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Impact of biochar on sorption of polycyclic aromatic hydrocarbons in water

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ABSTRACT

Biochar can be a relatively inexpensive and effective material for removing polycyclic aromatic hydrocarbons (PAHs) from aquatic environment. An evaluation of the sorptive possibilities of biochar to remove PAHs from the aquatic environment was conducted. The content of benzo(a)pyrene and the sum of four PAHs, such as benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene were determined in water. The sorption process was carried out for biochar doses of 25, 50 and 100 mg/L. For each biochar dose, the contact time with PAHs was: 30, 60, 90 and 120 min. The best results were obtained for a biochar dose of 100 mg/L and a contact time of 120 min. For benzo(a)pyrene, the concentration decreased up to 78%, while for the four recommended PAHs, the greatest changes were shown for benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, whose concentrations decreased by 81%. For the remaining PAHs, greater sorption was observed for dibenzo(a,h)anthracene, the concentration of this compound decreased by 81%.

Keywords: Biochar; Organic micropollutants; Removal efficiency

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are considered hazardous pollutants due to their carcinogenicity, mutagenic and toxic properties, and persistent nature [1]. Although there are more than 200 different types of PAHs, the United States Environmental Protection Agency (USEPA) has classified 16 PAHs on the priority list due to their high toxicity and possible mutagenic effects [2]. PAHs are released into the environment as a result of natural processes such as volcanic eruption, terrestrial vegetation synthesis, microbial synthesis, or reactions associated with the formation of minerals and fossil fuels [3–5]. However, it is anthropogenic sources that are responsible for more than 90% of the total amount of PAHs present in the environment. Of the anthropogenic sources, the most important is power generation processes at power plants and combined heat and power plants, gas and fume emissions from industrial plants, motorization (car exhaust, tire abrasion), and fumes from boiler rooms, and home furnaces. Other source is cigarette butts, contain high amounts of PAHs from incomplete tobacco leave burning [6]. Given the high level of littering with cigarette butts, PAHs may leach from this waste and enter the environment, which may pose a threat to the aquatic environment [7]. PAHs have been detected in air [5], soil, sediment [8,9], and water reservoirs [10,11] including animal and plant tissues [12,13]. In the air, PAHs may occur associated with particulate matter ($PM_{2.5}$, PM_{10}) [14,15] and microplastic (MS). In this form, they constitute a health risk via inhalation [14]. Studies of PAHs in surface sediments showed that contamination and PAH levels in industrial stations were much higher than in urban stations [16]. The wide spread of PAHs in the environment has resulted in the presence of these contaminants in meat and meat products [17]. The presence of PAHs has also been demonstrated in pregnant women and foetuses. Studies have shown transmission of PAHs from mother to foetus through the cord blood [18].

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To deal with the problem of PAHs present in the environment, various methods have been proposed for the removal of these compounds [19]. Coagulation, sorption, advanced oxidation processes (AOPs), membrane technologies and hybrid methods are used to remove PAHs from the aquatic environment [20]. Sorption is one of the methods widely used to eliminate PAHs because these compounds show high interaction to particulate matter, which is facilitated by their low solubility in water [3]. Studies have demonstrated the effectiveness of PAH removal with activated carbon [21]. Gong et al. [22] using columns with activated carbon demonstrated high efficiency of PAHs removal from vegetable oil in the range from 68.1% to 93.5%. According to the author's, activated carbon is a promising adsorbent because it can adsorb both high and low mass PAHs equally effectively. Sorbents vary in structure and chemical nature. Decisive factors in choosing sorbents are their high absorption capacity (the ability to take liquids or other substances in through a surface), versatility, ability to be disposed of after use, and economic considerations. All of these characteristics are met by biochar, which can be used as an inexpensive alternative sorbent for removing organic and inorganic contaminants [23].

Biochar is a carbon-rich product derived from biomass and produced from such organic materials as manure, leaves, crop residues, that is, straw from various types of cereals, cereal hulls, residues from paper mills, sludge, forestry waste, and organic fraction of sewage sludge. The materials are subjected to combustion under anaerobic conditions at temperatures usually between 350°C and 700°C. The conditions of the processing of organic materials are key factors influencing the efficiency of the process and biochar properties. The higher the process temperature, the greater the specific surface area of the product [24]. Literature reports confirm the sorption potential of biochar to remove PAHs from contaminated soils. Oleszczuk et al. [25] showed that biochar can reduce *ca.* 57% of PAHs present in sewage sludge. Beesley et al. [26] used biochar to remove PAHs from contaminated soil, reducing toxic effects on microorganisms and plants due to the immobilization of PAHs in the soil. The findings of the above-mentioned studies lead to the conclusion that biochar can be a relatively inexpensive and effective material for removing PAHs from aqueous solutions [3,27]. The sorption of organic pollutants on biochar depends on the types of feed stocks, production processes, sorbate concentration, and the ageing [28,29]. Biochar particle size has been shown to have little or no effect on PAH sorption [3,27]. However, the smaller the particle size, the shorter the time to achive sorption equilibrium [30]. A literature review by Ahmad et al. [31] on the sorption of organic pollutants on biochar allowed the researcher to propose three mechanisms of interaction between biochar and organic pollutants. The following interaction mechanisms can be distinguished in the process of sorption of hydrophobic organic compounds on carbon fractions of biochar: π–π or donor–acceptor interactions, hydrophobic interactions, hydrogen bond formation, pore filling, or simultaneous occurrence of several adsorption mechanisms. According to literature, the strong sorption of PAH on biochar is based on three processes: (1) π–π interaction between the benzene rings of PAH and biochar, (2) sorption of PAH into the nanopores of biochar, and (3) rapid adsorption at lower concentrations of PAHs in water and absorption at higher concentrations of PAH due to the maximum adsorption [32–35].

Schmidt & Noack [36] and Titirici et al. [37] showed that regardless of the raw material, biochar has the same chemical structure, oxygen-containing heterocyclic pyran, and furan rings of carbohydrates or phenol-like structure, which are the main components of lignin. Consequently, PAH sorption on biochar mainly depends on biochar production temperatures and PAH structure. Aromatic hydrocarbons, as compounds of low polarity, can be covalently bonded to the polar surface of biochar [33]. As a result, the sorption of PAHs on biochar is related to the aromaticity of these compounds. Due to its aromatic surfaces and aliphatic structures, which are a function of production temperature, biochar can bind PAHs ten times more than organic matter [32,33].

Gopinath et al. [38] proposed using biochar from sewage sludge to treat wastewater. This solution is in line with the objective of sustainable resource recovery and promotes a circular economy based on wastewater. The use of biochar derived from sewage sludge minimizes disposal costs and acts as a resource to remove toxic pollutants from water and wastewater. The ability to reuse and availability of this type of biochar irrespective of the season makes it an economically viable material for wastewater treatment. The properties of biochar from municipal sewage sludge largely depend on the properties of the sludge itself (especially the heavy metal content) and the temperature of the biochar production process [39,40]. Biochar obtained from municipal sewage sludge is characterized by a relatively high mineral content (e.g., biochar obtained at 450°C, 500°C, and 600°C is characterized by the mineral content of 68.1%, 69.3% and 74.3%, respectively), low carbon content, and low calorific value (about 5.3–5.9 MJ/kg) [41]. The efficiency of sorption of organic pollutants on biochar is also influenced by the contact time and biochar dose [28]. Since biochar from municipal sewage sludge may contain significant amounts of heavy metals, its use will be determined by its chemical composition. There are few studies in the literature on the efficiency of PAH removal from water and wastewater using biochar obtained from municipal sewage sludge, which offers an inexpensive solution for wastewater treatment in plants already in operation [38]. For this reason, the present paper proposes the use of biochar from municipal sewage sludge to remove PAHs from the aquatic environment as the first stage of research aimed at developing an effective method for removing PAHs from contaminated wastewater in the future [42]. The authors determined the sorption capacity of biochars originating from sewage sludge in relation to phenanthrene (3-ring PAH) and pyrene (4-ring PAH). The conversion of sewage sludge into biochar significantly increased its sorption capacity. Pyrene sorbed better on the tested materials than phenanthrene. On the basis of the obtained results, the sorption mechanism of the analysed compounds on biochars was determined in the context of their possible use for water and sewage treatment and immobilisation of pollutants in soils contaminated with these compounds. Due to the broad prospects of a wide use of biochar, research was undertaken on the use of this sorbent for the removal of PAHs from the aquatic environment.

Such a solution will also provide a sustainable solution to the problem of waste biomass. Therefore, the purpose of this study was to evaluate changes in the quantitative and qualitative composition of PAHs in water after adsorption on biochar obtained from municipal sewage sludge using different doses of biochar at different contact times, which is new knowledge in this field. The research carried out will help expand knowledge of the sorption capacity of biochar obtained from sewage sludge to produce water with environmentally safe PAH content. The findings offer theoretical and practical implications for research into new and cost-effective methods of removing PAHs from the aquatic environment.

2. Materials and methods

2.1. Materials

The sewage sludges were obtained from municipal (mechanical–biological) wastewater treatment plants (WTTPs) located in Silesia region of Poland: (GPS: 50°46′58.9″N, 18°59′48.8″E). The WTTPs use an anaerobic digestion process and dewatering. The activated sludge method is used for the wastewater treatment, along with the following processes: nitrification, denitrification and simultaneous chemical precipitation of phosphorus with iron(III) sulfate.

Sewage sludges were collected during summer 2021, at the end point, after the sewage sludge digestion process. A few representative subsamples were taken for the present experiments. Samples were mixed, dried in air (about 25°C for a few weeks) in the dark, ground and passed through a 2 mm sieve. Such pre-prepared sewage sludge samples were stored in glass containers, and then subjected to the process of pyrolysis.

Biochar was produced in a 30 min autothermal pyrolysis of biomass (in pellet form) under oxygen-limited conditions. The process was carried out in a reactor under pressure and flow conditions that ensure the maximum heating rate of the ground biomass. Details on the pyrolysis process have been published by the manufacturers of these biochars [43,44].

2.2. Experimental set-up

The biochar was characterized in terms of its chemical properties (ash content, pH, total carbon, sulfur, and hydrogen content). The ash content was determined by incineration in a muffle furnace. The biochar samples were burned for 6 h at 750°C. The pH value was measured electrochemically using a pH meter (pH-meter CX-505). Samples were stirred with deionized water at a ratio of 1:10, shaken for 1 h, and then the pH was measured. The total carbon content (C_{tot}) of the test material was determined using a C/N analyzer (TOC Multi N/C 2000 Analytik Jena, Germany). The elemental composition of the biochar was determined using a CHNS analyzer (2400 CHNS/O Analyzer Series II, PerkinElmer, Waltham, MA, USA).

Prior to the main research (adsorption), examinations were conducted to verify the PAH content of biochar obtained from municipal sewage sludge. For this purpose, fragmented and homogenized biochar (1 g) was extracted using the Soxlet method. The extraction process was carried out for 12 h with toluene at 110°C. The extract was then concentrated to 1 mL and purified with N,N-dimethylformamide (DMF). The resulting extracts were analyzed by CGC/MS. The experiments were carried out with 3 repetitions.

PAH sorption was examined using biochar for distilled water with RESTEK PAH MIX A standard mixture (model water). The total contents of the four normalized PAHs were twice as high as permissible levels in drinking water. The level of PAH concentration in water was selected on the basis of literature data on the effective sorption of these pollutants on activated carbon and biochar [3]. The biochar for the adsorption process was fragmented and thoroughly homogenized. For adsorption, biochar was added to each sample of model water of 500 mL in three doses of 25, 50, and 100 mg/L. Samples prepared in this way were subjected to mixing on a magnetic stirrer at 1,500 rpm. For individual doses of biochar, the contact time with PAH was 30 and 60, 90, and 120 min. The experiments were carried out with 3 repetitions.

2.3. Analytical procedure

The samples were then subjected to solid phase extraction (SPE) after the sorption process. For solid-phase extraction, BAKERBOND Speedisk® C18, 50 mm extraction discs were used, which had previously been conditioned with methanol. Then a sample of treated wastewater was passed through the extraction disc. The sample was eluted with 5 mL of methylene chloride followed by 2 mL × 3 mL portions of 1:1 ethyl acetate:methylene chloride. The extracts were combined and dried by passing them through a drying column containing 10 g of anhydrous sodium sulfate. The extracts were rinsed with 2 mL × 3 mL with 1:1 portions of ethyl acetate: methylene chloride and concentrated 0.5 to 1 mL under a stream of nitrogen. Qualitative and quantitative analysis was made using Fisons gas chromatograph (model CGC8000/MS800). Separation was performed using a DB-5 column (30 m × 32 mm × 1 μm). A quadruple mass spectrometer MS 800, working in a selective mode of ion monitoring, was used for detection. The analysis was conducted according to a programmed increase of temperature: 40°C–40°C/min, 120°C–5°C/min, 280°C–15 min.

The detection limit (signal-to-noise ratio) ranged from 5 pg/L for the least hydrophobic PAHs to 0.1 pg/L for the most hydrophobic. To verify the adopted procedure, recovery values were determined for aromatic hydrocarbons with low molar mass. For this purpose, standard RESTEK 16 PAH MIX A was introduced into a sample of distilled water and PAH determination was carried out according to the procedure described above. Recovery rates ranged from 50.4% for naphthalene to 92.8% for phenanthrene. Recovery values were included in calculating the contents of labeled PAHs. PAH determinations were performed in duplicate.

3. Results

Biochar from sewage sludge (obtained at 550°C) was characterized by a water content of 0.9% ± 0.3%, ash content of 43.25% at 550°C, total carbon content of 43.4% ± 3.0%, hydrogen content of 4.52% ± 0.90%, sulfur content of 0.400% ± 0.067%, chlorine content of 0.187%, and pH of 7.3.

Results of PAH concentration changes in model water after biochar adsorption at different doses and contact times are shown in Tables 1–3. The results of the tests verifying the PAH content in biochar from sewage sludge showed that the concentrations of these compounds were below the detection limit, that is, 0/01 ng/L. The effectiveness of the process was assessed on the basis of results of the analysis of PAHs concentration in water before and after the sorption process.

The Directive of the European Parliament and the EU Council regulates the permissible concentrations of PAHs in water intended for human consumption [45]. In Poland, the applicable legal act is the Ordinance of the Minister of Health on the quality of water intended for human consumption [46]. Both documents set out standards for benzo(a)pyrene and the total of four normalized PAHs, that is, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. In water intended for human consumption, the permissible concentration of benzo(a)pyrene amounts to 0.01 μg/L, and for the sum of the four PAHs it amounts to 0.1 μg/L. The results obtained showed that the application of biochar reduced the concentration of analyzed PAHs in the model water, but not for all tested doses and times of contact of biochar with PAHs. It was observed that increasing contact time improves the efficiency of PAH removal. The best results were obtained with a biochar dose of 100 mg/L and a contact time of 120 min (Fig. 1) where the concentration of PAHs standardized in water intended for human consumption decreased and was below the limit values. Under these conditions, the concentration of benzo(a)pyrene decreased by 82.3%, and the total of the four normalized PAHs decreased by 80.2%. For the limit values of PAHs in water for human consumption, which for benzo(a)pyrene is 0.01 μg/L and for the total of the four PAHs is 0.1 μg/L, the above conditions were effective in eliminating these compounds to below the limit values, with the concentrations of benzo(a)pyrene and the total of the four PAHs after the adsorption process under the above conditions of 0.008 and 0.039 μg/L, respectively. For the other PAHs recommended for analysis by EPA, concentrations after adsorption on biochar (dose 100 mg/L) decreased for 2-ring naphthalene by 67.6% for 3-ring PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) from 72.3% to 74.2%, for 4-ring PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene) by 75.0% to 77.5% and for 6-ring dibenzo(a,h)anthracene by 81.1% (Fig. 2). At the same dose and contact time of 90 min, the concentration of benzo(a)pyrene decreased by 56.1%, and the removal efficiency of the total of the four normalized PAHs was 58.5%. Analysis of the concentrations of normalized PAHs showed that the above conditions were effective in removing benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene while they were not sufficient to reduce the contents of benzo(a)pyrene below the permissible limits. For the other PAHs recommended for analysis by EPA, concentrations after adsorption on biochar decreased for 2-ring naphthalene by 25.9%, for 3-ring PAHs from 30.9% (anthracene and phenanthrene) to 34.5% (fluorene), for 4-ring PAHs up to 38.8% (pyrene), and for 6-ring dibenzo(a,h)anthracene by 50.7%. At a dose

Table 1
Polycyclic aromatic hydrocarbon concentration (ng/L) in model water and after adsorption with biochar dose 25 mg/L

Polycyclic aromatic hydrocarbon	Modified water	Contact time, min			
		30	60	90	120
Benzo(a)pyrene	48.56	46.29	42.13	39.13	30.6
Benzo(b)fluoranthene	48.92	48.22	43.13	39.26	31.10
Benzo(k)fluoranthene	50.22	48.32	44.23	38.46	32.60
Benzo(g,h,i)perylene	50.84	48.49	43.38	37.38	32.40
Indeno(1,2,3-cd)pyrene	49.69	47.37	43.25	36.28	32.70
Σ 4 WWA	199.67	192.4	173.99	151.38	128.80
Naphthalene	48.34	48.25	43.13	43.13	39.20
Acenaphthylene	45.48	46.63	44.15	44.15	39.20
Acenaphthene	46.6	42.27	43.34	43.34	40.30
Fluorene	45.37	42.38	43.01	43.01	39.40
Phenanthrene	45.01	41.49	40.67	40.67	33.20
Anthracene	44.73	41.57	40.90	40.9	38.50
Fluoranthene	45.24	39.25	39.16	39.16	35.30
Pyrene	44.23	42.37	40.49	40.49	35.70
Benzo(a)anthracene	42.27	44.25	40.43	40.43	34.40
Chrysene	43.35	45.56	40.61	40.61	32.20
Dibenzo(a,h)anthracene	42.40	44.21	39.82	39.82	33.50

Table 2
Polycyclic aromatic hydrocarbon concentration (ng/L) in model water and after adsorption with biochar dose 50 mg/L

Polycyclic aromatic hydrocarbon	Modified water	Contact time, min			
		30	60	90	120
Benzo(a)pyrene	48.56	42.48	40.15	36.24	29.27
Benzo(b)fluoranthene	48.92	41.90	41.33	35.37	30.10
Benzo(k)fluoranthene	50.22	42.87	41.20	34.12	28.20
Benzo(g,h,i)perylene	50.84	43.72	41.73	33.39	29.25
Indeno(1,2,3-cd)pyrene	49.69	43.77	39.25	33.83	26.59
Σ 4 WWA	199.67	172.26	163.51	136.71	114.14
Naphthalene	48.34	45.49	42.3	41.47	37.25
Acenaphthylene	45.48	45.61	42.11	40.47	35.17
Acenaphthene	46.6	46.69	41.57	40.79	34.59
Fluorene	45.37	46.74	41.48	39.92	34.35
Phenanthrene	45.01	41.92	38.1	39.51	33.16
Anthracene	44.73	41.88	37.25	35.89	31.49
Fluoranthene	45.24	40.00	35.42	33.48	27.83
Pyrene	44.23	42.06	37.51	35.24	30.10
Benzo(a)anthracene	42.27	43.47	38.15	36.8	29.36
Chrysene	43.35	41.92	38.37	36.2	29.49
Dibenzo(a,h)anthracene	42.40	42.02	37.13	36.85	28.38

Table 3
Polycyclic aromatic hydrocarbon concentration (ng/L) in model water and after adsorption with biochar dose 100 mg/L

Polycyclic aromatic hydrocarbon	Modified water	Contact time, min			
		30	60	90	120
Benzo(a)pyrene	48.56	40.47	36.91	21.34	8.59
Benzo(b)fluoranthene	48.92	42.35	35.53	22.24	10.52
Benzo(k)fluoranthene	50.22	43.58	37.59	22.45	10.46
Benzo(g,h,i)perylene	50.84	41.39	32.50	19.47	9.47
Indeno(1,2,3-cd)pyrene	49.69	41.60	29.83	18.69	9.00
Σ 4 WWA	199.67	168.92	135.45	82.85	39.45
Naphthalene	48.34	42.81	39.14	37.39	16.37
Acenaphthylene	45.48	47.64	44.74	33.29	13.57
Acenaphthene	46.6	45.49	42.38	33.34	13.72
Fluorene	45.37	44.05	41.76	33.92	11.84
Phenanthrene	45.01	45.72	41.52	33.46	12.79
Anthracene	44.73	43.50	40.49	33.74	12.58
Fluoranthene	45.24	44.61	35.26	31.58	12.31
Pyrene	44.23	45.06	36.27	30.79	12.58
Benzo(a)anthracene	42.27	48.48	40.58	32.50	11.40
Chrysene	43.35	44.82	40.26	33.15	11.40
Dibenzo(a,h)anthracene	42.40	46.49	29.50	25.29	9.68

of 100 mg and a contact time of 60 min, benzo(a)pyrene concentrations decreased by 24.0%. The concentration of the four normalized PAHs decreased from 25.1% (benzo(k)fluoranthene) to 40.0% (indeno(1,2,3-cd)pyrene) whereas their total concentration decreased by 32.2%. At the same biochar dose and a contact time of 30 min, the removal efficiency of PAHs was the lowest for the results for times of 60 and 90 min, indicating that increasing the contact time of biochar with PAHs in the aqueous environment improves their sorption efficiency. Consequently, after a time of 30 min, the results were least satisfactory, with the concentration of benzo(a)pyrene decreased by 16.7%, the concentration of the four normalized PAHs decreased from 13.2% (benzo(k)fluoranthene) to 18.6% (benzo(g,h,i)perylene), and total concentration reduced by 15.4%.

At the other doses, that is, 50 and 25 mg/L, PAH removal efficiency was lower compared to the 100 mg/L doses. A similar rule to the 100 mg/L dose was observed, with the increasing contact time improving PAH removal efficiency.

At a biochar dose of 50 mg/L and a contact time of 30 min, the concentration of benzo(a)pyrene decreased by 12.5% (Fig. 1). The concentration of the four normalized PAHs decreased from 11.9% (indeno(1,2,3-cd)pyrene) to 14.6% (benzo(k)fluoranthene), with their total concentration decreased by 13.7%. At the same biochar dose and a contact time of 60 min, benzo(a)pyrene concentration decreased by 17.3%. The concentration of the four normalized PAHs decreased from 15.5% (benzo(k)fluoranthene) to 21.0% (indeno(1,2,3-cd)pyrene) and their total concentration decreased by 18.1%. At the same biochar dose and a contact

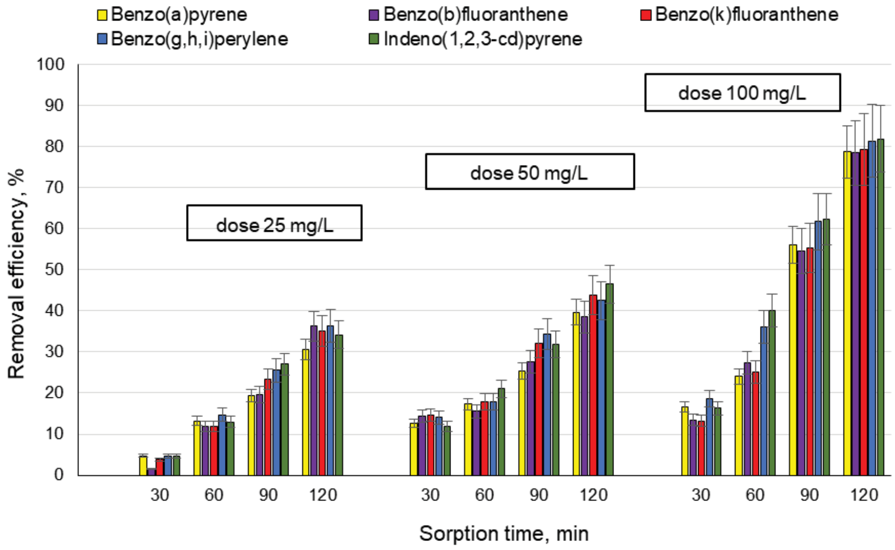

Fig. 1. Removal efficiency of normalized polycyclic aromatic hydrocarbons from water.

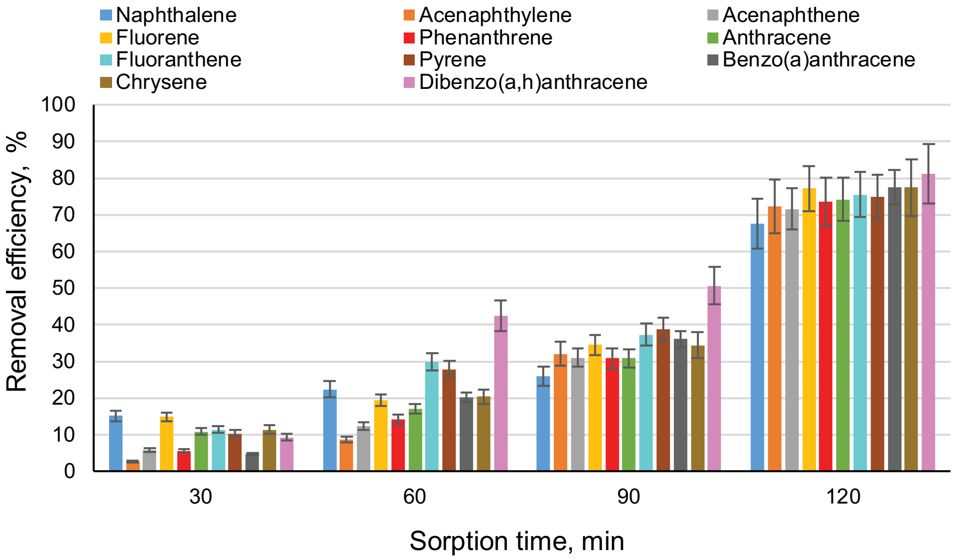

Fig. 2. Removal efficiency of polycyclic aromatic hydrocarbons from water with biochar dose 100 mg/L.

time of 60 min, benzo(a)pyrene concentration decreased by 17.4%. The concentration of the four normalized PAHs decreased from 15.5% (benzo(k)fluoranthene) to 21.6% (indeno(1,2,3-cd)pyrene) whereas their total concentration decreased by 18.1%. For the other PAHs recommended for analysis by EPA at a dose of 50 mg/L and a contact time of 60 min, the concentration after adsorption decreased for 2-ring naphthalene by 16.2%, for 3-ring PAHs from 14.0% (acenaphthene) to 23.7% (anthracene), for 4-ring PAHs from 24.2% (chrysene) to 29.7% (fluoranthene) and 6-ring dibenzo(a,h)anthracene by 27.6% (Fig. 3). For the same dose of biochar and contact time of 90 min, the concentration of benzo(a)pyrene was 36.24 ng/L (reduction by 25.4%), the total concentration of four PAHs was equal to 136.71 ng/L (reduction by 31.5%). Removal efficiencies for the other PAHs analyzed ranged from 17.2% (naphthalene) to 29.9% (pyrene). For this dose, as in the above tests, increasing the contact time improved PAH removal efficiency, and at the longest contact time of 120 min benzo(a)pyrene decreased by 39.7%. The concentration of the four normalized PAHs decreased from 38.5% (benzo(k)fluoranthene) to 46.5% (indeno(1,2,3-cd)pyrene), whereas their total concentration decreased by 42.8%. For the same biochar dose for the other PAHs recommended for analysis by EPA at a dose of 50 mg/L and a contact time of 120 min, the concentration after adsorption decreased for 2-ring naphthalene by 26.3%, for 3-ring PAHs from 28.3% (acenaphthene) to 33.3% (fluorene), for 4-ring PAHs from 40.1% (pyrene) to 44.7% (fluoranthene) and for 6-ring dibenzo(a,h)anthracene by 44.6%.

At a biochar dose of 25 mg/L and a contact time of 30 min, the concentration of benzo(a)pyrene decreased by only 4.7% (Fig. 1). Changes in the concentrations of the four normalized PAHs were within analytical error. At the same biochar dose and a contact time of 60 min, benzo(a)pyrene concentration decreased by 13.2%. The concentration of the four normalized PAHs decreased from 11.8% (benzo(b)fluoranthene) to 14.7% (benzo(g,h,i)perylene), whereas their total concentration decreased by 12.9%. At the same biochar dose and a contact time of 90 min, PAH removal efficiency was higher for times of 30 and 60 min. The concentration of benzo(a)pyrene decreased by 19.4%. The concentration of the four normalized PAHs decreased from 19.7% (benzo(b)fluoranthene) to 27.0% (indeno(1,2,3-cd)pyrene) whereas their total concentration decreased by 24.2%. For the other PAHs recommended for analysis by EPA at a dose of 25 mg/L and a contact time of 90 min, the concentration after adsorption decreased for 2-ring naphthalene by 14.5%, for 3-ring PAHs from 9.9% (acenaphthylene) to 17.0% (fluorene), for 4-ring PAHs from 19.5% (pyrene) to 22.3% (fluoranthene), and for 6-ring dibenzo(a,h)anthracene by 22.3% (Fig. 4). For this biochar dose, the best results were obtained after a contact time of 120 min, with the concentration of benzo(a)pyrene reduced by 37.1%, whereas the total of the four PAHs decreased by 35.5%. For the other PAHs recommended for analysis by EPA at a dose of 25 mg/L and a contact time of 120 min, the concentration after adsorption decreased for 2-ring naphthalene by 22.3%, for 3-ring PAHs from 16.8% (fluoranthene) to 31.4% (phenanthrene), for 4-ring PAHs from 29.0% (pyrene) to 36.4% (chrysene), and for 6-ring dibenzo(a,h)anthracene by 34.7%.

The research showed that better results were obtained for a higher dose of biochar (Fig. 1). These results can be explained by the fact that with the increase in biochar dose, the surface-active sites of the adsorbent increase, leading to greater availability of active adsorbent sites to adsorb PAHs from water. According to literature data [34], PAH sorption on biochar is based on: π–π interaction between PAH benzene rings and biochar, and PAH sorption in biochar nanopores. With the increase in the dose of biochar, the number of nanopores and the sorption capacity increased. Studies of changes in PAH concentration depending on contact time showed that with increasing time, the concentration of these pollutants in the model water decreased (Figs. 1–4) which could be due to the greater importance of migration effect for longer time on adsorption of PAHs [3]. According to Semple et al. [47] PAH take longer time to reach sorption equilibrium. This hypothesis was confirmed

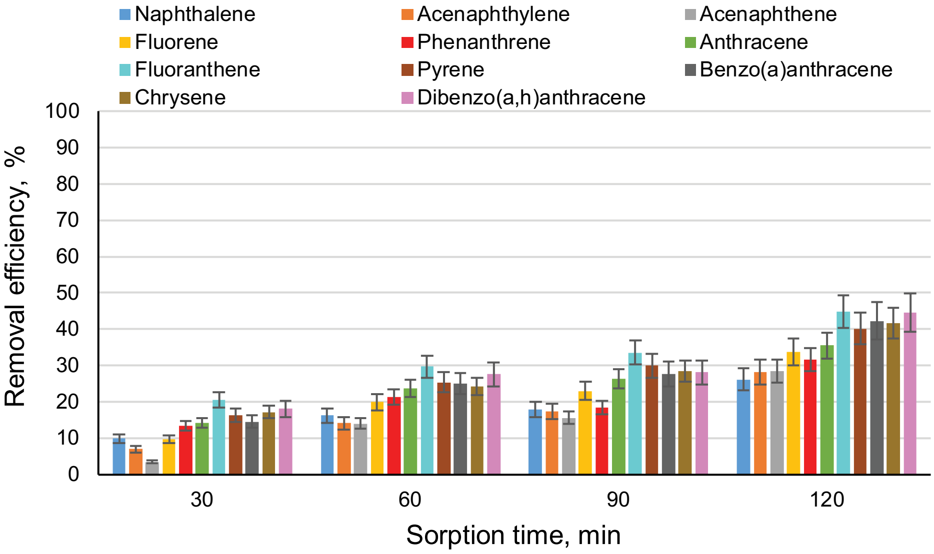

Fig. 3. Removal efficiency of polycyclic aromatic hydrocarbons from water with biochar dose 50 mg/L.

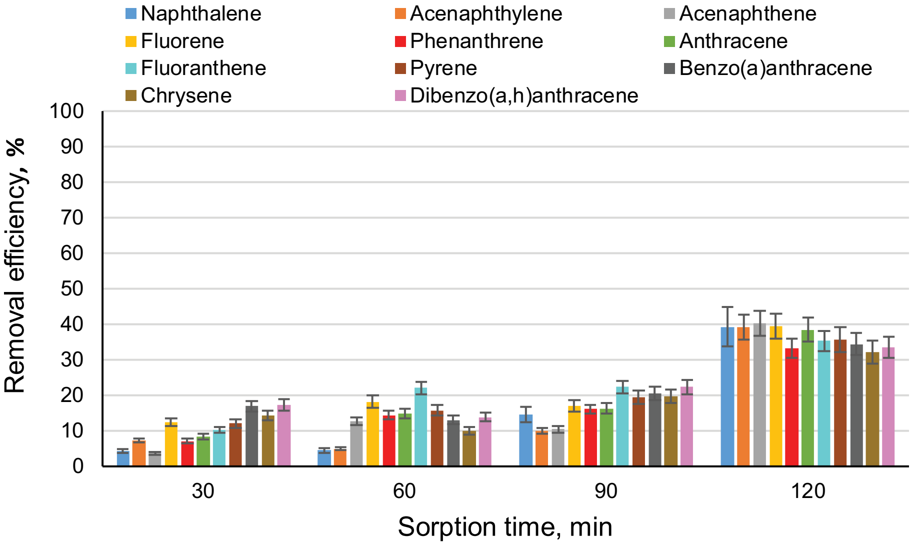

Fig. 4. Removal efficiency of polycyclic aromatic hydrocarbon from water with biochar dose 25 mg/L.

by research by Zeledon-Toruno et al. [48]. The authors conducted an experiment with pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and fluorene with an initial concentration equal to 100 mg/L. The studies have shown that 70% of PAHs removal was achieved within 2 h of contact time and then gradually reached to the equilibrium within 24 h with maximum removal efficiency of >82% for pyrene, benzo(k)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene and 78.4% for fluorine. Other studies on phenanthrene adsorption rate on mesoporous molecular sieve MC-41 showed that the adsorption process reached the equilibrium within 60 min and no further significant change in adsorption has been observed until 2 h [49]. Gupta [50] confirmed that the phenanthrene adsorption rate on activated carbon increased rapidly in the first 75 min of contact time, then reached to the equilibrium state at 150 min. In the case of model water for standardised PAHs, their adsorption on biochar after contact time of 90 min was not sufficient to lower the concentration below the limit values, the optimal time was 120 min (Fig. 1).

Since the literature does not provide examples of the use of biochar obtained from municipal sewage sludge for the sorption of PAHs from the aquatic environment, the results of the study were compared to the sorption data of these compounds on activated carbon [51,52]. The sorption of PAHs on activated carbon depends on factors such as PAH concentration, adsorbent surface area, contact time, type of carbon, dose, and temperature conditions. A very important parameter is also the size of the adsorbate particles (on which their transport in the adsorbent depends), which in turn, according to Hale et al. [27], is not important for biochar. Valderrama et al. [53] evaluated granular activated carbon (GAC) as a suitable sorbent for removing PAHs from aqueous solutions. The high efficiency of PAH removal from a standard aqueous solution (distilled water contaminated with PAH standard solution) on WG-12 activated carbon was confirmed by Smol et al. [51] examinations. The removal efficiency of carcinogenic PAHs was 100% for benzo(g,h,i)perylene, 99.8% for benzo(k)fluoranthene, 97.1% for benzo(a)pyrene, 96.7% for benzo(b)fluoranthene and dinenzo(a,h)anthracene, and 90.9% for indeno(1,2,3-cd)pyrene. In the case of the biochar used in the study, at a maximum dose of 100 mg and a contact time of 120 min for the enumerated PAHs, the removal efficiency of these compounds was lower and ranged from 78.5% (benzo(b)fluoranthene) to 82.3% (benzo(a)pyrene) but the concentrations of these PAHs after the sorption on the biochar were below the permissible levels for drinking water. The lower efficiency of PAH removal on biochar compared to literature data on the removal of activated carbon does not preclude the proposal to use biochar for PAH sorption. This recommendation is supported by the values obtained for the concentration of normalized PAHs after sorption on biochar, which was below the permissible levels specified in the relevant legal acts in drinking water, that is, below 0.01 µg/L for benzo(a)pyrene and 0.1 µg/L for the total of four PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene). Another argument for further research into the use of biochar for PAH sorption is their low cost compared to relatively expensive commercially available activated carbons.

It should be noted that the final recommendation of the use of biochar for the removal of PAHs from the aquatic environment or wastewater requires further research because the results presented in this paper were obtained for model water, which differs in quality composition from real water. It is known that the sorption of PAHs is affected not only by the properties of the adsorbent but also by water composition, pH, temperature, salinity, and environmental factors, so further research will be conducted on surface water. Another equally important aspect to consider when using biochar as an adsorbent is the likelihood of the presence of PAHs in biochar. As shown research, PAHs can be co-produced during substrate pyrolysis to obtain biochar [54]. The actual PAH content of biochar can range from negligibly low to alarmingly high depending on pyrolysis conditions and subsequent activation. Krzyszczak et al. [55] also reported that biochar may contain some potentially toxic compounds, such as PAH. However, by comparing the toxicity of sewage sludge and the biochar produced from sewage sludge, Zielińska and Oleszczuk [42,56] showed that the toxicity of biochar is much lower than that of sewage sludge. The content of soluble PAHs in biochar is 2.3–3.4 times lower than in raw sewage sludge. Gopinath et al. [38] indicated that further research is needed to improve the quality of biochar obtained from sewage sludge in order to increase its potential for real-world application. This can be achieved by controlling the temperature of pyrolysis and co-pyrolysis. Due to health risks, PAHs must be determined in biochar used as a sorbent to immobilize pollutants from various elements of the environment. This requires appropriate regulations and standardization of analytical methods for the determination of these compounds.

4. Conclusion and future work

Based on the obtained results, the following conclusions were formulated:

- The use of biochar reduced the concentration of analysed PAHs in the water.
- Extending the contact time and increasing the dose of biochar improves the effectiveness of PAH removal.
- The best results of PAH removal from water were obtained with biochar dose of 100 mg/L and contact time of 120 min. Under these conditions, the concentration of benzo(a)pyrene decreased by 82.3%, and the sum of the four standardized PAHs decreased by 94.5%.
- At the highest dose of biochar and after the contact time of 120 min, the concentrations of standardized PAHs after the sorption process were below the permissible levels specified in the relevant legal acts for drinking water.

The results obtained in the study support the use of biochar for the sorption of PAHs from the aquatic environment. The final recommendation of the use of biochar for PAH removal from the aquatic environment requires further research under real-world conditions. Given the likelihood of the presence of PAHs in biochar, which can be co-generated during the pyrolysis of the substrate, due to health risks, PAHs must be determined in biochar used as a sorbent to immobilize contaminants from various elements of the environment. In addition, future studies on biochars originating from sewage sludge should include: assessment of the impact of coexisting ions/compounds on adsorption on biochar, removal of PAHs from water both in laboratory and in real conditions (e.g., surface water), analysis of the impact of pyrolysis conditions and modification of physical and chemical parameters of biochar on the improvement of PAH removal efficiency.

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