Sorbent-Catalyst for Acceleration of The Iron Oxidation Process

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ABSTRACT

In this work, the process of water deironing by using magnetite as a catalyst to accelerate the oxidation of iron ions in an aqueous medium was investigated. It was shown that the efficiency of iron ion extraction depends on the solution concentration, sorbent dose and contact time. In all cases, the use of magnetite accelerated the process of extraction of iron by more than an order of magnitude in comparison with similar experiments on the oxidation of iron without the addition of a catalyst. At the pH values greater than 6, the use of magnetite as a catalyst contributes to the deep purification of water from iron ions.

Keywords: iron ions, magnetite, sorbent, catalyst, deironing, sorption capacity of magnetite

INTRODUCTION

Intense pollution of the surface and groundwater sources has led to deterioration in the drinking water quality. Most water resources, including artesian wells, are contaminated with iron compounds that accumulate in the human body and lead to the development of chronic diseases. Usually, iron in natural waters may be present in concentrations from 5 to 20 mg/dm³. The use of such water for drinking purposes without prior purification is impossible. The vast majority of water deironing technologies are obsolete. The characteristics of water at the outlet of treatment plants do not meet the requirements for the drinking water quality. In view of this, the search, development and implementation of efficient and energy-saving methods for deironing of drinking groundwater remain important tasks in the process of water treatment. That is why, the use of new high-performance materials with appropriate characteristics is promising and appropriate.

The problem of extracting iron from natural and wastewater remains unresolved, despite the large number of publications [Khatri et al., 2017; Ryzhenko et al., 2019]. If the known methods of water deironing are considered, the most common technique of groundwater deironing is the method of simplified aeration [Podgórni et al., 2014]. In this case, the oxidation of iron in water is realized through the contact of water with air and its subsequent settling and filtration. This method is dominated by ion exchange [Chaturvedi et al., 2012], sorption methods [Biela et al., 2016], electrocoagulation [Doggaz et al., 2018] and reverse osmosis [Goncharuk et al., 2011]. The ion exchange and sorption processes of iron extraction from water are complicated by significant concentrations of hardness ions in natural and wastewater. The concentrations of hardness ions are at least ten times higher than the concentrations of iron ions, so the use of resins and sorbents for deironing natural waters is extremely inefficient. In the case of sorption, ion exchange, the sorbents are poisoned by iron (III) compounds, which after their formation are difficult to remove from the resin or sorbent. Poisoning by iron (III) compounds also occurs when using membranes. Electrocoagulation requires complex hardware and significant energy consumption. The reagent removal of iron from water [Biplob Kumar

Pramanik, et al., 2016] is accompanied by water leaching and contamination with reagents.

In recent years, research has been actively conducted on the use of highly dispersed sorbents and catalysts that contain particles with magnetic properties. Such materials show increased activity under the conditions of catalytic reactions and promote acceleration of processes. One such material includes the nanoparticles formed on the basis of ferrites. Sorbents synthesized due to iron oxide compounds are actively used in various chemical technologies [Gomelya et al., 2020]. It was found that magnetite (Fe_3O_4) nanoparticles show sorption activity against heavy metal salts [Giraldo et al., 2013; Radovenchik et al., 2020].

The aim of this work was to study the oxidation of iron ions in the presence of magnetite and evaluate the effectiveness of its use as a sorbent-catalyst for deironing of water.

MATERIALS AND METHODS

Methods of work

In order to determine the effect and dose of the catalyst on the rate of oxidation of iron ions in an aqueous medium, the study was performed on model solutions, which were prepared in tap water with a concentration of iron ions from 5 to 30 mg/dm^3. Magnetite (Fe_3O_4) was used as a catalyst. In order to obtain magnetite in the form of a suspension used the method of precipitation of magnetic particles from a mixture of solutions of salts of ferrous sulfate (II) and ferric chloride (III) in an alkaline medium. The product yield was calculated at a ratio of $Fe^{2+}:Fe^{3+} = 1: 2$ by the reaction:

$$FeSO_4 \cdot 7H_2O + 2FeCl_3 \cdot 6H_2O + 8NaOH =$$
$$= Fe_3O_4\downarrow + NaCl + NaSO_4 + 4H_2O \quad (1)$$
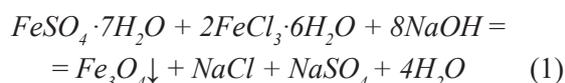
Magnetite nanoparticles were formed in the pH range of 9–10. For maturation, the synthesized magnetite particles were left in the mother liquor for one hour, after which the resulting suspension was washed with distilled water to a neutral pH value. Subsequently, the magnetic suspension was dosed into the model solutions at predetermined concentrations from 100 to 500 mg/dm^3 for Fe_3O_4, fixing the residual concentrations of iron ions every 30 min for 3 hours.

On the basis of the obtained data, the capacity of sorbent A (mg/g) was calculated for iron ions and the purification efficiency E (%) from iron ions:

$$A = \frac{(C_0 - C) \cdot V_s}{m}, \% \quad (2)$$

$$E = \frac{(C_0 - C)}{C_0} \cdot 100, \% \quad (3)$$

where: C_0 and C – initial and equilibrium concentration of iron ions in solution, mg/dm^3;
V_s – volume of solution, dm^3;
m – mass of the sorbent, g.

RESULTS AND DISCUSSION

Oxidation of iron in water is not as easy as it may seem at first glance. The oxidation processes of iron compounds in tap water were studied. In these experiments, the oxidation of iron was carried out with constant stirring of solutions of ferrous sulfate in tap water with magnetite as a catalyst. The results are shown in Figure 1. According to the results above, only at the initial concentration of iron (III) 5 mg/dm^3 for 3 hours of stirring the solution, the iron content in water was reduced to 0.6 mg/dm^3. The degree of purification reached 78.8%. In all other cases, at concentrations of 15–30 mg/dm^3, the efficiency of iron extraction after 3 hours of stirring did not exceed 46%. The efficiency of iron removal from water decreased with increasing its initial concentration from 15 to 30 mg/dm^3. The results obtained can be explained as follows. The concentration of oxygen in water at 20–25 ^{o}C does not exceed 8 mg/dm^3, or 1 mg-eq/dm^3. At an iron concentration of 15 mg/dm^3, its equivalent amount reaches 0.54 mg-eq/dm^3, and at 30 mg/dm^3 – 1.08 mg-eq/dm^3. That is, under these conditions, the excess oxygen is either insignificant or non-existent. In turn, at an iron concentration of 5 mg/dm^3 (0.1786 mg-eq/dm^3) the excess oxygen reaches 3 mg-eq per 1 mg-eq of iron. Stoichiometrically, 0.143 mg of dissolved oxygen is consumed per 1 mg of iron (III). It is known that iron (II) is practically not oxidized by oxygen in a weakly acidic environment. The rate of its oxidation increases significantly only in a slightly alkaline environment. In addition, in the process of oxidation of salts of iron (II) in water is the acidification of water:

$$4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^- \quad (4)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (5)$$
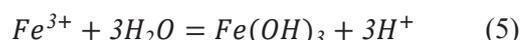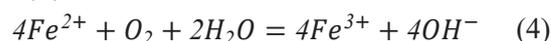
The general equation of the process is:

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ \quad (6)$$
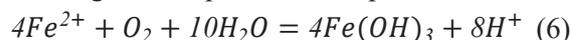
This is confirmed by the pH results obtained during the oxidation of solutions of iron in water (Fig. 1).
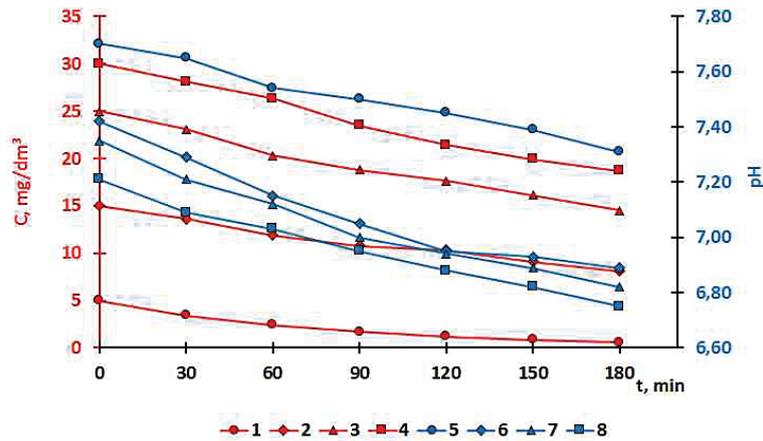
Fig. 1. Change in the concentration of iron ions (1; 2; 3; 4) and the pH of the medium (5; 6; 7; 8) with time of mixing of solutions of iron (II) in tap water at initial concentrations of iron, mg/dm^3: 5 (1; 5); 15 (2; 6); 25 (3; 7); 30 (4; 8)

When iron solutions come into contact with air, in the case of constant stirring, the pH of the medium decreases, as iron (II) and (III) ions oxidize and hydrolyze. At an initial concentration of iron ions of 5 mg/dm^3, the pH of the medium decreases the least, because the amount of iron in water is insignificant. Moreover, in the presence of bicarbonate anions in tap water, a significant proportion of protons are associated with the release of carbon dioxide. This process can be described by the equation:

$$4Fe^{2+} + 8HCO_3^- + O_2 + 2H_2O =$$
$$= 4Fe(OH)_3 + 8CO_2 \uparrow \qquad (7)$$
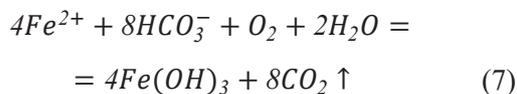
With an increase in the concentration of iron by 3–6 times, there is a more significant decrease in the pH of solutions (Fig. 1, curves 6; 7; 8), which in turn reduces the rate of iron oxidation (Fig. 1, curves 2; 3; 4) and decreases the efficiency of its removal from water (Fig. 2, curves 2; 3; 4).

Of course, with an increase in the concentration of iron in 3–6 times there is a more significant decrease in the pH of solutions (Fig. 1, curves 6; 7; 8), which in turn reduces the rate of iron oxidation (curves 2; 3; 4) and decreases efficiency removing it from the water.

It is known that the rate of iron (II) oxidation in water increases not only with increasing pH of the medium, but also with the use of catalysts. Even the products of iron oxidation can be catalysts for the oxidation of iron (II). Therefore, the efficiency of using magnetite as a catalyst for the removal of iron ions from water was investigated. The experiment was performed similarly to the previous studies, analyzing the samples of solutions for iron content every 30 minutes.

As can be seen from Figure 2, when using magnetite in the amount of 100 mg/dm^3, the oxidation rate increased significantly. At an iron concentration of 5 mg/dm^3, its bulk was oxidized in 30 minutes. At an iron (II) concentration of 15 mg/dm^3, it was completely oxidized in less than 120 minutes, at a concentration of 25 mg/dm^3, the iron was oxidized in less than 150 minutes, and at 30 mg/dm^3 in less than 180 minutes. At the same time, with increasing iron concentration, the residual pH decreased the more, the higher the iron concentration was. When using iron in concentrations of 5–30 mg/dm^3, the residual pH of the solutions decreased from 7.75 to 6.62. Before stirring, while diluting ferrous sulfate at an iron concentration of 5 mg/dm^3, the pH of the solution reached 7.75, at 15 mg/dm^3 – 7.51, at 25 mg/dm^3 – 7.32 and at 30 mg/dm^3 – 7.22. From the above-mentioned results it is seen that the rate of oxidation of iron when used as a catalyst for magnetite has increased significantly even during the process at pH 6.62–7.75. It is very important. After all, purifying large volumes of water to adjust the pH requires large amounts of alkali, soda or lime. In addition, it is necessary to use the equipment for obtaining and dosing solutions. Undoubtedly, the introduction of reagents can degrade the water quality, especially when treating water with high mineralization.

Even higher oxidation rates of iron were observed when using magnetite in the amount of 200 and 500 mg/dm^3 (Fig. 3). At a dose of magnetite of 200 mg/dm^3 (Fig. 3a), at an iron concentration of 5 mg/dm^3, its complete oxidation was achieved in less than 30 minutes. At a dose of magnetite of 500 mg/dm^3 (Fig. 3b), complete oxidation of
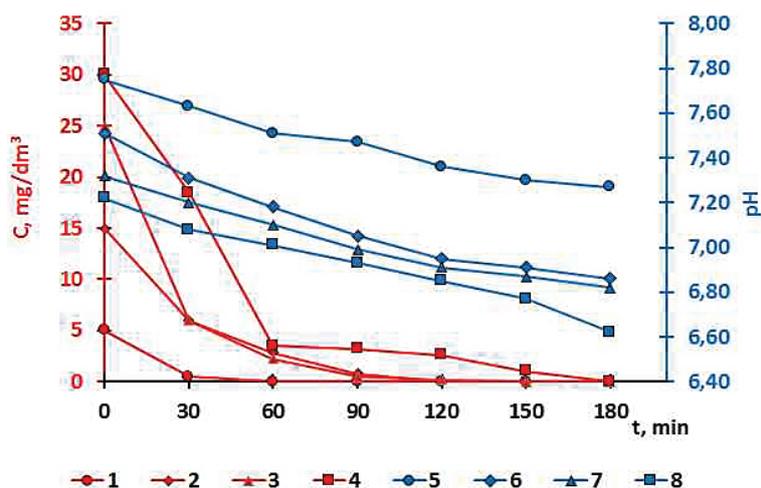
Fig. 2. Change in the concentration of iron ions (1; 2; 3; 4) and the pH of the medium (5; 6; 7; 8) with time of mixing of solutions of iron (II) in tap water at initial concentrations of iron, mg/dm³: 5 (1; 5); 15 (2; 6); 25 (3; 7); 30 (4; 8), at a dose of magnetite 100 mg/dm³
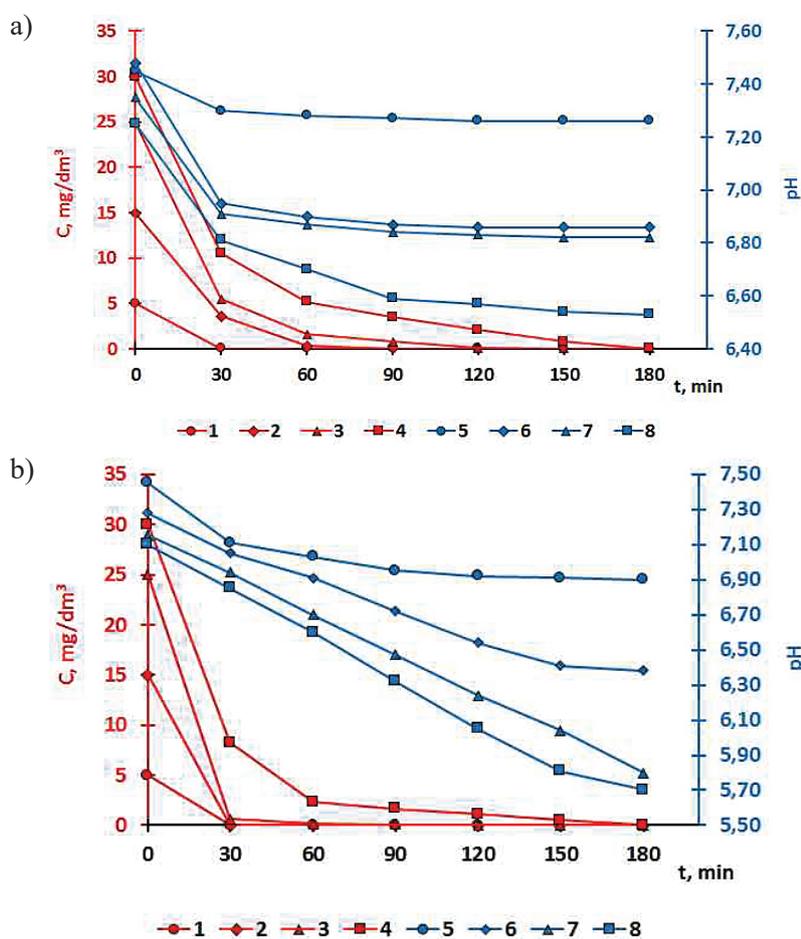
Fig. 3. Change in the concentration of iron ions (1; 2; 3; 4) and the pH of the medium (5; 6; 7; 8) with the mixing time of solutions of iron (II) in tap water at initial concentrations of iron, mg/dm³: 5 (1; 5); 15 (2; 6); 25 (3; 7); 30 (4; 8), at a dose of magnetite of 200 mg/dm³ (a) and 500 mg/dm³ (b)

iron was achieved in less than 30 minutes at iron concentrations of 5 and 15 mg/dm³. Iron was oxidized fairly quickly at iron concentrations of 25 and 30 mg/dm³.

It should be noted that at a dose of magnetite of 500 mg/dm³, effective oxidation of iron occurred at pH 5.70–6.05. It is obvious that magnetite is a complex reagent with sorption

and catalytic properties. This is due to the fact that iron (II) and iron (III) ions in the presence of oxygen can complete the crystal lattice of magnetite. That is, activated adsorption can be observed. However, it is known that magnetite nanoparticles are formed at high pH [Rashid et al., 2020]. In addition, activated adsorption is characterized by high activation energy and low process rates. On the other hand, the magnetite particles are 7–10 nm in size, which means that they have a highly developed surface. Due to the presence of iron (II) atoms, they can effectively sorb oxygen. On the other hand, magnetite also efficiently absorbs iron (II) ions from the solution. In general, iron (II) ions interact effectively with oxygen on the surface of magnetite to form iron (III) compounds. In [Ryzhenko et al., 2019] it was shown that the oxidation of $Fe(OH)_2$ precipitate produces magnetite Fe_3O_4. Thus, in this case, during the oxidation of iron on the surface of magnetite, a significant part of it is included in the crystal lattice of the catalyst. Therefore, along with the catalytic activity of magnetite, its sorption properties in relation to iron compounds in water can be observed.

From the data given in Table 1, the catalytic activity and sorption capacity of magnetite can be assessed. As can be seen from the table, with increasing initial concentration of iron in solution, the time of complete purification of water from iron increases. The rate of purification of water from iron increases along with the dose of magnetite. At a concentration of magnetite of 500 mg/dm³ for 30 minutes, iron was completely removed from the water at concentrations of 5 and 15 mg/dm³, and at a concentration of iron ions of 25 mg/dm³ for 30 minutes, the degree of iron recovery was reached at 97.6%.

The value of the sorption capacity of magnetite increases along with the concentration of iron in solution and with decreasing dose of magnetite with increasing mixing time and the degree of extraction of iron. This is quite logical and fully consistent with the idea of sorption processes, including activated adsorption. It should be noted that when adjusting the pH of iron solutions in water to values of 8.0 and when mixing solutions with a dose of magnetite 200 mg/dm³, no significant acceleration of the process and increase in the degree of iron extraction with increasing mixing time was observed (Fig. 4, Table 1).

The values of the sorption capacity of magnetite are close to the corresponding values in water purification without adjusting the pH. In this case, the dose of magnetite 200 mg/dm³ provides a

Table 1. Change in the degree of purification of water from iron, the sorption capacity of magnetite by iron ions with the time of mixing of solutions of ferrous sulfate in water at different doses of magnetite

Fe^{2+}, mg/dm³	Dose of magnetite, mg/dm³	Sorption capacity, mg/dm³						Level of purification, %					
		Time of contact, min						Time of contact, min					
		30	60	90	120	150	180	30	60	90	120	150	180
5	100	45	50	50	50	50	50	90	100	100	100	100	100
15		90	122	142	150	150	150	60	81	95	100	100	100
25		190	228	245	248	250	250	76	91	98	99	100	100
30		115	265	268	274	290	300	38	88	89	91	97	100
5	200	25	25	25	25	25	25	100	100	100	100	100	100
15		57	74	75	75	75	75	76	98	100	100	100	100
25		98	117	121	125	125	125	78	94	97	99	100	100
30		108	136	138	140	146	150	72	91	92	93	97	100
5	200*	23	24	25	25	25	25	90	96	100	100	100	100
15		67	73	75	75	75	75	89	97	100	100	100	100
25		90	110	120	125	125	125	72	88	96	99	100	100
30		98	110	135	143	149	150	65	73	90	95	99	100
5	500	10	10	10	10	10	10	100	100	100	100	100	100
15		30	30	30	30	30	30	100	100	100	100	100	100
25		38	50	50	50	50	50	98	99	99	100	100	100
30		44	55	57	58	59	60	73	76	78	80	83	84

* When bringing the initial pH of the solutions to 8.0.

sufficient increase in the rate of oxidation of iron and at pH 6.0–7.7.

In general, if the results given above are considered, it can be said that when using magnetite, the rate of oxidation and sorption of iron increases so much that in 30 minutes most of the processes are completed. Therefore, when using magnetite at doses of 200 and 500 mg/dm³, kinetic studies were performed with a time interval between the sample analyses of 10 minutes. The results are shown in Figure 5.

In this case, at a dose of magnetite of 200 mg/dm³ (Fig. 5a) and an iron concentration of 5 mg/dm³, purification took place in almost 10 minutes. Other experiments lasted 40–50 minutes. Within an hour, water purification from iron was noted in all experiments. At a dose of magnetite of 500 mg/dm³ (Fig. 5b) only at an iron concentration of 30 mg/dm³, the purification process lasted more than 40 minutes. In this case, as in previous experiments, there was a significant acceleration of the process of removing iron from water using catalyst sorbents.

In order to more fully evaluate the results of these kinetic studies, the oxidation rate constants (Table 2) of iron in water without the use of catalysts and when using them (Table 3) were calculated. The zero-order constant (K_0) was calculated based on the equation:

$$C = K_o \cdot t, \qquad (8)$$

The rate constants of the 1st (K_1), 2nd (K_2) and 3rd (K_3) orders were calculated based on the equations:

$$lnC = lnC_o - K_1 t, \qquad (9)$$

$$\frac{1}{c} = \frac{1}{c_0} + K_2 t, \qquad (10)$$

$$\frac{1}{c^2} = \frac{1}{c_0^2} + 2K_3 t, \qquad (11)$$

where: C is the concentration of iron (mg/dm³) after stirring for time t (min), C_0 is the initial concentration of iron (II), mg/dm³ (from 5 to 25 mg/dm³).

As can be seen from Table 3, the constants of the 1st and 2nd orders are closest in terms of rate constants for the oxidation of iron (II) without a catalyst for different periods of oxidation. The concentration of 5 mg/dm³ is better described by an equation of the 1st order. The constant K_1 is in the range of 0.0118–0.0122
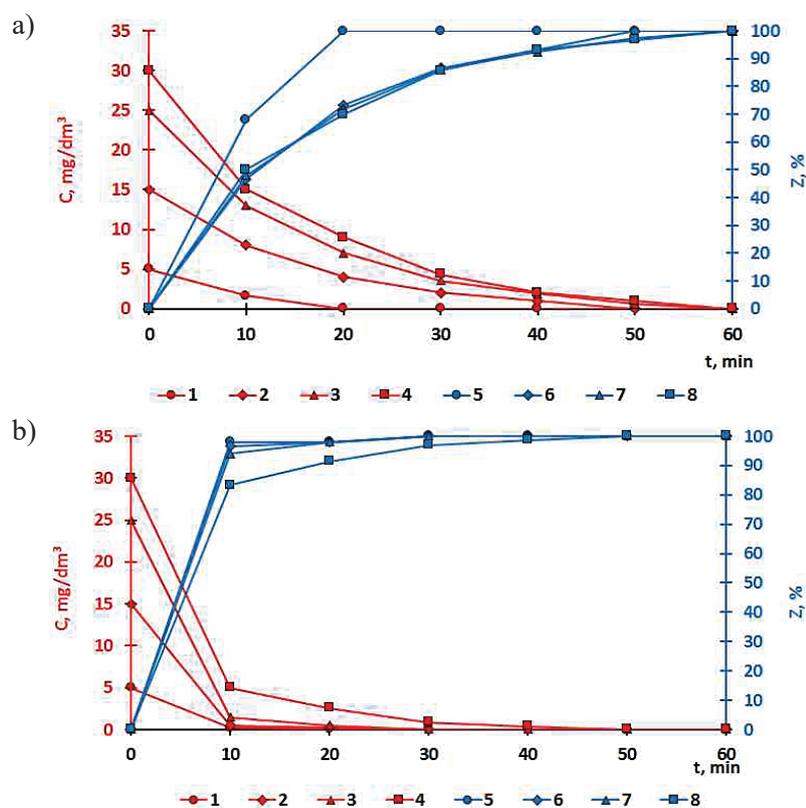
Fig. 5. Dependence of iron concentration (1; 2; 3; 4) and degree of iron extraction (5; 6; 7; 8) from solutions of ferrous sulfate in tap water on the time of mixing of solutions at initial iron concentration, mg/dm³: 5 (1; 5); 15 (2; 6); 25 (3; 7); 30 (4; 8), at doses of magnetite 200 mg/dm³ (a) (Final pH: 7.52 (1); 6.97 (2); 6.81 (3); 6.55 (4)) and 500 mg/dm³ (b) (Final pH: 7.24 (1); 6.90 (2); 6.79 (3); 6.24 (4))

Table 2. Dimensions of the rate constant of iron oxidation in water

К	K_0	K_1	K_2	K_3
Unit of measurement	$mg \cdot dm^{-3} \cdot min^{-1}$	min^{-1}	$mg \cdot dm^3 \cdot min^{-1}$	$dm^6 \cdot mg^{-2} \cdot min^{-1}$

Table 3. Rate constants for the oxidation of iron during mixing in tap water at different concentrations of iron and doses of magnetite

Dose of magnetite, mg/dm³	Fe^{2+}, mg/dm³	K	t, min					
			30	60	90	120	150	180
–	5	K_0	$1.03 \cdot 10^{-1}$	$3.00 \cdot 10^{-2}$	$1.90 \cdot 10^{-2}$	$8.00 \cdot 10^{-3}$	$7.00 \cdot 10^{-3}$	$6.00 \cdot 10^{-3}$
		K_1	$1.29 \cdot 10^{-2}$	$1.22 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$1.18 \cdot 10^{-2}$	$1.17 \cdot 10^{-2}$
		K_2	$3.1 \cdot 10^{-3}$	$3.60 \cdot 10^{-3}$	$4.30 \cdot 10^{-3}$	$5.20 \cdot 10^{-3}$	$6.50 \cdot 10^{-3}$	$8.10 \cdot 10^{-3}$
		K_3	$7.80 \cdot 10^{-4}$	$1.24 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$	$2.73 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$	$7.60 \cdot 10^{-3}$
	15	K_0	$4.53 \cdot 10^{-1}$	$1.98 \cdot 10^{-1}$	$1.20 \cdot 10^{-1}$	$8.61 \cdot 10^{-2}$	$6.11 \cdot 10^{-2}$	$4.51 \cdot 10^{-2}$
		K_1	$3.30 \cdot 10^{-3}$	$3.800 \cdot 10^{-3}$	$3.70 \cdot 10^{-3}$	$3.20 \cdot 10^{-3}$	$3.30 \cdot 10^{-3}$	$3.40 \cdot 10^{-3}$
		K_2	$2.80 \cdot 10^{-4}$	$2.90 \cdot 10^{-4}$	$2.90 \cdot 10^{-4}$	$3.00 \cdot 10^{-4}$	$2.90 \cdot 10^{-4}$	$3.00 \cdot 10^{-4}$
		K_3	$1.60 \cdot 10^{-5}$	$2.30 \cdot 10^{-5}$	$2.30 \cdot 10^{-5}$	$2.10 \cdot 10^{-5}$	$2.50 \cdot 10^{-5}$	$3.00 \cdot 10^{-5}$
	25	K_0	$9.37 \cdot 10^{-1}$	$4.38 \cdot 10^{-1}$	$2.61 \cdot 10^{-1}$	$1.78 \cdot 10^{-1}$	$1.33 \cdot 10^{-1}$	$1.01 \cdot 10^{-1}$
		K_1	$2.20 \cdot 10^{-3}$	$2.20 \cdot 10^{-3}$	$2.70 \cdot 10^{-3}$	$2.80 \cdot 10^{-3}$	$2.70 \cdot 10^{-2}$	$2.60 \cdot 10^{-3}$
		K_2	$1.40 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	$1.40 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	$1.60 \cdot 10^{-4}$
		K_3	$4.6 \cdot 10^{-6}$	$6.80 \cdot 10^{-6}$	$6.80 \cdot 10^{-6}$	$6.80 \cdot 10^{-6}$	$7.50 \cdot 10^{-6}$	$8.80 \cdot 10^{-6}$
100	5	K_0	$1.71 \cdot 10^{-2}$	-	-	-	-	-
		K_1	$7.67 \cdot 10^{-2}$	-	-	-	-	-
		К	$1.60 \cdot 10^{-1}$	-	-	-	-	-
		K_3	$6.60 \cdot 10^{-2}$	-	-	-	-	-
	15	K_0	$2.00 \cdot 10^{-1}$	$4.71 \cdot 10^{-2}$	$9.10 \cdot 10^{-3}$	-	-	-
		K_1	$3.05 \cdot 10^{-2}$	$3.05 \cdot 10^{-2}$	$3.26 \cdot 10^{-2}$	-	-	-
		K_2	$3.33 \cdot 10^{-3}$	$4.84 \cdot 10^{-3}$	$1.32 \cdot 10^{-2}$	-	-	-
		K_3	$3.89 \cdot 10^{-4}$	$1.03 \cdot 10^{-3}$	$8.66 \cdot 10^{-3}$	-	-	-
	25	K_0	$6.16 \cdot 10^{-1}$	$5.80 \cdot 10^{-2}$	$3.61 \cdot 10^{-2}$	$2.17 \cdot 10^{-2}$	$7.00 \cdot 10^{-3}$	-
		K_1	$4.75 \cdot 10^{-2}$	$4.05 \cdot 10^{-2}$	$4.65 \cdot 10^{-2}$	$4.02 \cdot 10^{-2}$	-	-
		K_2	$4.22 \cdot 10^{-3}$	$6.91 \cdot 10^{-3}$	$2.18 \cdot 10^{-2}$	$4.13 \cdot 10^{-2}$	-	-
		K_3	$4.36 \cdot 10^{-4}$	$1.71 \cdot 10^{-3}$	$2.22 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	-	-
200	15	K_0,	$1.20 \cdot 10^{-1}$	$5.10 \cdot 10^{-3}$	-	-	-	-
		K_1	$4.75 \cdot 10^{-2}$	$6.52 \cdot 10^{-2}$	-	-	-	-
		K_2	$7.03 \cdot 10^{-3}$	$5.44 \cdot 10^{-2}$	-	-	-	-
		K_3	$1.21 \cdot 10^{-3}$	$9.26 \cdot 10^{-2}$	-	-	-	-
	25	K_0	$2.83 \cdot 10^{-1}$	$4.71 \cdot 10^{-2}$	$2.80 \cdot 10^{-2}$	$1.81 \cdot 10^{-2}$	$5.10 \cdot 10^{-3}$	-
		K_1	$5.05 \cdot 10^{-2}$	$4.58 \cdot 10^{-2}$	$3.82 \cdot 10^{-2}$	$2.87 \cdot 10^{-2}$	-	-
		K_2	$4.73 \cdot 10^{-3}$	$9.75 \cdot 10^{-3}$	$1.34 \cdot 10^{-2}$	$8.30 \cdot 10^{-2}$	-	-
		K_3	$5.24 \cdot 10^{-4}$	$3.24 \cdot 10^{-3}$	$8.67 \cdot 10^{-3}$	$4.17 \cdot 10^{-1}$	-	-
500	25	K_0	$2.00 \cdot 10^{-2}$	$3.10 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	-	-	-
		K_1	$1.24 \cdot 10^{-1}$	$8.53 \cdot 10^{-2}$	$6.14 \cdot 10^{-2}$	-	-	-
		K_2	$5.42 \cdot 10^{-2}$	$1.11 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$	-	-	-
		K_3	$4.63 \cdot 10^{-2}$	$3.70 \cdot 10^{-1}$	$5.56 \cdot 10^{-1}$	-	-	-

min^{-1}. For iron concentrations of 15 and 25 mg/dm³, the processes best describe the 2nd order equations. For an iron concentration of 15 mg/dm³, the K_2 constant decreases in the range of $2.8 \cdot 10^{-4}$–$3.0 \cdot 10^{-4}$ dm³·mg⁻¹·min⁻¹, for 25 mg/dm³ $K_2 = 1.4 \cdot 10^{-4}$–$1,6 \cdot 10^{-4}$ dm³·mg⁻¹·min⁻¹. Obviously, at a low concentration of iron with a stable supply of oxygen molecules to the water

with a stable 3-fold excess, the rate of oxidation is determined only by the concentration of iron ions.

At iron concentrations of 15 and 25 mg/dm^3, the equivalent amounts of oxygen and iron are close. Therefore, the speed of the process depends on both the concentration of iron and the concentration of oxygen. Under these conditions, the reaction of the 2nd order is realized. The decrease in the rate constant with increasing iron concentration from 15 to 25 mg/dm^3 is due to a decrease in excess oxygen in the water, which generally slows down the oxidation of iron.

As can be seen from Table 3, it is difficult to compare the kinetic characteristics of the oxidation processes of iron without a catalyst and its use. It can be said that when using catalysts, the rate constants of the 1st and 2nd orders are more than an order of magnitude higher than when the catalyst was not used. Given that most processes were completed in 30–90 minutes, it is impossible to obtain the series in which the rate constants can be compared. Somewhat more interesting results were obtained when conducting the studies with sampling for analysis every 10 minutes. The calculated rate constants for these cases are given in Table 4.

As can be seen from Table 4, at initial iron concentrations of 15–30 mg/dm^3, the oxidation processes at a magnetite dose of 200 mg/dm^3 are best described by 1st order equations. The rate constants in this case do not depend on the mixing time and the initial concentration of iron and have fairly close values. This suggests that under conditions of intensive aeration of water, the amount of oxygen sorbed on the magnetite is constant and sufficient for the oxidation of sorbed iron (II) ions. Therefore, the speed of the process mainly depends on the concentration of iron ions. The rate constant of the 1st order in this case is more than 20 times higher than the rate constant of the oxidation of iron without the use of a catalyst.

It should be noted that magnetite is an effective catalyst for the oxidation of iron in an aquatic environment at pH>6. As a rule, in tap water at iron concentrations of 5–30 mg/dm^3 obtained by dissolving the appropriate amounts of ferrous sulfate, the pH almost never falls below 6.0. However, when dissolving ferrous sulfate in distilled water, the solution is acidified. Acidification is greater the higher the concentration of iron in the water. This is due to the partial hydrolysis of ferrous sulfate. In tap water, acidification is compensated by the interaction of protons with bicarbonates to release carbon dioxide. There are no hydrocarbons in distilled water, so at iron concentrations of 5, 15, 25 and 30 mg/dm^3, the pH decreases to 6.00, 5.44, 5.40 and 5.39, respectively. Under these conditions, even when using magnetite in the amount of 100 mg/dm^3, the oxidation of iron is inefficient (Fig. 6).

Table 4. Constants of the rate of iron (II) oxidation depending on the stirring time at iron concentrations of 5–30 mg/dm^3 at a dose of magnetite 200 mg/dm^3

Fe^{2+}, mg/dm^3	K	t, min				
		10	20	30	40	50
5	K_0	0.16000	-	-	-	-
	K_1	0.11394	-	-	-	-
	K_2	0.04250	-	-	-	-
	K_3	0.03500	-	-	-	-
15	K_0	0.70000	0.15000	0.08330	0.02500	-
	K_1	0.06290	0.06610	0.06720	0.06770	-
	K_2	0.00583	0.09170	0.10144	0.02350	-
	K_3	0.00160	0.00533	0.00519	0.02488	0.03122
25	K_0	0.90000	0.42500	0.11670	0.04750	0.01600
	K_1	0.06540	0.06360	0.06550	0.06440	0.06430
	K_2	0.00369	0.00514	0.00819	0.01220	0.03250
	K_3	0.00107	0.00061	0.00267	0.00689	0.03120
30	K_0	1.40000	0.50000	0.14330	0.05000	0.01800
	K_1	0.06930	0.06290	0.06470	0.06770	0.06800
	K_2	0.00333	0.00389	0.00664	0.01167	0.01933
	K_3	0.00382	0.00167	0.00036	0.00517	0.02380
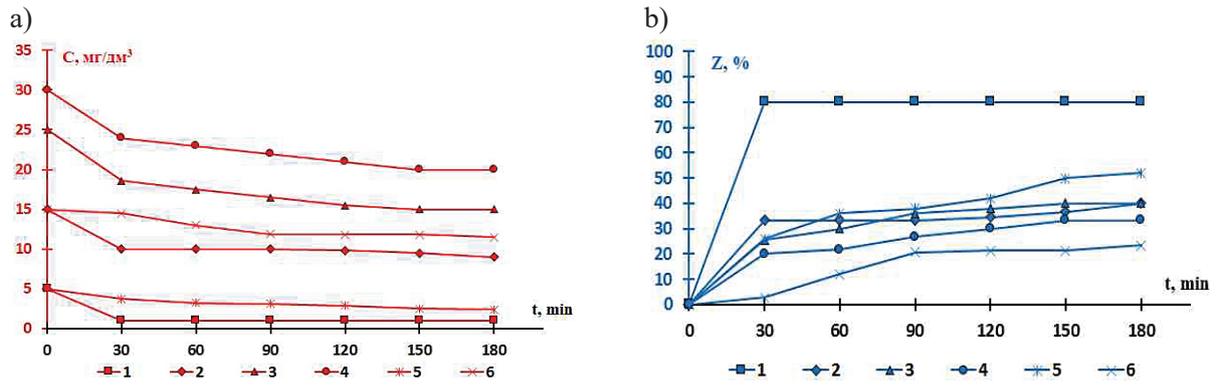
Fig. 6. The dependence of the residual concentration of iron (a) and the change in the degree of purification of water from iron (b) from solutions of ferrous sulfate in distilled water from the mixing time at the initial concentration of iron mg/dm^3: 5 (1; 5); 15 (2; 6); 25 (3); 30 (4), at a dose of magnetite 100 mg/dm^3 (1; 2; 3; 4) and without magnetite (5; 6) (pH of solutions 5.99 (1.5); 5.44 (2; 6); 5.40 (3); 5.39 (4)).
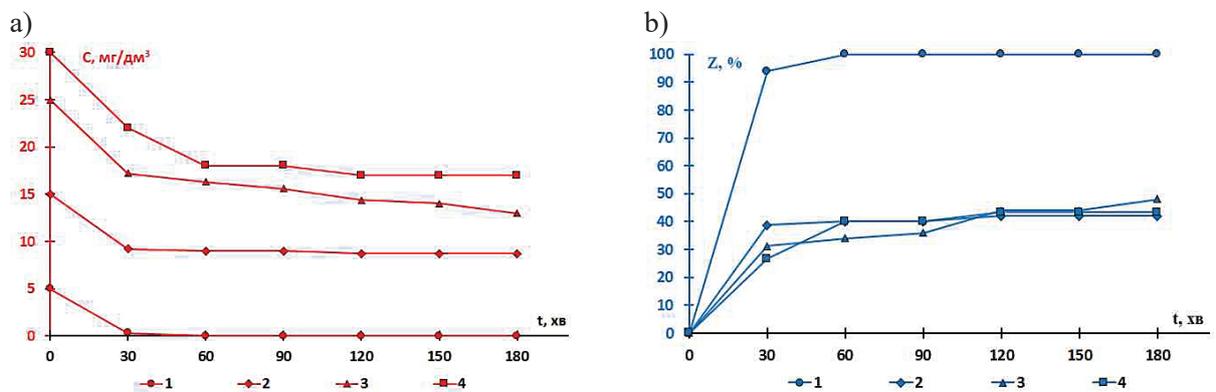
Fig. 7. The dependence of the residual concentration of iron (a) and the degree of purification of solutions of iron (b) from solutions of ferrous sulfate in distilled water on the time of mixing of solutions at initial concentrations of iron mg/dm^3: 5 (1); 15 (2); 25 (3); 30 (4), at a dose of magnetite 200 mg/dm^3 (pH of solutions 6.10 (1); 5.54 (2); 5.60 (3); 5.28 (4)).

In this case, water purification takes place only at an iron concentration of 5 mg/dm^3 (pH 6.00). At a dose of magnetite 100 mg/dm^3, the degree of iron removal reaches 80%.

Without magnetite, the maximum degree of iron removal reaches 52% (Fig. 6b). At higher concentrations of iron at pH<5.60, the oxidation of iron is inefficient both without magnetite and in its presence. Similar dependences were obtained at a dose of magnetite of 200 mg/dm^3 (Fig. 7). The complete removal of iron was achieved only at an iron concentration of 5 mg/dm^3 (pH 6.10). In all other cases, the degree of iron extraction reached 42–48%. As it is shown in Table 5, at pH>6.0, high efficiency of iron removal from distilled water was achieved.

Table 5. Dependence of the residual concentration of iron in distilled water depending on the dose of magnetite, pH and stirring time of the solution

Dose of magnetite, mg/dm^3	pH	Fe^{2+}, mg/dm^3				
		t, min				
		0	30	60	90	120
100	6.696	15.00	3.00	1.00	0.30	0.00
200	6.653	15.00	0.70	0.20	0.10	0.00
500	6.803	15.00	0.60	0.17	0.50	0.00
	7.050	15.00	0.60	0.15	0.10	0.00
	8.595	15.00	0.10	0.00	0.00	0.00
	9.232	15.00	0.00	0.00	0.00	0.00

CONCLUSIONS

It was shown that the oxidation of iron in solutions of ferrous sulfate in tap water depends on the concentration of iron. The oxidation efficiency decreases with increasing iron concentration from 5 to 30 mg/dm^3. At iron concentration of 5 mg/dm^3, the oxidation reaction of the 1st order prevails, at iron concentrations of 15 mg/dm^3 and above, the oxidation occurs by the reaction of the 2nd order.

The dependence of the oxidation efficiency of iron in tap water on the concentration of iron and the dose of magnetite when using the latter in the amount of 100, 200 and 500 mg/dm^3 was determined. In all cases, the use of magnetite accelerated the process of extracting iron by more than an order of magnitude.

It was established that when using a catalyst-sorbent based on magnetite, the oxidation of iron in tap water is a first-order reaction, which is due to the effective saturation of water and magnetite with oxygen.

It was shown that from the solutions of ferrous sulfate in distilled water, the extraction of iron on the catalyst sorbent is inefficient due to the lowering of the pH during hydrolysis of iron. The negative effect rises with increasing concentration of iron ions in water. In the case of adjusting the pH to the values greater than 6.5 when using magnetite as a catalyst, a deep purification of water from iron ions is achieved.

Acknowledgments

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