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Selection of Coagulants for the Removal of Chosen PAH from Drinking Water

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Abstract: The aim of the research was to determine the efficiency of a coagulation process with powdered activated carbon for the removal from surface water of benzo(a)pyrene and 16 polycyclic aromatic hydrocarbons (PAHs), including the sum of four standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. For the study, surface water was used, whose composition was modified with standard solution PAH MIX A. In the first stage, for water modified with standard PAH mixture, the coagulation process was conducted. As the coagulants $Al_2(SO_4)_3 \cdot 18H_2O$, hydrolysed salts, and polyaluminum chlorides (PAX1910 and PAX19F) were used. In the second stage, the adsorption process was conducted. Powdered activated carbon was used (CWZ-22 and CWZ-30). In the third stage, the coagulation process and the adsorption process were combined. The best effects for the reduction concentrations of the sum of four normalized PAHs, as well as of benzo(a)pyrene, were obtained by applying coagulation carried out with PAX19F and aided by powdered activated carbon CWZ-30. The removal efficiency for these compounds was, respectively, 93.8% and 95.8%.

Keywords: coagulation process; drinking water; polycyclic aromatic hydrocarbons; powdered activated carbon

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute a group of chemical compounds containing from two to seven condensed aromatic rings [1–7]. At present, in the environment there are over 300 different recognized compounds classified as polycyclic aromatic hydrocarbons, including 33 which are considered by the Scientific Committee on Food (SCF) to be particularly toxic. In the environment, PAHs do not occur separately, but always in a mixture [8]. The most extensively studied PAH is benzo(a)pyrene, which due to a strong carcinogenic effect and prevalence in the environment, has been recognized as an indicator for the whole group of these compounds [9,10]. For this reason, several regulations deal with PAHs in the environment. The first was the EPA Consent Decree by the Environmental Protection Agency of the USA (US EPA) in 1976 [11,12]. PAHs have been the object of many new or updated regulations. One example is the Council Directive 98/83/EC of 3 November 1998 [13], the Water Framework Directive of the European Union (EU) (Directive 2000/60/EC), that was updated in 2013 (2013/39/EU): another is the Ministry of Health Regulation of 7 December 2017 [14].

However, PAH reactivity and polarity may change depending on the type and presence of functional groups [15]. PAHs have low volatility and low water solubility, both of which decrease with increasing molecular weight [16]. These compounds are highly soluble in organic solvents, such as benzene, hexane, cyclohexane, and acetone. They demonstrate sensitivity to changes in temperature and the pH of the environment in which they occur, and to the co-presence of chemical compounds such as surfactants, pesticides, and oxidizing agents. PAHs show a high affinity for solid surface, which increases with the number of rings in the molecule. They occur mainly in a form adsorbed on the particles forming suspended solids. Naphthalene and acenaphthylene are impermanently bound to suspended solids, whereas the remaining hydrocarbons constitute a group of compounds which can occur in both dissolved and adsorbed form. PAHs get into the aquatic environment mainly from anthropogenic sources. The amount of PAH derived from natural sources is small compared to that resulting from human activity [17]. In water, the main sources of micropollutants of anthropogenic origin, including PAH, are dry and wet precipitation, wastewater, surface runoffs, and leachate from municipal and industrial landfills [18].

The permissible PAH content in water intended for human consumption is based on the sum of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)diperylene, and indeno(1,2,3-cd)pyrene; it amounts to 0.1 μg/L. The permissible content of benzo(a)pyrene, 0.01 μg/L, is stated separately. In Polish legislation, the permissible levels of benzo(a)pyrene and the sum of the four PAHs in drinking water are stated in The Ministry of Health Regulation of 7 December 2017 [14] on the quality of water intended for human consumption, and in the European legislation in the Council Directive 98/83/EC of 3 November 1998 [13] on the quality of water intended for human consumption.

Due to toxic, mutagenic, and carcinogenic properties of PAHs [19,20], it is necessary to remove these compounds from water intended for human consumption and undertake a health risk assessment [21,22]. For PAH removal from water, membrane processes, advanced oxidation processes, adsorption, and biodegradation, among others, are used. The efficiency of PAH removal in these processes amounts to 72–94%. In the case of water preparation for consumption, adsorption with activated carbon has practical applications [23,24]. The efficiency of adsorption is not always satisfactory, and it depends on the type of removed adsorbates. This process should be preceded by pre-treatment processes of water, in which coagulation plays an important role [25]. Coagulation-flocculation process is regarded as one of the most important and widely used treatment processes of drinking water [26] and industrial wastewater [27] due to its simplicity and effectiveness. In the literature, there are few examples of research on PAH removal from contaminated water using a coagulation process enhanced by adsorption on activated carbon.

The aim of this research was to evaluate the effectiveness of the coagulation process, adsorption and coagulation enhanced by powdered activated carbon for the removal from surface water of benzo(a)pyrene and 15 polycyclic aromatic hydrocarbons (PAH), including the sum of the four standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption: benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene [13].

2. Materials and Methods

2.1. Materials

For the research, surface water from the Kozłowa Góra dam reservoir was used. The Kozłowa Góra dam Reserovir is located on the south-east outskirts of Świerklaniec commune (Poland). This reservoir was formed due to the raised water level of the Brynica River. It covers approx. 5.5 km^2 of the area, and its volume is approx. 13 mln m^3. It is relatively shallow, with an average depth of 4.5 m. At present, the Kozłowa Góra dam Reservoir is a water source for the Water Treatment Plant in Wymysłów, which belongs to the Upper Silesia Water Supply Company. It also functions as flood control, and it may be used for tourist-recreational activities.

Water was modified with a PAH MIX A standard solution produced by AccuStandard, Inc company (New Haven, CT, USA), in order to obtain the total concentration of standardized PAHs higher than the permissible level in water intended for human consumption. Four PAHs were introduced into the water: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene, which are enclosed in the Directive (total concentration amounted to 0.20 μg L^{-1}), benzo(a)pyrene (0.05 μg L^{-1}) and the remaining 11 PAH recommended by the Environmental Protection Agency (EPA) for determination in environmental samples.

Nonhydrolyzed salt $Al_2(SO_4)_3 \cdot 18H_2O$, produced by POCH in Gliwice, and hydrolyzed salts, polyaluminum chlorides, with commercial names PAX-XL19F and PAX-XL1910, produced by KEMIPOL company in city Police (Poland), were used as coagulants. Aluminum sulphate is a commonly used coagulant for water treatment plants in Poland. However, more and more often it is replaced by pre-hydrolyzed coagulants, i.e. due to the fact that they reduce the dose of the applied reagents. Commercial solutions of polyaluminum chlorides had alkalinity equal to 85%. The alkalinity is determined by the ratio of the number of OH^- moles to Al^{3+} in the coagulant, defined as the coefficient $r = [OH^-]/[Al^{3+}]$. The relation between the "r" value and the alkalinity of the coagulant is: alkalinity (%) = r/0.03. A commercial solution of PAX-XL19F contained 16.0% Al_2O_3, while PAX-XL1910 contained 19.8% Al_2O_3. Polyaluminum chlorides and their doses were chosen based on previously conducted research [28] on the removal of turbidity, color and total organic carbon content. The recommended pH for conducting the coagulation process is 5.5–7.5; therefore, the recommended tests were carried out without pH correction. For the analyses, coagulant solutions were prepared by diluting commercial products so that they contained 1.0 g Al L^{-1}.

In the study, powdered activated carbons were also used, with trade names CWZ-30 and CWZ-22, manufactured by GRYFSKAND in Hajnówka city (Poland). The characteristics of the carbons are shown in Table 1. The carbons were characterized by the specific surface area of 920–1134 m^2 g^{-1}, iodine number 1032–1190 mg g^{-1}, and methylene number 29–30 cm^3.

Table 1. Selected properties of powdered activated carbons.

Properties	Unit	Powdered Activated Carbon	
		CWZ-22	CWZ-30
Specific surface area	m^2 g^{-1}	960	1134
Iodine number	mg g^{-1}	1032	1190
Methylene number	cm^3	29	30
Granulation < 0.06 mm	%	93	90

2.2. Jar Test Procedure

In the first stage, the coagulation process was conducted in 3 L glass beakers; to each beaker, 2 L of analyzed water was measured. The coagulants, 3 mg Al L^{-1}, were introduced, and with the use of a mechanical stirrer, fast stirring was executed for 2 min (applying 250 RPM), and then slow stirring for 15 min (25 RPM). After this time, the samples were subjected to 1 h sedimentation. Afterwards, 0.5 L of water was decanted and analyzed.

In the second stage of the research, the adsorption process was conducted. One liter of analyzed modified water was measured into glass beakers with a volume of 2 L, and powdered activated carbons were introduced. The applied dose of carbons was 30 mg L^{-1}. Using a mechanical stirrer, mixing was performed at 200 RPM for 15 min. Then, the carbon was separated from the water by filtration of the samples through a paper filter and analyzed.

In the third stage, the coagulation process was combined with the adsorption process. Among the tested coagulants, the highest removal efficiency of PAH was obtained using PAX-XL19F. Taking this into consideration, the efficiency of decreasing the sum of PAH concentrations standardized in the Council Directive 98/83/EC with studied activated carbons differed slightly, the efficiency of remaining PAH removal was higher with the usage of CWZ-30 carbon, CWZ-30 carbon was selected for enhancement of the coagulation process. Two liters of the analyzed modified water was measured into a glass beaker with a volume of 3 L. PAX-19F coagulant was introduced at the amount of 3 mgAl L^{-1}, and with the use of a mechanical stirrer, fast stirring was conducted for 2 min (applying 250 RPM).

Then, 30 mg L^{-1} carbon CWZ-30 was introduced, and the solution was stirred for a further 2 min. Next, slow stirring was carried out for 15 min (25 RPM). After this period, the samples were subjected to 1 h sedimentation. Then, 0.5 L of water was decanted and analyzed. Opinions regarding the order in which the coagulants are applied vary, and examples of the simultaneous introduction of coagulant and powdered activated carbon, application of coagulant first and then carbon, or the other way round, can all be found. Each of the mentioned methods has advantages and disadvantages. In water treatment plants in Poland, powdered activated carbon is most often introduced into rapid mixing chambers along with the coagulant.

2.3. Analytical Procedure

The physicochemical parameters of water were measured with the following methods: pH–potentiometrically; turbidity–with Instruments TN-100 nephelometer (Eutech Instruments Pte Ltd., Singapore), expressed in NTU–Nephelometric Turbidity Unit); color–colometrically with platinum-cobalt standard method; total organic carbon (TOC)–by infrared spectrophotometry with carbon analyzer Multi N/C (Analytic Jena, Germany), aluminum–with Aquaquant 14413 aluminum test.

For PAH separation from water, the solid phase extraction (SPE) method was applied, using Bakerbond company columns with Octadecyl C_{18} filling (J.T. Baker Mallinckrodt Baker, Inc. Phillipsburg, NJ, USA). For this purpose, 0.5 L of modified surface water was collected and 0.5 L of water after the coagulation, the adsorption and the coagulation enhanced by the adsorption. Propanol was added to the water samples. The samples were then passed through preconditioned Octadecyl C_{18} columns. PAHs were eluted from the column by filling with hexane (3 × 1 mL). The obtained eluate was gently evaporated to dryness under a stream of nitrogen, and then 1 mL acetonitrile was added to the test tube. The sample was analyzed by means of gas chromatography and mass spectrometer GC-MS (Fisons Instruments SpA, Rodano, Italy) [29–35]. Separation was conducted on a DB-5 column (30 m × 32 mm × 1 µm). A quadrupole mass spectrometer MS 800 (Fisons Instruments SpA, Rodano, Italy), working in a selective mode of ion monitoring was used for detection. Selective ion monitoring (SIM) m/z was applied. For each PAH, three representative ions were chosen. Identification ions of PAHs are shown in Table 2.

Table 2. Retention times and the strongest ions peaks for PAH.

PAH	Molecular Formula	Retention Times	The Strongest Ions
Naphthalene	$C_{10}H_8$	5.40	129 128 127
Acenaphtylene	$C_{12}H_8$	10.09	153 152 151
Acenaphtene	$C_{10}H_{10}$	10.76	154 153 152
Fluorene	$C_{13}H_{10}$	12.96	167 166 165
Phenanthrene	$C_{14}H_{10}$	17.48	179 178 176
Anthracene	$C_{14}H_{10}$	17.73	179 178 176

Table 2. *Cont.*

PAH	Molecular Formula	Retention Times	The Strongest Ions
Fluoranthene	$C_{16}H_{10}$	23.60	203 202 101
Pyrene	$C_{16}H_{10}$	24.77	203 202 101
Benzo(a)anthracene	$C_{18}H_{12}$	31.95	229 228 226
Chrysene	$C_{18}H_{12}$	32.95	229 228 226
Benzo(b)fluoranthene	$C_{20}H_{12}$	36.17	252 250 126
Benzo(k)fluoranthene	$C_{20}H_{12}$	36.17	252 250 126
Benzo(a)pyrene	$C_{20}H_{12}$	41.28	252 250 126
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	51.78	277 276 138
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	52.86	278 277 276
Benzo(g,h,i)perylene	$C_{22}H_{12}$	54.48	277 276 138

Determination was performed for each sample and each four injection of the obtained extract. In order to verify the applied procedure, values of recoveries for aromatic hydrocarbons with low molecular weights were determined. For this purpose, standard mixture 16 PAH MIX A by RESTEK company was introduced into a sample of distilled water and quantitative-qualitative assays of PAH were conducted, according to the procedure described above. The recovery ranged from 50.4% (naphthalene) to 92.8% (phenanthrene). The recovery values were taken into account during concentration calculations. PAH determinations were performed in duplicate.

3. Results and Discussion

Surface water was characterized by turbidity amounting to 7.5 NTU and color equal to 40 mg L^{-1}. The TOC content was 9.1 mgC L^{-1}. The water reaction was slightly alkaline.

The effectiveness of turbidity, color, and TOC removal by various coagulants and type powdered activated carbon are presented in Table 3.

Table 3. Effect of coagulation and adsorption with various agents on selected physicochemical properties of water.

Parameter	Unit	Surface Water	$Al_2(SO_4)_3$	PAX-XL1910	PAX-XL19F	PAX19F + CWZ-30	CWZ-22 *	CWZ-30 *
pH	-	7.28	6.92	7.08	7.12	7.16	7.23	7.26
Color	mgPt L^{-1}	40.0	20.0	15.0	10.0	5.0	15.0	10.0
Turbidity	NTU	7.5	2.1	1.6	0.8	1.3	-	-
TOC	mgC L^{-1}	9.1	6.9	6.1	5.6	5.1	7.4	7.0
Aluminum	mgAl L^{-1}	0.03	0.28	0.07	0.07	0	0	0

* analyzed in sample after adsorption filtered through filter paper.

The research results for a coagulant dose of 3.0 mgAl L^{-1} confirmed higher effectiveness in removal of turbidity, color and organic compounds with the usage of pre-hydrolyzed polyaluminum chlorides PAX-XL1910 and PAX-XL19F. 79% and 89% turbidity removal, 63% and 75% color reduction, were obtained. The efficiency of reduction of organic compound content assayed as TOC amounted to 33% and 38% using PAX, whereas with the application of $Al_2(SO_4)_3$ this was 24%. The higher effectiveness of pre-hydrolysed coagulants, in comparison to aluminum sulphate, is determined by the presence of polycations $Al_2(OH)_2{}^{4+}$, $Al_3(OH)_4{}^{5+}$ and $Al_{13}O_4(OH)_{24}{}^{7+}$, as well as by the difference in structure of precipitated aluminum hydroxide flocs formed during the hydrolysis of these coagulants [36,37]. Simultaneous use of powdered activated carbon CWZ-30 and coagulant PAX-XL19F improved color removal by 88%. No aluminum ions were present in water after coagulation supported by the addition of activated carbon.

PAH concentrations in modified surface water and in water after the coagulation process, the adsorption, and the coagulation enhanced by powdered activated carbon are presented in Table 4. In the results discussion, the analyzed PAH were divided into following groups:

- standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption: benzo(a)pyrene and the total of: benzo(b)fluoranthene, benzo(k)fluoranthene; benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene (compounds classified as 5- and 6-ring PAH);
- 2-ring PAH (naphthalene);
- 3-ring PAH: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene;
- 4-ring PAH: fluoranthene, pyrene, benzo(a)anthracene, chrysene;
- 6-ring PAH: dibenzo(a,h)anthracene.

Table 4. The concentration (ng L^{-1}) of PAH in water after the coagulation process, the adsorption and the coagulation enhanced by powdered activated carbon.

PAH	Detection Limit (ng L^{-1})	Water after Modification	$Al_2(SO_4)_3$	PAX-XL1910	PAX-XL19F	PAX19F + CWZ-30	CWZ-22	CWZ-30
Benzo(a)pyrene	0.01	50.85	8.06	15.96	18.33	2.15	25.70	17.22
Benzo(b)fluoranthene	0.01	49.76	18.03	10.01	11.50	2.74	11.78	13.71
Benzo(k)fluoranthene	0.01	51.99	26.44	9.62	8.83	2.74	26.55	5.58
Benzo(g,h,i)perylene	0.01	51.26	20.25	20.93	6.46	2.07	12.46	19.65
Indeno(1,2,3-cd)pyrene	0.01	50.85	18.06	25.97	4.83	5.16	11.10	27.23
Σ		203.86	82.78	66.53	31.62	12.71	61.89	66.17
Naphthalene	0.05	58.58	35.80	39.33	36.69	20.10	33.20	35.40
Acenaphthylene	0.01	48.83	20.18	24.13	22.60	11.61	28.90	19.01
Acenaphthene	0.01	49.24	15.50	20.38	19.4	13.77	27.12	20.95
Fluorene	0.01	52.59	22.84	12.81	21.01	10.63	22.58	20.59
Phenanthrene	0.01	48.39	17.88	14.43	16.32	13.77	20.68	18.00
Anthracene	0.01	48.52	20.03	16.01	16.49	9.73	17.77	17.70
Fluoranthene	0.01	51.99	20.44	9.61	8.82	2.53	16.69	5.87
Pyrene	0.01	51.27	20.25	17.93	6.46	2.06	12.45	5.99
Benzo(a)anthracene	0.01	50.88	18.06	21.76	6.63	2.15	13.04	8.12
Chrysene	0.01	50.59	15.50	15.08	17.18	2.01	13.20	8.37
Dibenzo(a,h)anthracene	0.01	51.26	19.15	19.03	6.32	2.10	19.35	17.64

In unmodified surface water, total concentration of analyzed PAH was 21.44 ng L^{-1}. The presence of compounds representing 3-ring PAH, i.e., acenaphthylene, acenaphthene, phenanthrene, and anthracene, and benzo(b)fluoranthene representing 5-ring PAH, was not determined. The concentration of PAH included in the Council Directive 98/83/EC on the quality of water intended for human consumption, i.e., benzo(a)pyrene and the sum of benzo(k)fluoranthene, benzeno(g,h,i)perylene and indeno(1,2,3-cd)pyrene, were below the permissible level, i.e., 0.05 μg L^{-1}. The concentration of the remaining PAH ranged from 0.59 (chrysene) to 8.58 ng L^{-1} (naphthalene). Using the coagulation process, the highest efficiency of reduction of benzo(a)pyrene concentration (by 84.2%) from modified water was obtained after the application of $Al_2(SO_4)_3$, and the lowest (by 63.9%) after the application of PAX-XL19F coagulant (Figure 1). The usage of powdered activated carbons reduced the concentration of this compound to within a range of between 49.5 and 66.1%. The usage of powdered activated carbon CWZ-30 was 17% more effective in decreasing the concentration of benzo(a)pyrene with regard to CWZ-22 carbon. Among the tested coagulants $Al_2(SO_4)_3$, PAX-XL1910, PAX-XL19F and powdered active carbons CWZ-22 and CWZ-30 for benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, a reduction in their concentration from 46.4 to 90.5% was obtained (Figure 1).

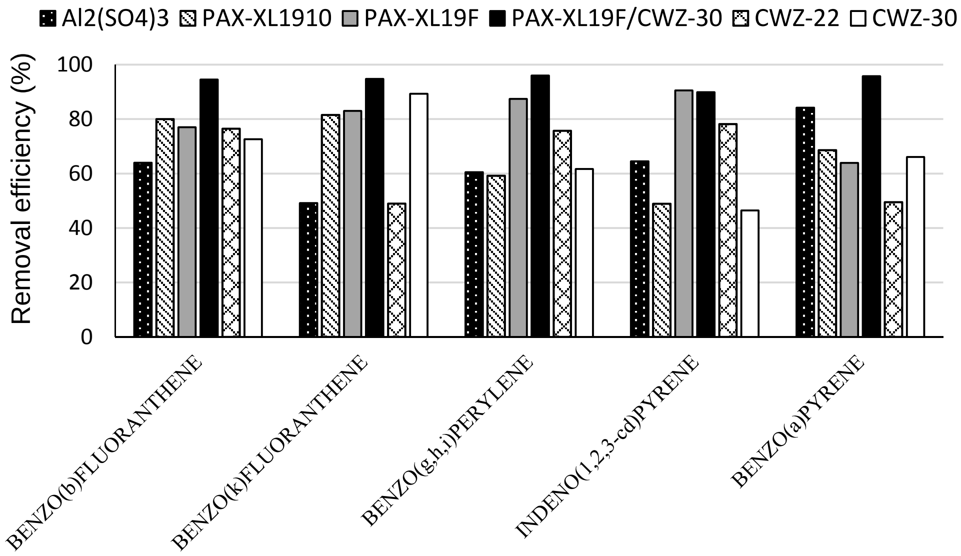

Figure 1. Removal efficiency of PAH standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption.

The highest efficiency of the reduction of the sum of four standardized PAH, i.e., benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, was obtained in the case of PAX-XL19F coagulant application (by 84.5%). With the usage of the remaining coagulants, $Al_2(SO_4)_3$ and PAX-XL1910, the efficiencies of reduction of total concentration of these compounds were 59.4% and 67.4%, respectively. The usage of powdered activated carbons CWZ-22 and CWZ-30 allowed a reduction in the sum of four PAH by 69.7% and 67.6%, respectively (Figure 2).

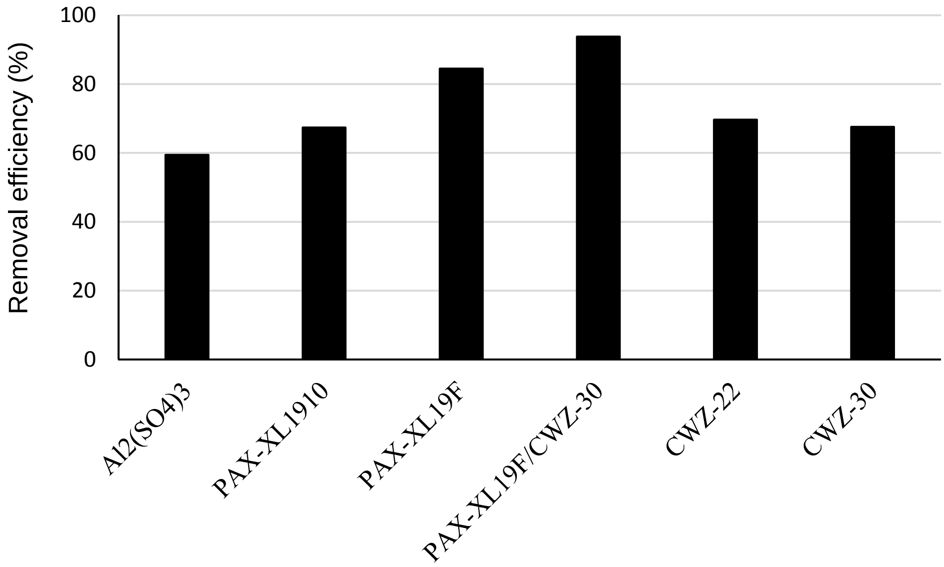

Figure 2. Removal efficiency of sum PAH standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption.

Among the tested coagulants $Al_2(SO_4)_3$, PAX-XL1910, PAX-XL19F and powdered active carbons CWZ-22 and CWZ-30, the lowest PAH removal from water efficiency was obtained for 2- and 3-ring compounds (Figure 3). In case of 2-ring naphthalene, the removal efficiency ranged from 34.9 ($Al_2(SO_4)_3$) to 57.8% (PAX-XL19F). For 3-ring PAH, a reduction in concentration by 54.8 to 71.1% was obtained. In this group of compounds, after application of $Al_2(SO_4)_3$ for coagulation, a reduction in concentration in the range of 56.6 (fluorene) to 69.0% (acenaphthene) was obtained. With the usage of PAX-XL1910 coagulant, the concentration of 3-ring PAH decreased from 51.7 (acenaphthylene) to 75.6% (fluorene). The application of PAX-XL19F influenced the decrease in the concentration of these compounds from 54.8 to 67.0%. The efficiency of removal from water of 3-ring PAH with powdered activated carbons CWZ-22 and CWZ-30 ranged from 42.2 to 64.6% (Figure 3).

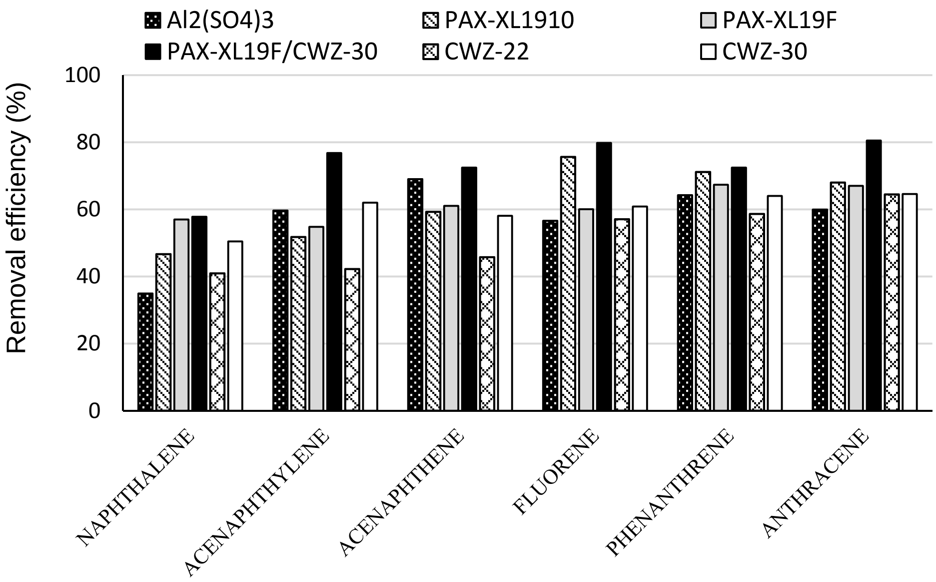

Figure 3. Removal efficiency of 2- and 3-ring PAH from surface water.

For 4-ring PAH, a reduction in concentration from 57.2 to 88.7% was obtained. In this group of compounds, with the usage of $Al_2(SO_4)_3$ for coagulation, a decrease in concentration in the range of 60.49% (pyrene) to 69.29% (chrysene) was obtained (Figure 4). After applying PAX-XL1910 coagulant, the concentration of 4-ring PAH decreased from 57.2 (benzo(a)anthracene) to 81.5% (fluoranthene). The usage of PAX-XL19F improved the PAH removal efficiency and a decrease in concentration from 66.0% (chrysene) to 87.4% (benzo(a)anthracene) was obtained. The efficiency of 4-ring PAH removal from water in the sorption process using powdered activated carbon CWZ-30 ranged from 83.4 to 88.7%, and was higher than the efficiency of CWZ-22 carbon (Figure 4).

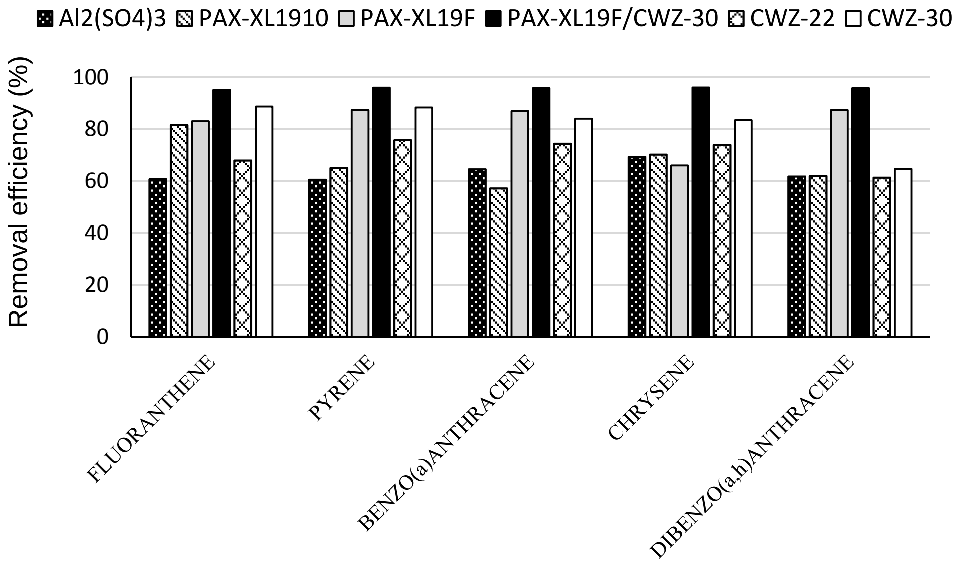

Figure 4. Removal efficiency of 4- and 5- ring PAH from surface water.

Among the tested coagulants $Al_2(SO_4)_3$, PAX-XL1910, PAX-XL19F, the highest removal efficiency of dibenzeno(a,h)anthracene (87.4%) was obtained using PAX-XL19F. In case of the application of powdered activated carbons CWZ-22 and CWZ-30, the removal efficiency of dibenzo(a,h)anthracene was comparable, and amounted to 61.3% and 64.7%, respectively.

The best results of reducing the concentration of benzo(a)pyrene, total of four standardized PAH, as well as concentration of the remaining PAH, were obtained using coagulation enhanced by powdered activated carbon (Figures 1–4). In the combined process, the application of PAX-19F coagulant, and subsequently CWZ-30 carbon, yielded a decrease in the concentration of analyzed compounds in the range of from 57.8 (naphthalene) to 96.0% (pyrene, chrysene). For benzo(a)pyrene, the removal efficiency was 95.8%, and the reduction of the sum of the four standardized PAH was 93.8%.

The obtained results indicate that the coagulation, the adsorption and the coagulation enhanced by powdered activated carbon are effective in the removal from water of polycyclic aromatic hydrocarbons, including benzo(a)pyrene, and four standardized in the Council Directive 98/83/EC on the quality of water intended for human consumption. It was observed that the selectivity of PAH removal from water depends on the physico-chemical properties of the compound (e.g., number of rings in the molecule, hydrophobicity). Similarly, according to the literature data, the efficiency of removal of organic micropollutants from water is affected by the type of process used, e.g., coagulation, filtration, adsorption, oxidation, or combined processes [23,38–40]), which is confirmed by the results of conducted research.

According to the literature, the efficiency of the coagulation process is influenced by (1) the type and dose of the coagulant; (2) treated water composition, including content and properties of organic contamination; (3) pH; (4) water alkalinity; and (5) physicochemical properties of removed organic micropollutants [25]. In the available literature, no studies were found on the effect of coagulant dose and water pH on the effectiveness of PAH removal in the coagulation process. The application of $Al_2(SO_4)_3$ or polyaluminum chlorides as coagulants for organic contaminant removal is recommended by many authors [25,41]. The obtained results suggest that, when using polyaluminum chlorides for organic micropollutant removal from water, their alkalinity is important, which should equal ca. 70%. Alkalinity of PAX-XL1910, PAX-XL19F was ca. 85%, which could affect the efficiency of the coagulation using these coagulants in PAH removal in comparison to the effects obtained during the coagulation with $Al_2(SO_4)_3$. The concentration of analyzed PAH decreased in the range of 32.9 (naphthalene) to 90.5% (indeno(1,2,3-cd)pyrene). The best results were obtained using PAX-XL19F for 4–6-ring PAH removal. The obtained results confirm the results of studies of other authors [42]. Higher removal efficiency of PAH containing 4–6 rings can be explained by their good sorption on particulates. Li and co-authors [43] demonstrated that during the coagulation of organic micropollutants, sorption of these compounds on particles of organic matter naturally occurring in water (NOM) plays an important role. The authors demonstrated that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) occur in water in a form bound to NOM, and during coagulation will be removed along with the NOM particulates. PAH strongly bonded to suspended solids and particulate surface, including indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)antracene, and benzo(k)fluoranthene. For these compounds, the removal efficiency in the coagulation process was higher than the removal efficiency of 2- and 3-ring PAH. The obtained results confirm the correlation between PAH hydrophobicity (expressed by the partition coefficient n-octanol/water i.e., $K_{o/w}$) and the coagulation effectiveness in removal of these pollutants from water. According to Tadkaew et al. [44], for compounds demonstrating log $K_{o/w} > 3.2$, higher efficiency of their removal in the coagulation process is achieved. The log $K_{o/w}$ value of analyzed PAH ranges from 3.30 to 6.58, which explains the good performance of the coagulation process in their removal. Generally, for analyzed compounds, it was demonstrated that along with increasing PAH, log $K_{o/w}$ efficiency of their removal increases.

The effectiveness of the adsorption process is influenced by the type of used carbon (specific surface area, porosity, polarity, and chemical nature of the carbon surface) and the properties of removed organic micropollutants (molar weight, spatial structure of the molecule, solubility, ionic strength), as well as the temperature of the solution in which the adsorption process occurs [23,38,45,46]. Unsatisfactory results of adsorption of naphthalene may arise from the nature of the applied powdered activated carbons. Research conducted by Anita and co-authors [47] has demonstrated that the adsorption capacity in different carbon materials depends not only on the textural characteristics of the material but also on the functionalities of the activated carbons. The micropores of the adsorbents, particularly those of narrower diameter, were found to be active sites for the retention of naphthalene. In the adsorption process, dispersion forces play an important role. The authors report that for the adsorption of naphthalene a carbon with higher non-polar character is effective.

The obtained results demonstrate a correlation between PAH adsorption effectiveness and specific surface area of the powdered activated carbon. Applied in the research powdered activated carbons, CWZ-22 and CWZ-30 were characterized by a specific surface area of 960 $m^2\ g^{-1}$ and 1134 $m^2\ g^{-1}$, respectively. The best results were obtained using activated carbon CWZ-30, which was characterized by a greater specific surface area. Upon application of this sorbent, a decrease in analyzed PAH concentration in water was obtained, ranging from 46.5 for indeno(1,2,3-cd)pyrene to 88.7% for fluoranthene. Similar results for organic micropollutants were obtained by Liyan and co-authors [48]. The authors conducted a research on the removal of hydrophobic organic chemicals (HOCs) using powdered activated carbon and granular-activated carbon. The effectiveness of adsorption of these compounds ranged from 73.4 to 89.2%.

The research results did not confirm that an increase in molecular weight of the compound causes an increase in the adsorption efficiency. It has to be noted, however, that adsorption is affected not only by molar weight, but also by the spatial structure of the molecule, and above all, by specific interactions between the basal planes of activated carbon and the polyaromatic structure of PAH [47]. Research conducted by Guo and co-authors [49] have demonstrated that adsorbent pore structure characteristics (i.e., pore shape and pore size distribution) and adsorbate molecular conformation are important in determining the adsorption of aromatic synthetic organic compounds (SOCs) by porous carbonaceous adsorbent.

Based on the research, it was concluded that an improvement in the efficiency of PAH removal from water may be achieved by using a coagulation process enhancement with powdered activated carbon. The usage of PAX-XL19F coagulant and powdered activated carbon CWZ-30 has improved the efficiency of PAH removal max. up to 96.0% for benzene(g,h,i)perylene. It has been shown that the combination of the coagulation with the adsorption increases the efficiency of PAH removal from contaminated water. For the practical application of the results, it would be necessary to verify the research by the determination of the optimal coagulant dose and the pH of water.

4. Conclusions

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

- the application of coagulants $Al_2(SO_4)_3$, PAX-XL1910, PAX-XL19F and powdered activated carbons CWZ-22 and CWZ-30 was effective in PAH removal in the range of 32.9 (naphthalene) up to 90.5% (indeno(1,2,3-cd)pyrene);
- in the coagulation process, high efficiency of reduction of the sum of the four standardized PAH, i.e., benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, was obtained using PAX-19F coagulant (84.5%); the usage of $Al_2(SO_4)_3$ or PAX-XL1910 obtained an efficiency of removal of these compounds of 59.4% and 67.4%, respectively;
- a good efficiency of removal of benzo(a)pyrene (84.2%) was obtained during coagulation using $Al_2(SO_4)_3$;
- among the applied coagulants, good removal for most PAHs was obtained in the coagulation process with polyaluminum chloride PAX-XL19F;
- the application of powdered activated carbons CWZ-22 and CWZ-30 reduced the concentrations of benzo(a)pyrene by 49.5% and 66.1%, respectively, while the total concentration of four PAH decreased by 69.7% and 67.6%, respectively;
- better removal efficiency for micropollutants in the process of coagulation and adsorption was demonstrated for PAH containing 4–6 rings;
- the adsorption on powdered activated carbon reduced the concentrations of analyzed PAH max. up to 89.3%; the best results were obtained using activated carbon CWZ-30, which was characterized by a higher specific surface area;
- the combination of the coagulation and the adsorption increased the efficiency of removal of PAH from contaminated water; the best results of removal of analyzed PAH were obtained using polyaluminum chloride PAX-XL19F and powdered activated carbon CWZ-30; a decrease in benzo(a)pyrene concentration and total concentration of four PAH in water by 95.8% and 93.8%, respectively, was obtained.

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