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## The effectiveness adsorption of carcinogenic PAHs on mineral and on organic sorbents

Efektywność adsorpcji rakotwórczych WWA  
na sorbentach mineralnych i organicznych

### Abstract

This paper presents the results of the effectiveness of PAHs removal from a model aqueous solution, during the sorption on the selected sorbents. Six carcinogenic PAHs listed by EPA for the analysis in the environmental samples were determined (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). In this study, model aqueous solution was prepared with RESTEK 610 mix PAHs standard (distilled water with standard of PAHs). Three types of sorbents: quartz sand, mineral sorbent and activated carbon, was used. The decrease in the concentration of all hydrocarbons was observed after sorption processes. The removal percentage was dependent on the type of sorbent. The highest efficiency (96.9%) was observed for activated carbon. The results shows that the sorption processes can be used in aqueous solutions treatment procedures.

**Keywords:** *carcinogenic PAHs, adsorption, quartz sand, mineral sorbent, activated carbon*

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## Streszczenie

Celem badań było określenie efektywności usuwania wielopierścieniowych węglowodorów aromatycznych (WWA) w procesie adsorpcji. Oznaczono sześć kancerogennych związków 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 trakcie eksperymentu wykorzystano trzy rodzaje adsorbentów: piasek kwarcowy, sorbent mineralny oraz węgiel aktywny. W czasie procesu adsorpcji odnotowano obniżenie stężenia poszczególnych węglowodorów. Skuteczność usuwania WWA zależała od rodzaju zastosowanego sorbentu. Największą efektywność, wynoszącą 96,9%, uzyskano dla węgla aktywnego. Otrzymane wyniki wskazują, iż proces sorpcji może być stosowany w celu usunięcia węglowodorów aromatycznych z roztworów wodnych.

**Słowa kluczowe:** *kancerogenne WWA, adsorpcja, piasek kwarcowy, sorbent mineralny, węgiel aktywny*

## 1. Introduction

The widespread occurrence of persistent organic pollutants (POPs) in soil and groundwater is a major environmental concern. A group of chemical substances highly resistant to degradation in the wastewaters, are hydrophobic organic compounds (HOCs). Due to a high toxicity and an ability to bioaccumulation, this contaminants are a significant threat to the health of living organisms [1-3]. One of the most commonly present in environment HOCs are polycyclic aromatic hydrocarbons (PAHs). PAHs are formed during the incomplete combustion of carbonaceous materials [4]. Several of them have been found to induce a number of adverse effects as immunotoxicity, genotoxicity, mutagenicity and carcinogenicity. PAHs, exemplified by benzo(a)pyrene, have been shown to be causative agents of lung, esophageal, gastric, colorectal, bladder, skin, prostate and cervical cancers in humans and animal models. The general population is primarily exposed to PAHs through inhalation of polluted air or cigarette smoke and through ingestion of PAH-containing foods [5, 6]. Depending on the mode of cooking, preservation and storage, aromatic hydrocarbons are found in substantial quantities in some foods and are detected in a wide range of matrices; meats, fishes, vegetables and fruits. Those detected in vegetables have been attributed to the deposition of airborne-PAHs from such various sources as vehicular exhaust and those present in fish and mussels, from contaminated waters [7]. However, during industrial smoking, heating and drying processes, combustion products come into direct contact with food and PAHs contaminations can occur. PAHs have generated considerable interest due to their carcinogenic and mutagenic potential and the fact that humans are exposed to PAHs on a daily basis [8]. Due to those properties, PAHs are priority pollutants. The 16 PAHs considered as priority by the United States Environmental Protection Agency (U.S. EPA) are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene,

dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene [9, 10]. The selected physicochemical properties of carcinogenic PAHs are show in Table 1.

Table 1. Physicochemical properties of carcinogenic PAHs [11]

Tabela 1. Fizykochemiczne właściwości kancerogennych WWA [11]

PAH	Molecular weight (g/mol)	Sobullity in water (25°C) (ng/l)	log (K <sub>ow</sub> )	Carcinogenicity/ Mutagenicity*
Benzo(a)anthracene	228	14000	5.61	+ / ++
Chrysene	228	2000	5.63	+ / ++
Benzo(b)fluoranthene	252	1200	6.57	+++ / +++
Benzo(k)fluoranthene	252	550	6.84	+ / ++
Benzo(a)pyrene	252	3800	6.06	++++ / +++++
Dibenzo(a,h)anthracene	278	500	6.86	++ / ++
Indeno(1,2,3-cd)pyrene	276	62000	7.23	+ / +
Benzo(g,h,i)perylene	276	260	7.66	+++ / ++

\* + poorly active carcinogen/mutagen; ++ medium active; +++ highly active; ++++ strongly active

It is proved that transformation products of PAHs could be 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 [12, 14]. The removal of these toxic organic pollutants from water is a problem, particularly when they are present in low concentrations. 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 [13, 15, 16]. An important phenomenon is biosorption, which involves the use of the ability of microorganisms to the collection and accumulation of PAHs in cells. However, sorption by the microorganisms is not stable, and these compounds may be released to the environment during cell lysis [18, 19]. An important advantage of adsorption lies in the fact that the persistent compounds are removed, rather than being broken down to potentially dangerous metabolites with may occur in result of oxidation and reductive processes [20]. 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. [21, 22]. The use of sedimentation process in the sand traps and preliminary septic for the removal of PAHs from urban wastewater allowed to reduce the amount of PAHs in wastewater by 45%, due to the adsorption of this pollutants on particule matter. During biological treatment PAHs sorption on activated sludge particles can also take place. Therefore, in earlier studies a significant accumulation of PAHs in sewage sludge (raw and excessive) was observed [14, 23].

An activated carbon is widely adjudged to be the most effective and widely used adsorbent in the adsorption treatment of water/wastewater containing high concentration of PAHs [10, 24]. The removal efficiency 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. The particle size of the adsorbate determines internal transport of mobile phase within adsorbent matrix [24, 25]. The various adsorbents have been studied for the removal of PAHs from the environment amongst which are: zeolite [26], other organic-free hydrophilic minerals like silica, alumina and talc [27, 28], solid residue from agricultural activities like ash waste, and pine bark [29, 30]. 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 [31]. 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 545.4 ng/l. This results are treated as relative values, which allow to compare the properties of selected adsorbents.

### **2.2. Analyses of PAHs**

Qualitative and quantitative identification of PAHs was carried out in the aqueous solution and after the sorption processes – fig. 1. 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. Next, samples were being shaken in an automatic shaker.

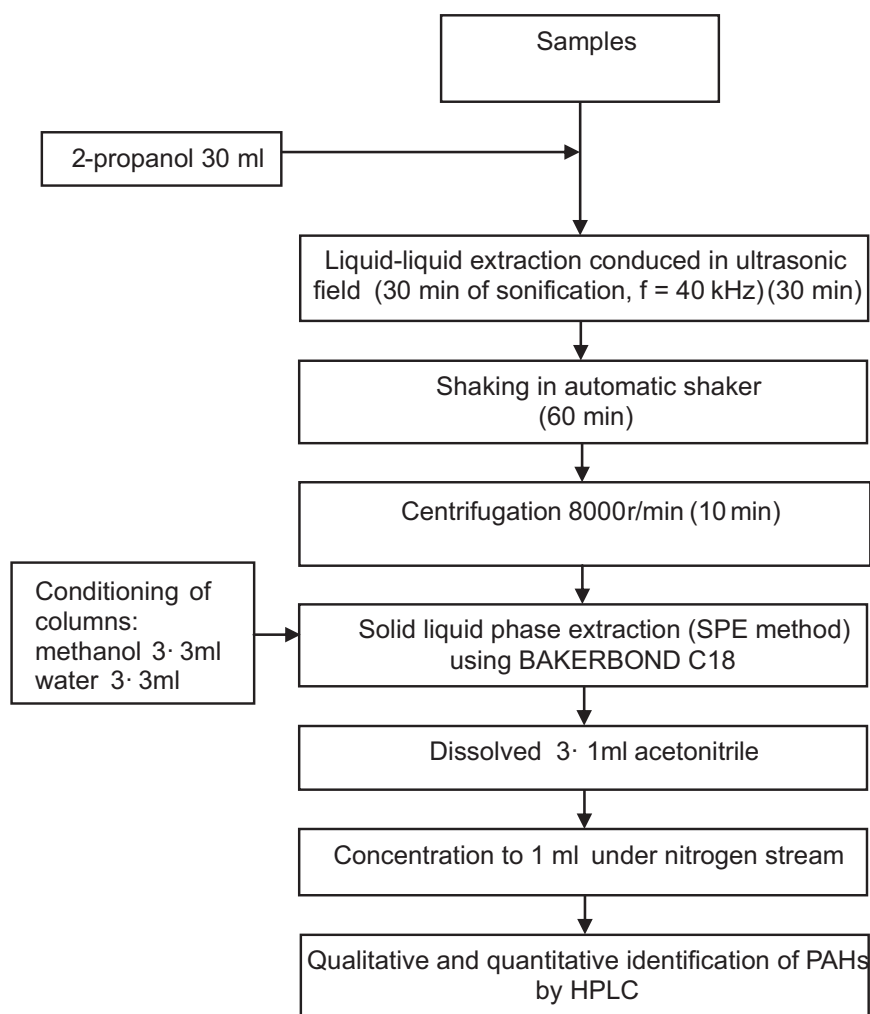


Fig. 1. Diagram of sample preparation to the determination of PAHs

Rys. 1. Schemat przygotowania próbki do oznaczenia WWA

The obtained extracts were poured into centrifugal test-tubes and were centrifuged for 10 minutes with 8000 rev/min. After that, 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 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 FL3000 and UV-Vis UV5000 detectors. PAHs were separated on Restek Pinnacle® II PAH 4 µm, 150×10 mm column. Column was filled with C18 silica gel. The temperature of the column during the analysis was 30° C. Elution was conducted by using a gradient technique with three solvents water - A, acetonitrile - B and methanol - C (start 0 min - 20/20/60 A<sub>v</sub>/B<sub>v</sub>/C<sub>v</sub>; 20 min - 5/95/0 A<sub>v</sub>/B<sub>v</sub>/C<sub>v</sub>). The flow rate was 0,80 ml/min. The loop volume was 10 µl. Detection of the data was carried out on both UV-Vis and fluorescence detectors. Wavelength used for UV

detection was 254 nm. The analysis time was 40 minutes [17]. The HPLC was calibrated with a diluted standard solution of 16 PAH compounds (PAH 610 Calibration Mix, Restek) recommended by US EPA. The following 6 PAHs listed by U.S. EPA were analyzed: 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. In order to verify the adopted procedures the recoveries of PAHs were determined. A detection limits for each hydrocarbons and its recovery were shown in Table 2.

Table 2. Validation of method for the determination of PAHs  
Tabela 2. Wewnętrzna walidacja metody oznaczania WWA

PAHs	Molecular formula	Symbol	Detection limit (ng/l)	Recovery [%]
Benzo(b)fluoranthene	C <sub>20</sub> H <sub>12</sub>	BbF	1.64	64.2
Benzo(k)fluoranthene	C <sub>20</sub> H <sub>12</sub>	BkF	1.64	83.7
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	BaP	1.89	90.8
Dibenzo(a,h)anthracene	C <sub>22</sub> H <sub>14</sub>	DahA	1.23	87.6
Indeno(1,2,3-cd)pyrene	C <sub>22</sub> H <sub>12</sub>	IP	1.41	58.4
Benzo(g,h,i)perylene	C <sub>22</sub> H <sub>12</sub>	Bper	1.96	72.1

### 2.3. Adsorption studies

PAHs removal process was carried out using sorption columns prepared in laboratory in Institute of Environmental Protection. Diagrams of the six prepared columns are shown in Fig. 2. In the study, three types of sorbents and mixtures thereof were used: quartz sand, activated carbon WG-12 and mineral sorbent ABSODAN PLUS. A sorbent samples with a mass 50g were placed in a sorption columns with a diameter of  $\varnothing=4$  cm. Then, the model solutions were 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.

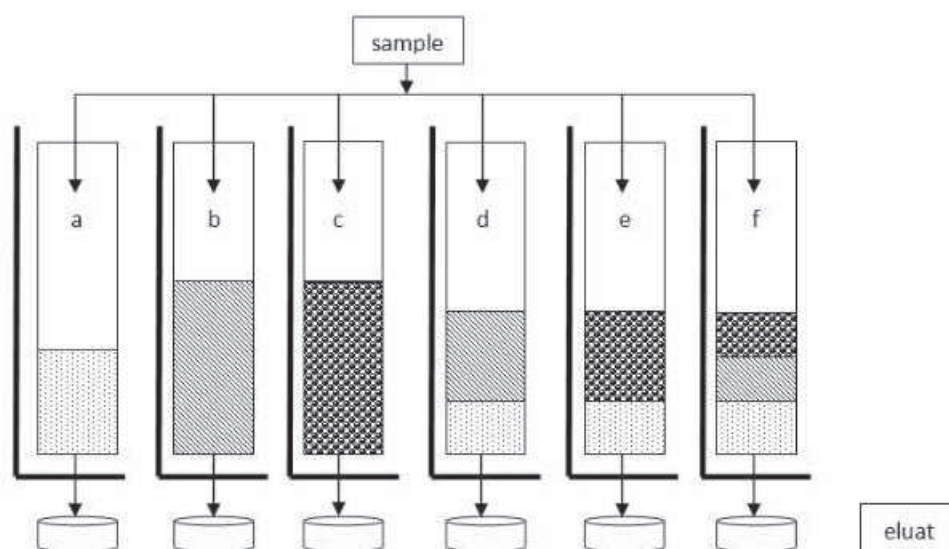


Fig. 2. Diagram of laboratory sorption columns

Rys. 2. Schemat laboratoryjnych kolumn sorpcyjnych

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

The percentage of PAHs in the tested mixtures was calculated using the equation [32]:

$$Removal = \frac{c_0 - c}{c_0_{eq}} \times 100 (\%) \quad (1)$$

where  $c_0$ —the initial concentration of the PAHs in solution, (mg/l),  $c_{eq}$  — the equilibrium concentration of the PAHs in solution (mg/l).

### 3. Results and discussion

The decrease in concentration of all hydrocarbons was observed during sorption processes. The amount of PAHs removed was calculated by comparing the initial concentration of the compounds with the concentration remaining in the solution after 6 h of contact time. The sorption of PAHs on sorbents was studied at pH 7. It was noted that the pH range is not a determining factor in removing all PAHs on leonardite. Results suggest that the prevalent mechanism in the uptake of PAHs is a physical adsorption caused by the aromatic nature of PAHs, probably combined with Van der Waals strength [33]. The total concentration of PAHs in eluat after adsorption on quartz sand was equal to 90.6 ng/l. The largest decline in the concentrations was reported for activated carbon – 17.9 ng/l. The mean concentration of PAHs after sorption on CQ bed was equal to 28.8 ng/l. The decrease in PAHs content on QAC bed was maintained at 42.1 ng/l. The decline in the concentrations of analyzed PAHs for QA bed was equal to 37.0 ng/l. Concentrations of PAHs after sorption on mineral sorbent was the lowest and it amounted to an average of 251.0 ng/l. Changes in the

concentration of naphthalene and 3 ring hydrocarbons after adsorption are presented in figure 3.

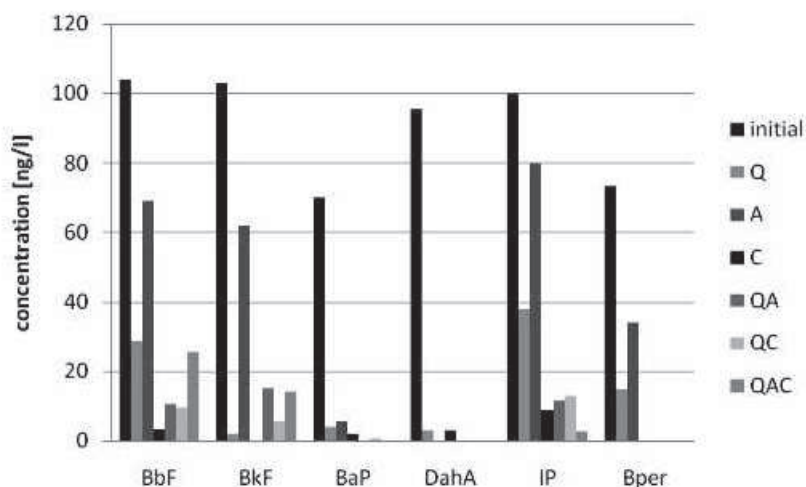


Fig. 3. Concentrations of PAHs in eluats

Rys. 3. Stężenia WWA w eluatach

Table 3 shows the degree of removal of PAHs on each sorbent.

Table 3. Removal of PAHs from aqueous solution

Tabela 3. Stopień usunięcia WWA z modelowego roztworu wodnego

PAHs	The degree of removal [%]					
	Q	A	C	QA	QC	QAC
Benzo(b)fluoranthene	72.2	33.5	96,7	89.9	90.7	75.5
Benzo(k)fluoranthene	98.1	39.8	99.8	85.3	94.5	86.4
Benzo(a)pyrene	94.2	91.7	97.1	99.9	99.2	99.8
Dibenzo(a,h)anthracene	96.8	99.8	96.7	100	100	100
Indeno(1,2,3,cd) pyrene	62.1	20.0	90.9	88.6	87.1	97.5
Benzo(ghi)perylene	80.0	53.5	100	100	100	100
Σ 6PAHs	83.9	56.4	96.9	94.0	95.3	93.2

Q - quartz sand bed, A- mineral sorbent bed (ABSODAN PLUS), C- activated carbon bed, QA - quartz sand/ mineral sorbent bed (ABSODAN PLUS), QC- quartz sand/ activated carbon bed, QAC- quartz sand/ mineral sorbent (ABSODAN PLUS)/ activated carbon bed

The ability to PAHs adsorption on the solid particles is determined by the octanol/water coefficient. PAHs have partition coefficients ( $K_{ow}$ ) greater than 1000. This number expresses their hydrophobic behavior and will be greater when increasing the number of aromatic rings in the molecule. Therefore, both the different values of this coefficient and the various binding force of each sorbent may influence obtained results [34]. There was no correlation between the degree of removal and the molecular



weight of the analyzed compounds. The greatest efficiency of PAHs removal 96.9% was recorded for the activated carbon. It is noted that activated carbon has the best adsorption capacity. The largest reduction is achieved for benzo(ghi)perylene and amounted to 100%. The concentration of B(a)P – the highest of carcinogens was reduced by 97.1%. 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 [2, 35]. The degree of removal of PAH from water ranged from 62.0 to 100% [20, 22]. In technical conditions, this process needs to be preceded by the removal of PAHs media, such as coagulation, filtration, sedimentation [10]. An adsorption on the surface of the sand bed particles was equal to 83.9%. For individual hydrocarbons it was in the range of 62.1-98.1%. The literature data indicate the possibility almost complete sorption of PAHs by the fraction of sand free of organic carbon [12]. The previous studies the authors of this publication have confirmed high values of PAHs removal by sand bed column. [12, 32]. During the research, the lowest degree of removal of PAHs was achieved for sorbent ABSODAN PLUS - 56.4%. The weakest effect of adsorption was found for indeno(1,2,3, cd)pyrene, which was reduced by 20%. The efficiency in the removal of analyzed compounds on QC bed was high and it was equal to 95.3%. The lowest efficiency (87.11%) was observed for the compound with the highest number of rings - indeno(1,2,3,cd)pyrene. The increased in the efficiency of removal of PAHs was achieved by combining traditional sand bed with sorbent ABSODAN PLUS. The degree of removal of PAHs characterized by the best solubility in water was 94%. A very high degree of removal of PAHs – 95.3% was achieved using a combination of sand bed with activated carbon. Also, a high degree of removal of PAHs 93.2% was achieved using combined adsorption bed containing a mixture of: activated carbon, sand and mineral sorbent (QAC).

The study confirms that the greatest degree in the removal of organic pollutants such as PAHs can be obtained by using activated carbon as absorption material. The use of carbonaceous adsorbents to remove contaminants from liquid and gas phases, gives very good results, difficult to achieve using other methods [36, 39]. It was also shown that preparation of filter beds WG-12 and sand did not significantly influence to the efficiency of the sorption process. The use of those combined bed can help to reduce the operating costs of the sorption process. The effect of water/wastewater treatment on a sorbent bed can be easily and effectively increase by the extending of sorption column height, and thus the contact time: the bed with the flowing medium. The effectiveness of the process is also determined by the amount of pollutants and flow parameters. In the case of wastewater containing the suspension, they should be pretreated - the removal of a considerable part of the solids (for example during coagulation and sedimentation processes) [10, 37]. Adsorption is nowadays considered effective for removing persistent organic pollutants and is regarded superior to other techniques, due to its low cost, simplicity of design, high efficiency, ease of operations and ability to treat a selection of PAHs in variety of concentrated forms [15, 38]. Moreover, it removes the complete PAHs molecule unlike certain methods which destroy the molecule and leave harmful residues.

## 4. Summary

The study confirms that the high degree in the removal of organic pollutants such as PAHs can be obtained during adsorption process. Six carcinogenic PAHs were analyzed (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). The highest degree of removal of studied hydrocarbons was obtained after the sorption on activated carbon (96.9%) and the lowest - for sorbent ABSODAN PLUS - 56.4%. The degree of removal of PAHs on the sand bed particles was equal to 83.9%. The changes in the efficiency of removal of PAHs was achieved using combined adsorption beds. The high degree of removal of PAHs 93.2% was achieved using combined adsorption bed containing a mixture of: activated carbon, sand and mineral sorbent (QAC), 94% - quartz sand/ mineral sorbent bed (QA) and 95.3% - quartz sand/ activated carbon bed (QC). The studies confirmed the possibility of using adsorption process for cleaning the aqueous solutions containing high concentrations of PAHs.

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