadmium intoxication [4, 6, 10]. According to the dose of cadmium, the number and size of lysosomes are increased, indicating a subtile cell damage. Therefore, NAG is a recognized marker of the cytotoxic effects of heavy metal compounds [11–13]. The increased levels of urinary N-acetyl-β-D-glucosaminidase observed in cadmium-exposed workers could be used as biomarkers for suggesting preventive measure [14, 15].

Besides NAG, other lysosomal enzymes such as: β-galactosidase, α- and β-mannosidase, arylsulphatase were also used for the diagnosis of multiple tissues damage [12, 16–18]. Since then, the presence of glycosidases and arylsulphatase has been demonstrated only in reproductive tissues and semen of pheasant [19].

In this work the suitability of using chosen acid hydrolases from pheasants tissues as biomarkers of environmental exposure of birds to heavy metals pollution was studied.

Materials and methods

1-year old male pheasants (n = 10) were shot by hunters using lead shots in February (the mean body weight 1.20 ± 0.26 kg). Birds originated from the urban area of Rzeszow (group A, n = 5), and from clear region (group B, n = 5) both localized in South-Eastern Poland (Podkarpacie region). Tissue samples were collected immediately and transported on ice to the laboratory. They were stored at 20 ^{o}C until analyzed. Heavy metals and enzyme assays were performed on livers, kidneys and testes of birds.

Cadmium (Cd) and lead (Pb) concentrations were assayed by AAS method using Hitachi Z-2000 (Japan) spectrophotometer equipped with a graphite furnace after prior microwave mineralization in HNO_3 (Speedwave Four, Berghof, German). The metal concentrations were expressed on a wet weight basis (mg/kg).

The activity of five lysosomal enzymes: N-acetyl-β-D-glucosaminidase (NAG; EC 3.2.1.30), α- and β-D-mannosiadase (α-MAN; EC 3.2.1.24, β-MAN; EC 3.2.1.25), β-galactosidase (β-GAL; EC 3.2.1.23) and arylsulphatase (ARYL; EC 3.1.6.1) was determined. Enzymatic activities were tested in the supernatant of tissues homogenates (10% w/v in a saline with 0.1% Triton additive), according to the method of Barrett and Heath [20]. Arylsulphatase activity assay was performed according to the Baum method [21]. The synthetic substrates (Sigma, USA) in optimum pH were used and the absorbance of released 4-nitrophenol was measured at 400 nm (for ARYL 4-nitrocatechol at 515 nm). The enzymatic activity was expressed in units (U) [$\text{mmol} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$]. Determination of the protein content of the tissues was performed by the Lowry method [22] using bovine serum albumin as a standard.

Differences between tissues were assessed using Kruskal-Wallis and Mann-Whitney U-tests ($P < 0.05$). Coefficients of correlation were calculated using Spearman's correlation analysis.

Results and discussion

Enhanced levels of both heavy metals were observed mainly in kidneys, following by liver and testes (Table 1). The levels of Cd found in liver and gonads were 5-fold and 30-fold lower ($P < 0.05$) than observed in kidneys, respectively. Similarly, Pb concentrations observed in the liver and testes were respectively 1.5-fold and 6-fold lower than in kidneys ($P > 0.05$). There was no synergistic relationship between lead and cadmium tissue concentration ($P > 0.05$).

Table 1

Concentrations of cadmium and lead (means ±SD; mg/kg wet weight) in tissues of pheasants derived from urbanized area (Group A) and clear region (Group B)

Heavy metal	Tissues		
	Liver	Kidneys	Testes
	Cadmium		
Total	0.67 ± 0.84^{a}	$3.33 \pm 2{,}76^{b}$	0.07 ± 0.16^{c}
Group A	1.08 ± 0.80*	5.73 ± 0.69*	0.11 ± 0.13
Group B	0.25 ± 0.08	0.92 ± 1.25	0.03 ± 0.18
	Lead		
Total	0.17 ± 0.03	0.25 ± 0.04	0.04 ± 0.06
Group A	0.16 ± 0.13	0.24 ± 0.04	0.06 ± 0.08
Group B	0.18 ± 0.04	0.17 ± 0.04	0.02 ± 0.03

* – significant differences between A and B groups ($P < 0.05$); [a, b, c] – significant differences between concentrations of heavy metals in tissues ($P < 0.05$).

The cadmium concentration in liver and kidneys of pheasants coming from urbanized area (group A) was significantly higher ($P < 0.05$), but great individual variability in Cd level was observed (Table 1). This tendency was not occurred for lead content in all tissues studied.

These results are in agreement with other authors finding that birds from urban areas have higher tissues concentrations of both lead and cadmium [23, 24]. Moreover, the elevated levels of cadmium damage mainly the kidneys of birds and mammals, although the male reproductive system was also affected. Probably this metal is co-responsible for a decrease in the number of population of Mallard observed in wetlands in North-Western Poland [25].

Table 2

The specific activity of hydrolytic enzymes [mU/mg protein] in tissues of shot pheasants (*Phasianus colchicus* L.) (n = 10)

Enzyme	Activity of hydrolytic enzymes [mU/mg protein]		
	Liver	Kidneys	Testes
NAG			
mean ±SD	348.54 ± 70.42[a]	744.21 ± 115.18[b]	1104.04 ± 203.12[c]
min.	265.62	530.72	907.28
max.	435	861.92	1413.64
variability [%]	20.2	15.5	18.4
β-GAL			
mean ±SD	36.35 ± 8.44[a]	43.32 ± 6.37[a]	233.91 ± 56[b]
min.	21.60	35	161.8
max.	47.80	50.87	295.86
variability [%]	23.2	14.7	23.9
α-MAN			
mean ±SD	44.71 ± 8.04[a]	52.17 ± 7.08[a]	34.87 ± 7.87[a]
min.	34.14	41.25	25.87
max.	54.09	62.52	47.1
variability [%]	18	13.6	22.6
β-MAN			
mean ±SD	18.55 ± 3.98[a]	18.3 ± 2.82[a]	27.35 ± 3.82[a]
min.	14.21	14.89	23.97
max.	24.66	23.04	34.5
variability [%]	21.5	15.4	14
ARYL			
mean ±SD	24.26 ± 6.42[a]	22.4 ± 4.43[a]	65.63 ± 16.38[b]
min.	16.58	17.28	41.33
max.	31.84	29.26	84.55
variability [%]	26.5	19.8	25

[a, b, c] – significant differences between activity of enzymes in tissues ($P < 0.05$).

Research carried out by Toman et al [5] showed that the cadmium concentrations in kidneys and liver increased significantly in adult pheasants. The metal was accumulated especially in kidneys of the adult pheasants and reached levels up to 9.64 mg/kg wet weight after the 3 months daily cadmium intake in drinking water. Similarly, the highest cadmium concentrations were also found in the kidneys (up to 117.6 mg/kg dry weight) and liver (37.1 mg/kg dry weight) of voles fed with cadmium [2]. Moreover, histological examination of the tissues revealed some pathological changes in the structure of kidneys, liver and testes of voles after chronic exposure.

Among the analyzed enzymes NAG showed the highest activity in all examined organs of pheasants while the lowest value was marked for β-MAN (Table 2). The activity of enzymes in examined tissues of birds declined in the following order:

liver: NAG > α-MAN > β-GAL > ARYL > β-MAN,
kidneys: NAG > α-MAN > β-GAL > ARYL > β-MAN,
testes: NAG > β-GAL > ARYL > α-MAN > β-MAN.

The highest activity of enzymes was noted in the testes of birds, excluding α-MAN. Significant differences in the activity of hydrolytic enzymes ($P < 0.05$) were determined for NAG in the all studied organs of birds and for ARYL and β-GAL in the testes (Table 2). The ratio between NAG and other studied enzymes activity was much higher in liver and kidneys tissues. These results are similar to earlier research [19, 26]. In all studied organs, the lowest activity was found for β-MAN and was lower about 59% in liver, 65 % in kidneys, 22% in testes than the activity of a-MAN. A similar relationship was observed for the activity of these enzymes in testes of duck during breeding season [26].

Significant decrease ($P < 0.05$) in the level of NAG activity was observed in the liver of pheasants inhabiting the contaminated area (group A) as compared to the clear region (Fig. 1a). An adverse effect for ARYL in testes was demonstrated ($P < 0.05$) (Fig. 1b).

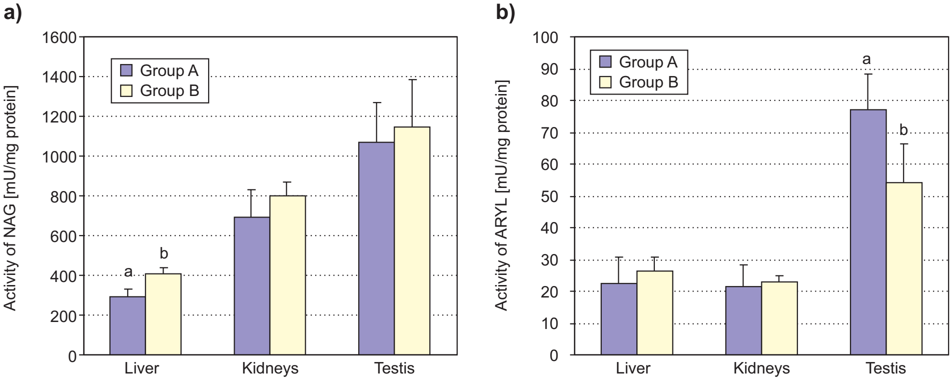

Fig. 1. The effect of environmental pollution on the activity of NAG (a) and ARYL (b) (mU/mg protein) in tissues of pheasants derived from urbanized area (Group A) and clear region (Group B); $^{a,\,b}$ – significant differences ($P < 0.05$)

Other studied enzymes, such as: β-GAL, α-MAN, β-MAN and ARYL were characterized by lower activity (Table 2). Their level in the liver and kidneys was

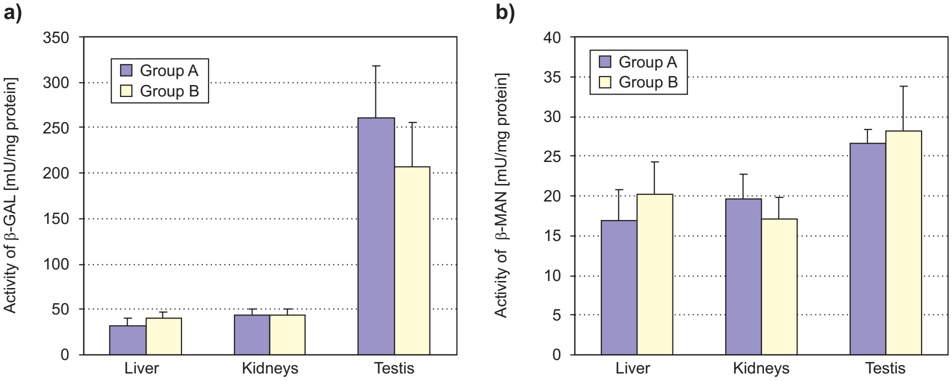

Fig. 2. The effect of environmental pollution on the activity of β-GAL (a) and β-MAN (b) (mU/mg protein) in tissues of pheasants derived from urbanized area (Group B) and clear region (Group A)

comparable and independent on the origin of birds (Fig. 1, 2a and 2b). The level of NAG activity was inversely correlated with the contents of cadmium and lead only in the liver (Table 3).

Table 3

Spearman correlation analysis of enzyme – metal interactions in pheasants tissues

Tissue/Metal	Enzyme				
	NAG	β-GAL	α-MAN	β-MAN	ARYL
Liver					
Cd	–0.71	–0.37	–0.43	–0.20	0.09
Pb	–0.77	–0.89	–0.31	–0.71	–0.54
Kidneys					
Cd	0.43	–0.26	–0.20	0.26	–0.37
Pb	0.12	0.23	0.38	0.46	0.38
Testes					
Cd	0.43	0.66	0.60	0.37	0.77
Pb	–0.31	0.37	0.94	0.14	0.54

Our findings are in agreement with study carried out by Bairati et al [11], who observed a significant decrease in activity of NAG and activity of glucuronidase with the maximum concentration of lead and manganese *in vivo* in blood plasma and *in vitro* in cultures of mitogen-activated lymphocytes.

In the opposite, Dzugan et al [12] showed an increase in the activity of NAG, β-MAN and ARYL in plasma of day-old chicks which indicated to damage kidneys and liver caused by toxicity of cadmium. Moreover, multiple researchers reported a positive correlation between excretion of cadmium ions and urinary NAG activities in humans environmentally exposed to Cd as well as in Cd-workers [10, 14, 15].

Many studies have confirmed the usefulness of NAG activity in the assessment of renal damage by impact of heavy metals such as cadmium and lead [8, 15, 27]. Brzoska et al [6] have used an experimental model of rats chronically exposed to cadmium. They observed, the increased urinary activities of NAG and its specific form (NAG-B), which were well correlated with early lesions in the main renal tubules. The enhanced excretion of enzyme due to Cd influence resulted from their leakage into cytoplasm via damage of lysosomal cellular membranes. The damage of the lysosomes and other cellular organelles, was demonstrated using well known biochemical markers of kidney status such as: low molecular weight serum protein in urine (α_1-microglobulin, β_1-microglobulin, retinol binding protein) and enzymes from the renal cortex (N-acetyl-β-D-glucosaiminidase) [28]. Therefore, the observed decrease in NAG activity in liver may be connected with excretion of lysosomal enzymes to blood.

Conclusions

It was firstly shown that cadmium and lead accumulation in tissues of pheasant affected the activity of the most active acid hydrolases NAG and this effect was significant for liver. The determination of NAG activity in pheasants liver can be suitable for monitoring of heavy metals in the environment. Due to a small birds population used in experiment it requires a further study.

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ZMIANY AKTYWNOŚCI KWAŚNYCH HYDROLAZ W TKANKACH DZIKICH BAŻANTÓW WYWOŁANE PRZEZ METALE CIĘŻKIE

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Abstrakt: Celem badań było oznaczenie aktywności wybranych kwaśnych hydrolaz w tkankach bażantów (*Phasianus colchicus* L.) oraz zastosowanie po raz pierwszy tych enzymów jako biomarkerów narażenia środowiskowego ptaków na metale ciężkie. Próbki wątroby, nerek oraz jąder zostały pobrane z bażantów odstrzelonych na Podkarpaciu w rejonie zurbanizowanym (n = 5) i ekologicznym (n = 5). Analizy tkanek obejmowały oznaczenie zawartości metali ciężkich (Cd, Pb) metodą AAS oraz aktywności kwaśnych hydrolaz.

Głównym narządem docelowym akumulacji metali ciężkich były nerki, zawartość kadmu w wątrobie oraz jądrach była niższa odpowiednio 5- i 30-krotnie. Podobną zależność zaobserwowano dla ołowiu, koncentracja tego metalu w jądrach i nerkach była niższa odpowiednio 1.5- i 6-krotnie. We wszystkich badanych tkankach stwierdzono obecność czterech glikozydaz i arylosulfatazy, przy czym najobfitszym źródłem enzymów były jądra, a najbardziej aktywnym enzymem we wszystkich tkankach była N-acetylo-β-D-glukozaminidaza (NAG). Wykazano istotne różnice ($P < 0.05$) w poziomie aktywności NAG w wątrobie bażantów bytujących na terenie zurbanizowanym w porównaniu do regionu ekologicznego. Aktywność NAG w tkankach ptaków może być przydatnym biomarkerem środowiskowego narażenia na kadm.

Słowa kluczowe: bażant, metale ciężkie, biomarker, kwaśne hydrolazy

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STEAM GASIFICATION OF MULTIWIRE LiYCY TYPE ELECTRICAL CABLE

ZGAZOWANIE PARĄ WODNĄ WIELOŻYŁOWEGO KABLA ELEKTRYCZNEGO TYPU LiYCY

Abstract: Original, non-separated pieces of the LiYCY cable (with multilayer metal/plastic (copper/PVC) structure) were gasified by steam in an excess at atmospheric pressure. Conversion of the gaseous stream was enhanced by catalytic bed of original granulated material, prepared from aluminosilicate (local clay) and calcium carbonate. In the process metal (Cu) preserved unchanged form of cords and braids and was quantitatively separated (49 % of original mass of the cable). Non-metal components (51 % of original mass of the cable) were converted to a slightly sintered non-metallic powder (3.3 % of original mass of the cable) and gaseous phase. Condensation of steam facilitated elimination of tars and oils as well as hydrochloride from the gas. It was estimated that only 5 % of carbon (from the cable components) was retained in the cooling/condensing line, mostly as water non-soluble phases. Efficiency of absorption of hydrochloride by catalytic bed and aqueous condensate was almost the same (but only 50 % of estimated total chlorine quantity was finally balanced).

Keywords: waste, electrical cables, pyrolysis, gasification

Introduction

Processing of electrical cable and wire waste is usually set to recover of metals, in the first place of copper, although recycling of some polymers has been also developed [1]. The process involves numerous mechanical operations, such as grinding, size classification, separation according to physical properties etc. Recovered metal is recycled as a copper scrap. Multiwire flexible cables represent a significant part of the electronic waste stream, which is processed especially due to high content of precious metals and copper. Recycling of electronic waste is extensively discussed in the literature, with a special attention to thermal processes [2–7]. In dedicated technologies,

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processing of these waste is carried out in reactors with molten metal bath with firing of plastics in oxygen enriched atmospheres; examples are: Noranda process, Kaldo furnace of Boliden or Umicore Isasmelt furnace [3]. In more typical copper pyrometallurgy, the presence of halides is strongly unwanted (however, volatilization of metal chlorides as a method of metal recovery is also considered in the literature [8]). On the other hand, steam gasification of electronic waste was discussed in the literature only for the supercritical state [9, 10]. Multiwire, layered, thin cables with polyvinyl chloride shielding are probably one of the major sources of chlorine in electronic waste processing. Moreover, they are combination of PVC and copper. It was reported in the literature [11] that co-presence of PVC and copper metal results in high emission of chlorinated species under pyrolytic conditions, with dominance of furans over dioxins, as well as high chlorination degree of organic compounds. Gasification with steam enables almost complete elimination of char from metals/inorganic structure and at the same time high concentration of oils and tars (condensing phases) in the product gas may be significantly reduced by catalysts [12].

Laboratory experiment described in this paper was conceived as a high temperature steam gasification (HTSG) processing of original PVC cable waste with the intention of copper components recovery and co-condensation of low-volatile species with excess of the steam in an external cooler.

Experimental section

Gasified material

Gasification experiment was performed with the LiYCY cable cut into four pieces of approximately 10 cm length. The cable was composed of 5 tinned copper multiwire cords (25 wt. %) in a colored polyvinyl chloride (*polwinit*) shielding (17 wt. %). The cords were wrapped with polyester foil (1 wt. %) and screened by the copper braid (24 wt. %). External coating of the cable was also made from polyvinyl chloride (*polwinit*) (32 wt. %).

Catalyst

Equilibration of gaseous phase was promoted by catalytic granules with diameter of approximately 5–10 mm. The height of the catalytic bed was approximately 10 cm. Granules were prepared by mixing calcium carbonate (p.a. POCH S.A.) with clay from local deposit (*Dzierzoniow county*), which was previously dried at ambient temperature and pulverized below 0.25 mm. The mixture was blended with polyethylene glycol (Carl Roth GmbH, ROTH 600, molar mass: 57–630 g/mol) and water, then homogenized. Proportion by weight of clay / carbonate / glycol / water was equal to 21/52/11/16. Catalytic granules were formed from this soft and plastic material and dried in 24 hours at 120 ^{o}C, then fired 9 hours at 950 ^{o}C and cooled down in several hours to ambient temperature. Weight losses at drying and firing were equal to 16 and 46 %, respectively. Preparation procedure was based on the one given in the literature

[13]. There was similar concentration of Al and Si (9.0 and 11.6 wt. %, respectively) in the final product and high concentration of Ca (21 wt. %). Concentrations of Fe and Mg were equal to 2.2 and 1.4 wt. %, respectively. Specific surface area (S_{BET}) was equal to approximately 16 m^2/g, the value typical for macroporous solids (with domination of pores with diameter >0.05 μm and clearly smaller share of mesopores with diameter below 0.05 μm, according to porosimetric analysis).

Reactor and experimental procedure

Gasification experiment has been performed in a quartz reactor which was a simple construction with quartz tubes of different diameters and lengths (Fig. 1).

Gasified sample of the cable pieces was placed on the perforated spacer made of heat-resistant steel (2), supported on the quartz tube with diameter of 22 mm and length of 500 cm (1c). This tube was inserted in the next one (1b) of 30 mm of diameter and 750 cm length, also covered by the perforated spacer (2). This spacer supported the catalytic bed. The third tube (1a), with diameter of 38 mm and 1000 cm length, was the external wall of the reactor. The reactor was sealed at the bottom by water sealing (5) and at the top with the temperature-resistant (up to 285 °C, Sodual Ltd.) polysiloxane sealing (4). Temperatures of catalytic bed, upper and bottom parts of the sample were measured by three thermocouples K-type (8), placed in the center of the reactor in a quartz tube shielding (3). Temperatures were registered with digital recorder APAR, AR 206/8. Water for generation of steam was supplied by tube (1d) at the bottom of the reactor. Reactor was heated by three tube furnaces (7a, b, c) separately powered by electronic controllers RE31 and RE15 with SSR units (furnaces 7c and 7b, respectively) and autotransformer (7a furnace). Temperatures of the furnaces were controlled by K-type thermocouples (6a, b, c). Polysiloxane sealing (4) was enforced at the bottom by mineral wool layer, and gases flowed from the reactor passing through the glass tube fixed in the

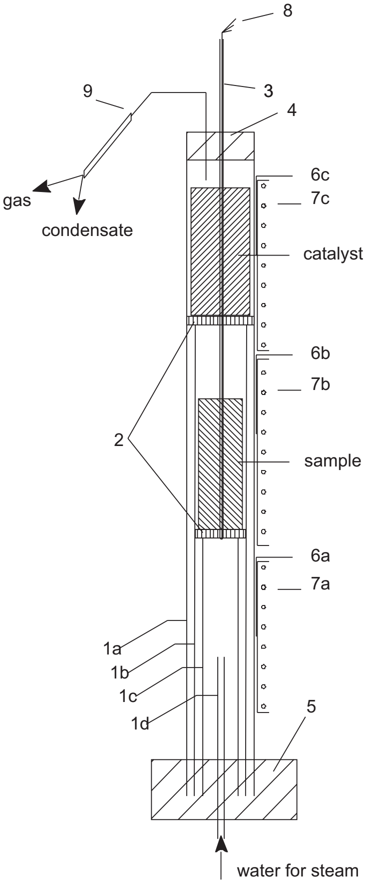

Fig. 1. Reactor used in the experiment: (1) – quartz tubes, (2) – perforated steel spacers, (3) – quartz shielding for thermocouples, (4) – polysiloxane sealing, (5) – bottom water sealing, (6) – thermocouples for controlling of the furnaces, (7) – tube furnaces, (8) – thermocouples for registering temperatures of the sample and catalytic bed, (9) – Liebig condenser

sealing. The tube was fitted to the Liebig condenser (9) with the ground glass joint. Excess of unreacted steam and non-volatile species (tars/oils) condensed in the Liebig condenser (9) and were collected in the glass flask. Non-condensing gases passed out the condensing line through the final water sealing (water flask) and were burned in a micro-flare, if necessary.

Completed reactor (with the sample of the cable and catalyst) as well as condensing line was flushed with argon for 1 hour before the experiment. Then the heating of the catalytic bed and the sample (furnaces 7c and 7b in the Fig. 1) was started. Supply of water for steam generation was started when the temperature of the cable sample was equal to 40–70 ^{o}C. The rate of the water supply controlled by peristaltic pump was equal to 0.59 cm^3/min, during the whole experiment. The highest temperature of the section with gasified sample was equal to 780 ^{o}C. This temperature was kept for 2 hours to almost complete decay of the gas evolution. Finally the reactor was cooled down to the temperatures: 190 ^{o}C of the catalytic bed and 125 ^{o}C of the gasified material (supply of water was finished when temperature of gasified material was equal to 400 ^{o}C). In order to avoid water absorption by the sample and catalyst, reactor was disassembled at this temperature gradient. Precise temperature profiles of the sample and catalytic bed are presented in Fig. 2.

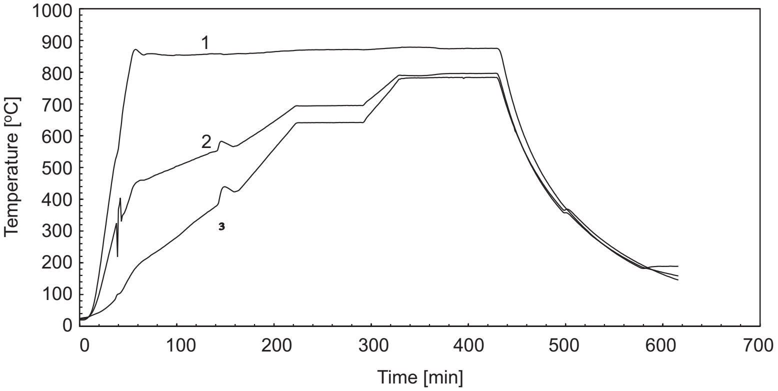

Fig. 2. Temperature profiles of the gasification run: 1 – temperature of the catalyst bed, 2 – temperature of the top of the sample, 3 – temperature of the bottom of the sample

Results and discussion

There were three products of the gasification experiment: (a) non-condensing gases, (b) aqueous condensate, oils and tars and (c) the solid residue in the reactor, dominated by metallic copper.

Non-condensing gases

At the beginning of experiment, reactor and condensing line were flushed by argon. The process started by pyrolysis of PVC, which proceeded, at temperatures above

200 °C, according to the ‘phase chain radical mechanism’ [14]. There were two major degradation steps of (poly)vinyl chloride. During the first step, dehydrochlorination and formation of polyene structures was accompanied by formation of benzene, naphthalene and phenanthrene. In the second phase, there was rearrangement of polyene molecules in the Cl-free melt and cyclization/cross-linking resulting in aromatic hydrocarbons and char residue formation. In a rough temperature scale, dehydrochlorination proceeded between 250–350 °C, formation of polyene structures between 300–450 °C and char/tar formation between 400–500 °C.

Thermal degradation of PVC is a complex process, with a large number of intermediate and final components. Considering presented in the Fig. 2 temperature gradient of the sample during the first 2–3 hours of the experiment, it may be concluded that the process started with dechlorination of the upper part of the sample approximately after 30 minutes from the beginning of the experiment. Then dechlorination proceeded down with successful release of aromatics as well as char formation in the sample sections with the higher temperature. Consequently, gaseous phase which reached catalytic bed was composed of hydrochloride, organic species (probably with a large ratio of aromatics) and steam. With increasing temperature of gasified sample the release of HCl and organic compounds decreased. It may be assumed, that nearly 450–500 °C the pyrolytic decomposition was finished and gasification of the char was started. Intensity of gas emission was noticeably smaller, despite the fact that increasing temperature caused intensification of char transformation process. Hence composition and volume of the gas leaving the reactor and condensing line was steadily changing (and it was qualitatively observed). The main objective of the experiment was to eliminate organic components from the cable and to convert them to non-condensing species, thus the final gas composition was not determined. Moreover, the process in the non-laboratory scale should be continuous and with a specific, stable composition of the

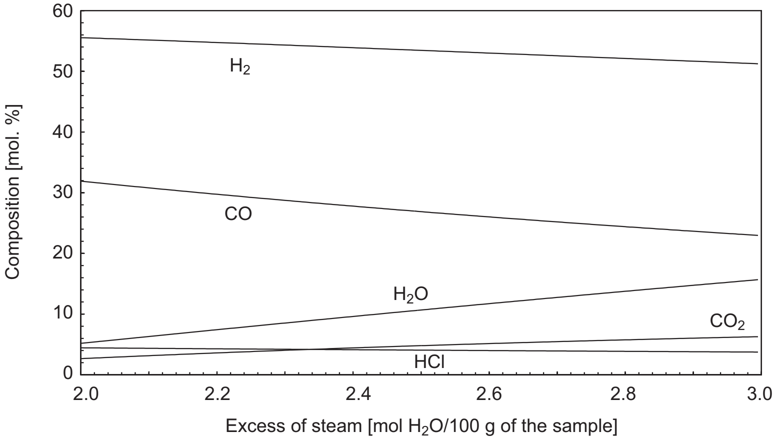

Fig. 3. Major components of the gaseous phase in thermodynamic equilibrium for steam gasification of the cable sample at 850 °C. Calculations have been carried out with HSC Chemistry® for Windows software [15] for an excess of steam (stoichiometric demands are equal approximately to 1.66 moles H_2O/100 g of the sample)

gas, characteristic for the flow reactor. Such calculated gas composition, assuming that the system is in the thermodynamic equilibrium, is presented in Fig. 3 (it should be noted that HCl concentration varies from 3.8 to 4.5 mol. %).

Condensate

Condensation of the steam excess began when temperature of the bottom part of the cable sample exceeded 120 ^{o}C. The condensate, colorless and clear at the beginning, became slightly darker and pink with time and separation of small amounts of light oils as well as sediments was observed at the end of experiment (it should be noted that condensing steam washed oils and sediments from the Liebig condenser). The smell of condensate was typical aromatic (naphthalene) and the solution was acidic (pH was approximately 1.0).

Detailed analysis of organic compounds in condensate was performed with mass spectrometry – gaseous chromatography (GC-MS, HP6890/HP5973 and capillary column HP1701 30 m × 0.25 mm with 14%-cyanopropylphenyl-86%-Poly(dimethylsiloxane), He carrier gas, sensitivity of 15–400 u). Four samples of different origins were analyzed: KCa1 – tars/sediments from the container walls, KCa2 – filtered aqueous condensate, KCaS – sediments separated from condensate by filtration and KCaW – tars/sediments from the Liebig condenser. Samples were extracted with diethyl ether (p.a. POCH S.A.) and NIST database was used to identify the species. Results of GC-MS analysis are presented in Table 1.

Table 1

Results of GC-MS analysis of the condensed fractions. KCa1 – tars/sediments from the container walls, KCa2 – filtered aqueous condensate, KCaS – sediments separated from condensate by filtration, KCaW – tars/sediments from the Liebig condenser

No.	Compound	CAS	KCa1	KCa2	KCaS	KCaW
			Mass [mg]			
1	Toluene	000108-88-3	0.12	0.32	0.00	0.06
2	Phenylethyne	000536-74-3	0.04	0.10	0.00	0.03
3	Styrene	000100-42-5	0.26	0.24	0.00	0.16
4	Benzene, 1-ethenyl-2-methyl-	000611-15-4	0.02	0.00	0.00	0.03
5	Indene	000095-13-6	0.45	0.11	0.14	0.74
6	Dodecane	000112-40-3	0.02	0.04	0.02	0.02
7	Naphthalene	000091-20-3	24.72	3.11	10.38	58.79
8	Naphthalene, 2-methyl-	000091-57-6	2.31	0.07	1.18	3.36
9	Naphthalene, 1-methyl-	000090-12-0	1.29	0.04	0.66	1.76
10	Naphthalene, 2-ethenyl-	000827-54-3	4.11	0.08	2.36	5.33
11	Naphthalene, 2,7-dimethyl-	000582-16-1	0.04	0.00	0.02	0.05
12	Naphthalene, 1,7-dimethyl-	000575-37-1	0.13	0.00	0.09	0.16
13	Biphenylene	000259-79-0	0.10	0.00	0.06	0.12
14	Naphthalene, 1-ethenyl-	000827-54-3	0.71	0.00	0.49	0.94
15	Acenaphthylene	000208-96-8	5.44	0.11	3.44	6.99

Table 1 contd.

No.	Compound	CAS	KCa1	KCa2	KCaS	KCaW
			Mass [mg]			
16	Diphenylmethane	000101-81-5	0.07	0.00	0.05	0.09
17	Acenaphthene	000083-32-9	0.06	0.66	0.04	0.07
18	Dibenzofuran	000132-64-9	0.21	0.00	0.15	0.26
19	1,1’-Biphenyl, 3-methyl-	000643-93-6	0.03	0.00	0.00	0.03
20	1H-Phenalene	000203-80-5	0.07	0.00	0.06	0.09
21	Fluorene	000086-73-7	1.75	0.19	1.30	2.07
22	1,1’-Biphenyl, 4-ethenyl-	002350-89-2	0.06	0.00	0.06	0.07
23	9H-Fluorene, 2-methyl-	001430-97-3	0.03	0.00	0.00	0.04
24	Dibenzothiophene	000132-65-0	0.07	0.46	0.05	0.06
25	9H-Fluoren-9-one	000486-25-9	0.43	0.13	0.32	0.47
26	Phenanthrene	000085-01-8	11.95	1.10	9.37	13.53
27	Anthracene	000120-12-7	3.57	0.15	3.20	7.68
28	1H-Indene, 1-(phenylmethylene)-	005394-86-5	0.52	0.00	0.42	0.58
29	Anthracene, 1-methyl-	000610-48-0	0.28	0.00	0.21	0.35
30	Anthracene, 2-methyl-	000613-12-7	0.34	0.00	0.26	0.43
31	Phenanthrene, 3-methyl-	000832-71-3	0.12	0.00	0.09	0.19
32	Naphthalene, 2-phenyl-	000612-94-2	1.81	0.00	1.38	2.22
33	1H-Phenalen-1-one	000548-39-0	0.11	0.00	0.06	0.23
34	9,10-Anthracenedione	000084-65-1	0.09	0.00	0.00	0.10
35	Naphthalene, 1-phenyl-	000612-94-2	0.16	0.00	0.08	0.19
36	Pyrene	000129-00-0	5.45	0.22	3.51	6.73
37	Fluoranthene	000206-44-0	2.10	0.11	1.42	2.57
38	Benzo[b]naphtho[2,3-d]furan	000243-42-5	0.24	0.00	0.09	0.16
39	p-Terphenyl	000092-94-4	0.14	0.59	0.00	0.16
40	Triphenylene	000217-59-4	0.10	0.00	0.05	0.00
41	11H-Benzo[b]fluorene	000243-17-4	0.63	0.00	0.36	0.83
42	Pyrene, 2-methyl-	003442-78-2	0.33	0.00	0.18	0.42
43	Pyrene, 1-methyl-	002381-21-7	0.25	0.00	0.13	0.30
44	Benz[a]anthracene	000056-55-3	0.12	0.00	0.06	0.13
45	Cyclopenta[cd]pyrene	027208-37-3	0.35	0.00	0.23	0.52
46	1,2’-Binaphthalene	004325-74-0	0.08	0.00	0.06	0.10
47	Triphenylene	000217-59-4	1.17	0.00	0.69	1.86
48	Chrysene	000218-01-9	1.96	0.51	1.10	3.01
49	7H-Benz[de]anthracen-7-one	000082-05-3	0.12	0.00	0.07	0.18
50	2,2’-Binaphthalene	000612-78-2	0.09	0.00	0.00	0.19
		Total	74.62	8.34	43.89	124.45

Total mass of identified species (presented in the Table 1) was equal to 251.3 mg. Fractionation of these species was very characteristic: only 3 % was found in filtered aqueous condensate, 17 % in filtered sediments, 30 % in sediments from the container walls and up to 50 % in sediments from the Liebig condenser. To evaluate the amount (percentage) of carbon isolated from cable plastic in cooling/condensing line, two parameters were considered: composition of *poliwinit* (discussed later) and average concentration of carbon. The latter was assumed to be equal to 90.0; 38.4 and 73.8 wt %, respectively in compounds listed in Table 1, PVC, and plasticizer (DEHP). Based on these data it was evaluated that 5.3% of carbon was isolated, mostly as water insoluble individuals. Accordingly, 94.7 % of the carbon was converted into non-condensing species.

Solid residue

Gasification experiment was carried out in order to extract metallic copper in the original form (*ie* without melting) and to eliminate the char from metal/inorganic residue. The solid products of gasification are presented in Fig. 4.

a) b) c) d)

Fig. 4. The solid residue of gasification experiment: a) non-metallic residue (with small pieces of copper), b) copper braids, c) cooper cords, d) pieces of cooper manually separated. Copper cords were removed from copper braids after experiment, for better presentation

They are: copper metal in the form of braids (48 % of the metal), cords (52 % of the metal) as well as manually separated little pieces (0.30 % of the metal) and a small amount of gray, slightly sintered powder with slight admixture of tiny pieces of copper. Masses of the original cable sample and fractions of the solid residue of gasification are given in Table 2.

Table 2

Mass balance of gasified sample of the LiYCY cable. The cable was cut into four pieces and placed in the reactor without additional treatment

Unit	Gasified cable	Solid residue	Deficit of mass	Solid residue	
				Non-metal fraction	Metal (Cu)
m [g]	18.0912	9.4692	8.622	0.5991	8.8701
wt. %	100	2.3	47.7	6.3	93.7

Fractionation of chlorine

It was discussed above that decomposition of PVC involves dehydrochlorination as an initial phase of destruction [14]. It seems that there is agreement in the literature that

HCl is the major chlorine product of PVC pyrolysis [16, 17], although temperature range of maximum emission of this compound depends on the material. It was also reported that emission of HCl was accompanied by emission of light hydrocarbons (in the first place benzene) as well as chlorinated light hydrocarbons, with domination of C_3H_5Cl [16]. In the presented here experiment gases from decomposition of PVC were forwarded together with steam to catalytic bed heated to 850 ^oC. Calculations performed with HSC software [15] revealed that equilibrium concentration of chlorinated organic species is negligible in comparison with hydrochloride. The same calculations show that calcium oxide (in the catalyst granules) should be chlorinated to $CaCl_2$. Additionally, PVC additives (*eg* calcium carbonate or dolomite in a form of fillers) may also react with hydrochloride [18]. Unfortunately, there was no information on such additives to *polwinit* (PVC in the cable shielding). Therefore, it was assumed that the chlorine from gasified PVC should be principally in the form of HCl and should be captured by: catalytic bed, aqueous condensate and mineral wool, located between catalytic bed and polysiloxane sealing. Analysis of the chloride ions content was performed by Mohr method, after leaching of the wool and the sample of catalyst granules with hot water. Non-soluble sediments from aqueous condensate were separated by filtration. Results of analysis are presented in Table 3.

Table 3

Distribution of chlorine between aqueous condensate, catalytic bed and mineral wool (support of the polysiloxane sealing)

Constituent	pH	Cl^- [mg]
Leaching of the catalyst	~9–10	603
Leaching of the mineral wool	~5–6	23
Aqueous condensate (filtered)	~1	604
	Total	1230

There was no available information on *polwinit* composition, therefore it was assumed that the material was composed of 50 % PVC, 40 % plasticizers (in the first place phthalates, *eg* diethylhexyl phthalate, DEHP), 2–4 % stabilizers (*eg* metal stearates or carboxylates) and fillers (chalk, talc, dolomite, quartz powder) to the balance. Considering amount of *polwinit* in the cable sample and chlorine content in (poly)vinyl chloride (56.8 wt %), the mass of 1.23 g Cl^- corresponds to only 50 % of expected chlorine quantity. Because there was only 0.6 g of non-metallic fraction from the solid residue after gasification, it seems that (1) significant amount of chlorine was not captured by alkaline component of catalytic bed and steam condensation or (2) assumed composition of *polwinit* was not correct. Anyway, the chlorine distribution should be investigated more carefully, taking into account additional alkaline gas-washing and reaction with PVC fillers. Moreover, replacing of calcium oxide by magnesium oxide as catalytic active component should be considered ($p_{H_2O} / p^2_{HCl} = 2.56 \cdot 10^4$ for the reaction $CaO + 2HCl = CaCl_2 + H_2O$ at 850 ^oC whereas relevant equilibrium constant for $MgO + 2HCl = MgCl_2 + H_2O$ reaction is equal to $6.79 \cdot 10^{-2}$). Rare earth oxychlorides seems also interesting as possible active components.

Conclusions

It has been shown that multilayer metal/plastic (copper/PVC) structure of the LiYCY cable was efficiently gasified by steam in an excess to metal (Cu) and non-metallic solid residue. Gasification was enhanced by catalytic bed of original granules prepared from local clay and calcium carbonate. In the process, metal (Cu) remained unchanged and was quantitatively separated (49 % of the original mass of the cable). Non-metal components of the cable (51 % of the original mass) were converted to non-metallic solid residue (3.3 % of the original mass of the cable) and gaseous phase. Condensation of steam facilitated elimination of tars and oils as well as hydrochloride from the gas. It was estimated that 95 % of carbon (from the cable components, particularly (poly)vinyl chloride) was converted to non-condensing species and only 5 % of carbon retained in the cooling/condensing line as (mostly) water non-soluble phases. Efficiency of absorption of hydrochloride by catalytic bed and aqueous condensate was almost the same (but only 50 % of estimated chlorine quantity in the sample was finally balanced).

Acknowledgement

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ZGAZOWANIE PARĄ WODNĄ WIELOŻYŁOWEGO KABLA ELEKTRYCZNEGO TYPU LiYCY

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Abstrakt: Oryginale, nie rozdzielone (w całości) kawałki kabla LiYCY (kabel wielożyłowy, kombinacja warstw metal/tworzywo sztuczne (Cu/PCW)) zgazowywano w nadmiarze pary wodnej pod ciśnieniem normalnym. Konwersję strumienia gazów prowadzono na złożu katalitycznym z oryginalnego, granulowanego materiału glinokrzemianowego (lokalna glina), z dodatkiem węglanu wapnia. W procesie zgazowania metal (Cu) zachował oryginalną postać linek i oplotów i został ilościowo wydzielony (49 % wag. kabla przed zgazowaniem). Niemetaliczne składniki kabla (51 % wag. kabla przed zgazowaniem) zostały przekształcone do nieznacznie spieczonego, niemetalicznego proszku (3,3 % wag. kabla przed zgazowaniem) i gazu. Kondensacja pary wodnej wspomagała usuwanie z gazu substancji smolistych i olejowych, a także chlorowodoru. Oszacowano, że tylko 5 % węgla (zawartego w tworzywach kabla) zostało zatrzymane w układzie chłodzenia/kondensacji, w zdecydowanej większości jako nierozpuszczalne w wodzie fazy. Skuteczność absorpcji chlorowodoru przez złoże katalityczne i kondensat wodny była praktycznie taka sama (ale zbilansowano ostatecznie tylko 50 % oszacowanej ogólnej zawartości chloru).

Słowa kluczowe: odpady, kable elektryczne, piroliza, zgazowanie

Varia

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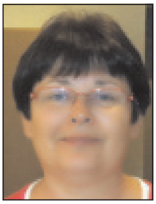

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MONITORING OF DIFFERENT HEAVY METALS IN SOIL/PLANT/WATER SYSTEMS

Miroslav ČERNÍK[1], Jaroslav HRABAL[2] and Martina VOTRUBOVA[2]
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CASE STUDY OF A COMBINED NANO-, BIO- AND ELECTRIC REMEDIATION METHODS ON THE MARS SVRATKA SITE

Marek JÓŹWIAK
Department of Environment Protection and Modelling
of the Jan Kochanowski University in Kielce, PL

BIOINDICATION AS CHALLENGE IN MODERN ENVIRONMENTAL PROTECTION

Paweł KAFARSKI
Wroclaw University of Technology
and Opole University, PL

HOW CAN WE USE SURVIVAL STRATEGIES OF ORGANISMS TO DEVELOP NEW TECHNOLOGIES

Short Conference Report

The Conference ECOpole ’14 was held in 15–18 X 2014 in Hotel Ziemowit in Jarnoltowek, PL. It was the twenty third ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL. 117 participants, including delegates representing following countries: Czech Republic, Germany, Great Britain, Hungary and Poland, took part in the event and presented 17 oral contributions and 107 posters.

The Abstracts of the Conference contributions were available on the Conference website

ecopole.uni.opole.pl

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* containing among others Keynote Speakers papers, was distributed at the Conference Reception desk together with a CD-ROM (containing short info on Keynote Speakers,

Abstracts of the Conference presentations as well as ECOpole ’14 Conference Programme).

On Wednesday (15th October 2014) at 19.00 after a brief Opening Ceremony performed by prof. Maria Waclawek, Chairperson of the Organising Committee and prof. Witold Waclawek, Chairman of the Conference Scientific Board and President of the Society of Ecological Chemistry and Engineering, the participants were invited for the Musical Soiree by the String Quartet (Emilia Kos – violin, Agnieszka Newiger – violin, Malgorzata Redzinska – viola and Barbara Kowalska – cello) of the Jozef Elsner Philharmonic in Opole. The Programme contained works by Johannes Brahms, Jules Massenet, Wolfgang Amadeus Mozart, Modest Mussorgsky, Johann Strauss and also Carlos Gardel, Astor Piazzolla, Frank Sinatra and Angel Villoldo. The audience applauded the players and claimed for encore.

The Conference Agenda was divided into 4 sections:
- – SI Ecological Chemistry and Engineering,
- – SII Environment Friendly Production and Use of Energy,
- – SIII Forum of Young Scientists and Environmental Education,
- – SIV Health, Ecology and Agriculture.

On Thursday, 16th October 2014 at 9.00 a.m. **prof. Gerhard ERTL** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, DE) – **the Nobel Prize Winner in Chemistry 2007** initiated the First Plenary Session with the invited lecture: *Elementary steps in heterogeneous catalysis: The basis for environmental chemistry*. During the conference the plenary lectures were also delivered by other invited lecturers: **Agnes BALINT** (Obuda University, Institute of Environmental Engineering, Budapest, HU): *Monitoring of different heavy metals in soil/plant/water systems*, **Miroslav CERNIK** (Technical University of Liberec, Liberec, CZ): *Case study of a combined nano-, bio- and electric remediation methods on the MARS Svratka site*, **Marek JOZWIAK** (Department of Environment Protection and Modelling of the Jan Kochanowski University in Kielce, PL): *Bioindication as challenge in modern environmental protection*, **Paweł KAFARSKI** (Wroclaw University of Technology and Opole University, PL): *How can we use survival strategies of organisms to develop new technologies*.

There were also presented very interesting lectures, *eg* by **P.P. WIECZOREK** (Faculty of Chemistry, Opole University, Opole, PL): *Solid phase extraction and liquid membranes as sample preparation methods in environmental analysis*, **S. FRANZLE** (Zittau International School (Dresden Tech), Zittau, DE): *New features of chitin-based biomonitoring of metal ions/complexes and semi-metal toxicants in different speciation forms*, **T. OLSZOWSKI** (Chair of Thermal Engineering and Industrial Facilities, Opole University of Technology, Opole, PL): *Comparison of the effect of emissions from individual heating systems on the concentration of* PM_{10} *in a rural area during extreme winter weather conditions* and **Z.A. SZYDLO** (Highgate School, London, UK): *History of explosives* – this contribution was met with great interest of the audience.

Thursday, a day of hard work, was finished with the second Poster Session. Many of the discussions started at the posters, lasted until the evening hours.

As usually during the ECOpole Conferences, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists' and Environmental Education Poster Session 30 posters were presented.

The Scientific Board: **Maria Waclawek** (Opole University, Opole, PL) – Chairperson, **Daniela Szaniawska** (Maritime University of Szczecin, Szczecin, PL), **Stefan Franzle** (IHI, Zittau, DE) and **Zbigniew A. Szydlo** (Highgate School, London, UK) granted awards (sponsored by the Society of Ecological Chemistry and Engineering) for the best presentations. The awards for oral presentations were given to: **Dariusz Poplawski**, M. Sc., Eng. (Wroclaw University of Technology, Wroclaw, PL) for the lecture: **D. Poplawski**, **D. Grzesiak**, **J. Hoffmann**, **K. Hoffmann**, **P. Falewicz**: *Evaluation of selected dolomites suitability for use as a filler in nitrogen fertilizers*; **Karina Snochowska**, M. Sc., Eng. (Lodz University of Technology, Lodz, PL), for the presentation: **K. Snochowska**, **M. Tylman**, **W. Kaminski**: *Ethanol recovery from low-concentration water solution using membrane contactors with ionic liquids*, **Michal Rybak**, M. Sc. (Adam Mickiewicz University, Poznan, PL) for the lecture: **M. Rybak**, **T. Joniak**, **T. Sobczynski**: *The monitoring of nitrogen and phosphorus content in without-flow lake during the time after elimination of wastewater inflow (Western Poland).*

The awards for poster presentations were given to **Magdalena Koszalkowska**, M. Sc. (Opole University, Opole, PL) for the poster: **M. Koszalkowska**, **L. Krecidlo**, **T. Krzysko-Lupicka**: *Decontamination of social area in food facility by using thyme essential oil*; **Martyna Blus,** M. Sc., Eng. (Lodz University of Technology, Lodz, PL) for the poster: **E. Tomczak, M. Blus**: *Study of the dynamics of dye's adsorption on natural porous deposits* and **Bartosz Ciorga,** M. Sc., Eng. (Poznan University of Life Sciences, Poznan, PL) for the poster: **B. Ciorga**, **M. Beszterda**, **E. Rusinek-Prystupa**, **A. Perczak**, **A. Waskiewicz**, **P. Golinski**: *The presence of toxic trace metals in dried tea samples.*

On Saturday morning an excursion was organised to the Underground Tourist – Educational Route in the Old Uranium Mine in Kletno.

Closing the conference, prof., prof. Maria and Witold Waclawek made short recapitulation. In general, ECOpole '14 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

They expressed gratitude to all participants for coming and taking active part in the Conference and thanked Sponsor (Ministry of Science and Higher Education, Warszawa, PL) as well as all Chairpersons of Sessions.

The organizers informed that the electronic version of the presented contributions (lecture or poster) could be published on the Conference website. They announced, that full texts of the presented papers will be published (after obtaining reviewers' positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants. The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

At the end they invited all Colleagues to attend the ECOpole '15 Conference, which will be held in Hotel "Ziemowit" in Jarnoltowek, PL in the next October.

Maria Wacławek

INVITATION FOR ECOpole ’15 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 24th annual Central European Conference ECOpole ’15, which will be held in 14–17.10.2015 (Wednesday–Saturday) in Hotel Ziemowit in Jarnoltowek, PL.

The Conference Programme includes oral presentations and posters and will be divided into four sections:

- SI Chemical Pollution of Natural Environment and Its Monitoring
- SII Environment Friendly Production and Use of Energy
- SIII Forum of Young Scientists and Environmental Education in Chemistry
- SIV Impact of Environment Pollution on Food and Human Health

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format),
- extended Abstracts (5–8 pages) in the semi-annual journal *Proceedings of ECOpole*,
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15th July 2015** and for the Extended Abstracts: **1st October 2015**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2015**) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole ’15 website).

After the ECOpole '15 Conference **it will be possible to publish electronic version of presented contributions** (oral presentations as well as posters) on this site.

Further information is available from:
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ZAPRASZAMY DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole ’15

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

w dniach 14–17 X 2015 r. w hotelu Ziemowit w Jarnoltówku

Będzie to **dwudziesta czwarta z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotyczącym różnych aspektów ochrony środowiska przyrodniczego.

Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’15 będą zgrupowane w czterech Sekcjach:

– SI Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring
– SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie
– SIII Forum Młodych (FM) i Edukacja prośrodowiskowa
– SIV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi

Materiały konferencyjne będą opublikowane w postaci:

– abstraktów (0,5 strony formatu A4) na CD-ROM-ie,
– rozszerzonych streszczeń o objętości 5–8 stron w półroczniku *Proceedings of ECOpole,*
– artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/ Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) ser. A i S oraz w półroczniku *Chemistry – Didactics – Ecology – Metrology* (*Chemia – Dydaktyka – Ekologia – Metrologia*).

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa) planowanych wystąpień upływa w dniu 15 lipca 2015 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 31 lipca 2015 r. na stronie webowej konferencji. Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach *Ecological Chemistry and Engineering* ser. A oraz S, które są dostępne w wielu bibliotekach naukowych w Polsce i za granicą. Zalecenia te są również umieszczone na stronie webowej Towarzystwa Chemii i Inżynierii Ekologicznej:

tchie.uni.opole.pl

Po konferencji zostaną wydane 5–8-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2015 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej.

Wszystkie streszczenia oraz program konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie webowej konferencji:

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Po konferencji **będzie możliwość opublikowania elektronicznej wersji prezentowanego wystąpienia** (wykładu, a także posteru) na tej stronie.

Prof. dr hab. inż. Maria Wacławek
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Konferencji ECOpole '15

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– Main text (usually divided into: Experimental – you describe methods used; Results and Discussion);

– Conclusions: you summarize your paper;

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[1] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.

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