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Concentrations of PCBs and heavy metals in water of the dam reservoir and use of pre-hydrolyzed coagulants to micropollutants removal from surface water

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ABSTRACT

The aim of the presented research work was to analyze the pollution in the Kozłowa Góra Dam Reservoir (Poland) with indicative Polychlorinated biphenyls (PCBs) (28, 52, 101, 118, 138, 153, 180) and heavy metals (Zn, Cu, Ni, Cd, Pb, Cr). Aluminum sulfate and pre-hydrolyzed polyaluminium chloride (PAX-XL1, PAX-XL19) were used as coagulants, and the following parameters were analyzed in the water samples from the Kozłowa Góra Dam Reservoir: turbidity, color, and concentrations of PCBs and heavy metals (Ni, Cd, Pb). The concentrations of Zn, Cu, Ni, Cd, Pb, and Cr in the water were as follows: 0.022; 0.012; 0.015; 0.01; 0.014; $<0.01\,mg\,L^{-1}$. The total concentration of PCBs in the water amounted to $6.0\,ng\,L^{-1}$. The highest concentration was shown for PCB 28 ($1.6\,ng\,L^{-1}$), while the lowest concentration was shown for PCB 180 ($0.5\,ng\,L^{-1}$). After the application of PAX19, polyaluminum chloride with the highest alkalinity, the best results (among the investigated coagulants) for the chosen contaminants' removal were obtained; 98% decrease of turbidity and 86% lead concentration were acquired. The highest removal rates for the indicator PCBs were obtained using aluminum sulfate. The total concentration of PCBs was reduced by 71%. The removal efficiency for particular congeners ranged from 57% (PCB 28) to 90% (PCB 153).

Keywords: Polychlorinated biphenyls; Heavy metals; Water; Coagulation; Polyaluminum chloride

1. Introduction

Polychlorinated biphenyl (PCB) and heavy metal contamination of water and bottom sediments is harmfully affecting the biological environment and often indirectly human health. Currently in water ecosystems, the PCBs may be adsorbed by suspended solids or by organic matter in sediments. Some of the 209 PCB congeners are toxic or potentially carcinogenic substances with high bioaccumulation potential and are also highly persistent in a natural environment [1]. Based on the solubility and octanol–water partition coefficient (K_{ow}) for individual congeners, PCBs can be classified into two groups: lower chlorinated PCBs (LCBs), which have a low sorption rate, and higher chlorinated PCBs (HCBs), which have a high sorption rate [2–4]. HCBs' persistence in environ-

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ment, especially in bottom sediments, is determined by low solubility and therefore strong adsorption shown by organic matter particles. Ecosystems, which are particularly subject to PCB contamination, are low-lying dam reservoirs. Slowing down of river stream, long water retention time, and a large amount of organic matter, which is carried away by the river to the reservoir, are creating suitable conditions for the sedimentation and accumulation of PCBs in bottom sediments. It is estimated that up to 97% of chloro-organic substances introduced to the water environment is deposited as bottom sediments in the dam reservoir. Therefore, these ecosystems are becoming a repository of PCBs, acting as a sustainable PCB source, and posing a danger to water organisms.

The evaluation of PCB and heavy metal contamination is especially important for dam reservoirs, which serve as sources of drinking water to people. The research carried out in 2009–2010 for a particular dam reservoir in Poland, which is a water source for the drinking water purification plant, has shown that water and bottom sediments are contaminated by the PCBs and heavy metals. The PCB concentration in water ranged from 7.3 to 8.1 ng L^{-1}, whereas the concentration in the bottom sediments ranged from 0.12 to 2.78 μg kg^{-1}. In water, the LCB and HCB concentrations were comparable, while in bottom sediments the HCB was the dominant factor (86%). Zinc, copper, nickel, cadmium, lead, and chromium concentrations in bottom sediments amounted to respectively: 125–200; 7.1–8.6; 5.5–7.3; 1.7–4.4; 92–109; 4.9–5.5 mg kg^{-1} [5].

Coagulation is the most commonly used process for removing inorganic and organic colloidal contaminants and difficult-to-settle suspensions from water. Decrease of turbidity, color of water, and content of organic matter (e.g., humic substances, which are precursors of the oxidation by-products) are the result of effective coagulation [6–9]. A properly performed coagulation can also ensure a heavy metal removal [10–12].

Aluminum sulfate ($Al_2(SO_4)_3$) is the most often used coagulant at the water purification plants in Poland. There are ongoing studies on the application of preliminary hydrolyzed coagulants e.g. polyaluminum chlorides with the general structure of $Al_n(OH)_mCl_{3n-m}$. Although the coagulation mechanism with non-hydrolyzed and preliminary hydrolyzed aluminum salts is the same, the presence of polymeric species of aluminum in solutions of polyaluminum, chlorides results in their higher stability in water and thus more efficient contaminants removal can be performed.

The present work was carried out to estimate the usability of pre-hydrolyzed polyaluminum chlorides as regards turbidity, color, heavy metal, and PCB removal from the surface water.

2. Materials and methods

2.1. Materials

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 approximately 5.5 km^2 of the area and its volume is approximately 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 Silesian Water Supply Company. This reservoir also helps to control flood apart from serving as a spot for tourist recreational activity.

In the present study [5], the distribution of particular heavy metals between chemical fractions of the investigated bottom sediments from the Kozłowa Góra Dam Reservoir was analyzed. The mobility of metals and the possibility of secondary contamination were also estimated. It was shown that in an unstable environment (e.g. change of pH, oxidation, salinity of water), there is a potential risk of releasing high quantities of lead, cadmium, and nickel from the bottom sediments of the reservoir.

The surface water samples from the Kozłowa Góra Dam Reservoir collected in March 2011 were used for the experiment. The sampling spots were located in the southern part of the dam reservoir, at the outflow (at the dam). The localization of the sampling spots is shown in Fig. 1. Twenty litres of water was taken from each sampling spot.

The composition of water was modified to obtain concentrations of each heavy metal of ca. 0.3 mg L^{-1} with implementation of particular amounts of cadmium-, lead nitrate ($Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$), and nickel chloride ($NiCl_2{\cdot}6H_2O$).

To obtain a concentration of 300 ng L^{-1} in the case of each congener, a standard mixture PCB MIX3, which consisted of indicator congeners, was added to water.

The coagulants included $Al_2(SO_4)_3{\cdot}18H_2O$ manufactured by the POCH in Gliwice, and hydrolyzed polyaluminum chlorides (PAX-XL1, PAX-XL19) manufactured by KEMIPOL in Police (Poland). Commercial solutions of polyaluminum chlorides PAX-XL1 and PAX-XL19 have an alkalinity of 70 ± 5%, 85 ± 5%, respectively, and their Al_2O_3 content is 10 ± 0.6%, and 23 ± 0.6%, respectively. The alkalinity of polyAlumi-

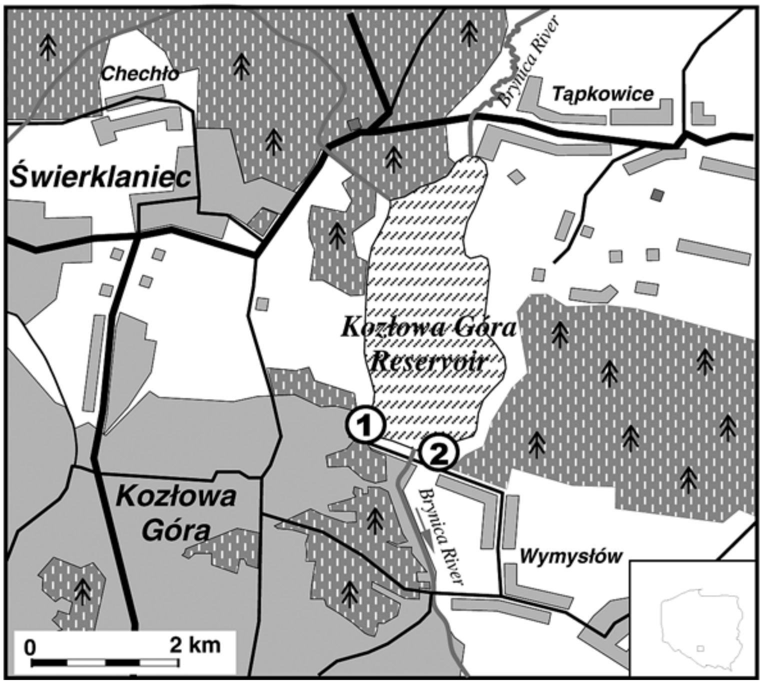

Fig. 1. Location of the Kozłowa Góra Dam Reservoir with the sampling points (1) and (2).

num chlorides is defined by the ratio of OH^- to Al^{3+} in a coagulant. The ratio is defined as the coefficient $r = [OH^-]/[Al^{3+}]$ and is treated as a measure of polymerization degree. There is a following dependence between r and coagulant alkalinity: alkalinity (%) = $r/0.03$.

While undertaking studies 1% solution of aluminum sulfate and solutions of polyaluminum chlorides were prepared by diluting the commercial products to obtain 1.0 gAl L^{-1} in them.

2.2. Laboratory test of coagulation

The process of coagulation was carried out in glass beakers with a capacity of 3 L. Each beaker was filled with 2 L of sampled water. Then, the coagulants with amounts of 1, 2, 3, and 4 mgAl L^{-1} were added and were quick mixed with a mechanical stirrer within 1 min (with 200 rpm) followed by slow mixing within 15 min (20 rpm). Afterwards, the samples were subject to sedimentation for 1 h. Then, 0.7 L of water was decanted.

2.3. Analytical methods

The following analytical methods were performed: pH—potentiometrically, turbidity—nephelometric method (nephelometer TN-100, Eutech Instruments), color—by comparing to the pattern scale (platynic–cobaltic), aluminum—spectrophotometric method using eriochrome cyanine (Helios Epsilon Spectrophotometer, Thermo Electron Corporation) and heavy metals—by means of atomic absorption spectrometry (spectrometer novAA 400, Analytik Jena).

The PCB analysis was carried out only for a coagulant dose of 3 mgAl L^{-1}. PCB analysis in water methodology was described in the literature [5]. To determine the PCBs in the sampled water, the solid-phase extraction (SPE) was applied. Sampled water (0.5 L) was passed through the Bakerbound columns with the Octadecyl C_{18} filling. After that, the columns were rinsed with 6 cm^3 of distilled water and air-dried. The PCB fraction was eluted with hexane and the extract was subsequently concentrated to a volume of 0.1 cm^3. The extract was condensed in vacuum and then subject to qualitative and quantitative analyses by gas chromatography and mass spectrometry (GC 8000 series, MS-MD 800, Fisons Instruments) [5,13].

3. Results and discussion

The water had a slightly alkaline pH (7.85), while the color index was at the level of 30 mgPt L^{-1} and turbidity of 16.8 NTU. The concentrations of zinc, copper, nickel, cadmium, lead, and chromium were as follows: 0.022; 0.012; 0.015; 0.01; 0.014; <0.01 mg L^{-1}. The total concentration of seven indicative PCBs in water amounted to 6.0 ng L^{-1}. The highest concentration was shown for PCB 28 (1.6 ng L^{-1}), while the lowest was shown for PCB 180 (0.5 ng L^{-1}).

The results of the removal of turbidity, color, Ni, Cd, and Pb from surface water enriched with metals during the coagulation process are presented in Table 1.

The results of turbidity measurements revealed that the most efficient way to remove turbidity under the conditions of coagulation (pH 7.72–7.38) was the use of PAX-XL19, on account of which the turbidity was reduced from 16.8 to 0.4 NTU. The most intensive reduction in colour from 30 to 5 mgPt L^{-1} was obtained after the use of PAX-XL19. After the use of aluminum sulfate, the color was reduced to a value of 15 mgPt L^{-1} and turbidity from 16.8 to 2.7 NTU. Better efficiency of PAX-XL19 coagulant might result from the fact that polymerized products of pre-hydrolysis with high positive charge were present in solutions of this reagent, which created more favorable conditions for destabilization of negatively charged pollutants, which cause water turbidity and color. Another favorable aspect of coagulation carried out using PAX-XL19 was low concentration of aluminum which remained after the process (below 0.1 mgAl L^{-1}).

In the range of surface water pH and when water alkalinity was sufficient, the hydrolysis of aluminum cations to $Al(OH)_3$ takes place almost immediately after the addition of aluminum sulfate to the treated water. The precipitating aluminum hydroxide in the pH range of 5.5–7.5 has positive surface charge: however, its destabilizing force is definitely smaller than those of Al^{3+} ion and its hydroxyl complexes with a positive charge. In polyaluminum chloride solutions, next to monomers Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$ (also present in solutions of non-preliminary hydrolyzed aluminum coagulants), the presence of many polymerized aluminum hydroxyl complexes with a positive charge: $Al_2(OH)_2^{4+}$, $Al_3(OH)_3^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$ was identified. The last one, called polymer $Al_{13,}$ is believed, among aluminum polymers, to be the most stable one and the most effective polymer during destabilization of negative colloids [14], which cause particularly a very high turbidity of water [15]. In the case of the aluminum preliminary hydrolysis, the polycation products formed during the process hydrolyse to Al $(OH)_3$ definitely slower after the addition of polyaluminum chloride to the treated water than aluminum in the solution of aluminum sulfate. This fact indicates that the application of polyaluminum chlorides, when comparing with the effects obtained during aluminum sulfate addition, is more effective in destabilizing the negative colloids, which are mainly responsible for the color and turbidity of water.

In the case of heavy metals, the best effects were obtained for lead, cadmium, and nickel removal using PAXL-XL19. Concentration of these metals was reduced from 0.3 mg/L to 0.04, 0.07, and 0.22 mg L^{-1}, respectively. Good results of lead removal were also obtained with the use of other coagulants such as: PAX-XL1 and aluminum sulfate; its concentrations were decreased to the following values: 0.05 and

Table 1
The values of analyzed indicators, before and after coagulation process

Coagulant	Dose mgAl L^{-1}	pH-	Turbidity NTU	Color mgPt L^{-1}	Al mg L^{-1}	Heavy metals (mg L^{-1})		
						Ni	Cd	Pb
Water surf.	–	7.85	16.8	30	<0.05	0.31	0.30	0.28
$Al_2(SO_4)_3$	1	7.72	6.1	25	0.40	0.31	0.24	0.25
	2	7.68	3.9	20	0.47	0.28	0.25	0.22
	3	7.55	3.2	20	0.28	0.28	0.20	0.16
	4	7.38	2.7	15	0.32	0.26	0.17	0.09
PAX-XL1	1	7.81	3.5	20	0.12	0.28	0.23	0.13
	2	7.74	2.9	15	0.16	0.27	0.22	0.11
	3	7.66	2.0	10	0.19	0.23	0.19	0.06
	4	7.52	1.6	10	0.12	0.24	0.20	0.05
PAX-XL19	1	7.78	2.6	15	0.22	0.25	0.12	0.11
	2	7.75	1.3	10	0.15	0.23	0.09	0.08
	3	7.63	0.8	5	<0.10	0.23	0.10	0.07
	4	7.56	0.4	5	0.10	0.22	0.07	0.04

0.09 mg L^{-1}, respectively. In the case of cadmium, better results were obtained when aluminum sulfate was used rather than PAX-XL1: however for nickel, the results were opposite. The quality of treated water did not meet the standard requirements for drinking water [16]. It may be assumed that an additional coagulation enhancement with activated carbon could result in obtaining the required concentrations [17,18].

The percentage of removal of turbidity, color, nickel, cadmium, and lead from surface water during the process of coagulation is presented in Fig. 2.

The highest decrease of turbidity (98%), lead and cadmium concentrations (86 and 77%, respectively) were acquired with PAX-XL19. The lowest degree of contaminant removal was observed when aluminum sulfate was used. During those tests, the turbidity was decreased by 84%, lead and cadmium concentrations were decreased by 68 and 43%, respectively. Only decrease of nickel concentration was independent of the applied coagulant and a small (about 16–29%) decrease in the concentration was observed.

The degree of heavy metal removal depends on the form of their occurrence in water and on the pH value. During the performed tests in the pH range of 7.7–7.4, the analyzed metals could be found mainly in the form of cations (Cd^{2+}, $CdCl^{+}$, $Pb(OH)^{+}$, Ni^{2+}) [19]. Therefore, it can be stated that the metal removal was determined by adsorption, surface complex formation and ion exchange. Among the investigated metals, the best results were obtained for lead removal.

The results of indicator PCB removal from water for a coagulant dose of 3 mgAl L^{-1} with an additional amount of PCB MIX3 standard mixture are presented in Table 2.

The highest removal rates for indicator PCBs were obtained with the use of aluminum sulfate (Fig. 3). The concentrations of PCB congeners with codes: 28, 52, 101, 118, 138, 153 decreased from ~300 ng L^{-1} to 129.0, 117.1, 62.0, 44.1, 31.4, 31.3 ng L^{-1},respectively. The total concentration of PCBs was reduced by 71%. The removal efficiency for particular congeners amounted from 57% (PCB 28) to 90% (PCB 153). Using aluminum sulfate was insufficient only in the case of removal of heptachlorobiphenyl—congener with code 180, whose concentration was reduced by 34%. The best results for this congener elimination were obtained with the use of PAX1. Employing PAX1 as a coagulant led to decreasing the total PCB concentration by 52%. The removal efficiency for particular congeners amounted from 40% (PCB 28) to 83% (PCB

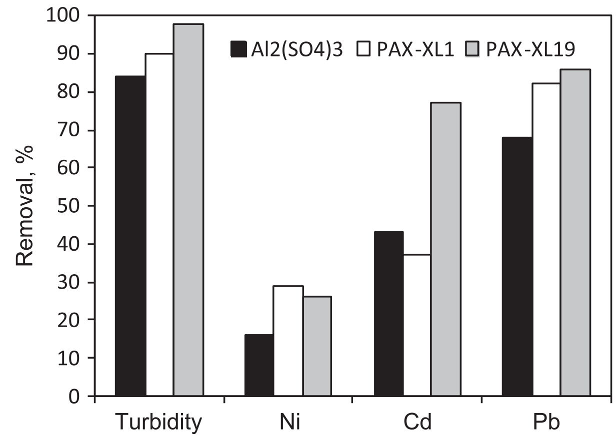

Fig. 2. The percentage of the removal of turbidity, color, and heavy metals from surface water (PAX—polyAluminum chlorides).

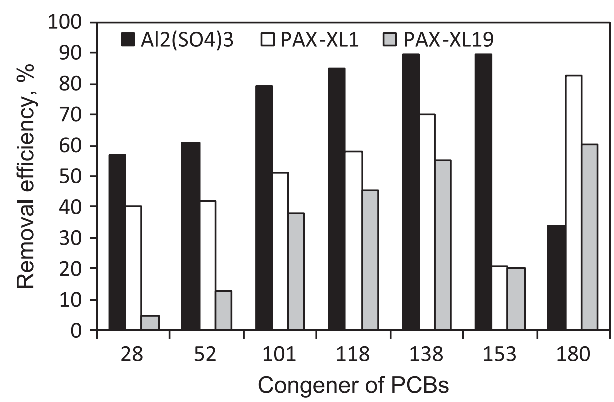

Fig. 3. The removal efficiency of PCBs from surface water (PAX—polyAluminum chlorides).

Table 2
The concentration of indicator PCB in water after the coagulation process

Coagulant	Concentration (ng L^{-1})						
	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
$Al_2(SO_4)_3$	129.0	117.1	62.0	44.1	31.4	31.3	198.0
PAX-XL1	178.9	174.4	146.4	125.6	89.0	240.0	52.1
PAX-XL19	285.9	261.9	185.5	164.0	134.9	230.0	118.8

180). The lowest removal rate was observed after using PAX19, when the congener concentrations were reduced from 5 to 60%. Total PCB concentration decreased only by 34%. For applied coagulants, a higher efficiency in the PCB removal was observed in the case of HCBs, which was a result of a higher adsorption on the suspended particles, in comparison with the LCBs [2,20]. The HCBs are characterized by low solubility in water and high values of the octanol–water partition coefficient (K_{ow}) [3]. Along with the increasing number of chlorine atoms in a biphenyl molecule, the distribution coefficient K_p, which describes the hydrophobic sorption of PCB congeners, increases. The utilization of the coagulants in a polychlorinated congener removal from water was shown by Li et al. [21]. In their study a 95% reduction of total polychlorinated dibenzo-p-dioxin concentration in drinking water was achieved.

4. Conclusions

The application of pre-hydrolyzed salts—polyAluminum chlorides-resulted in better effect of water purification than when non-hydrolyzed salt—aluminum sulfate-was used. The following conclusions can be drawn from the present study:

(1) after the application of PAX-XL19, polyAluminum chloride with the highest alkalinity, the best results (among the investigated coagulants) for the chosen contaminant removal were obtained; more than 85% decrease of turbidity, color, and lead concentration was acquired;
(2) when PAX-XL19 was applied, the residual Aluminum concentration in purified water was below $0.1\,mg\,L^{-1}$, whereas when Aluminum sulfate was used, the concentration was below $0.3\,mg\,L^{-1}$;
(3) the best results of indicator PCB removal (71%) were observed with application of aluminum sulfite, whereas PAX-XL1 and PAX-XL19 coagulants decreased total PCB concentration by 52 and 34%, respectively. For applied coagulants, a better removal efficiency was observed for HCBs in comparison with LCBs.

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