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EVALUATION OF THE CONTRIBUTION OF ION EXCHANGE IN THE PROCESS OF DEMANGANIZATION WITH MODIFIED CATION EXCHANGE RESIN KU-2-8

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Abstract

An effective method of water purification from manganese compounds is the use of magnetite, so it is advisable to improve the way it is used. The main disadvantage of using dispersed microcrystalline magnetite is the difficulty of implementing water purification in dynamic conditions, due to the significant resistance to water filtration. In the case of the use of magnetite in static conditions, there is a constant consumption of magnetite after settling and filtration, and the demanganization process requires the use of bulky and poorly mobile installations (mixers, settling tanks and filters). Therefore, water purification from manganese ions was carried out under dynamic conditions by filtering water through a layer of strong acid cation exchange resin KU-2-8 in H^+, Na^+, Ca^{2+} forms modified with magnetite. This allows constant contact of the solution with the ion exchange material and reduces the role of the limiting diffusion factor on the water purification process. When evaluating the effectiveness of cation exchange resin KU-2-8 in the extraction of Mn^{2+} ions from water depending on the form of the resin, it was found that the FEDC for the resin in H^+ form is 2198 mg-eq/dm³, for Na^+ it is 2175 mg-eq/dm³ and for Ca^{2+} the value is 1717 mg-eq/dm³. Therefore, during the transition from H^+ to Na^+ and to Ca^{2+} form there is a decrease in the sorption capacity for Mn^{2+} ions in the cation exchange resin KU-2-8. On the cation exchange resin in Ca^{2+} form the efficiency of demanganization decreases with increasing concentration of manganese ions. When increasing the initial concentration from 5 to 10 and 30 mg/dm³ in distilled water, the residual concentration increases from 0.14 to 0.35 and up to 1.95 mg/dm³ when filtered through 10 cm³ of resin in Ca^{2+} form. When removing Mn^{2+} ions from artesian water, the residual concentration was 4.0; 7.0 and 27.0 mg/dm³ respectively. Thus, on magnetite-modified cation exchange resin, manganese ions are removed only partially due to ion exchange and their complete removal from water is possible only due to catalytic oxidation and deposition on magnetite.

Keywords: demanganization; ion exchange; catalytic oxidation; artesian water; magnetite.

ОЦІНКА ВКЛАДУ ІОННОГО ОБМІНУ В ПРОЦЕСАХ ДЕМАНГАНАЦІЇ МОДИФІКОВАНИМ КАТІОНІТОМ КУ-2-8

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Анотація

Ефективним методом очищення води від сполук марганцю є застосування магнетиту, тому доцільним було вдосконалення методу його використання. В роботі очищення води від іонів марганцю проводили в динамічних умовах при фільтруванні води через шар сильнокислотного катіоніту КУ-2-8 в H^+, Na^+, Ca^{2+} формах модифікованого магнетитом. Це дозволяє забезпечити постійний контакт розчину з іонообмінним матеріалом та знижує роль лімітуючого дифузійного фактору на процес очищення води. При оцінці ефективності катіоніту КУ-2-8 при вилученні іонів Mn^{2+} із води в залежності від форми іоніту було встановлено, що ПОДЄ для іоніту в H^+, формі становить 2198 мг-екв/дм³, Na^+ – 2175 мг-екв/дм³, Ca^{2+} – 1717 мг-екв/дм³. Отже, при переході від H^+ до Na^+ і до Ca^{2+} форми відбувається зниження сорбційної здатності катіоніту КУ-2-8 по іонах Mn^{2+}. При підвищенні початкової концентрації з 5 до 10 та 30 мг/дм³ в дистильованій воді залишкова концентрація зростає від 0.14 до 0.35 та до 1.95 мг/дм³ при фільтрування через 10 см³ іоніту в Ca^{2+} формі. При вилученні іонів Mn^{2+} із артезіанської води залишкові концентрація становили 4.0; 7.0 та 27.0 мг/дм³ відповідно. Отже, на модифікованому магнетитом катіоніті іони марганцю вилучаються лише частково за рахунок іонного обміну, а повне вилучення їх із води можливе лише за рахунок каталітичного окислення та висадження на магнетиті.

Ключові слова: деманганація; іонний обмін; каталітичне окислення; артезіанська вода; магнетит

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ОЦЕНКА ВКЛАДА ИОННОГО ОБМЕНА В ПРОЦЕССАХ ДЕМАНГАНАЦИИ МОДИФИЦИРОВАННЫМ КАТИОНИТОМ КУ-2-8

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Аннотация

Эффективным методом очистки воды от соединений марганца является применение магнетита, поэтому целесообразным было совершенствование метода его использования. В работе очистку воды от ионов марганца проводили в динамических условиях при фильтровании воды через слой сильнокислотного катионита КУ-2-8 в H$^+$, Na$^+$, Ca^{2+} формах модифицированного магнетитом. Это позволяет обеспечить постоянный контакт раствора с ионообменным материалом и снижает роль лимитирующего диффузионного фактора на процесс очистки воды. При оценке эффективности катионита КУ-2-8 при изъятии ионов Mn^{2+} из воды в зависимости от формы ионита было установлено, что ПОДЕ для ионита в H$^+$, форме составляет 2198 мг-экв/дм^3, Na$^+$ – 2175 мг-экв/дм^3, Ca^{2+} – 1717 мг-экв/дм^3. Следовательно, при переходе от H$^+$ к Na$^+$ и к Ca^{2+} форме происходит снижение сорбционной способности катионита КУ-2-8 по ионам Mn^{2+}. При повышении начальной концентрации с 5 до 10 и 30 мг/дм^3 в дистиллированной воде остаточная концентрация возрастает от 0.14 до 0.35 и до 1.95 мг/дм^3 при фильтрации через 10 см^3 ионита в Ca^{2+} форме. При изъятии ионов Mn^{2+} с артезианской воды остаточные концентрации составляли 4.0, 7.0 и 27.0 мг/дм^3 соответственно. Итак, на модифицированном магнетитом катионите ионы марганца изымаются лишь частично за счет ионного обмена, а полное извлечение их из воды возможно лишь за счет каталитического окисления и осаждения на магнетите.

Ключевые слова: деманганация; ионный обмен; каталитическое окисление; артезианская вода; магнетит.

Introduction

The number of water supply sources in Ukraine with high quality water is quite limited. Among other pollutants of natural waters, a significant place is occupied by ions of iron, manganese, nitrates, humic sunstances [1–3]. Water lighting and decolorization technologies are widely used today [4; 5]. Purification of water from iron can be achieved by aeration of water and its filtration [6–8]. Anion exchangers provide efficient removal of nitrates, phosphates and sulfates from water [9; 10].

It is much more difficult to solve the problem of water demanganization, as manganese (II) ions are oxidized in water very slowly: hundreds of thousands of times slower than iron (II) ions [11–13].

Ion exchange and reverse osmosis are not selective for manganese ions, which leads to a deep softening of water desalination, when there is no need to completely remove carbonates, hardness ions and other water-soluble substances from the water [14; 15]. The presence of manganese in concentrations greater than 0.2 mg/dm^3 is not allowed in potable water [14]. However, the concentrations of manganese in water can be in much higher concentrations (0.5–5 mg/dm^3) due to natural factors and anthropogenic impact. [16–19]

Recently, many works have been published describing the processes of extraction of manganese ions from water by sorption methods [20–22]. Sorbents with a deposited catalyst film, preferably manganese oxide, are often used to increase the purfication efficiency [23, 24]. A catalyst for the oxidation of manganese ions based on manganese ore was also developed [25].

It should be noted that the oxidation of Mn^{2+} ions, even in the presence of catalysts, largely depends on a set of factors, such as: pH of the medium, redox potential of the medium, the concentration of manganese and oxygen ions [26, 27]. The author has concluded that the auto-oxidative reaction between Mn^{2+} and MnO$_2$ in solutions does not occur at pH below 9.0.

In general, the oxidation processes of manganese (II) ions on the surface of catalysts are accompanied by the formation of MnO$_2$. Although in the complete absence of chlorides, the formation of Mn$_2$O$_3$ is possible [28].

Recently, more and more attention is paid to biological methods of water demanganization [29–31]. However, the biochemical oxidation of manganese is a more complex process than sorption and chemical oxidation and is often much slower than these processes [32]. At the same time, the enzymatic oxidation of manganese can take place in high yield.

However, sorption-catalytic extraction of manganese (II) ions from water can be more technological. This process involves the sorption of Mn^{2+} ions on the catalyst and their oxidation to MnO$_2$ in the presence of oxygen. The best results were obtained using magnetite. This sorbent catalyst is effective in the oxidation of iron ions and manganese [33].

However, the use of magnetite is possible only in static conditions. Adding to the water of fine magnetite and its separation in settling tanks and filters is needed. This complicates the water purification technology. The filtration of water

through the magnetite layer is too slow, as the magnetite particles are very fine (they are nanoparticles in size) [34]. Therefore, magnetite-modified cation exchange resins, such as KU-2-8 cation exchange resin, are used to remove magnetite under dynamic conditions. However, in the process of modifying the cation exchange resin, it is treated with alkali at the last stage, which leads to the transition of the resin to the Na^+ form. In this case, the extraction of manganese can occur due to sorption and oxidation on magnetite, or due to sorption on cation exchange resin, which is the basis of the catalyst. When studying the mechanism of manganese ion extraction, it was noted that conversion of cation exchange resin into Ca^{2+} form did not guarantee complete exclusion of ion exchange from the process of manganese (II) ion separation from water. Therefore, to clarify the mechanism of the extraction of manganese (II) ions from water, it was expedient to study in detail the mechanism, including the use of Ca^{2+} form of the resin.

The aim of the work was to study the processes of ion exchange extraction of manganese (II) ions from water, taking into account the dependence of the process on the concentration of manganese (II) ions, the form of ion exchanger, the presence of hardness ions in water.

To achieve this goal, the following tasks were set:

- Evaluate the effectiveness of cation exchange resin KU-2-8 in the extraction of manganese (II) ions from water, depending on the form of the resin;

- To determine the efficiency of the extraction of manganese ions from water, taking into account the level of manganese concentration in water;

- Evaluate the effect of hardness ions on the sorption of manganese ions from dilute solutions.

Materials and methods

Strong acid cation exchange resin in H^+, Na^+, Ca^{2+} forms was used. As working media solutions of manganese sulfate in distilled and artesian water were used. Artesian water had the following characteristics: hardness H = 4.0 - 5.3 mg-eq/dm³, alkalinity A = 4.0 - 5.2 mg-eq/dm³, pH = 7.20–7.87, [Ca^{2+} = 3.0 - 4.1 mg-eq/dm³, [Cl^-] = = 25.0–75.0 mg/dm³, [SO_4^{2-}] = = 15.0–48.0 mg/dm³, the concentration of manganese ions was at the level of 5 to 300 mg/dm³.

Solutions of manganese sulfate in distilled and artesian water with concentrations of Mn^{2+} from 5 to 300 mg/dm³ were filtered during the studies on the extraction of manganese ions on the KU-2-8 cation exchange resin (V_i = 10 cm³). The resin was used in H^+, Na^+, Ca^{2+} forms. Consumption of solutions was 10 cm³/min. The sample volume was 250–500 ml. Manganese concentration, pH and calcium ion concentration were monitored in the selected samples.

Results and Discussion

The known order of selectivity of double-charged cations for strongly acidic cation resins is following:

$Hg^{2+} < Cd^{2+} < Mn^{2+} < Mg^{2+} < Zn^{2+} < Cu^{2+} < Ni^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Ba^{2+}$
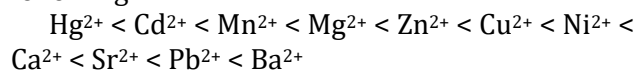
According to this data, the cation exchange resin KU-2-8 has a much higher selectivity for calcium ions compared to manganese ions. However, this does not mean that in the Ca^{2+} form the cation exchange resin will not sorb manganese ions. Especially in conditions when solutions of manganese (II) salts do not contain calcium ions, and the concentration of manganese ions is significant. In this case, the course of ion exchange will be determined to a lesser extent by selectivity and to a greater extent by the process of equalization of the concentration between the solution and the sorption volume of the resin. Thus, during the sorption of manganese ions from solutions of manganese sulfate in distilled water at a concentration of the latter 280 - 300 mg/dm³ on the cation exchange resin KU-2-8 in H^+, Na^+ and Ca^{2+} forms (Fig. 1, Fig. 2, Fig. 3), full exchange dynamic capacity (FEDC) of the cation exchange resin was the same for H^+ and Na^+ forms and reached its limit values: 2198 and 2175 mg-eq/dm³ respectively. For cation exchange resin in Ca^{2+} FEDC was slightly lower and reached 1717 mg-eq/dm³. The solution was acidified only when using cation exchange resin in H^+ form due to the exchange of Mn^{2+} ions for counterions. For the resin in the Na^+ and Ca^{2+} form, the sorption process had little effect on the pH of the solution.

To mathematically describe the initial sorption curves under dynamic conditions (dependence between the concentration of ions in the eluate and the sorption time, or the consumed volume of the solution) at a given constant filtration rate of the solution through the column with cation exchange resin most often the Thomas model is used. It is one of the most reliable models, which is quite simple and easy to use. The Thomas model is described by the dependence:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(K\left(\frac{Q \cdot M}{V} - C_0 \cdot t\right)\right)},$$

where K is the constant of the Thomas model, $dm^3/mg \cdot h$; Q is the maximum concentration of metal in the solid phase, mg/g; V is the volumetric rate of filtration of the solution through the column (flow rate of the solution through the column), dm^3/h; m is the mass of the sorbent, g; t – time, year.

When controlling the process by measuring the volumes of filtered solutions at a constant filtration rate, the filtration time (h) can be calculated by the formula:

$$t = \frac{V_s}{V},$$

where V_s is the volume of the filtered solution

The application of the Thomas model, which describes the dynamic initial sorption curves, is reduced to determining the constant of the Thomas model by experimental results. The kinetic coefficient and sorption capacity of the column can be determined by the linear dependence of $\ln(C/C_0 - 1)$ on 1 (or on V_s/V). The dependence can be represented as:

$$\ln\left(\frac{C_0}{C} - 1\right) = K\left[\frac{Q \cdot M}{V} - C_0\left(\frac{V_s}{V}\right)\right]$$

$$K = \frac{\ln\left(\frac{C_0}{C} - 1\right)}{\left[\frac{Q \cdot M}{V} - C_0\left(\frac{V_s}{V}\right)\right]}$$

The coefficient of determinism (correlation) R^2 was calculated by the formula:

$$R^2 = \frac{\sum_{i=1}^{n}(y_i - \bar{y})}{\sqrt[a]{\sum_{i=1}^{n}(y_i - \bar{y})^2}}$$

where y is the average value of the function (in this case the calculated value of the concentration of metal ions in the solution C, mg/dm^3) at a given value of the argument x (in this case the volume of the solution passed through the ion exchanger V_s, dm^3); y_i is the value of the function (C) at a given value of x (V_s).

For 10 cm^3 of cation exchange resin, the mass was calculated based on the specific volume of 2.7 cm^3/g, M = 3.7 g. In the case of the sorption of manganese ions under dynamic conditions, the kinetic coefficient (Thomas model constant) was equal to 0.01394 $dm^3/mg \cdot h$ for the resin in H^+ form, 0.00729 $dm^3/mg \cdot h$ for the resin in Na^+ form, 0.00370 $dm^3/mg \cdot h$ for the resin in Ca^{2+} form. The maximum concentration of the metal at the selected concentrations of C_0 was determined by FEDC.

$$Q = E_f \frac{V_i \cdot N}{1000 \cdot M},$$

where E_f – FEDC, mg-eq/dm^3; N is the equivalent weight of the metal; for Mn^{2+} it is 27.45 mg; M is the mass of the resin, g (for this case 3.7 g); V_i is the volume of the resin, cm^3.

For manganese ions, based on equation 1, the Thomas model can be written as:

$$C = \frac{C_0}{1 + \exp\left[0.00976\left(\frac{Q \cdot M}{V} - C_0\left(\frac{V_p}{V}\right)\right)\right]}$$

As it can be seen from Fig. 1 – 3, calculated dependences of C on V_s according to the Thomas model correlate well with experimental data not only for ion exchanger in H^+ and Na^+ forms, but also for ion exchanger in Ca^{2+} form, and therefore adequately describe the processes of the sorption of manganese ions on cation exchange resin KU-2-8 in dynamic conditions.
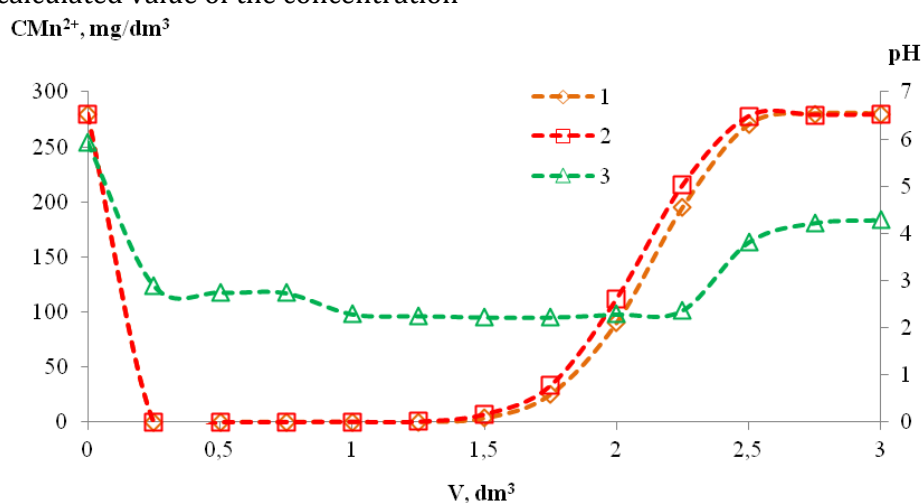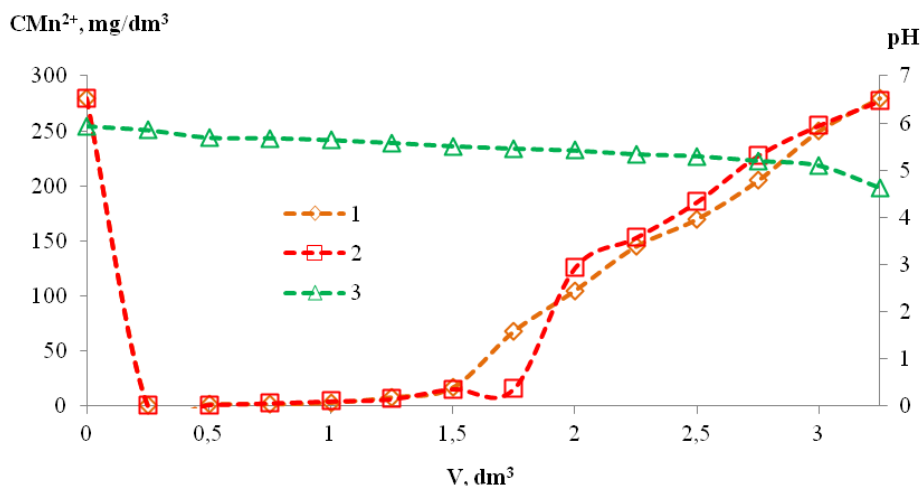

Fig. 1. The dependence of the concentration of manganese ions (1; 2) and the pH (3) of a solution of manganese sulfate (C (Mn^{2+}) = 280 mg/dm^3) in distilled water on the filtration rate through the cation exchange resin KU-2-8 in H^+ form (V_i = 10 cm^3) at a solution flow rate of 10 cm^3/min. (curve 2 is calculated according to the model of Thomas) (FEDC = 2198 mg-eq/dm^3)

Fig. 2. The dependence of the concentration of manganese ions (1; 2) and the pH (3) of a solution of manganese sulfate (C (Mn²⁺) = 280 mg/dm³) in distilled water on the filtration rate through the cation exchange resin KU-2-8 in Na⁺ form (Vᵢ = 10 см³) at a solution flow rate of 10 cm³/min. (curve 2 is calculated according to the model of Thomas) (FEDC = 2175 mg-eq/dm³)
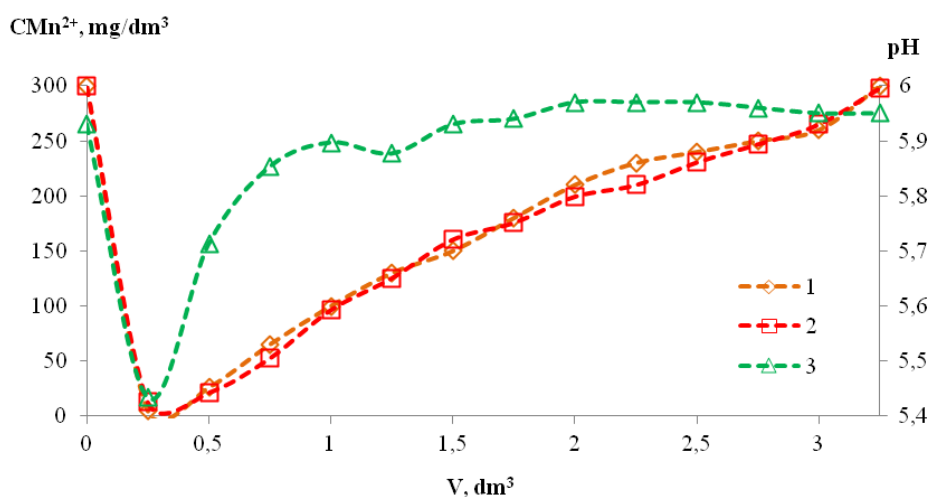
Fig. 3. The dependence of sorption of manganese ions (1; 2) and the pH (3) from a solution of MnSO₄ (C (Mn²⁺) = 300 mg/dm³) in distilled water on the cation exchange resin KU-2-8 (Vᵢ = 10 см³) in Ca²⁺ form on the volume of the passed solution (U = 10 см³/min) (curve 2 is calculated according to the model of Thomas) (FEDC = 1717 mg-eq/dm³)

It should be noted that for the cation exchange resin KU-2-8 in H⁺, Na⁺, Ca²⁺ forms, the coefficients K in the Thomas model differ from each other, due to the fact that despite the close initial concentrations of manganese, experimental sorption curves are different. Despite the fact that FEDC for cation exchange resin in H⁺ and Na⁺ forms do not differ, the initial sorption curves for different forms are different (Fig. 1 and Fig. 2). In the first sample (Vₛ = 0.25 dm³) for cation exchange resin in Na⁺ form the concentration of manganese reaches 1.3 mg/dm³, while for H⁺ form the excess of manganese concentration (1.0 mg/dm³) occurs when passing more than 1.5 dm³. For cation exchange resin in Ca²⁺ form, the concentration of manganese in the first sample (Vₛ = 0.25 dm³) reaches 5.0 mg/dm³.

It is interesting to note that when the concentration of manganese in distilled water is reduced to 30.0 mg/dm³, its sorption on the cation exchange resin KU-2-8 in the Ca²⁺ form is quite effective (Fig. 4). When filtering 4.0 dm³ of the solution through 10 cm³ of cation exchange resin at a flow rate of 10 cm³/min, the concentration of manganese on the initial sorption curve increases from 0.6 mg/dm³ to 1.95 mg/dm³. The sorption curve calculated according to the Thomas model at a value of the coefficient K = 0.0037 dm³/mg·h is quite close to the curve obtained experimentally.

Similar results were obtained at a concentration of manganese (II) in distilled water of 5.0 and 10.0 mg/dm³ during sorption on cation exchange resin in the Ca²⁺ form (Fig. 5). And in this case, the initial curves calculated by the

Thomas model are close to the experimental dependences. In all cases (Fig. 4 and Fig. 5) the concentration of calcium ions desorbed from the ion exchanger exceeds the equivalent amount of sorbed manganese ions. It is possible that in this case, when converting the cation exchange resin to the Ca^{2+} form, an excess of calcium sorption took place, which was accompanied by leaching of excess calcium ions with distilled water.
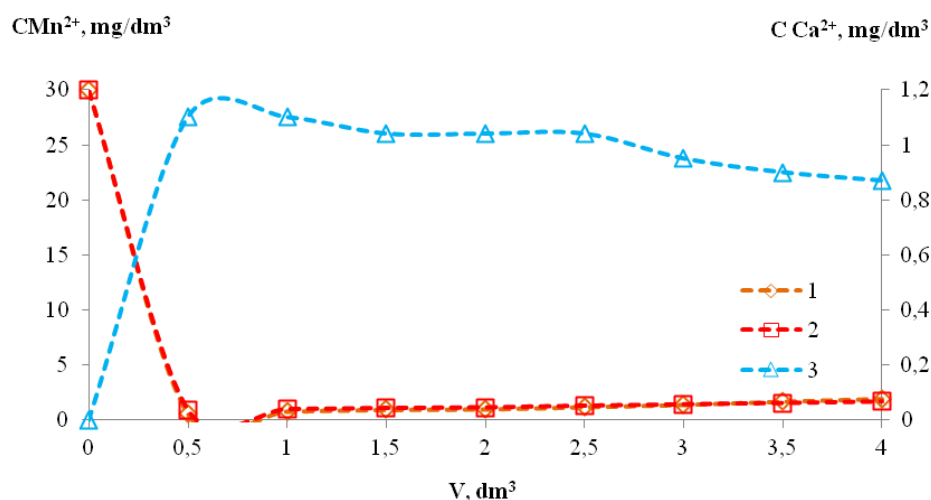

Fig. 4. Dependence of the concentration of manganese (1; 2) and calcium ions (3), on the volume of the solution of manganese sulfate (C Mn^{2+} = 30 mg/dm³) passed through the cation exchange resin KU-2-8 in Ca^{2+} form (V_i = 10 см³) (curve 2 is calculated according to the model of Thomas)
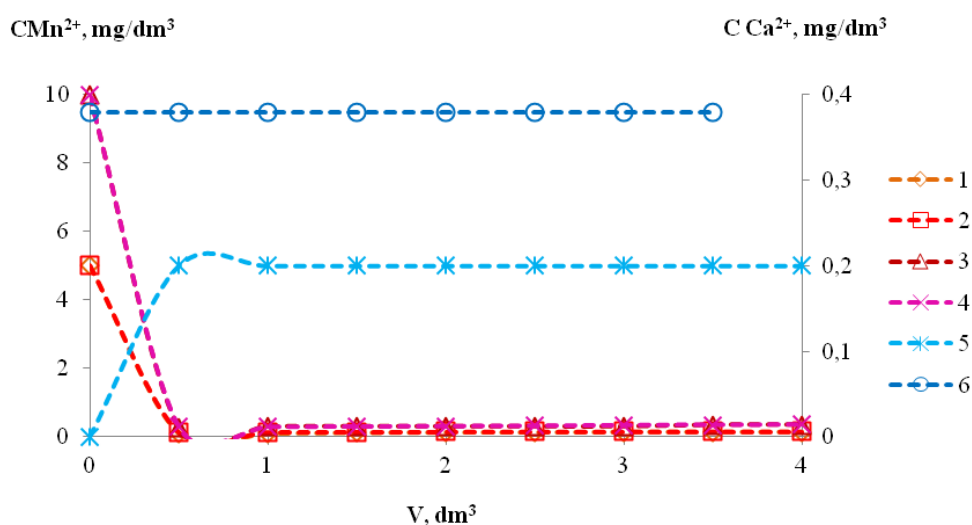

Fig. 5. The dependence of the concentration of manganese (1; 2; 3; 4) and calcium ions (5; 6), from a solution of manganese sulfate in distilled water (C Mn^{2+} = 5 mg/dm³ (1; 2; 5) C Mn^{2+} = 10 mg/dm³ (3; 4; 6)) on the volume passed through the cation exchange resin KU-2-8 in Ca^{2+} form (V_i = 10 см³) at a solution flow rate of 10 cm³/min. (curves 2 and 4 are calculated according to the Thomas model)

Sorption of manganese ions from solutions with concentration of 5, 10 and 30 mg/dm³ in tap water was much less effective when they were filtered through cation exchange resin KU-2-8 in Ca^{2+} form (Fig. 6). As it can be seen from Fig. 6, the concentration of manganese in the solution with an initial concentration of 5 mg/dm³ after passing 4 dm³ of the solution increases to 4.0 mg/dm³. At an initial concentration of 10 mg/dm³ under these conditions it increases to 7 mg/dm³ and at an initial concentration of 30 mg/dm³ it increases to 27 mg/dm³. If we compare with the data of [35], where it was clearly shown that when passing a solution of manganese sulfate in artesian water (C Mn^{2+} = 5 mg/dm³) through 10 cm³ of magnetite-modified cation exchange resin KU-2-8 in Ca^{2+} form (volume 8 dm³), the concentration of manganese in the source water was 0 mg/dm³.
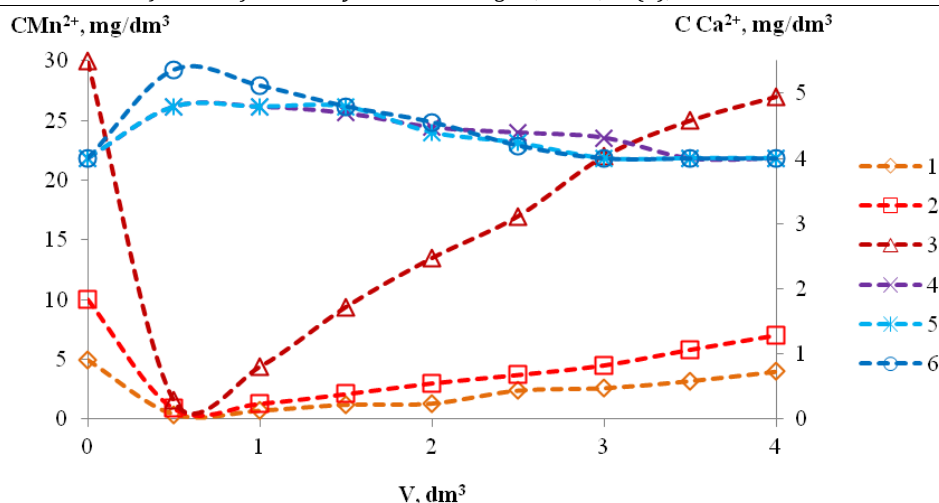
Fig. 6. Change in the concentration of manganese (1; 2; 3) and calcium ions (4; 5; 6), from a solution of manganese sulfate in artesian water (C Mn^{2+} = 5 mg/dm^3 (1; 4); C Mn^{2+} = 10 mg/dm^3 (2; 5); C Mn^{2+} = 30 mg/dm^3 (3; 6); C Ca^{2+} = 4,0 mg/dm^3) when filtering them through the cation exchange resin KU-2-8 in Ca^{2+} form (V$_i$ = 10 см^3)

It is clear from Fig. 6 (curve 1) that when passing such a solution through the unmodified cation exchange resin KU-2-8 in Ca^{2+} form with a volume of the passed solution of 4 dm^3, the concentration of manganese increases from 0.4 to 4.0 mg/dm^3. It can be assumed that the extraction of manganese from water during its filtration through magnetite-modified cation exchange resin is partly due to ion exchange, but the biggest part is removed due to catalytic oxidation on magnetite.

Conclusions

1. It is shown that cation exchange resin KU-2-8 provides extraction of Mn^{2+} ions from water. FEDC for ion exchanger in H$^+$, Na$^+$, Ca^{2+} form is 2198, 2175, 1717 mg-eq/dm^3 respectively. The concentration of manganese in the initial solutions reaches 0.01 - 280 mg/dm^3, for the resin in the Na$^+$ form it is 1.3 - 280 mg/dm^3, and 5.0 - 300 mg/dm^3 for the resin in the Ca^{2+} form at a volume of solutions of 3.25 dm^3. This indicates a decrease in the sorption capacity of the cation exchange resin KU-2-8 on Mn^{2+} ions during the transition from H$^+$ to Na$^+$ and to Ca^{2+} form.

2. It is established that during sorption of manganese (II) ions from distilled water on cation exchange resin in Ca^{2+} form, the efficiency of water purification decreases with increasing concentration of manganese ions. When filtering 4 dm^3 of Mn^{2+} solutions with concentrations of 5, 10 and 30 mg/dm^3, respectively, through 10 cm^3 of ion exchanger in Ca^{2+} form, the residual manganese concentration increases from 0.14 to 0.35 and up to 1.95 mg/dm^3. When the concentration of Mn^{2+} is 300 mg/dm^3, the residual concentration of manganese reaches 26

mg/dm^3 at a volume of filtered solution of 0.5 dm^3.

3. The influence of hardness ions on the sorption of manganese (II) ions on the KU-2-8 cation exchange resin in Ca^{2+} form has been determined. It is shown that under these conditions the efficiency of manganese sorption decreases due to competitive sorption of hardness ions. At initial concentrations of Mn^{2+} being 5, 10 and 30 mg/dm^3, the concentrations of manganese leakage reach 4.0, 7.0 and 27.0 mg/dm^3 respectively. This confirms the conclusion that on magnetite-modified cation exchange resin manganese ions are removed only partially due to ion exchange and their complete removal from water is possible only due to catalytic oxidation and deposition on magnetite.

4. It is known that the concentration of Mn^{2+} ions in natural water does not exceed 8 mg/dm^3 at concentrations of hardness ions greater than 4 mg-eq/dm^3, which significantly reduces the efficiency or makes ion exchange purification of water impossible. The use of magnetite-modified cation exchange resin in the demanganization of aerated water provides complete removal of Mn^{2+} ions due to catalytic oxidation without restriction of the filter cycle.

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