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Removal of natural organic matter from groundwater by coagulation using prehydrolysed and non-prehydrolysed coagulants

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ABSTRACT

The aim of the present study was to compare the effectiveness of coagulation process carried out using non-prehydrolysed coagulants (iron (III) sulphate (VI) and aluminium sulphate (VI)) and prehydrolysed polyaluminium chlorides differing in basicity in the removal of natural organic matter (NOM) from groundwater. Volume coagulation was carried out in groundwater samples after aeration at natural pH or at pH adjusted to 6.0–8.5. The Al species (Al_a-monomeric, Al_b-polymerized, Al_c-colloidal) distribution in the aluminium coagulants were analyzed by the Ferron complexation timed spectrophotometry. The fraction distributions of NOM and residual aluminium after coagulation were analyzed as changes of coagulant dose and pH. The efficiency of polyaluminium chlorides in the removal of NOM was found to increase with the polymerization of the products of aluminium prehydrolysis. Prehydrolysed coagulants were of greater utility than non-prehydrolysed coagulants in removing not only non-dissolved, but also dissolved fractions of NOM, and they were efficient over a wider range of pH. When the proportion of dissolved organic carbon in the total organic carbon load increased, the efficiency of total organic carbon removal decreased regardless of the type of coagulant tested. The worst results in the removal of NOM were produced by the iron coagulant.

Keywords: Groundwater; Natural organic matter; Coagulation; Non-prehydrolysed coagulants; Prehydrolysed coagulants

1. Introduction

Natural organic matter (NOM) is present in all natural water sources in varying concentration. The concentration, composition and chemistry of NOM are highly variable and depend on the environmental conditions under which it has been formed. Amongst main NOM constituents low molecular weight components such as hydrophilic acids, proteins, amino acids as well as macromolecular compounds like humic substances (HS) are worth mentioning [1,2]. Aquatic HS constitute 40–60% of dissolved organic carbon and are the largest fraction of natural organic matter in water [3]. HS are considered as the natural polyelectrolytic organic compounds of complex structure involving a proportion of more or less condensed aromatic rings with a large number of attached -OH and -COOH groups [4,5]. The presence of HS causes many problems in the quality of drinking water. Water quality problems associated with HS are colour, taste and odor and the formation of disinfection by-products like trihalomethanes (THM) and haloacetic acids are the most common. The disinfection by-products have become a focus of attention in water treatment, since they have been reported to have adverse health effects. HS can also form complexes with heavy metals and organic micro pollutants and enhance bacterial regrowth in distribution system [6–10].

NOM should be removed from water during treatment to the level compliant with drinking water quality standards: TOC (total organic carbon) ≤ 5 mg C/L [11]. Various processes are employed to achieve this goal, with coagulation, actived carbon adsorption, oxidation, ion exchange and membrane filtration as those in common use [12–15]. Despite the increasingly wide introduction of membrane technologies for water treatment, coagulation is still a fun-

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damental a unit process used to remove NOM from raw water. Most of the NOM can be removed by the coagulation method, although, the hydrophilic, low molecular weight fractions of NOM is apparently removed less efficiently than the hydrophobic, high molecular weight compounds [16–18].

The problem of how to increase the efficiency of coagulation for the removal of natural organic matter is still raising interest. According to Libecki and Dziejowski [19] aluminium salts remove natural organic matter from water better than iron salts because Fe^{3+} ions or the hydrolysis products of iron (III) salts interact more strongly with organic substances, compared to Al^{3+} ions. Matilainen et al. [16] and Cheng and Ghi [20] are of the opinion that iron (III) salts have been noted to be better in removing NOM than aluminium salts in many investigations. Especially the removal of middle size NOM fractions is noted to be more efficient. According to Ghernaout et al. [21] coagulation of dissolved organic matter is best at pH values around pH 5 for Al(III) and around pH 4 for Fe(III). Cheng et al. [22] and Libecki and Dziejowski [19] states that coagulation of natural organic matter is best at pH values of about 5–6 with aluminium sulphate (VI) and pH of 4.5–5.5 with iron (III) sulphate (VI). Although the mechanisms for organic matter removal by metal coagulants are not yet fully understood, two mechanism are likely to occur. According to Pernitsky and Edzwald [8] the first mechanism is adsorption of positively charged coagulant species to sites on the negatively charged natural organic matter to obtain charge neutralization and the formation of insoluble complexes. The second mechanism is adsorptions of natural organic matter to, or enmeshment in, the metal hydroxide precipitates (adsorption/sweep coagulation). The first mechanism is generally more dominant at lower coagulant dosage and pH conditions, and for coagulation by prepolymerized coagulants. For the second mechanism, which predominates at higher coagulant dosage and pH, it is important to notice that hydroxides cannot precipitate until most of the natural organic matter have been complexed.

In recent years, the prehydrolysed aluminium coagulants, e.g. polyaluminium chloride and polyaluminium sulphate have been developed and researched. In water treatment plants in order to improve the efficiency of coagulation process, the use of prehydrolysed coagulants in place of aluminium sulphate (VI) is common practice. Prehydrolysed reagents based on polymerized forms of aluminium generally are more effective in removing natural organic matter compared to non-prehydrolysed coagulants e.g. aluminium sulphate (VI) [23–31]. Polyaluminum chlorides represented by the general formula $Al_n(OH)_mCl_{3n-m}$ are primarily used. The alkalinity of polyaluminium chloride is determined by the quotient of the number of moles OH^- to Al^{3+} in a coagulant, referred to as the alkalinity ratio (r), which is approached as a coagulant polymerization degree measure. "Al_{13}" polymer ($Al_{13}O_4(OH)_{24}{}^{7+}$) is the most stable and efficient in colloid destabilization of all aluminium polymers and its amount increases along with the alkalinity ratio (r) increase to 2.1. The degree of polymerization can be determined by means of ferron-timed spectroscopy method. The different species can be classified into three categories: the mononuclear (Al_a), medium polynuclear (Al_b) and precipitated/colloidal (Al_c) species, in which the Al_b species are considered to be the most efficient species for DOC (dissolved organic carbon) removal [16]. These coagulant species (Al_b) are considered to be the most efficient Al-species due to their larger size and higher positive charges. A large number of investigations and practical applications show that the ($Al_{13}O_4(OH)_{24}{}^{7+}$) (simplified as Al_{13}) is the most efficient species for organic matter removal because of its high stability and positive electric charge [32–40]. The prehydrolysed coagulants cause smaller consumption of the natural water alkalinity and lower its pH reaction to a smaller extent than coagulants that are non-prehydrolysed. Increased efficacy of reagent containing prehydrolysis products implies the possibility of reduction of the required dose [41,42]. The polymeric structure of the hydrolysis products causes that polyaluminium chlorides show agglomerating properties, thus improving flocculation conditions. The effectiveness of coagulation to remove NOM depends on several factors, including coagulant type and dose, mixing conditions, pH, temperature, particle and NOM properties. In spite of the development of new separation techniques for water treatment, the coagulation process will continue to be the most important water-treatment process for removal of NOM.

The goal of the present study was to compare the effectiveness of coagulation process carried out using classical hydrolyzing coagulants (iron (III) sulphate (VI) and aluminium sulphate (VI)) and prehydrolysed coagulants differing in basicity in the removal of NOM from groundwater. In this study the effect of Al species (Ala-monomeric, Alb-polymerized, Alc-colloidal) distribution in the aluminium coagulants on the coagulation performance of NOM was also evaluated. The fraction distributions of NOM (TOC, DOC, colloidal organic carbon, UV absorbance at 254 nm) and residual aluminium after coagulation were analyzed as changes of coagulant dose and pH.

2. Materials and methods

2.1. Water samples used to coagulation

Water used in coagulation process was groundwater from Quaternary formations characterized by a increased amount of natural organic matter (TOC from 5.70 to 7.00 mg C/L, DOC from 4.00 to 4.60 mg C/L, colloidal organic carbon (COC) from 1.70 to 2.40 mg C/L, UV absorbance at 254 nm from 0.198 to 0.295 cm^{-1}) and also a high concentration of total iron - amounting to 7.20 mg Fe/L, more intensive colour - up to 33 mg Pt/L, turbidity up to 30 NTU and manganese (up to 0.39 mg Mn/L). Iron (II) from 5.00 to 6.00 and iron (III) from 1.00 to 2.00 mg Fe/L compounds were present in the water. These characteristics of the water were the cause of the unfavorable extent of the removal of iron compounds from it in the conventional system of underground water treatment. The turbidity and intensity of apparent and real colour of water proved the occurrence of iron in the form of colloidal and dissolved bonds with NOM, for the removal of which the coagulation process was used.

2.2. Experimental procedure of coagulation

In the research the effectiveness of volumetric coagulation in groundwater treatment was determined. In order to oxidise the Fe(II) to Fe(III) before the coagulation process samples of groundwater was aerated with compressed air for 15 min until a concentration of about 10 mg O_2/L i.e. ca.100% saturation of water with oxygen has been obtained. The aeration of the water caused an increase in turbidity, colour and pH of the water by one unit within the range of 7.0–8.0. Jar tests were carried out by using a 1 L six-place paddle stirrer (Flocculator Kemira 2000, Sweden). Coagulation was carried out in water samples with aeration of 1 L through 1 min. fast mixing at a speed of 250 rpm and 25 min. flocculation with an intensity of mixing of 30 rpm. The coagulants used were classical hydrolyzing coagulants: iron (III) sulphate (VI) - PIX112 and aluminium sulphate (VI) (SAL) as well as prehydrolysed polyaluminium chlorides with the trade names PAX XL19H and Flokor 1A that had different alkalinity and aluminium content (Table 1). The experiments involved a natural pH or a pH adjusted to 6.0–8.5, using aqueous solutions of HCl, H_2SO_4 or NaOH. The doses of coagulants were expressed in mg Fe/L or mg Al/L and varied from 1 to 5 mg Al(Fe)/L. After coagulation the samples were subject to sedimentation process for 1 h.

2.3. Analytical methods

The physical-chemical composition of both the raw groundwater as well as treated water was determined according to the International Standard methods. The NOM concentration was monitored by measuring the TOC, DOC, colloidal organic carbon (COC) and UV absorbance at 254 nm. The TOC, DOC and COC were measured using the thermal method and a Shimadzu TOC analyzer. DOC was analyzed by the TOC analyzer after filtration through 0.45 μm pore diameter membranes. Water samples subjected to filtration on 1.2 μm pore diameter membranes were used to establish the sum of COC and DOC and thereafter to calculate COC. In the data analysis, the quotient of DOC to TOC concentrations was defined as the coefficient B. UV absorbance at 254 nm (UV_{254}) was measured by a UV-VIS spectrophotometer Agilent Cary 60 using a quartz cell with 1 cm path length after filtration through 0.45 μm membrane. The colour (according to Pt scale), total iron, iron (II) concentrations were determined with the Dr 3900 (HACH Lange) spectrophotometer. Iron (II) was measured using the 1,10 phenanthroline method. Total iron was measured using the same method. As a reducing agent of ferric ions to the ferrous ions, hydroxylamine hydrochloride was used. Aluminum and manganese concentrations were determined with the atomic emission spectroscopy (ISP-OES, 5300DV, Perkin Elmer Company, US). Total aluminium and dissolved aluminium concentrations were measured before and after sample filtration through a 0.45 μm membrane, respectively. The temperature and pH of the raw water and the purified water was determined with an WTW Multi Line P4 with an combination pH electrode with temperature corrections. The dissolved oxygen of the raw water and the purified water was determined with an WTW Multi 3410 SET 4 with an optical oxygen sensor FDO^R 925 (Germany). Turbidity was measured using the Hach 2100N Turbidimeter. The alkalinity was determined with a titrimetric method against methyl orange using 0.1 M aqueous solutions of HCl. The Al species distribution in the PACls (Flokor 1A, PAXXL19H) and aluminium sulphate (VI) samples were analyzed by the Ferron complexation timed spectrophotometry [35,42]. Al(III) reacts with Ferron reagent to form Al-Ferron complex at pH = 5, λ = 370 nm. Agilent Cary 60 spectrophotometer was used to measure the Al-Ferron kinetics. Based on the kinetic difference of reactions between Ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid) with different hydrolyzed species, hydrolyzed Al species can be divided into three types: monomeric Al species (Al_a) (instantaneous reaction: 0–1 min), medium polymerized Al species (Al_b) (reaction within 120 min) and species of colloidal (Al_c) (no reaction in 120 min). The results are shown in Table 2.

Table 1
Selected properties of the coagulants tested [43,44]

Indicator	Type of coagulant			
	Flokor 1A	PAX XL19H	SAL	PIX 112
Alkalinity ratio, $[OH^-]/[Al^{3+}]$	2.40	2.55	0	–
Alkalinity, %	80.0	85.0	–	–
Al^{3+}, %	11.0	12.5	4.3	–
Fe_{tot}, %	–	–	< 0.007	12
Cl^-, %	6.5	8.5	< 0.1	< 0.1
SO_4^{2-},%	–	–	22.5	30.0

3. Results and discussion

During the studies, the course and effectiveness of volumetric coagulation after aeration in groundwater was determined.

3.1. The effect of the type and dose of a coagulant on the efficiency of removing NOM

The scope of the analytical research carried out made it possible to assess the effect of the type and dose of a coagulant, pH of the treated water and a degree of polymerization of the tested aluminium coagulants on the efficiency of removing natural organic matter from groundwater in the coagulation process.

Regardless of the physical-chemical composition of the water being purified, the effectiveness of removing NOM (TOC, DOC, COC, UV_{254}) and reducing colour increased as the doses of the coagulants tested increased (Figs. 1 and 2).

The effects of the research presented in Fig. 1 and Fig. 2 also prove that the efficiency of the tested aluminium coagulants in removing NOM (TOC, DOC, COC, UV_{254}) as well

Table 2
The degree of polymerization of the aluminium coagulants tested according the conventional ferronometry

Al species	Flokor 1A	PAX XL19H	SAL
Monomeric Al species (Al_a), %	3	38	91
Polymerized Al species (Al_b), %	54	35	9
Colloidal Al species (Al_c),%	43	27	0

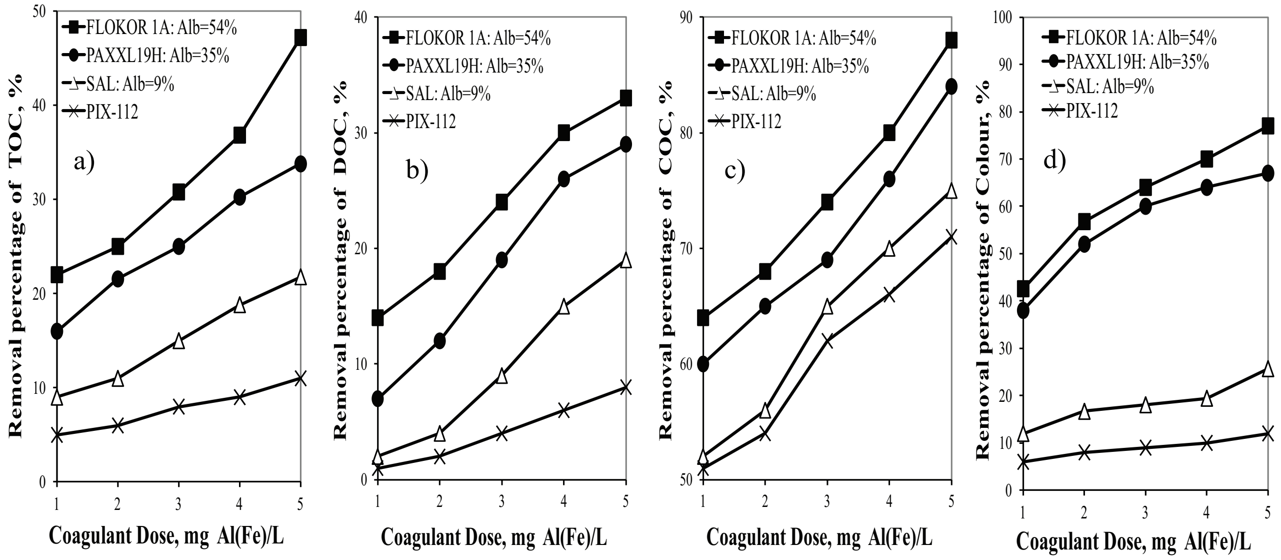


Fig. 1. The effect of the type and dose of a coagulant on the efficiency of removing TOC (a) DOC (b) COC (c) and colour (d).

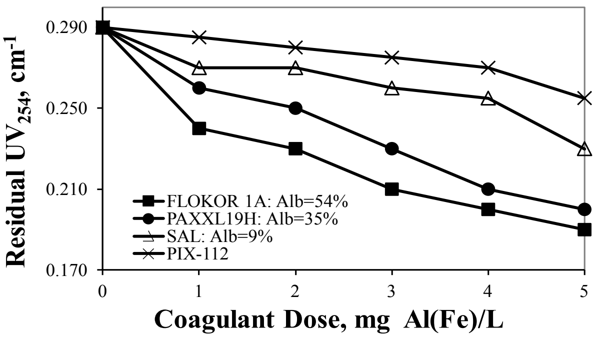


Fig. 2. The effect of the type and dose of a coagulant on the residual UV absorbance at 254 nm in treated water.

as in decreasing the colour intensity increased along with an increase of polymer aluminium forms in the tested coagulants (Table 2). The least efficient coagulant was the iron coagulant PIX-112 and, from among the tested aluminium coagulants, the worst effects were produced by classical hydrolyzing coagulant aluminium sulphate (VI) characterised by the smallest contents of polymer aluminium forms (Al_b = 9%). The lowest effectiveness of the iron coagulant PIX-112 at removing NOM and reducing colour was caused by the occurrence of coloured combinations of natural organic matter present in the water being purified with Fe(III) introduced into the water with this coagulant. The concentration of iron residual in water after coagulation exceeded the value of 0.2 mg Fe/L, yet it was about twice smaller in samples of water treated with aluminium coagulants (0.60–0.27 mg Fe/L - SAL; 0.40–0.22 mg Fe/L - Flokor 1A and PAXXL19H) than with iron coagulant PIX-112 (1.20–0.60 mg Fe/L). According to Libecki and Dziejowski [19] iron and aluminum coagulants react differently with organic matter in water. Riedel and Biester [40] and Albrektiene et al. [6] demonstrated that the ability to bind organic ligands in surface water increases as follows: $Ca^{2+} < Al^{3+} < Fe^{3+}$. According to Albrektiene et al. [6] humic acid-Fe chelate complexes are formed when two or more coordination positions about the iron species are occupied by donor groups of humic acid (HA) ligand to form an internal ring structure. The compexing ability of HA results largely from their content of oxygen -containing functional groups, such as the COOH, phenolic OH and C=O. Iron species directly produce insoluble complexes with HA oxygen-containing functional groups which can be removed by sedimentation. The relations presented in Fig. 1b and Fig. 2 show that, polyaluminium chlorides are more efficient in removing DOC than aluminium sulphate (VI) and they also decrease UV absorbance at 254 nm. The relations illustrated in Fig. 2 also lead to the conclusion, that polyaluminium chlorides remove natural organic matter characterised by high contents of aromatic rings, such as humic substances, more effectively than hydrolyzing coagulants. From among the analysed polyaluminium chloride, the highest efficiency in removing DOC, COC, lowering UV absorbance at 254 nm and decreasing colour intensity was shown by Flokor 1A characterised by much higher contents of polymer aluminium forms (Al_b = 54%) than PAXXL19H (Al_b = 39%). Many studies [8,31,32,42] have confirmed that the content of preformed Al_b in polyaluminium chlorides is correlated well to the tridecamer ($Al_{13}O_4(OH)_{24}^{7+}$), often denoted as Al_{13}. In addition, preformed Al_b species possess high stability when dosed into water and it is the species formed when traditional aluminium salts were added into water under certain conditions. The differences between the efficiency of polyaluminium chlorides in removing DOC and in lowering UV absorbance at 254 were, generally, higher for smaller doses (Fig. 1b and Fig.2). Increasing a dose of sulphate (VI) iron (III) increased the efficiency of removing DOC (the most difficult fraction to remove) only to a small extent (Fig. 1b). With dosage gradually increased to 5 mg Al/L, aluminium sulphate (VI) becomes more efficient in DOC removal. Note that the solution pH drops with aluminium sulphate (VI) dosage increases (pH in water after coagulation: 7.75-7.20.), while only slight pH changes were observed for the polyaluminium chlorides (pH in water after coagulation: 8.00–7.70 Flokor 1A; 8.00–7.75 PAXXL19H). When considering the distribution of Al species (Table 2), the Al_b content in polyaluminium chlorides is correlated well with the removal of DOC due to its high charge neutralization ability. In the low dosage situation, more Al_b species is present in the solution to neutralize the negatively charged organic matter to enhance to removal. In the aluminium sulphate (VI) case, higher DOC removal under high dosage conditions could result from the in situ formation of Al_b under low pH conditions. Although the removal behaviour of the in situ formed Al_b has not been well identified, it is believed that its charge neutralization ability could also be relatively high [42]. Of the organic carbon fractions examined, COC was removed with the highest efficiency (Fig. 1), according to expectations. In terms of the efficiency of removing NOM (TOC, DOC, COC, UV_{254}) and lowering the colour intensity, the efficiency of the tested coagulants decreased according to the below presented series:

FLOKOR 1A (Al_b=54%) > PAXXL19H (Al_b=35%)>SAL (Al_b=9%) > PIX –112 (Al_b=0) that illustrates the decreasing contents of polymer aluminium forms (Al_b,%) in the tested coagulants.

The comparison of the doses of iron coagulant-PIX112, aluminium sulphate (VI) and polyaluminium chlorides used for treating the same groundwater ensuring a comparable efficiency of removing TOC (25%), DOC (19%), COC (72%), UV_{254} (17%) and colour (64%) presented in Table 3, indisputably indicates the greatest efficiency of the pre-hydrolyzed coagulant Flokor 1A possessing the highest amount of polymerized Al species (Al_b) - Table 2.

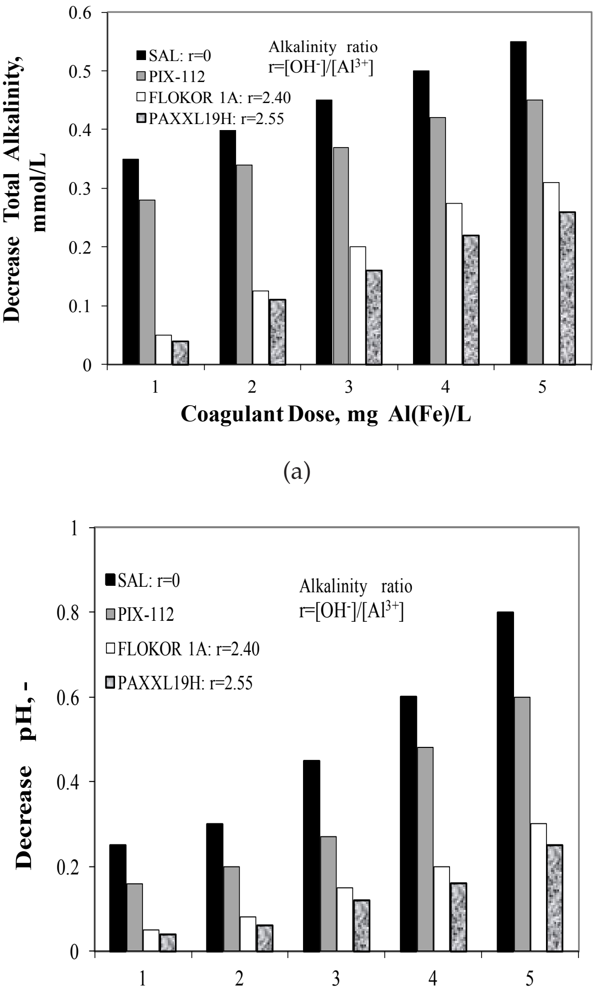
The studies conducted by Nowacka et al. [28] proved that the optimal doses of prehydrolysed coagulants were much lower than in the case of aluminium sulphate (VI) and of iron (III) sulphate (VI). As a result of the coagulation process with all types of the tested coagulants, water alkalinity was used up and the concentration of hydrogen ions increased. Polyaluminium chlorides caused much lower water acidification and lowering of alkalinity than aluminium sulphate (VI) and iron (III) sulphate (VI) for all the range of the doses of the tested coagulants (D_c = 1÷5 mg Al(Fe)/L), which is important in terms of water chemical stability. Differences in lowering water total alkalinity and water pH in relation to the type and dose of the coagulant used are shown in Figs. 3a and 3b. The dependencies presented in Figs. 3a and b show that an increase in the alkalinity ratio of the prehydrolysed coagulants decreased water acidification and consumption of its total alkalinity.

Table 3
The required doses of coagulants (D_{re}) ensuring comparable efficiency of removing TOC and components of groundwater causing colour

Type of coagulant	D_{re}, mg Al(Fe)/L :			
	TOC	DOC	UV_{254}	Colour
PIX112	$D_{re} > 5$	$D_{re} > 5$	$D_{re} > 5$	$D_{re} > 5$
SAL	$D_{re} > 5$	$D_{re} > 5$	$D_{re} > 5$	$D_{re} > 5$
PAXXL19H	3	3	3	4
FLOKOR 1A	2	2	2	3

The studies conducted by Pernitsky and Edzwald [34] proved also that the prehydrolysed coagulants cause smaller consumption of the natural water alkalinity and lower its pH reaction to a smaller extent than coagulants that are non- prehydrolysed. The effects of the research presented in Fig. 4 also prove that the efficiency of TOC removal was affected not only by coagulant type, but also by the percentage of DOC in the total organic matter in the water to be treated. When the value of coefficient B increased, the efficiency of TOC removal decreased although the doses the investigated coagulants remained unchanged (Fig.4).

During the research the concentration of aluminium residual in the water after coagulation with aluminium coagulants: aluminium sulphate (VI) and polyaluminium chlorides was also determined. It was found that also in this aspect polyaluminium chlorides had been more effective. The obtained results are confirmed by the literary data Sillanpää et al. [31] substitution of aluminium sulphate (VI) by polyaluminium chlorides reduced the concentration of



(a)

(b)

Fig. 3. The effect of the type and dose of coagulant on decreasing total alkalinity (a) and pH (b) of the treated water.

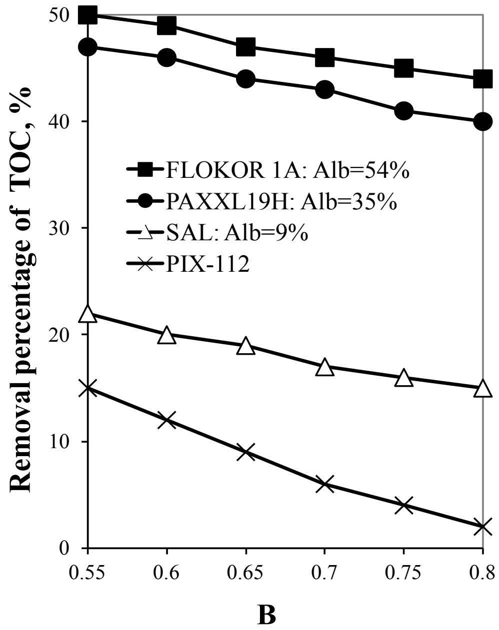


Fig. 4. The effect of percentage of DOC in total organic matter (B) on the efficiency of TOC removal (D_c = 3 mg Al(Fe)/L).

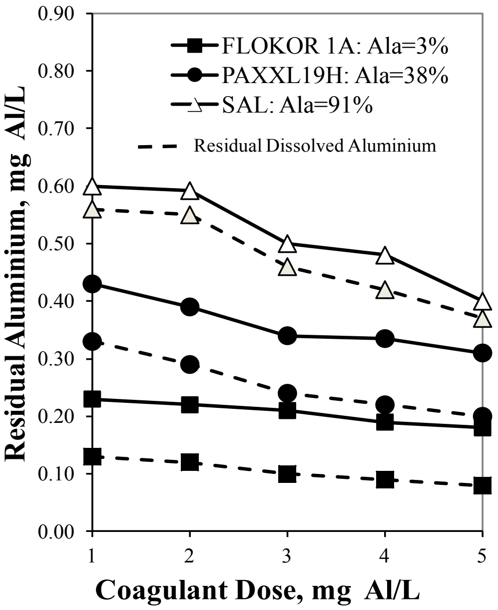


Fig. 5. The effect of the type and dose of coagulant on the residual aluminium content and on the residual dissolved aluminium content in the treated water.

aluminium residual in water after coagulation. As shown in Fig. 5 the residual aluminium and the residual dissolved aluminium changes also with various aluminium coagulants. The higher the content of Al_a, the higher the residual dissolved aluminium. The residual aluminium as high as more than 0.1 mg/L is obviously greater than the theoretical value calculated based on the solubility of $Al(OH)_3$. It implies that Al_a might be able to form soluble complexes with some organic matters, while the floc of Al_b and Al_c could be larger than the spore size of the 0.45 µm membrane and filtered off by the membrane. According Wang and Tang [42] for Al_a, the most reactive species out of the three, it is less efficient and can result in high residual aluminium in the finished water due to the complexation with organic matter.

3.2. The effect of pH correction on efficiency of removing NOM in the coagulation process

The value of pH of treated water affects greatly the course and the efficiency of coagulation process in removing NOM, because it decides about a form, thereby, about the stability of organic components removed as well as about the type and charge of the products of coagulant hydrolysis [25–27,39]. Therefore, the next tests were performed in order to determine the effect of water alkalization or water acidification on the efficiency of removing NOM from groundwater in the process of coagulation with aluminium coagulants. The tests on the effects of pH correction on the efficiency of removing natural organic matter, did not comprise investigating iron coagulant due to its lowest effectiveness in removing the above mentioned NOM shown in the previous tests. The test results obtained show, that the efficiency of removing natural organic matter from groundwater was also affected, apart from the type of the aluminium coagulant, by pH value of the treated water.

Water acidification before the coagulation process increased the efficiency of removing natural organic matter (TOC, DOC and COC) and in lowering colour intensity (Figs. 6a, b and c). Beneficial effect of water acidification (up to pH = 6) in case of removing organic matter and colour compounds was found for all tested coagulants and it was the highest when using the non-prehydrolysed coagulant aluminium sulphate (VI) possessing the highest contents of monomer aluminium forms (Al_a = 91%) (Figs. 6a, b and c, Table 2). At pH 6.0 aluminium sulphate (VI) becomes the most efficient coagulant for DOC removal. Increasing H^+ ion concentration in treated water provides conditions for forming cationic products of the hydrolysis of the non-prehydrolysed coagulant e.g. aluminium sulphate (VI). In acid environment, apart from providing favourable conditions for formation of polymer products of aluminium sulphate (VI) hydrolysis, there are conditions of decreased dissociation of NOM, which improved the efficiency of lowering organic matter and colour compounds [31–33]. Wang and Tang [42] have observed that the lower the alkalinity ratio of prehydrolysed coagulants, the more the Al_b formed in situ at acid pH range. DOC was removed most efficiently at pH 6, at which the content of Al_b reached the maximum. The opposite dependence, in case of removing natural organic matter (TOC, DOC and COC) and lowering colour intensity, was brought about by water alkalization. Water alkalization to pH = 8.5 led to a decrease in TOC removal efficiency in case of all tested coagulants as well as to the absence of DOC removal by aluminium sulphate (VI). The negative effect of alkalization from pH = 8.0 to pH = 8.5 on removal of organic matter and colour compounds was the smallest for Flokor 1A coagulant (Fig. 6, Table 4) possessing the highest contents of polymer aluminium forms (Al_b=54%) - Table

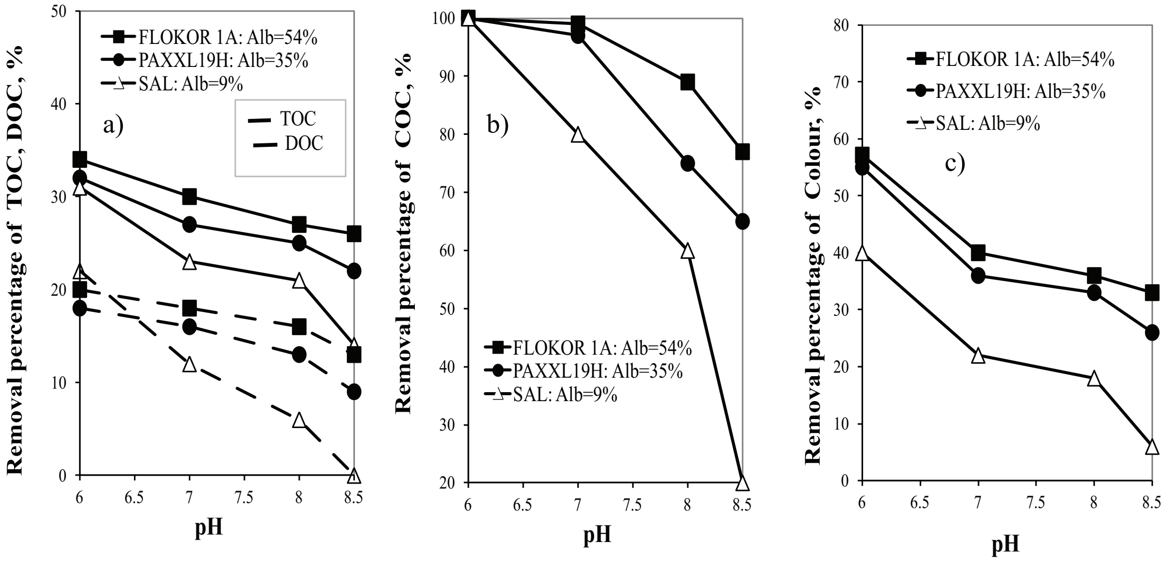


Fig. 6. The effect of pH correction and coagulant type (D_c = 3 mg Al/L) on the efficiency of removing TOC, DOC (a) COC (b) and colour (c).

2. This confirms reports in the literature, that prehydrolysed coagulants are less sensitive to changes in pH value because products of initial hydrolysis (occurring during coagulant formation) are more stable in water [25–28,34]. According Wang and Tang [42] the DOC removal efficiency is the lowest at pH 8.5 for all prehydrolysed coagulants, where most of Al_b transforms into Al_c.

The adjustment of pH to alkaline levels before coagulation reduced the efficiency of NOM removal. This is possibly due to the following mechanism: the rise in pH is concomitant with the increase in the dissociation of organic matter on one hand; on the other hand, there is a decrease in quantity of positively charged polymeric products of aluminium hydrolysis, which form in the course of coagulation [25,38,39]. The analysis of the results of tests also shows, that the pH correction, and especially alkalization, influences concentration of residual aluminium in water after coagulation (Fig. 7) which is very important due to the fact, that increased aluminium concentration may pose a potential risk to human health, causing brain lesions characteristic for the Alzheimer's disease. The suggested negative effect of the aluminium presence in water on human health as well as its allowable concentration in water intended for human consumption of ≤ 0.2 mg Al/L in Poland as well as the recommendations of WHO and EU impose and obligation to guarantee the minimum aluminium content in water intended for human consumption [36]. The highest concentration of residual aluminium was found in samples treated with aluminium sulphate (VI) for the whole pH range (pH = 6–8.5). Wang and Tang [42] attributed the higher residual aluminium concentrations in water to the high content of monomeric the aluminium species (Al_a) in the non-prehydrolysed coagulants. In case of prehydrolysed coagulants within the range of pH from 6 to 8, the concentration of residual aluminium was ≤ 0.2 mg Al/L, whereas at pH = 8.5 the allowable concentration of residual aluminium (0.2 mg Al/L) was obtained only after coagulation with Flokor 1A coagulant. Generally, in case of all the tested coagulants, the lowest concentration of residual aluminium was found in water samples with pH = 7, and the highest at pH = 8.5.

Table 4
Effect of water alkalization from pH = 8.0 to pH = 8.5 on coagulation efficacy (D_c = 3 mg Al/L)

Type of coagulant	Reduce the removal efficiency (Δη, %)		
	TOC	DOC	Colour
SAL	7	6	12
PAX XL19H	3	4	6
FLOKOR 1A	1	3	3

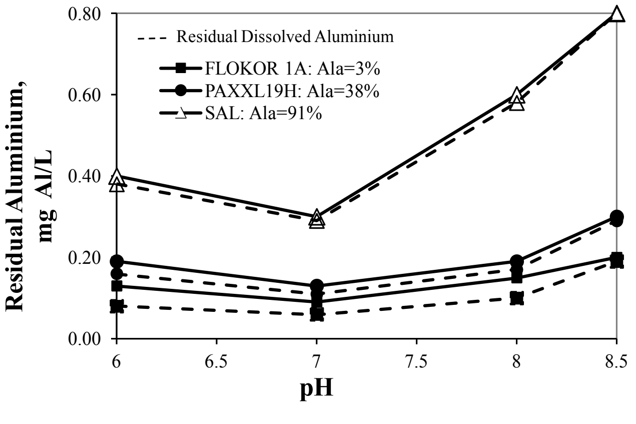


Fig. 7. The effect of pH correction and coagulant type (D_c = 3 mg Al/L) on the residual aluminium content and on the residual dissolved aluminium content in the treated water.

The increase in the concentration of aluminium left within the range of pH from 8 to 8.5 was caused by formation of $Al(OH)_4^-$ [8,25–27]. The negative effect of alkalization from pH = 8 to pH = 8.5 on removal of natural organic matter or the contents of residual aluminium in the treated water was, however, smaller in case of using polyaluminium chlorides than aluminium sulphate (VI) (Fig. 7). Control of solution pH is key to minimizing the aluminium concentration. According Sillanpää et al. [31] and Pernitsky and Edzwald [34] the use aluminium coagulants at around pH 6.5–7.0 is one approach for minimizing residual aluminium concentrations.

4. Conclusions

The studies performed on the effectiveness of non-prehydrolysed coagulants (iron (III) sulphate (VI) and aluminium sulphate (VI)) and prehydrolysed aluminium coagulants PAXXL19H and Flokor 1A in the removal of natural organic matter from groundwater led to the following conclusions:

- Prehydrlolysed coagulants were greater utility than non-prehydrolysed in removing not only non-disolved, but also dissolved fractions of natural organic matter, natural organic matter characterised by high contents of aromatic rings and they were efficient over a wider range of pH. When the proportion of dissolved organic carbon in the total organic carbon load increased, the efficiency of total organic carbon removal decreased in the course of the coagulation process. The worst results in the removal of natural organic matter in the coagulation process were produced by the iron coagulant.
- The removal efficiencies of natural organic matter correlate well with the aluminium species distribution of aluminium coagulants. Al_b was the most efficient for natural organic matter removal especially DOC. The best results in removing natural organic matter were produced by polyaluminium chloride Flokor 1A possessing higher contents of polymer aluminium forms ($Al_b = 54\%$) than PAXXL19H ($Al_b = 35\%$).
- Adjustment of pH to 6.0 increased the efficiency of total organic carbon and dissolved organic carbon removal, but the effect of this adjustment on removal efficiency was more distinct in the presence aluminium sulphate (VI) than in the presence of polyaluminium chlorides. Water alkalization to pH = 8.5 had negative effect on the removal of natural organic matter in the course of coagulation. At pH 8.5 mainly non-disolved fractions were removed, which was particularly evident after the use of aluminum sulphate (VI).
- The concentration of residual aluminium of the treated water decreased with an increase in polymerization degree of aluminium coagulants. The amount of Al_a in aluminium coagulants mainly determined the dissolved residual aluminum concentration after coagulation.

References

[1] A. Urbanowska, M. Kabsch-Korbutowicz, Characteristics of natural organic matter removed from water along with its treatment, Environ. Protect. Eng., 42 (2016) 183–195.

[2] B. Bazrafkan, Q. Wei, R. Fabris, C.W.K. Chow, J. Leeuwen, D. Wang, M. Drikas, Assessment of a new combined fractionation technique for characterization of the natural organic matter in the coagulation process, Desal. Water Treat., 48 (2012) 252–260.

[3] J.A. Leenheer, J.P. Croué, Characterizing aquatic dissolved organic matter, Environ Sci. Technol., 37 (2003) 18–26.

[4] A. Ziółkowska, The role of humic substances in detoxification process of the environment, Environ. Protect. Nat. Resour., 26 (2015) 1–5.

[5] I. Krupińska, Effect of organic substances on the efficiency of Fe(II) to Fe(III) oxidation and removal of iron compounds from groundwater in the sedimentation process, Civil Environ. Eng. Reports, 26 (2017) 15–29.

[6] R. Albrektiene, M. Rimeika, R. Grazeniene, Organic fractions and metal-organic complexes in the groundwater. The 9th International Conference "Environmental Engineering" 22–23 May 2014, Vilnius, Lithuania.

[7] M. De Julio, L. Di Bernardo, T.S. De Julio, S.X. de Campos, E.M. Vieira, Removal of humic substances with different apparent molecular sizes using Fenton's reagent, Desal. Water Treat., 46 (2012) 139–148.

[8] D.J. Pernitsky, J.K. Edzwald, Solubility of polyaluminium coagulants, J. Water Supply: Res. Technol., – AQUA 52 (2003) 395–406.

[9] A. Matilainen , E.T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, M. Sillanpää, An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment, Chemosphere, 83 (2011) 1431–1442.

[10] M. Kabsch-Korbutowicz, A. Urbanowska, Comparison of polymeric and ceramic ultra filtration membranes for separation of natural organic matter from water, Environ. Protect. Eng., 36 (2010) 125–135.

[11] Regulation of the Minister of Health dated December 7, 2017 amending the regulation on the quality of drinking water mean for human consumption.

[12] K. Choi, B. Dempsey, In-line coagulation with low-pressure membrane filtration, Water Res., 38 (2004) 4271–4281.

[13] M. Kabsch-Korbutowicz, J. Wiśniewski, S. Łakomska, A. Urbanowska, Application of UF, NF and ED in natural organic matter removal from ion-exchange spent regenerant brine, Desalination, 280 (2011) 428–431.

[14] M. Kabsch-Korbutowicz, A. Urbanowska, Effect of ion-exchange for NOM removal in water treatment with ceramic membranes ultra filtration, Membr. Water Treat., 3 (2012) 211–219.

[15] A. Urbanowska, M. Kabsch-Korbutowicz, Influence of operating conditions on performance of ceramic membrane used for water treatment, Chem. Pap., 68 (2014) 190–196.

[16] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interfac., 159 (2010) 189–197.

[17] T. Tuhkanen, A. Ketonen, L. Gilberg, J. Jahela, Removal of different size fractions of natural organic matter in drinking water by optimized coagulation, Chem. Water Wastewater Treat., VII (2004) 201–208.

[18] B. Aftab, J. Hur, Fast tracking the molecular weight changes of humic substances in coagulation/flocculation processes via fluorescence EEM-PARAFA, Chemosphere, 178 (2017) 317–324.

[19] B. Libecki, J. Dziejowski, Optimization of humic acids coagulation with aluminum and iron (III) salts, Pol. J. Environ. Stud., 17 (2008) 397–403.

[20] W. Cheng, F. Ghi, A study of coagulation mechanisms of polyferric sulfate reacting with humic acid using a fluorescence-quenching method, Water Res., 36 (2002) 4583–4591.

[21] D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electro coagulation, Desal. Water Treat., 2 (2009) 203–222.

[22] Y.L. Cheng, R.J. Wong, J.Ch. Te Lin, Ch. Huang, D.J. Lee, J.Y. Lai, Pre-Treatment of natural organic matters containing raw water using coagulation, Sep. Sci. Technol., 45 (2010) 911–919.

[23] L. Dąbrowska, Removal of organic matter from surface water using coagulants with various basicity, J. Ecol. Eng., 17 (2016) 66–72.

[24] W. Wang, H. Yang, X. Wang, J. Jiang, W. Zhu, Effects of fulvic acid and humic acid on aluminum speciation in drinking water, J. Environ. Sci., 22 (2010) 211–217.

[25] I. Krupińska, The influence of aeration and type of coagulant on effectiveness in removing pollutants from groundwater in the process of coagulation, Chem. Biochem. Eng. Q., 30 (2016) 465–475.

[26] I. Krupińska, The impact of potassium manganate (VII) on the effectiveness of coagulation in the removal of iron and manganese from groundwater with an increased content of organic substances, Civil Environ. Eng. Reports, 27 (2017) 29–41.

[27] I. Krupińska, The impact of the oxidising agent type and coagulant type on the effectiveness of coagulation in the removal of pollutants from underground water with an increased content of organic substances, J. Environ. Eng. Landsc., 24 (2016) 70–78.

[28] A. Nowacka, M.W. Makuła, B. Macherzyński, Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants, Desal. Water Treat., 52 (2014) 3843–3851.

[29] A. Nowacka, M. Włodarczyk-Makuła, B. Tchórzewska-Cieślak, J. Rak, The ability to remove the priority PAHs from water during coagulation process including risk assessment Desal. Water Treat., 57 (2016) 1297–1309.

[30] E. Sogaard, Production of the coagulation agent PAX-14. Contents of polyaluminium chloride compounds, Chem. Water Wastewater Treat., VII (2002) 3–16.

[31] M. Sillanpää, M. Ch. Ncibi, A. Matilainen, M. Vepsäläinen, Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review, Chemosphere, 190 (2018) 54–71.

[32] J.M. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid. Interfac., 100 (2003) 475–502.

[33] S. Hussain, J. van Leeuwen, Ch. Chow, S. Beecham, M. Kamruzzaman, D. Wang, M. Drikas, R. Aryal, Removal of organic contaminants from river and reservoir waters by three different aluminum-based metal salts: Coagulation adsorption and kinetics studies, Chem. Eng. J., 225 (2013) 394–405.

[34] D. Pernitsky, J. Edzwald, Selection of alum and polyaluminum coagulants: Principles and applications, J. Water Supply Res. T., 55 (2006) 121–141.

[35] W. Zhou, B. Gao, Q. Yue, L. Liu, Y. Wang, Al-Ferron kinetics and quantitative calculation of Al(III) species in polyaluminum chloride coagulants, Colloid Surface A., 278 (2006) 235–240.

[36] J.M. Sieliechi, G.J. Kayem, I. Sandu, Effect of water treatment residuals (aluminium and iron ions) on human health and drinking water distribution systems, Int. J. Conserv. Sci., 1 (2010) 175–182.

[37] J. Piekutin, I. Skoczko, K. Ignatowicz, Use of integrated process of petroleum removal from water, Desal. Water Treat., 57 (2016) 1593–1597.

[38] J. Lin, Ch. Huang, B. Dempsey, J.Y. Hu, Fate of hydrolyzed Al species in humic acid coagulation, Water Res., 56 (2014) 314–324.

[39] M. Wolska, Removal of precursors of chlorinated organic compounds in selected water treatment processes, Desal. Water Treat., 52 (2013) 3938–3946.

[40] T. Riedel, H. Biester, Molecular fractionation of dissolved organic matter with metal salts, Environ. Sci. Technol., 46 (2012) 4419–4426.

[41] H. Tang, Z. Luan, Differences in coagulation efficiencies between PACl and PICl, J. AWWA, 1 (2003) 79–86.

[42] D. Wang, H. Tang, J. Gregory, Relative importance of charge neutralization and precipitation on coagulation of Kaolin with PACl: effect of sulfate ion, Environ. Sci. Technol., 36 (2002) 1815–1820.

[43] Manufacturer's specification (Coagulants: iron (III) sulphate(VI), aluminium sulphate (VI), PAX XL19H).

[44] Manufacturer's specification (Coagulant: Flokor 1A).