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INFLUENCE OF SELECTED COAGULANTS OF INDICATOR AND DIOXIN-LIKE PCB REMOVAL FROM DRINKING WATER

WPŁYW WYBRANYCH KOAGULANTÓW NA USUWANIE WSKAŹNIKOWYCH I DIOKSYNOPODOBNYCH PCB Z WODY PRZEZNACZONEJ DO SPOŻYCIA

Abstract: The aim of the research was to compare selected coagulants efficiency in indicator and chosen dioxin-like PCB removal from surface water. As coagulants, there were used aluminium sulfate and 5 hydrolyzed polyaluminium chlorides, with trade names: PAX-XL1, PAX-XL10, PAX-XL19, PAX-XL60, PAX-XL69. For the research, surface water was used, collected from dam reservoir. The water composition was modified with standard mixtures PCB MIX24 and MIX13, in order to obtain concentration of each congener equal to 300 ng/dm^3. The PCB MIX24 mixture was composed of indicator congeners solution: 28, 52, 101, 118, 138, 153, and 180, whereas the MIX13 mixture - solution of three dioxin-like PCB 77, PCB 126, and PCB 169. It was demonstrated that the application of aluminium sulfate allowed for reaching better effects for purifying water of PCB, than with the usage of pre-hydrolyzed salts, polyaluminium chlorides. Out of the studied coagulants, the best effects for indicator PCB removal were obtained with the application of aluminium sulfate, total PCB concentration was decreased by 65%. The highest efficiency for indicator congeners removal (90%) was obtained for PCB 138 and 153. After the application of hydrolyzed polyaluminium chlorides PAX-XL1, PAX-XL10 decrease in higher chlorinated PCB concentration was obtained, in the range of 23 to 74%. Selectivity of chosen PCB congener removal, depending on applied coagulant, was demonstrated; with the usage of aluminium sulfate, removal of heptachlorobiphenyl PCB 180 at the level of 34% was obtained, whereas with the application of PAX-XL1 and PAX-XL10 higher reduction efficiency for this congener was obtained, *ie* 83 and 74% respectively. For dioxin-like PCB, after application of aluminium sulfate, total concentration reduction by 74% was obtained, efficiency of this congeners removal amounted to from 54 (PCB 77) up to 72% (PCB 126), similar results were obtained after the usage of PAX-XL1. The lowest PCB removal from water rate was stated for coagulants PAX-XL60 and PAX-XL69.

Keywords: polychlorinated biphenyls, coagulation, aluminium sulphate, hydrolyzed polyaluminium chlorides, removal efficiency, drinking water

Introduction

In recent years, significant increase in interest in micropollutants present in water can be observed. For this purpose, further normative quality indicators for drinking water and water for economical purposes are being introduced in proper pieces of legislation. Moreover, worldwide tendency can be observed to reduce their permissible concentration to a level, at which no pathological changes in water consumers are discovered. Micropollutants occurring in water are divided into several categories, one of the classification is division into organic micropollutants (*eg* polycyclic aromatic hydrocarbons, polychlorinated biphenyls, surface active substances, pesticides) and inorganic micropollutants, primarily heavy metals [1-3].

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209 polychlorinated biphenyl (PCB) congeners are known, a number of which are characterized by high bioaccumulation, toxicity or potential carcinogenicity, and simultaneously high persistence in the environment. So called dioxin-like PCB, which include coplanar congeners with codes: 77, 81, 126, 169, are considered to be the most toxic [4]. Three of them (PCB 77, PCB 126 and PCB 169) are spatial analogues of the most toxic dioxin, *ie* 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). According to the U.S. Environmental Protection Agency, 7 indicator congeners should be determined in the environment, with codes: 28, 52, 101, 118, 138, 153, and 180. Water ecosystems pollution occurs indirectly (from the atmosphere) or directly (discharge of waste water containing PCB, run-off from fields, leakages from transformers and condensers, landfills). Because of hydrophobic properties, PCB have a strong tendency to transition from liquid phase to phases with higher hydrophobicity, *eg* through bioaccumulation or sorption, by binding to sediment particles or to suspended solids present in water [5].

Negative influence of micropollutants on water consumers health causes the need to remove these substances from drinking water. The choice of micropollutant removal processes is determined by their type, properties, and form of occurrence. Current literature reports emphasize the need for basic research regarding the removal mechanism of trace organic pollutants, using different coagulants. In recent years the use of new generation coagulants, with high efficiency, can be observed [1]. These coagulants reflect the properties of trace organic pollutants which are being removed (*eg* hydrophobicity, charge, polarizability, the presence of particular functional groups). It was also demonstrated that combined processes have a high efficiency in removal of organic micropollutants from water [6, 7]. In the literature there are few examples of research regarding PCB removal from contaminated surface water. Due to the similarities in chemical properties of PCB and PCDD, for removing polychlorinated biphenyls from water, research developments in PCDD/Fs removal [7] can be used.

PCB pollution monitoring is particularly important for reservoirs, which are sources of drinking water for supplying the population. Research conducted in 2009-2011 for chosen water reservoir in Poland, which is the source of water for water treatment plant, showed that the water and the bottom sediments are contaminated with PCB [8]. The scope of PCB concentration in the reservoir water ranged from 1.0 to 8.1 ng/dm^3, whereas the concentration of these compounds in the bottom sediments ranged from 0.12 to 2.78 μg/kg. The most commonly used coagulant in water treatment plants in Poland is aluminium sulphate $Al_2(SO_4)_3$. Also, there are studies conducted regarding the application of pre-hydrolyzed coagulants, *ia* polyaluminium chlorides with general formula $Al_n(OH)_mCl_{3n-m}$. The mechanism of coagulation with aluminium salts, non-hydrolyzed and pre-hydrolyzed, is the same, however the presence of aluminium polymeric forms in polyaluminium chloride solutions cause them to be more stable in water, resulting in more efficient removal of pollutants [1, 9].

The aim of this research was to compare the efficiency of chosen coagulants in removal of indicator and dioxin-like PCB from surface water.

Materials and methods

Research material

Kozlowa Gora water reservoir is created by damming the river Brynica. It is located on the south-eastern edge of Swierklaniec municipality. It occupies an area of approx. 5.5 km^2, its capacity equals to approx. 13 millions m^3, and its average depth is 4.5 m. Currently it constitutes water source for water treatment plant in Wymyslow, which belongs to Gornoslaskie Przedsiebiorstwo Wodociagow. The reservoir also fulfils flood prevention objectives, and it is used, to a limited extend, for touristic and recreational purposes.

Water from the reservoir, sampled in November 2011, was used for the research. Positions were situated in southern, outlet (by the dam) part of the reservoir. At each measuring point, 20 dm^3 of water was collected. The water composition was modified in order to obtain concentration of each PCB congener equal to 400 and 300 ng/dm^3 respectively, by introducing to water appropriate amounts of standard solutions - PCB MIX 13 and MIX 24.

As the coagulants there were used $Al_2(SO_4)\cdot 18H_2O$ produced by Przedsiebiorstwo Handlowe Polskie Odczynniki Chemiczne in Gliwice, and five hydrolyzed polyaluminium chlorides with trade names Kemira: PAX-XL1, PAX-XL10, PAX-XL19, PAX-XL60, PAX-XL69 produced by KEMIPOL in Police. Commercial solutions of polyaluminium chlorides were characterized by alkalinity equal to respectively 70 ±5%; 70 ±10%; 85 ±5%; 40 ±10%; 60 ±10%; 85 ±5%, and contained respectively 10.0 ±0.6%; 9.4 ±0.4%; 9.4 ±0.4%; 14.4 ±0.6%, and 11.3 ±0.9% of Al_2O_3 [10]. For the research, 1% solution of aluminium sulphate, and solutions of polyaluminium chlorides were prepared, by diluting commercial products so that they contained 1.0 g Al/dm^3.

Coagulation process

The coagulation process was conducted in glass vessels, to each 2 dm^3 of studied water was measured. The coagulants were introduced in the amount of 4 mg Al/dm^3, and fast stirring was performed for 2 minutes (applying 250 rpm) with the use of mechanical stirrer. Next slow stirring (20 rpm) was conducted for 15 minutes. After this time the samples were subjected to 1-hour sedimentation. Then 0.7 dm^3 of water was decanted. Before and after the coagulation process, water analysis was performed, including determination of: pH, turbidity, colour, total organic carbon (TOC), and PCB analysis [8, 11].

Analysis methodology

For the PCB analysis, hexane was added to 0.5 dm^3 of sampled water, and it was stirred with magnetic stirrer. Next, after separation of hexane fraction in a separator, the solution was mixed with fresh batch of hexane. Hexane extracts were combined. The extract was dried by seeping it through a layer of anhydrous Na_2SO_4. Hexane was evaporated near to dryness from the dried extract under vacuum, and it was poured into a tube. The flask was further washed with hexane, and combined with the solution, and then transferred into the tube. For mineralization of organic compounds, obtained solution was shaken with concentrated H_2SO_4. After separation of the mixture, 5% solution of KOH in ethanol was added to hexane layer. The tube was closed tightly and heated in a water bath.

After cooling, ethanol-water solution was added (1:1, v/v). Next, the hexane layer was separated, which was concentrated in a vacuum evaporator to a volume of 1 cm^3. The obtained extracts were analyzed qualitatively and quantitatively by means of capillary gas chromatography with mass spectrometry (CGC/MS) according to literature data [12]. For the chromatographic analysis there were used standards by dr Ehrenstorfer company, *ie* PCB MIX24 mixture, which was a solution of indicator congeners: 28, 52, 101, 118, 138, 153 and 180, and PCB MIX13 solution, which contained three coplanar PCB congeners with codes: 77, 126 and 169. For their chromatographic separation, a DB-5 column was used. For detection, quadrupole mass spectrometer MS 800 by Fisons was used, which was operating in a selective ion monitoring mode. PCB quantification was achieved by single ion monitoring (SIM) [13].

Results and discussion

The analysed surface water had slightly alkaline pH (7.9), colour equal to 30 mg Pt/dm^3, and turbidity of 17 NTU [8].

Total concentration of indicator and dioxin-like PCB in sampled water was low and amounted to 32.3 and 4.7 ng/dm^3 respectively. Research results of PCB removal from water, for the coagulant dose of 4 mg Al/dm^3 with additional amount of standard solutions of indicator and dioxin-like PCB are presented in Table 1.

Table 1

PCB concentration in modified surface water after coagulation process

Congeners	**Concentration [ng/dm^3]**					
	$Al_2(SO_4)_3$	**PAX-XL1**	**PAX-XL10**	**PAX-XL19**	**PAX-XL60**	**PAX-XL69**
Indicator						
PCB 28	165.7	178.9	186.3	285.9	290,4	287.9
PCB 52	159.2	174.4	180.4	261.9	272.5	274.8
PCB 101	62.0	146.4	157.5	185.5	210.8	215. 6
PCB 118	44.1	125.6	138.9	164.0	195.3	202.7
PCB 138	31.4	89.0	95.3	134.9	180.5	192.6
PCB 153	31.3	240	235.9	230.0	252.0	263.0
PCB 180	198.0	52.1	78.7	118.8	164..6	170.3
Dioxin-like						
PCB 77	138.0	140.6	179.7	236.3	262.1	260.0
PCB 126	84.5	74.9	119.4	179.5	211.7	214.3
PCB 169	90.0	110.7	173.2	180.3	184.9	187.5

Out of studied coagulants better effects of indicator PCB removal were obtained after the usage of aluminium sulphate, total PCB concentration decreased by 65%. The highest efficiency of indicator congener removal was obtained for PCB 138 and 153, which amounted to 90% (Fig. 1). The concentrations of other PCB were reduced in the range of 85 (PCB 118) to 34% (PCB 180).

Among hydrolyzed polyaluminium chlorides, the best results of indicator PCB removal were obtained after application of PAX-XL1 and PAX-XL10. For these coagulants, decrease in total PCB concentration by 53 and 50% respectively was obtained.

Greater reduction of higher chlorinated congener, *ie* PCB 180, 138 and 118, concentration was achieved, in the range of 54 to 83%.

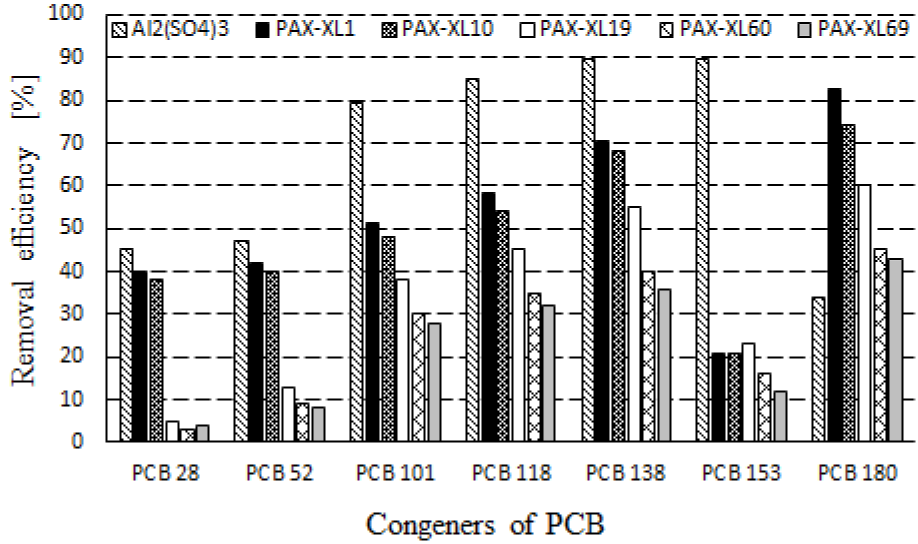

Fig. 1. Removal efficiency of indicator PCBs from water

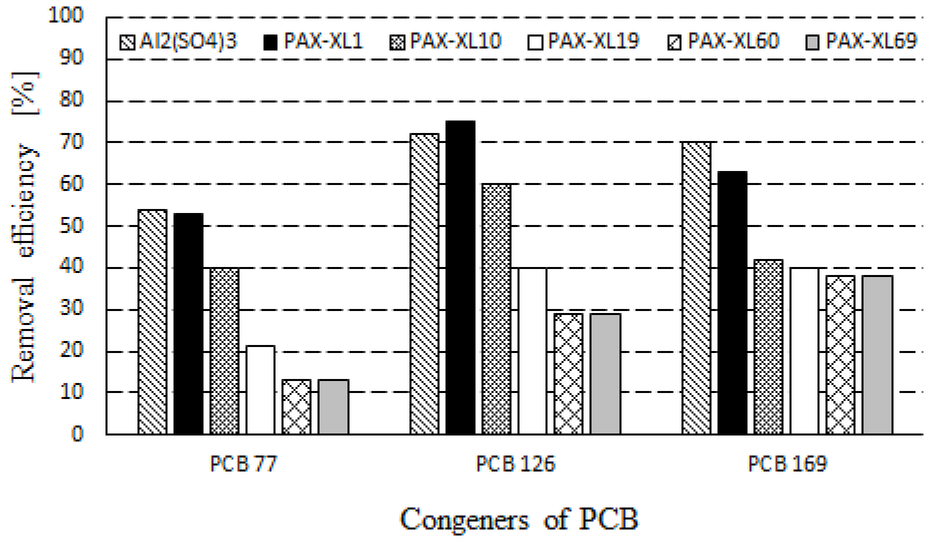

Fig. 2. Removal efficiency of dioxin-like PCBs from water

Selectivity in removal of chosen PCB congeners, depending on applied coagulant, was demonstrated; the usage of aluminium sulphate resulted in achieving heptachlorobiphenyl

PCB 180 removal rate at the level of 34%, while using PAX-XL1 and PAX-XL10 resulted in obtaining higher reduction efficiency for this congener, *ie* 83 and 74% respectively.

For dioxin-like PCB after the application of aluminium sulphate total concentration reduction by 74% was obtained, congener removal efficiency amounted to from 54 (PCB 77) to 72% (PCB 126) (Fig. 2). Similar effects were achieved after the usage of PAX-XL1, total PCB concentration decreased by 73%, reduction of PCB 77, 126 and 169 concentration amounted to 53, 75 and 63% respectively.

The smallest degree of removal from water, both for indicator and dioxin-like PCB, was stated for coagulants PAX-XL60 and PAX-XL69. After the application of these coagulants, decrease in PCB concentration in the range of 3 to 45% (indicator PCB), and 13 to 38% (dioxin-like PCB), was obtained.

According to the literature data, the coagulation process with aluminium sulphate, apart from desirable effects, may cause negative changes in physico-chemical composition of purified water, *eg* an increase in aluminium ion concentration or intensification of water corrosivity [1]. Increased aluminium ion concentration in drinking water may also pose a potential threat to human health. Therefore, despite demonstrated in the research, higher efficiency of aluminium sulphate in PCB removal from water, it is suggested to use polyaluminium chlorides PAX-XL1 and PAX-XL10, which have alkalinity equal to 70 ±5%, 85 ±5% respectively, and which contain approx. 10 and 3% of Al_2O_3. The application of polyaluminium chlorides as coagulants for organic pollutant removal, is recommended by many authors [1, 2]. Higher efficiency is explained by the fact that polyaluminium chloride solutions contain more polycationic and polymerized products of controlled prehydrolysis than aluminium sulphate. In the pH range of natural waters and with their alkalinity, hydrolysis of aluminium cations present in aluminium sulphate occurs almost immediately after their contact with treated water, therefore the precipitation of aluminium hydroxide occurs faster than the desired reaction of colloids and organic pollutant anions neutralization [2].

The obtained results suggest that in case of removal from water indicator and dioxin-like PCB using polyaluminium chlorides, their alkalinity is important, which should amount to approx. 70%. Alkalinity of PAX-XL60 and PAX-XL69 was lower and amounted to approx. 40 and 60%, which can explain lower efficiency of these coagulants in PCB removal. PAX-XL1 coagulant efficiency in congener removal is confirmed by results obtain for dioxin-like PCB. Also the literature data confirm the effectiveness of polyaluminium chloride in dioxin and dioxin-like compound removal. Li et al [7] demonstrated 99% efficiency in PCDD/Fs removal after application of ferric chloride and polyaluminium chloride, slightly lower (97-98%) was obtained for aluminium sulphate. Applied coagulants were selective in removal of chosen PCDD/Fs. The literature data and own research indicate that significant improvement of polyaluminium chloride efficiency in PCB removal from water is achieved by application of coagulation process enhancement with powder-activated carbon. Liyan et al. [14] demonstrated the effectiveness of powder-activated carbon (PAC), granular-activated carbon (GAC) in hydrophobic organic chemicals (HOCs) removal, in the range of 73.4 to 89.2%, which is the next stage of own research.

Conclusions

Conducted research allowed for formulating the following conclusions:

- good effects of indicator and dioxin-like PCB removal from surface water were obtained after the application of aluminium sulphate, and hydrolyzed polyaluminium chlorides PAX-XL1 and PAX-XL10,
- after the coagulation process using aluminium sulphate and coagulants PAX-XL1 and PAX-XL10, total concentration of indicator PCB decreased in water by 65, 53, and 50% respectively,
- for dioxin-like PCB, after using aluminium sulphate and hydrolyzed polyaluminium chloride PAX-XL1, total concentration reduction by 74 and 73% was achieved,
- selectivity in chosen PCB congener removal was demonstrated, depending on applied coagulant; with the usage of aluminium sulphate removal of heptachlorobiphenyl PCB 180 at the level of 34% was obtained, whereas with the application of PAX-XL1 and PAX-XL10 higher efficiency of this congener reduction was obtained, *ie* 83 and 74% respectively.

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WPŁYW WYBRANYCH KOAGULANTÓW NA USUWANIE WSKAŹNIKOWYCH I DIOKSYNOPODOBNYCH PCB Z WODY PRZEZNACZONEJ DO SPOŻYCIA

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Abstrakt: Celem badań była porównanie efektywności wybranych koagulantów w usuwaniu z wody powierzchniowej wskaźnikowych i wybranych dioksynopodobnych PCB. Jako koagulanty wykorzystano siarczan glinu oraz 5 zhydrolizowanych chlorków poliglinu o nazwach handlowych: PAX-XL1, PAX-XL10, PAX-XL19, PAX-XL60, PAX-XL69. Do badań wykorzystano wodę powierzchniową. Skład wody zmodyfikowano mieszaniną wzorcową PCB MIX24 oraz MIX13 w celu uzyskania stężenia każdego kongeneru 300 ng/dm^3. Mieszaninę PCB MIX24 stanowił roztwór wskaźnikowych kongenerów: 28, 52, 101, 118, 138, 153 i 180, a mieszaninę MIX13 roztwór trzech dioksynopodobnych PCB 77, PCB 126 oraz PCB 169. Wykazano, że zastosowanie siarczan glinu pozwoliło na uzyskanie lepszych efektów oczyszczania wody z PCB niż przy wykorzystaniu wstępnie zhydrolizowanych soli, chlorków poliglinu. Z przebadanych koagulantów najlepsze efekty usuwania wskaźnikowych PCB otrzymano po zastosowaniu siarczanu glinu, sumaryczne stężenie PCB zmniejszyło się o 65%. Najwyższą efektywność usuwania wskaźnikowych kongenerów (90%) uzyskano dla PCB 138 i 153. Po zastosowaniu zhydrolizowanych chlorków poliglinu PAX-XL1, PAX-XL10 uzyskano obniżenie stężenia wyżej chlorowanych PCB w zakresie od 23 do 74%. Wykazano selektywność usuwania wybranych kongenerów PCB w zależności od zastosowanego koagulantu; przy wykorzystaniu siarczanu glinu uzyskano usunięcie heptachlorobifenylu PCB 180 na poziomie 34%, natomiast przy wykorzystaniu PAX-XL1 i PAX-XL1o uzyskano większą efektywność redukcji tego kongeneru, tj. odpowiednio 83 i 74%. Dla dioksynopodobnych PCB po zastosowaniu siarczanu glinu uzyskano redukcję sumarycznego stężenia o 74%, efektywność usuwania tych kongenerów wynosiła od 54 (PCB 77) do 72% (PCB 126), podobne rezultaty otrzymano po zastosowaniu PAX-XL1. Najmniejszy stopień usuwania PCB z wody stwierdzono dla koagulantów PAX-XL60 i PAX-XL69.

Słowa kluczowe: polichlorowane bifenyle, koagulacja, siarczan glinu, zhydrolizowane chlorki poliglinu, efektywność usuwania, woda pitna