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The ability to remove the priority PAHs from water during coagulation process including risk assessment

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ABSTRACT

The aim of the study was to determine extent, in which coagulation can affect to the risk reduction of human exposure to the consumption of water containing polycyclic aromatic hydrocarbons (PAHs). The paper presents results of research on the removal of priority PAHs (naphthalene, anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo (k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene) from water in the volumetric coagulation and sedimentation process. For analysis were chosen coagulants such as aluminum(VI)sulfate and two pre-hydrolyzed coagulants—PAX XL 19H and FLOKOR 1ASW/B. Water samples subjected to coagulation were collected from selected water treatment plant following the pre-ozonation process. Tested coagulants were dosed at optimal doses (2.8; 3.6 mg Al^{3+}/L). Summary concentration of eight hazardous PAHs in water after pre-ozonation amounted to 60.78 ng/L. After volumetric coagulation using selected coagulants was in the range of 31.51–33.64 ng/L. The highest efficiency in the removal of 8 PAHs was obtained after application of FLOKOR 1 ASW/B (48.2%). Also in the removal of benzo(a)pyrene FLOKOR 1ASW/B was the most effective (decrease by 89.9%). The risk analysis was carried out for five hydrocarbons: benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.

Keywords: Coagulation; HPLC; PAHs; Water treatment; Risk assessment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemical compounds containing two or more fused aromatic rings with a different laying of the benzene rings in the molecule [1]. Lipophilicity and resistance to PAH degradation increases with the increase of the number of aromatic rings [2]. Biodegradation resistance increases proportionally to the octanol/water partition coefficient and increase of the molar mass, and inversely proportional to solubility in water. PAHs have hydrophobic properties and the ability to sorb on solid particulates. Octanol/water partition coefficient determines PAHs propensity to deposit at the solids. Therefore, PAHs in surface water

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are adsorbed on the particles of suspensions and accumulate in the bottom sediments. This is confirmed in the literature data that the concentration of these compounds in bottom sediments is several times higher than in the waters [3]. PAHs may be subjected to transformation under the influence of suitable microorganisms. In the water purification technology, biological activated carbon filters have a main significance in the removal of PAHs. Biodegradation may occur with the use of bacteria, fungi, actinomycetes, and some algae. The microorganisms are not capable to direct degradation of PAHs. Although the probable biodegradability pathways are defined, the ability of microorganisms for the production of the corresponding enzymes is required to occurring biodegradation. It is not always possible during the process in the technological conditions. It is necessary to adapt the microflora to biodegradation of the aromatic hydrocarbons present in the environment. Therefore, microorganisms isolated from the environment where they were exposed to the presence of PAHs are biodegradable [4–6]. To other processes of PAHs degradation in the waters are also included: photodegradation and sonodegradation [7,8].

PAHs have the ability to accumulate in the organisms. Some of them are known to have mutagenic, carcinogenic, and teratogenic properties. PAHs are toxic to the indicator organisms. The toxicity grade is dependent on the nature of the compound, the nature of the organism, and the environmental conditions [9]. The values of relative ratios of carcinogenicity for individual PAHs have been identified by Nisbet and LaGoy [10]. Benzo(a)pyrene was found to be the primary compound with carcinogenicity equal to 1. The strength of carcinogenic effects of other compounds is calculated in relation to benzo(a)pyrene [11]. Carcinogenicity and mutagenicity of selected PAHs are presented in Table 1. The strongest carcinogenicity effect is characterized by benzo(a)pyrene [12].

PAHs can cause harm on reproduction and heritable genetic defects [14]. These compounds can also induce in humans mutagenic changes and cancer. PAHs can penetrate into the human body by three pathways: ingestion, inhalation, and skin contact. The last one is the least important in the case of environmental exposure [15]. According to reports of WHO, 99% of PAHs penetrates into the body with food and 0.1–0.3% with the contaminated water [16,17]. Carcinogenic doses of selected PAHs for animals are presented in Table 2. The impact on the human body can be estimated on the basis of the data contained in this table (for mice or rats), because research on human can be conducted in that case.

Quality standards for water intended for human consumption are provided in Directive 98/83/EC of the Council [29]. The allowable concentration of benzo(a)pyrene, amounting to 10.0 ng/L, was specified in this Directive. Also, the total concentration of 4 PAHs—benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene was determined at the level of 100.0 ng/L. In Table 3, there are also presented concentrations of selected PAHs in bodies of surface waters and in inland/other surface waters. Five hydrocarbons, important from the point of view of the quality of water intended for human consumption, were selected to assess the risk.

Risk analysis and evaluation is the most important procedure in water supply system safety management. Access to safe drinking water is essential to health, a basic human right and a component of effective policy for health protection [32]. In 2004, in the third edition of Guidelines for drinking-water Quality the WHO presented guidelines for the development of the so-called water safety plans [33].

Danger and hazard are the factors that determine the magnitude of the risk. Danger is considered a cause of loss. It is characterized by some kind of arranged time sequence of successive phases. In the first phase, threat appears, which creates danger (e.g. an incidental water pollution in a source). In the second phase, danger becomes real (e.g. polluted water appears in the distribution subsystem). In the third phase, the effects of real danger are revealed (e.g. water consumers' gastric problems). Hazard is identified as a set of conditions and factors that have a direct impact on the second phase of danger. The severity of any given danger is fundamentally based on the hazard. Hazard as a risk factor determines the magnitude of losses resulting from risk realization [34]. The measure of the loss of consumer safety is the risk that water quality parameters required for tap water will not be filled.

Risk is defined as the probability of exceeding the quality parameters, which may result in a real threat to the consumers' health or lives, considered in a short as well as a long period of time. Risk means the deviation from the expected value of assumed objective [35–37].

The risk analysis is conducted in order to determine risk by estimating the probability of undesirable events occurrence and their consequences. The principle that risk cannot be eliminated is applied. You can only take various actions aiming at minimizing it to an acceptable level in terms of safety and necessary costs, which is said in the ALARP (as low as reasonably practicable) principle [38]. An acceptable level of tap water quality, acceptable quality level (AQL),

Table 1
Carcinogenicity and mutagenicity of selected PAHs and its classification

PAH	Symbol	Classification according Regulation 1272/2008/EC [13]*	Carcinogenicity**	Mutagenicity**
Naphthalene	Nap	Carc. 2, H351	–	–
Anthracene	Ant	–	–	–
Fluoranthene	Fl	–	–	+
Benzo(a)pyrene	BaP	Carc. 1B, H350, Muta. 1B, H340	++++	++++
Benzo(b)fluoranthene	BbF	Carc. 1B, H350	+++	++
Benzo(k)fluoranthene	BkF	Carc. 1B, H350	+	++
Benzo(g,h,i)perylene	BgP	–	+++	++
Indeno(1,2,3-cd) pyrene	IcP	Carc. 2, H351	+	+

*carc./muta.1A—substances for target organ toxicity on the basis of reliable and good quality evidence from human cases or epidemiological studies; carc./muta. 1B—substances for target organ toxicity on the basis of observations from appropriate studies in experimental animals; carc./muta. 2—substances for target organ toxicity on the basis of observations from appropriate studies in experimental animals; H350—may cause cancer; H351—suspects that causes cancer; H340—may cause genetic defects.
**– no carcinogen/mutagen activity; + poorly active; ++ medium active; +++ highly active; ++++ strongly active.

Table 2
Carcinogenic doses of selected PAHs

PAH	Carcinogenic dose for animals [μg/kg b.w.] [18]	LD_{50} (For mice or rats) [μg/kg] [19,20]	LD_{50} (For rats) [μg/kg] [21–28]
Nap	–	–	>490,000 (Oral)
Ant	–	430,000 (Intraperitoneal)	Not available
Fl	–	2,000,000 (oral)	2,000 (Oral)
BaP	2	232,000 (7)* (intraperitoneal) 259,000 (4)* (intraperitoneal)	1 (Oral, for human)
BbF	40,000	–	980,000 (oral)
BkF	72,000	–	Not available
BgP	–	–	Not available
IcP	72,000	–	Not available

*The number of days after which half of animals fell.

means water quality shown in laboratory tests and in compliance with existing standards. AQL [39,40], however, in the context of the analysis of the health risk, can be considered in relation to substances that are not currently standardized, but conducted studies indicate their potential health threat (e.g. genotoxic and carcinogenic). Such substances are substances from the group of PAHs. In the safety analysis, assuming the appearance of undesirable events according to the exponential distribution of failure-free operation time, the probability of such an event (failure) is determined by the formula [34]:

$$Q = 1 - \exp(-\lambda\, t) \tag{1}$$

where Q—probability of event, λ—value of the failure intensity, t—time.

In risk assessment $\lambda t << 1$, then the probability Q can be approximated.

$$Q = \lambda\, t \tag{2}$$

It allows concluding that, regardless of the value of the failure intensity λ = const, an increase in the risk exposure is associated with time and always results in an increase of that risk.

The classic definition of a quantitative risk r is the product of the probability of incident P and its negative consequences C [36,38].

$$r = PC \tag{3}$$

The consequences can be determined in the range from zero to one, while $C = 1$ is attributed to decrease. In this way, limited to such case, $r = P$.

Table 3
Allowable concentrations of selected PAHs in: drinking water, bodies of surface waters, inland and other surface waters

	Concentration [ng/L]				
		In bodies of surface waters: stream, creek, river, canal, lake, natural and artificial water reservoirs [30]		In inland and other surface waters [31]	
PAH	In drinking water [29]	Annual average	Maximum allowable concentration	Annual average	Maximum allowable concentration
Nap	Not specified	2,400	*	2,000	130,000
Ant	Not specified	100	400	100	100
Fl	Not specified	100	1,000	6.30	120
BaP	10	50	100	0.17	270 (Inland waters) 27 (Other surface waters)
BbF	BbF+BkF+BghiP+IcP = 100	BbF+BkF = 30	*	Not specified	17
BkF				Not specified	17
BgP		BghiP+IcP = 2	*	Not specified	8.20 (inland waters) 0.82 (other surface waters)
IcP				Not specified	

*It is assumed that the average annual concentration protect also against short-term increase in concentrations at constant discharge.

The aim of the study was to determine to what extent coagulation can affect to the risk reduction of human exposure to the consumption of water containing PAHs. During the first stage of study was determined the effectiveness of selected aluminum coagulants: aluminum (VI) sulfate and two pre-hydrolyzed coagulants: PAX XL 19H and FLOKOR 1ASW/B, in the removal of priority PAHs from water in the coagulation process. On the basis of obtained values risk assessment for five selected PAHs (three 5-ring and two 6-ringed compounds with large toxicity) was calculated.

2. Materials and methods

2.1. Water used for coagulation

Water for the coagulation process was collected from a selected water treatment plant (WTP) (i.e. a single collection in one day) in southern Poland following the pre-ozonation process. Instantaneous samples were taken in summer. Samples were stored at +4°C. Water sampling site and technological scheme of WTP is presented in Fig. 1. The physico-chemical characteristic of water following pre-ozonation (before coagulation jar tests) is presented in Table 4.

2.2. Coagulants

In selected WTP, aluminum(VI)sulfate is used in coagulation process. Doses of ALK are in the range of 14–37 g/m^3 in first production line and 14–26 g/m^3 in the second production line.

Three coagulants were used in the study:

(1) $Al_2(SO_4)_3 \times 14H_2O$—ALK, in solid form and
(2) Two pre-hydrolyzed coagulants:
    (a) polyaluminium chloride–PAX XL 19H,
    (b) dialuminium chloride hydroxide sulfate—FLOKOR 1ASW/B.

The characteristics of the tested coagulants are presented in Table 5. To ensure easier application, 1% solutions of the tested coagulants were prepared.

2.3. Experimental procedure of coagulation

The study was carried out with the use of a six-beaker flocculator. The coagulant was introduced as a 1% solution at the optimum doses to water samples (volume: 2 L). The optimum doses of the coagulants and the optimum process parameters were determined on the basis of indicators such as color, turbidity, and UV_{254} absorbance in earlier studies of current authors, which have not been published yet. The optimum doses of the coagulants used amounted to:

(1) Aluminum(VI) sulfate: 3.6 mg Al^{3+}/L and
(2) Pre-hydrolyzed aluminum coagulants: 2.8 mg Al^{3+}/L.

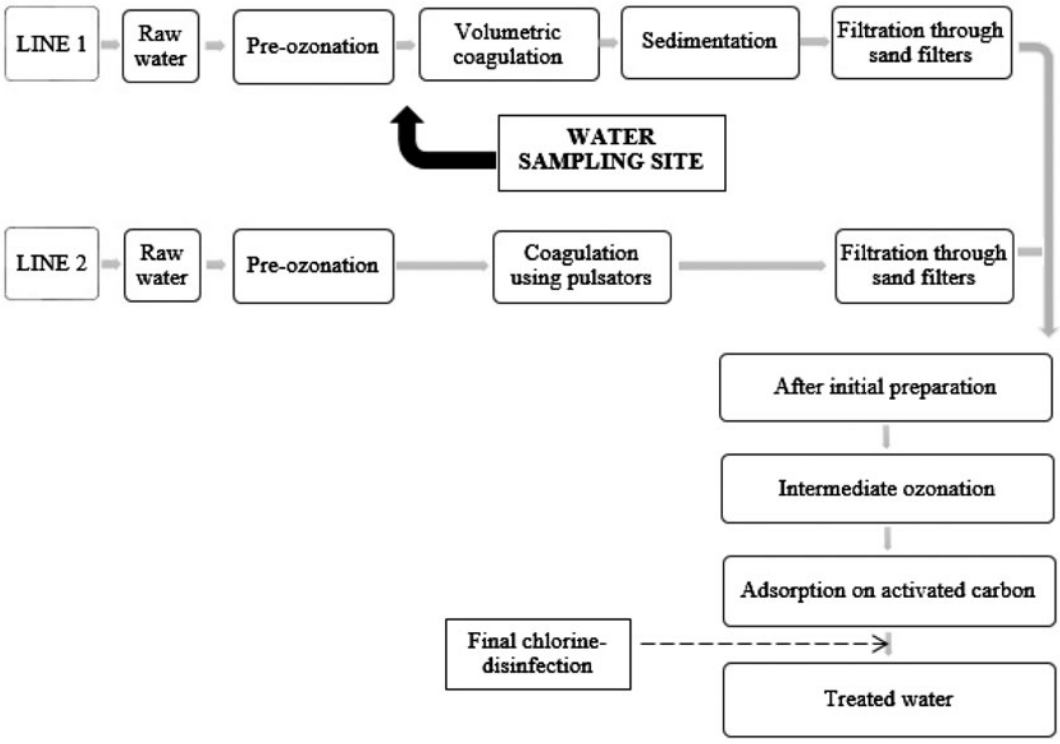

Fig. 1. Technological scheme of selected WTP with marked water sampling site.

Table 4
The physico-chemical characteristic of water following pre-ozonation

Indicator	Unit	Average value
pH	–	7.5
Temperature	℃	19.0
Alkalinity	mval/L	1.4
True colour	mg Pt/L	9
Turbidity	NTU	13.9
Absorbance UV_{254}	cm^{-1}	0.074
Total organic carbon (TOC)	mgC/L	5.16
Dissolved organic carbon (DOC)	mgC/L	4.93
SUVA	$m^3/gC{\cdot}m$	1.50

Optimum doses of coagulants were added to a beaker and were quick mixed with a mechanical stirrer for 3 min (at 200 rpm) followed by slow mixing for 10 min (at 30 rpm). Afterward, the samples were subjected to sedimentation for 60 min. Following sedimentation, 1.2 L of water was decanted for analysis of the concentrations of selected priority PAHs (Fig. 2). Optimum duration time of each coagulation stages is determined in earlier research of authors [41] of present study.

2.4. Analysis of PAHs

The concentration of PAHs known as priority substances was determined in this research. The content of selected PAHs in water samples before and after volumetric coagulation was determined through HPLC-FTD method. For the research, 500 mL of a water sample was collected. A quantity of 88 mL of 2-propanol (HPLC purity) was added to the sample. An extraction column C18 was used to isolate extracted analytes from other organic substances

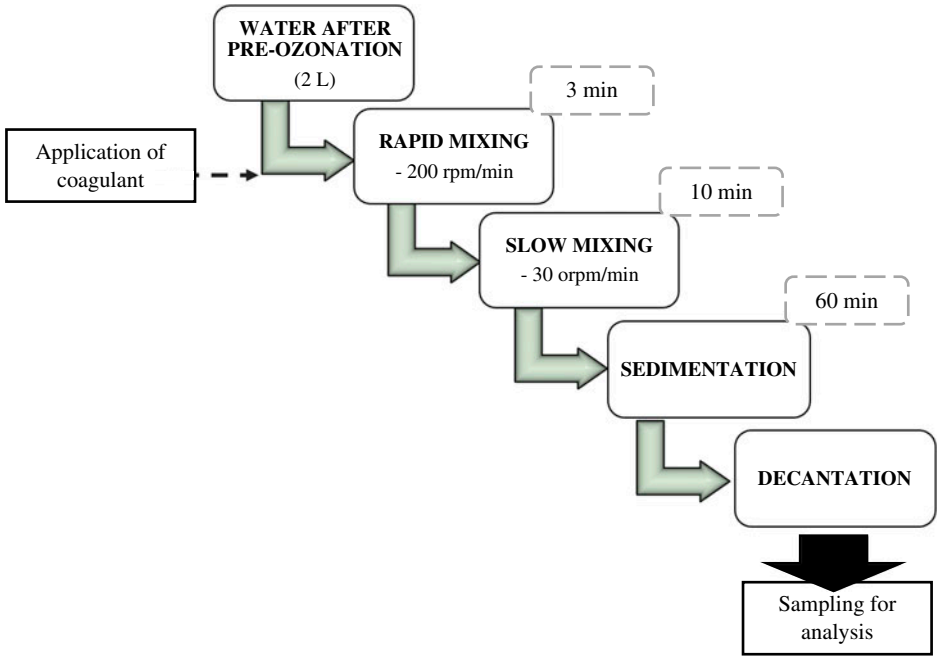

Fig. 2. Schematic diagram of technological research.

extracted at the same time. Through the column 6 mL of hexane was slowly passed, then column was dried under vacuum for 2 min, to prepare it to use. Prior to introduction of the extracts, the column was conditioned with methanol (6 mL) and HPLC water (6 mL). The analyzed sample was passed through the column, maintaining the vacuum and aspiration rate of 10 mL/min. Then, the sample was dried under vacuum for 30 min, and the PAHs were eluted with hexane (3 × 1 mL). The resulting eluate was gently evaporated until dry in a stream of nitrogen. The dry residue was dissolved in acetonitrile in amount of 1 mL. The tested sample was analyzed chromatographically. Indications were performed on a liquid chromatography (Waters Alliance 2695 with a Supelcosil LC-PAH column, 15 cm × 4.6 mm × 5 mm). The identification was performed in duplicate.

In order to verify the procedure were designated recovery values for priority PAHs. For this purpose into the sample of distilled water was introduced a standard mixture of 16 PAHs (Restek PAHs Mix). Then quantitative and qualitative determinations of the PAHs were carried out in accordance with the procedure described for tested samples. The recovery rate ranged from 40.6% (naphtalene) to 109.0% (fluoranthene). Recovery rates and limits of quantification (LOQ) for individual PAHs are presented in Table 6. Calculations of concentration take these recovery rates into account.

The examples of chromatograms obtained after volumetric coagulation and sedimentation following application of three aluminum coagulants are presented in Fig. 3.

Table 5
The characteristics of the tested coagulants (referring to commercial preparations)

	Coagulant		
Parameter	ALK	PAX XL 19H	FLOKOR 1ASW/B
Density (20°C), g/mL	1.580	1.340	1.200
pH	3.4	3.5	3.9
Basicity, %	0.0	85.0	70.0
[Al], wt.%*	9.1	12.5	8.0
[Al_2O_3], wt.%	17.20	23.60	15.12
[Cl^-], wt.%	0.0	8.5	5.2
[Al]/[Cl]	0	1.47	1.54

*wt.—mass fraction in %.

2.5. Risk assessment

The statistical analysis of the quality of tap water takes into account the average values x_a for the standard deviation σ (obtained during the study).

For the normal distribution, the following relations are valid:

(1) $x_a \pm \sigma$ means that 68.27% of the results of chemical analysis of water composition is within tolerance zone, thus 31.73% of exceeded quality is permitted,

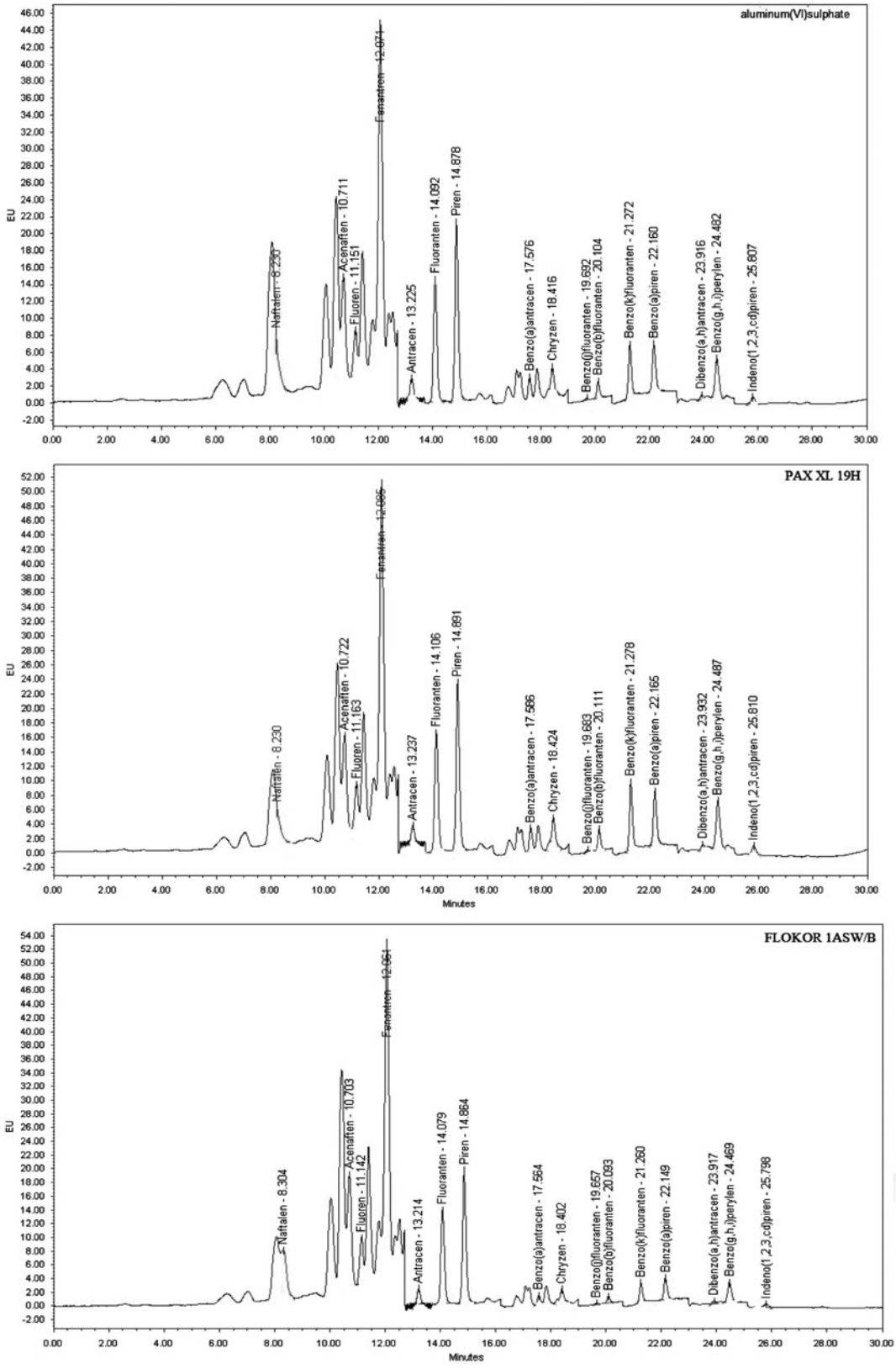

Fig. 3. Examples of chromatograms obtained for samples of water after coagulation with ALK, PAX XL 19H, and FLOKOR 1ASW/B.

Table 6
Limits of quantification (LOQ) and recoveries of priority PAHs from water sample

PAH	Average recovery [%]	Limit of quantification (LOQ) [ng/L]
Naphtalene	40.6	1.0
Anthracene	65.1	2.0
Fluoranthene	109.0	16.0
Benzo(a)pyrene	57.5	2.0
Benzo(b)fluoranthene	72.0	3.0
Benzo(k)fluoranthene	66.0	1.0
Benzo(g,h,i)perylene	49.5	0.6
Indeno(1,2,3-cd)pyrene	46.6	0.6

(2) $x_a \pm 2\sigma$ means that 95.46% of the results of chemical analysis of water composition is within tolerance zone, thus 4.54% of exceeded quality is permitted, and
(3) $x_a \pm 3\sigma$ means that 99.73% of the results of chemical analysis of water composition is within tolerance zone, thus 0.27% of exceeded quality is permitted.

The risk was estimated based on the assumption that the larger the standard deviation, the larger the risk connected with the probability that an undesirable event occurs, i.e. occurrence of exceeding of the value PAHs in tap water. In this sense, the risk is interpreted as the expected value of losses associated with the occurrence of an undesirable event, e.g. as a result of inadequate selection of technological parameters of selected water treatment process or unsuitable type/dose of coagulant. The likelihood that the losses C are located in the indicated ranges are as follows:

$$E(C) \pm \sigma = 0.6827$$

$$E(C) \pm 2\sigma = 0.95445$$

$$E(C) \pm 3\sigma = 0.9973$$

where $E(C)$ is the expected value of losses.

Positive values of deviations indicate that the losses are larger than average, and they are primarily a negative phenomenon. Because the unacceptable risk is associated with undesirable events that cause large losses, in the analysis, the extraordinary losses are considered. Thus, in the risk analysis the so-called standard semideviation determined by Eq. (4).

$$\sigma_S = \sqrt{\sum_{i=1}^{n} p_i \cdot d_i^2} \tag{4}$$

where σ_S is the standard semideviation, p_i—the likelihood that the losses C_i occur, d_i—the positive deviation from the expected loss.

The criterion values for the risk assessment are presented in Table 7.

The risk analysis was carried out for the five hydrocarbons from group of carcinogenic PAHs for which possible probability of exceeding the standard values have been found. The analysis was carried out after coagulation using selected three types of coagulants. PAHs selected for risk assessment are compounds rated in as toxic, and their concentration in the water should be standardized. In accordance with Polish law, allowable concentration, in bodies of surface waters, of BbF and BkF amounted to 30 ng/L (1)-AQL, while for BgP and IcP is equal to 2 ng/L (2)-AQL [30]:

In case of benzo(a)pyrene, allowable concentration of this PAH in drinking water amounted to 10 ng/L,

Table 7
The risk assessment criterion

Description	Risk
If the calculated value ($x_a + 3\sigma_s$) is in the range of AQL	Tolerable (T)
If the calculated value ($x_a + 2\sigma_s$) is in the range of AQL	Controlled (C)
If the calculated value ($x_a + \sigma_s$) is or not in the range of AQL	Unacceptable (UN)

while in inland and other surface water is equal 0.17 ng/L (annual average) and to benzo(a)pyrene:

(1) AQL_1 (according to Directive 2013/39/EU) = 0.17 and
(2) AQL_2 (according to Directive 98/83/EC in drinking water) = 10.

3. Results

3.1. Concentrations of priority PAHs in water intended to coagulation and following the process

The results of qualitative–quantitative determination of eight priority PAHs in water following pre-ozonation process and after coagulation are presented in Table 8. The summary concentration of 8 PAHs amounted to 60.78 ng/L. In case of 4 PAHs, it was equal to 19.10 ng/L. In water following pre-ozonation process (before volumetric coagulation), dominant was naphthalene. The lowest concentration were obtained for anthracene and benzo(k)fluoranthene. Concentration of benzo(a)pyrene amounted to 4.80 ng/L.

Following coagulation using the optimal dose of aluminum(VI)sulfate, the total concentration of 8 PAHs amounted to 33.64 ng/L and was 44.7% less than in water before the process. In case of summary concentration of 4 PAHs, concentration following volumetric coagulation was lower by 67.4%. The anthracene concentration in the water samples was below the detection limit. For another 3-ring hydrocarbon fluoranthene, there was a concentration decrease by 64.9%. In the case of 4-ring hydrocarbons was observed decrease in the content of these compounds in water samples in the range of 63.9–65.0%. The contents of 5-ring hydrocarbons (68.1–69.8%) and 6-ring PAHs (68.5%) also decreased following the use of ALK. The best results were obtained for benzo(a)pyrene and benzo(g,h,i)perylene. After the application of the formulation PAX XL 19H, the total concentration of 8 and 4 WWA was at the level of 33.64 and 6.23 ng L, respectively. There has been however loss of 45.2 and 58.4% relative to the water before the process. In the case of naphthalene, there was a decrease in content of this hydrocarbon by 27.6%. Similarly as in case of using ALK, also after application of PAX XL 19H do not found in water samples the presence of anthracene. In the case of fluoranthene and 4-ring PAHs, degree of removal of these compounds does not exceed 54.3%. Higher efficiency (62.7–63.9%) was obtained for 5- and 6-ring hydrocarbons. The dominant hydrocarbon in water samples after the coagulation process using the formulation FLOKOR 1ASW/B was naphtalene. As in the case of other coagulants, following application of the FLOKOR 1 ASW/B formulation, no anthracene content was observed. Following coagulation with that coagulant from the group of FLOKOR, the total concentration of 8 PAHs was at the level of 31.51 ng L. This constituted a loss of48.2% in comparison with the water before the process. In case of summary content of 4 PAHs, it obtained a decrease by 89.9%. For fluoranthene, removal efficiency amounted to 69.0%. After application of this coagulant was observed higher effectiveness in the removal of 4-, 5-, and 6-ring aromatic hydrocarbons than for ALK and pre-hydrolyzed PAX XL 19H. In all examined cases, beyond naphthalene, the FLOKOR 1ASW/B formulation was the most

Table 8
Average concentration of priority PAHs in water before and after coagulation

	Concentration [ng/L]			
		Following coagulation		
PAH	Before coagulation	ALK	PAX XL 19H	FLOKOR 1ASW/B
Naphtalene	27.80 ± 0.29	23.17 ± 0.39	20.12 ± 0.07	26.61 ± 0.80
Anthracene	1.51 ± 0.60	Below detection limit	Below detection limit	Below detection limit
Fluoranthene	7.57 ± 1.57	2.66 ± 0.28	3.46 ± 0.16	2.35 ± 0.28
Benzo(a)pyrene	4.80 ± 1.25	1.53 ± 0.67	1.79 ± 0.51	0.64 ± 0.11
Benzo(b)fluoranthene	5.77 ± 1.44	2.02 ± 0.72	2.71 ± 0.46	0.58 ± 0.07
Benzo(k)fluoranthene	2.94 ± 0.78	1.06 ± 0.41	1.47 ± 0.37	0.41 ± 0.13
Benzo(g,h,i)perylene	4.82 ± 0.97	1.52 ± 0.86	1.74 ± 0.54	0.30 ± 0.32
Indeno(1,2,3-cd)pyrene	5.56 ± 1.40	1.68 ± 1.04	2.02 ± 0.56	0.63 ± 0.14
∑4 PAHs*	19.10 ± 4.58	6.23 ± 3.03	7.94 ± 1.93	1.92 ± 0.12
∑8 PAHs	60.78 ± 7.71	33.64 ± 4.37	33.31 ± 2.67	31.51 ± 0.53

*Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(g,h,i)perylene, and Indeno(1,2,3-cd)pyrene.

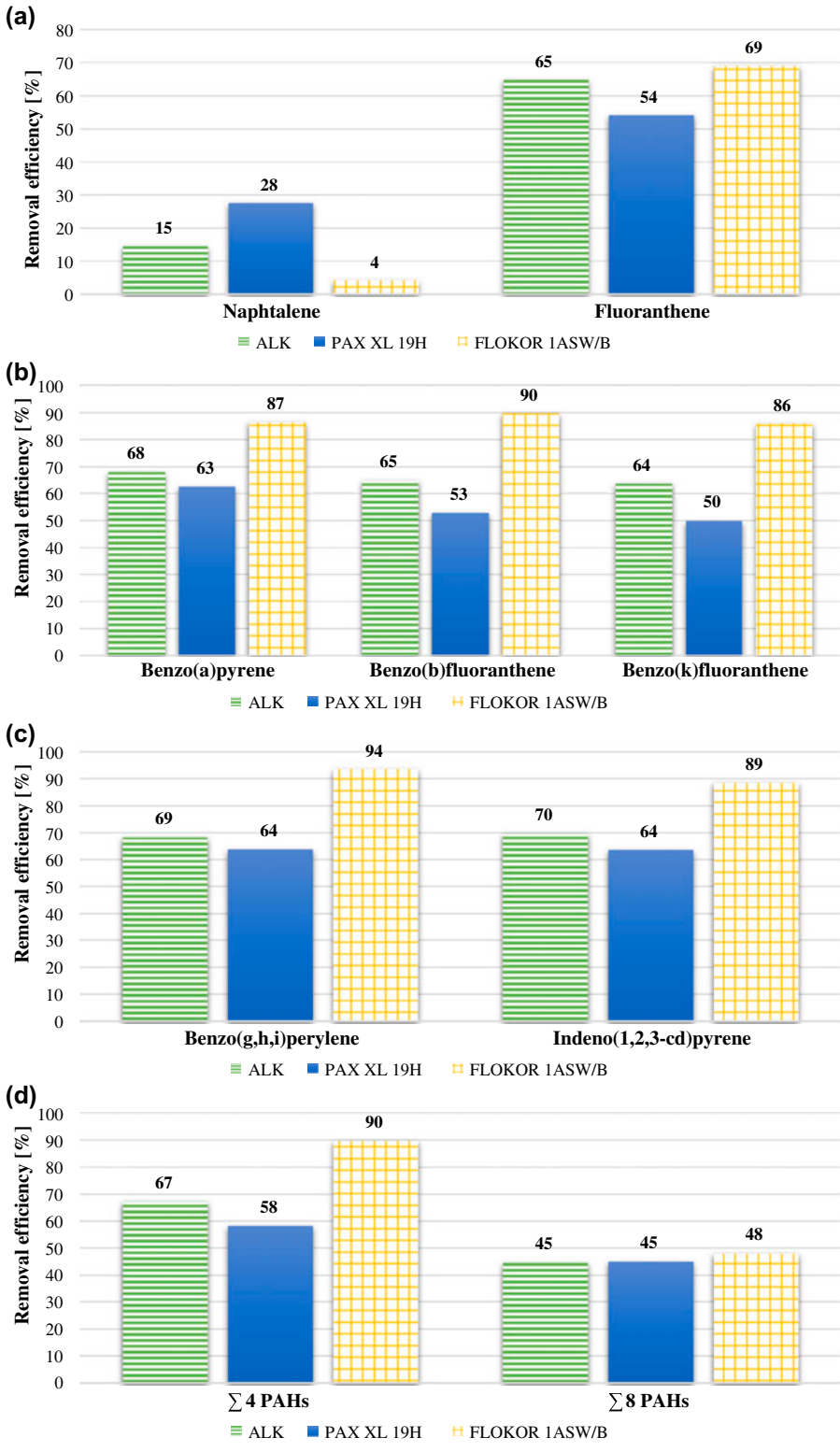

Fig. 4. Removal efficiency of selected priority PAHs following application of ALK, PAX XL 19H, and FLOKOR 1ASW/B: (a) low molecular weight PAHs, (b) 5-ring PAHs, (c) 6-ring PAHs and (d) summary concentration of 4 and 8 PAHs.

Table 9
The risk assessment

PAH	ALK				PAX XL 19H				FLOKOR 1ASW/B			
	$(x_a + \sigma_s)$	$(x_a + 2\sigma_s)$	$(x_a + 3\sigma_s)$	Risk	$(x_a + \sigma_s)$	$(x_a + 2\sigma_s)$	$(x_a + 3\sigma_s)$	Risk	$(x_a + \sigma_s)$	$(x_a + 2\sigma_s)$	$(x_a + 3\sigma_s)$	Risk
BbF + BkF (1)	4.21	5.34	6,47	T	5.01	5.84	6.67	T	1.19	1.39	1.59	T
BgP + IcP (2)	5.1	7	8,9	UN	4.86	5.96	7.06	UN	1.39	1.85	2.31	C
B(a)P	2.2	2.87	3.54	UN_{AQL1} T_{AQL2} C	2.48	2.99	3.5	UN_{AQL1} T_{AQL2} C	0.75	0.86	0.97	UN_{AQL1} T_{AQL2} T

effective in the removal of priority PAHs from water following volumetric coagulation and sedimentation. Removal efficiency of priority PAHs following application of selected coagulants was presented in Fig. 4(a)–(d). Knowing the percentage of removal efficiency of benzo(a)pyrene from water, coagulants can be ranked as follows:

$$\text{FLOKOR 1ASW B}\,(86.7\%) > \text{ALK}\,(68.1\%) > \text{PAX XL 19H}\,(62.7\%)$$

After the coagulation process, this hydrocarbon concentration was below the limit specified for water intended for human consumption. The regulation also governed the total concentration of 4 PAHs. Also in this case, there were no exceedances of the limit content after coagulation and sedimentation. Coagulants can be ranked as follows:

$$\text{FLOKOR 1ASW B}(89.9\%) > \text{ALK}(67.4\%) > \text{PAX XL 19H}(58.4\%)$$

As was written in earlier paragraph PAHs have ability to sorb on solid particulates. Therefore, it can be removed during the coagulation and sedimentation process. The lowest tendency to adsorb on solid particles has naphthalene (log K_{OW} = 3.37). Octanol/water partition coefficient for anthracene and fluoranthene amounted 4.54 and 5.22, respectively. The strongest affinity for solid particles have 5- and 6-rings PAHs (log K_{OW} in the range of 6.06–7.66). This may explain the high removal degree of these hydrocarbons in comparison with naphthalene.

Comparison of the results obtained with data in the literature is difficult, because there were found no other studies on the removal of priority PAHs from water during coagulation. Removal of PAHs during coagulation and other water treatment processes was investigated in earlier studies by the present authors [42]. Research was performed in autumn. In research, removal efficiency of selected 2- and 3-ring aromatic hydrocarbons (naphthalene, acenaphthene, fluorene, phenanthrene, and anthracene) was investigated. The highest effectiveness in the removal of Σ 3-ring PAHs was obtained after the application of PAX XL 19H and FLOKOR 1ASW/B (decrease by 56 and 49.3%, respectively).

3.2. Risk assessment

The Table 9 shows the calculated values $(x_a + \sigma_s)$, $(x_a + 2\sigma_s)$ and $(x_a + 3\sigma_s)$ for the risk assessment according to the Table 7.

The risk analysis carried out for two 5-ring polycyclic hydrocarbons (BbF and BkF) showed that risk was acceptable regardless of the coagulant type. In the case of the 6-ring hydrocarbons, concentrations determined in water after coagulation process were unacceptable for the aluminum (VI)sulfate and PAX XL 19H. In the case of FLOKOR 1ASW/B, risk was tolerable. For the benzo(a)pyrene, risk assessment was calculated according to the two different AQL values and finally accepted that the risk is tolerable only for the coagulant FLOKOR 1ASW/B.

4. Conclusion

The research performed on the effectiveness of aluminum(VI) sulfate and the pre-hydrolyzed aluminum coagulants PAX XL 19H and FLOKOR 1ASW/B led to the following conclusions:

(1) The highest efficiency in the removal of priority aromatic hydrocarbons was obtained after application of the coagulant FLOKOR 1 ASW/B. The decrease in the total concentration of 8 PAHs amounted to 48.2% and for 4 PAHs to 89.9%.

(2) The greatest effectiveness in the removal of individual priority PAHs was obtained with the application of coagulant FLOKOR 1ASW/B (using a lower coagulant dose than in the case of ALK). Effectiveness was higher than in case of two other coagulants by:

(a) fluoranthene: 4.1–14.7%,
(b) benzo(a)pyrene: 18.6–24.0%,
(c) benzo(b)fluoranthene: 24.9–36.9%,
(d) benzo(k)fluoranthene: 22.2–36.1%,
(e) benzo(g,h,i)perylene: 25.3–29.9% and
(f) indeno(1,2,3-cd)pyrene: 18.9–25.0%.

(3) Risk analysis showed that the coagulant with the lowest risk indicator for the five analyzed PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene) is FLOKOR 1ASW/B. For the benzo(a)pyrene, risk assessment is tolerable only for the coagulant FLOKOR 1ASW/B.

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