

The Influence of Aeration and Type of Coagulant on Effectiveness in Removing Pollutants from Groundwater in the Process of Coagulation

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The subject of research was groundwater from Quaternary formations with high concentration of total iron, increased colour and turbidity, and an increased amount of organic substances and manganese. Successful purification of such water creates technological problems and is practically impossible to achieve by applying traditional groundwater treatment processes. One of the ways recommended for intensifying the removal of iron that occurs in the form of stable iron-organic compounds is the application of the coagulation process. The paper discusses the effectiveness of coagulation with iron(III) sulphate and with two aluminium coagulants: aluminium sulphate and polyaluminium chloride in purifying groundwater without aeration and groundwater aerated for 15 minutes. The aeration of water increased the removal rate of iron and pollutants causing colour and turbidity, but it decreased effectiveness in removing organic substances. The efficiency in purifying water increased as the dose of coagulants increased, and the most effective was polyaluminium chloride. The least effective in removing iron compounds and organic substances, and at the same time in decreasing the intensity of the colour of the water, was iron(III) sulphate.

Key words:

groundwater, aeration, coagulation, iron(III) sulphate, aluminium sulphate, polyaluminium chloride

Introduction

Groundwater is often the only source of water for humans, which is why they have to be used regardless of their quality.

A technological system of groundwater treatment depends on its chemical-physical composition and largely on the concentration of organic pollutants in the water. In the case of water with an increased content of organic substances, iron compounds, and increased turbidity and colour intensity, the application of conventional groundwater treatment does not ensure the required treatment efficiency¹⁻⁶. Organic compounds delay, and sometimes even render the oxidation of iron(II) ions impossible. It has been shown that 1 gram of humic acids at pH = 3 causes the reduction of 0.03 mmol of Fe(III), and 1 gram of fulvic acids at pH = 5.5–5.7 reduces 0.5 mol of Fe(III)⁷. The use of aeration for oxidizing Fe(II) present in groundwater is insufficiently effective when organic substances are also present, because sedimentation agglomerates of iron(III) hydroxide do not precipitate easily, but there appear colloidal and water-soluble coloured iron-organic

compounds, and the groundwater being purified is characterised by a higher intensity of colour and turbidity⁸. It has also been shown that the stability of iron-organic compounds increases when the concentration of organic ligands increases, and in order to remove them, coagulation is necessary, most preferably with aluminium coagulants^{9,10}. Regardless of the kind of coagulant used, before the process of coagulation, it is necessary to oxidise Fe(II) ions occurring in non-organic compounds, after which the process of sedimentation is not necessary^{2,4,5}. Some authors¹¹ recommend the use of chemical oxidants for oxidizing Fe(II), dosed in quantities greater than stoichiometric quantities, which enable a high value of oxidation-reduction potential to be obtained. However, the use of chlorine compounds is not advisable for this purpose because of the risk of occurrence of chloric organic compounds, including trihalomethanes. The use of oxidants, such as hydrogen peroxide or ozone, is also questionable. The oxidation mechanism consists of de-fractionating large organic particles into smaller ones. However, this is not necessarily the same as breaking up iron-organic complexes and freeing Fe(II) ions into the solution, and first of all, removing organic ligands from the water. Because of this, a technological system for purifying this

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kind of groundwater should include a method for the efficient removal of iron occurring together with organic compounds. This condition is probably satisfied by the right process of coagulation^{2,4,5}. Iron and aluminium salts are especially effective coagulants. Many researchers have reported^{1,4,5} that iron coagulants are more effective in respect to manganese removal than aluminium coagulants. Laboratory tests conducted by Albrektiene *et al.*² revealed that the coagulation process markedly increased efficacy in iron-organic complexes removal. The efficacy depended on coagulant type and increased with their dose. According to Libeck *et al.*¹⁰ aluminium salts remove iron-organic complexes from groundwater 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. Coagulation guaranteed the effective elimination of colloidal iron-organic compounds and essentially had no impact on the dissolvent iron-organic compounds concentrations. During coagulation, the possibility of neutralising a negative charge of colloidal iron-organic compounds by coagulant cations or their positively charged hydroxy-complexes is used and a large absorption capacity of precipitated aluminium or iron(III) hydroxides. Among the major factors that contribute to the compression of the diffusion layer of the colloids are the type and dose of the coagulant applied and pH of the water being treated. The pH value is not only a decisive contributor to the form in which the colloidal pollutants occur in the water, and to the sign and value of their electric charges, but also substantially influences the form of occurrence as well as the sign and value of the electrical charges of the products generated during hydrolysis of the coagulants used. When the concentration of the OH^- ions in the water increases due to the adsorption of these anions on the surfaces of the colloidal particles (in the case of organic colloids also due to their enhanced dissociation), the negative charges of the colloids increase, whereas the positive charges of the ionic forms of aluminium or iron responsible for the destabilization of the colloids decrease^{12–15}. Within the range of $\text{pH} = 4–6$ the neutralisation of the negative charge of the pollution being removed dominates, including organic anions, and the adsorption of pollutants on metal hydroxides of the coagulants⁹ used is less important. According to Jekel¹⁶, adsorption on $\text{Al}(\text{OH})_3$ is very important at $\text{pH} > 7$, and in Dempsey's opinion^{17,18} and Eikebrokk¹⁹ at $\text{pH} > 6.25$. It has been found that the importance of the pH value is greater in the case of removing pollution that determines the colour and the level of organic pollution than in the case of pollution that determines turbidity^{4,5}. In the case of non-prehydrolysed coagulants (e.g. aluminium sulphate or

iron(III) sulphate), decreasing the pH value below 6 is a condition for obtaining a sufficient number of hydrolysis products, which unfortunately causes the intensification of water corrosivity^{20–21}. According to a number of authors^{4,5} optimum pH values for purifying “coloured” waters with the process of coagulation are within the range of $\text{pH} = 5–6$ and $\text{pH} = 4–5$, respectively for aluminium and iron coagulants. Black and Packham⁴ obtained the best results in decreasing colour within the range of $\text{pH} = 4.5–5.5$ for $\text{Fe}(\text{III})$ salt and $\text{pH} = 5–6$ for aluminium salt. The high effectiveness of the process of coagulation at removing pollution determining colour and the level of organic pollution in water in the aforementioned pH ranges is a result of decreasing the rate of dissociation of organic substances and the presence of a large number of poly-cations of iron and aluminium, which determine effective neutralisation of the charge of colloids being removed. The research results have also shown that the pH ranges of effective coagulation used to reduce the colour and turbidity are not the same, and in order to effectively reduce colour, lower pH values are required^{2,4}. It has also been found that within the range of $\text{pH} = 6–10$, iron(III) sulphate is much less useful than aluminium sulphate, especially for reducing the intensity of colour. This is caused by the appearance of coloured and not settling easily combinations of Fe^{3+} ions with organic substances, most frequently with humic acids^{10,22}. The risk of such coloured chelates appearing exists when an insufficient dose of an iron coagulant is used or the value of pH environment is inappropriate^{4,5}. It has also been found that polymerised polyaluminium chlorides are more effective in removing organic substances and reducing turbidity than aluminium sulphate^{20–24}. Better effectiveness of pre-hydrolysed aluminium coagulants is caused by the presence of polymeric aluminium complexes with large positive charges, which effectively destabilise and bridge the coloured organic pollution being removed^{25–28}. The research determined the effectiveness of the process of coagulation, and the oxidation of $\text{Fe}(\text{II})$ ions with dissolved oxygen in purifying groundwater.

Materials and methods

Water samples

The subject of research was groundwater from Quaternary formations characterised by a high concentration of total iron (Fe) – amounting to $7.19 \text{ mgFe dm}^{-3}$, more intensive colour – up to 33 mgPt dm^{-3} and turbidity up to 30 NTU , and also a high quantity of organic substances (TOC from 4.900 to $5.420 \text{ mgC dm}^{-3}$) and manganese (up to $0.39 \text{ mgMn dm}^{-3}$). Iron(II) and iron(III) compounds

Table 1 – Groundwater quality indicators

Parameter	Unit	Value		
		Minimum	Average	Maximum
Temperature	°C	11.3	12.4	13.8
pH	–	6.97	–	7.14
Dissolved Oxygen	mgO ₂ dm ⁻³	0.50	1.24	1.53
Colour	mgPt dm ⁻³	19	28	33
Turbidity	NTU	9.41	20.13	30.00
Iron total	mgFe dm ⁻³	5.47	6.10	7.19
Iron(II) – Fe(II)	mgFe dm ⁻³	2.64	3.39	4.36
Iron(III) – Fe(III)	mgFe dm ⁻³	1.11	2.70	4.13
Alkalinity	mval dm ⁻³	3.60	3.62	3.70
Manganese	mgMn dm ⁻³	0.32	0.36	0.39
Aluminium	mgAl dm ⁻³	0.09	0.13	0.17
TOC	mgC dm ⁻³	4.900	5.157	5.420
TOC/Iron total (D)	–	0.550	0.770	0.995

were present in the water. The temperature changed within the range of 11.3 to 13.8 °C, the concentration of dissolved oxygen changed within the range of 0.50 to 1.53 mgO₂ dm⁻³, and the pH value within the range of 6.97 to 7.14 (Table 1). The water samples examined differed in terms of the value of the ratio of the TOC concentration and the concentration of total iron (D).

Experimental procedure

In the research, the effectiveness of volumetric coagulation in raw groundwater treatment and after aeration was determined. The effects of water treatment in technological systems were assessed:

- coagulation, sedimentation and filtration,
- oxidation of Fe(II) by dissolved oxygen, coagulation, sedimentation and filtration.

Samples of groundwater (treatment line with aeration) was aerated with compressed air for 15 minutes until a concentration of about 10 mgO₂ dm⁻³ i.e. ca.100 % saturation of water with oxygen had been obtained. Jar tests were carried out by using a 1 dm³ six-place paddle stirrer (Flocculator Kemira 2000, Sweden). Coagulation was carried out in water samples (with and without aeration) of 1 dm³ 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 iron(III) sul-

phate– (PIX-112) and aluminium coagulants: aluminium sulphate– (SAL) and polyaluminium chloride – (PAX XL-60), dosed in the form of water solutions. The doses of coagulants were expressed as mgFe dm⁻³ or mgAl dm⁻³. Six different doses of coagulants were selected 1, 2, 3, 4, 5 and 6 mgFe(Al) dm⁻³. After the process of coagulation, the water samples underwent 2 hours of sedimentation, and filtration through a soft filter.

Analytical methods

The physical-chemical composition of both the raw as well as treated water was determined according to the International Standard methods. The temperature and pH of the raw water and the purified water was determined with a WTW Multi Line P4 with a combination pH electrode with temperature corrections. The instrument was standardized daily using a two-point calibration with pH 4 and 7 standard solutions. The dissolved oxygen of the raw water and the purified water was determined with a WTW Multi 3410 SET 4 with an optical oxygen sensor FDO^R 925 (Germany). The turbidity was determined by means of 2100P HACH turbidimeter. The colour (according to Pt scale), total iron, iron(II) concentrations were determined with the Dr 3900 (HACH Lange) spectrophotometer. For determination of water colour, water samples were filtrated through 0.45 µm membrane filters. Water colour was measured in 5 cm cell with 390 nm wavelength) spectrophotometer. Iron(II) was measured using the 1,10 phenanthroline method. Total iron was measured using the same method except that a reducing reagent was also included in a reagent powder pillow to convert Fe(III) to Fe(II). Iron(III) was determined from the difference in the content of iron total and iron(II). Aluminium and manganese concentrations were determined with the atomic absorption method (ISP-OES, 5300DV, Perkin Elmer Company, US). The alkalinity was determined with a titrimetric method against methyl orange. The organic carbon content was measured with a Shimadzu TOC apparatus. Prior to TOC measurement, the samples were acidified and bubbled with air containing no CO₂, in order to remove the inorganic carbon. Raw and treated water samples were analyzed in the laboratory of University of Zielona Góra, Institute of Environmental Engineering (Poland). When interpreting the test results in order to assess the organic pollution level of water samples and its effect on the process and efficiency of coagulation, the organic substance and total iron coexistence ratio D was applied, which was calculated as: $D = [\text{TOC}]/[\text{Fe}_{\text{tot}}]$ (mgC/mgFe). For simplifying the records, this article does not list the D coefficient unit.

Results and discussion

The research determined the effectiveness of coagulation and oxidation of Fe(II) with dissolved oxygen in purifying raw groundwater.

Treatment without aeration

Regardless of the physical-chemical composition of the water being purified, the effectiveness in removing iron compounds, organic pollution, and reducing colour and turbidity increased as the doses of the coagulants tested increased (Figs.1 and 2).

Analysis of the dependence presented in Figs. 1 and 2 also indicates that the effectiveness of the coagulants under research had decreased as the value of the ratio of TOC and concentration of total iron (D) increased. The effectiveness of the coagulants under research in removing different pollution can be ordered as follows:

- removing iron, coloured pollution and organic pollution: PAX XL-60 > SAL > PIX-112.
- decreasing turbidity: PAX XL-60 > PIX-112 > SAL.

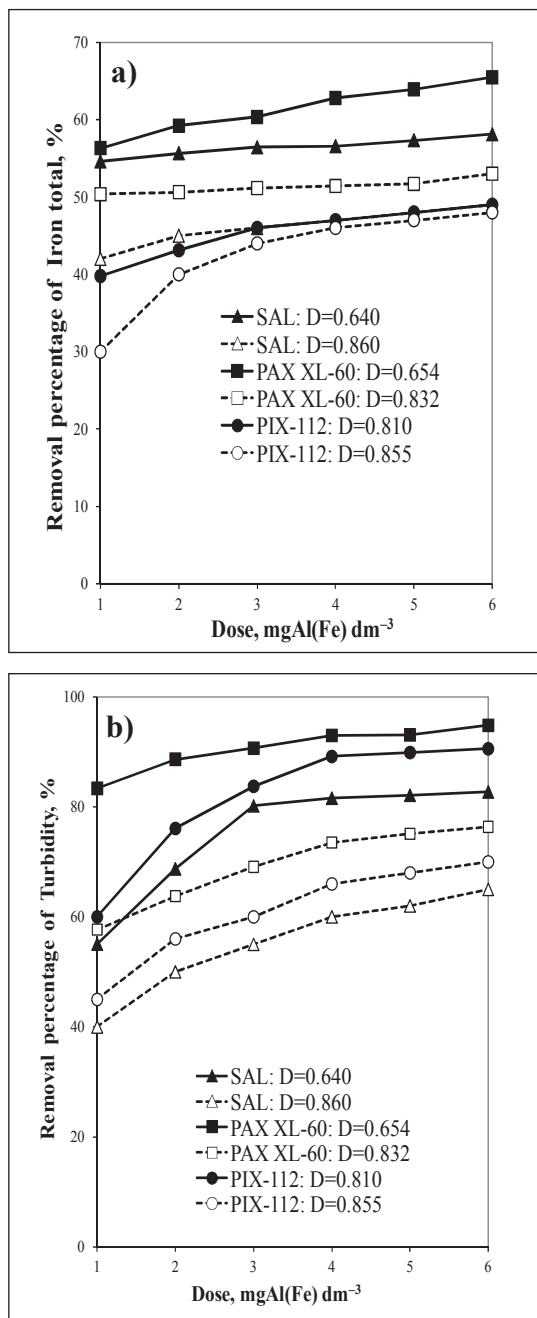


Fig. 1 – Effect of the type and dose of coagulant on the efficiency in removing total iron (a) and decreasing the turbidity (b)

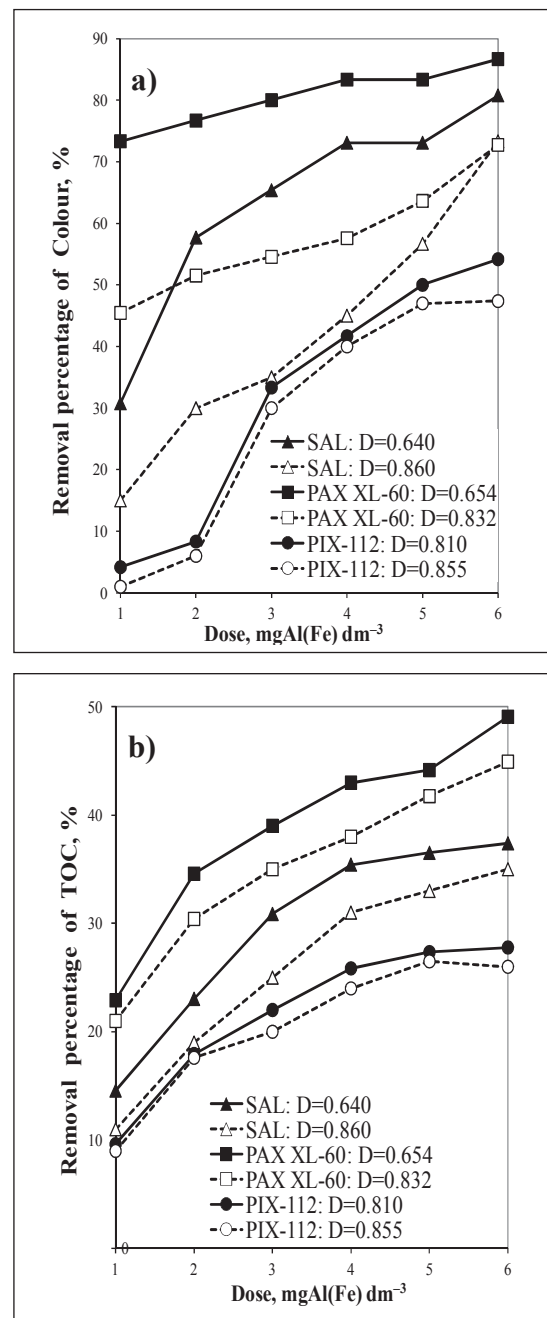


Fig. 2 – Effect of the type and dose of coagulant on the efficiency in removing colour (a) and decreasing TOC (b)

In accordance with scientific literature, the lowest effectiveness of the iron coagulant PIX-112 in removing iron compounds, organic substances, and reducing colour was probably caused by the occurrence of coloured combinations of organic compounds present in the water being purified with Fe(III) introduced into the water with this coagulant^{4,10,22}. According to Piekutin *et al.*²⁹, iron and aluminium coagulants react differently with organic matter in water. Libecki *et al.*¹⁰ and Kaiser³⁰ demonstrated that the ability to bind organic ligands in surface water increases as follows: $\text{Ca}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+}$. Results of analysis confirmed the research conducted by Świdorska-Bróz²² that the iron coagulant was only more effective in reducing turbidity, which resulted from better sedimentation characteristics of $\text{Fe}(\text{OH})_3$ than of $\text{Al}(\text{OH})_3$. The pre-hydrolysed aluminium coagulant (PAX XL-60) was the most effective among the coagulants tested because of a higher content of polymeric aluminium complexes with a high positive charge, which effectively destabilized colloidal pollution, and also the content of silica, which improved the process of flocculation^{23,31}. The studies conducted by Nowacka *et al.*^{32–34} proved that the optimal doses of pre-hydrolyzed coagulants were much lower than in the case of aluminium sulphate and iron(III) sulphate. Edzward *et al.*²⁴ make it clear that, among the aluminium polymers, Al_{13} is the most effective destabilizer of negatively charged colloids. Upon its addition to the water being treated, the polycationic products of aluminium prehydrolysis are hydrolyzed to $\text{Al}(\text{OH})_3$ at a remarkably slower rate as compared with the aluminium present in the aluminium sulphate. Moreover, they preserve their dissolved and polymerized (“primary”) form over a wider range of pH as compared to aluminium sulphate when used as a coagulant³⁵. The effectiveness of non-pre-hydrolysed coagulants, aluminium sulphate and iron(III) sulphate, in removing organic pollution increased as their dose increased, and at the same time, the pH value decreased (Fig. 3).

In general, aluminium sulphate, which caused higher acidity in the water being purified, was more effective than iron(III) sulphate. According to Nowacka *et al.*³², the importance of pH value is greater in the case of removing organic pollution than in the case of pollutants responsible for turbidity. Decreasing the pH value has a favourable influence on the removal of organic pollution because it both increases the quantity of hydrolysis products with a positive charge, which destabilises organic colloids, and decreases the dissociation rate of organic pollution, which assists its removal^{4,5,15,16}. Regardless of the type of coagulant, increasing its dose resulted in a reduction in pH value of the water, and at the same time, in decreasing effectiveness in re-

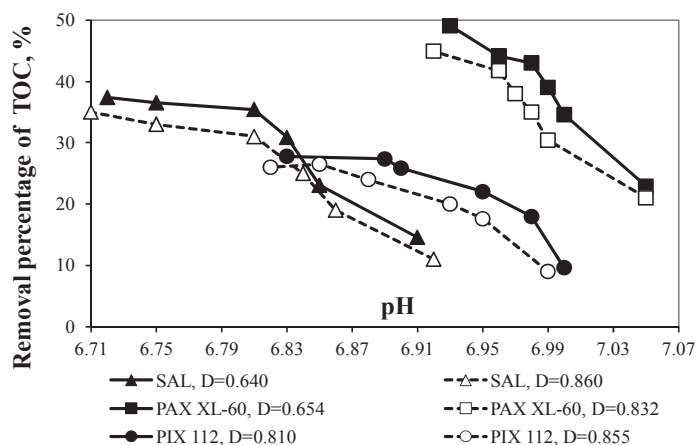


Fig. 3 – Influence of the pH value on effectiveness in decreasing TOC (Dose = 1-6 mgAl(Fe) dm⁻³)

moving Fe(II). The influence of increasing the dose of coagulants and the concentration of H^+ ions was opposite in the case of effectiveness in removing iron(III) and organic pollution. In all the research series effectiveness in removing manganese compounds was insufficient, and decreased as the dose of the coagulants under research increased, and at the same time the pH value decreased. From among the coagulants under research, the best results in removing manganese were achieved by the iron coagulant PIX-112 (Table 4 and Fig. 8).

The importance of the filtration process in terms of the total efficiency in reducing turbidity and reducing iron compounds was the least after applying a prehydrolyzed coagulant PAX XL-60. On the other hand, the greatest contribution of filtration in total efficiency of reducing the turbidity was found after applying aluminium sulphate, and in the case of removing iron compounds, the greatest contribution of filtration in total efficiency was found after applying iron(III) sulphate, which is illustrated in Table 2.

In the case of non-aerated water, even after additional filtration through filter tissue, the coagu-

Table 2 – Effect of the type of coagulant ($D_c = 4 \text{ mgAl(Fe) dm}^{-3}$) on the contribution of filtration in the total efficiency in removing total iron and turbidity

Type of coagulant	Efficiency of:					
	Coagulation and sedimentation, %		Coagulation, sedimentation and filtration, %		Filtration, %	
	Iron total	Turbidity	Iron total	Turbidity	Iron total	Turbidity
PAX XL-60	70	83	83	95	13	12
SAL	50	60	79	92	29	32
PIX-112	40	68	77	93	37	25

lants used did not decrease the concentration of total iron and manganese, and turbidity to values required for drinking water specified in the regulation by the Health Minister of 29 April 2010, which are respectively 0.2 mgFe dm^{-3} , $0.05 \text{ mgMn dm}^{-3}$ and 1 NTU^{36} . During the research, the concentration of aluminium residual in the water after coagulation with aluminium coagulants aluminium sulphate and polyaluminium chloride was also determined. It was found that, also in this aspect, polyaluminium chloride had been more effective. The concentrations of aluminium in the water after coagulation with (polyaluminium chloride) PAX XL-60 and 2 hours of sedimentation were over twice lower ($0.20\text{--}0.28 \text{ mgAl dm}^{-3}$) than in the water purified with aluminium sulphate ($0.40\text{--}0.70 \text{ mgAl dm}^{-3}$). Filtration through soft filter resulted in further elimination of post-coagulation suspensions, and decreasing the concentration of residual aluminium to the value of $0.15\text{--}0.25 \text{ mgAl dm}^{-3}$ (SAL) and $0.11\text{--}0.14 \text{ mgAl dm}^{-3}$ (PAX XL-60).

Treatment with aeration

In order to oxidise Fe(II) to Fe(III), the raw water samples were aerated for 15 minutes to obtain an effectiveness of iron(II) oxidation of about 88–95%. The rate of oxidation of Fe(II) during aeration was determined by the value of the coefficient of co-occurrence of TOC and total iron in raw water (D). As it increased, the effectiveness of the oxidation of Fe(II) with oxygen dissolved in the water decreased, which was especially clear in the case of the water samples which differed in the value of the coefficient D. These dependences are presented in Fig. 4.

Although the organic substances present in the treated water did not decrease significantly the efficiency of Fe(II) to Fe(III) oxidation, the oxidation products were colour, difficult to agglomerate and sedimenting Fe(III) bonds. According to a number of authors^{4,5,7,23,37–40}, organically complexed iron can sometimes be oxidized by oxygen from simple aeration. In this state, its size is usually very fine or colloidal, so it is too small to be removed by a gran-

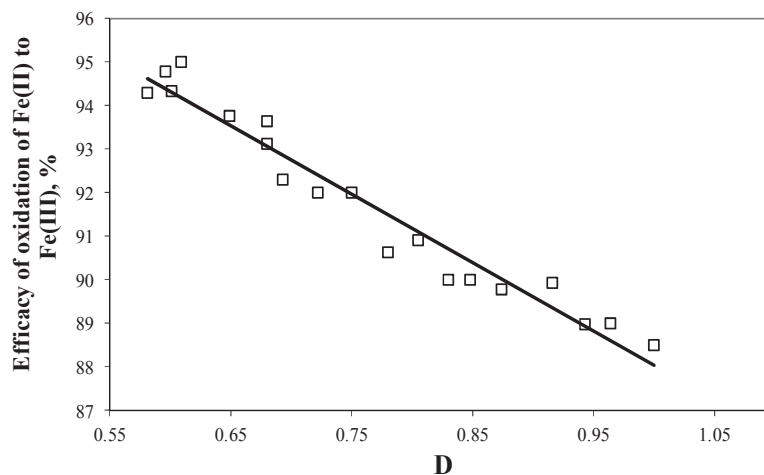


Fig. 4 – Effect of coexistence ratio of TOC concentration and concentration of total iron (D) on efficacy in oxidising Fe(II) to Fe(III) (aeration)

ular media filter. One removal option is to neutralize the surface charge using coagulants.

Like in the case of non-aerated water, the amount of pollution removed increased as doses of the coagulant increased. In samples of aerated water, unlike in the case of raw water, as doses of the coagulant increased, the effectiveness in removing Fe(II) also increased. A comparison of results obtained for raw water and aerated water clearly showed that it had been necessary to precede coagulation with aeration of the water in order to increase effectiveness in removing iron compounds and decreasing colour and turbidity (Fig. 5a and b, and 6a). Just the opposite was found in the case of organic substances (Fig. 6b).

This relationship was confirmed by the content of organic substances (which increased together with the dose of the coagulant) in post-coagulation sludge separated from non-aerated water and after aeration (Table 3).

Increasing the pH value of the water (by about 1 unit – pH from 7 to 8), as a result of aeration in accordance with scientific literature^{4,32–34}, caused simultaneously a decrease in the amount of products of the hydrolysis of coagulant cations with a positive charge (e.g. AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$) which destabilised organic colloids and an increase in the rate of dissociation of organic compounds. As a result (Fig. 6b), the rate of remov-

Table 3 – pH in water after coagulation and content of organic substances in the dry mass of post-coagulation sediments (Dose = $1\text{--}6 \text{ mgAl}(\text{Fe}) \text{ dm}^{-3}$) released from raw water and aerated water

Kind of water being purified	pH in water after coagulation			Organic substances % in the dry mass of post-coagulation sediments		
	SAL	PAX XL-60	PIX-112	SAL	PAX XL-60	PIX-112
Raw water	6.92–6.71	7.05–6.93	7.00–6.83	14.3–31.4	16.3–33.8	11.0–25.0
Aerated water	7.75–7.08	8.06–7.56	7.84–7.33	8.1–19.0	14.9–21.1	7.0–16.0

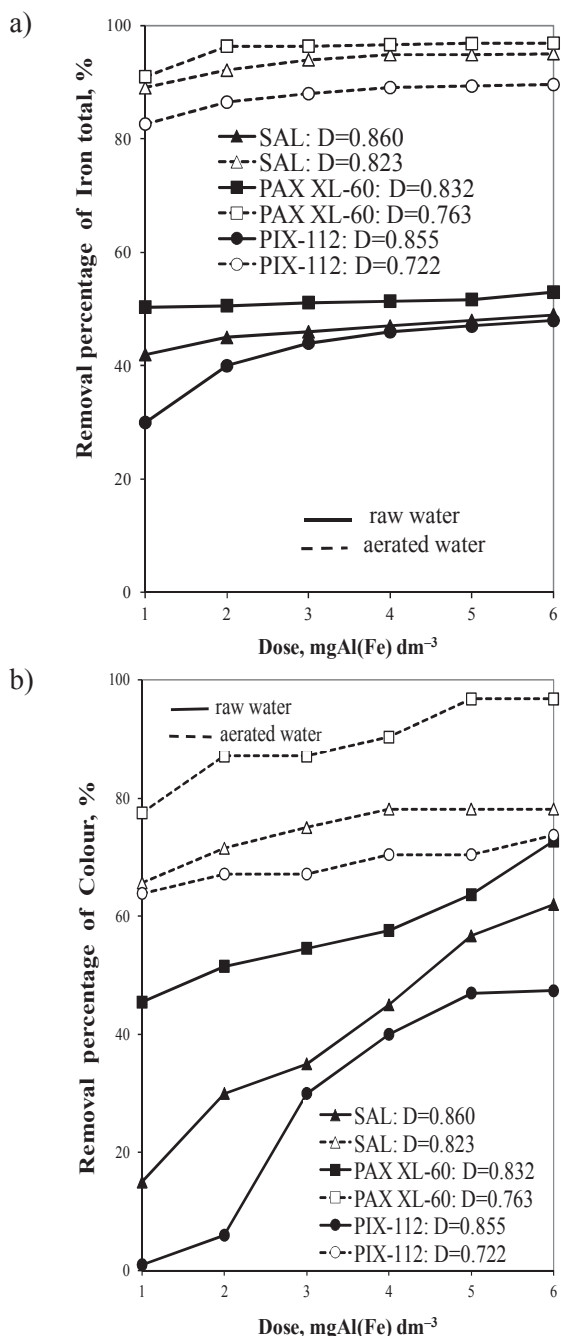


Fig. 5 – Effect of the type and dose of coagulant on the efficiency in removing total iron (a) and decreasing the colour (b) during treatment with or without aeration

ing TOC was lower. According to various book references^{4,5,10,14}, it is presumed that one of the ways recommended for intensifying the removal of pollutants from underground water with an increased content of organic substances is the use of chemical oxidising agents instead of aeration before the coagulation process. A comparison between the effectiveness of the coagulants under research showed that, especially in the case of the smallest doses, the pre-hydrolysed coagulant PAX XL-60 had been the most effective. An advantage of polyaluminium chloride was lower acidity of the water (Table 3)

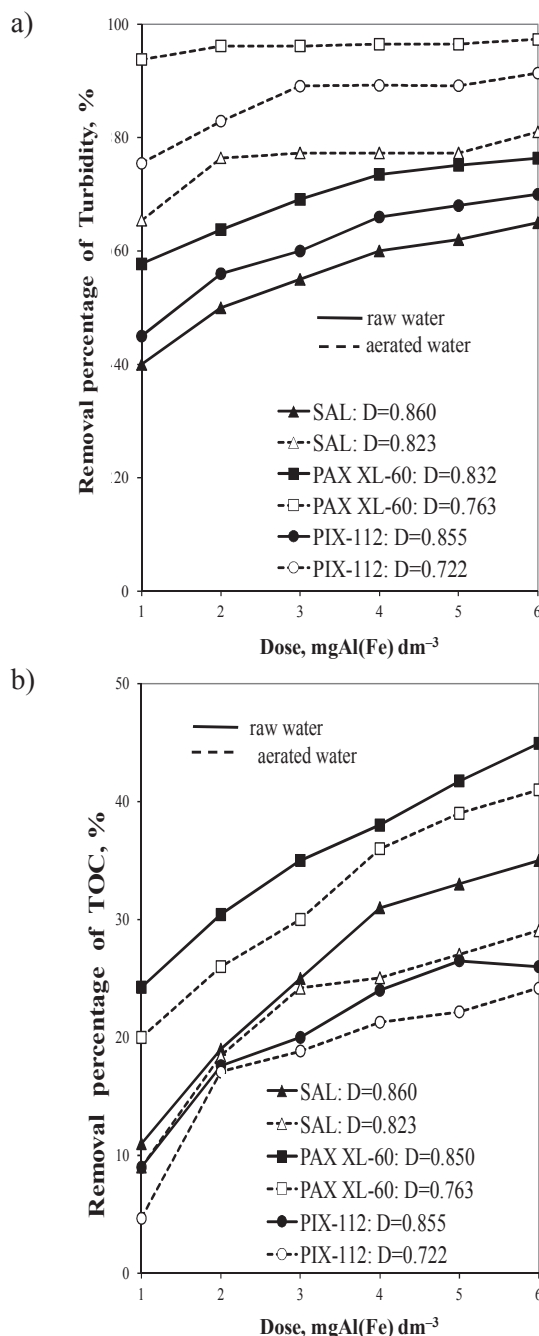


Fig. 6 – Effect of the type and dose of coagulant on the efficiency in removing turbidity (a) and decreasing TOC (b) during treatment with or without aeration

and a lower consumption of alkalinity (Fig. 7), which was important in the aspect of the chemical stability of the water.

The studies conducted by Edzwald *et al.*²⁴ and Nowacka *et al.*^{32–34} proved that the pre-hydrolyzed coagulants cause smaller consumption of the natural water alkalinity and lower its pH reaction to a smaller extent than coagulants that are not prehydrolyzed. The effectiveness of iron(III) sulphate, regardless of the kind of water being purified (with and without aeration), was only higher than the effectiveness of aluminium sulphate (SAL) in reduc-

Table 4 – Influence of the value of coefficient D ($\text{TOC}/\text{Fe}_{\text{tot}}$) and the type of coagulant ($\text{Dose} = 3 \text{ mgAl(Fe) dm}^{-3}$) on effectiveness in removing pollution (η , %) from raw water or aerated water

Type of coagulant	Type of oxidant	D	η_{Fe}	η_{Colour}	$\eta_{\text{Turbidity}}$	η_{TOC}	η_{Mn}
SAL	–	0.640	56.42	65.38	80.21	30.87	5.41
		0.860	47.00	35.00	55.00	25.00	5.41
	O_2	0.780	95.16	76.92	85.02	24.17	14.71
		0.823	93.97	75.00	77.29	21.11	14.71
PIX-112	–	0.810	46.00	33.33	83.74	22.01	13.51
		0.855	44.00	30.00	60.00	20.00	13.51
	O_2	0.650	88.74	70.00	90.36	20.25	19.00
		0.722	88.00	67.14	89.07	18.85	17.00
PAX XL-60	–	0.654	60.33	80.00	90.67	39.02	5.88
		0.832	51.16	54.55	69.10	35.00	5.88
	O_2	0.763	96.38	87.10	96.17	30.00	15.00
		0.840	94.01	81.48	94.68	25.21	15.00

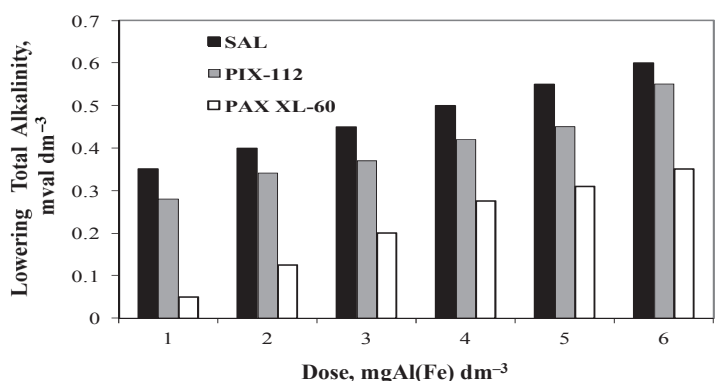


Fig. 7 – Effect of the type and dose of coagulant on lowering total alkalinity of the treated water

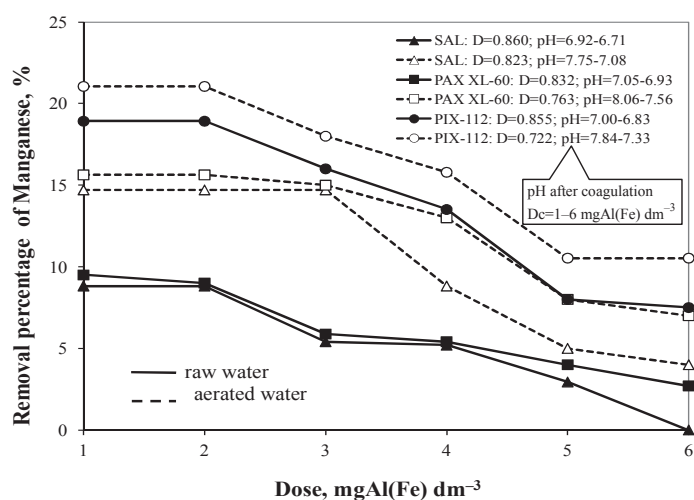


Fig. 8 – Effect of the type and dose of coagulant on the efficiency of removing manganese during treatment with or without aeration

ing turbidity (Fig. 6a and Table 4), and in removing manganese compounds even higher than the effectiveness of the coagulant PAX XL-60 (Fig. 8).

The results showed that coagulation with the coagulants under research was ineffective in removing manganese compounds both from non-aerated water and aerated water, and effectiveness in removing manganese decreased as doses of the coagulants increased, and simultaneously the concentration of H^+ ions increased (Fig. 8). The greatest but insufficient effectiveness of coagulant PIX-112 in removing the manganese compounds (Table 4 and Fig. 8) in accordance with scientific literature^{1,4,5}, was probably due to the effect of the adsorption of manganese on iron(III) hydroxide, whose additional amounts were produced in samples of water treated with iron(III) sulphate. Same as in the case of non-aerated water, the concentration of aluminium remaining in the water after coagulation exceeded the amount of 0.2 mgAl dm^{-3} , but it was twice lower in the water samples purified with polyaluminium chloride than in those purified with aluminium sulphate. A decrease in the concentration of aluminium ions to an acceptable value ($\text{Al} = 0.13\text{--}0.16 \text{ mg dm}^{-3}$) was achieved by additional filtration of the water samples purified with all the doses of polyaluminium chloride. In the case of aluminium sulphate, a sufficient decrease in the concentration of residual aluminium ($0.17\text{--}0.19 \text{ mgAl dm}^{-3}$) was achieved by filtration of the water samples purified with doses of 3 to 6 mgAl dm^{-3} . The obtained results are confirmed in literature Nowacka *et al.*³² reported that the lowest concentration of residual aluminium in the water samples was achieved after

Table 5 – Parameters of linear correlations between the amount of TOC removed and the amount of total iron or Fe(III) removed in the coagulation process

Type of		Linear correlation equation	Coefficient of the Pearson correlation (<i>R</i>)
Water	Coagulant		
Raw water	SAL	$\eta\text{Fe} = 0.420\eta\text{TOC} + 51.160$	0.9648
		$\eta\text{Fe(III)} = 1.3496\eta\text{TOC} + 47.663$	0.9929
	PAX-XL60	$\eta\text{Fe} = 0.1530\eta\text{TOC} + 51.860$	0.9664
		$\eta\text{Fe(III)} = 0.9145\eta\text{TOC} + 50.145$	0.9839
	PIX-112	$\eta\text{Fe} = 0.2530\eta\text{TOC} + 60.860$	0.9648
		$\eta\text{Fe(III)} = 2.3701\eta\text{TOC} - 1.9562$	0.9916
Aerated water	SAL	$\eta\text{Fe} = 0.2627\eta\text{TOC} + 88.966$	0.9250
		$\eta\text{Fe(III)} = 0.4477\eta\text{TOC} + 84.412$	0.8240
	PAX-XL60	$\eta\text{Fe} = 0.3744\eta\text{TOC} + 85.028$	0.9570
		$\eta\text{Fe(III)} = 0.7124\eta\text{TOC} + 74.654$	0.9696
	PIX-112	$\eta\text{Fe} = 0.1530\eta\text{TOC} + 51.860$	0.9647
		$\eta\text{Fe(III)} = 2.3701\eta\text{TOC} - 1.0062$	0.9918

the coagulation process using pre-hydrolyzed coagulants Flokor 1.2A. This concentration was about 53 % lower than in the case of aluminium sulphate. Also, according to Van Benschoten *et al.*²⁸, substitution of aluminium sulphate with polyaluminium chlorides reduced the concentration of aluminium residual in water after coagulation. A comparison between effectiveness in removing pollution from raw underground water or aerated water (Table 4) differing in terms of values of coefficients of co-existence of organic pollution and total iron ($D = \text{TOC}/\text{Fe}_{\text{tot}}$), showed that, regardless of the type of coagulant, the effectiveness in reducing the concentration of total iron, decreasing colour, turbidity, and removing organic substances, was lower for greater values of coefficient *D*.

The regularities found indicate that organic substances stabilise iron compounds. The regularity found is proven in references^{17–19,23,24}, stating that an increase in the amount of organic ligands in raw water strengthens durability/life of organoferric combinations as well as the contribution of dissolved coloured, organoferric complexes, difficult to remove in the coagulation process. Also, according to Stumm and Lee³⁷, in many natural waters, organic matter may stabilize ferric oxide colloids or may increase the Fe(III) solubility by complex formation. Generally, iron removal is very slow under such conditions. Regardless of the kind of water being purified (raw or aerated) and the coagulant used, the rate of reduction of total iron, mainly Fe(III), correlated with the effectiveness in removing organic substances (Table 5). This was not the case for Fe(II).

Analysis results confirmed the research conducted by Sommerfeld³⁸, that organic substances in water may interfere with the iron removal process, forming stable complexes with iron. The Fe(III)-organic complexes are stronger and more stable as compared to Fe(II)-organic complexes^{38,39}.

Conclusions

Laboratory tests showed that the process of coagulation is necessary for eliminating colourful colloid connections of iron with organic compounds. Independently of the coagulants used, iron compounds were removed together with organic substances, which proved that they are present in water in the form of colloidal iron-organic compounds. Efficiency in disposal of wastes in the process of coagulation depended on the type and dose of coagulant and coefficient of coexistence of organic substances and total iron in raw water. Among the coagulant types under analysis, the best results in removing iron compounds and organic contamination, and which also ensured the colour as well as the turbidity, were guaranteed by polyaluminium chloride. For removal of manganese, iron(III) sulphate was more effective than aluminium coagulants. The research results also show that when groundwater, having a high concentration of total iron and an increased content of organic substances is treated, the process of coagulation with aeration, regardless of the type and dose of coagulant, had considerably improved effectiveness in removing iron compounds and decreasing colour and turbidity, at the same time reducing the degree of organic pollution removal.

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