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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

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Abstract. The article presents the results of studies concerning the impact of the method of Fe(II) ion oxidisation on the effectiveness of coagulation in the removal of pollutants from underground water with an increased content of organic substances (TOC up to 5.338mgC/dm^3). In order to oxidise the Fe (II) ions before the coagulation process, the underground water was subjected to aeration, or either potassium manganate (VII) or hydrogen peroxide were dosed in the stoichiometric amount in view of the concentration of Fe (II). The efficiencies of three coagulants were compared: that of aluminium sulphate (VI), polyaluminium chloride (PAX XL-60) and iron (III) sulphate (VI) – PIX-112. Coagulant doses expressed in mgAl/dm^3 or mgFe/dm^3 and changed within the range of 1 to 6 mgAl(Fe)/dm^3. Volume coagulation was performed in 1-dm^3 groundwater samples using 1-minute rapid mix (250 rpm) and 25-minute slow mix (30 rpm) followed by 2-hour sedimentation. It has been proven that the type of oxidising agent and coagulant, as well as their dose, co-determines the effectiveness of the removal of the pollutants. Among the used methods of iron (II) oxidisation, the best effects have been achieved by potassium manganate (VII) with regards to the effects of the reduction of colour, turbidity, concentration of manganese and organic substances, and with regards to the extent of total iron removal, oxidisation with dissolved oxygen was the most effective solution. Hydrogen peroxide was the least useful oxidising agent. Regardless of the oxidising agent the best results in the removal of pollutants in the coagulation process were produced by the coagulant: pre-hydrolysed polyaluminium chloride PAX XL-60, and the worst by the iron coagulant: iron (III) sulphate (VI). Analysis of the results of the studies also showed that the effectiveness of pollutant removal from the underground water in the coagulation process was decreased together with an increase in the value of the TOC/Fe$_{tot}$ only in the case of water samples which, after aeration, differed in terms of the coefficient of organic substances and total iron (D). Such a relationship was not found when potassium manganate (VII) and hydrogen peroxide were used for oxidisation before the coagulation process.

Keywords: groundwater, organic substances, volume coagulation, aeration, potassium manganate (VII), hydrogen peroxide.

Introduction

Poland is one of the countries whose water reserves are relatively small. This is especially true as far as surface water is concerned. The usable reserves of groundwater are estimated in Poland as 15.6 km^3, 65% of which is water from the quaternary aquifer. 85% of abstracted water is used for drinking and economic purposes and 15% for manufacturing purposes. In Poland, groundwater is used by 185 enterprises and water supply companies, surface water by 10 water supply companies and both sources are used by 29 water supply companies. Very few of the water supply companies abstract groundwater whose physical-chemical composition satisfies the requirements for water for human consumption, and about 34% of abstracted groundwater is low quality water with an increased content of iron, manganese and organic substances and it has to be treated in a number of stages with costly and technologically difficult methods (Gimbel *et al.* 2008). In the case of underground waters containing increased concentrations of organic compounds, Fe(II) and Fe(III) ions as well as their hydrocomplexes create stable iron-organic bonds and the water is characterised by its raised colour

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and turbidity. Depending on the type and concentration of the organic substances, the pH, the oxidising-reduction potential and the ionic composition of water, the iron ions and their hydro complexes may, together with organic ligands, create compounds or complexes can form colloidal solution. Of major significance in the creation of ion-organic compounds are the humic acids (Krupińska *et al.* 2013; Calace *et al.* 2001; Jobin, Ghosh 1972). Based on the analysis of a number of vulnerabilities of metals to create bonds with humic acids, a conclusion may be drawn that both the Fe^{2+} ions and the Fe^{3+} ions create complexes with the humic acids (Frimmel 1979; Munter *et al.* 2005; Albrektiene *et al.* 2014). There is no unequivocal theory explaining the mechanism of the creation of ion-organic bonds. In the opinion of many authors (Arnold *et al.* 1998; Hrubec 1995), the iron ions are bound by the humic acids as a result of the electrostatic impact of the metal cation with the negatively charged function groups, and especially the carboxylic groups. According to Gonczarow and Pandey (Gonczarow *et al.* 2003; Pandey *et al.* 2000) the formation of chelate complexes with the humic acids in natural waters occurs as a consequence of the reaction of exchanges between the hydrogen ions from the carboxylic and phenolic groups of humic acids, and the ion cations occurring in these conditions, mainly in the form of hydro complexes $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$. Also, it has been concluded that the complex stability constant is increased with an increase in the pH, which is probably caused by the growing dissociation of function groups, i.e. –COOH and –OH and smaller competitiveness of H^+ ions in relation to iron cations, which is present under acid conditions. It is claimed that the strongest water-soluble complexes of iron and humic acid are formed at a pH of 7 (Rahman *et al.* 2010; Theis, Singer 1974). In the opinion of many authors (Krupińska *et al.* 2013; Gonczarow *et al.* 2003; Calace *et al.* 2001; Jobin, Ghosh 1972), one of the reasons for iron stabilisation by organic substances in underground waters may also include the formation of"protective colloids" of a hydrophilic nature, which result from the adsorption of organic substances on the surface of the iron (III) hydroxide. The dispersion degree of bonds of iron and organic substances and their stability in water depends on the value of the quotient of organic ligand concentrations in relation to the metal in complex compounds. As the amount of organic substances increases, the stability and degree of the dispersion of iron-organic bonds also increases. Thus, the possibility of their removal within the framework of the conventional process system of underground water treatment is decreased (Krupińska *et al.* 2013; Gonczarow *et al.* 2003; Pandey *et al.* 2000). Knocke *et al.* (1992) report that, in treated water, if dissolved substances are dominant among the organic substances, iron demonstrates a high degree of complexation, and the forming iron-organic bonds significantly decrease the effectiveness of the oxidisation of Fe^{2+} to Fe^{3+} with dissolved oxygen. The application of aeration in such a case is not sufficiently effective, as the sedimenting iron (III) hydroxide agglomerates are not easily precipitated, and only colloidal and water-soluble colourful iron-organic bonds are created (Krupińska *et al.* 2013; Libecki, Dziejowski 2010). Therefore, various attempts at the intensification of the removal of iron occurring in bonds with organic ligands are made. One of these is the use of chemical oxidising agents instead of aeration (Krupińska *et al.* 2013; Stępniak *et al.* 2008). Such technological solutions do not always guarantee the effective removal of iron compounds and organic substances, and in the case of the introduction of chloric oxidising agents into the water, there is a risk of its secondary contamination with side chlorination products (Stępniak *et al.* 2008; Lytle *et al.* 2004). The underlying purpose of using ozone or hydrogen dioxide is also arguable, as it may cause the fractionation of large organic particles into smaller particles, and the intermediary organic products from the oxidisation of organic compounds which remain in the water may still stabilise the iron, forming iron-organic bonds, for which the removal via the sedimentation and filtration processes are not sufficient. In an environment that is neutral or close to neutral, and such environments usually occur in natural waters, for the oxidisation of Fe(II) ions occurring in bonds with organic substances, it is advantageous to use potassium manganate (VII), because $MnO_{2,}$ which improves the sedimentation of iron-organic agglomerates by acting both as the weight and the adsorbent (Krupińska *et al.* 2013; Ficek, Vella 2000; Knocke *et al.* 1991; Knocke *et al.* 1992; Singer *et al.* 1980), is another product of reaction except $Fe(OH)_3$. The studies conducted by Knocke *et al.* (1992) proved that the molecular weight of organic ligands determined the effectiveness of the chemical oxidisation of complexed Fe(II). A significantly greater effectiveness of the oxidisation of Fe(II) to Fe(III) and its removal in the sedimentation process was obtained as a result of chemical oxidisation by means of potassium manganate (VII) or chlorine dioxide, when low-molecular and not high-molecular compounds were dominant among the organic ligands as part of the iron-organic complex. One of the ways recommended for intensifying the removal of iron that occurs in a form of stable ferro-organic compounds is application of the coagulation process, preferably with aluminium salt (Krupińska 2012; Albrektiene *et al.* 2011; Libecki, Dziejowski 2010; Libecki, Dziejowski 2008; Potgieter *et al.* 2005; O'Melia *et al.* 1999; Huang, Shiu 1996; Jekel 1986; Dempsey *et al.* 1984). It has also been found that polymerised polyaluminium chlorides are more effective at removing organic substances and reducing turbidity than aluminium sulphate (VI) (Krupińska 2014; Eikebrokk, Fettig 1990; Dempsey *et al.* 1985). 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 (Edzwald *et al.* 2000; Edwards, Amirtharajah 1985; Edzwald, Van Benschoten 1990; Tuhkanen *et al.* 2004; Van Benschoten, Edzwald 1990). The article presents the results of studies concerning the impact of the method of Fe (II) ion oxidisation on the effectiveness of coagulation in the removal of pollutants from underground water with an increased content of organic substances.

1. Materials and methods

The subject of the studies was underground water with variable physico-chemical composition (Table 1), characterised by raised colour (up to 38 mgPt/dm^3), turbidity (38.80 NTU) and a significant content of iron compounds (up to 7.84 mgFe/dm^3) and manganese (up to 0.42 mgMn/dm^3). The water contained iron (II) and (III) compounds and dissolved oxygen in the amount of 0.50–1.56 mgO$_2$/dm^3, as well as a periodically increased content of organic substances (TOC up to 5.338 mgC/dm^3). These characteristics of the water were the cause of the unfavourable 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 colours of water proved the occurrence of iron in the form of colloidal and dissolved bonds with organic compounds, for the removal of which the coagulation process was used. The effectiveness of voluminal coagulation in raw water treatment, after aeration and chemical oxidisation, was determined in the studies. The raw water was aerated with compressed air for a period of time of (t$_n$) 15- minutes, obtaining a dissolved oxygen concentration at a level of about 10 mgO$_2$/dm^3, that is, about 100 % water saturation with oxygen. Also, chemically pure solutions of KMnO$_4$ or H$_2$O$_2$ were used to oxidise the Fe(II) ions; the oxidisation time amounted to 5 min, and the doses of oxidising agents were determined in view of the concentration of Fe(II) at an amount equal to 100% of the stoichiometric demand. In certain measurement series after coagulation and 2-hour sedimentation, filtration of samples through a soft filter was additionally added.

Table 1. Groundwater quality indicators

Indicator	Unit	Value		
		Minimum	Average	Maximum
Temperature	°C	6.9	11.8	17.8
pH	–	6.88	–	7.25
Dissolved Oxygen	mgO$_2$/dm^3	0.50	0.93	1.56
Colour	mgPt/dm^3	10	20	38
Turbidity	NTU	2.81	16.82	38.80
Iron total	mgFe/dm^3	2.48	5.03	7.84
Iron (II)	mgFe/dm^3	1.20	2.80	5.84
Iron(III)	mgFe/dm^3	0.95	2.22	4.20
Alkalinity	mval/dm^3	3.40	3.60	3.70
Manganese	mgMn/dm^3	0.20	0.32	0.42
Aluminum	mgAl/dm^3	0.09	0.13	0.17
TOC	mgC/dm^3	3.495	4.285	5.338
D = [TOC] / [Iron total]	–	0.640	0.860	0.943

The coagulation was performed in water samples with a volume of 1-dm^3, applying 1-minute of rapid stirring at an intensity of 250-rev./min and 25-minute of flocculation with a stirring intensity of 30-rev./min. Aluminium sulphate (VI) (SAL), polyaluminium chloride (PAX XL-60) and iron (III) sulphate (VI) – PIX-112, dosed in the form of water solutions were used as coagulants. The doses of coagulants (D$_c$) were expressed in mgAl/dm^3 or mgFe/dm^3 and changed within a range of 1 to 6 mgAl(Fe)/dm^3. 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 an WTW Multi Line P4 with an 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 an 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 Dr 3900 (HACH Lange) 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). Aluminum and manganese concentrations were determined with the plasma emission method (ICP-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, which did not contain any CO$_2$, 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).The coefficient of the co-occurrence of organic substances and total iron D, calculated as D = [TOC]/[Fe_{tot}] (mgC/mgFe) was used in the interpretation of the results of the studies, for the assessment of the level of organic pollution of the water samples and its impact on the course and effectiveness of the coagulation process, whereby in order to simplify the formula, the unit of the coefficient D was not given in the article. A decrease in the values of the studied water quality indicators in relation to the values permissible in the water for human consumption was assumed as the required effectiveness of water treatment.

2. Results and discussion

During the studies, the course and effectiveness of coagulation in raw water treatment and after Fe (II) oxidisation was determined. The effects of water treatment in technological systems were assessed:

- coagulation, 2-hour sedimentation;
- Fe (II) oxidisation, coagulation, 2-hour sedimentation (additional filtration through soft filter paper).

2.1. The impact of water aeration on the effectiveness of its treatment

Comparison of the effects of raw and aerated water showed unambiguously that in view of the necessity of increasing the degree of the removal of iron compounds and reducing the intensity of the colour and turbidity of water, its aeration was required before the coagulation process (Figs 1a, b and 2b).

The water aeration was, on the other hand, disadvantageous in terms of the removal of organic substances (Fig. 2a). This relationship was confirmed by the contents 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 2).

Table 2. Content of organic substances in the dry mass of post-coagulation sludge (D_c = 1–6mgAl/Fe/dm³) separated from raw water and aerated water

Kind of water being purified	Organic substances % in the dry mass of post-coagulation		
	SAL	PAX XL-60	PIX-112
Non-aerated	14.3–31.4	16.3–33.8	11.0–25.0
Aerated	8.1–19.0	14.9–21.1	7.0–16.0

An increase in the pH of the water (by about 1 unit) as a result of aeration probably caused a simultaneous decrease in the amount of products of the hydrolysis of coagulants with positive charges (e.g. $AlOH^{2+}$, $Al(OH)_2^+$, $FeOH^{2+}$, $Fe(OH)_2^+$) and an increase in the degree of the dissociation of organic compounds, which decreased the effectiveness of the removal of organic pollutants (Krupińska 2012; Libecki, Dzejowski 2008). Comparison of the effectiveness of the studied coagulants showed the greatest effectiveness using the prehydrolyzed coagulant (PAX XL-60), especially in terms of small doses. The advantages of polyaluminium chloride also included the decreased acidification of water and a smaller consumption of total alkalinity, which is significant in the aspect of the removal of iron and manganese compounds and the chemical stability of water. Within the range of doses used, an average unit consumption of total alkalinity was: 0.10 mval/mgAl (SAL), 0.07 mval/mgAl (PAX XL-60) and 0.09 mval/mgFe (PIX-112). The studies conducted by Edzwald *et al.* (2000) 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 pre-hydrolyzed.

The effectiveness of iron (III) sulphate (VI), irrespective of the type of polluted water (raw or aerated water),

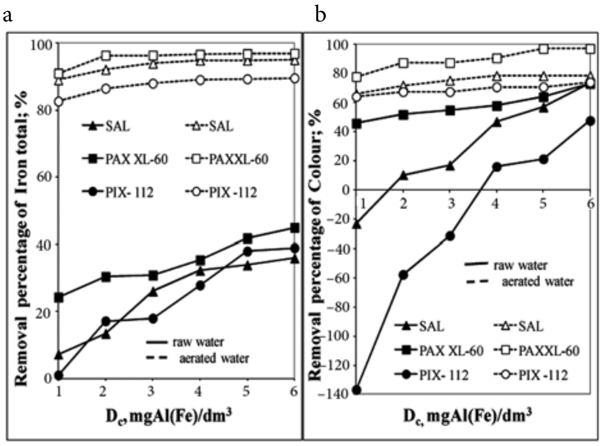

Fig. 1. Comparison of effectiveness of coagulation and 2-hour sedimentation in the reduction of: (a) the concentration of total iron and (b) colour in raw water or after aeration

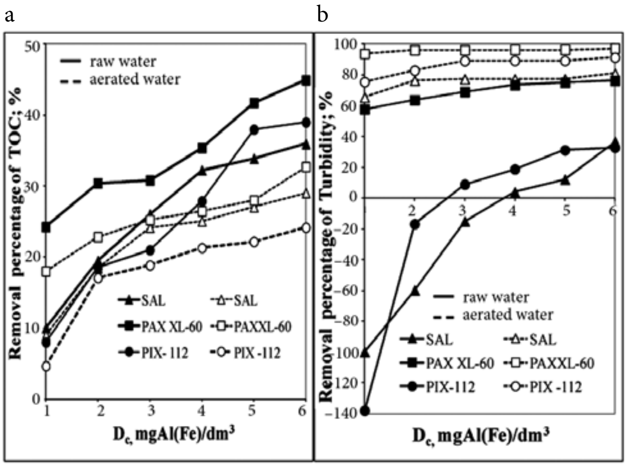

Fig. 2. Comparison of the effectiveness of coagulation and 2-hour sedimentation in the reduction of (a) TOC and (b) turbidity in raw water or after aeration

Table 3. The impact of the value of coefficient D (TOC/Fe_{og}) and the type of coagulant (D_k = 3 mgAl(Fe)/dm^3) on the effectiveness of the removal of pollutants (η) from raw water and from water after aeration

Type of coagulant	Type of oxidant	D	η_{Feog}	η_B	η_M	h_{TOC}	η_{Mn}
SAL	–	0.640	56	65	80	31	5
		0.846	27	17	15	26	5
	O_2	0.780	95	77	85	24	15
		0.823	90	73	77	21	15
PIX-112	–	0.810	50	33	84	22	13
		0.838	25	31	80	20	13
	O_2	0.601	89	70	90	20	20
		0.722	85	67	87	17	20
PAX XL-60	–	0.654	60	80	91	39	7
		0.832	51	54	69	31	7
	O_2	0.763	96	87	97	28	17
		0.943	94	81	94	25	17

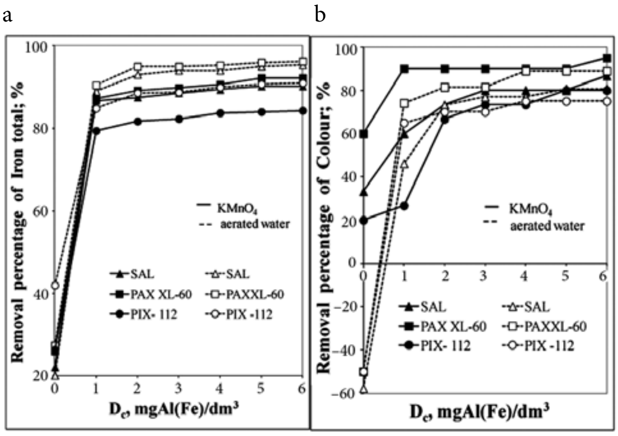

Fig. 3. Comparison of the effectiveness of coagulation and 2-hour sedimentation in the reduction of the total iron concentration (a) and colour (b) in water after oxidisation with $KMnO_4$ or after aeration

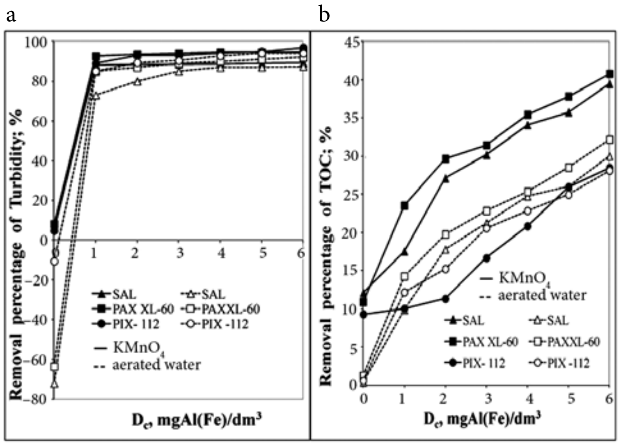

Fig. 4. Comparison of the effectiveness of coagulation and 2-hour sedimentation in reducing the turbidity (a) and concentration of total organic carbon (b) in water after oxidisation with $KMnO_4$ or after aeration

was only greater than that of the aluminium coagulant of aluminium sulphate (VI) (SAL) in reducing the turbidity and removing the manganese compounds, and even greater than PAX XL-60 coagulant. The greater effectiveness of iron (III) sulphate (VI) than aluminium sulphate (VI) in reducing the turbidity was probably caused by the greater density of $Fe(OH)_3$ than $Al(OH)_3$, and thus meaning better sedimentation properties of post-coagulation suspensions. The results of the studies have shown that coagulation with the studied coagulants was completely ineffective in removing manganese compounds from both non-aerated water and aerated water. This was caused by the low pH content, which was confirmed by an increase in the concentration of manganese in the treated water as the dose of coagulants and concentration of H^+ ions increased. The greatest but insufficient effectiveness of coagulant PIX-112 in removing the manganese compounds (Table 3) was probably 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 (VI). Comparison of the effectiveness of the removal of pollutants from underground raw or aerated water (Table 3), differing in terms of the values of the coefficients of the co-occurrence of organic pollutants and total iron (D = TOC/Fe_{tot}) proved that, irrespective of the type of the coagulant, the effectiveness of decreasing the concentration of total iron, reducing the colour and the turbidity and removing the organic substances was lower for the greater values of coefficient D.

The relationships found prove the stabilisation of iron compounds by organic substances. The regularity found proves book references (Eikebrokk, Fettig 1990; Dempsey *et al.* 1985; Edzwald *et al.* 2000; Krupińska 2014) stating that an increase of 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.

2.2. The effects of the removal of pollutants from water after oxidisation using potassium manganate (VII)

The effects of the removal of pollutants from the water after oxidisation with potassium manganate (VII) showed that the precipitating manganese (IV) oxide increased the effectiveness of the removal of pollutants from the water. Comparison of the effects of coagulation and sedimentation in the treatment of aerated water and water after oxidisation with potassium manganate (VII) showed that the application of $KMnO_4$ as an oxidising agent was much better than oxidisation with regards to the degree of the reduction in colour, turbidity and concentration of manganese and organic substances (except coagulant PIX-112), but unfortunately worse with respect to iron removal (Figs 3 and 4).

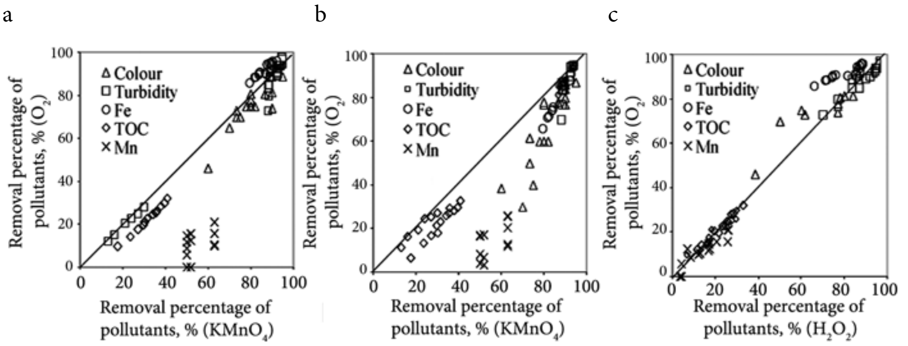

Fig. 5. The impact of the type of oxidising agent: a) dissolved oxygen and $KMnO_4$, b) H_2O_2 and $KMnO_4$, c) dissolved oxygen and H_2O_2 on the effects of the removal of pollutants in the coagulation process (SAL, PAX XL-60, PIX-112) and 2-hour sedimentation

The probable reason for the worse effects of the removal of iron from water after oxidisation with $KMnO_{4,}$ was the decrease in the efficiency of oxidisation of the Fe(II) to Fe(III),(($\eta_{Fe(II)\text{-}Fe(III)}$ = 92% (O_2); $\eta_{Fe(II)\text{-}Fe(III)}$ = 86% ($KMnO_4$)); caused by the lower pH value than in the water samples after aeration ((pH = 8 (O_2); pH = 7 ($KMnO_4$)).

The lack of any increase in the pH in water after oxidisation with potassium manganate (VII) additionally precipitated manganese (IV) oxide was, on the other hand, favourable in terms of the removal of the organic substances. According to Ficek and Vella (2000) application of potassium manganate (VII) to drinking water treatment systems can help solve a number of problems. It is a versatile oxidant that will react with organic compounds easily breaking carbon-carbon double bonds and oxidizing functional groups. The comparison of the usefulness of the studied coagulants in the removal of pollutants from water after oxidisation of Fe(II) with potassium (VII) manganate, just as in the case of the treatment of raw and aerated waters, confirmed the greatest effectiveness of coagulant which was prehydrolyzed with PAX XL-60. Also, the concentration of the residual aluminium was determined in the studies. It was ascertained that also in this aspect, polyaluminium chloride was more useful than aluminium sulphate (VI). The lowest aluminium concentrations (0.28–0.22 mgAl/dm^3) were found in water after oxidisation with potassium (VII) manganate and coagulation with coagulant PAX XL-60 (D_c = 1–6mgAl/dm^3) (see Fig. 7). Also according to Van Benschoten, Edzwald (1990), substitution of aluminium sulphate(VI) by polyaluminium chlorides reduced the concentration of aluminium residual in water after coagulation. The conducted studies also showed that if $KMnO_4$ was used for the oxidisation of the Fe(II) before the process of coagulation with aluminium sulphate (VI), polyaluminium chloride and iron (III) sulphate (VI), the impact of the coefficient D on the effectiveness of the removal of pollutants was not unambiguous.

2.3. The impact of oxidisation with hydrogen peroxide on the degree of removal of pollutants

Analysis of the relationships presented in Figure 5 proved that the worst effects regarding the removal of pollutants from water were obtained as a result of the application of H_2O_2 for the oxidisation of Fe(II). The application of aeration before the coagulation process was the most effective in view of the removal of iron compounds, and potassium manganate (VII) – with regards to reducing the colour, turbidity and concentrations of the total organic carbon and manganese.

The degree of the removal of manganese from water samples in which $KMnO_4$ was applied as the oxidising agent was constant and did not depend on the dose of the coagulant. On the other hand, in the case of preceding the coagulation with aeration or oxidisation with hydrogen peroxide, the effectiveness of the removal of manganese was reduced together with an increase in the dose of the studied coagulants (Fig. 6).

Irrespective of the type of the oxidising agent (O_2, $KMnO_4$, H_2O_2) used, with regards to the concentration of

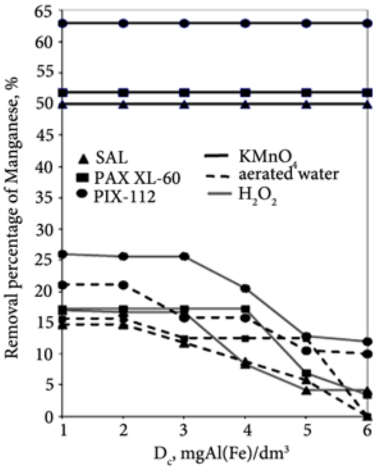

Fig. 6. The impact of the type and dose of coagulant and the oxidising agent used on the effectiveness of the removal of manganese from water (2-hour sedimentation)

aluminium left in the water treated with aluminium coagulants, coagulant PAX XL-60 was more effective than aluminium sulphate (VI). Eikebrokk and Fettig (1990) and Edzwald *et al.* (2000) believe that polyaluminium chlorides are more effective than aluminium sulphate (VI). The higher efficiency of polyaluminium chloride than aluminium sulphate (VI) is attributable to the fact that the solutions of polyaluminium chloride contain (in addition to aluminium monomers) large quantities of polycationic products generated during prehydrolysis of aluminium, which effectively neutralize the negative charges of the colloids (Krupińska 2014; Eikebrokk, Fettig 1990; Dempsey *et al.* 1985). On top of this, irrespective of the type of oxidising agent (O_2, $KMnO_4$, H_2O_2) used, the concentration of residual aluminium after coagulation with polyaluminium chloride was reduced together with an increase in the dose of the coagulant, and after the coagulation with aluminium sulphate (VI), the reverse relationship was found (Fig. 7).

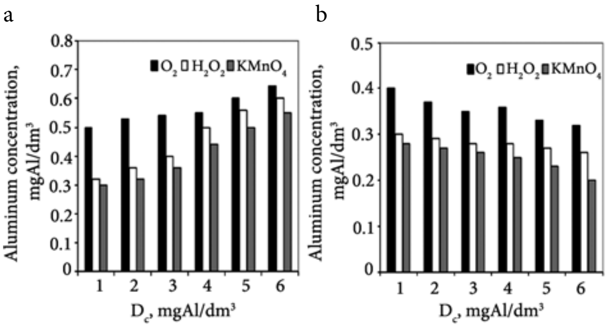

Fig. 7. The impact of the type and dose of coagulant and the oxidising agent on the change of aluminium concentration: a) SAL; b) PAX XL-60

Table 4. Required doses of coagulants (D_{re}) ensuring a comparable degree of reduction in the concentration of total iron and organic pollutants, and causing colour and water turbidity in coagulation and sedimentation

Type of coagulant	D_{re} mgAl(Fe)/dm³			
	Iron total	Colour	Turbidity	TOC
SAL	$D_c < 1$	$1 < D_c < 2$	$D_c > 6$	$4 < D_c < 5$
PIX-112	$D_c = 6$	$D_c = 6$	$D_c = 6$	$D_c = 6$
PAX XL-60	$D_c < 1$	$D_c < 1$	$3 < D_c < 4$	$4 < D_c < 5$

Table 5. Parameters of lineral regression between the amount of TOC removed and the amount of Fe(III) removed in the coagulation proces

Type of oxidant	Type of coagulant	Linear regression equation	Coefficient of determination (R^2)
O_2	SAL	hTOC = 1.8127η Fe(III) −147.12	0.9465
	PAX XL-60	hTOC = 1.3197η Fe(III) −97.101	0.9401
	PIX-112	hTOC = 1.9361ηFe(III) − 143.74	0.9631
$KMnO_4$	SAL	hTOC = 1.505ηFe(III) −88.805	0.9457
	PAX XL-60	hTOC = 1.826 ηFe(III) −121.40	0.9588
	PIX-112	hTOC = 2.2558 ηFe(III) −133.13	0.9483
H_2O_2	SAL	hTOC = 1.7238ηFe(III) − 110.34	0.9493
	PAX XL-60	hTOC = 2.0134η Fe(III) − 161.71	0.9843
	PIX-112	hTOC = 1.0709η Fe(III) − 39.416	0.9793

Comparison of the doses of coagulants ensuring a similar degree of reduction in the concentration of total iron (76%), colour (60%), turbidity (95%) and TOC (27%) in water samples in which hydrogen peroxide was used as the oxidising agent, confirmed unambiguously the greatest effectiveness of coagulant PAX XL-60, and among the non-hydrolyzed coagulants, a preliminarily greater effectiveness of aluminium sulphate (VI) than iron (III) sulphate (VI) (except for reduction in turbidity) (Table 4).

Analysis of the results of the studies presented in Table 5 showed that irrespective of the oxidising agent used, an increase in the effectiveness of coagulation and sedimentation in the removal of Fe(III) resulted in an increase in the degree of the removal of TOC, which proves the removal of Fe(III) together with the organic substances, and thus, the occurrence of iron in iron-organic bonds in water. In the water samples in which H_2O_2 or $KMnO_4$ were used for oxidisation of Fe(II), no relationship between the effectiveness of the removal of pollutants and the value of the quotient of the TOC concentrations to total iron (D) were found. The required values of colour (15 mg Pt/dm³), turbidity (1NTU) and concentrations of total iron (0.2 mg Fe/dm³) and residual aluminium (0.2 mg Al/dm³) were obtained only after additional filtration through a soft filter. To obtain the required degree of water treatment, the filtration of water samples after sedimentation of post-coagulation suspensions was redundant only after using $KMnO_4$ and the most effective coagulant (PAX XL-60 (D_c = 5mgAl/dm³)).

Conclusions

The test results analysis leads to the following conclusions:

1. In the case of treatment of groundwater with an increased content of organic substances and iron, it was necessary to oxidise Fe (II) ions prior to the coagulation process.
2. The application of potassium manganate (VII) for oxidation of Fe (II) ions produced the best results

in terms of reduction in colour, turbidity and concentration of manganese and organic substances. Hydrogen peroxide was the least useful oxidising agent.

3. In the case of the treatment of raw water or aerated water, the effectiveness of the coagulation process was determined by the value of the coefficient of the co-occurrence of organic substances and total iron. As its value in the treated water increased, the effectiveness of coagulation and sedimentation in the removal of pollutants (except manganese compounds) decreased. This regularity was not observed when hydrogen peroxide and potassium manganate (VII) was used to oxidise Fe (II).
4. Regardless of the oxidising agent the best results in the removal of pollutants in the coagulation process were produced by the coagulant: pre-hydrolysed polyaluminium chloride PAX XL-60, and the worst by the iron coagulant: iron (III) sulphate (VI). The lowest usefulness of the iron coagulant for removing iron and organic compounds, and for decreasing the colour intensity in water was probably caused by the interaction of organic ligands and Fe(III) ions introduced into the water with the coagulant.
5. In the coagulation process Fe (III) compounds were removed together with organic substances, which means that they occurred in the water undergoing treatment in the form of colloidal ferrous-organic compounds which could only be removed in the coagulation process.
6. An analysis of the research results also shows that when groundwater with an increased content of organic substances is treated, the coagulation process for polyaluminium chloride should be aided with a chemical oxidising agent, preferably with a potassium manganate (VII) because apart from iron(III) hydroxide, manganese (IV) oxide is also produced in the process of oxidation. It acts as an extender and adsorbent improving the sedimentation characteristics of ferrous-organic agglomerates, which are difficult to remove in a conventional technological system for groundwater treatment.

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