

ADSORPTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) FROM AQUEOUS SOLUTIONS ON DIFFERENT SORBENTS

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Abstract

This paper presents the results of the possibility and effectiveness of PAHs removal from a model aqueous solution, during the sorption on the selected sorbents. Six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) listed by EPA for the analysis in the environmental samples were determined. Model aqueous solution was prepared with RESTEK 610 mix PAHs standard. After the sorption process, decrease in the concentration of individual hydrocarbons was observed. The removal percentage was dependent on the type of sorbent (quartz sand, mineral sorbent, activated carbon). The highest efficiency (98.1%) was observed for activated carbon.. The results shows that the sorption processes can be used in aqueous solutions treatment procedures.

Keywords: 2- and 3-rings of PAHs, adsorption, quartz sand, mineral sorbent, activated carbon

1. INTRODUCTION

In recent years, the growth of intensive human activity has led to the formation of a significant amount of wastewater, which is one of the largest environmental hazards. These wastes are mainly industrial wastewaters, surface water runoff from agricultural land and domestic wastes generated by households. A group of

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chemical substances highly resistant to degradation in the wastewaters, are persistent organic pollutants (POPs)[1-2]. One of the most commonly present in environment POPs are polycyclic aromatic hydrocarbons (PAHs). Due to carcinogenic, mutagenic, and teratogenic properties, PAHs are priority pollutants. The 16 PAHs considered as priority by the United States Environmental Protection Agency (U.S. EPA) [3-5].

It is also suspected that transformation products of PAHs are more toxic than the parent molecules. The high values of coefficient octanol/water confirmed that PAHs are easily adsorbable. They have hydrophobic properties and in solutions containing a suspension of these compounds they mainly occur in the adsorbed form. PAHs are often resistant to biological degradation and are not efficiently removed by conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration or ozonation [5, 6]. The currently used methods of those pollutants removal from water and wastewater are also expensive and required a complicated technology. Therefore, an interesting solution in the removal of PAHs is the use of adsorption process [7-10]. Due to high organic matter removal efficiency adsorption based technique are one of the most interesting available options for PAHs removal. The research shows that PAHs present in surface water are adsorbed on the surface of the solid particles, and next they fall down with solid particles and become a component of bottom sediments [11, 12].

An activated carbon is widely adjudged to be the most effective and widely used adsorbent in the adsorption treatment of wastewater containing high concentration of PAHs [4, 13]. It is confirmed that PAHs are present in activated carbons, however, they do not affect the sorption capacity of this material and also do not cause any noticeable contamination of water [14]. The degree of the removal of PAHs on activated carbon depends on their content in water/wastewaters, contact time, the type of used material, the dose and efficacy of water/wastewater pre-treatment. An important parameter is the particle size of the adsorbate, which determines internal transport of mobile phase within adsorbent matrix. It should be noted, that reported in the literature results concerns mainly research conducted in the laboratory conditions [13, 15]. The other adsorbents have been also studied for the removal of PAHs from the environment amongst which are: zeolite [16], other organic-free hydrophilic minerals like silica, alumina and talc [17, 18], solid residue from agricultural activities like ash waste, and pine bark [19, 20]. Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method. The development of low-cost adsorbents has led to the rapid growth of research interests in this field [21]. The aim of this study was to

evaluate the effectiveness of selected sorbents in the removal of PAHs from model aqueous solutions.

2. MATERIALS AND METHODS

2.1. Experimental procedure

In these studies, model aqueous solution containing standard of PAHs RESTEK 610 PAH Mix was prepared: distilled water with standard of PAHs. The concentration of six PAHs was equal to 1000 ng/L. The results should be treated as relative values, which allow to compare the properties of selected adsorbents. In the study three types of sorbents and mixtures thereof were used: quartz sand, activated carbon WG-12 and mineral sorbent ABSODAN PLUS. PAHs removal process was carried out using sorption columns prepared on a laboratory scale. Diagrams of the six prepared columns are shown in Fig. 1.

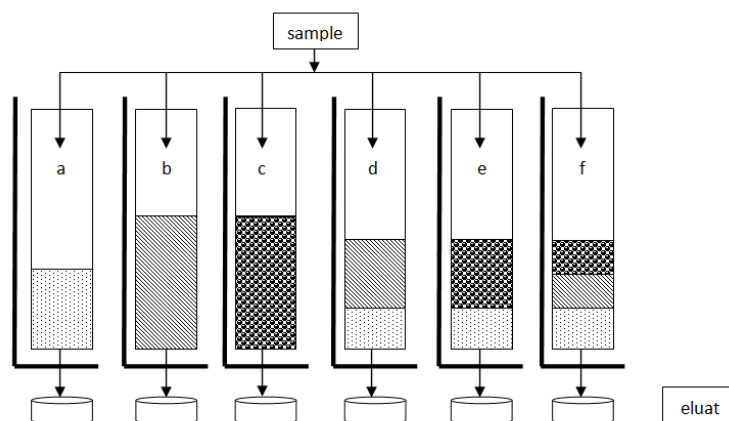


Fig. 1. Diagram of laboratory sorption columns

(a-quartz sand bed (50g), b-mineral sorbent bed (ABSODAN PLUS) (50g),
 c-activated carbon bed (50g),
 d-quartz sand/ mineral sorbent bed (ABSODAN PLUS) (25g/25g),
 e-quartz sand/ activated carbon bed (25g/25g),
 f-quartz sand/ mineral sorbent (ABSODAN PLUS)/ activated carbon bed
 (25g/12,5g/12,5g))

A sorbent samples with a mass 50g were placed in a sorption columns with a diameter of $\varnothing=4$ cm. Then, the model solution was poured into the column to the total saturation of pores. The height of the filtration layer was 2-4cm, depending on the type of sorbent. The volume of the filtration bed in a

cylindrical shape, was 10-25ml. Ambient temperature during the experiment was 20°C (room temperature). The flow rate of the model solution by the bed was varied and amounted to 0.2-0.5 ml/min.

2.2. Analyses of PAHs

Qualitative and quantitative identification of PAHs was carried out in the aqueous solution and after the sorption processes. Preparation of samples for the PAHs determination was carried out by the solid-liquid phase extraction. 2-propanol as an extrahent was used. The extraction process was been conducted in an ultrasonic bath (30 min of sonification, $f = 40$ kHz). After that, samples were being shaken for 60 minutes in an automatic shaker. The obtained extracts were poured into centrifugal test-tubes and were centrifuged for 10 minutes with 8000 rev/min. Next, they were dissolved in distilled water 250 ml. Then, samples were subjected to concentration and purification using SPE columns. For this purpose, Bakerbond C18 columns were used. For the extraction from the SPE resin, acetonitrile was used (3•1ml). Subsequently, the extracts were concentrated to the volume of 1 ml under a nitrogen stream. The liquid chromatographic techniques are complementary methods that are commonly used in the characterization of PAHs in environmental samples. The relevant part of the analysis was conducted using high performance liquid chromatography (HPLC), THERMO Scientific HPLC system consisting of a pump P4000, autosampler AS3000 and fluorescence detector FL3000. PAHs were separated on Restek Pinnacle® II PAH 4 μ m, 150×10 mm column by using the gradient elution technique. As for the mobile phase mixture of water, methanol and acetonitrile were used. The temperature of the column was 30°C, and the analysis time was 40 minutes [26]. The HPLC was calibrated with a diluted standard solution of 16 PAH compounds (PAH 610 Calibration Mix from Restek) recommended by US EPA. The following 6 PAHs listed by U.S. EPA were analyzed: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene. In order to verify the adopted procedures the recoveries of PAHs were determined.

3. RESULTS AND DISCUSSION

During sorption processes, the decrease in concentration of all hydrocarbons was observed. Changes in the concentration of all studied hydrocarbons after adsorption on each sorbent is shown in figure 2. The total concentration of PAHs in eluat after adsorption on quartz sand was equal to 237.5 ng/L. The largest decline in the concentrations was reported for activated carbon - 22.2 ng/L. Concentrations of PAHs after sorption on mineral sorbent amounted to an

average of 484.7 ng/L. The mean concentration of PAHs after sorption on CQ and QAC beds were maintained at 237.0 ng/L and 351.0 ng/L, respectively. The lowest decline in the concentrations of analyzed hydrocarbons was observed for QA bed - 499.0 ng/L.

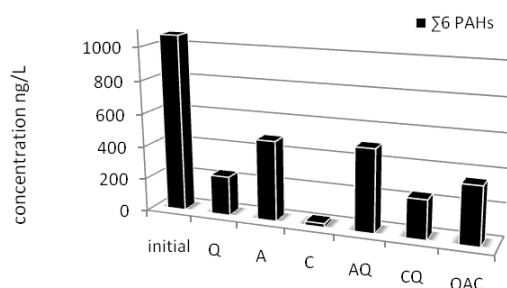


Fig. 2. Concentration of $\Sigma 6$ PAHs in eluats (Q - quartz sand bed, A- mineral sorbent bed, C- activated carbon bed, SQA - quartz sand/ mineral sorbent bed, QC- quartz sand/ activated carbon bed, QAC- quartz sand/ mineral sorbent/ activated carbon bed)

Changes in concentration of individual hydrocarbons after adsorption are presented in figures 3-4. The ability to PAHs adsorption on the solid particles is determined by the octanol/water coefficient. Therefore, both the different values of this coefficient and the various binding force of each sorbent may influence obtained results. It is worth mentioning that the solubility of naphthalene is the highest and amounts to 31,700 mg/l and a low value of octanol/water coefficient (3.36) indicates a low capacity of naphthalene to sorb on the suspended particles [22, 23].

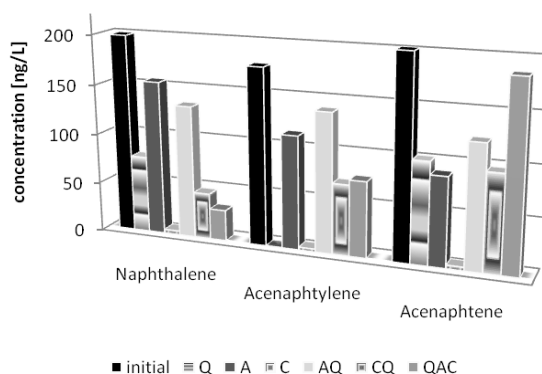


Fig. 3. Concentration of naphthalene, acenaphthylene and acenaphthene in eluats (Q - quartz sand bed, A- mineral sorbent bed, C- activated carbon bed, SQA - quartz sand/ mineral sorbent bed, QC- quartz sand/ activated carbon bed, QAC- quartz sand/ mineral sorbent/ activated carbon bed)

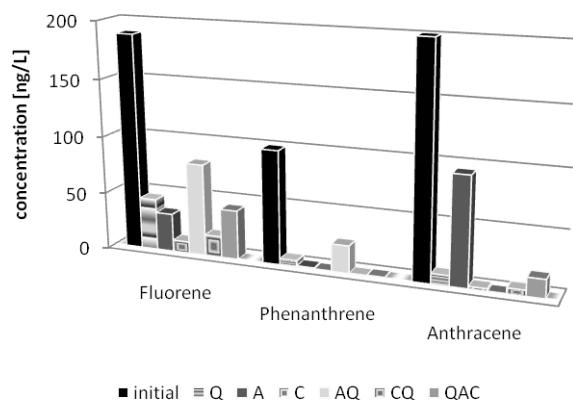


Fig. 4. Concentration of fluorene, phenanthrene and anthracene in eluats (Q - quartz sand bed, A- mineral sorbent bed, C- activated carbon bed, SQA - quartz sand/ mineral sorbent bed, QC- quartz sand/ activated carbon bed, QAC- quartz sand/ mineral sorbent

Table 1. Removal of PAHs from aqueous solution

PAHs	The degree of removal [%]					
	Q	A	C	QA	QC	QAC
Naphthalene	61.3	22.3	98.1	33.3	76.8	84.5
Acenaphthylene	-	35.9	98.4	21.1	60.1	57.3
Acenaphthene	49.8	56.8	98.2	39.0	51.9	7.8
Fluorene	76.1	82.3	94.7	57.4	90.3	77.2
Phenanthrene	94.6	99.5	100	75.9	99.7	99.4
Anthracene	95.6	53.6	98.9	-	97.5	92.1
Σ 6PAHs	75.5	58.2	98.1	45.4	79.4	69.7

Q - quartz sand bed, A- mineral sorbent bed, C- activated carbon bed, SQA - quartz sand/ mineral sorbent bed, QC- quartz sand/ activated carbon bed, QAC- quartz sand/ mineral sorbent/ activated carbon bed

The greatest efficiency of PAHs removal 98.1% was recorded for the activated carbon. Therefore it may be stated that the activated carbon has the best adsorption capacity. The previous studies demonstrated that PAHs with low molecular weight are easily absorbed on the activated carbons [24]. The largest reduction is achieved for phenanthrene and amounted to 100%, for the naphthalene this value was equal to 98.1%. The partial losses of naphthalene and 3-ring compounds can be associated with the oxidation of these compounds due to the volatile properties of low molecular weight PAHs. Activated carbon WG12 is a very good adsorbent for polycyclic aromatic hydrocarbons from

aqueous solutions. The efficiency of adsorption of PAHs on activated carbons can be increased after the chlorination process [23, 24]. The literature data confirm the high efficiency of activated carbon in the removal of PAHs from water. The degree of removal of PAH ranged from 62.0 to 100% [12, 14]. In technical conditions, this process needs to be preceded by the removal of PAHs media, such as coagulation, filtration, sedimentation [4].

The efficiency of PAHs removal by a sand bed was equal to 75.5%. There was no correlation between the degree of removal and the molecular weight of the analyzed compounds. For naphthalene removal efficiency was equal to 61.3%. For the anthracene removal efficiency was equal to 95.6%. Leichtle and Totsche noted the almost complete sorption of PAHs by the fraction of sand free of organic carbon [5]. The previous studies the authors of this publication have confirmed a high degree of removal of PAHs from raw coking wastewater in the process of sorption on a sand-gravel bed - 51% [25]. During the research, the lowest degree of removal of PAHs was achieved for sorbent ABSODAN PLUS. The average removal efficiency of PAHs from a model aqueous solution was 58.2%. The highest values 99.1% and 82.3% were obtained for the phenanthrene and fluorene, respectively. The weakest effect of adsorption was found for naphthalene, which was reduced by 22.3%. The lowest efficiency of removal of PAHs was achieved by combining traditional sand bed with sorbent ABSODAN PLUS. The degree of removal of PAHs was 45.4%. The lowest values 21.4% was obtained for acenaphthylene. A very high degree of removal of PAHs - 79.4% was achieved using a combination of sand bed with activated carbon. For individual hydrocarbons it was in the range of 51.9-99.7%. Also, a high degree of removal of PAHs 69.7% was achieved using combined adsorption bed containing a mixture of: activated carbon, sand and mineral sorbent.

4. CONCLUSIONS

During the experiment a decrease in concentration of studied hydrocarbons was observed. The highest degree of removal of PAHs was obtained after the sorption on activated carbon (for individual hydrocarbons were in the range 94.7-100%). The studies have confirmed the possibility of using adsorption processes to the removal of PAHs from aqueous solutions due to a degree of removal of PAHs (45.4-98.1%). PAHs negative impact on the aquatic environment is the cause of the need to remove these compounds from aqueous solution. It is necessary to undertake further study in order to better understand the mechanism of sorption of PAHs in natural and synthetic sorbents and their possible applications.

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ADSORPCJA WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW
AROMATYCZNYCH (WWA) Z ROZTWORÓW WODNYCH NA RÓŻNYCH
SORBENTACH

Streszczenie

Celem badań opisanych w pracy było określenie skuteczności adsorpcji wielopierścieniowych węglowodorów aromatycznych (WWA). Oznaczono sześć związków (naftalen, acenaftylen, acenaften, fluoren, fenantren, antracen) spośród szesnastu wskazanych przez EPA do analizy w próbkach środowiskowych. Do badań sporządzono modelowy roztwór wodny z dodatkiem wzorca WWA - Restek 610 Calibration Mix. W czasie procesu adsorpcji odnotowano obniżenie stężenia poszczególnych węglowodorów. Skuteczność usuwania WWA zależała od rodzaju zastosowanego sorbentu (piasek kwarcowy, sorbent mineralny, węgiel aktywny). Największą efektywność, wynoszącą 98,1%, uzyskano dla węgla aktywnego. Otrzymane wyniki wskazują, iż proces sorpcji może być stosowany w celu usunięcia węglowodorów aromatycznych z roztworów wodnych.

Słowa kluczowe: 2- i 3-pierścieniowe WWA, adsorpcja, piasek kwarcowy, sorbent mineralny, węgiel aktywny

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