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Removal of PAHs from Municipal Wastewater during the Third Stage of Treatment

Usuwanie WWA ze ścieków komunalnych w trzecim etapie oczyszczania

The investigations were carried out using wastewater received from a municipal wastewater treatment plant. The samples of wastewater were primarily characterized for concentration of selected physicochemical parameters. Next, a standard mixture of PAHs was added to the samples. Chemical oxidation process was performed using two doses of hydrogen peroxide. Changes in concentration of PAHs were determined in the wastewater samples before addition of the chemical reagent and after the oxidation process. A quantitative analysis of PAHs was provided by GC-MS. The extraction of organic matrices from the wastewater samples was performed using a mixture of organic solvents: methanol, cyclohexane and dichloromethane. The extracts were separated from samples, purified on silica gel and concentrated under nitrogen stream. Concentrations of 16 PAHs according to EPA were determined. The detection limit ranged from 0.14 to 0.59 µg/L. Total concentration of 16 PAHs in wastewater sampled from the treatment plant were 1.4 µg/L on average. Total concentration of 16 PAHs in wastewater with the standard mixture was 561 µg/L on average. A decrease in PAHs concentration was observed in the samples after chemical oxidation process. Addition of hydrogen peroxide resulted in a decrease of 16 PAHs concentration in wastewater coming from the wastewater treatment plant to 61±74%. The efficiency of hydrocarbons removal, grouped according to the number of rings, ranged from 35 to 90%.

Keywords: PAHs, GC-MS, wastewater, oxidation process, hydrogen peroxide

Introduction

Identification of PAHs in wastewater has been frequently demonstrated in the literature and our previous studies [1, 2]. The wastewater with the highest content of these compounds comes from fuel processing industry, especially coke wastewater and petrochemical wastewater. Lower concentrations of these compounds have been documented in municipal and domestic wastewater [3, 4]. Therefore, the percentage of industrial wastewater and its type is a significant factor that impacts on PAH content in wastewater that inflow at a treatment plant. Furthermore, in combined sewer systems, stormwater (including meltwater) containing PAHs also flows to the treatment plant [5]. Current legal regulations on conditions that have to be met for wastewater discharge to the environment stipulate permissible levels only for volatile aromatic hydrocarbons (BTX), petroleum hydrocarbons and adsorbable

organic halides (AOX). No permissible levels have been specified with respect to PAHs enumerated on the US EPA or WHO lists. However, due to carcinogenic, mutagenic and teratogenic properties which have been extensively explored, one should number PAHs among compounds that are particularly hazardous to the water environment and should be eliminated [6, 7]. On the other hand, PAHs have been mentioned in legal regulations concerning monitoring of surface water and groundwater [8].

Few studies have examined PAHs content in municipal wastewater. Most studies have concerned PAHs in industrial wastewater and sewage sludge [9, 10], where PAHs are accumulated during treatment, or surface water and bottom sediments [11, 12]. Available results of examinations discussed in the literature and our own research indicate that PAHs are not removed in conventional sewage treatment processes to a sufficient degree despite a relatively high level of organic compounds removal rates expressed by COD and BOD₅. Therefore, the treated wastewater discharged to receiving water bodies represents a source of these pollutants to the water environment [2, 13]. Torret [13] indicated that PAHs contents in raw sludge sampled from two Italian treatment plants ranged from 2.6 to 4 µg/L. Concentrations of individual compounds ranged from 21 to 750 ng/L [13]. Mezzanotte et al. [14] demonstrated that PAHs concentration in wastewater from municipal treatment plants ranged from 1.1 to 9.3 µg/L. The effectiveness of PAHs removal during biological treatment processes reached 97%. Qiao et al. [15] evaluated concentrations of PAHs in raw sewage treated in Beijing. Concentrations of these compounds in the influent ranged from 0.4 to 0.7 µg/L, whereas values in the effluent were from 0.2 to 0.3 µg/L. According to the authors, low molecular weight compounds were removed through biodegradation and adsorption under anaerobic conditions and volatilization in aerobic conditions. High molecular weight of PAHs are mainly removed by adsorption. Total load received with the treated wastewater ranged from 66 g/d in summer and 148 g/d in winter [15].

In raw wastewater in Japan, concentration of PAHs was below 0.42 µg/L, whereas in the effluent - below 0.1 µg/L. Effectiveness of PAH removal in the treatment processes, such as biological and chemical changes and volatilization, did not exceed 63%. With the accumulation of PAHs in sewage sludge at 9%, around 28% of the load received at a treatment plant was discharged to receiving waters [16]. Similar findings were published by Manoli and Samara [17]. In a treatment plant operating based on activated sludge technology, the PAH load was removed from 28 to 67% during initial treatment, and from 1 to 61% during the final treatment. Total percentage removal of PAHs did not exceed 89% [17]. In a wastewater treatment plant in Jordan, PAH removal did not exceed 40% of total PAHs [18]. Results of the study by Alawi et al. [19] suggested substantially greater concentrations of PAHs in wastewater: 1 to 2.9 mg/L in raw wastewater and from 0.5 to 1.6 mg/L in the effluent. Total PAHs removal during treatment ranged from 28 to 72% depending on physico-chemical properties and treatment technology [19].

In surface waters, PAHs migrate and/or settle sediment in the adsorbed form on suspended matter and undergo physical, chemical and biological changes [20-23].

For example, in surface waters and bottom sediments, concentration of PAHs ranged from 13 to 26 mg/L and from 27 to 55 mg/kg, respectively [23]. Biological changes consist in enzymatic decomposition of these compounds. However, this is possible in the case of relatively low concentrations of PAHs (below tolerance threshold for microorganisms) and presence of microflora capable of production of suitable enzymes. Among abiotic processes one should also stress those which lead to transfer to other environments and those causing destruction of PAHs. Migration to other environments occurs during volatilization of PAHs to the atmosphere [20, 24]. However, this concerns mainly hydrocarbons with high vapour pressure. The processes of PAHs destruction are focused on chemical oxidation and photodegradation [25, 26]. However, it should be noted that these processes lead to formation of new compounds, often with toxicity higher than the basic ones. PAHs derivatives are formed not only as a result of their degradation but also as a result of reaction with other matrix components (halogenation, nitration, sulfonation, acylation). In the natural environment, photolysis has a significant impact on PAHs destruction. However, this concerns only the compounds which are dissolved in the surface layer of water [26].

Efficiency of PAHs removal from municipal and industrial wastewater in the process of oxidation has been the focus of our previous studies [2, 27, 28]. With reference to wastewater, it is justified to use final chemical treatment of effluents from a wastewater treatment plant that limits PAHs load discharged to surface waters. Chemical oxidation is performed using oxidizers which initiate formation of hydroxyl radicals (Fenton's reagent, ozone, permanganate, hydrogen peroxide) [29]. Previous studies concerning oxidation of organic compounds, including PAHs have used treated municipal wastewater sampled from the effluent of the secondary settlement tank [27]. Total initial PAH content in effluents was at the level of 1.39 µg/L. The oxidant was hydrogen peroxide, which was introduced to wastewater with concentration of 1 mmol/L with two doses - 20 and 40 mg/L. Efficiency of PAH removal was different for individual hydrocarbons and ranged from several to several tens of percent. The efficiency was the highest (64%) in the case of the most volatile hydrocarbon (naphthalene). A reduction in total concentration of 16 compounds was 51 and 59% for smaller and greater doses of oxidizer, respectively [27]. Since initial concentrations of PAHs in the examinations discussed in the literature may be greater than in this study, the examinations of PAH removal from wastewater were conducted after introduction of an additional amount of PAHs to wastewater in the form of a standard mixture.

1. Research methodology

1.1. Materials

The examinations were conducted using treated wastewater sampled from the municipal wastewater treatment plant receiving domestic wastewater mixed with industrial wastewater. Population equivalent (PE) for this treatment plant is

over 100,000. Technology of wastewater treatment consists in mechanical and biological processes combined with simultaneous precipitation of phosphates. Oxidation of organic compounds and nitrogen compounds occurs in bioreactors with activated sludge divided into anaerobic, anoxic and aerobic zones. The examinations were conducted for wastewater sampled from the overflow of the secondary settlement tank. In practice, according to the permit required by the Water Law Act, this wastewater is discharged to a surface receiver. The wastewater was initially characterized by performing determination of such parameters as content of suspended matter, concentrations of organic (and some inorganic) compounds determined as COD, and value of pH. Analysis were performed according to the procedure designed by Hermanowicz et al. [30]. The content of 16 PAHs was evaluated according to the methodology described in 1.3.

1.2. Technological examinations

After averaging of the composition of wastewater sampled from the treatment plant, four samples were prepared for technological examinations. Furthermore, the 16 PAHs standard mixture was added (mixture of benzene and dichloromethane, 1:1). Concentration of PAHs in the standard mixture was 2 µg/mL for each of the 16 compounds. Next, 4 µg/L of each hydrocarbon and solution of dihydrogen dioxide were added to wastewater samples. Concentration of the oxidant was 1 mmol/L. Doses of reagent added to wastewater were: 20 mg/L (oxidation I) and 40 mg/dm³ (oxidation II). Next, the samples were mixed and left for 1 hour in laboratory settings. After this time, concentration of PAHs in the wastewater was determined. The experiments were carried out with two replicates. Changes in concentration of PAHs were determined based on the analysis of the concentration of these compounds in samples before and after oxidation. Significance of changes in concentration of PAHs was verified by means of the Student's t-test. Using the tables, a critical value was adopted for the degrees of freedom (n-2) and level of confidence of 95% [31]. Furthermore, the effect of oxidant on microflora was examined each time by evaluation of the number of colony-forming units cultured on Petri dishes. No bacteria were grown during incubation conducted for temperatures of 20 and 37°C.

1.3. Analytical methodology for PAHs

Preparation of the samples for quantitative determination of PAHs consisted in separation of the organic matrix from wastewater by liquid-liquid extraction using the mixture of organic solvents. Cyclohexane, dichloromethane and methanol (which are solvents with different polarities) were used [32]. The extracts separated from wastewater were next cleaned on silica gel in vacuum conditions. The cleaned extracts were concentrated to the volume of 1 mL in the nitrogen stream. Quantitative determinations were performed by means of capillary gas chromatography using a gas chromatograph coupled with mass detector (GC8000/MS800 manufactured

by Fisons). Determination consisted in injection of the prepared sample with the dose of 2 μ l on a DB column with the length of 30 m, diameter of 0.25 mm, and film thickness of 1 μ m. Helium was used as a carrier gas, with flow rate of 0.5 mL/min. The analysis was conducted at temperature of 280°C. The temperature program for the column furnace was chosen based on the analysis of model mixtures: 40°C/min, heating at 5°C/min to 120°C. Finally temperature 280°C was kept for 60 min. Qualitative and quantitative determinations were performed for 16 compounds enumerated on the list published by the US EPA. This concerns the following hydrocarbons: naphthalene Naf, acenaphthylene Acyl, acenaphthene Ac, phenanthrene Fen, anthracene Ant, fluorene Flu, pyrene Pir, fluoranthene Fl, benz[a]anthracene BaA, chrysene Ch, benzo[b]fluoranthene BbF, benzo[k]fluoranthene BkF, benzo(a)pyrene BaP, dibenz[a,h]anthracene DahA, benzo[ghi]perylene Bper and indeno[1,2,3-cd]-pyrene IP. Eight of the listed hydrocarbons (from BaA to IP) were considered carcinogenic in the description of the results. Table 1 presents certain properties of PAHs, parameters of chromatographic analysis and initial concentrations of PAHs in wastewater sampled from the treatment plant.

Table 1. Characteristics of PAHs, hydraulic retention time, standard mixture recoveries and initial concentration of PAHs in wastewater samples

WWA	CAS No.	Abbreviation	L ¹⁾	R ²⁾ μg/L	Log K _{ow} ³⁾	Recovery rate %	C ⁴⁾ μg/L [27]
Naphthalene	91-20-3	Naf	2/0	31700	3.37	19.8	1.235
Acenaphthylene	208-96-8	Acyl	2/1	3930	4.07	19.1	0.009
Acenaphthene	83-32-9	Ac	2/1	3900	4.33	29.8	0.015
Fluorene	86-73-7	Flu	2/1	1980	4.18	67.9	0.007
Phenanthrene	08/01/1985	Fen	3/0	1290	4.57	74.5	0.034
Anthracene	120-12-7	Antr	3/0	73	4.54	87.9	0.005
Fluoranthene	206-44-0	Fl	3/1	260	5.22	98.1	0.018
Pyrene	129-00-0	Pir	4/0	135	5.32	102.9	0.019
Benzo[a]anthracene	205-99-2	BaA	4/0	14	5.61	90.4	0.006
Chrysene	218-01-9	Ch	4/0	2.0	5.63	96.8	0.010
Benzo[b]fluoranthene	207-08-9	BbF	4/1	1.2	6.57	93.6	0.007
Benzo[k]fluoranthene	207-08-9	BkF	4/1	0.55	6.84	85.4	0.008
Benzo[a]pyrene	50-32-8	BaP	5/0	3.8	6.06	68.4	0.006
Dibenz[a,h]anthracene	53-70-3	DahA	5/0	0.5	6.86	105.2	0.003
Benzo[ghi]perylene	191-24-2	BghiP	6/0	62.0	7.66	70.2	0.004
Indeno[123cd]pyrene	193-39-5	IP	5/1	0.26	7.23	107.8	0.005

¹⁾ Number of benzene/cyclopentane rings, ²⁾ R - solubility at temperature of 25°C

³⁾ logarithm of octanol/water partition coefficient, ⁴⁾ initial concentration of PAHs

The parameters concern the properties of PAHs which have an effect on concentrations determined in wastewater (solubility), tendency for adsorption on sus-

pensions (value of octanol/water partition coefficient). However, PAHs solubility in water can increase in the presence of surfactants, which is especially important to domestic wastewater containing substantial amounts of surface-active agents. In order to verify the adopted methodology of wastewater preparation for PAHs determination, the recovery rates were evaluated for a standard mixture of these compounds. Mean recovery rate for the standard mixture without the most volatile compounds was high and exceeded 93%. The results obtained are within the range cited in the literature for wastewater containing the suspension composed mainly of organic parts (38÷95%) [3, 5].

2. Results and discussion

Initial examinations of the wastewater demonstrated that concentration of total suspension was at the level of 24 mg/L, whereas pH was 7.4. Content of organic (and some inorganic) pollutants analysed as COD was 75 mg/dm³. After completion of the oxidation process, concentration of the above compounds was below 40 mg/L.

Total concentration of 16 PAHs in the treated wastewater was 1.4 µg/L on average. Table 1 presents concentrations of individual hydrocarbons. In total amount, 2-ring naphthalene (89%) was dominant in total amount, with its concentration substantially exceeding other compounds. 3-ring hydrocarbons accounted for 5% of total amount of PAHs, whereas concentrations of other hydrocarbons were below 20 ng/L (Tab. 1) [27].

After adding a standard mixture, total concentration of PAHs in wastewater was 56 µg/L on average. 3-, 4- and 5-ring hydrocarbons had similar percentages of total content of PAHs (26÷27%). Concentrations of naphthalene, acenaphthylene and acenaphthene were low, which is likely to have resulted from high loss during application of the standard mixture to wastewater. These are hydrocarbons with the highest values of vapour pressure, highest solubility in water and small value of the Nernst partition coefficient. Therefore, the recovery of these compounds from wastewater was the lowest (Table 1). Figure 1 presents changes in naphthalene and tricyclic hydrocarbons before and after oxidation.

Efficiency of naphthalene removal was the highest and reached 80%. The decline of 3-ring hydrocarbons ranged from 57 to 79% and was directly proportional to the oxidant dose. Both naphthalene and 3-ring hydrocarbons are characterized by the highest volatility and susceptibility to decomposition. Compared to the results of previous studies, where standard mixture of PAHs has not been added to wastewater samples, naphthalene loss was below 64%, whereas the decrease of 3-ring compounds was substantially lower (below 27%) [27]. It should be noted that a statistically significant decline was observed already after introduction of a lower dose of oxidizer (oxidation I). The increase in the dose of hydrogen peroxide was not statistically significant for acenaphthene, for which oxidation efficiency increases only by 9%. Changes in concentration of 4-ring hydrocarbons in wastewater subjected to oxidation are presented in Figure 2.

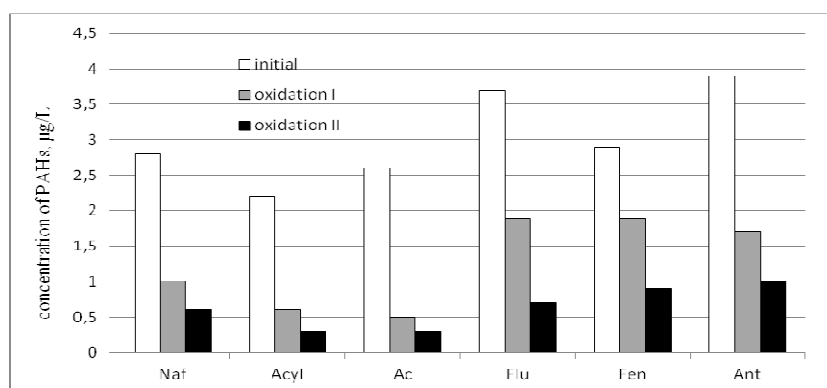


Fig. 1. Concentrations of naphthalene and 3-ring PAHs in wastewater during oxidation

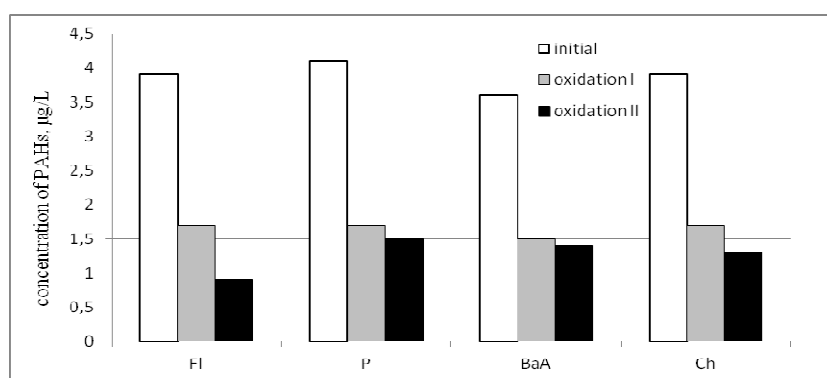


Fig. 2. Concentrations of 4-ring PAHs in wastewater during oxidation

Total concentration of 4-ring hydrocarbons was at the level of 15.5 µg/L. After oxidation, lower concentrations were observed in wastewater, by 43 and 34% for the decreasing oxidant dose. Therefore, removal rate depended, similarly to the above compounds, on the amount of hydrogen peroxide. Statistically significant differences were found for concentrations after adding a lower dose of oxidant. Of 4-ring compounds, an increase in the dihydrogen dioxide dose had a significant effect on oxidation only for fluoranthene. Figure 3 presents changes in 5-ring and 6-ring compounds during oxidation.

Similar to other hydrocarbons, efficiency of removal of 5-ring and 6-ring hydrocarbons depended on the oxidant dose: during oxidation I, it was 69 and 59%, whereas during oxidation II, this was 79 and 70%, respectively. With total concentration of 16 compounds, one can conclude that mean degree of degradation was at the level of 61 and 74%, for oxidation I and oxidation II, respectively. A statistically significant decrease in PAHs was observed following oxidation I, whereas the increase in the oxidant dose was statistically significant only for 6-ring hydrocarbons. Efficiency of oxidation of the latter increased by 15÷16%, whereas for the other compounds it did not exceed 10%. The differences were also found

in efficiency of oxidation of compounds containing benzene rings compared to oxidation of hydrocarbons containing cyclopentane rings. In the case of the latter, loss was higher by 10%, regardless of the oxidant dose. This means that these compounds were more susceptible to decomposition.

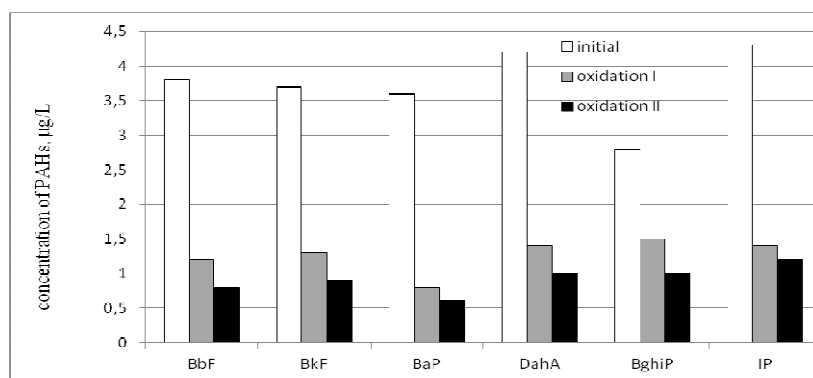


Fig. 3. Concentrations of 5-ring and 6-ring PAHs in wastewater during oxidation

Table 2 presents efficiency of removal of 16 PAHs during examinations compared to the results obtained for wastewater where standard PAH mixture was not added and literature data concerning the efficiency of PAHs removal from water solutions.

Table 2. Efficiency of PAHs removal from municipal wastewater during oxidation

WWA	The present study		Previous studies [27]		Literature data Decline of PAHs AOP process
	Oxidation I	Oxidation II	Oxidation I	Oxidation II	
Naphthalene	68	80	56	64	1. 9÷91%, 8 PAHs, UV [5] 2. 80÷90%, 16 PAHs, UV/H ₂ O ₂ [11] 3. 41÷75%, 18 PAHs, O ₃ /UV [25] 4. 10÷70%, 3 PAHs, O ₃ 5. 40÷80%, 3 PAHs, UV 6. 85÷99%, 16 PAHs, UV/O ₃ , UV/H ₂ O ₂ 7. 70÷100%, 6 PAHs, Fenton's process 8. 38÷90%, 3 PAHs, Photo-Fenton process [29]
Acenaphthylene	73	87	33	44	
Acenaphthene	80	89	27	40	
Fluorene	48	80	29	29	
Phenanthrene	35	7	15	18	
Anthracene	56	74	20	20	
Fluoranthene	58	76	6	17	
Pyrene	57	63	5	11	
Benzo[a]anthracene	59	62	0	33	
Chrysene	55	66	10	30	
Benzo[b]fluoranthene	68	79	0	29	
Benzo[k]fluoranthene	65	76	13	25	
Benzo[a]pyrene	78	83	17	17	
Dibenz[a,h]anthracene	67	76	17	33	
Benzo[ghi]perylene	47	63	0	25	
Indeno[123cd]pyrene	64	79	0	20	

Results of the study obtained for wastewater with addition of the standard mixture did not reflect the quantitative changes in PAHs documented during oxidation of wastewater without an additional amount of PAHs. After oxidation I, total concentration of 16 PAHs was by 61% lower than initial (around 22 $\mu\text{g/L}$). Initially, the highest loss was found for naphthalene and 5-ring compounds. Efficiency of removing these hydrocarbons was 69%. However, in previous studies, decrease of naphthalene did not exceed 55%, whereas for 5-ring compounds, this value was below 10% [27]. Increasing the oxidant dose (oxidation II) led to the increase in efficiency of removal of PAHs to 74% with reference to total content of 16 compounds. However, decreases for individual hydrocarbons ranged from 66 to 80%. Efficiency of removal was significantly higher especially for 3-ring hydrocarbons (from 57 to 79%).

As mentioned above, most studies in the literature have concerned treatment of industrial wastewater or landfill leachates where efficiency of oxidation has been analysed mainly with respect to COD. Results of these studies have shown that oxidation efficiency depends on a type of oxidant, pH of the reaction environment and process condition. For example, Deng et al. [33] described the results of other researchers during oxidation of landfill leachate at a mean level of 53% for ozonation, 43% for application of ozone and hydrogen peroxide, 52% for O_3/UV , 77% for $\text{O}_3/\text{H}_2\text{O}_2$ oxidation, and 71% for Fenton's reaction [33]. Other studies in the literature have mainly focused on oxidation of individual hydrocarbons (or several compounds) and have been often conducted using clean matrices without PAHs to which a specific amount of hydrocarbons is added and changes in concentration are monitored for the adopted oxidation conditions. Process conditions are diversified and oxidation efficiency also varies for individual hydrocarbons, from several percent to 100% depending on the oxidant type, its dose, examination matrix, temperature, reaction time and pH of the environment [25, 26, 29, 34]. Examinations described in the present paper were conducted using municipal wastewater containing a certain amount of suspensions and other compounds, both organic and inorganic. Therefore, PAHs removal efficiency in this study was in most cases lower than in the studies discussed in the literature since a specific amount of oxidant is consumed for oxidation of other organic pollutants. It should be emphasized that intermediate products are periodically formed during decomposition of complex organic compounds such as PAHs. In the case of PAHs, oxidation products include diols, quinones and aldehydes. For example, benzo[a]pyrene-1,6-dione and benzo[a]pyrene-3,6-dione were identified during oxidation of BaP [10, 29]. Therefore, further research on identification of derivatives of hydrocarbon oxidation and toxicity of these compounds is needed, since it has been shown in the literature that products of PAHs degradation can be more toxic than basic compounds. Analysis of the results obtained for the adopted experimental conditions leads to the following conclusions:

- oxidation by means of hydrogen peroxide can be used at the third stage of treatment of municipal wastewater in order to oxidise organic pollutants, including PAHs,

- efficiency of PAHs oxidation reached 74% for total concentration of 16 compounds, whereas for individual hydrocarbon, it ranged from 35 to 89% which confirms varied susceptibility to decomposition of the compounds from the PAH group,
- hydrocarbons containing cyclopentane rings are degraded faster than the compounds containing only benzene rings in their structure,
- further research on identification of intermediate products of oxidation and toxicological examinations are needed.

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References

- [1] Kumar A., Sengupta B., Kannaujia M.Ch., Priyadarshinee R., Singha S., Dasguptamandal D., Mandal T., Treatment of coke oven wastewater using ozone with hydrogen peroxide and activated carbon, *Desalin. Water Treat.* 2017, 69, 352-365.
- [2] Smol M., Włodarczyk-Makula M., Włóka D., Adsorption of polycyclic aromatic hydrocarbons (PAHs) from aqueous solutions on different sorbents, *Civil Environ. Eng. Rep. CEER* 2014, 2, 86-97.
- [3] Perez S., Guillamon M., Barcelo D., Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants, *J. Chromatogr. A* 2001, 938, 57-65.
- [4] Busetti F., Heitz A., Cuorno M., Badoer S., Traverso P., Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant, *J. Chromatogr. A* 2006, 1102, 04-115.
- [5] Forsgren Wastewater Treatment, Occurrence and Fate of Polycyclic Aromatic Hydrocarbons (PAHs), ed. J. Amy, CRC Press, 2015.
- [6] Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, *Dz.U.* 2014, poz. 1800.
- [7] Rozporządzenie Ministra Środowiska z dnia 6 maja 2016 r. w sprawie wykazu substancji priorytetowych, *Dz.U.* 2016, poz. 681.
- [8] Rozporządzenie Ministra Środowiska z dnia 19 lipca 2016 r. w sprawie form i sposobu prowadzenia monitoringu jednolitych części wód powierzchniowych i podziemnych, *Dz.U.* 2016, poz. 1178.
- [9] Meng X., Zhang H., Li Y., Cao H., Sheng Y., Analysis of polycyclic aromatic hydrocarbons (PAHs) and their adsorption characteristics on activated sludge during biological treatment of coking wastewater, *Desalin. Water Treat.* 2016, 57, 23633-23643.
- [10] Lawal A., Polycyclic aromatic hydrocarbons, A review, *Cogen Environ. Sci.* 2017, 3, 1339841 (1-89).
- [11] Malakahmad A., Hoe Ho L.L., UV/H₂O₂ oxidation process optimization by response surface methodology for removal of polycyclic aromatic hydrocarbons (PAHs) from water, *Desalin. Water Treat.* 2017, 65, 408-417.
- [12] dos Santos I.F., Ferreira S.L.C., Dominquez C., Bayona J.M., Analytical strategies for determining the sources and ecotoxicological risk of PAHs in river sediment, *Microchem. J.* 2018, 137, 90-97.

- [13] Torreta V., Katsoyiannis A., Occurrence of polycyclic aromatic hydrocarbons in sludges from different stages of a wastewater treatment plant in Italy, *Environ. Technol.* 2013, 34, 5-8, 937-943.
- [14] Mezzanotte V., Anzano M., Collina E., Marazzi F.A., Lasagni M., Distribution and removal of polycyclic aromatic hydrocarbons in two Italian municipal wastewater treatment plants in 2011-2013, *Polycyc. Aromat. Comp.* 2016, 36, 3, 213-228.
- [15] Qiao M., Qi W., Liu H., Qu J., Occurrence, behavior and removal of typical substituted and parent polycyclic aromatic hydrocarbons in a biological wastewater treatment plant, *Water Res.* 2014, 52, 11-19.
- [16] Ozaki N., Takamura Y., Kojima K., Kindaichi T., Loading and removal of PAHs in a wastewater treatment plant in a separated sewer system, *Water Res.* 2015, 80, 337-345.
- [17] Manoli E., Samara C., The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: Experimental calculations and model predictions, *Environ. Pollut.* 2008, 151, 3, 477-485.
- [18] Hussain H., Lintelmann J., Determination of polycyclic aromatic hydrocarbons in wastewater, sediments, sludge and plants in Karak Province, Jordan, *Water, Air, Soil Pollut.* 2000, 121, 1-4, 217-228.
- [19] Alawi M.A., Tarawneh I.N., Ghanem Z., Removal efficiency of PAH's from five wastewater treatment plants in Jordan, *Toxin Rev.* 2018, 37, 2.
- [20] Traczewska T., *Aspekty ekologiczne zanieczyszczenia środowiska wodnego wielopierścieniowymi węglowodorami aromatycznymi*, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2000.
- [21] Haddox D.C., Cutright T.J., Evaluation of two bacterial delivery systems for in-situ remediation of PAH contaminated sediments, *Soil. Sedim.* 2003, 3(1), 41-48.
- [22] Haftka J.J.H., Govers H.A.J., Parsons J.R., Influence of temperature and origin of dissolved organic matter on the partitioning behaviour of polycyclic aromatic hydrocarbons, *Environ. Sci. Pollut. Res.* 2010, 17, 1070-1079.
- [23] Edokpayi J.N., Odiyo J.O., Popoola O.E., Msagati T.A.M., Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in Vhembe District, South Africa *Inter. J. Environ. Res. Public Health* 2016, 13, 387 (1-12).
- [24] Lepri L., Bubba M.D., Masi F., Udristi R., Cini R., Particle size distribution of organic compounds in aqueous aerosols collected from above sewage aeration tanks, *Aerosol Sci. Technol.* 2000, 32, 404-420.
- [25] Lin C., Zhang W., Yuan M., Feng C., Ren Y., Wei C., Degradation of polycyclic aromatic hydrocarbons in a coking wastewater treatment plant residual by an O₃/ultraviolet fluidized bed reactor, *Environ. Sci. Pollut. Res. Int.* 2014, 21(17), 10329-10338.
- [26] Little C., Hephher M.J., El-Sharif M., The sono-degradation of phenanthrene in an aqueous environment, *Ultrasonics* 2002, 40, 667-674.
- [27] Włodarczyk-Makula M., Zmiany ilościowe WWA w ściekach oczyszczonych podczas utleniania, *Rocz. Ochr. Środ.* 2011, 13, 2, 1093-1104.
- [28] Włodarczyk-Makula M., Wiśniowska E., Turek A., Obstój A., Removal of PAHs from coking wastewater during photodegradation process, *Desalin. Water Treat.* 2016, 57, 1262-1272.
- [29] Rubio-Clemente A., Torres-Palma R.A., Penuela G.A., Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: A review, *Sci. Total Environ.* 2014, 478, 201-225.
- [30] Hemanowicz W., *Fizyczno-chemiczne badanie wody i ścieków*, Arkady, Warszawa 1999.
- [31] Zgirski A., Gondko R., *Obliczenia biochemiczne*, Wydawnictwo Naukowe PWN, Warszawa 2010.
- [32] Włodarczyk-Makula M., Preparation of wastewater samples for GC analysis of PAHs, *Arch. Environ. Prot.* 2008, 34, 3, 259-264.

- [33] Deng Y., Zhao R., Advanced Oxidation Processes (AOPs) in wastewater treatment, *Curr. Pollut. Rep.* 2015, 1, 167-176.
- [34] Torreta V., PAHs in wastewater: removal efficiency in a conventional wastewater treatment plant and comparison with model predictions, *Environ. Technol.* 2012, 33, 8, 851-855.

Streszczenie

Celem badań było określenie efektywności usuwania WWA ze ścieków podczas ich doczyszczania. W pracy przedstawiono wyniki badań zmian ilościowych WWA w poddawanych utlenianiu ściekach komunalnych oczyszczonych odpływających z miejskiej oczyszczalni ścieków. Oczyszczalnia pracuje jako mechaniczno-biologiczna z chemicznym usuwaniem fosforu. Badania prowadzono po wprowadzeniu do ścieków oczyszczanych dodatkowej ilości WWA w postaci standardowej mieszaniny. Następnie prowadzono proces utleniania zanieczyszczeń organicznych ze szczególnym uwzględnieniem zmian w stężeniu WWA, z wykorzystaniem nadtlenu wodoru. Utleniacz stosowano w postaci 30% roztworu w dawkach wynoszących 2,5 i 5 mg/dm³. Efektywność usuwania WWA określano z uwzględnieniem zawartości początkowej badanych związków oraz dodanej w postaci wzorca. Analizowano stężenia 16 WWA zgodnie z listą EPA. Oznaczenia jakościowo-ilościowe prowadzono z wykorzystaniem chromatografu gazowego ze spektrometrem masowym. W procesie utleniania odnotowano znaczny spadek stężenia badanych WWA w ściekach. Ubytek sumarycznej ilości WWA w ściekach wzbogaconych WWA był w zakresie od 61 do 74%, lecz dla poszczególnych węglowodorów efektywność usunięcia wahała się od 35 do 90%.

Słowa kluczowe: WWA, GC-MS, ścieki, proces utleniania