DOI 10.31891/2307-5732-2022-315-6-234-239
UDC 628.161.2:546.71

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EVALUATION OF THE EFFICIENCY OF SORBENTS-CATALYSTS FOR THE PURIFICATION OF WATER FROM MANGANESE COMPOUNDS

The condition of sources and central water supply systems does not guarantee the required quality of drinking water. A large part of the population of Ukraine uses drinking water that does not meet hygienic requirements according to various indicators. Manganese compounds are quite often present in natural waters. Their quantitative content can vary in a wide range, depending on the region, it can be 5-6 mg/dm^3. Manganese in underground waters is presented as ion Mn^{2+}, salts of which are soluble. To remove manganese from water one should transfer it to insoluble state by oxidation. Today, there are a number of typical technologies of demagnetization of water. Many works have also been published which describe the purification of water from manganese ion. It is worth noting that with a high content of manganese compounds in water, their removal is a rather difficult task. Removal of manganese compounds from water can be implemented using the ion exchange method, which consists of filtering water through loading in salt or acidic form. At the same time, softening and desalination of water can occur simultaneously. Therefore, the ion exchange method should be used for comprehensive water purification, softening, and removal of manganese compounds.

In order to study the oxidizing capacity of catalytic loading with respect to manganese compounds in water were used as a catalytic load KU-2-8 cationite modified with magnetite and manganese oxide in H^+, Na^+, and Ca^{2+} forms. To modify cationite with magnetite under static conditions, it was treated with a solution containing a mixture of Fe^{2+} and Fe^{3+} ions in a ratio of 1:2. The research was also carried out on the preparation of catalysts based on cationites by modifying them with manganese compounds.

The purpose of this article is to evaluate the efficiency of manganese removal from water when using a catalyst sorbent. The article presents the results of research on water purification from manganese compounds using sorbents-catalysts modified with iron and manganese compounds. It was established that in static and dynamic conditions, complete extraction of manganese ions can be achieved using sorbents based on polymer resin and magnetite. When using cation exchange resin modified with magnetite, the removal of Mn^{2+} ions from aqueous solutions occurs both due to ion exchange, regardless of the form of the ion exchanger, and due to oxidation on the catalyst (magnetite) in the presence of dissolved oxygen. Modified cation exchange resin in Na^+ form leads to the extraction of manganese due to sorption and oxidation of Mn^{2+}. In this case, sorption of calcium and magnesium ions, which is known to be accompanied by an increase in pH. The pH of the medium increased, which increased the efficiency of oxidation of manganese ions on magnetite. Under these conditions, the sorbent catalyst provides complete removal of manganese ions due to catalytic oxidation and sorption of manganese ions on magnetite.

Keywords: *manganese ions, magnetite, sorbent, catalyst, cationite, aeration.*

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ОЦІНКА ЕФЕКТИВНОСТІ СОРБЕНТІВ-КАТАЛІЗАТОРІВ ДЛЯ ОЧИЩЕННЯ ВОДИ ВІД СПОЛУК МАНГАНУ

Стан джерел та систем центрального водопостачання не гарантує необхідної якості питної води. Велика частина населення України використовує питну воду, яка не відповідає гігієнічним вимогам за різними показниками. Сполуки марганцю досить часто присутні в природних водах. Їх кількісний вміст може коливатися у широкому діапазоні залежності регіону може становити – 5-6 мг/дм^3. Варто зазначити, що при високому вмісті сполук марганцю у воді, їх видалення представляє достатньо складну задачу. Видалення сполук марганцю з води може бути реалізоване за допомогою методу іонного обміну, що полягає у фільтруванні води через завантаження в сольовій або кислій формі. При цьому може одночасно відбуватися пом'якшення та знесолення води. Тому, іонообмінний метод доцільно застосовувати для комплексного очищення води, її пом'якшення та видалення сполук марганцю. В статті представлені результати досліджень з очищення води від сполук марганцю із застосуванням сорбентів-каталізаторів модифікованих сполуками заліза та марганцю. Встановлено, що в статичних та динамічних умовах повного вилучення іонів марганцю можна досягти із застосуванням сорбентів на основі полімерної смоли та магнетиту.

Ключові слова*: іони марганцю, магнетит, сорбент, каталізатор, катіоніт, аерація.*

Introduction

Intensive pollution of water supply sources, their inadequacy, and limitation every year lead to the deterioration of the quality of drinking water. As a result, groundwater and surface water can contain a variety of organic and inorganic chemicals. Some of them exceed the permissible norms of presence in the water.

An excess of manganese compounds in water for drinking and domestic purposes leads to the development of many diseases. In accordance with the sanitary and hygienic requirements of Ukraine, the allowable norms for the presence of manganese in water are ≤ 0.1 mg/dm^3. Instead, due to natural factors or anthropogenic influence, manganese present in water can be in concentrations of 0.5-5 mg/dm^3.

Numerous literary data testify to the development of new directions in the purification of water from manganese compounds in recent years [1]. Effective methods of removing soluble manganese compounds from water include those that involve the use of filter loads with an oxidizing film applied to the granules of the material [2]. It acts as an oxidation catalyst. As a rule, in this case, the granules of the filter load are covered with higher metal oxides – most often, manganese oxide. For this purpose, natural materials and modified sorbents, such as basalt gravel, anthracite, quartz sand, dolomite [3], polymeric materials, cinder, zeolite [4, 5], expanded clay, quartzite, and clays of various origins are used as the basis of the filter load [6].

Modification of zeolite with manganese oxide or iron oxide leads to an increase in its sorption and catalytic properties. Conducted studies on the extraction of manganese ions using such sorbents showed that zeolite modified with potassium permanganate has a higher sorption capacity than zeolite coated with iron oxide [7].

Filter loads of Birm and Greensand brands are widely used abroad. Granular filter load Birm, made by artificially applying a film of manganese dioxide MnO_2 on the surface of the material. Another close analog is the glauconite mineral activated by potassium permanganate - Greensand. The sorbent-catalyst synthesized by Ukrainian scientists from natural manganese ore has similar properties to the proposed analogs of foreign manufacturers. However, all these catalysts are quite expensive, as they use deficient manganese compounds in their production.

Magnetic sorbents based on iron oxide have proven themselves quite well in the process of extracting dyes and oil products from water [8]. The most acceptable magnetic modifier is magnetite Fe_3O_4. Analysis of literature data shows that magnetic composites based on silica gel, activated carbon, carbon nanotubes and clay minerals coated with magnetite are quite effective in extracting heavy metals [9]. Previously conducted studies on the extraction of iron compounds from water using a sorbent-catalyst based on ion-exchange resin modified with magnetite showed that such a sorbent has quite good oxidizing properties for iron ions [10]. Therefore, research was conducted using a modified sorbent for water purification from manganese compounds.

Research methods and techniques.

In order to study the oxidizing capacity of catalytic loading with respect to manganese compounds in water, 10 cm^3 of catalytic sorbent was added to solutions prepared in tap water with initial concentrations of 1–30 mg/dm^3, after which they stood for 4 hours, determining the residual manganese concentrations every hour. KU-2-8 cationite modified with magnetite and manganese oxide in H^+, Na^+, and Ca^{2+} forms were used as a catalytic load (Fig. 1). To intensify the oxidation process, solutions with a sorbent were aerated using a porous aerator with a water saturation rate of 0.5 dm^3/min.

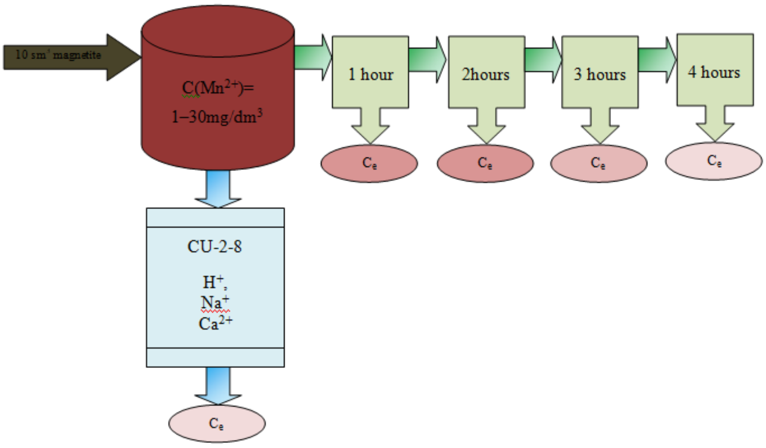

Figure 1. Process diagram

To modify cationite with magnetite under static conditions, it was treated with a solution containing a mixture of Fe^{2+} and Fe^{3+} ions in a ratio of 1:2. The mixture was stirred until the cationite was saturated with iron ions. After that, the cationite was treated with a 10% solution of sodium hydroxide. The mixture was stirred until complete hydrolysis of iron ions with the formation of magnetite in the pores of the cationite. The processes implemented in this case can be described by equations:

$$8\left(\Pi - SO_3^-\right)H^+ + Fe^{2+} + Fe^{3+} \rightarrow \left(\Pi - SO_3^-\right)_8 Fe^{2+}, Fe^{3+} + H^+ \quad (1)$$

$$\left(\Pi-SO_3^-\right)_8 Fe^{2+},Fe^{3+}+8NaOH\rightarrow 8\left(\Pi-SO_3^-\right)Na+Fe_3O_4 \tag{2}$$

where *П* is the polymer residue of the cationite.

The research was also carried out on the preparation of catalysts based on cationites by modifying them with manganese compounds. For this, cationite KU-2-8 was converted into Mn^{2+} form, after which it was treated with a 1% solution of potassium permanganate. The process goes according to the scheme:

$$2\left(\Pi-SO_3^-\right)H^+ + Mn^{2+}\rightarrow\left(\Pi-SO_3^-\right)_2 Mn^{2+}+2H^+ \tag{3}$$

$$3\left(\Pi-SO_3^-\right)_2 Mn^{2+}+2KMnO_4\rightarrow 5MnO_2+2\left(\Pi-SO_3^-\right)K^+ + 4\left(\Pi-SO_3^-\right)H^+ \tag{4}$$

The degree of extraction of Mn^{2+} ions was calculated according to the formula:

$$A=\frac{C_{in}-C_e}{C_{in}}\cdot 100\%$$

C_{in}, C_e – initial and equilibrium concentration of manganese (II) ions in solution, mg/dm^3.

Presenting main material

When using cationite modified with manganese compounds to remove manganese ions from water under static conditions, the efficiency of the process was insignificant. The degree of purification did not exceed 67% at initial concentrations of manganese ions of 1.5 - 30.0 mg/dm3. The best results were obtained when the water purification process was carried out in static conditions with mixing and aeration (tables 1, 2)

Table 1

Dependence of the residual concentration of manganese (II) and pH in tap water on the time of contact with the modified cationite KU-2-8 in the Mn^{2+} form treated with $KMnO_4$

Process conditions	C_{in}	contact time					pH	
		1	2	3	4	24	initial	final
		C (Mn^{2+}), mg/dm^3						
mixing	5,0	3	2,75	1,6	1,0	0,5	8,058	3,141
	15,0	6,0	2,3	1,8	1,2	0,85	8,031	3,134
aeration	5,0	2	1,75	0,75	0,7	0,25	8,074	3,022
	15,0	5,0	2,6	1,4	1,0	0,80	8,023	2,937

Table 2

Dependence of the degree of extraction of manganese (II) in tap water on the time of contact with the modified KU-2-8 cationite in Mn^{2+} form treated with $KMnO_4$

Process conditions	C_{in}	contact time				
		1	2	3	4	24
		A, %				
mixing	5,0	40	45	68	80	90
	15,0	60	85	88	92	94
aeration	5,0	60	65	85	86	95
	15,0	67	83	91	93	95

The degree of manganese extraction in the case of mixing or air aeration of the solution reached 90-95%. It is obvious that the limiting stage of the process is the diffusion of manganese ions to the ionite grains, therefore, when the solution is mixed or aerated, the process is significantly accelerated. This is due to maintaining the oxygen concentration at a constant level. However, if we take into account that the pH of the medium decreased after water purification to 2.94 – 3.89, it can be said that the water purification process is largely influenced by ion exchange:

$$\left(\Pi-SO_3^-\right)H^+ + Ca^{2+}+Mg^{2+}\rightarrow\left(\Pi-SO_3^-\right)_2 Ca^{2+},Mg^{2+}+H^+ \tag{5}$$

To prevent acidification of the pH of the water medium during purification from manganese ions after modification, the sorbent was treated with an alkali solution to convert the ionite into the salt form (Na^+). The results are presented in Tables 3-4.

The efficiency of water purification from manganese (II) ions was the same as in the previous case when the process was carried out without stirring. But in this case, the pH of the medium after cleaning was at the level of 6.0–7.5. In all cases, the lowest residual concentration was 0.5–0.75 mg/dm^3.

When using magnetite-modified cationite KU-2-8 in static conditions for the extraction of manganese compounds from water, a certain decrease in manganese concentration was noted in 4 hours. The degree of water purification did not exceed 30%. The interaction of modified cationite with solutions of Mn^{2+} ions within 24 hours ensured water purification from manganese by 55-63%. At the same time, the modified cationite was in contact with the solution without mixing, which made it difficult for the diffusion of manganese ions to the ionite grains.

Table 3

Dependence of the residual concentration of manganese (II) and pH in tap water on the contact time with the modified cationite KU-2-8 in the $H^+ \rightarrow Mn^{2+}$ form treated with $KMnO_4$/NaOH

C_{in}	contact time					pH	
	1	2	3	4	24	initial	final
	C (Mn^{2+}), mg/dm^3						
1,0	0,73	0,57	0,53	0,53	0,33	7,901	3,889
5,0	4,55	3,40	3,20	3,20	2,20	7,813	3,839
15,0	13,5	12,5	11,0	11,0	5,0	7,883	3,724
30,0	28,0	24,0	23,0	23,0	11,0	7,882	3,343

Table 4

Dependence of the degree of extraction of manganese (II) in tap water on the time of contact with the modified cationite KU-2-8 in the $H^+ \rightarrow Mn^{2+}$ form treated with $KMnO_4$/NaOH

C_{in}	contact time				
	1	2	3	4	24
	A, %				
1,0	27	43	47	47	67
5,0	9	32	36	36	56
15,0	10	17	27	27	67
30,0	7	20	23	23	63

When supplying air through a porous aerator for aerating a solution with a modified cationite KU-2-8, the degree of extraction of manganese ions from water increased significantly (Tables 5, 6).

Table 5

Dependence of the residual concentration of manganese (II) and pH in tap water on the contact time with the modified cationite KU-2-8 and the intensity of air bubbling 0.5 dm^3/dm^{3}min

C_{in}	contact time					pH	
	1	2	3	4	24	initial	final
	C (Mn^{2+}), mg/dm^3						
1,0	0,50	0,30	0,25	0,25	0,10	8,998	7,736
5,0	0,85	0,50	0,25	0,25	0,10	8,989	7,743
15,0	5,00	1,30	0,80	0,40	0,15	8,947	7,711
30,0	10,00	3,50	1,50	0,60	0,20	8,878	7,696

Table 6

Dependence of the degree of extraction of manganese (II) in tap water on the contact time with the modified cationite KU-2-8 and the intensity of air bubbling 0.5 dm^3/dm^{3}min

C_{in}	contact time				
	1	2	3	4	24
	A, %				
1,5	50	70	75	75	90
5,5	83	90	95	95	98
15,0	67	91	95	97	99
30,0	67	88	95	98	99

During 5 hours of water treatment, the degree of purification from manganese ions reached 90-99% with initial manganese concentrations from 1 to 30 mg/dm3. At the same time, the residual concentration of manganese was 0.1–0.2 mg/dm^3. It is quite likely that this cationite in dynamic conditions will ensure the complete extraction of manganese (II) ions from water. An important aspect of the process is that it takes place in a neutral environment (pH=7.2 - 7.7).

Purification of water from manganese ions in dynamic conditions was carried out by filtering water through a layer of sorbent treated with magnetite. This ensures constant contact of the solution with the ion-exchange material and reduces the role of the limiting diffusion factor on the water purification process. It is known that when cationite is modified according to reactions 1 and 2, it changes to the Na+ form when Fe_3O_4 magnetite ionite grains are formed in the pores. When using such a cationite, both the oxidation of manganese ions on magnetite and their partial sorption on ionite together with hardness ions is possible. The results of water purification from manganese (II) ions are presented in Fig. 2, 3.

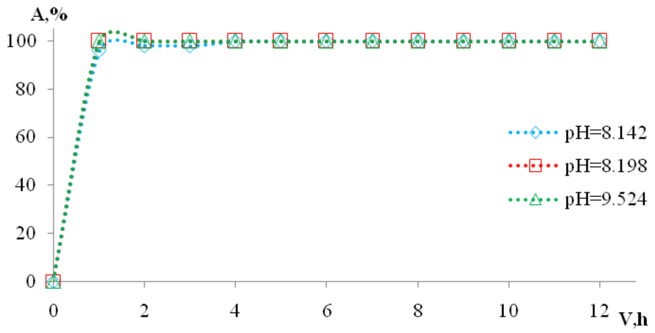

Fig. 2. Dependence of the extraction efficiency of manganese (II) on the volume of artesian water passed through at a manganese concentration of 5.0 mg/dm^3 through cationite KU-2-8 modified with magnetite in the Na$^+$ form (pH=8.142, pH=9.524), Ca^{2+} form (pH=8.198)

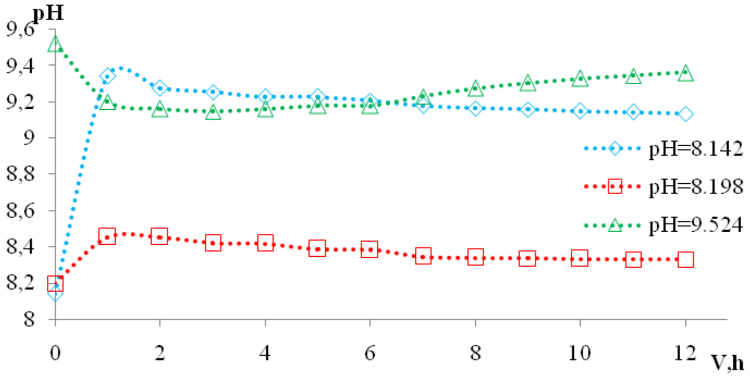

Fig. 3. Dependence of the pH of the medium on the volume of artesian water passed at a manganese concentration of 5.0 mg/dm^3 through cationite KU-2-8 modified with magnetite in Na$^+$ form (pH=8.142, pH=9.524), Ca^{2+} form (pH= 8.198)

When filtering the solution of manganese sulfate through cationite KU-2-8 in the Na$^+$ form modified with magnetite, complete extraction of manganese ions from the solution was achieved. This happened due to their oxidation on the magnetite film and possibly due to ion exchange. The pH of the solution during the filtration process increased from 8.14 to 9.342, which was due to the exchange of Ca^{2+} and Mg^{2+} ions for Na$^+$ ions. At the same time, sodium bicarbonate was mainly formed in the water. During its hydrolysis, the solution becomes alkaline. The alkalinity of water helps to accelerate the process of oxidation of manganese ions but is not desirable for drinking water. Therefore, cationite after modification with magnetite was treated with a 10% solution of calcium chloride. The results of using modified cationite in Ca^{2+} form for water purification from manganese(II) ions are presented in Fig. 5.

In this case, when filtering water through modified cationite, it was completely purified from manganese ions. At the same time, the pH of the environment practically did not change and was in the range of 8.2–8.45.

Thus, it can be said that the cationite modified with magnetite in the Ca^{2+} form provides high efficiency of water demanganation, without affecting the pH level of the medium and the hardness of the water. This filtering loading also delays the bulk of the manganese oxide obtained during oxidation.

Conclusions. A study of the use of KU-2-8 cationite modified with potassium permanganate or iron compounds with the production of manganese oxide and magnetite on its surface was conducted. It was established that, under static conditions, the best results in the extraction of manganese ions from water were achieved using a sorbent catalyst modified with magnetite. The use of cationite modified with magnetite with additional aeration significantly accelerated the process of water purification from manganese compounds. The degree of purification in 5 hours of water treatment reached 90 – 99% with initial manganese concentrations of 1–30 mg/dm^3, while residual manganese concentrations were lower than 0.1 mg/dm^3. When using cationite modified with magnetite in Ca^{2+} form under dynamic conditions at an initial manganese (II) concentration of 5 mg/dm^3, its complete extraction was achieved. The pH of purified water was in the range of 8.2–8.5.

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