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Removal of PAHs from coking wastewater during photodegradation process

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ABSTRACT

The results of investigations on the efficiency of the removal of polycyclic aromatic hydrocarbons (PAHs) from wastewater exposed to UV radiation are presented. The investigations were carried out using wastewater originating from an industrial treatment plant. Samples of wastewater were exposed to UV rays for 30, 60, and 90 s. After exposition to UV rays, PAHs concentration was determined in the samples. Extraction of PAHs from samples was made with the mixture of: cyclohexane and dichloromethane. The quantitative analysis of PAHs by high performance liquid chromatography with a fluorimetric detector was carried out. After exposition to ultraviolet rays, a decrease in PAHs concentration in the samples was observed. Exposure of wastewater to UV-rays resulted in a decrease in the concentration of PAHs in wastewater from an industrial wastewater treatment plant up to 50%. The efficiency of the removal for individual hydrocarbons was varied as it was in the range of 5–67%. The half-life time of hydrocarbons (without naphthalene) was in the range of 64–123 s under exposition to UV rays.

Keywords: PAHs; HPLC-DAD; Photodegradation; Coking wastewater; Half-life time

1. Introduction

Industrial wastewater is the main vehicle for polycyclic aromatic hydrocarbons (PAHs). The highest concentrations of PAHs are found in a coke plant and crude oil refining plant wastewater [1–3]. Removal efficiency of biochemical treatment processes in wastewater treatment plants towards PAHs is insufficient. In the case of municipal wastewater, as it was stated previously, about 15% of an influent PAHs load is present in the treated effluent [4]. As far as a big municipal wastewater treatment plant is considered, daily several tens grams of 16 EPA-PAHs may be discharged into surface water. According to Polish law regulations, no limit values for PAHs in treated effluents are established. It is only mentioned that carcinogenic compounds should be eliminated from wastewater [5]. Simultaneously, however, selected PAH compounds are considered by legislation as indicators of surface and underground water pollution [6]. PAHs are also represented as indicators in regulations concerning water quality monitoring [7]. Thus, elaboration and implementation of effective processes of PAHs removal from treated effluents is of great importance in order to

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protect the quality of surface water. PAHs are classified as permanent environmental pollutants, but under unstable conditions they undergo biological and physicochemical degradation [2,8–10]. Among the abiotic processes which are involved in PAHs degradation, there are included both the ones making it possible to relocate these micropollutants from one environment to the other and the ones bringing on destruction of PAHs (destructive processes are mainly chemical oxidation and photodegradation). During degradation processes, new compounds are generated [11–14]. Due to such chemical reactions as halogenation, nitration, sulfonation, alkylation, or arylation, derivative compounds are generated. Up to now, their identification has been, however, only fragmentary [15]. Photodegradation and oxidation are regarded as the most effective PAHs degradation methods, but in natural environment they may occur only in surface layers of water and soil. During photolysis, benzene ring cleavage takes place and, consequently, destruction of PAHs occurs. When exposed to light, oxygen aromatic hydrocarbons relatively easily form such epoxy compounds as: chinones, dihydric alcohols, phenols, aldehydes, and nitrogen derivatives, e.g. 1,5-dihydrohynaphthene, carbazole, acridine, 9-fluorenon, 9-hydroxyphenanthrene, 4-hydroxyacridine, xanthone, antraquinone, 1,8-dihydroxyantraquinone, and 1-nitropirne. As the number of condensed rings in PAHs particle increases, it undergoes oxidation easier (also elecrophilic substitution). The results of research works indicate that PAHs are degraded under UV radiation of wavelength in the range of 10–400 nm, as well as under electromagnetic radiation (gamma rays of wavelength lower than 124 pm) [16–18]. As a result of breakdown of this compound 1,6-, 3,6-, and 6,12-BaP-quinones were identified as by-products [19]. The effect of photooxidation on PAHs removal from water which contained fulvic acids was investigated by Xia et al. [20]. During the research work, the samples were exposed to UV-A rays (of the wavelength 365 nm). The radiation was emitted by a xenon lamp. Hydrocarbons arranged in order of degradation rate were as follows [20]:

acenaphthene > pyrene > phenanthrene > fluorene > fluoranthene

As fulvic acids concentration increased, the degradation rate of acenaphthene, fluorene, and phenanthrene decreased. It was suggested that it was due to the fact that acids contributed to generation of active oxygen. Reactive oxygen presence increased the degradation rate from 33 to 69% [20]. Distinct order of hydrocarbons as a function of their degradation susceptibility was stated by Cataldo and Keheyan [21]. It was connected with the difference in reaction environment conditions including an alternative source of radiation. To irradiate the samples, a cobalt lamp (it emitted gamma rays; the source of radiation was 60 Co radioisotope, which emitted 2.7 kGy/h) was used. PAHs (17 compounds) were by contrast dissolved in acetonitrile. The intensity of irradiation was 100, 200, and 300 kGy. Coronene was the most persistent PAH compound. Based on the susceptibility to degradation, the following rank of order was established (from the most to the least persistent compound) [21]:

Coronene > chryzen > fluorene > 2-methylphenanthrene > acanaphthylene > pyrene > 3-metylphenenthrene > fluoranthene > phenanthrene > 1-metylnaphtalene > anthracene > naphtalene.

Complete degradation of selected PAHs was achieved as a result of ozone oxidation and radiation intensity 200 kGv. Ozone and oxygen mixture was also effective under these radiation conditions. Fluorene and chrysene were completely degraded in both cases. PAHs can be degraded during ozonization, but by-products of ozonization alone and ozonization supported by radiation are diversified. It is connected with the fact that PAH derivatives which are generated under irradiation are further oxidized when ozonization is involved in the process [21]. UV radiation was used to research degradation of PAHs adsorbed on fly ash particles. Effectiveness of photodegradation decreased as molecular weight of PAH compounds increased. UV B radiation speeded up degradation of these micropollutants [22]. In relation to soil samples, the effect of temperature, particles size, soil depth, and humic acids concentration on pyrene degradation was proved. Half-life time ($T_{1/2}$) of pyrene was dependent mainly on soil depth and as it increased from 1 to 4 mm, $T_{1/2}$ increased from 20 to 38 d. The presence of humic acids significantly increased the yield of pyrene photodegradation on the surface of soil (when the soil was exposed to UV radiation) [23–25]. Jamroz et al. [11] investigated oxidation of selected PAHs with hydrogen peroxide, ozone, and under UV radiation. The process parameters which allowed for complete degradation of benzo(a)pyrene, chrysene, and fluorine in water were set (at pH 7). It was shown that during photochemical processes, toxic by-products were generated. Toxicity of by-products to indicators was diversified. It was stated that when H_2O_2 was used as an oxidation agent, the most toxic products were formed [11]. During the earlier investigation, the removal of PAHs from treated municipal wastewater during the photodegradation process occurred [26]. The aim of the present investigation was to evaluate the effectiveness of PAHs degradation in coke plant wastewater exposed to UV radiation.

2. Materials and methods

2.1. Materials

Coke plant wastewater used in the study was taken from a coking factory wastewater treatment plant (FWTP). A coke plant produces high quality coke, coal chemicals, and coke oven gas. The wastewater was chosen as a substratum in research work due to high concentration of PAHs. In FWTP, wastewater is biologically oxidized as well as nitrified with an activated sludge method. The wastewater used in the study was the one utilized in closed quenching of the coke system. To limit PAHs emission to the atmosphere, it is crucial to determine the technological parameters which allow one to minimize the concentration of these micropollutants in wastewater. Coke plant wastewater was analyzed for selected physicochemical properties including organic compounds content (as TOC and COD). TOC concentration was equal to 185 mg/L and COD was equal to 1,242 mg/L. These values were in the range typical for coke plant wastewater.

2.2. Experimental procedure

Coke plant wastewater was irradiated by UV rays. Before irradiation, selected PAHs were analyzed in wastewater samples. The control sample (which was not irradiated) was prepared to evaluate the effectiveness of UV rays in PAHs destruction. The other samples of coke plant wastewater were exposed to UV rays (UV-C; wavelength 264 nm) for 30, 60, and 90 s. Wastewater samples were placed in a porcelain roller tray which was used as an open UV reactor; the depth of wastewater was equal to 2 mm. UV lamp was placed closely above the wastewater level. Changes in PAHs concentration were evaluated based on the analysis of these micropollutants before and after photodegradation.

2.3. PAHs analysis

In order to analyze PAH concentration in wastewater, the samples were extracted using liquid–liquid technique. Wastewater samples were mixed with cyclohexane/dichloromethane mixture (v/v = 5:1) and then they were shaken on a shaker with horizontal motion for 60 min. Organic extracts were separated from the water-phase and cleaned with SPE columns packed with silica gel. SPE columns were conditioned 3 × 3 mL of dichloromethane/cyclohexane mixture. Cleaned extracts were evaporated to dryness under a nitrogen stream. Dry residue was diluted with acetonitrile and chromatographically qualified and quantified for PAHs. The reversed phase high performance liquid chromatography (HPLC) was used to separate PAHs mixture. Quantification of PAHs was done with DAD detector. HPLC chromatograph (Waters model Aliance 2695) with Supelcosil LC-PAH column (15 cm × 4.6 mm × 5 μm), a fluorimetric detector (Waters 2475), and a photodiode detector (Waters 2998) were used during the study. The parameters of the method were as follows: time of analysis 40 min, time of stabilization —8 min. The flow rate through the column: 1.5 mL/min, temperature of column thermostating: 25°C. A flurimetric detector was calibrated so that the excitation wavelength would be equal to 275 nm, and the emission wavelength (emission WL) to 350 nm. The qualification of individual compounds was made by comparing their retention times with retention times set for standard solutions. Also, a specific PAHs fluorescence phenomenon was used (Fig. 1). The basic standard mixture of 16-PAHs with the concentration 2,000 μg/mL was used. For each PAH compound, five solutions were made (with concentrations 5,10,20,30, and 50 ng/mL. Some basic parameters of the mobile chase flow are listed in Table 1.

The following compounds were analyzed: naphthalene; 3-ring PAHs (acenapthene, fluorene, phenanthrene, anthracene); 4-ring-PAHs (fluoranthene pyrene, benzo(a)anthracene, chrysene,); 5-ring PAHs (benzo(b)fluoranthene, (benzo(k)fluoranthene, benzo(a) pyrene, dibenzo(ah)anthracene), and 6-ring ones (indeno(1,2,3 cd)pyrene, benzo(ghi)perylene) 77–103%. It means that they are within the range obtained by other authors for matrices containing suspended solids and diluted contaminants (literature data range is from 38 to 125%) [2,18].

The Student *t*-test was used in order to evaluate the statistical significance of the results. Comparison of affectivities of PAHs degradation in the wastewater exposed to UV rays was calculated according to *t*-test. The critical value was read from tables for the specified degree of freedom ($n-2$) and at a confidence level of 95%. The theoretical value of decomposition t_d ranged 4,303.

2.4. Calculation of PAHs half-life

Assuming that the speed of decomposition of a substrate PAHs takes place according to the first-order reaction, half-life $T_{1/2}$ of hydrocarbons was calculated according to the following equations [10]:

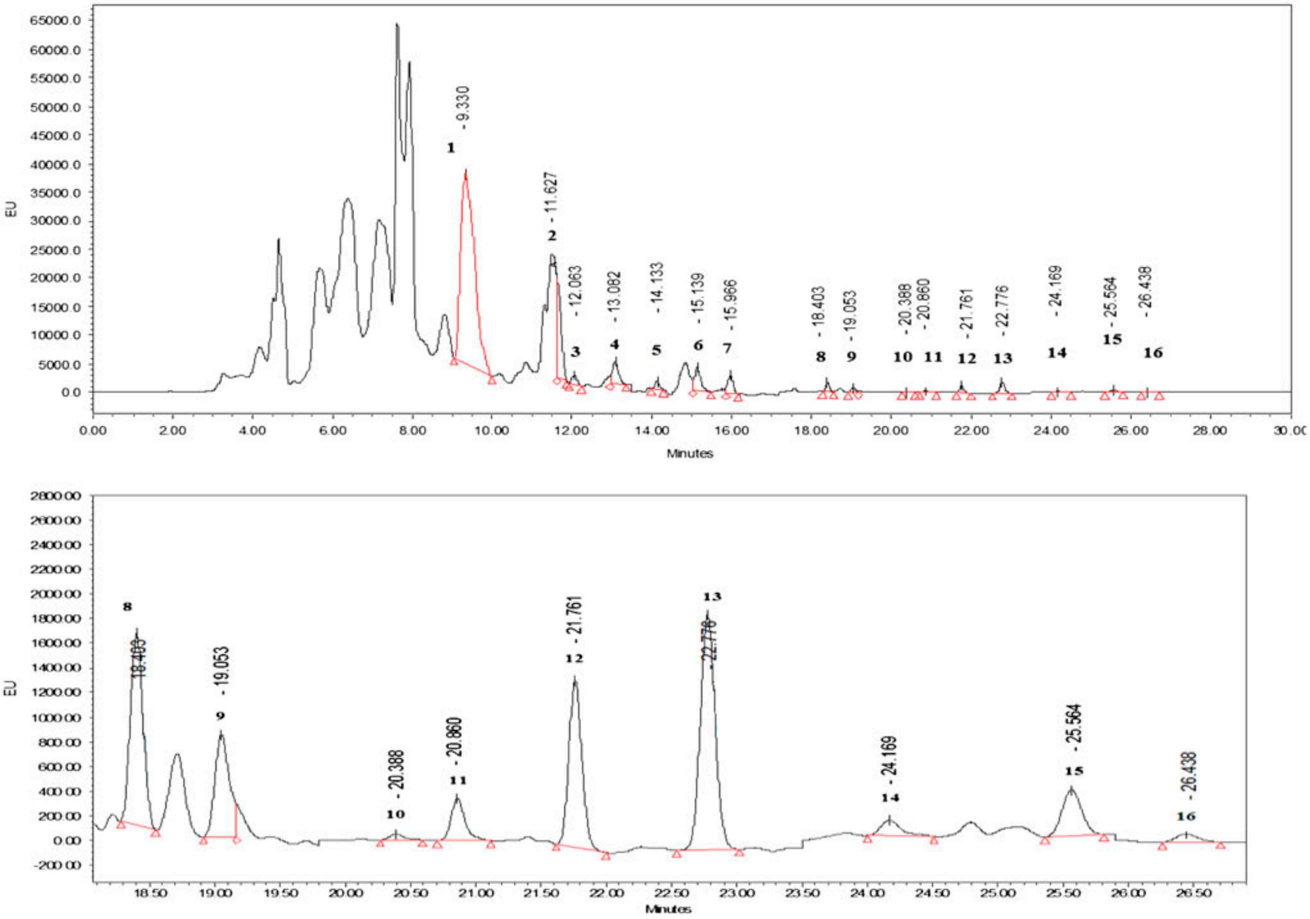

Fig. 1. Chromatograms of wastewater samples.
Notes: 1—Naphthalene, 2—Acenaphthene, 3—Fluorene, 4—Phenanthrene, 5—Anthracene, 6—Fluoranthene, 7—Pyrene, 8—Benzo(a)anthracene, 9—Chrysene, 10—Benzo(j)fluoranthene, 11—Benzo(b)fluoranthene, 12—Benzo(k)fluoranthene, 13—Benzo(a)pyrene, 14—Dibenzo(a,h)anthracene, 15—Benzo(g,h,i)perylene, 16—Indeno(1,2,3,c,d)pyrene.

Table 1
The flow of the mobile phase HPLC analysis

Time (min)	Flow rate (mL/min)	% A, acetonitrile	% B, methanol
0	1.5	55	45
5	1.5	55	45
30	1.5	0	100
36.10	1.5	55	45

$$T_{1/2} = \frac{\ln 2}{k} \quad (1)$$

and

$$\ln \frac{C_0}{C_t} = k \cdot t \ \ [\mathrm{s}] \quad (2)$$

where C_0—initial concentration of PAHs (μg/L); C_t—PAHs concentration in wastewater exposed UV rays (μg/L); t—time of exposition on UV (s); k—the reaction rate constant (s^{-1}).

3. Results

The total concentration of 15 analyzed PAHs in coke plant wastewater at the beginning of the experiment was in average equal to 323 μg/L. The most abundant compound was naphthalene (88% of total concentration) which is the best water soluble PAH compound of the analyzed ones during the study. Initial concentration of naphthalene in wastewater was high and it reached 286 μg/L. Concentration of 3-ring compounds was lower and it did not exceed 10% of the total PAHs concentration. Domination of low molecular weight hydrocarbons in wastewater discharged after thermal treatment of coal is typical since the main source of this wastewater is treatment of coke–oven gas. Coke–oven gas contains high quantities of these volatile and relatively well water soluble hydrocarbons. The percentage share of the remaining PAH compounds in the total concentration was at the level of fractional percent. Exposure of wastewater to UV radiation resulted in a decrease or fluctuation of individual compounds concentration. In Fig. 2, naphthalene concentration changes during UV exposure are presented.

No linear relationship between time of exposure and naphthalene concentration was stated under experimental conditions. The highest removal efficiency was not higher than 10%, and decreased as exposure time increased. Increases in naphthalene concentration were not statistically important (5.0–9.1%). An increase of naphthalene concentration in wastewater caused by increasing time of exposure could be a consequence of naphthalene formation as a product of higher molecular weight compounds degradation. Some literature data signalize that it is possible for such a mechanism to take place [11].

In Fig. 3 concentration changes of 3-ring compounds during exposure to UV irradiation are presented. The total concentration of 3-ring compounds decreased from 29 to 14 μg/L. For individual compounds, fluctuations of concentrations were stated. The highest removal efficiency was, however, observed for the shortest exposure time. Extension of exposure time to 9 s resulted only in 2–8% increase in removal efficiency. 3-ring hydrocarbons are relatively well water soluble (compared to other EPA PAHs) and have high vapor pressures, which results in their well volatility. These characteristics had some effect on their behavior during UV exposition of wastewater.

In Fig. 4 concentration changes of 4-ring PAHs are presented. The total concentration of these compounds reached 12 μg/L. A significant decrease (up to 40%) in total 4-ring compounds was stated after 30 s. exposure. Photodegradation efficiency of individual compounds was diversified and varied from 32 to 52%. It confirms that susceptibility of 4-ring compounds for photodegradation is not identical. The most resistant to UV rays compound was benzo(a)anhracene.

The total concentration of 5-ring hydrocarbons (BbF, BkF, BaP, and DahA) was low and did not exceed 2 μg/L. Since these compounds show high toxicity to living organisms, their removal from wastewater discharged into surface waters is of very high importance. In Fig. 5 concentration changes of 5-ring compounds are presented. Removal of total 5-ring PAHs as a result of UV rays exposure did not exceed 43% (for individual compounds it was in the range from 41 to 48%). The total concentration in coke plant wastewater before UV rays exposure was the lowest of all groups of hydrocarbons analyzed during the experiment (at level 0.2 μg/L). Similarly, as in the case of other hydrocarbons as a result of UV rays exposure, a decrease in benzo(ghi)perylene and indeno(123 cd)pyrene was stated (removal efficiency was, respectively, equal to 39 and 41% (Fig. 6).

In Fig. 7 changes in concentrations of PAH-compounds grouped according to the number of rings in particle are presented. As can be seen in Fig. 7, compounds which were the most resistant to photodegradation were 5-ring and 6-ring PAHs. Effectiveness of 5- and 6-ring PAHs degradation was not affected by time (changes in concentration were not statistically important in the function of time). In the

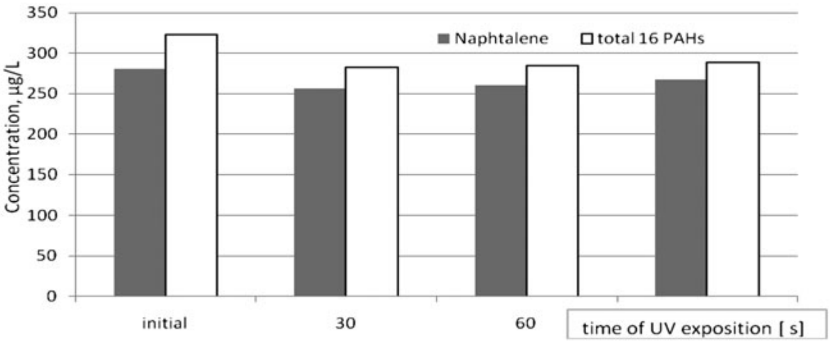

Fig. 2. Changes in the concentration of naphthalene in the UV irradiation and changes in the concentration of 16 PAHs degradation in UV irradiation.

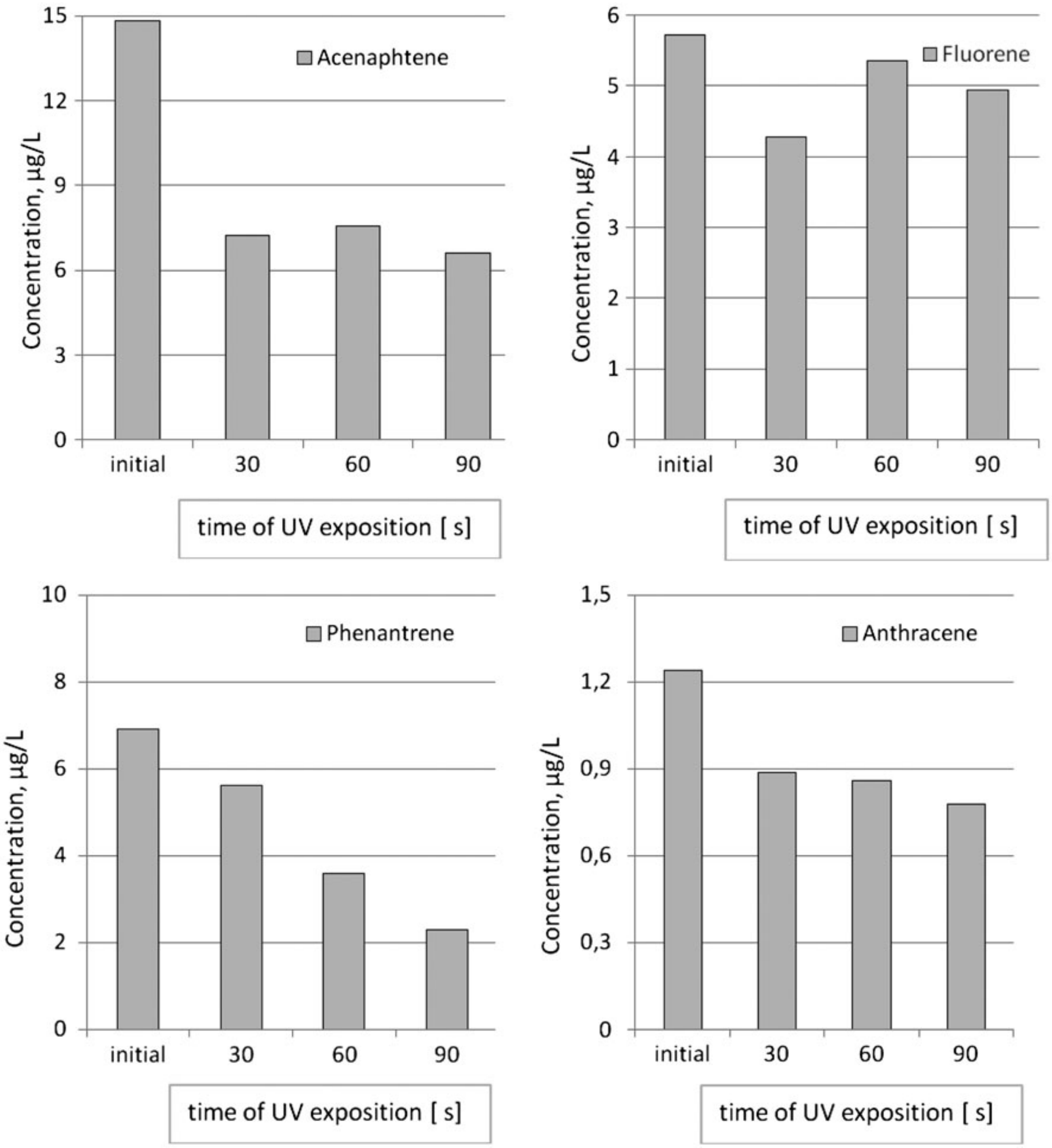

Fig. 3. Changes in the concentration of 3-ring of PAHs in the UV irradiation.

case of other hydrocarbons, the losses of their concentration were statistically important after 30 s exposure. Extension of exposure time apparently caused some improvement in removal efficiency, but the changes were not statistically important.

In Fig. 2, concentration changes of both naphthalene and the total concentration of 15 analyzed PAHs are presented. During exposition of wastewater to UV rays, an increase in naphthalene percentage share (up to 93%) in total PAH concentration was observed (in wastewater before exposure to UV percentage share of naphthalene was equal to 87%). Percentage shares of the other hydrocarbons fluctuated insignificantly after UV rays exposure.

Stable maintenance of naphthalene during UV exposure is decisive in interpretation of obtained results. In Table 2, effectiveness of photodegradation of individual compounds as well as half-life times are listed. Degradation efficiency for selected 15 PAHs was within the range 10–12%, whereas, effectiveness of 14 PAHs (excluding naphthalene) reached 50%.

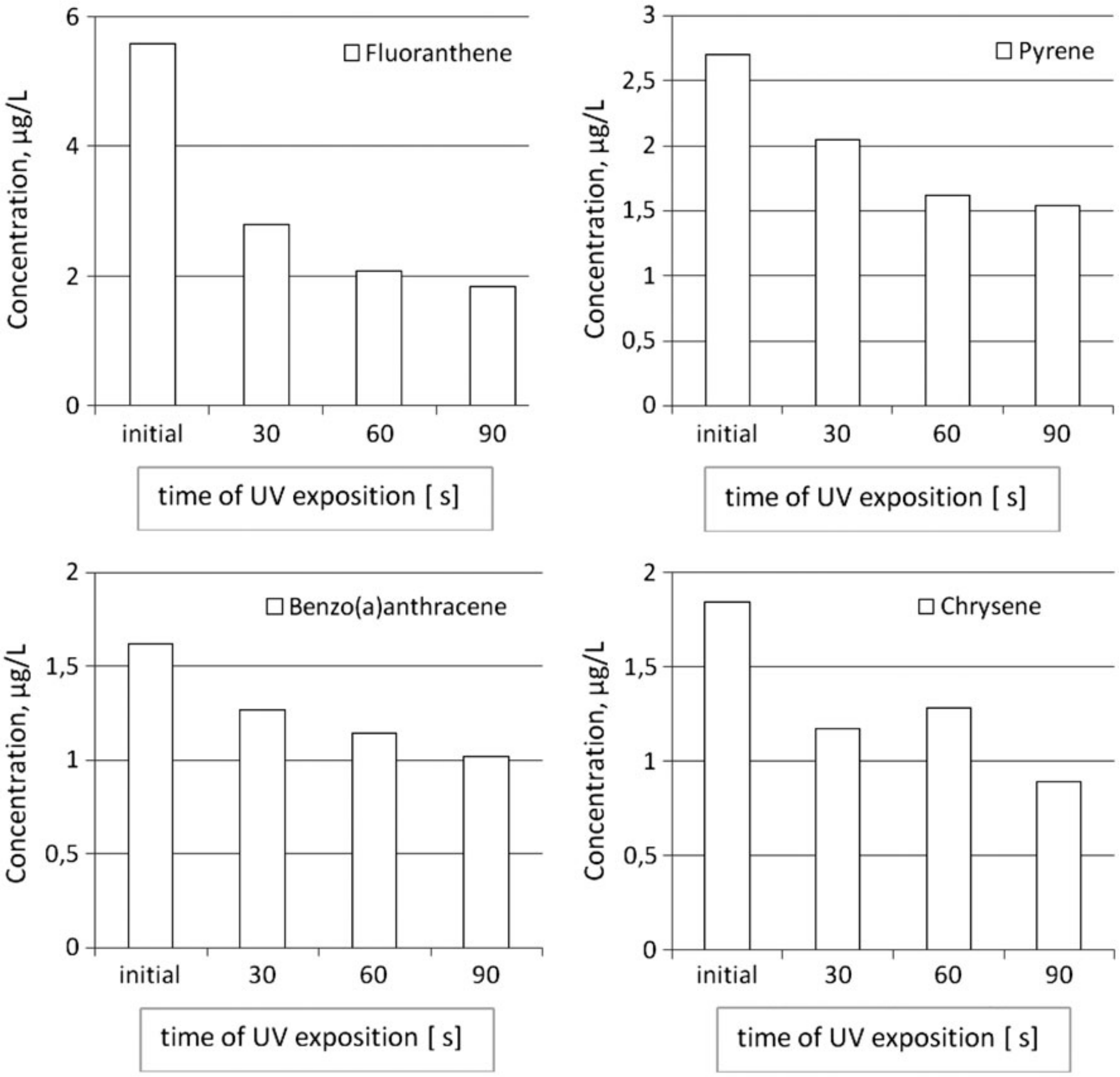

Fig. 4. Changes in the concentration of 4-rings of PAHs in the UV irradiation.

The half-times of hydrocarbons were in the range of 64–701 s (Table 2). The most persistence compound was naphthalene with a half-life time value equal to 701 s. Taking into consideration physicochemical properties of naphthalene (such as solubility in water, volatility) and also the possibility of generating this compound as a by-product of other compounds degradation value of half life presented above cannot be considered as credible. Among other compounds the most resistant to photodegradation were benzo(b) fluoranthene, fluorene, anthracene, and benzo(a)pyrene with half-life times higher than 100 s. Half-life times for remaining compounds were within the range 64–99 s (under experimental conditions). Taking into consideration the lowest concentration values obtained during the study, chemical reactivity of analyzed PAHs was as follows:

phenanthrene, fluoranthene > acenaphtene > chrysene > dibenzo(ah)anthracene > benzo(a)pyrene > pyrene > benzo(b)fluranthene > benzo(k)fluoranthene, indeno(123 cd)pyrene> benzo (ghi)perylene > benzo(a) anthracene > fluorene > naphtalene

In scientific literature, only fragmentary data on PAHs photodegradation mechanism are available. Most research works are focused on chlorine derivatives and on determination of degradation efficiency under various conditions [12,16,18–20,23]. It has been confirmed that removal of PAHs from water solutions exposed to oxygen and light are partially the

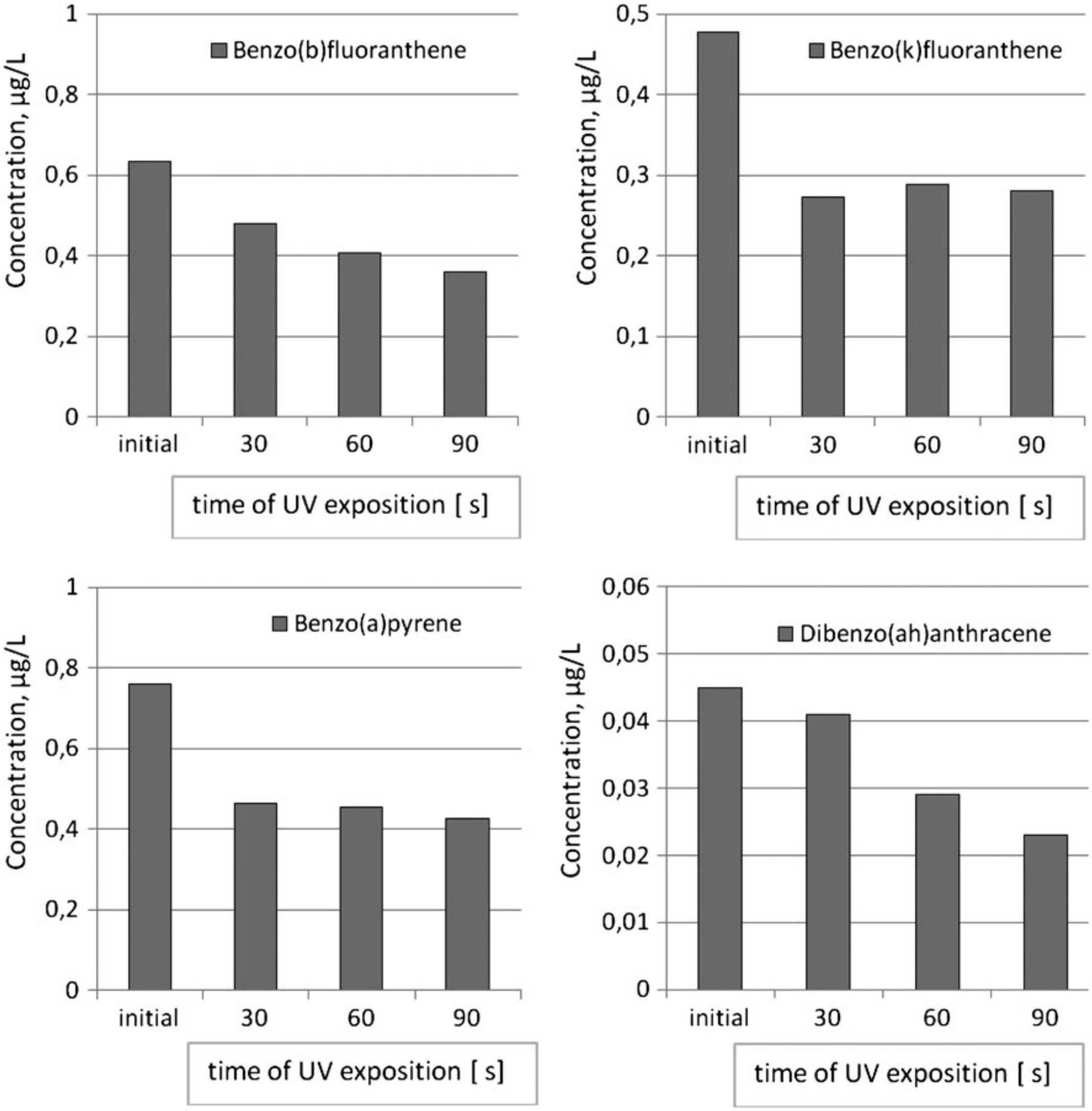

Fig. 5. Changes in the concentration of 5-rings of PAHs in the UV irradiation.

result of oxidation (in the case of highly volatile hydrocarbons) and partially are caused by forming by-products during degradation processes; e.g. during research of bezno(a)pyrene photodegradation two by-products were identified—benzo(a)pyrene-1,6-dione and benzo(a)pyrene-3,6-dione [22]. Zander [14] stated that as a result of photooxidation of dissolved benzo (a)pyrene mixture of three quinines are generated. Some data also confirm that in the presence of light and oxygen PAHs undergoing photodegradation generate not only quinines, but also dihydric alcohols and aldehydes [9]. It is believed that photodegradation is more effective when PAHs are adsorbed on solid particles. Then degradation time of BaP (under various conditions) was lower than one day. BaP half-life time during photolysis when there is more sunshine can be about two orders of attitude shorter than during other transformation processes [17,18]. Little et al. [16] conducted an experiment on the degree of phenanthrene degradation under various temperatures. At 20˚C about 3% degradation effectiveness was obtained at the presence of light, at 40˚C degradation effectiveness increased to 88% (but when degradation occurred in dark, the effectiveness was lower (up to 78%) [16].

It is hard to compare the results obtained in our study with the literature data because during the

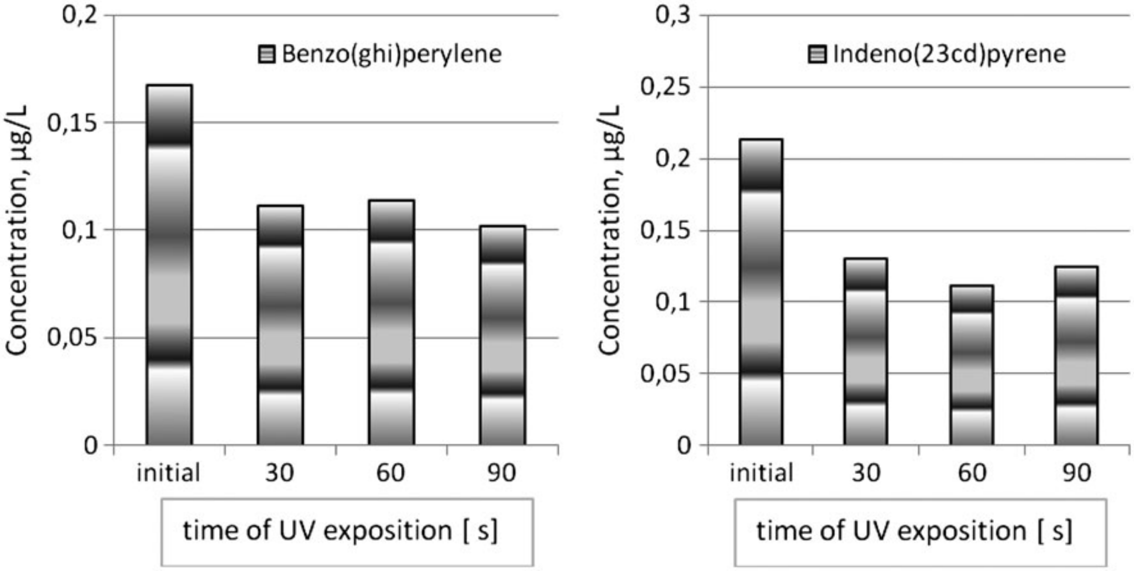

Fig. 6. Changes in the concentration of 6-rings of PAHs in the UV irradiation.

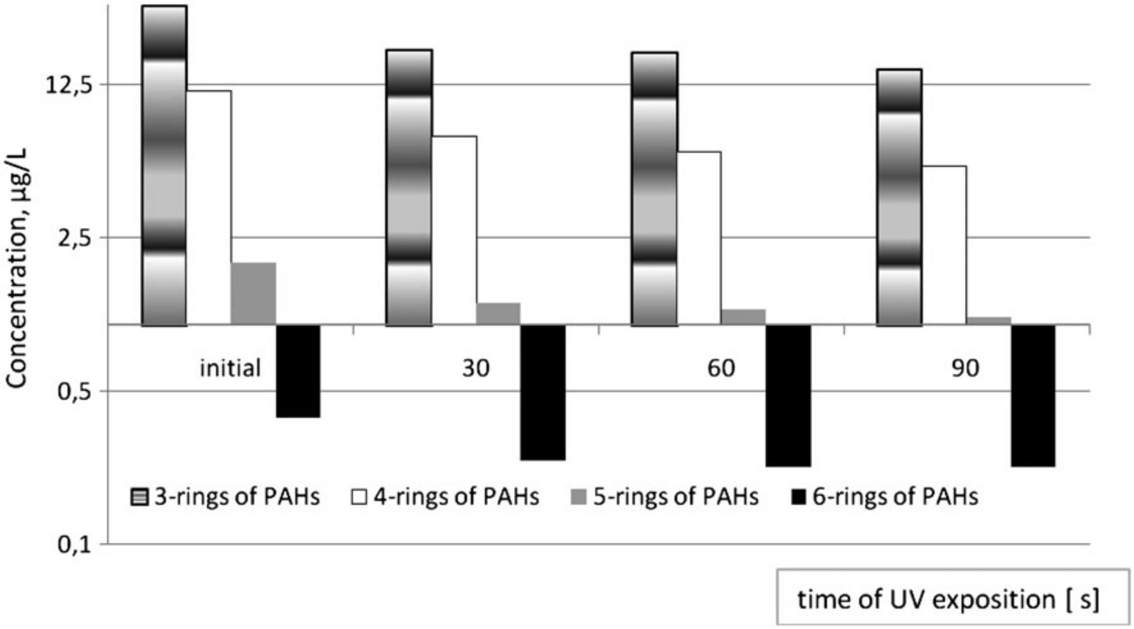

Fig. 7. Comparison of PAHs degradation in the UV irradiation.

experiment being described, real wastewater was used (interfering compounds present in sewage could affect the results). Whereas, data available in literature concern mainly water solutions of standard PAHs mixtures (less often environmental matrices), frequently, only one compound (representative for the group of PAHs) is investigated. Based on the literature data concerning environmental samples, PAHs photodegradation can only occur in surface layers of water and soil. Earlier research work of the co-author concerned PAHs degradation in municipal wastewater [24]. Degradation effectiveness of 16 PAHs did not exceed 65% for real wastewater. When wastewater was enriched with the standard mixture of PAHs, the effectiveness increased to 84%. Degradation efficiency of 3-ring PAHs was within the range of 50–64% and was

Table 2
The effectiveness of photodegradation process of PAHs and half-life of PAHs

PAHs	Effectivenes of PAHs photodegradation (%)	Half-life time (s)	PAHs	Effectivenes of PAHs photodegradation (%)	Half-life time (s)
Naphtalene	**5.0–9.1**	701	Benzo(b)fluoranthene	24.4–43.2	123
Acenaphtene	48.6–56.0	64	Benzo(b)fluoranthene	40.1–42.9	85
Fluorene	6.5–24.5	115	Benzo(a)pyrene	38.9–44.1	103
Phenantrene	19.0–67.0	82	Dibenzo(ah)anthracene	**8.9–49.0**	**92**
Anthracene	28.9–37.6		**5-ring of PAHs**	**34.4–43.0**	
3-ring of PAHs	**38.0–50.0**		Benzo(ghi)perylene	33.5–38.9	96
Fluoranthene	50.0–67.1	46	Indeno(123 cd)pyrene	39.0–47.8	99
Pyrene	24.9–43.0	**74**	**6-ring of PAHs**	**36.6–40.0**	
Benzo(a) anthracene	22.0–37.0	**82**	**Total of 15 PAHs**	**10.0–12.3**	
Chrysene	32.0–51.8	**88**	**Total of 14 PAHs (Without naphtalene)**	**37.1–50.1**	
4-ring of PAHs	**26.0–45.0**				

Note: The bold values signify the group of PAHs.

several times higher than the one obtained for 5- and 6-ring compounds. Research work carried out by Salihoglu et al. [12] concerned photocatalytic oxidation of PAHs in sewage sludge from municipal wastewater. The results obtained by these authors also showed that 3-ring compounds were degraded more efficiently than 5- and 6-ring compounds. Degradation efficiency of total 12 PAHs was not higher than 77% [12].

4. Conclusions

The most important sources of PAHs in water environment are discharges of insufficiently treated wastewater. The highest concentrations of PAHs are present in coke-plant wastewater. The total concentration of PAHs in coke-plant wastewater used in the study was equal to 323 μg/L. The most abundant compound was naphthalene with concentration equal to 286 μg/L. Concentration of the remaining 14 PAHs (without naphthalene) was not higher than 43 μg/L (which was equivalent to 12% of the total PAHs concentration). Research on photodegradation of these compounds was undertaken in order to reduce PAHs concentration in wastewater. During the experiment, it was stated that it is possible to minimize PAHs concentration in coke-plant wastewater via exposure on UV irradiation. Not all hydrocarbons are equally susceptible to photodegradation. When the total concentration of 15 PAHs degradation is considered, its effectiveness was equal to 50%. For individual compounds, the removal efficiency varied from 5 to 67%. The most resistant to photodegradation compounds were benzo(b)fluoranthene and benzo(a)pirene with half-life times equal to 123 and 103 s, respectively. It can be emphasized that photodegradation of PAHs lead to generation of by-products and, therefore, some further studies on their identification are of great importance.

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