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EFFECTIVENESS IN THE REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS FROM INDUSTRIAL WASTEWATER BY ULTRAFILTRATION TECHNIQUE

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Abstract: The paper presents the results of studies on the changes in the PAHs concentration during pre-filtration and ultrafiltration (UF) processes. In the study, biologically treated wastewater (after denitrification and nitrification processes), discharged from the biological treatment plant and used in coke plant, was used. A gas chromatography-mass spectrometry (GC-MS) was used in order to qualify and quantify the PAHs. Sixteen PAHs listed by EPA were determined. The wastewater samples were collected three fold and initially characterized for the concentration of nitrate nitrogen, ammonium nitrogen, COD, TOC and pH. In the first step, wastewater was filtrated on the sand bed. Total concentration of 16 PAHs in the treated wastewater before initial filtration was in the range of 44.8−53.5 mg/L. During the process the decrease in the concentration of the most studied hydrocarbons was observed. Concentration of PAHs after initial filtration ranged from 21.9 to 38.3 μg/L. After the initial filtration process the wastewater flew to the ultrafiltration module and then was separated on the membrane (type ZW-10). The total concentration of 16 PAHs in the process of ultrafiltration was in the range of 8.9−19.3 mg/L. The efficiency of removal of PAHs from coke wastewater in the process of ultrafiltration equaled 66.6%. Taking into account the initial filtration, the total degree of removal of PAHs reached 85%. The obtained results indicate the possibility of using the ultrafiltration process with the initial filtration as additional process in the coke wastewater treatment.

INTRODUCTION

In the literature there is a limited number of publications describing the study of concentration of PAHs in contaminated wastewater. General information indicates that the determined concentrations of PAHs in different urban wastewaters depend on the diversified composition and the amount of industrial wastewater [20]. The level of PAHs concentration in urban wastewaters depends on the sewerage discharge system, wastewater treatment as well as the weather conditions. During rainless days concentration of compounds reaches the above mentioned value of 800 ng/L, whereas during heavy rain days it is over 100 times higher [10]. The average of total PAHs concentration in industrial wastewater is at the level of 100 μg/L. However, this is the estimated value,

since the composition of industrial wastewater may vary due to the type of industry, raw materials, technologies and forming products. The previous studies proved that the main source of compounds is wastewater originating from the treatment of fuels [20]. These include coke wastewater, resulting from cooling and cleaning of coke oven gas. Wastewater is loaded not only with PAHs but with organic substances such as aliphatic, aromatic, heterocyclic compounds, oils, tars and inorganic: cyanides, sulfides, sulfates, thiosulfates, ammonia and heavy metals as well. Due to the pollution load, waste coke is usually subjected to treatment at the plant, and then introduced into the sewer system or applied in a company [15].

In the case of industrial wastewater input to sewer, PAHs permissible concentration in industrial wastewater is equal to 0.2 mg C/L according to legislation [17]. The usage of treated wastewater containing PAHs for coke quenching may result in air pollution. Therefore, it is necessary to recognize the possibility of application of efficient methods for cleaning the wastewater contaminated with PAHs.

Biological, physicochemical and combined methods can be applied for the degradation or removal of polycyclic aromatic hydrocarbons from wastewater. The removal of PAHs from wastewater in a physical processes is carried out by using membrane techniques. The possibility of application of an individual processes is limited by the size of particles retained on the membrane. For this reason, the most important techniques applied in the removal of PAHs are: nanofiltration (NF), reverse osmosis (RO) and ultrafiltration (UF). [2, 3, 7, 13, 14].

In the literature ultrafiltration processes are often used for the removal of organic contaminants such as polycyclic aromatic hydrocarbons (PAH), trihalomethanes (THMs) and phthalates from water. Separation abilities and the possibility of using different ultrafiltration membranes were evaluated in order to chose the best PAHs removal technique. A determined retention coefficient for PAH, THM and phthalates is in the range of 50.0−99.9% [6]. Other studies were conducted on the use of UF membranes for the treatment of PAH in the presence of humic substances. The application of the afore mentioned method allowed to reduce anthracene by over 40%, while the same method in presence of humic substances increases the effectiveness up to 97% [9]. The literature data indicate a high degree of removal of PAHs exceeding 80% from aqueous solutions in the ultrafiltration process [8]. Ultrafiltration membranes are characterized by "cut-off" which is the lowest molecular weight retained by UF membrane with a specific retention coefficient. Most UF membranes have molecular weight cut-off values between 1,000 and 100,000 Da [6, 8, 12, 16]. Ultrafiltration membranes have the following properties: high hydraulic efficiency, good separating properties, resistance to mechanical, thermal and chemical factors. Pre-treatment should be applied in order to protect the membrane. This process allows for removal of suspended solids, colloids and a variety of dissolved compounds, which during the adsorption on the surface of the membrane may contribute to reducing the hydraulic efficiency [2, 4, 12, 19]. The most common applications of ultrafiltration are: treatment of natural water, brackish water pre-treatment before desalination by reverse osmosis, purification of macromolecular solutions and industrial wastewater also contaminated with oil derivatives [6, 7]. Previous studies of the authors of this paper showed that in raw wastewater influent to the treatment plant the concentration of PAH was equal to 240 μg/L. The degree of removal of hydrocarbons from wastewater in filtration and ultrafiltration processes was equal to 78% [21].

The aim of this paper is to determine the efficiency of PAHs removal from coke wastewater after biological treatment in wastewater treatment plants during initial filtration and ultrafiltration processes.

METHODS AND MATERIALS

The investigations were carried out using treated coke wastewater coming from a treatment plant. In the studied wastewater treatment plant the technological processes of treatment contain: biological processes involving the separate denitrification, nitrification and carbon oxidation. The wastewater samples were collected three fold from the plant and characterized for concentration of nitrate nitrogen, ammonium nitrogen, chemical oxygen demand (COD), total organic carbon (TOC) and pH according the procedures described by Hermanowicz [5]:

- pH – potentiometric method;
- COD, with the American-short method;
- TOC – gas chromatography;
- nitrate-nitrogen by the colorimetric method;
- ammonium nitrogen by Nessler reagent method.

The concentrations of determined PAHs were treated as initial values.

METHODOLOGY

The investigations were conducted using the cylindrical ultrafiltration module. This module was submerged in the cylindrical tank of 70 L. The performance range of the pump (Vogeslang company) operating in the ultrafiltration system was in the range of 8–72 L/h. During the tests these efficiency was kept at 10 L/h. The installation worked at a transmembrane pressure of 0.02 MPa. The membrane separation process was based on capillary membrane type ZW-10 selective for suspended solids, colloids, viruses and bacteria. The diameter of pores in the skin layer of the membrane was 0.04 μm and a total surface of membrane was 0.93 m². A mean volumetric flux of permeate was $2.99*10^{-6}$ m³/m²*s (an arithmetical average of obtained results during filtration process). The time of experimental was 8 h. The permeate was intermittently extracted with a suction mode of 15 min extracting/45 seconds backwashing, according to the producer's recommendation.

The wastewater samples after ultrafiltration were collected using a pressure pump. A scheme of the ultrafiltration process is shown in Figure 1.

Wastewater was initially filtrated on the sand bed before ultrafiltration. The bed was a cylinder shape container filled with three layers of gravel and sand. The layers consist of bottom layer gravel Ø = 1.0 cm, middle layer gravel Ø =0.6 cm, and upper layer sand Ø = 0.1−2.0 mm. The total amount of the filters layer was 50 cm, and the volume of the filter bed was 25 L. The flow velocity of wastewater through the bed was equal to 40 L/h. The wastewater after the initial filtration process were pumped to the ultrafiltration module.

PAHs ANALYSIS

Qualitative and quantitative identification of PAHs was carried out in the treated wastewater originating from the treatment plant, after the initial filtration process and
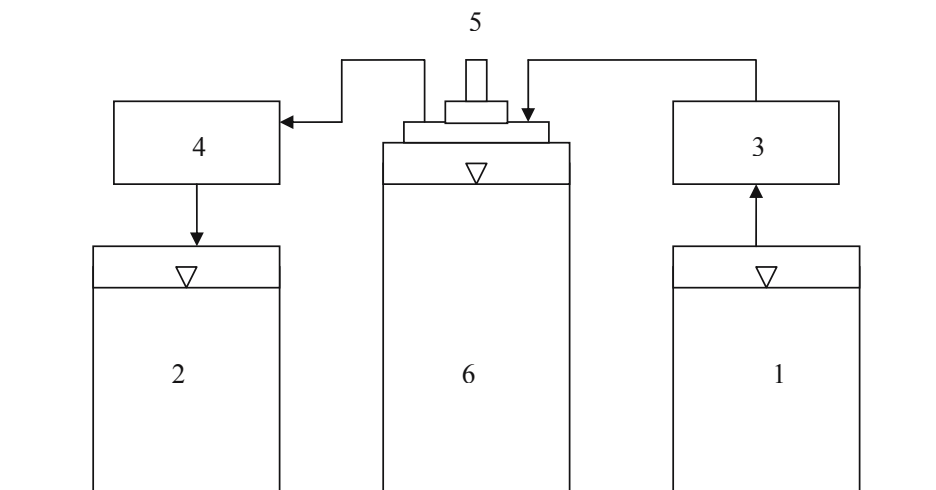
Fig. 1. Scheme of the ultrafiltration

1 – tank of raw wastewater; 2 – tank of final treatment; 3 – dosing pump (wastewater to the UF module);
4 – pressure pomp; 5 – monomers; 6 – ultrafiltration module

after the ultrafiltration process. The investigations were conducted three times, and samples were prepared in duplicates. In the first step the selection of the organic matrix from the wastewater was carried out. Extraction of organic materials was applied by adding the following organic solvents with the different polarity: methanol, cyclohexane and dichloromethane (v/v 20:5:1). The extraction was carried out mechanically by shaking for 60 minutes in order to adjust the constant amplitude. Then the solvent fraction was separated from the wastewater in a laboratory divider. The prepared extracts were purified using SPE columns packed with silica gel under vacuum conditions. The extracts were concentrated to the volume of 2 mL under nitrogen stream. Qualitative and quantitative analysis of 16 PAHs was carried out using gas chromatography method coupled with mass spectrometry (GC-MS system Fisons model GC 800/MS 800). The following hydrocarbons were determined: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chryzen, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene. PAH separation was done on the DB-5 column with a length of 30 m, diameter 0.25 mm, film thickness of 1 μm. The temperature range of the column was 40–280°C, and the time analysis was 60 minutes.

RESULTS AND DISCUSSION

Efficiency of membrane filtration process was determined by the analysis of changes in the concentration of selected physico-chemical properties, changes in concentration of individual PAHs as well as the retention coefficient based on the following equation:

$$R = (1-c/c_n)100[\%]$$

where:

c_n − concentration of the compound in the feed solution, g/m^3

c − concentration of the compound in the permeate, g/m^3.

Preliminary studies

The selected physical-chemical properties during technological research in the coke wastewater are shown in Table 1.

Table 1. Characteristics of treated coke wastewater

Determination	Unit	Raw biologically purified wastewater	Treated wastewater after prefiltration	Treated wastewater after ultrafiltration	Allowable values of sewage pollution [17]
pH	-	6.9	7.4	7.9	6.5-9.0
COD	mg O_2/L	441.3	369.3	298.6	125
Nitrate nitrogen	mg NO_3^-/L	4.1	2.6	1.8	30
Ammonium nitrogen	mg NH_4^+/L	80.1	56.2	48.2	10
TOC	mg C/L	185.8	157.4	144.4	30

The pH of the wastewater from biological treatment works was equal to 6.9. This value increased slightly during the prefitration to the value of 7.4 and ultrafiltration to 7.9, respectively. It did not exceed the permissible values of 6.5−9.0 in the treated wastewater [18]. This value of pH was also in the range given by Bartkiewicz (7.5−9.1) [1]. Following the prefiltration and ultrafiltration processes, a decrease of nitrate nitrogen concentration from 4.1 to 1.8 mg NO_3^-/L occurred, but the total concentration did not exceed the permissible values [18]. The concentrations of other indicators exceeded the permissible values [18]. The concentration of ammonium nitrogen decreased during the prefiltration and ultrafiltration processes, and finally reached the value of 48.2 mgNH_4^+/L after ultrafiltration. The permissible value of the concentration of ammonium nitrogen for wastewater entering the receiving surface water and sewage system was equal to 200 mg mg NH_4^+/L [17]. Bohdziewicz and Mielczarek indicate that during the treatment of raw coke wastewater in the process of ultrafiltration the concentration of ammonia nitrogen was equal to 70.0 mgNH_4^+/L [16]. The concentration of total nitrogen in coke wastewater after mechanical treatment may be as high as 2042 mg N/L [15]. The value of COD decreased from 441.3 to 298.6 mg O_2/L, while TOC decreased from 185.8 to 144.4 mg C/L.

Changes in the concentration of PAHs

Changes in the concentration of 2−3 ring, 4-ring and 5–6-ring hydrocarbons are presented in Figures 2–4, respectively. The following representative hydrocarbons were determined:

the representative of 2-ring hydrocarbon was naphthalene, the representatives of 3-ring hydrocarbons were acenaphthylene, acenaphthene, flouren, phenanthrene and anthracene, the representatives of 4-ring hydrocarbons were: fluoranthene, pyrene, benzo(a) anthracene and chrysene, the representatives of 5-ring hydrocarbons were: benzo(a) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(a, h)anthracene, and the representatives of 6-ring hydrocarbons were: indeno(1,2,3,c,d)pyrene and benzo(g,h,i) perylene.

The concentrations of 16 PAHs in wastewater from biological treatment works varied from 44.8 to 53.5 µg/L. It was found that the largest participation (70%) in wastewater had 3-ring PAHs with the highest solubility. Percentage of individual PAHs in coke wastewater and obtained retention coefficients are shown in Table 2.

Table. 2. Percentage of PAHs in coke wastewater treated

PAH	The average participation of PAHs (%)			The degree of removal (%)	Retention coefficient, R (%)
	Wastewater collected from the plant	Wastewater after prefiltration	Wastewater after ultrafiltration	Wastewater after prefiltration	Wastewater after ultrafiltration
Naphthalene	14.4 ± 17.2	10.1 ±3.2	17.3 ± 7.3	59.8	19.9
Acenaphthylene	1.7 ±1.0	2.5 ±1.9	1.6 ± 0.9	13.4	70.8
Acenaphthene	42.8 ± 25.2	32.3 ±24,2	22.9 ± 2.0	57.0	66.9
Fluorene	12.3 ± 5.3	12.9 +/-3.2	9.7 ± 4.0	40.0	64.8
Phenanthrene	12.3 ± 7.9	30.7± 19.8	39.1 ± 7.9	-	40.5
Anthracene	0.6 ± 0.6	1.2 ±0.7	1.8 ± 1.4	-	28
Fluoranthene	3.6 ± 1.4	2.6 ± 0.8	2.5 ± 0.8	58.3	54.2
Pyrene	2.4 ± 0.9	1.5 ± 0.1	1.3 ± 0.4	65.5	57.1
Benz[a]anthracene	1.2 ± 0.5	0.8 ± 0.3	0.7 ± 0.3	59.6	59.6
Chrysene	1.4 ± 0.6	0.7 ± 0.5	0.5 ± 0.2	70.4	66.8
Benz[b]fluoranthene	1.8 ± 1.1	0.9 ± 0.4	0.8 ± 0.2	71.6	58.1
Benz[k]fluoranthene	1,6 ± 0,5	1.1 ± 0.4	0,6 ± 0.1	59.7	72.8
Benz[a]pyrene	2.1 ± 1.4	1.3 ± 0.4	0.8 ± 0.3	64.8	71.7
Dibenz[a,h]anthracene	0.1 ± 0.1	0.0	0.0	75.0	100
Indeo[1,2,3,-cd]pyrne	1.3 ± 1.1	0.6 ± 0.3	0.2 ± 0.3	71.4	91.3
Benzo[ghi]perylene	0.4 ± 0.4	0.6 ± 0.3	0.1 ± 0.2	23.8	94.3

The highest concentration of 21.0 µg/L was found for acenaphthene. The participation of 4-ring PAHs was 8.6%, and 5-ring PAHs 5.6%, respectively. The lowest percentage was observed for the 6-ring PAHs and it was equal to 1.7%. Compounds with carcinogenic properties: benzo(a)anthracene, chryzen, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3,c,d)pyrene,
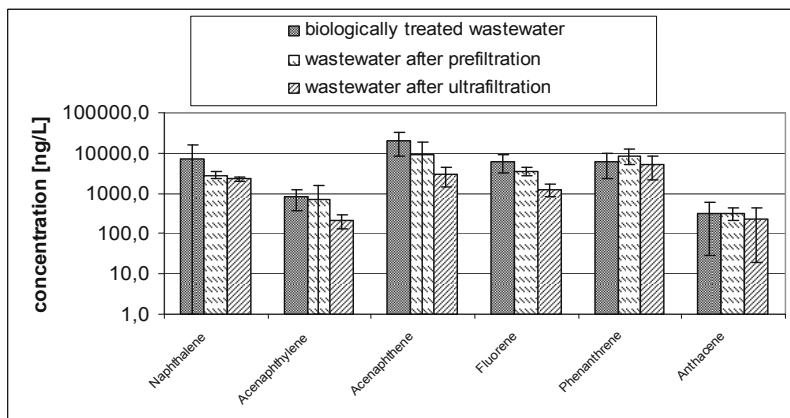
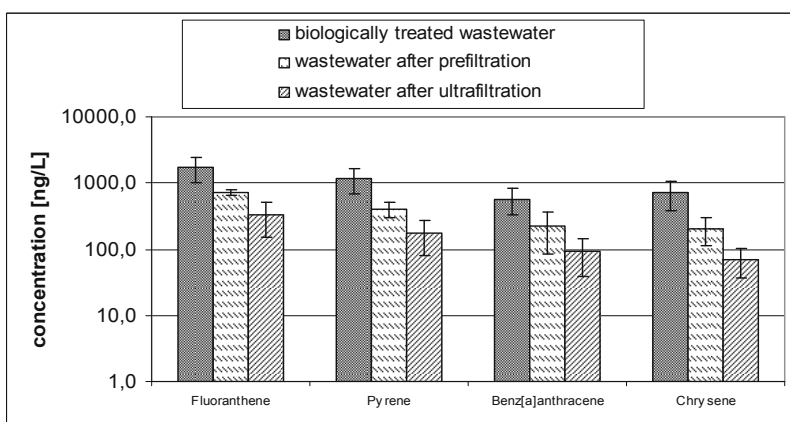Fig. 2. Average concentrations of 2 and 3-ring PAHs in treated coke wastewater

Fig. 3. Average concentrations of 4-ring PAHs in treated coke wastewater

benzo(g,h,i)perylene amounted for 10% of the total PAH content in the wastewater after biological treatment. It was found that in the wastewater after the initial filtration and ultrafiltration processes the concentrations of the studied hydrocarbons gradually lowered. The total concentration of 16 PAHs in coke wastewater after initial filtration was in the range of 21.9–38.3 μg/L. The highest concentration in the wastewater was on average 22.3 μg/L. It was observed for 3-ring PAHs with the highest concentration of 20.5 μg/L for acenaphthene. The lowest concentrations were found for 6- and 5-ring hydrocarbons and were in the range of 0.3 μg/L, 0.9 μg/L, respectively. The mean concentration of naphthalene was equal to 2.8 μg/L, whereas for the 4-ring PAHs the concentration was equal to 1.6 μg/L.

The highest decline in the concentrations was reported for 5-ring and 4-ring hydrocarbons and ranged between 67.8% and 63.5%, respectively. The decrease in the concentration of 6-ring was 47.6%. The lowest decline in the concentration was observed for 3-ring PAHs and it was equal to 12.4%. The concentration of naphthalene declined
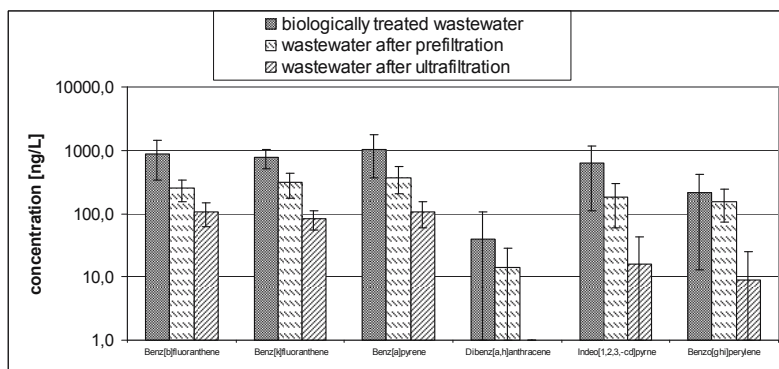
Fig. 4. Average concentrations of 5 and 6-ring PAHs in treated coke wastewater

by an average of 59.8%. It should be pointed out that the solubility of naphthalene is the highest and amounts to the value of 31 700 μg/L, whereas the value of coefficient octanol/water is low and it is equal to 3.36. It indicates that there is a limited ability of adsorption of naphthalene on a particle [20]. PAHs have hydrophobic properties and in solutions containing a suspension of these compounds they mainly occur in the adsorbed form [11]. It can be assumed that the decrease in the concentration after prefiltration results from adsorption on the surface of the sand bed particles.

During UF changes in PAH concentration in the wastewater the decrease of all studied hydrocarbons was observed. It was also found that mass molecular of PAHs resulted in the degree of removal. The retention coefficients of 3-ring PAHs were 54%, of 4-ring PAHs 59%, and of 5-ring PAHs 76%, respectively. The highest value of the retention coefficient of 93% was observed for macromolecular 6-ring compounds. In the case of UR membrane, the retention coefficient increased with the molecular weight of the removal compound. Benzo(g,h,i)perylene should be the most efficiently removed due to the highest molecular weight of the studied PAHs. Naphthalene should be the least efficiently removed due to the molecular weight of the analyzed PAHs. The studies of other authors confirm the above mentioned dependence [8]. The concentration of B(a)P – the highest of carcinogens was reduced by 70%. The treatment of coke wastewater in the process of ultrafiltration allowed for the removal of an average of 66.6% of PAHs. Including the prefiltration the overall level of PAHs removal reached 85%. The efficiency in removal of PAHs from water reached 80% and 90%, respectively [2, 8]. In UF the relatively high degree in removal of PAHs from the wastewater was observed, despite the fact that the molar mass PAHs are much lower than the "cut-off" (70 kDa) and the pore radius of applied membrane. It could be the result of interaction between the retained particles and an ultrafiltration membrane – an adsorption of PAHs on the surface and inside the membrane pores caused basically by fouling. Membrane fouling involves the deposition of substances existing in the filtrated sample on the membrane surface and/or in the pores of the substances presented in filtrated sample. In the course of UF separation it caused a decrease in permeate flux volume over time and it is a disadvantageous phenomenon.

Table 3 shows the critical values of Student's t test, determining the significance of the process used in the treatment of PAH concentrations for the studied wastewater.

Table 3. Values of Student-t distribution (td = 2.776) by the number of rings

PAHs	Prefiltration	Ultrafiltration (UF)
Naphthalene	4.5	**7.96**
3-rings	**9.5**	5.4
4-rings	3.92	3.44
5-rings	5.46	3.28
6-rings	4.78	3.68
Sum of PAHs	3.32	4.8

The type of coke wastewater treatment process was statistically significant in determination of the total concentration of PAHs (determined value of td is greater than the critical value). For prefiltration process the greatest statistical significance for 3-ring compounds was indicated. The UF had a statistically significant effect on the concentrations of all studied hydrocarbons. The greatest statistical significance was found for naphthalene. The use of wastewater treatment processes play a statistically significant role in the removal of PAHs from coke wastewater.

CONCLUSIONS

1. The total concentration of PAHs in the coke wastewater originating from the biological wastewater treatment works was in the range of 44.8−53.5 µg/L.
2. After the initial filtration on the sand bed 50% decrease in the concentrations of most hydrocarbons was observed, and total concentration of 16 compounds ranged from 21.9 to 38.3 µg/L. This study confirmed necessity of using sand bed in order to protect the membrane from pollution.
3. In the process of ultrafiltration a further reduction in the concentration of PAHs was achieved and the final total content ranged from 8.9 to 19.3 µg/L. The treatment of coke wastewater in the process of ultrafiltration allowed to remove 66.6% of PAHs.
4. The total removal of PAHs during initial filtration and UF equaled to 85%, whereas for individual hydrocarbons it was in the range of 27−100%.
5. The carried out investigations indicate a high efficiency of ultrafiltration in wastewater treatment of PAHs. The studies confirmed the possibility of using ultrafiltration process for cleaning the wastewater containing high concentrations of PAHs.

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