

## THE COAGULANT TYPE INFLUENCE ON REMOVAL EFFICIENCY OF 5- AND 6-RING PAHS DURING WATER COAGULATION PROCESS

Anna NOWACKA<sup>1,1</sup>, Maria WŁODARCZYK-MAKUŁA<sup>2</sup>

<sup>1</sup> Częstochowa University of Technology,

Institute of Environmental Engineering, Poland

<sup>2</sup> Częstochowa University of Technology; Department of Chemistry,

Water and Wastewater Technology, Poland

### Abstract

The article presents results on investigation of the removal efficiency of selected 5- and 6-ring polycyclic aromatic hydrocarbons (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene) from water during coagulation and sedimentation process. Two pre-hydrolyzed aluminum coagulants: PAX XL 19H and FLOKOR 105V were chosen for research. Process was carried out at optimum process parameters: rapid-mixing - 3 min at the rotational speed of 200 rpm, slow mixing - 10 min at 30 rpm, sedimentation - 60 min. The removal effectiveness was dependant on coagulant type and its composition. Better results in the removal of 5-and 6-ring PAHs were obtained after application of FLOKOR 105V (lower aluminum content) than after using PAX XL 19H.

Keywords: 5- and 6-ring PAHs, coagulation, pre-hydrolyzed coagulants, water treatment

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are classified as group of organic micro-pollutants of anthropogenic origin [3,18]. Despite the fact that there are known over 300 compounds from this group, only 16 of them are designated the

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<sup>1</sup> Corresponding author: Czestochowa University of Technology, Institute of Environmental Engineering, 60a Brzeznicza Str., Czestochowa 42-200, Poland  
e-mail: anowacka@is.pcz.czest.pl , tel. +48343250919

most common [11]. PAHs are included into a group of primary environmental pollutants due to the toxic, mutagenic and carcinogenic properties [2,6,13,14]. The occurrence of these compounds in groundwater and surface water has been confirmed by many authors [10,16,17]. Although PAHs are classified as persistent and difficult degradable pollutants they are subjected to constant physico-chemical and biological changes. PAH are easily soluble in organic solvents, such as benzene, hexane, cyclohexane, acetone and slightly soluble in water [4,7]. Properties of selected for research 5- and 6-ring PAHs are presented in the Table 1. High octanol/water partition coefficient of investigated PAHs indicates that they are easily adsorbable compounds. The analyzed polycyclic aromatic hydrocarbons have a strong affinity for solid particles (log  $K_{ow}$  in the range of 6.06 to 7.66).

Table 1. Properties of selected 5- and 6-ring PAHs [15]

PAH	Molecular formula	Number of rings	Molecular weight [g/mol]	Solubility in water (25°C) [ng/L]	log $K_{ow}$
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	5	252	3800	6.06
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	5	252	1200	6.57
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	5	252	550	6.84
Benzo[j]fluoranthene	C <sub>20</sub> H <sub>12</sub>	5	252	2500	6.11
Dibenzo[a,h]anthracene	C <sub>22</sub> H <sub>14</sub>	5	278	500	6.86
Benzo[g,h,i]perylene	C <sub>22</sub> H <sub>12</sub>	6	276	260	7.66
Indeno[1,2,3-cd]pyrene	C <sub>22</sub> H <sub>12</sub>	6	276	62000	7.23

The most frequently used coagulant in water treatment plants has so far been aluminum(VI)sulfate. Currently it is replaced by a pre-hydrolyzed coagulants. They are more effective in the removal of water turbidity, colour and organic impurities and more resistant to changes in pH and temperature [1,5,8,12,19]. Despite research confirming their greater effectiveness there found in the available literature no information concerning PAHs removal from the water in coagulation process.

The purpose of the research was to determine the influence of coagulant type PAX XL 19H and FLOKOR 105V on removal efficiency of 5- and 6-ring polycyclic aromatic hydrocarbons (benzo[a]pyrene - BaP, benzo[b]fluoranthene - BbF, benzo[k]fluoranthene - BkF, benzo[j]fluoranthene - BjF, dibenzo[a,h]anthracene - DaA, benzo(g,h,i)perylene - BgP, indeno(1,2,3-cd)pyrene - IcP) during water coagulation process.

## 2. MATERIALS AND METHODS

### 2.1. Materials (water, coagulants)

Water for coagulation and sedimentation process was collected once after pre-ozonation process from chosen water treatment plant (WTP) in Poland. Instantaneous samples were taken in autumn season. Water samples intended to coagulation were collected from waterworks taps. Samples were stored at +4°C. In selected WTP there are two production lines running simultaneously. Water samples for analysis were collected after pre-ozonation in first treatment line.

In research studies were used two pre-hydrolyzed aluminum coagulants:

- polyaluminum chloride - PAX XL 19H,
- dialuminium chloride hydroxide sulfate - FLOKOR 105V.

Characteristics of tested coagulants is presented in Table 2. To ensure easier application 1% solutions of tested coagulants were prepared.

Table 2. Characteristics of tested coagulants

Parameter	Unit	Coagulant	
		PAX XL 19H	FLOKOR 105V
Density (20°C)	g/mL	1.340	1.100
pH	-	3.5	3.5
Basicity	%	85.0	70.0
[Al]	wt. %	12.5	6.5
[Al <sub>2</sub> O <sub>3</sub> ]	wt. %	23.6	12.28
[Cl]	wt. %	8.5	4.5
[SO <sub>4</sub> <sup>2-</sup> ]	wt. %	0.0	2.8
[Al]/[Cl]	-	1.47	1.44

### 2.2. Experimental procedure

The research in a laboratory scale was carried out using a six beaker flocculator. To 2 L water samples optimal dose of coagulant (as a 1% solution) was introduced. The optimal doses and the optimum process parameters were determined in previous authors studies. There were determined on the basis of indicators such as: turbidity, colour and UV<sub>254</sub> absorbance. The optimum doses of tested pre-hydrolyzed coagulants amounted 1.2 mg Al<sup>3+</sup>/L. Designated doses of coagulants were added to beaker and then were quick mixed within 3 min with 200 rpm followed by slow mixing within 10 min with 30 rpm. Afterwards, the samples were subject to sedimentation for 60 min. Next 1.2 L of water was decanted for analysis on the content of selected 5- and 6-ring PAHs. The scheme of research process was presented in Fig. 1.

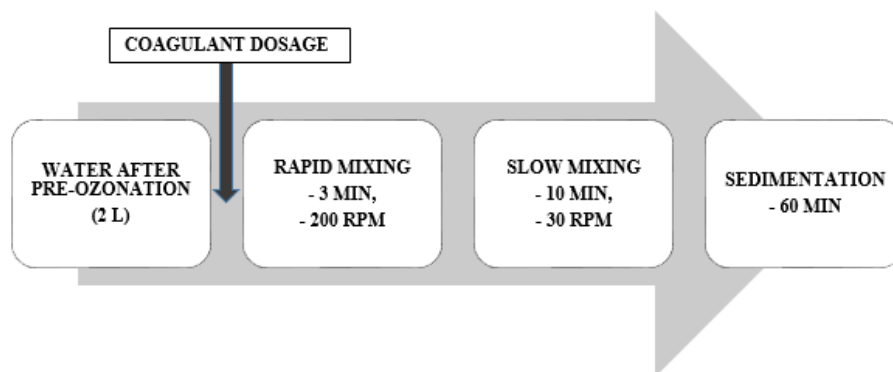


Fig. 1 The scheme of research process

### 2.3. PAHs analysis

Qualitative and quantitative determination of PAHs was carried out before and after coagulation and sedimentation process. Content of selected 5- and 6-ring PAHs was investigated. Determination of polycyclic aromatic hydrocarbons in the water samples was performed using high performance liquid chromatography with fluorescence detector (HPLC-FTD). To the sample of water before and after coagulation (500 mL) 87.5 mL of 2-propanol (17.5 mL per 100 mL of sample) was added. To isolate extracts analytes from simultaneously extracted other organic substances extraction column C18 was used (solid phase extraction SPE). After that 6 mL of hexane was slowly passed through the column. Then dried under vacuum for 2 minutes. Column was conditioned with methanol (6 mL) and HPLC water (6 mL) before the introduction of extracts. The test sample was passed through the column in the vacuum and with aspiration rate of 10 mL/min. The sample was then dried in vacuum for 30 minutes and eluted PAHs with hexane (3 x 1 mL). The resulting eluate was evaporated to dryness gently in a stream of nitrogen and then acetonitrile was added in an amount of 1 mL. The prepared sample was analyzed by HPLC. Indications was performed on liquid chromatograph (Waters Alliance 2695 with column Supelcosil LC-PAH 15 cm x 4.6 mm x 5 mm). Designation of PAHs were performed in duplicate.

In order to verify the adopted procedure, values of recovery for priority PAHs have been designated. The recovery ranged from 47.7% for dibenzo[a,h]anthracene to 73.1% for benzo[b]fluoranthene. The calculation of concentration takes into account the recoveries.

Table 3. Recovery of 5- and 6-ring PAHs from water samples

PAH	Recovery [%]
Benzo[a]pyrene	58.9
Benzo[b]fluoranthene	73.1
Benzo[k]fluoranthene	67.4
Benzo[j]fluoranthene	60.2
Dibenzo[a,h]anthracene	47.7
Benzo[g,h,i]perylene	50.3
Indeno[1,2,3-cd]pyrene	48.3

### 3. RESULTS AND DISCUSSION

The results of qualitative-quantitative determination of 5- and 6-ring PAHs in water after pre-ozonation process were presented in Fig.2. Summary concentration of analyzed PAHs amounted 13.5 ng/L (9.1 ng/L - 5-ring PAHs and 4.4 ng/L - 6-ring PAHs). The lowest concentration was observed in the case of dibenzo[a,h]anthracene (0.2 ng/L). Quantitative investigations showed that benzo[b]fluoranthene (2.67 ng/L) and benzo[j]fluoranthene (2.47 ng/L) were dominated in water intended to coagulation and sedimentation process. Average concentration of benzo[a]pyrene was equal 2.12 ng/L.

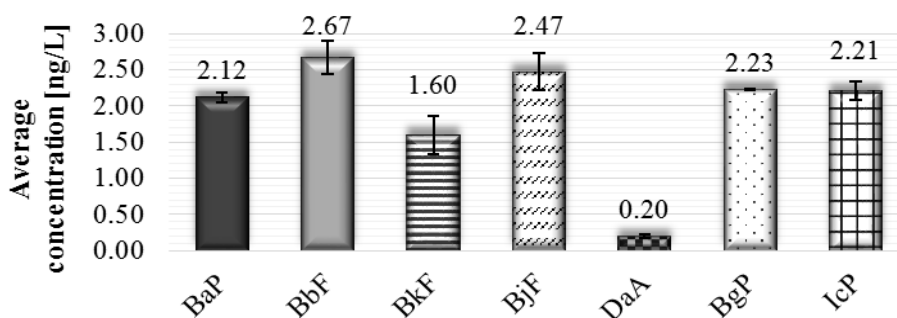


Fig.2. Average concentration of 5- and 6-ring PAHs in water samples after pre-ozonation (before coagulation)

Changes in concentration of individual 5- and 6-ring polycyclic aromatic hydrocarbons after coagulation using optimal dose of coagulant PAX XL 19H was shown in Fig.3. The value of octanol/water coefficient indicates a capacity of PAHs to sorb on the surface of the solid particles. All analyzed PAHs has strong ability to sorb on flocs. Summary concentration of 5- and 6-ring hydrocarbons amounted 8.7 ng/L and 4.4 ng/L, respectively. Total concentration was equal 13.1 ng/L (decrease of 3.0% in comparison to concentration in water

after pre-ozonation process). Summary concentration was comparable to to this before coagulation and sedimentation - there was no significant decrease. Also in case of individual PAHs there was no significant reduction of its concentration after coagulation process. There has been slight decrease in the contents of 5-ring hydrocarbons (1.4-19.4%) and 6-ring PAHs (0.5-1.5%) after using PAX XL 19H. The highest decrease was obtain for benzo[k]fluoranthene (19.4%).

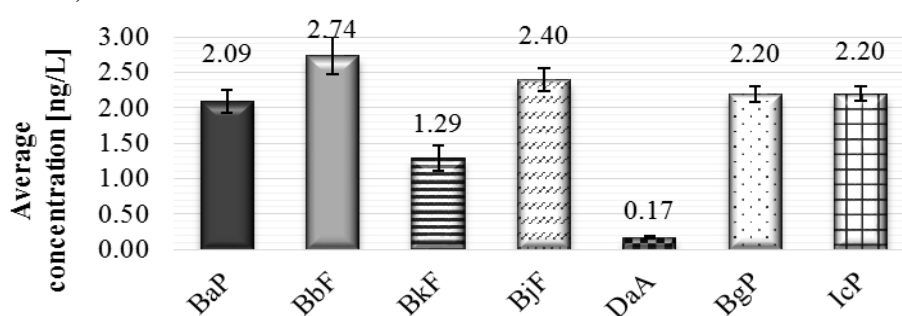


Fig.3. Average concentrations of individual 5- and 6-ring PAHs after coagulation using PAX XL 19H

Average values of concentration of the selected 7 PAHs in water samples after the coagulation process using FLOKOR 105V were presented in Fig.4. Summary concentration of all individual PAHs amounted 8.3 ng/L (5.4 ng/L and 2.9 ng/L for 5- and 6-ring PAHs respectively). The dominant hydrocarbon, like in water after pre-ozonation and after coagulation using PAX XL 19H, was benzo[b]fluoranthene. After the process there was a concentrations decrease of all analyzed PAHs. Decrease in the contents amounted 15.0-47.5% and 34.1-36.7% for 5-ring for 6-ring hydrocarbons after application of FLOKOR 105V, respectively.

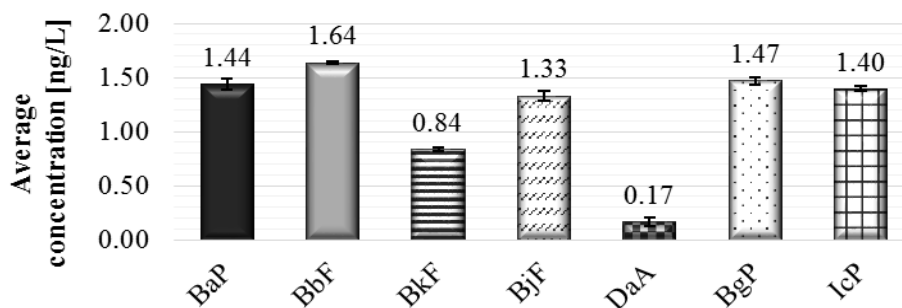


Fig.4. Average concentrations of individual 5- and 6-ring PAHs after coagulation using FLOKOR 105V

The percentage of the removal of individual 5- and 6-ring PAHs from water after coagulation was shown in Fig.5.

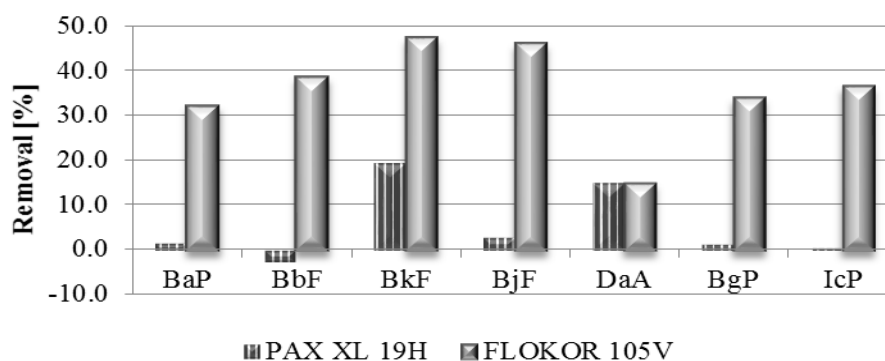


Fig.5. The percentage of the removal of selected PAHs from water after coagulation and sedimentation using PAX XL 19H and FLOKOR 105V

The most effective coagulant in the removal of selected PAHs from the water in the autumn season was FLOKOR 105V. Greater efficiency of this aluminum pre-hydrolyzed formulation could be affected by the appropriate content of aluminum,  $\text{Al}_2\text{O}_3$  and Cl (lower by 47-48% than in case of PAX XL 19H). Dialuminium chloride hydroxide sulfate has also lower basicity than polyaluminum chloride, and additional content of  $\text{SO}_4^{2-}$ . Highest effectiveness of FLOKOR 105V in the removal of selected 5- and 6-ring PAHs may also be related to the structure and properties of the flocs resulted after coagulation using this formulation. The highest efficiency in the case of FLOKOR 105V was obtained for 5-ring PAHs such as: benzo[k]fluoranthene (47.5%) and benzo[j]fluoranthene (46.2%). Comparison of the obtained results with the literature data is difficult because there found no research concerning removal of PAHs from water in coagulation process using pre-hydrolyzed coagulants. PAHs removal during coagulation and sedimentation process was investigated in other authors studies [9]. In those studies removal effectiveness of 4-ring hydrocarbons such as: pyrene, benzo[a]anthracene and chrysene was determined. The greatest efficiency in the removal of 4-ring aromatic hydrocarbons were obtained also after application of the coagulant FLOKOR 105V (decrease in the concentration of 30%).

#### 4. CONCLUSIONS

The research performed on the influence of coagulant type (PAX XL 19H and FLOKOR 105V) on removal efficiency of 5- and 6-ring polycyclic aromatic hydrocarbons led to the following conclusions:

1. The coagulant type and its content has impact on coagulation and sedimentation efficiency in removal of analyzed PAHs,
2. The highest efficiency in the removal of 5- and 6-ring PAHs was obtained after application of the FLOKOR 105V. Decrease in the total concentration of all examined PAHs amounted 38.6%.
3. In case of summary content of 5- ring PAHs and summary concentration of 6-ring hydrocarbons reduction after using dialuminium chloride hydroxide sulfate amounted 40.2% and 64.4%, respectively,
4. The most effectiveness in the removal of individual PAHs was obtained after the application of coagulant FLOKOR 105V (using the same coagulant dose than in case of PAX XL 19H), as evidenced by loss of concentrations:
  - benzo[a]pyrene: 32.1%,
  - benzo[b]fluoranthene: 38.6%,
  - benzo[k]fluoranthene: 47.5%,
  - benzo[j]fluoranthene: 46.2%,
  - dibenzo[a,h]anthracene: 15.0%,
  - benzo[g,h,i]perylene: 34.1%,
  - indeno[1,2,3-cd]pyrene: 36.7%,

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#### WPLYW RODZAJU KOAGULANTU NA SKUTECZNOŚĆ USUWANIA 5- i 6-PIERŚCIENIOWYCH WWA Z WODY W PROCESIE KOAGULACJI

##### Streszczenie

W pracy przedstawiono wyniki badań dotyczące skuteczności usuwania wybranych 5- i 6-pierścieniowych węglowodorów aromatycznych (benzo[a]piren, benzo[b]fluoranten, benzo[k]fluoranten, benzo[j]fluoranten, benzo[g,h,i]perylen, indeno[1,2,3-cd]piren, dibenzo[a,h]antracen) z wody w procesie koagulacji. Do badań wybrano dwa koagulanty glinowe wstępnie zhydrolizowane: PAX XL 19H oraz FLOKOR 105V. Próbki wody pobrano po procesie ozonowania wstępnego w wybranym zakładzie uzdatniania wody. Poboru dokonano w sezonie jesiennym. Celem badań było określenie wpływu rodzaju koagulantu na skuteczność usuwania 5- i 6- pierścieniowych węglowodorów aromatycznych. Proces prowadzono przy zastosowaniu optymalnych dawek koagulantów ( $1.2 \text{ mg Al}^{3+}/\text{L}$ ) i przy optymalnych parametrach procesowych: szybkie mieszanie - 3 min, 200 obr/min, wolne - 10 min, 30 obr/min, sedymentacja - 60 min. Przeprowadzone badania pozwoliły na stwierdzenie, że skuteczność usuwania wybranych 5- i 6- pierścieniowych WWA zależała od rodzaju stosowanego koagulantu. Większą efektywność (38.6% ) w usuwaniu tych węglowodorów uzyskano po aplikacji preparatu FLOKOR 105V mimo mniejszej zawartości glinu i zastosowaniu identycznej dawki w porównaniu z PAX XL 19H. Po zastosowaniu koagulantu o nazwie FLOKOR 105V

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spadki stężenia 5- i 6-pierścieniowych WWA wynosiły odpowiednio o 40.2% oraz 64.4%.

Słowa kluczowe: 5- i 6-pierścieniowe WWA, koagulacja, koagulanty wstępnie zhydrolizowane, uzdatnianie wody

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