

POTASSIUM PERMANGANATE AS AN OXIDIZING AND FLOCCULATING AGENT IN GROUNDWATER TREATMENT

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The effectiveness of groundwater treatment with a high amount of organic substances and general iron depended on the kind of oxidizing agent, the kind and dose of coagulant, and the time of sedimentation. The effectiveness of the sedimentation process increased with the length of time of the process, and its results depended most on the method of oxidizing Fe(II). From among the oxidizing agents used before the coagulation process the best results in terms of a decrease in colour, turbidity, the concentration of manganese and organic substances were obtained in the case of oxidization with potassium permanganate, and as far as the effectiveness of removing general iron was concerned oxidizing with dissolved oxygen.

Keywords: potassium permanganate, groundwater, coagulation

1. INTRODUCTION

Potassium permanganate was first used for the purification of water intended for people in London in 1913, in order to oxidize compounds giving water taste and smell [3]. Nowadays, potassium permanganate is mainly used as an oxidizing agent for the treatment of water with an unacceptable taste and smell, most often together with processes of sorption with activated carbon. It can also be used as a strong oxidizing agent stimulating the process of coagulation, and also as an oxidizing agent in the treatment of groundwater. Chemical oxidizing agents such as: potassium permanganate, chlorine or chlorine dioxide cause faster oxidization of Fe(II) to Fe(III) than dissolved oxygen [7]. It was confirmed by the results of research carried out by Lytle et al., who found that molecules of

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$\text{Fe}(\text{OH})_3$ created as a result of oxidizing $\text{Fe}(\text{II})$ with chlorine and chlorine dioxide had a lower density and were more difficult to remove in the process of filtration than products of oxidizing with dissolved oxygen. They also proved that the presence of organic compounds in water makes the removal of iron much more difficult. Organic compounds lengthen the time oxidization of $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$ and decrease its effectiveness, and oxidization products are colloidal in character [4, 7, 14]. Results obtained by a number of authors [1, 2, 5, 6, 7, 8, 9, 10, 11, 13] showed that for the oxidization of $\text{Fe}(\text{II})$ present in groundwater in the form of compounds with organic substances it is good to use potassium permanganate, because the oxidization process is stimulated in addition by sorptive and catalytic characteristics of precipitating MnO_2 . An advantage of the use of potassium permanganate is also the fact that unlike oxidization it does not cause the pH of water to increase, which would be unfavourable to the removal of organic pollutants [14]. There is very little information about the kinetics of oxidizing $\text{Fe}(\text{II})$ by means of potassium permanganate. It is believed that the reactions take place quickly with $\text{pH} > 7$. In an environment with neutral reaction, which is usual in natural water, potassium permanganate is reduced to manganese oxide (IV). The hydrated colloidal manganese oxide (IV) which appears has a negative charge with $\text{pH} < 8$, and a positive charge with $\text{pH} \geq 8$ and a vast specific surface with good sorptive characteristics [7, 8, 9]. The use of potassium permanganate is particularly favourable if there is $\text{Mn}(\text{II})$ in the water being purified, because apart from $\text{Fe}(\text{OH})_3$ a product of the reaction is MnO_2 which catalyses the oxidization of $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$. The catalytic oxidization of $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ ions makes it possible to decrease the dose of potassium permanganate below stoichiometric amounts if there are not any other reduced substances [7] in the water being purified. The article presents results of research into the oxidization of $\text{Fe}(\text{II})$ ions with oxygen and potassium permanganate and the influence of oxidization on the effectiveness of removing pollutants from groundwater.

2. AIM AND METHODOLOGY OF RESEARCH

The research substrate was groundwater from Quaternary formations with a high concentration of general iron (Fe_{og}) amounting to $7,84 \text{ mgFe/dm}^3$, increased colour (B) – up to 38 mgPt/dm^3 and turbidity (M) up to 38.8 NTU , and also an increased amount of organic substances (OWO from 3.495 to 5.338 mgC/dm^3), and manganese (up to 0.42 mgMn/dm^3). There were iron compounds (II) and (III) in the water. The concentration of dissolved oxygen varied within the range of 0.50 to $1.56 \text{ mgO}_2/\text{dm}^3$, and the pH value was between 6.88 and 7.25 (table 1). In the research the effectiveness of the technological system was specified: sedimentation and filtration and the system: volume coagulation,

sedimentation and filtration in the treatment of water after its aeration and oxidization with potassium permanganate. Raw water was aired with compressed air in the time (t_a) from 10 s to 15 minutes, the compression of oxygen obtained was from about $1.82 \text{ mgO}_2/\text{dm}^3$ to about $10 \text{ mgO}_2/\text{dm}^3$ i.e.. from about 18 to about 100 % saturation of the water with oxygen.

Table 1. Groundwater characteristics

Parameter	Unit	Value		
		Minimum	Average	Maximum
Temperature	$^{\circ}\text{C}$	6.9	11.8	17.8
pH	-	6.88	-	7.25
Dissolved Oxygen	mgO_2/dm^3	0.50	0.93	1.56
Colour (B)	mgPt/dm^3	10	20	38
Turbidity (M)	NTU	2.81	16.82	38.80
Iron (Fe)	mgFe/dm^3	2.48	5.03	7.84
Iron (II) – Fe(II)	mgFe/dm^3	1.20	2.80	5.84
Iron(III) – Fe(III)	mgFe/dm^3	0.95	2.22	4.20
Alkalinity	mval/dm^3	3.40	3.60	3.70
Manganese (Mn)	mgMn/dm^3	0.20	0.32	0.42
TOC	mgC/dm^3	3.495	4.285	5.338
TOC/Iron (D)	-	0.633	1.073	1.613

In the case of the use of potassium permanganate the oxidization time was 5 minutes, and the dose was determined on the basis of the concentration of Fe(II), in the amount equal to 100% of the stoichiometric demand. After aeration, or chemical oxidization KMnO_4 the sedimentation process was used for 1 to 24 h. Coagulation was carried out in water samples of 1 dm^3 , with the application of 1 minute's fast mixing with the intensity of 250 rev/min. and the time of flocculation of 25 minutes with the intensity of mixing of 30 rev/min. Aluminium sulphate (VI) (SAL) and chloride of polyaluminium (PAX XL-60) were used as coagulants, and they were dosed as water solutions. The coagulant doses were changed within the range of 1 to $6 \text{ mgAl}/\text{dm}^3$. The physical and chemical constitution of the raw and purified water was specified according to the current National Standards. A decrease in the values of the indicators of the quality of water under research to values acceptable in water intended for people [12] was adopted as the required water purification effectiveness. In the interpretation of the research results the ratio of coexistence of organic substances and general iron D calculated as $D = \text{TOC}/\text{Fe}$ (gC/gFe) was used to assess the level of organic pollutants in the water samples and their influence on the course and effectiveness of the processes under research.

3. RESEARCH RESULTS

The results of groundwater purification were evaluated by research in the following technological configurations:

- oxidation of Fe(II) by dissolved oxygen or potassium permanganate;
- oxidation of Fe(II) by dissolved oxygen, sedimentation ($t_s=1\div 24$ h) and filtration;
- oxidation of Fe(II) by potassium permanganate, sedimentation ($t_s=1\div 24$ h) and filtration;
- oxidation of Fe(II) by dissolved oxygen, coagulation, 2 hours' sedimentation and filtration;
- oxidation of Fe(II) by potassium permanganate, coagulation, 2 hours' sedimentation and filtration.

The process of filtration of the water samples was carried out through soft filter paper.

3.1. Oxidation of Fe(II) to Fe(III)

In order to oxidize Fe(II) to Fe(III) the groundwater samples were aerated or treated with potassium permanganate in a stoichiometric amount in comparison to the concentration of Fe(II). Regardless of the oxidizing agent which was used the oxidization rate was greater than 82,50%. However, the difference in the time of the oxidization of Fe(II) during aeration and oxidization with potassium permanganate was important. After aeration a further increase in colour was observed in the water samples during two hours' sedimentation in comparison to 15 minutes' aeration, which meant that there was further oxidization of Fe(II) to Fe(III) – fig.1. This phenomenon was not observed when potassium permanganate was used as an oxidizing agent. Potassium permanganate caused a decrease in the colour of the water, and also a slower increase in the turbidity of the water in comparison to the water samples after aeration (tab.2).

Table 2. Influence of the kind of oxidizing agent on the average unit change in colour ($\Delta B/\Delta Fe(III)$) and turbidity ($\Delta M/\Delta Fe(III)$) of the water samples

Type of oxidant	$\Delta M/\Delta Fe(III)$	$\Delta B/\Delta Fe(III)$
Dissolved Oxygen	6.52	5.86
KMnO ₄	1.28	-2.66

In the case of aeration, the rate of oxidization of Fe(II) to Fe(III) increased with the time of aeration (t_a), and at the same time with the concentration of oxygen dissolved in the water and the pH value (fig.2).

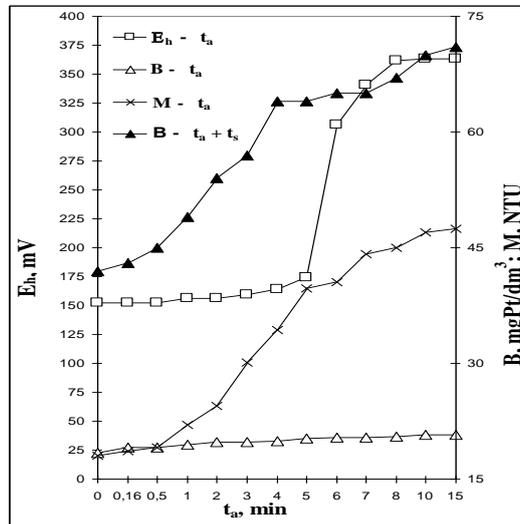


Fig. 1. Influence of the aeration time (t_a) on changes in the value of the oxidizing – reduction potential and the colour and turbidity of the water samples

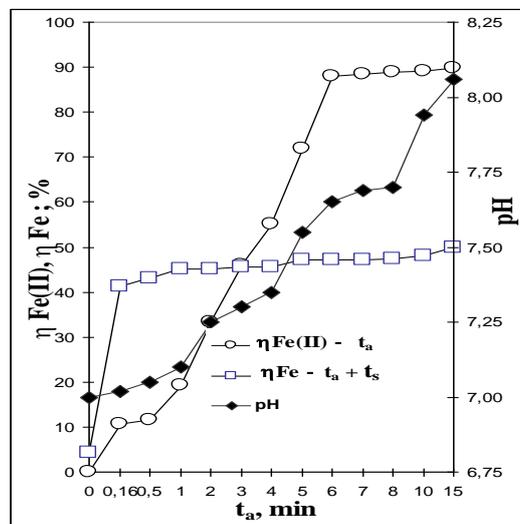


Fig. 2. Influence of the aeration time (t_a) on the effectiveness of the oxidation of Fe(II) to Fe(III), and the rate of removal of general iron in the process of sedimentation (t_s)

The value of the ratio of coexistence of organic substances and iron in raw water (D) also determined the rate of oxidation of Fe(II) during aeration. As

its value increased the effectiveness of oxidizing Fe(II) with oxygen dissolved with water decreased. These dependences have been presented in figure 3.

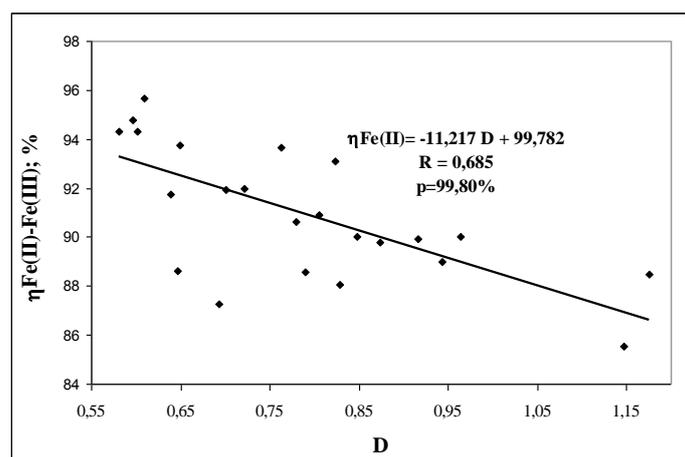


Fig. 3. Influence of the value of the ratio of coexistence of organic substances and general iron (D) on the rate of oxidization of Fe(II) to Fe(III)

In the water samples in which potassium permanganate was used to oxidize Fe(II) a dependence between the value of the ratio of coexistence of organic substances and general iron, and the rate of oxidization of Fe(II) to Fe(III) was not observed.

3.2. Influence of aeration or oxidization with potassium permanganate on the effectiveness of removing pollutants in the process of sedimentation

The aeration of water with compressed air for 15 minutes caused 101.6 % saturation of water with oxygen, an increase in pH by about 1 unit (to 8.16), 88.5 % oxidization of Fe(II) to Fe(III), and an increase in colour to 23 mgPt/dm³ and turbidity to 20.2 NTU. After 1 hour's sedimentation the effectiveness of water purification was very low; the water had the colour (B=25mgPt/dm³) and turbidity (M=19.6 NTU) greater than raw water, the rate of removing general iron was 12.7 %, and the decrease TOC was 6.8 %. Lengthening the time of sedimentation improved the results of water purification, but even 24 hours' sedimentation and additional filtration did not result in a sufficient rate of removal of general iron, manganese compounds and a decrease in turbidity. The final concentrations were respectively: Fe=0.38 mg/dm³, Mn=0.12 mg/dm³, M=3.40 NTU. The results of the researches have been presented in fig. 4.

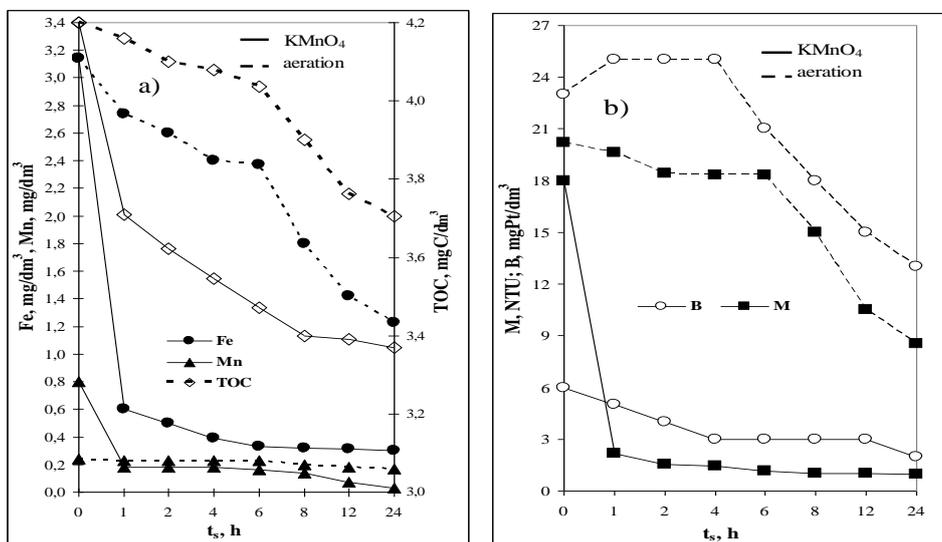


Fig. 4. Influence of the kind of oxidizing agent and sedimentation time on the values of: a) concentrations of general iron, manganese and TOC and b) water colour and turbidity after sedimentation

After potassium permanganate had been used as an oxidizing agent, in the amount of $1.92 \text{ mgKMnO}_4/\text{dm}^3$ (100% of stoichiometric demand as far as the concentration of Fe(II) was concerned), and after a contact time of 5 minutes a decrease in the pH value by about 0.04 was observed and an increase in the value of the oxidation-reduction potential of the water being purified from $E_h=255 \text{ mV}$ to $E_h=399\text{mV}$. Oxidation with potassium permanganate, contrary to aeration, caused a decrease in colour by $10 \text{ mgPt}/\text{dm}^3$ (to $6 \text{ mgPt}/\text{dm}^3$) and a considerably smaller increase in turbidity (to 18 NTU) - fig.4. During sedimentation an increase in the intensity of the colour of the water was not observed, which was the case during oxidizing iron (II) with oxygen dissolved in the water. The colour of the water corresponded to the acceptable value just after the process of oxidization with potassium permanganate alone.

The required efficiency of removing general iron ($\text{Fe}= 0.17 \text{ mg}/\text{dm}^3$) and turbidity ($M= 0.86 \text{ NTU}$) were obtained after oxidization with potassium permanganate, 4 hours' sedimentation and additional filtration. The effectiveness of removing manganese compounds from the water after oxidization with potassium permanganate was considerably higher than after aeration and was from 25.0 to 87.5%, and after additional filtration from 66.7 to 87.5%. The required concentration of manganese ($\text{Mn}=0.05\text{mg}/\text{dm}^3$) was obtained after 8 hours' sedimentation and additional filtration (fig.4a). It was also found that the effectiveness of removing general organic carbon was higher

in the water samples after oxidization with KMnO_4 than after aeration and was respectively from 11.7 to 19.8% and from 0.95 to 11.7% for sedimentation time from 1 to 24 h. The higher effectiveness of water purification with the use of KMnO_4 in comparison to the use of oxygen was probably caused by the adsorptive values of precipitating MnO_2 in comparison to manganese, iron and organic compounds, and also oxidization, which improved the sedimentation properties of the products of oxidization. The use of KMnO_4 was also favourable because of the lack of an increase in the pH value of the water being purified, which would cause an increase in the rate of dissociation of organic substances. After the use of potassium permanganate as an oxidizing agent and 1 hour's sedimentation the concentration of general iron, iron (III) and the turbidity and colour were about twice lower than after aeration and 24 hours' sedimentation. The effectiveness of removing organic compounds from the water after aeration was comparable with the effectiveness obtained after oxidization with potassium permanganate and 1 hour's sedimentation only after 24 hours' sedimentation.

3.3. Influence of aeration or oxidization with potassium permanganate on the effectiveness of removing pollutants in the process of coagulation

Low effectiveness of water purification, and especially of the removal of iron compounds in the technological system: the oxidation of Fe(II) (by dissolved oxygen or potassium permanganate), sedimentation and filtration caused the process of coagulation to be included in the technological system. Comparison of the results of coagulation and sedimentation in the purification of water after aeration and oxidization with potassium permanganate showed that the use of KMnO_4 as an oxidizing agent resulted in greater effectiveness of decreasing colour, the concentration of manganese and organic substances. That oxidizing agent, in comparison to oxygen, caused a comparable decrease in turbidity, but unfortunately a worse result as far as the removal of iron was concerned (fig.5a and b, 6a and b as well as 7a). The reason for the lower effectiveness of removing iron from the water after oxidization with KMnO_4 (fig.5b), was probably a decrease in the rate of oxidization of Fe(II) caused by a lower pH value of the water than after the process of aeration. The lack of an increase of the pH value and the precipitating manganese dioxide were particularly favourable in terms of removing organic substances (fig.6 b).

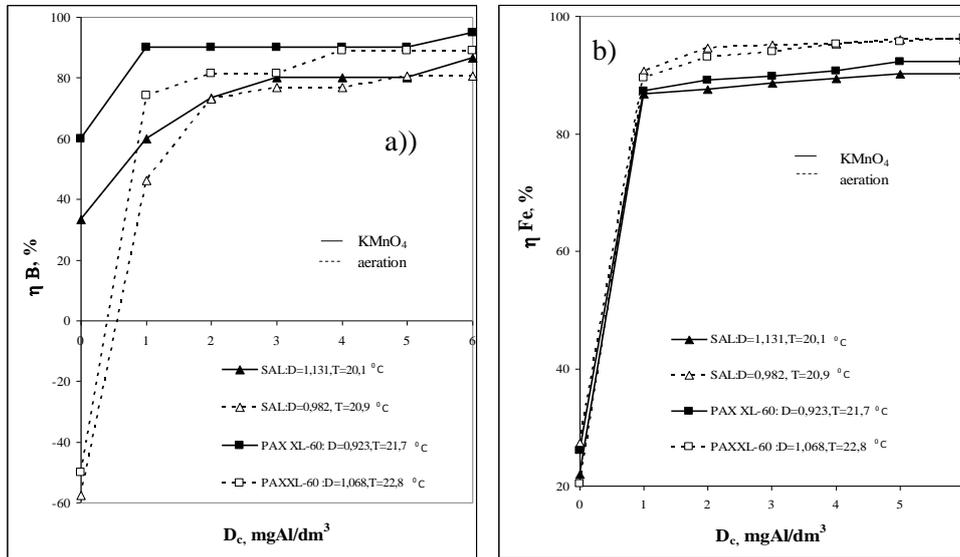


Fig. 5. Comparison of the effectiveness of coagulants in decreasing colour (a) and the concentration of general iron (b) in the water after oxidation with (KMnO_4 or O_2)

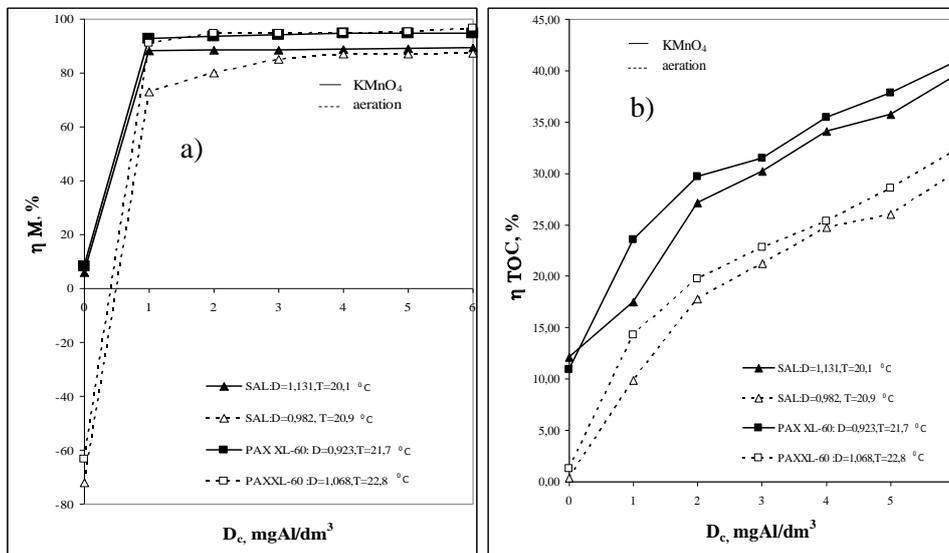


Fig. 6. Comparison of the efficiency of coagulants in decreasing (a) turbidity and the concentration of general organic carbon (b) in the water after oxidation with (KMnO_4 or O_2)

A comparison of the effectiveness of the coagulants which were tested: sulphate (VI) of aluminium and chloride of polyaluminium PAX XL-60 for the removal

of pollutants from water after oxidation with KMnO_4 or oxidation with oxygen, showed that the effectiveness of chloride of polyaluminium was much higher than that of sulphate (VI) of aluminium. The rate of removing manganese compounds from the water after oxidation with a fixed dose of potassium permanganate was considerably higher than from the water after the process of aeration (fig.7 a and b).

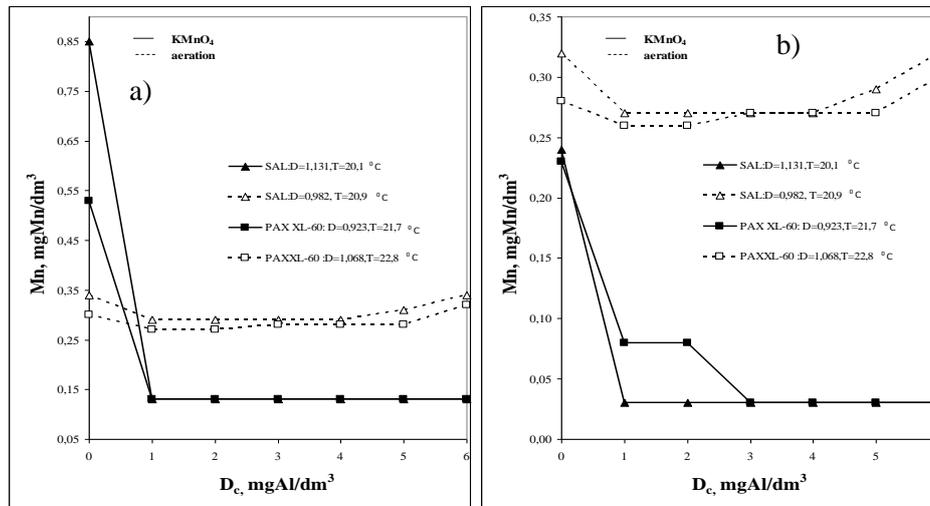


Fig. 7. Influence of the kind and dose of coagulant and the kind of water to be purified on the concentration of manganese remaining in the purified water: a) after sedimentation and b) after additional filtration

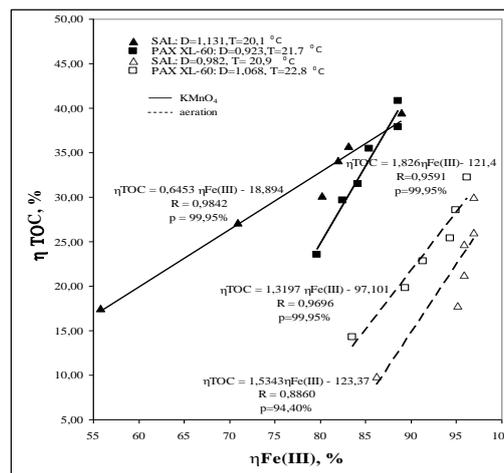


Fig. 8. Dependence of decreasing TOC on the rate of removing general iron

After oxidization with potassium permanganate, the effectiveness of removing manganese did not depend on the dose of coagulant but the removal of manganese depended on the amount of precipitated MnO_2 . Independently of the kind of oxidizing agent used organic substances were removed together with iron (III) compounds, which is confirmed by the linear correlations shown in fig. 8.

Together with an increase in Fe(III) which was removed in the process of coagulation the amount of pollutants causing colour and turbidity of the water which were removed also increased (table 3).

Table 3. Parameters of linear correlation between a decrease in the concentration of Fe(III), and a decrease in the turbidity and colour of the water in the processes of: aeration or oxidization with $KMnO_4$, coagulation and sedimentation

Type of oxidant	Type of coagulant	Linear regression	The correlation coefficient	Probabilities
$KMnO_4$	SAL	$\Delta M = 1.5624\Delta Fe(III) + 11.2190$ $\Delta B = 2.6118\Delta Fe(III) + 2.4847$	R=0.9088 R=0.7132	p=98.6% p=88.0%
	PAX XL-60	$\Delta M = 2.3991\Delta Fe(III) + 19.0710$ $\Delta B = 2.1167\Delta Fe(III) + 1.3760$	R=0.9372 R=0.9100	p=98.8% p=98.6%
Dissolved Oxygen	SAL	$\Delta M = 9.5473\Delta Fe(III) - 8.5578$ $\Delta B = 13.5450\Delta Fe(III) - 8.4861$	R=0.9220 R=0.9772	p=98.6% p=99.95%
	PAX XL-60	$\Delta M = 4.1383\Delta Fe(III) + 16.9500$ $\Delta B = 28.7320\Delta Fe(III) - 59.8930$	R=0.9440 R=0.9981	p=98.6% p=99.95%

The amount of organic substances removed from Fe (III) ($\Delta TOC/\Delta Fe(III)$) - table 4 and the amount of colour substances removed from Fe(III) ($\Delta B/\Delta Fe(III)$) were greater in the water samples after oxidization with $KMnO_4$ than after aeration and they increased together with a dose of coagulants (tables 4 and 5).

Table 4. Influence of the kind of dose of coagulant and the kind of oxidizing agent on the amount of organic pollutants (mg) removed from 1 mg of Fe(III) ($\Delta TOC C/\Delta Fe(III)$)

Type of coagulant	Type of oxidant	$\Delta TOC/\Delta Fe(III)$					
		$D_c, mgAl/dm^3$					
		1	2	3	4	5	6
SAL	Dissolved Oxygen	0.095	0.165	0.197	0.229	0.238	0.275
	$KMnO_4$	0.228	0.350	0.385	0.432	0.448	0.495
PAX XL-60	Dissolved Oxygen	0.170	0.227	0.259	0.285	0.319	0.356
	$KMnO_4$	0.249	0.307	0.323	0.361	0.379	0.408

Table 5. Influence of the kind and dose of coagulant and the kind of oxidizing agent on the amount of colour pollutant (mg) removed from 1 mg of Fe(III) ($\Delta B/\Delta Fe(III)$)

Type of coagulant	Type of oxidant	$\Delta B/\Delta Fe(III)$					
		$D_c, mgAl/dm^3$					
		1	2	3	4	5	6
SAL	Dissolved Oxygen	4.800	6.884	7.194	7.194	7.636	7.664
	KMnO ₄	9.375	9.016	8.690	8.510	8.390	8.496
PAX XL-60	Dissolved Oxygen	9.184	8.867	8.696	8.571	8.257	8.450
	KMnO ₄	9.524	9.821	9.998	10.126	10.200	10.250

4. CONCLUSIONS

- Together with increasing values of coexistence ratios of organic substances and iron in the water, the effectiveness of oxidizing ions of Fe(II) to Fe(III) with oxygen decreased and the time of oxidization increased. This phenomenon was not observed when potassium permanganate was used, because unlike dissolved oxygen it decreased the intensity of colour and caused a smaller increase in the turbidity of the water.
- Regardless of the method of oxidizing ions of Fe(II) (dissolved oxygen, potassium permanganate) the products of oxidization were finely dispersed and had bad sedimentation properties.
- During sedimentation only non-organic forms of iron were removed from the water and colloidal and dissolved fractions of iron remained in it (mainly Fe(III)) and were stabilized by organic substances.
- Oxidization of ions of Fe(II), 25 minutes' flocculation and sedimentation did not result in a sufficient decrease in the concentration of iron compounds and a decrease in the turbidity of the water.
- The effectiveness of the process of coagulation for the removal of pollutants from underground water depended on the kind of oxidizing agent used and the kind of coagulant, and it increased together with the dose of coagulants. Better results in purifying the water were obtained with the use of a pre-hydrolysed coagulant PAX XL-60 than sulphate (VI) of aluminium.
- From among the oxidizing agents used before the coagulation process the best results in terms of a decrease in colour, turbidity, the concentration of manganese and organic substances were obtained in the case of oxidization with potassium permanganate, and as far as the effectiveness of removing general iron was concerned oxidizing with dissolved oxygen.

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MANGANIAN (VII) POTASU JAKO UTLENIACZ I FLOKULANT W OCZYSZCZANIU WÓD PODZIEMNYCH

Streszczenie

Skuteczności usuwania zanieczyszczeń z wody podziemnej o podwyższonej zawartości substancji organicznych i żelaza ogólnego zależała od rodzaju stosowanego utleniacza, czasu sedymentacji oraz rodzaju koagulantu i jego dawki. Skuteczność procesu sedymentacji zwiększała się wraz z czasem trwania procesu, a o jej efektach w największym stopniu decydował sposób utleniania Fe(II). Lepsze efekty oczyszczania wody podczas procesu sedymentacji uzyskano stosując manganian (VII) potasu jako utleniacz niż tlen rozpuszczony, ponieważ wytrącający się z wody MnO_2 , działając jako obciążnik i adsorbent, poprawił właściwości sedymentacyjne aglomeratów $Fe(OH)_3$. Ilość żelaza ogólnego usuniętego z wody w wyniku utleniania Fe(II) tlenem rozpuszczonym a następnie jego sedymentacji, zmniejszała się wraz ze wzrostem współczynnika współwystępowania substancji organicznych i żelaza ogólnego w wodzie surowej. Spośród stosowanych sposobów utleniania żelaza (II) przed procesem koagulacji lepsze efekty z uwagi na efekty zmniejszenia barwy, mętności, stężenia manganu i substancji organicznych zapewniło utlenianie manganianem (VII) potasu natomiast z uwagi na skuteczność usuwania żelaza ogólnego utlenianie tlenem rozpuszczonym.