 USING FILTER LOADING FOR IRON REMOVAL FROM WATER
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Received 20 April 2023; accepted 4 June 2023; available online 25 July 2023

Abstract
To purify water from iron compounds, were used granulated zeolite and zeolite modified with potassium permanganate. The experimental results showed that when filtering water, the modified zeolite removes iron from the aqueous environment better. The filtration cycle time depends on the initial concentrations of iron compounds in the water and continue until the critical level of resistance in the filtering unit is reached, due to the accumulation of sediment in the filter column. The calculation of the sedimentation rate on the surface of modified and unmodified zeolite has been carried out. The rate of formation of such a layer affects the efficiency of iron compound oxidation during water filtration. The rate of film formation on the loading surface in the case of filtration through the modified zeolite is greater, which indicates a more complete extraction of iron ions. After washing the filter, the modified zeolite did not lose its oxidizing power.

Keywords: iron, zeolite; filter; dirt capacity; adsorption film; water purification.

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**Introduction**

Nowadays, the rational use of water resources in conditions of water scarcity, also the significant deterioration of its quality, is a complex scientific and technical problem [1–3]. Therefore, an important issue is the purification of natural waters through the improvement of water treatment technologies and the development of new effective resource-saving methods [4–7].

Iron (Fe$^{2+}$) is a typical inorganic water pollutant. Iron occurs in both surface and groundwater [8–10]. Among various water sources, groundwater due to the leaching of Fe$^{2+}$ rocks and minerals have a greater amount of them.

Although iron is necessary for human life, it causes problems in high concentrations [11; 12]. At high concentrations of iron, various diseases occur – hemochromatosis, which damages various organs of the body, eye problems such as conjunctivitis, and heart disease, affects the gastrointestinal tract and the central nervous system.

Iron also affects the color, taste and smell of water, giving the water a metallic taste and red color [14; 15].

For water purification, physicochemical and biological methods are used to remove heavy metals from water [16–18].

Chemical redox reaction, coagulation, ion exchange, electrodialysis, chemical and physical precipitation, evaporation, adsorption, solvent extraction, membrane filtration and electrochemical processes are the most common methods of cleaning water sources containing heavy metals. Although most of these methods have certain advantages, they have some limitations that prevent their application.

Chemical precipitation is a simple and economical method, but requires alkaline conditions that lead to the formation of sediment, which leads to secondary pollution [19]. Methods of aeration oxidation of iron do not always achieve the required efficiency [20; 21].

Electrochemical [22–24], ion-exchange, membrane [25; 26] methods can selectively remove heavy metals, but they are not often used due to high capital or operating costs and limitations in low metal concentration.

Recently, biological methods of water deironing have been widely used, but they are quite complex [27–30]. The use of materials with capillary properties is difficult when using significant volumes of water [31–33].

Therefore, adsorption has become the most promising method due to its simplicity, wide adaptability and high efficiency. Adsorbents play a more significant role in the adsorption method. Recently, numerous adsorbents have been tested to remove heavy metal ions, including mesoporous silica, organometallic scaffolds (MOF) [34], carbon nanotubes [35; 36], activated carbon, clays [37], hydrogel [38], biosorbents (e.g., seaweed, chitosan and chitin) [39–41], biochar from banana peels and agricultural waste [42; 43], sorption on manganese sand [44] and magnetite [45–47], zeolite [48–53].

Natural zeolites are used as inexpensive and effective adsorbents to purify water from various pollutants [54]. However, the adsorption capacity of natural zeolites to certain elements may be limited. To increase the sorption capacity of zeolites, mechanical, thermal or chemical treatment is used to improve the physicochemical properties and adsorption capacity for removing pollutants [48–53].

The objective of our work was to evaluate the effectiveness of using a zeolite filter medium for removing iron from water.

This paper was focused on tasks that include:

1. Determine a method of zeolite modification to increase the efficiency of iron removal from water.
2. Determine the main parameters of the water filtration process through such a filter loading.
3. Investigate the possibility of multiple use of a zeolite-based filter load.

**Materials and methods**

A granular zeolite and a modified zeolite were used as the filter charge. The modified zeolite was obtained by treating a certain volume of the filter charge with a modifying reagent in a predetermined sequence. Potassium permanganate K$\text{MnO}_4$ was used as a modifying reagent. To do this, 20 cm$^3$ of CPS zeolite with a fractional composition of 3–5 mm, under statistical conditions, was treated with a 5 % K$\text{MnO}_4$ solution, thawed during the day. Then it was washed with distilled water until complete removal of permanganate residues. The installation diagram is shown in Fig. 1.
To determine the efficiency of extracting iron compounds from water under dynamic conditions, an iron sulfate solution prepared on tap water was passed through a layer of filter load with a volume of 20 cm$^3$. Samples were taken in a volume of 1 dm$^3$, with a solution flow rate of 10–15 cm$^3$/min. The concentration of iron ions at the inlet and outlet of the filter unit was controlled. After accumulation of the precipitate in the volume of the filter charge, the filter was washed by reverse water supply.

Mass of oxidized iron $m_{Fe}$ (mg) determined by the formula:

$$m_{Fe} = (C_{in} - C_i) \cdot V_s,$$

(1)

where $C_{in}$ – initial concentration of ions in solution, mg/dm$^3$; $C_i$ – ion concentration in sample i, mg/dm$^3$; $V_s$ – sample volume, dm$^3$.

The total weight of oxidized iron was determined as the sum of oxidized iron from all samples taken:

$$m_{Fe}^{tot} = \sum_{i=1}^{n} m_{Fe}^i.$$

(2)

The recovery of Z ions (%) of iron was determined by the formula:

$$A = \frac{(C_{in} - C_o)}{C_{in}} \cdot 100\%.$$

(3)

Specific dirt content of the filter during the filter cycle was determined by the formula:

$$G_k = K_n U_f \frac{\sum_{i=0}^{T_f} (C_o - C_f)}{T_f} T \cdot \frac{mg}{m^2},$$

(4)

where $C_o$ i $C_f$ – average iron content in the source and filtered water, respectively, over the time interval between adjacent measurements, mg/m$^3$; $U_f$ – speed of water filtration, m/h; $T_f$ – duration of water filtration, h; $K_n$ – conversion factor considering the ratio of molecular weight of iron hydroxide Fe(OH)$_3$ to the atomic mass of ferrous iron:

$$K_n = \frac{M[Fe(OH)_3]}{AFe^{2+}} = \frac{107}{56} = 1.91.$$

(5)

Based on experimental data obtained during water filtration, the rate of formation of a catalytic (chemisorption) layer on the surface of the filter bed was calculated. The specific rate of formation of the filter layer was determined by the formula:

$$V_{form.layer} = \frac{m_{ret.ions}}{t_i S_f} \cdot \frac{mg}{min \cdot m^2},$$

(6)

where $m_{ret.ions}$ – mass of retained iron ions; $t_i$ – filtration time; $S_f$ – filter area.

Weight of adsorption film ($m_{ads.fil}$), water formed during the filtration period was determined by mass balance using the concentration of iron ions in the initial solution.
and in the filtrate, as well as the volume of the filtrate ($V_f$):

$$m_{ads,film} = K \cdot \left( C_0 \cdot V_f - C_f \cdot V_f \right),$$  \hspace{1cm} (7)

where $K$ - coefficient taking into account the ratio of the molecular weight of iron hydroxide Fe(OH)$_3$ to the atomic weight of ferrous iron, $K=1.91$.

Results and Discussion

In groundwater, which are sources of water supply, the concentration of iron can reach 1-10 mg/dm$^3$. In the process of water treatment, oxidation of iron compounds occurs due to free oxygen or additional aeration of water, as a result of which insoluble suspended forms are formed with gradual precipitation and a decrease in the total concentration of metal in water.

$$4\text{Fe}(	ext{HCO}_3)_2 + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 8\text{CO}_2,$$

$$4\text{FeSO}_4 + \text{O}_2 + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + \text{H}_2\text{SO}_4.$$  \hspace{1cm} (8)

$$4\text{FeSO}_4 + \text{O}_2 + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + \text{H}_2\text{SO}_4.$$  \hspace{1cm} (9)

Thus, it can be said that all Fe$^{2+}$ ions in different states participate in the reaction with oxygen, which is the sum of independent, simultaneously occurring oxidation reactions of iron ions.

At the same time, intermediates such as Fe (OH)$^{2+}$ and Fe (OH)$^{2+}$ and slightly water-soluble Fe(OH)$_3$ will be present. The formation of iron (III) hydroxide depends on many parameters, such as temperature, pH of the medium, the concentration of iron ions and oxidizing agent, as well as the presence of other compounds.

Such iron hydrolysis intermediates may act as a catalyst for the oxidation reaction of iron in water. Given that the simplest method of extracting iron is the oxidation of Fe$^{2+}$ ions to Fe$^{3+}$, followed by hydrolysis and precipitation of the resulting iron hydroxide (Fe(OH)$_3$), studies have been conducted on the use of various filter feeders for water deironing. Oxidized iron in the form of Fe(OH)$_3$ hydroxide creates an autocatalytic film on the surface of the charge grains. The simplest filter material can be quartz sand. Natural sorbents such as glauconite, dolomite, zeolite, mordenite, etc. are also used.

To evaluate the effectiveness of this process, water was decontaminated by filtering it through a layer of granulated zeolite. At iron concentration in water at 10–15 mg/dm$^3$ (Fig. 2) aeration occurs due to contact with solution air for 10 - 60 min before filtration. As can be seen from the graph, the efficiency of cleaning water from iron in this case was not high. Iron recovery gradually decreased from 52.0 % to 42.5 % and 48.7 to 37.3 for initial concentrations 10.0 and 15.0 mg/dm$^3$ according. In the case of using potassium permanganate-modified zeolite, the recovery at the initial stage was higher than 96.7 % and gradually decreased to 81.0–83.0 % (Fig. 3).

In the process of treating the zeolite with potassium permanganate, manganese oxide was formed on its surface, which in the presence of oxygen dissolved in water provided catalytic oxidation of iron. At the same time, iron passed into an insoluble state and iron hydroxide was retained on the zeolite, worsening the contact of water with the surface of the filter material.

![Fig. 2. Change in iron concentrations (1; 2) in water and degree of iron extraction from water (3; 4) from the solution volume passed through the granular zeolite ($V_i$= 20 cm$^3$) (1; 4), at baseline concentration of 10.0 (1; 3) (pH = 7.67) and 15.0 mg/dm$^3$ (2; 4) (pH = 7.73)](image-url)
The filter cycle continues until the critical resistance level in the filter unit increases, due to the accumulation of sediment in the filter column [55, 56]. The loading volume, grain size, filtration rate and iron content of the source water also affect the process speed. To assess the effect of iron hydroxide precipitate, the specific dirt content of the filter was calculated, showing the amount of precipitate Fe(OH)$_3$ per 1 m$^2$ of its area. Also, on the basis of experimental data obtained during water deironing by filtering through a load of zeolite and modified zeolite with potassium permanganate, the rate of formation of a catalytic (chemisorption) layer on the surface of the sorbent was calculated. The rate of formation of such a layer affects both the oxidation efficiency of iron compounds in the thickness of the filter, and actually depends on the rate of water filtration (Fig. 4).

When filtering water through the modified zeolite, the dirt content index is greater than in the case of filtering through the granulated zeolite. That is, the formation and accumulation of precipitates in the filter bed of the modified zeolite is faster. The initial concentration of iron in water also plays a large role in the rate of sediment formation. The higher the concentration, the greater the mass of retained iron hydroxide formed during the oxidation process.

To clarify the rate of oxidation of iron compounds and, accordingly, the rate of formation of the precipitate, the rate of formation of the filter layer and the weight of the adsorption film were calculated (Fig. 5, Tables 1, 2).

![Fig. 3. Change in iron concentrations (1; 2) in water and degree of iron extraction from water (3; 4) of the solution volume passed through the zeolite modified with potassium permanganate (V$_i$ = 20 cm$^3$) (1; 4), at baseline concentration 10.0 (1; 3) (pH = 7.67) and 15.0 mg/dm$^3$ (2; 4) (pH = 7.73)](image)

![Fig. 4. Dependence of filter specific dirt content on filtration time through granular zeolite (1; 2) and a modified zeolite (3; 4) at an initial concentration of 10.0 (1; 3) and 15.0 mg/dm$^3$ (2; 4)](image)

![Fig. 5. Dependence of the sediment layer formation rate on the volume of solution passed through the granular zeolite (1; 2), modified zeolite (3; 4) at an initial concentration of 10.0 (1; 3) and 15.0 mg/dm$^3$ (2; 4)](image)
Based on the obtained dependencies, we can say that in the case of filtering through a modified zeolite, the film formation rate on the loading surface is higher. However, in all cases, this figure decreases with an increase in the amount of water passed. Thus, even when a catalytic film is formed, iron ions are not completely oxidized and hydrolyzed, which over time leads to a decrease in the efficiency of water deironing and an increase in residual concentrations.

In the case of filtering water through the modified zeolite, the mass of the adsorption film formed on the loading surface is twice as large as that formed on the surface of the granular zeolite, which leads to faster contamination of the filter and increased resistance.

The formation of a chemisorption layer on the surface of the modified zeolite is more intense, since at the beginning of filtration, oxidation of iron compounds occurs almost completely due to contact with the formed catalytic film of manganese oxide. When accumulating a layer of iron hydroxide precipitate, the area of free contact of water with manganese oxide overlaps. The formed layer of iron hydroxide, which also has catalytic properties, does not have time to completely oxidize the iron ions present in the solution. Obviously, this is due to kinetic factors when the rate of oxidation of iron is lower than the rate of its presence on the surface of the filter load. It is this that causes a decrease in the degree of water purification during filtration. To avoid this effect, the loose precipitate of iron hydroxide must be periodically removed by backwashing the filter with water.

### Table 1

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<thead>
<tr>
<th>Calculation of filter bed formation rate (initial iron concentration (C_{Fe} = 10.0 \text{ mg/dm}^3))</th>
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<tr>
<td>Filtration medium</td>
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<td>(V_0) solution, dm(^3)</td>
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<td>1</td>
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<td>(\Sigma) = 62.839</td>
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### Table 2

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<thead>
<tr>
<th>Calculation of filter bed formation rate (initial concentration of iron (C_{Fe} = 15.0 \text{ mg/dm}^3))</th>
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<tbody>
<tr>
<td>Filtration medium</td>
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<tr>
<td>(V_0) solution, dm(^3)</td>
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<td>(\Sigma) = 51.18</td>
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After achieving a critical filtration resistance and a sharp decrease in the concentration of iron ions in filtered water, the filtration process was completed. The filter was washed by water return. After that, the water filtration process was repeated using the modified zeolite as a catalytic
charge for water deironing. In this case, it was important to investigate the oxidative loading capacity after the first filter cycle.

When filtered through modified zeolite after washing from sediment Fe(OH)$_3$ concentrations were reduced from 10.0 and 15.0 mg/dm$^3$ to 0.34 and 0.51 mg/dm$^3$ according (Fig. 6).

The calculated weight of the adsorption film and the rate of film formation on the loading surface (Table 1, Table 2) are almost the same as during the first filter cycle. Graphical relationships reflect similar patterns of iron ion oxidation and sediment formation during water filtration (Fig. 7, Fig. 8).

During the second filter cycle, as in the first case, it is noted that as the sediment layer increases, the rate of its formation decreases. Repeated studies confirm the fact that iron hydroxide, which is retained on the loading surface in this case, acts as a weak catalyst for the oxidation of iron ions. There is not complete oxidation and hydrolysis of iron ions entering with an increase in the volume of the passed solution.
The use of the modified zeolite as a filter bed for water decontamination is effective until excessive accumulation of precipitate as iron hydroxide occurs in the background of the bed. After washing, the modified charge does not lose its oxidizing power.

Conclusions
1. To remove iron from water, zeolite modified with potassium permanganate was used as a filter load. In the process of treating the zeolite with potassium permanganate was used as a filter load. In the process of treating the zeolite with potassium permanganate, manganese oxide was formed on its surface, which in the presence of oxygen dissolved in water provided more complete oxidation of iron.

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