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Simultaneous oxidation and adsorption of PAHs in effluents from industrial treatment plant

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ABSTRACT

The aim of the study was to determine the removal of polycyclic aromatic hydrocarbons (PAHs) during oxidation as well as simultaneous process of oxidation and adsorption in effluents coming from industrial treatment plant. Technological research was conducted with the use of biologically treated coking wastewater. Advanced oxidation was carried out by dihydrogen peroxide. The adsorption process was carried out with activated carbon. Gas chromatograph and mass spectrometer system was applied for quantitative and qualitative determination of PAHs. 16 hydrocarbons according to US EPA list were analyzed. The changes in the PAHs concentration were determined after: 1, 4 and 24 h. The experiments were conducted at constant: pH and temperature. After 24 h the effectiveness of PAHs degradation during oxidation process reached 59%. Removal efficiency of the sum of 16 hydrocarbons under oxidation and adsorption integrated process was higher and reached 82%. The degradation of individual compounds in the oxidation process varied from 28% to 68%, respectively. During integrated process of oxidation and adsorption on activated carbon, the PAHs removal was in the range 55%–88%. During oxidation process, higher concentration of two- and three-ring PAHs was found when compared with the initial concentration. The reason is that low molecular weight PAHs can occasionally arise from the decomposition of high molecular weight hydrocarbons and degradation of other organic compounds. In the removal of high molecular hydrocarbons, adsorption process was significant and then, the adsorbed PAHs were decomposed.

Keywords: Oxidation; Dihydrogen peroxide; Adsorption; Activated carbon; GC-MS; PAHs

1. Introduction

Application of additional treating processes in third step of treating wastewater is of increasing importance in wastewater technology. This is because the effectiveness of removal of organic micropollutants in wastewater treatment plants is not sufficient [1–3]. Recently, contaminants determined in micro- and nanogram concentrations in effluents from wastewater treatment plants become increasingly important. At present, attention is paid into the efficient removal of organic and inorganic pollutants from effluents to obtain lower load of pollutants entering surface waters. That is important as surface waters are sources of water for water supply systems. Among organic pollutants, polycyclic aromatic hydrocarbons (PAHs) composed of two or more condensed aromatic rings can be distinguished. The presence of PAHs in water and wastewater was found in many literature data [1–4]. In Polish regulations, the permissible values of five PAHs in waters intended for human consumption included in effluents coming from wastewater treatment plant are omitted [5]. The former investigations carried out by the researchers on treated wastewater proved that removal of PAHs is not sufficient although high level of wastewater treatment is carried out [6–9]. This trend is observed both in effluents originating from municipal and industrial wastewater treatment plants. Only certain load

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of micropollutants is removed in the industrial wastewater treatment plants. The requirements of best available techniques (BATs) for effluents quality force to apply the advanced methods and processes intended for removal or decomposition of pollutants entering the receiver. It is mainly aimed to organic pollutants not only PAHs but also organic chlorine, phosphorus and bromide derivatives, coloring agents and other contaminants as well [3,4,10,11]. Some of them have carcinogenic and mutagenic or teratogenic impact on the organisms. They accumulate in organisms leading to damages of the genetic material. Hydrocarbon derivatives have also carcinogenic properties that occur in environment or in organism as a result both of metabolic or co-metabolic fates [12–14]. PAH derivatives may be formed during reaction with other components of the matrix such as: halogenation, nitration, sulfonation, alkylation and acylation. They also form products of oxidation reactions and photochemical degradation. Oxidation of hydrocarbons can provide the following products: diols, quinones and aldehydes. For example, benzo(a)pyrene can be transformed into benzo(a)pyrene-1,6-dione and benzo(a)pyrene-3,6-dione. In literature there are many available information on the analysis of PAH derivatives, that are formed during decomposition [4,8,9,12–14]. Literature data and own studies indicate that PAHs can be effectively removed in physical and chemical processes. In processes of sorption or membrane separation, hydrocarbons are only removed from the solution but are not degraded. Decomposition of the aforementioned persistent compounds is possible during advanced oxidation processes (AOPs) [15–20]. This is according to the IED (Industrial Emissions Directive 2010/75/EU) aimed at integrated prevention and reduction of industrial emissions, where the application of BATs is required [21].

Activated carbons are mostly used in the removal of organic compounds including PAHs. Currently, the results of investigation of applying other sorbents are reported in literature data. Activated carbon is produced from the following waste materials: nut shells, fruit waste, etc. The information of applying activated carbon in the removal of PAHs from wastewater is limited [22–28]. The results of studies and own studies confirm that activated carbons may be successfully applied in the removal of organic compounds from water solutions. It should also be highlighted that mixture of various organic compounds in water solutions results in limited efficiency of sorption of selected compounds due to the competitive sorption of other compounds. In water PAHs are eliminated during conventional chemical oxidation processes: ozonation and direct photolysis [26–30]. AOPs are regarded to be alternative methods in the removal of organic compounds from water solutions (industrial wastewater, landfill leachate) [31–35]. Advanced oxidation methods are more often used in the treatment of industrial wastewater. The literary sources indicate high efficiency of AOPs in removal of organic substances with a special attention to those resistant to biodegradation (PAHs, pesticides, etc.) [10–14,16–20]. AOPs rely on the production of hydroxyl radical that decomposes organic compounds and their intermediate products of decomposition to CO_2, H_2O and inorganic ions (Cl^-, NH_4^+, SO_4^{2-}). Ozone, dihydrogen dioxide, Fenton reagent, permanganate, UV radiation and ultrasound are responsible for the generation of hydroxyl radicals. Total decomposition of organic contaminants can be obtained using photocatalysis (TiO_2 + UV) [12,13]. In the Fenton reaction (Fe^{2+}/H_2O_2), the efficiency of process depends on:

- dose of Fe^{2+} and H_2O_2 (the value of the ratio between the amount of iron Fe^{2+} ions and hydrogen peroxide), pH, reaction time, temperature of the reaction environment,
- characteristic of the oxidized substance and the presence of other inorganic and organic compounds [16–20,34–36].

Application of the Fenton's reagent in oxidation of selected PAHs can be found in a wide range of literary sources. Studies on the advanced oxidation of PAHs have been carried out in water solutions with individual or a few hydrocarbons only. It should be pointed out that PAHs are found in the environment as a mixture of various compounds. Thus, the experiments with aqueous solutions of PAHs do not reflect the real environmental conditions. The results are also divergent due to various conditions of the process. Many scientific data are available about the removal organic compounds in two-step process: sorption process and advanced chemical oxidation process [14,24,31]. Simultaneous sorption and oxidation can be regarded as another system. In integrated process, activated carbon plays a role of the sorbent of organic compounds as well as a catalyst in the formation of hydroxyl radicals. In this case the adsorbed organic compounds may be oxidized on surface of adsorbent. The dissolved organic compounds may undergo degradation by hydroxyl radical in liquid phase [14,24]. Studies aiming at the determination of removal efficiency of hydrocarbons by combing both processes have been undertaken due to satisfactory effects of the removal of PAHs during the sorption and oxidation of these compounds as well as under oxidation conditions [24,37–39]. The decomposition of PAHs in industrial wastewater under oxidation in the presence of activated carbon has not been considered so far despite the fact that many investigations into AOPs and adsorption have been carried out. The monitoring of changes in PAH concentration during these processes was also not investigated. Advanced oxidation methods seem to be promising ones due to sufficient treatment of industrial wastewater after biological treatment. Numerous experiments aiming to determine the mechanisms of transformation and PAHs removal from industrial wastewater are carried out in Poland and other countries [14]. It should be pointed that among 16 aromatic compounds listed by US EPA (United States Environmental Protection Agency), 8 of them have carcinogenic and/or mutagenic and teratogenic properties. The former studies included:

- PAHs chemical oxidation (dihydrogen dioxide) in the presence of catalysts (titanium or platinum or cobalt catalyst) in aqueous solutions [36].
- PAHs photo-oxidation in treated municipal and coke wastewater with the use of dihydrogen dioxide [38–40]. Therefore, the aim of the investigation was to monitor PAHs concentration during simultaneous chemical oxidation and adsorption processes. The effectiveness of PAHs removal/degradation under oxidation condition in the presence of activated carbon was determined.

2. Materials and methods

2.1. Materials and reagents

The experiments were carried out using biologically treated coke plant wastewater. Samples of wastewater effluents were taken from an industrial wastewater treatment plant. Coke wastewater originating from technological processes with activated sludge and nitrification of ammonia nitrogen removal were investigated. The wastewater samples were taken once.

2.1.1. Reagents

- Standard mixture of 16 PAHs (produced by Ultra Scientific);
- 30% solution of pure dihydrogen dioxide (POCH, Poland);
- Powdered activated carbon C 2186 (Merck).

2.1.2. Solvents

- Methanol of chromatographic purity – 99.9% (POCH, Poland);
- Dichloromethane of chromatographic purity 99.8% (POCH, Poland);
- Cyclohexane of chromatographic purity 99.5% (POCH, Poland);
- Columns filled with silica gel (JT Baker).

2.2. Experimental procedure

In raw wastewater samples coming from industrial treatment plant, the initial organic matter was determined by chemical oxygen demand (COD), total organic carbons (TOCs) and PAHs. The experiments were carried out using dihydrogen dioxide (30%) – strong oxidant. The amount of the oxidant equal to 10 mL/L was previously adjusted [36,38–40]. The sorption in the amount of 1 g/L was carried out using powdered activated carbon (Merck: No 2186). The dose of activated carbon was chosen based on the previous studies as well as literature data [23,24,38].

According to the data given by Merck, the amount of adsorbed blue methylene and iodine was higher than 120 and 70 mL/g, respectively. Heavy metals content (such as Pb) did not exceed 0.003%, whereas content of Fe and Zn did not exceed 0.03% and 0.001%, respectively. The content of sulfur and chloride was low and did not exceed 0.01%. The water content was below 10%, water solubility and acid soluble were below 0.5% and 1%, respectively [41].

The experiment was carried out at a constant temperature of 20°C, pH of wastewater was 7.2 on average. The period of carrying the simultaneous process of oxidation and adsorption was constant and equal to 24 h. The wastewater samples taken from industrial treatment plant were not filtered before oxidation. After adding oxidant and activated carbon, samples were mixed for 1 h. Concentration of PAHs and COD was determined threefold after: 1, 4 and after 24 h of oxidation process. Concentration of organic compounds (given as COD) was determined. Samples were performed in duplicate to determine the significant changes in the concentration of PAHs. Student's *t*-test was used in order to determine the confidence level 0.95 and degree of freedom 2 for the results performed in duplicates. The theoretical value of t_d was equal to 4.303.

2.3. Analytical methods of PAHs

PAH analysis included the initial sample preparation as well as chromatographic quantitative and qualitative determination. The preliminary preparation of wastewater samples was carried out during extraction of organic substances by liquid–liquid method. Solvents: methanol, cyclohexane, dichloromethane (v/v 20:5:1) were added to 500 mL of wastewater. Then, samples were shaken for 60 min at constant amplitude. Then, extracts were separated from wastewater by centrifugation. Samples containing activated carbon were filtered and then, both solution and suspension samples were further analyzed. In this case mixture of solvents was added to the suspension. The extraction was conducted by shaking samples on the linear shaker within 1 h. Afterwards, extract was separated in glass classifier by flushing the walls few times. Then, anhydrous sodium sulphate was added to bind the remaining wastewater. Then, the extracts were purified in vacuum (solid-phase extraction) using columns filled with silica gel (fill conditioning was performed with a mixture of dichloromethane and cyclohexane, v/v 1:5, 3 × 3 mL). The extracts were concentrated to the volume of 2 mL under a nitrogen stream. PAHs were determined quantitatively and qualitatively using gas chromatography coupled with mass spectrometer (GC–MS). The analysis was performed on a column DB-5 ms, length of 30 m and a diameter of 0.25 mm. Helium was used (with flow rate 1.08 mL/min) as a carrier gas. The time of analysis was equal to 50 min. The flow rate of samples was 1.5 mL/min. Qualitative and quantitative determination was carried out using external standard of 16 PAHs at a concentration of 200 ng/mL each. The recovery values were determined for individual PAHs, and then the average concentration of the following PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene and indeno(1,2,3 c,d)pyrene was calculated. In Table 1 selected properties of individual PAHs and recovery values are included. The reference value of each hydrocarbon was equal to 200 ng/mL. The recoveries for individual PAHs were in range 38%–118%. Recovery values were determined for series of triplicate samples. The average concentrations of individual PAH were calculated. In further experiment, the obtained hydrocarbons concentration was taken as the initial one.

3. Results and discussion

The content of organic compounds in wastewater taken from coke wastewater treatment plant expressed by COD was equal to 412 mg/L, whereas the TOC value was equal to 256 mg/L. During oxidation process both COD and TOC value decreased. After 24 h of oxidation process, COD decreased to the value of 146 mg/L. In the presence of activated carbon, COD dropped to the value of 123 mg/L. The results of organic compounds removal of this study correspond with the results of other studies [14,24]. The dihydroxen dioxide

Table 1
Selected properties and recoveries of PAHs

PAHs	Number of rings/ benzene rings	Solubility at temperature 25°C	Octanol/water coefficient	Value (ng/L)	Recovery (%)
Naphthalene Naph	2/2	31.7	3.37	76	38
Acenaphthylene Acyl	3/2	3.93	4.07	84	42
Acenaphthene Ac	3/2	3.9	4.33	124	62
Fluorene Flu	3/2	2.0	4.18	143	72
Anthracene Ant	3/3	0.07	4.54	182	91
Phenanthrene Phen	3/3	1.3	4.57	146	73
Fluoranthene Fl	4/3	0.3	5.22	219	109
Pyrene P	4/4	0.14	5.32	236	118
Benzo(a)anthracene BaA	4/4	0.012	5.61	196	98
Chrysene Ch	4/4	0.002	5.61	201	100
Benzo(b)fluoranthene BbF	5/4	0.0012	6.57	186	98
Benzo(k)fluoranthene BkF	5/4	0.00055	6.84	224	112
Benzo (a)pyrene BaP	5/5	0.003	6.04	179	89
Dibenzo(a,h)anthracene DahA	5/5	0.0005	6.75	183	92
Indeno(1,2,3,c,d)pyrene IP	6/5		6.91	152	76
Benzo(g,h,i)perylene BghiP	6/6	0.00026	7.23	162	81
16 PAHs				∑16 PAHs – 2,693	Average 85

is the strong oxidant (Eh value equal to 2.7 mV) and many organic compounds undergo degradation under oxidation conditions [40].

The initial concentration of 16 PAHs ranged the average value of 19,637 µg/L. Three-ring hydrocarbons (9,357 µg/L) comprised 48% of the total analyzed PAHs. Four-ring and five-ring hydrocarbons constituted 35% and 13% of the total PAHs content, respectively. Concentration of naphthalene was the lowest (270 µg/L). Concentration of carcinogenic compounds ranged the value of 4,849 µg/L. During oxidation process and simultaneous oxidation and adsorption process, the total concentration of PAHs decreased. However, the concentration of individual hydrocarbons fluctuated, mainly low molecular mass compounds such as: naphthalene, acenaphthylene, acenaphthene.

3.1. Changes in the concentration of two- and three-ring PAHs

The initial concentration of two- and three-ring PAHs ranged the value of 9,357 µg/L. In Fig. 1 changes in the concentration of naphthalene and anthracene during oxidation process and during integrated oxidation and adsorption process are given. After 1 h of experiment, the concentration of naphthalene was higher than initial one. Naphthalene concentration was two times higher than initial one. It is probably due to the fact that naphthalene is a by-product of decomposition of high molecular mass hydrocarbons. Under oxidation conditions, the hydrocarbons were decomposed and naphthalene was identified as the product. This phenomenon was observed in the previous studies carried out by Kozak and Włodarczyk-Makuła [38].

After 4 and 24 h the concentration of naphthalene was lower than after 1 h of process. The final naphthalene concentration under oxidation conditions and under oxidation process in the presence of activated carbon was 194 and 121 µg/L, respectively. The effectiveness in the removal of naphthalene was low and did not exceed 28% during oxidation process. In the presence of activated carbon, effectiveness in the removal of hydrocarbons achieved 55%. Considering three-ring hydrocarbons, changes in the concentration of anthracene was similar to the changes in the naphthalene concentration. After 1 h of oxidation process, the concentration of anthracene was higher than initial one. After 4 and 24 h, the concentrations were lower than the concentration after 1 h of conducting experiment. The efficiency of anthracene removal during oxidation and during simultaneous oxidation and adsorption process was 48% and 78%, respectively. In Fig. 2 changes in the concentration of anthracene and fluorene are presented. During process similar changes in the concentration of acenaphthene and fluorene were observed. The highest concentration of these compounds was determined after 4 h of experiment. The effectiveness in the removal of acenaphthene under oxidation process was equal to 61%. In the presence of activated carbon, the effectiveness in the removal of hydrocarbons achieved 91%. The efficiency of the fluorene removal during oxidation and during oxidation coupled adsorption process achieved 59% and 86%, respectively.

The concentration of acenaphthylene increased gradually within time. It is confirmed that acenaphthylene is a by-product of decomposition of high molecular mass hydrocarbons. The presence of activated carbon did not affect the concentration of this compound during 4 h of oxidation. After 24 h of oxidation, the concentration of acenaphthylene was lower than after 4 h but higher than the initial one. The increase of acenaphthylene concentration was significant compared with the initial one. In Fig. 6 changes in the concentration of phenanthrene are presented.

In Fig. 3 changes in the concentration of acenaphthylene and phenanthrene are presented.

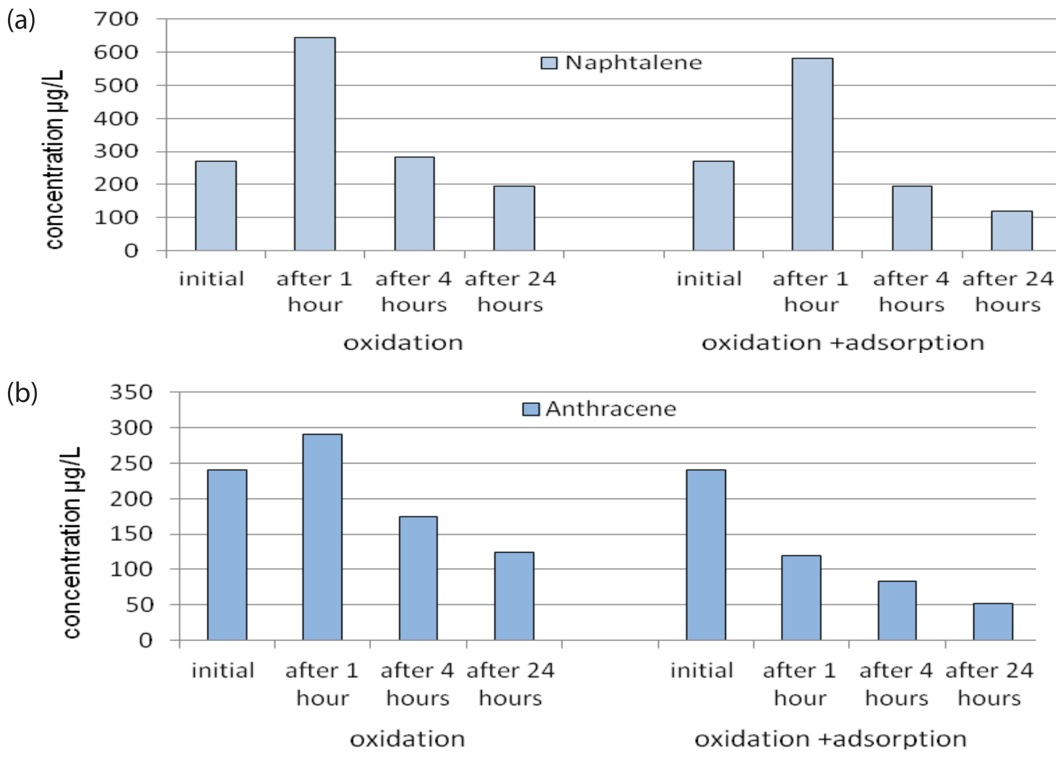

Fig. 1. Changes in the concentration of (a) naphthalene and (b) anthracene during oxidation process and during simultaneous oxidation and adsorption process.

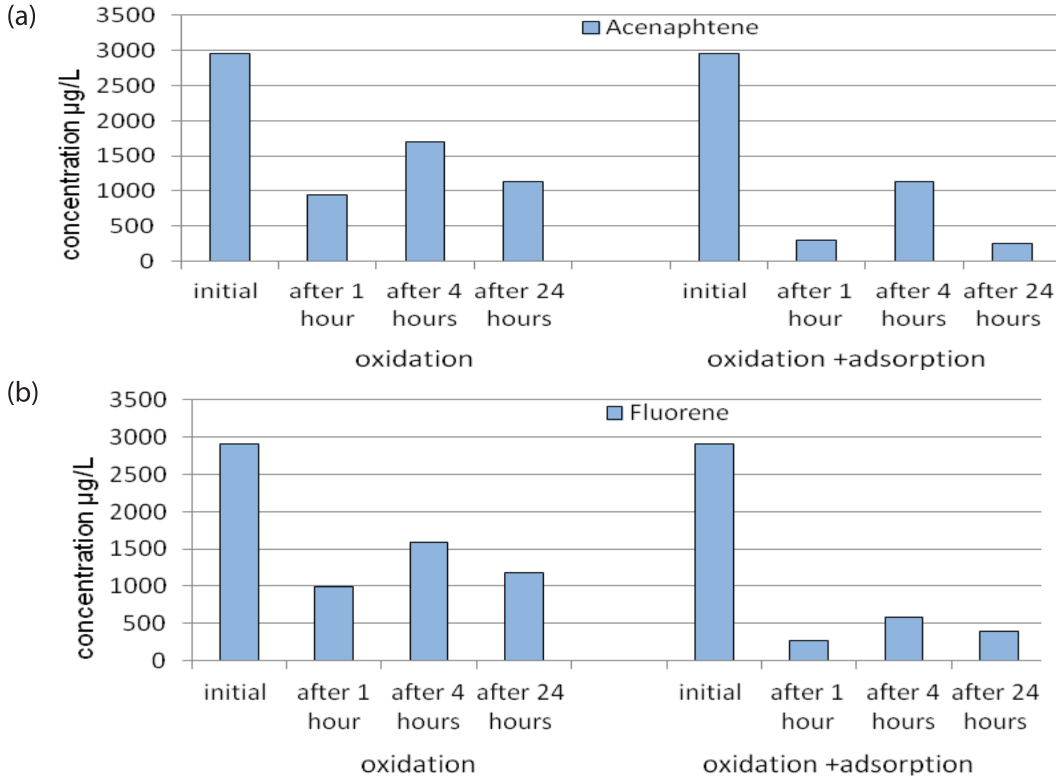

Fig. 2 Changes in the concentration of (a) acenaphthene and (b) fluorene during oxidation process and during simultaneous oxidation and adsorption process.

During oxidation with dihydrogen dioxide, the total concentration lowered. After 24 h the concentration of phenanthrene was lower than the initial one of 51%. The addition of activated carbon increased the efficiency of PAHs removal of 87%. During integrated processes, the concentration of phenanthrene was lower than the concentration under oxidation conditions of 20%. The efficiency of three-ring PAHs removal during oxidation and adsorption process achieved 57% and 87%, respectively. In Table 2 percentage of PAHs removal is given.

3.2. Changes in the concentration of four-ring PAHs

The initial concentration of four-ring PAHs ranged the average value of 6.906 µg/L. That constituted 35% of total content of hydrocarbons. The initial concentration of fluoranthene and pyrene ranged values: 2,820 and 2,341 µg/L, respectively. Changes in the concentration of fluoranthene and pyrene are included in Fig. 4.

After 24 h of oxidation process with dihydrogen dioxide, the concentration of fluoranthene was lower than the initial

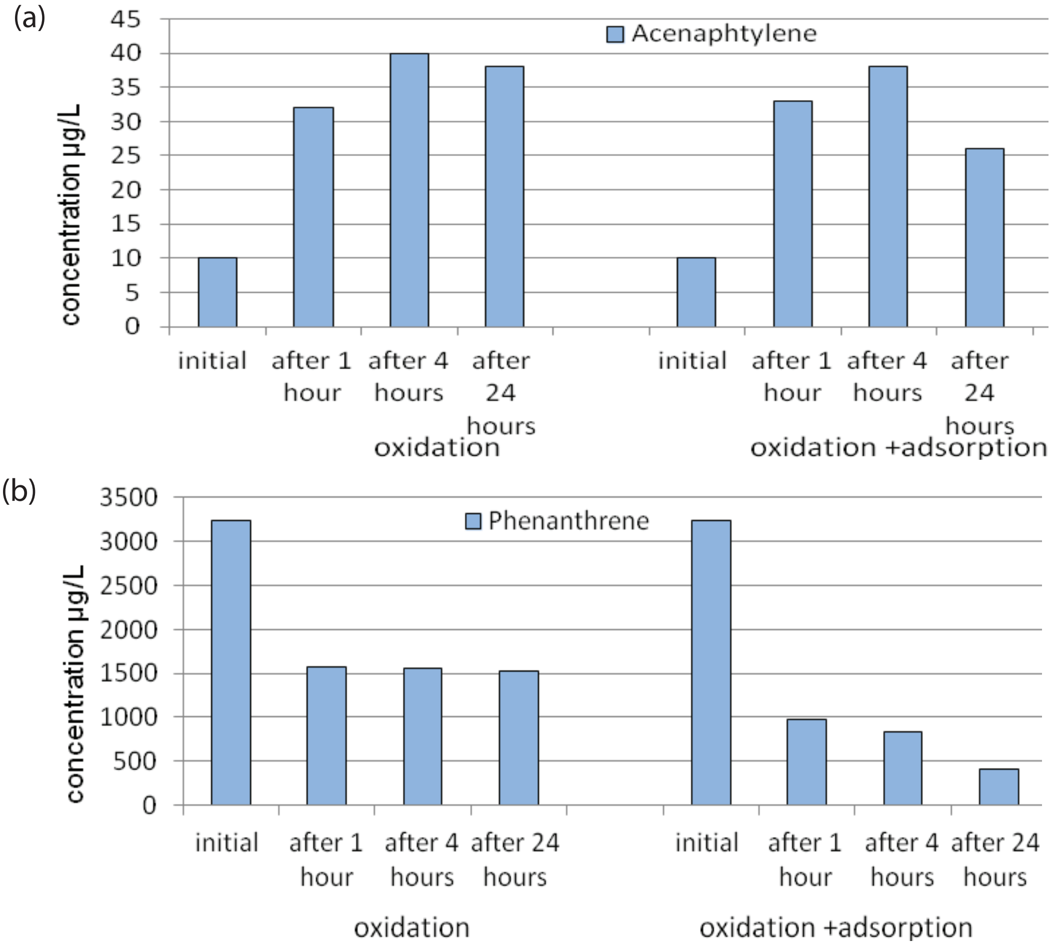

Fig. 3 Changes in the concentration of (a) acenaphthylene and (b) phenanthrene during oxidation process and during simultaneous oxidation and adsorption process.

Table 2
Effectiveness of PAHs removal (%) under oxidation and simultaneous process (the average values)

PAHs	Oxidation process				Oxidation and adsorption process			
	After 1 h	After 4 h	After 24 h	Result of test	After 1 h	After 4 h	After 24 h	Result of test
Naphthalene	–	–	28	+	–	28	55	+
3-ring of PAHs	59	46	57	+	82	71	88	+
4-ring of PAHs	19	39	62	+	58	67	80	+
5-ring of PAHs	35	54	68	+	37	64	75	+
6-ring of PAHs	26	38	43	+	36	66	70	+
Total 16 compounds	38	44	59	+	64	68	82	+

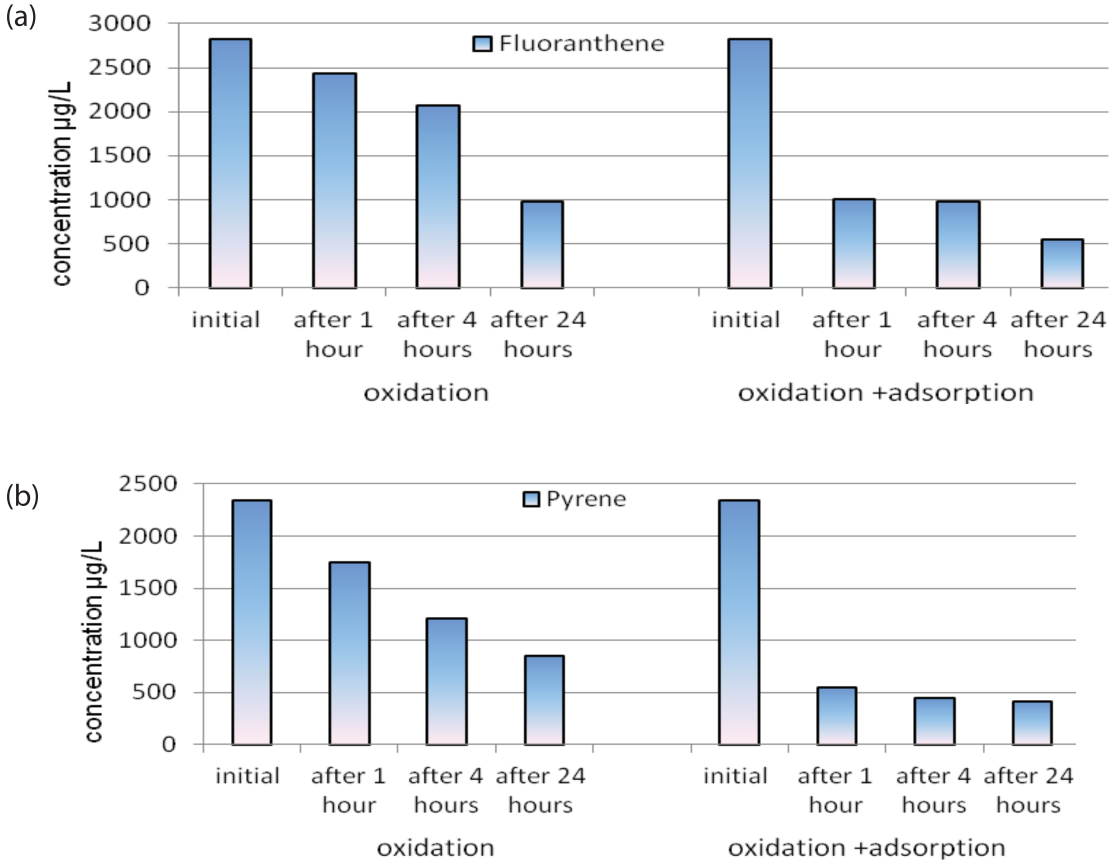

Fig. 4. Changes in the concentration of (a) fluoranthene and (b) pyrene during oxidation process and during simultaneous oxidation and adsorption process.

one of 65%. The addition of activated carbon improved the efficiency removal of 15%. The efficiency of pyrene removal during oxidation and adsorption processes achieved 64% and 83%, respectively. In Fig. 5 changes in the concentration of benzo(a)anthracene and chrysene during oxidation process and during integrated oxidation and adsorption processes are presented.

The efficiency of benzo(a)anthracene removal during oxidation and adsorption processes achieved 25% and 49%, respectively; the final concentration of benzo(a)anthracene was equal to 382 and 259 µg/L, respectively. Similar changes in concentration of chrysene and anthracene were noted. The final concentrations of chrysene were lower than the initial concentrations of 65% and 87% under oxidation and simultaneous oxidation and adsorption process, respectively. The efficiency of four-ring hydrocarbons removal during oxidation and adsorption processes achieved 62% and 80%, respectively (Table 2). The final concentration of four-ring PAHs did not exceed the values of 2,600 and 1,400 µg/L, respectively.

3.3. Changes in the concentration of five-ring PAHs

The initial total concentration of five-ring hydrocarbons ranged the value of 2,462 µg/L. After adding dihydrogen dioxide to wastewater 68% decrease of hydrocarbons was noted. During simultaneous processes of oxidation and adsorption, the decrease in the five-ring PAHs content ranged 75% (Table 2). Monitoring of five-ring hydrocarbons concentration in wastewater showed a gradual decrease similar to four-ring compounds. Changes in benzo(b)fluoranthene and benzo(k)fluoranthene concentration during oxidation and adsorption process are given in Fig. 6.

The percentage of benzo-fluoranthene compounds removal was equal to 68% and 75% under oxidation and adsorption condition, respectively. In Fig. 7 changes in the concentration of benzo(a)pyrene and dibenzo(ah)anthracene during oxidation process are included, respectively.

Removal of five-ring PAHs was the most significant under oxidation process. Under oxidation process in the presence of activated carbon, the removal of five-ring PAHs increased to only 7%. It was surprised because the coefficients of octanol/water values of five-ring PAHs are high and the hydrocarbons adsorbed onto solid particles very quickly and tightly.

3.4. Changes in the concentration of six-ring PAHs

In Fig. 8 changes in the concentration of benzo(ghi)perylene and indeno(123cd)pyrene during oxidation and during simultaneous oxidation and adsorption process are included. The initial concentration of six-ring compounds ranged the value of 642 µg/L.

After oxidation with dihydrogen dioxide, the total concentration was lower than the initial one of 43%. The addition of activated carbon improved PAHs removal efficiency of 27%.

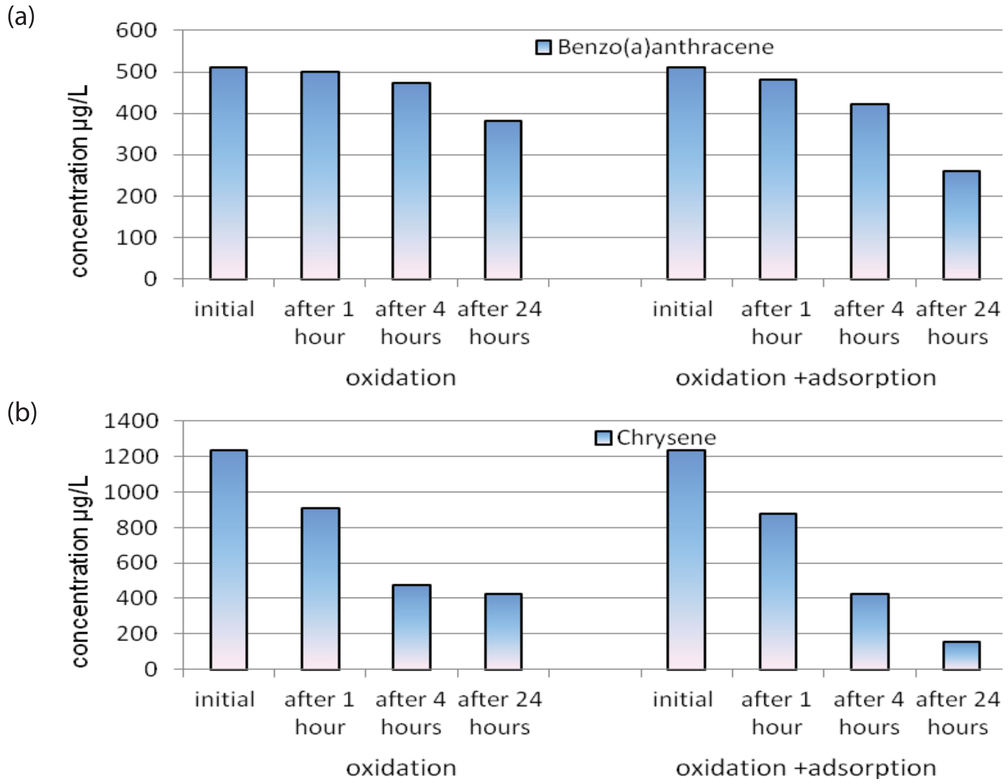

Fig. 5 Changes in the concentration of (a) benzo(a)anthracene and (b) chrysene during oxidation process and during simultaneous oxidation and adsorption process.

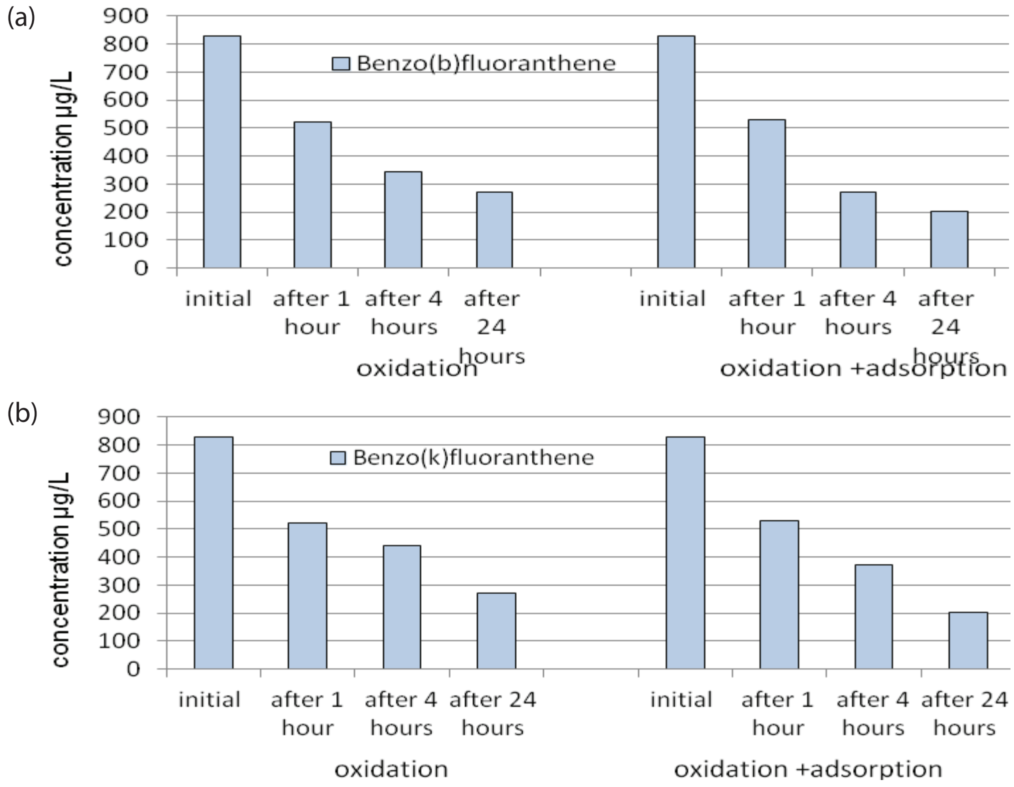

Fig. 6 Changes in the concentration of (a) benzo(b)fluoranthene and (b) benzo(k)fluoranthene during oxidation process and during simultaneous oxidation and adsorption process.

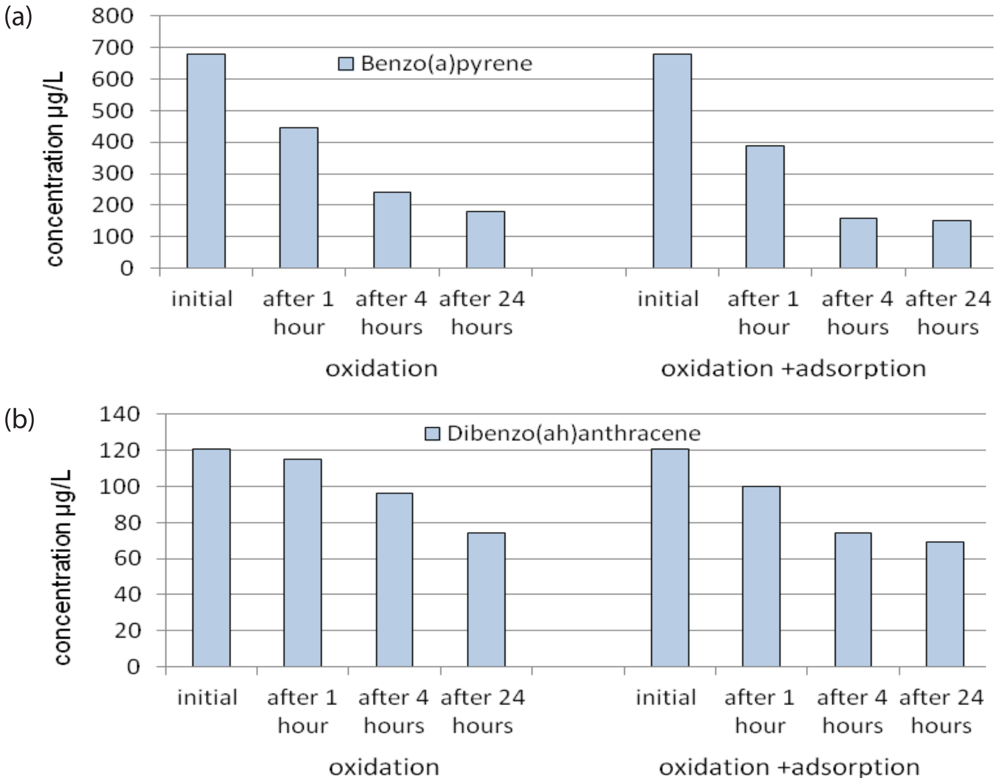

Fig. 7. Changes in the concentration of (a) benzo(a)pyrene and (b) dibenzo(ah)anthracene during oxidation process and during simultaneous oxidation and adsorption process.

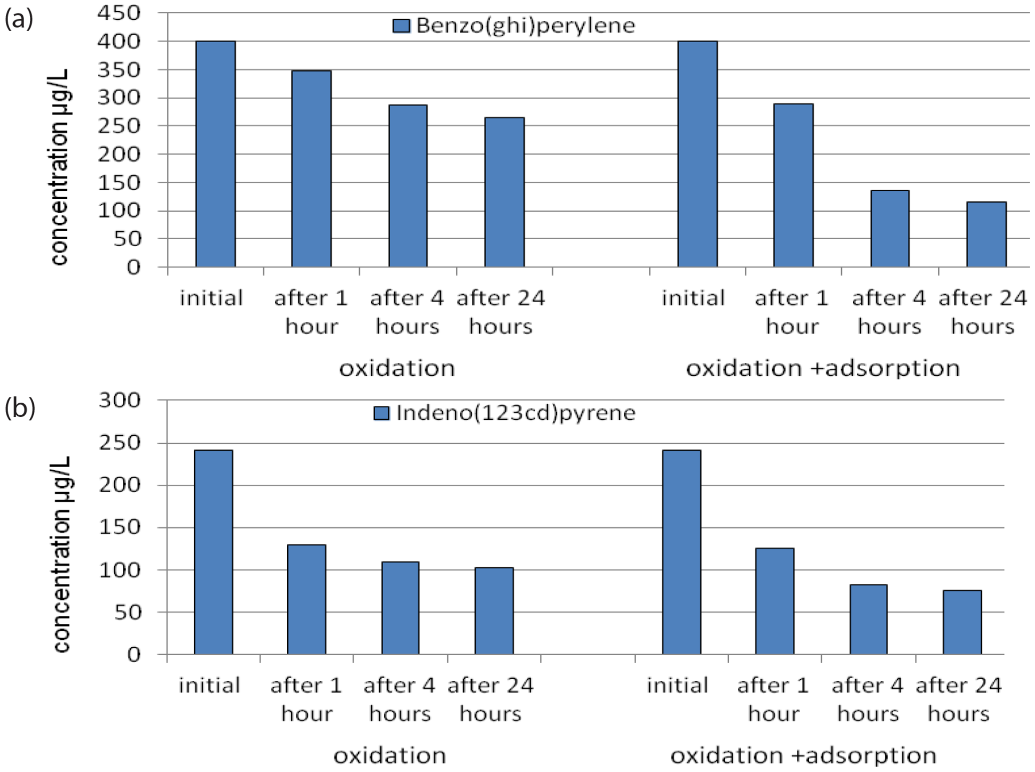

Fig. 8. Changes in the concentration of (a) benzo(ghi)perylene and (b) indeno(123cd)pyrene during oxidation process and during simultaneous oxidation and adsorption process.

In simultaneous adsorption and oxidation process, the decrease of PAHs was higher than during only oxidation and ranged the value of 70%. Under oxidation process independent of activated carbon, presence of the degradation of PAHs was observed. After adding dihydrogen dioxide, the concentration of analyzed hydrocarbons decreases of 59%. During simultaneous process of oxidation and adsorption, the decrease in PAHs content ranged 82%. After 24 h the concentration of 16 PAHs ranged the value of 8,007 and 3,448 μg/L under oxidation and simultaneous process, respectively. The efficiency of degradation of individual compounds was diversified. The results indicate that more favorable conditions of two- and three-ring hydrocarbons removal appeared during simultaneous oxidation and adsorption in the initial step of investigations. This was also observed in former studies but for shorter period of experiment (2 h) [37–39]. In the previous studies, the decrease in the concentration of hydrocarbons occurred after 4 h. Adsorption process was important in the removal of PAHs. The presence of activated carbon enhanced the degradation of analyzed compounds. The increase of percentage of PAHs removal in the presence of adsorbent varied from 7% to 31%. The presence of activated carbon was not statistically significant in the removal of five-ring PAHs. In contrast to these hydrocarbons, the presence of adsorbent was statistically significant for other compounds. The most persistent were six-ring PAHs. The percentage of oxidation of hydrocarbons did not exceed 43%. Effectiveness of PAHs degradation increased with the increase of molecular weight, number of rings in the molecule and the value of octanol/water coefficient, respectively.

In the studies the applied activated carbon has physical–chemical parameters recommended for determination of adsorbable organic halogens according to the standard German method. The carbon has qualities parameters certified by Merck [41].

In order to carry out the proper process of oxidation, it is necessary to form hydroxyl radicals under optimal conditions: temperature of 20°C, pH 7.2 and time from few to several minutes. Therefore, it can be concluded that in the conducted experiment, first sorption on activated carbon took place probably whereas, PAHs oxidation occurred in solution and on activated carbon surface, that could also played a role of catalyst. The studies of PAHs concentration adsorbed on activated carbon were also analyzed during former studies. The PAHs content extracted from adsorbent after 1 h of oxidation was compared with PAHs concentration in the solution. PAHs balance indicates that PAHs losses occurred both in solution and onto adsorbent [4]. In order to confirm this hypothesis, further experiment is required including monitoring of PAHs changes in the solution and onto activated carbons carried out in shorter time intervals.

The statistical calculations (Table 2) show that changes in the total concentration of 16 PAHs were significant with respect to applied adsorbent (calculated t_d value was greater than the critical value). Statistics showed that application of activated carbon resulted in significant changes of three-, five- and six-ring hydrocarbons concentration. It should be pointed out that under experimental conditions the highest decrease was found for hydrocarbons including cyclopentane ring. The cyclopentane ring is included in the structure of acenaphthylene, acenaphthene, fluorene, fluoranthene, benzo(b and k)fluoranthene and indeno(123cd)pyrene. The removal percentage of hydrocarbons was the highest and independent on adsorbent presence. The results indicate significant impact of sorption despite the high solubility in the water.

Literature data obtained with applying AOP for the removal of organic compounds are widely found. Mainly the removal of organic compounds as a COD indicator in adsorption or oxidation process separately can be found. For example, coking wastewater treatment in adsorption process was investigated by Choudhary and Chaudhari [23]. It was found that removal of COD by adsorption using fly ash was in the range 17%–24%. The percentage of phenol removal on activated carbon did not exceed 37% [23]. Advanced catalytic oxidation of coking wastewater with photo-Fenton process was examined by Zhang et al. [34]. Both TOC and COD removal rates reached 65% within 2 h. The catalytic dosage of 1 g/L and the H_2O_2 concentration was 14.68 mmol/L [34]. Meng et al. [42] investigated PAHs removal during biological treatment of coking wastewater during adsorption process onto activated sludge. The adsorption effectiveness of PAHs depended on sorption time and on activated sludge concentration. The concentration of PAHs in coking wastewater sludge was in the range 0.6–2.2 mg/g [42]. In the previous studies, COD value was reduced of 40%–63% [38,39]. In integrated systems, the removal of organic substances in several literary sources is described. For example, treatment of coke wastewater using ozone and activated carbon was examined by Kumar et al. [24]. The percentage degradation of organic compounds was similar. COD removal was 77% and 76% in integrated process and in oxidation process, respectively [24]. The removal of organic compounds, including PAHs in integrated processes was previously studied but time of reaction was shorter. After 2 h of oxidation process, COD value decreased by 40%–48%. PAHs concentration after 2 h was lower than the initial one of 4%–81% under oxidation condition and of 17%–100% during simultaneous process [39].

4. Conclusion

It can be concluded as follows:

- efficiency of degradation of 16 studied hydrocarbons (total concentration) did not exceed 59% on average under oxidation conditions whereas, under simultaneous oxidation and adsorption onto activated carbon was equal to 82%.
- efficiency of degradation of individual hydrocarbons (except acenaphthylene) was in the range 28%–73% under oxidation conditions whereas, under simultaneous oxidation and adsorption onto activated carbon was in the range 55%–91%, respectively.
- simultaneous oxidation and adsorption may be effectively applied in the last step of coke wastewater treatment.

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