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Removal of turbidity, colour and organic matter from surface water by coagulation with polyaluminium chlorides and with activated carbon as coagulant aid

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ABSTRACT

The aim of the research work was to evaluate the capability of pre-hydrolysed aluminium salts to reduce turbidity, colour and organic matter from surface water. The coagulants used in the study were $Al_2(SO_4)_3$ and hydrolysed polyaluminium chlorides: PAX18, PAX-XL3, PAX-XL10, PAX-XL 19F, PAX-XL1905, PAX-XL61 and PAX-XL69. Using pre-hydrolysed salts—polyaluminium chlorides—made it possible to obtain better effects of surface water treatment compared with the results accomplished with non-hydrolysed aluminium salt (aluminium sulphate). At a dose of 3 mg Al L^{-1} the best effects of turbidity, colour and organic matter removal were obtained using PAX-XL1905, which is polyaluminium chloride of high alkalinity. Under these conditions, 89% reduction in turbidity and 50% in colour was achieved. Moreover, the total organic carbon (TOC) value decreased by 26%. When pH was decreased from 8.2 to 6.2 the effectiveness of TOC removal increased (upto 37%). The addition of powdered activated carbon to water during coagulation did not significantly affect the effectiveness of organic compounds removal.

Keywords: Surface water; Coagulation; Polyaluminium chlorides; Organic matter

1. Introduction

Application of the coagulation process in surface water treatment allows for a decrease in turbidity and colour of water, as well as the organic matter content and the concentration of heavy metal ions [1–5]. A dose of the coagulant and technical parameters of the coagulation process must be determined experimentally for each water. In Poland, most drinking water treatment plants (WTPs) use aluminium sulphate as a coagulant. Research works on pre-hydrolysed coagulants, e.g. polyaluminium chlorides (general formula $Al_n(OH)_mCl_{3n-m}$) are also carried out. These products contain high positive charge which creates good conditions for destabilisation of negatively charged contaminants which cause turbidity and colour of water. In the solutions of polyaluminium chlorides besides monomers, such as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ (they

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are also present in solutions of non-hydrolysed aluminium coagulants), positively charged polymerised hydroxyl complexes of aluminium were identified: $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ [6]. Although coagulation processes using non-hydrolysed and pre-hydrolysed aluminium salts share the same mechanism, the presence of polymeric aluminium compounds in solutions of polyaluminium chlorides causes their better stability; as a result the effectiveness of pollutants removal is higher. $Al_{13}O_4(OH)_{24}^{7+}$ is called polymer A_{13} and is considered to be the most stable and effective in destabilisation of negatively charged colloids, especially, the colloidal particles which causes high turbidity of water [7].

It is also possible to apply adsorption and coagulation processes simultaneously by adding both powdered activated carbon and coagulant. The main parameters that affect the process are a dose of adsorbent, retention time and whether the carbon is dosed before or after coagulant. It was stated that simultaneous coagulation and adsorption was effective primarily in organic compounds and heavy metal ions removal [8–11].

The aim of the present investigation was to evaluate the capability of pre-hydrolysed aluminium salts applied alone as well as supported by powdered activated carbon to reduce turbidity, colour and organic matter from surface water.

2. Experimental procedures

2.1. Materials and jar test procedure

Surface water was collected three times, in October 2013, from Kozłowa Góra dam reservoir (Silesian voivodenship, Poland). The reservoir is a water supply for Wymysłów WTP, in which coagulation is carried out for treatment of drinking water.

The coagulants used in the study were $Al_2(SO_4)_3{\cdot}18H_2O$ (POCh™—Avantor Performance Materials Poland S.A.) and pre-hydrolysed polyaluminium chlorides (commercial agents PAX18, PAX-XL3, PAX-XL10, PAX-XL19F, PAX-XL1905, PAX-XL61 and PAX-XL69) manufactured by Kemipol (Police, Poland). The summary of the coagulants characteristics is given in Table 1. Alkalinity of commercial products varied from 41 to 85%. They contained 9.4–17.0% of Al_2O_3. The alkalinity of polyaluminium chlorides is defined by the ratio of OH^- moles to Al^{3+} moles in coagulant. The ratio is defined as coefficient $r = [OH^-]/[Al^{3+}]$ and it is used as a measure of polymerisation degree. There is the following dependency between "r" and alkalinity of coagulant: alkalinity (%) $= r/0.03$. During the study, 1% solution of aluminium sulphate was used. Solutions of polyaluminium chlorides were prepared by diluting commercial products to obtain concentration equal to 1.0 g of Al L^{-1}.

The research was divided into three stages: coagulation with aluminium salts, adsorption with powdered activated carbon and combined processes.

Coagulation was carried out in 2 L glass beakers which were filled with 1 L of surface water. Then, the coagulants in amounts of 1, 2 and 3 mg Al L^{-1} were added and rapid mixing with mechanical stirrer was performed for 3 min (at 200 rpm) followed by slow mixing (for 15 min, at 20 rpm). After mixing, the flocs were allowed to settle for 1 h and then carefully 200 mL of supernatant was decanted and analysed for selected physicochemical properties. Additional tests on the effectiveness of coagulation under pH lower than in collected surface water (after acidification pH was equal to 7.1 and 6.2) were carried out for aluminium sulphate, and the most effective polyaluminium chloride (PAX-XL1905). The advantage of PAX-XL1905 use was the low concentration of residual aluminium in the treated water (it was lower than 0.1mg L^{-1}).

The adsorption process was carried out in 1 L glass beakers. They were filled with 0.5 L of surface water and after that powdered activated carbon were added (at concentration 15, 30 and 45 mg L^{-1}). The samples were stirred mechanically for 10 min at 300 rpm. Afterwards, they were filtered through a paper filter (Munktell, Grade 3 W). Commercial powdered activated carbon (CWZ 30 and AKPA 22) produced by Gryfskand (Hajnówka, Poland) were used in the study. They had specific area equal to 1,134 and 914 g m^{-2} for the CWZ 30 and AKPA 22, respectively. The iodine value was 1,190 mg g^{-1} for CWZ 30 and 940 mg g^{-1} for AKPA 22. The methylene value was, respectively, 30 and 28 cm^3.

Table 1
Characteristics of the coagulants used during experiments

Parameter	PAX18	PAX-XL3	PAX-XL10	PAX-XL19F	PAX- XL1905	PAX-XL61	PAX-XL69
Alkalinity (%)	41.0 ± 3	70.0 ± 5	70.0 ± 10	85.0 ± 5	85.0 ± 5	70.0 ± 10	60.0 ± 10
Al_2O_3 (%)	17.0 ± 0.6	10.0 ± 0.6	9.4 ± 0.4	16.0 ± 0.9	11.3 ± 0.9	10.2 ± 0.4	11.3 ± 0.9
Chlorides (%)	21.0 ± 2	13.0 ± 2	11.5 ± 1	5.5 ± 0.5	5.0 ± 1	11.0 ± 2	11.0 ± 2
pH	1.0 ± 0.2	2.5 ± 0.5	2.5 ± 0.5	4.0 ± 0.5	3.6 ± 0.4	3.0 ± 0.5	2.5 ± 0.5

Tests on the effectiveness of simultaneous coagulation (with aluminium sulphate and PAX-XL 1905) and adsorption with powdered activated carbon (CWZ 30) at natural pH and at pH equal to 6.2 were also undertaken. Powdered activated carbon was added into the water during a fast stirring phase, 1 min after coagulant addition. The dose of activated carbon was equal to 30 mg L^{-1}.

2.2. Analytical procedure

The physicochemical parameters of water were measured with the following methods: pH—potentiometrically; turbidity—with Eutech Instruments TN-100 nephelometer (expressed in NTU—Nephelometric Turbidity Unit); colour—colometrically with platinum–cobalt standard method; dissolved (DOC) and total organic carbon (TOC)—by infrared spectrophotometry (with carbon analyser Multi N/C, Analytic Jena)—to measure DOC concentration the samples of water were filtered through 0.45 µm filter paper (DOC content was analysed in a filtrate); permanganate value (PV) by potassium permanganate method and aluminium—with Aquaquant 14413 aluminium test (by visual comparison of the colour of the analysed solution with colour fields of a colour card; in weakly acidic acetate buffered solution aluminium forms blue–violet colour lacquer with chromazurol S). The analyses were carried out before and after coagulation as well as adsorption.

3. Results and discussion

During the first stage of research work (coagulation with aluminium salts) raw surface water was alkaline (pH 7.8); a colour of the water was 30 mg Pt L^{-1} and turbidity was equal to 8.8 NTU. TOC concentration was equal to 14.8 mg L^{-1}, whereas DOC was 12.6 mg L^{-1}.

The effectiveness of turbidity and colour removal by various coagulants as well as the changes in PV and TOC concentration during coagulation are presented in Table 2. It summarises the results for the remaining aluminium concentrations, too. Based on the results of turbidity removal efficiency, it was stated that the most effective agent (under the conditions of coagulation process: $T = 18-20$°C and pH 7.8−7.5) was PAX-XL1905. The application of this product at a dose of 3 mg Al L^{-1} decreased turbidity of water from 8.8 to 1.9 NTU. Also, PAX18 agent was effective in removing of turbidity (decreased turbidity to 2.1 NTU). With aluminium sulphate (non-hydrolysed) 3.7 NTU value was obtained in treated water.

PAX-XL1905 was also the most effective product for colour removal (decreased colour from 30 to 10 mg L^{-1}). PAX-XL3, 10, 61, 69 and PAX-XL19F agents reduced colour to 15 mg Pt L^{-1}, whereas aluminium sulphate to 20 mg Pt L^{-1}. Better effectiveness of PAX products was probably connected with the fact that in solutions of these compounds polymerised products of preliminary hydrolysis are present. Higher effectiveness of hydrolysed coagulants compared with aluminium sulphate results not only from the presence of Al_{13} polycations, but also from the difference in a structure of the aluminium hydroxides which are generated during hydrolysis of these coagulant agents [12,13].

Organic compounds (measured as TOC) content after coagulation with aluminium sulphate decreased from 14.8 to 10.8 mg L^{-1}, whereas the use of pre-hydrolysed products reduced the concentration of TOC to 10.2–11.1 mg L^{-1}. The advantage of PAX-XL1905 use was that, it has low concentration of residual aluminium in the treated water (it was lower than 0.1 mg L^{-1}).

Fig. 1 presents percentage removal of turbidity and TOC from surface water during the coagulation process with a dose of 3 mg Al L^{-1}. Using 3 mg Al L^{-1} of PAX-XL1905 allowed for a decrease in turbidity by 78% and TOC by 31%. The other PAX products reduced turbidity by 64/76% and TOC by 25/28%. Aluminium sulphate decreased turbidity and TOC by 58 and 27%, respectively.

Effectiveness of the coagulation process in removal of organic pollutants increases together with the molecular weight. The same relationship can be observed between the effectiveness of coagulation and a degree of aromaticity. The best effectiveness of pollutants removal is achieved in the case of large-molecular hydrophobic aromatic compounds, the worst one for low-molecular and non-ionic hydrophilic fractions [14]. In this study, the reason for low effectiveness of organic compounds removal during coagulation was a high share (over 85%) of DOC in TOC.

The effects of coagulation of surface water were compared with efficiency of the adsorption process (the second stage of research work). The effectiveness of turbidity, colour and DOC removal according to the type and dose of powdered activated carbon is presented in Table 3.

It was stated that as the dose of powdered activated carbons (both CWZ 30 and AKPA 20) increased, the effectiveness of DOC removal from sample also increased, but it was not a very significant change. DOC concentration decreased by 20–23%. It could be caused by sorption of larger organic particles onto mesopores. As a result, the access of smaller particles

Table 2
Effect of coagulation with various agents on selected physicochemical properties of water

Coagulant	Dose mg Al L^{-1}	pH –	Turbidity NTU	Colour mg Pt L^{-1}	PV mg O$_2$ L^{-1}	TOC mg L^{-1}	Aluminium mg L^{-1}
Raw water	–	7.8	8.8	30	6.6	14.8	0
$Al_2(SO_4)_3$	1	7.6	6.7	25	5.8	14.1	0.35
	2	7.5	5.5	20	5.0	12.5	0.30
	3	7.5	3.7	20	4.6	10.8	0.35
PAX18	1	7.6	4.9	25	5.6	12.6	0.30
	2	7.6	3.4	20	4.8	11.3	0.26
	3	7.6	2.1	20	4.1	10.9	0.20
PAX-XL3	1	7.6	4.9	20	5.6	13.1	0.20
	2	7.6	4.5	20	5.1	12.3	0.20
	3	7.6	2.6	15	4.8	11.1	0.12
PAX-XL10	1	7.6	4.6	20	5.2	12.2	0.16
	2	7.5	4.2	20	4.9	11.6	0.16
	3	7.5	3.2	15	4.3	10.7	0.20
PAX- XL19F	1	7.7	6.7	20	5.3	13.8	0.12
	2	7.7	5.3	20	4.7	11.7	0.12
	3	7.7	3.0	15	4.4	11.1	0.16
PAX- XL1905	1	7.7	3.9	20	4.9	11.5	0.07
	2	7.7	3.0	15	4.4	10.7	0.07
	3	7.7	1.9	10	3.5	10.2	0.04
PAX- XL61	1	7.5	5.1	25	5.7	12.6	0.20
	2	7.5	4.5	20	5.3	12.0	0.20
	3	7.5	2.7	15	4.5	10.9	0.16
PAX- XL69	1	7.6	4.8	20	5.4	12.3	0.16
	2	7.6	4.0	15	4.7	12.1	0.12
	3	7.5	2.8	15	4.2	10.6	0.16

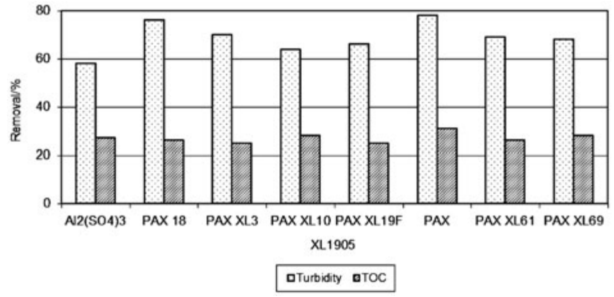

Fig. 1. Removal of turbidity and TOC from raw water during coagulation with various coagulants at dose equal to 3 mg Al L^{-1}.

was blocked. Simultaneously, CWZ 30 made it possible to decrease the colour of water by 70%.

During the third stage of the study, coagulation was enhanced by a powdered activated carbon addition. The process was investigated under decreased pH of water (the value of the parameter was equal to 6). This parameter was decreased because as it was stated by other researchers, a decrease in water pH can improve the results of this process regarding organic contaminants removal [14,15]. It is connected with the fact that pH value is the factor which affects the mechanism of coagulation. The mechanism of the process is connected both with kind of coagulation products and with a form of organic pollutants present in water.

Values of selected properties of water (turbidity, colour, DOC and TOC) before and after coagulation as a function of pH, coagulant type and powdered activated carbon CWZ 30 are listed in Table 4.

The experiments confirmed that lowering the value of pH made it possible to increase the effectiveness of organic compounds removal. Coagulation of water with PAX-XL1905 (dose 3 mg Al L^{-1}) and at pH 6.2 resulted in a decrease in TOC value from 25.9 to 16.3 mg L^{-1}. Using aluminium sulphate (at the same pH value) decreased TOC to 17.5 mg L^{-1}. DOC value decreased from 18.3 to 10.1 and 10.6 mg L^{-1} in the case of PAX-XL1905 and aluminium sulphate, respectively. When pH of water was lower than it was of natural water, percentage removal of TOC was about 11–12% higher and DOC removal was about 31–32% higher.

Table 3
Effect of adsorption with activated carbon on selected physicochemical properties of water

Activated carbon	Dose mg L^{-1}	pH –	Turbidity[a] NTU	Colour[a] mg Pt L^{-1}	DOC[b] mg L^{-1}
Raw water	–	8.2	26.7	40	18.3
CWZ 30	15	8.2	3.3	20	14.3
	30	8.3	2.8	15	14.2
	45	8.5	3.1	12	14.5
AKPA 22	15	8.1	4.4	30	14.6
	30	8.1	5.2	25	14.4
	45	8.2	4.6	20	14.1

[a] Analysed in sample after adsorption filtered through filter paper.

[b] Analysed in sample after adsorption filtered through 0.45 μm filter.

Table 4
Effect of pH and activated carbon addition on selected physicochemical properties of water during coagulation with $Al_2(SO_4)_3$ and PAX-XL1905 at doses equal to 3 mg Al L^{-1}

Coagulant + activated carbon	pH initial –	pH –	Turbidity NTU	Colour mg Pt L^{-1}	DOC mg L^{-1}	TOC mg L^{-1}	Aluminium mg L^{-1}
Raw water	8.2	–	26.7	40	18.3	25.9	0
$Al_2(SO_4)_3$	8.2	7.3	5.3	30	16.2	20.7	0.22
	7.1	6.8	4.2	25	13.7	20.4	0.20
	6.2	6.1	3.4	25	10.6	17.5	0.26
$Al_2(SO_4)_3$ + CWZ 30	8.2	7.3	8.7	25	16.2	19.6	0.16
	6.2	6.1	3.8	15	10.5	16.6	0.07
PAX- XL1905	8.2	7.9	2.9	20	15.9	19.2	0.07
	7.1	7.2	2.3	20	13.9	19.0	0.07
	6.2	6.4	2.1	10	10.2	16.3	0.04
PAX- XL1905 + CWZ 30	8.2	7.8	5.6	15	15.5	18.7	0
	6.2	6.4	4.0	5	10.0	15.1	0

Correction of pH caused better susceptibility of humic compounds for removal during the coagulation process.

The use of powdered activated carbon (CWZ 30) did not affect significantly the efficiency of organic compounds removal. Concentrations of TOC and DOC were comparable in water treated with aluminium sulphate alone, PAX-XL1905 alone and with aluminium sulphate and PAX-XL1905 with a powdered activated carbon amendment. Decreasing of water pH to the value of 6.2 also did not enhance the effectiveness of organic compounds removal in the samples with CWZ 30 addition. Changes in the effectiveness of organic compounds removal were not significant (about 4–5%) for both coagulants. However, contemporaneously it was observed that the effectiveness of turbidity removal was lower.

A simultaneous use of powdered activated carbon and coagulants improved; however, the colour removal by 88 and 63% in the case of PAX-XL1905 and $Al_2(SO_4)_3$, respectively. No aluminium ions were present in water after coagulation with PAX XL1905 supported by addition of activated carbon CWZ 30.

As it was stated by [16] coagulation was more effective in removal of the high molecular weight organic compounds (from 2.1 to 5.3 kDa). The concentration of the mentioned compounds decreased by 70%, whereas in the case of low-molecular weight compounds (1.5–2.1 kDa and 1.0–1.5 kDa) was reduced by 26 and 3.5%, respectively. Addition of powdered activated carbon at a dose of 30 mg L^{-1} increased removal efficiency to 39 and 17.5%. This phenomenon confirms the fact that a number of organic compounds present in water was not susceptible for removal both using coagulation and adsorption processes [16].

4. Conclusions

The use of pre-hydrolysed salts—polyaluminium chlorides—allowed one to obtain better effects of surface water treatment compared with non-hydrolysed aluminium salt (aluminium sulphate). The conclusions are as follows:

(1) at the dose of $3\,\mathrm{mg\,Al\,L^{-1}}$, the best effects of turbidity, colour and organic matter removal were obtained using polyaluminium chloride of high alkalinity (89% reduction in turbidity and 50% in colour was achieved; TOC value decreased by 26% and DOC by 13%);
(2) when pH decreased from 8.2 to 6.2 the effectiveness of organic compounds removal increased (upto 37 and 44%, for TOC and DOC respectively);
(3) the use of polyaluminium chloride made it possible to obtain residual aluminium concentration lower than $0.1\,\mathrm{mg\,L^{-1}}$, whereas when aluminium sulphate was used it was equal to $0.3\,\mathrm{mg\,L^{-1}}$;
(4) the addition of powdered activated carbon to water during the coagulation process did not significantly affect the effectiveness of organic compounds removal, both at natural pH 8.2 and pH equal to 6.2.

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