TECHNOLOGY ORGANIC AND INORGANIC SUBSTANCES

EVALUATION OF CATIONITE EFFICIENCY DURING EXTRACTION OF HEAVY METAL IONS FROM DILUTED SOLUTIONS

Досліджено процеси іонообмінного вилучення іонів важких металів на слабо- та сильнокислотних катіонітах. При концентрації міді 10^{-2} мкг/дм³ мідь не сорбується при використанні фільтрів змішаної дії. При видаленні іонів свинцю ступінь вилучення зростає. При використанні 2М розчину соляної кислоти ефективність десорбції іонів свинцю сягає 100 %. Ступінь десорбції іонів міді сягає приблизно 90 %

Ключові слова: важкі метали, іонний обмін, сорбція, регенерація іоніту, фільтр змішаної дії

Исследованы процессы ионообменного извлечения ионов тяжелых металлов на слабо- и сильнокислотных катионитах. При концентрации меди 10^{-2} мкг/дм³ медь не сорбируется при использовании фильтров смешанного действия. При удалении ионов свинца степень извлечения увеличивается. При использовании 2М раствора соляной кислоты эффективность десорбции ионов свинца достигает 100 %. Степень десорбции ионов меди достигает примерно 90 %

Ключевые слова: тяжелые металлы, ионный обмен, сорбция, регенерация иони-та, фильтр смешанного действия

N. Gomelya
Doctor of Technical Sciences,
Professor, Head of Department*
E-mail: m.gomelya@kpi.ua

V. Ivanova
Postgraduate Student*
E-mail: veronika_m_p@ukr.net

V. Galimova
PhD, Associate Professor
Department of analytical and
bioinorganic chemistry and quality water
National University of Life and
Environmental Sciences of Ukraine
Heroyiv Oborony str., 15, Kyiv, Ukraine, 03041
E-mail: galimovav@yandex.ua

J. Nosachova
PhD, Associate Professor*
E-mail: j.nosachova@gmail.com

T. Shabliy
Doctor of Technical Sciences, Professor*
E-mail: dsts1@ukr.net
*Department of Ecology and technology of Plant Polymers
National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

1. Introduction

The end of XX and the beginning of XXI century brought not only outstanding scientific and technological achievements, but also a considerable deterioration in the condition of environment as a result of its significant pollution.

Ukraine has limited supplies of fresh water and has almost lost the clean surface water that would meet the requirements for water quality for household and drinking purposes. Surface water of rivers, lakes, underground water, moderate artesian water used for drinking water supply has largely lost quality due to excessive contamination with sewage. Very often technogenic loading on water reservoirs exceeds their ability to self-purification.

Most often, pollution of water bodies leads to a significant increase in the level of mineralization of the reservoir, to a significant increase in the hardness of water. There are acute problems related to water contamination by heavy metals [1]. Even though the compounds that are formed during the hydrolysis of heavy metals are difficult to solve, the fact that contributes to the creation of false notions about the low content of heavy metals in natural waters, the real situation is much more complicated. That is why reliable control over the content of heavy metals in water is a relevant issue, as well as determining efficiency of the known methods for purifying water at low concentrations of the ions of heavy metals.

2. Literature review and problem statement

It is known that because of anthropogenic influences, the content of ions of heavy metals often exceeds permissible standards [2]. But even at allowable concentrations of heavy metals in natural waters, their content periodically increases significantly as a result of the processes of eutrophication

[3]. This is contributed to by a considerable accumulation of heavy metals in hydrobionts and bottom sediments [4]. To a large extent, nuclear power plants, along with other industrial enterprises, affect the introduction of heavy metals into water [5, 6]. These industrial facilities are characterized by a high level of thermal pollution, and large amount of wastewater discharged into reservoirs. Thus, Zaporizhzhya Nuclear Power Plant discharges 10 m³ of water per second into the river Dnieper, which amounts to about 800.000 m³ per day. In this case, the content of copper ions in such waste water reaches 20–100 mkg/dm³.

Today, there are no available effective methods for water purification from heavy metal ions under such low concentrations in the presence of hardness ions.

As noted by the authors of article [7], selectivity of the cationite KU-2-8 to the ions of copper at its low concentrations is close to the selectivity to the ions of hardness. That is why, during sorption of copper from waste or natural waters with a hardness of 4–18 mg-equiv/dm³ at copper concentration 1–2 mg/dm³, the ionite capacity for copper is about as many times less as its concentration relative to the concentration of hardness ions. In other words, deep water purification from the ions of copper by using an ion-exchange method is impossible without full water softening. This is also true in relation to weak-acid cationites [8]. That is why, authors of [9] propose organizing closed cycles in galvanic production without discharge of wastewater.

At the same time, when employing the ion-exchange materials modified with compounds of manganese and iron [10], the authors managed to improve efficiency of extracting the ions of heavy metals from water. In addition, when the ionite capacity is not exhausted during sorption of other dominant ions (for example, the hardness ions), ionites quite effectively sorb the ions of heavy metals even at low concentrations. This applies for both strong- and weak-acid cationites. The weak-acid cationites have high capacity for doubly charged cations even at high concentrations of competing one-charge ions [11]. That is why the ion-exchange methods are widely used both in the processes of deep softening and in the process of practically full deionization of water. These methods are promising also at the concentration of ions and salts in analytical methods, when extracting rare metals.

However, at present, the analyzed data from the scientific literature fail to evaluate the efficiency of extraction from water the ions of heavy metals employing an ionic exchange at concentrations lower than 1 mg/dm³ (at and below the level of their boundary admissible concentration (BAC) in natural waters). This happens to be extremely important given the concentration of heavy metals in trophic chains in natural water bodies and a varying increase in their concentration during eutrophication of water bodies [3]. Given this situation, it is rather promising to determine the limit of effectiveness in the ion-exchange purification from the ions of heavy metals as one of the most efficient methods for water deionization.

3. The aim and objectives of the study

The aim of present work was to determine effectiveness of the ion-exchange resins during sorption of heavy metal cations from strongly diluted solutions. This implied establishment of threshold concentrations of the ions of metals, at which the sorption capacity of cationites is reduced to zero, as well as determining the capability of cationites to concentrate cations of heavy metals during water analysis.

To achieve the set aim, the following tasks have been solved:

– to study the processes of copper ions sorption ($1 \cdot 10^{-1}$– -1×10^{-6} mg/dm³) on strong- and weak-acid cationites from distilled and tap water, to evaluate effectiveness of the filters with combined action during extraction of copper ions from water;

– to examine the processes of cation-exchange extraction of lead ions (0.01–100 mkg/dm³) from tap and distilled water on weak- and strong-acid cationites, to determine efficiency of lead ion desorption from cationites when using solutions of hydrochloric acid;

– to assess prospects of the ion-exchange methods in the processes of concentration of heavy metal ions from strongly diluted solutions.

4. Materials and methods to study the extraction of heavy metal ions from water using the method of ion exchange

4. 1. Materials and equipment used in the experiment

We used as ion-exchange materials the weak-acid cationite DOWEX MAC-3, the strong-acid cationite KU-2-8, the high-base anionite AV-17-8. Cationites were used in the H^+- and Na^+-forms, anionite – in the OH^--form. We applied as model solutions the solutions of copper sulphate and lead nitrate with concentrations by the ions of heavy metals from $1 \cdot 10^{-2}$–$1 \cdot 10^{-3}$ mkg/dm³ from distilled and tap water.

Characteristics of tap water:

H=4.8–5.2 mg-equiv/dm³,

$[Ca^{2+}]$=3.64–4.0 mg-equiv/dm³,

A=4.7–5.2 mg-equiv/dm³,

$[Cl^-]$=37–50 mg-equiv/dm³,

$[SO_4^{2+}]$= 47–65 mg/dm³,

pH=7.10–7.57.

Concentration of the ions of copper and lead were determined by the method of inverse chronopotentiometry in line with the procedure described in paper [12]. Such method of analysis enabled accuracy in determining copper and lead at the level of 10^{-6} mg/dm³ (10^{-3} mkg/dm³).

4. 2. Design of experiment for the removal of heavy metals from water on different cationites

Sorption was carried out under dynamic conditions. Volume of ionite was 10–20 cm³. The column is 2 cm in diameter. Consumption of the solution at sorption was 10–15 cm³/min, at regeneration – 1–2 cm³/min. Regeneration was conducted by the 2M solution of hydrochloric acid.

Hardness of the solutions and pH were determined by known procedures [13]. The degree of desorption of metal ions was calculated as the ratio of mass of the desorbed ions to the total mass of sorbed ions.

5. Results of research into removal of copper ions (II) and lead ions (II) using an ion-exchange method

Strong- and weak-acid cationites sorb the ions of heavy metals in the presence of hardness ions. But the capacity of cationites for the ions of heavy metals decreases with increasing concentration of competing ions – of calcium and magnesium. However, even at low concentrations of copper ions, they sorb in the presence of hardness ions in a proportional amount with the latter [7, 8]. In this case, at low amounts of solutions filtered through ionites, when the ionite capacity for the total quantity of cations is exhausted partially, they can sorb from the solutions almost up to exhaustion of the ionite capacity. However, as shown by the conducted studies (Fig. 1), at the first stage of sorption (V_{filter}=0.6–1.8 dm^3) on the weak-acid cationite DOWEX MAC-3 in the H$^+$-form (V_i=20 cm^3), there occurs a reduction in the concentration of copper ions from 0.1–0.2 mg/dm^3 to (1.6–9.4)·10^{-3} mg/dm^3 at a simultaneous reduction of hardness of the solution from 4.8 mg-equiv/dm^3 to 0.40–0.46 mg-equiv/dm^3 (Fig. 1).
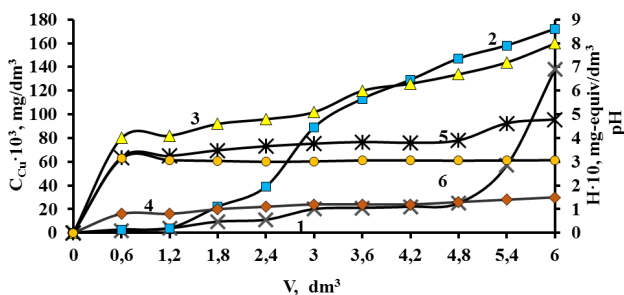

Fig. 1. Dependence of concentration of copper ions (1; 2), hardness (3; 4) and pH (5; 6) of the solution of copper sulphate in tap water ([Cu^{2+}], mg/dm^3: 0.138 (1; 3; 5); 0.172 (2; 4; 6), H=4.8 mg-equiv/dm^3 on volume of the solution passed through the cationites DOWEX MAC-3 (1; 3; 5) and KU-2-8 (2; 4 ; 6) in the H$^+$-form (V_i=20 cm^3) (EDC$_1$=32 mg/dm^3; EDC$_2$=25.3 mg/dm^3; EDC$_3$=1269.6 mg-equiv/dm^3; EDC$_4$=1405.5 mg-equiv/dm^3)

On the strong-acid cationite KU-2-8, under the same conditions, the concentration of copper decreased to (2.8–22.0)× ×10^{-3} mg/dm^3 while hardness fell to 0.08–0.10 mg-equiv/dm^3. This is predetermined by the selectivity of ionite for the given ions, by the starting concentration of ions, by a decrease in pH of the medium to 3.00–3.14, and the competing sorption of hardness ions. Experimental data proved that flashing by copper ions in the cationite DOWEX MAC-3, equal to the starting concentration of the given ions in the solution, occurred during filtration of only 6.0 dm^3 of water when filled with cations by only 31.5 % of the capacity of ionite. On the KU-2-8, copper ions passed through the cationite without sorption when also exposed to 6.0 litres of the solution when filled with cations by approximately 58 % of the capacity of cationite. It is obvious that effectiveness of the extraction of copper cations in the given case depends both on kinetic and thermodynamic factors. However, if a significant portion of the caionite capacity is not used, then efficiency of the sorption removal of copper ions depends largely on the concentration of the given cations in water. Thus, at starting concentration of copper 0.331–1.569 mkg/dm^3 during sorption on the cationite DOWEX MAC-3 in the H$^+$- and Na$^+$-form from tap and distilled water, exchange dynamic

capacity for copper was only 2.5·10^{-6}–2.14·10^{-3} mg/dm^3 at the filled capacity of ionite to 15 % (Fig. 2).
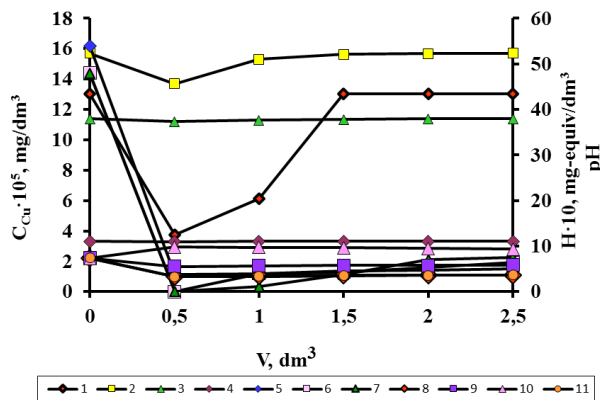

Fig. 2. Dependence of starting values of the concentration of copper ions (1—4), hardness (5—7) and pH (8—11) of the solutions of copper sulphate in tap (1; 2; 4—8; 10; 11) and distilled (2; 9) water on volumes of the solutions passed through the cationite DOWEX MAC-3 (V_i=20 cm^3) in the H$^+$- (1; 2; 4; 5; 7—9; 11) and Na$^+$-form (3; 10) (EDC$_1$=2.14× ×10^{-3} mg/dm^3; EDC$_2$=6.15·10^{-4} mg/dm^3; EDC$_3$=8.25× ×10^{-5} mg/dm^3; EDC$_4$=2.5·10^{-6} mg/dm^3; EDC$_5$=619.5 mg-equiv/dm^3; EDC$_6$=550 mg-equiv/dm^3; EDC$_7$=551 mg-equiv/dm^3)

The lowest values of the ionite capacity were registered at starting concentration 0.3 mkg/dm^3, as well as at sorption on cationite in the Na$^+$-form. It is obvious that at concentration of copper ions in water approximately 0.3 mkg/dm^3, sorption does not actually occur because the given content corresponds to the equilibrium concentration of copper in the solution for ionites with carboxylic groups. Copper does not sorb also on the cationite in the Na$^+$-form due to the relatively higher selectivity of cationite for the Na$^+$ ions in comparison with the H$^+$ ions and low concentration of the Cu^{2+} ions in water. The diffusion factor here is of little effect for the process of exchange since under static conditions at the time of contact between the solution and ionite, similar results were obtained [8].

The sorption of copper ions practically did not occur on the cationite in acidic form from distilled water at a concentration of 1.569 mg/dm^3 due to the reduced capacity of cationite in acidic medium. Although in this case, because of low sorption of copper ions, acidification of the solution was practically not observed (Fig. 2, curve 9). pH reached 5.52–5.83. Acidification of the copper solution in tap water was due to the sorption of hardness ions from water (Fig. 2, curve 8, 11).

It should be noted that the utilized concentration of copper ions (3.31–13.02)·10^{-5} mg/dm^3, or (1.04–4.10)·10^{-9} g-equiv/dm^3, is 3 to 2 orders of magnitude lower than the concentration of protons in distilled water. That is why a concentration factor, in this case, contributes to the desorption of copper ions rather than to their sorption. It is obvious that a small sorption of copper ions at a concentration of 13,02·10^{-5} mg/dm^3 occurs only at the expense of a much higher selectivity of ionite on copper ions compared to protons. During sorption of copper ion on the cationite in the Na$^+$-form, the exchange of sodium ions for copper ions does not occur at a concentration of copper 15.69·10^{-5} mg/dm^3, which is caused by a slightly higher selec-

tivity of ionite for sodium cations compared to protons. Even lower is sorption capacity of the cationite KU-2-8 for copper ions compared to DOWEX MAC-3 during sorption from strongly diluted solutions (Fig. 3).
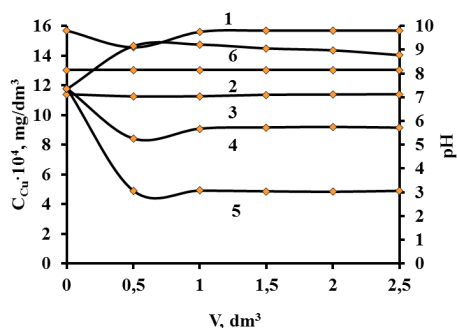

Fig. 3. Change in the concentrations of copper ions (1; 2; 3) and pH of the medium (4; 5; 6) depending on the volume of copper sulphate solution in distilled water ([Cu^{2+}]=1.569× ×10^{-3} mg/dm^3) (1; 4) and tap water (H=5.20 mg-equiv/dm^3, [Cu^{2+}]=1.302·10^{-3} mg/dm^3 (2; 5); [Cu^{2+}]=1.139·10^{-3} mg/dm^3 (3; 6)) passed through the cationite KU-2-8 (V_i=20 cm^3) in the H$^+$-form (1; 2; 4; 5) and the Na$^+$-form (3; 6)

Thus, with a concentration of $(1.302-1.569) \cdot 10^{-3}$ mg/dm^3, copper ions practically do not sorb on cationite in the H$^+$- and Na$^+$-form from both distilled and tap water. In this case, during sorption of copper ion from distilled water on cationite in the H$^+$-form, lowering of pH from 7.36 to 5.25–5.74 occurs due to the sorption of residual hardness ions in distilled water. As a rule, in the distillate without additional purification, residual hardness amounts to 0.01–0.02 mg-equiv/dm^3. When passing the tap water through ionite in acidic form, pH reduces to 3.02–3.07 at the expense of changing hardness ions to protons. When using ionite in the Na$^+$-form, there is an exchange of sodium ions to the hardness ions, which leads to an increase in pH to 8.77–9.21, which agrees with data from the scientific literature [14].

During desorption of copper ions from the cationites KU-2-8 and DOWEX MAC-3 we used the 2M solution of hydrochloric acid (Fig. 4).
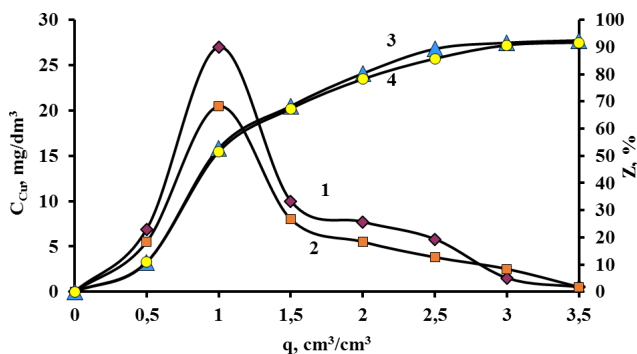

Fig. 4. Dependence of starting concentration of copper ions (1; 2) and the degree of their desorption (3; 4) from the cationites DOWEX MAC-3 (1; 3) and KU-2-8 (2; 4) in the Ca^{2+}-, Mg^{2+}-, Cu^{2+}-form at a mass of the sorbed copper ions of 0.643 mg (1; 3) and 0.503 mg (2; 4) in 20 cm^3 of ionite on the 2M HCl specific consumption

In this case, concentration of the acid was chosen based on the fact that the solutions of HCl with such concentration are used when running an analysis on the device M-HA1000-5.

In general, despite a scant amount of the sorbed copper, its desorption proceeds rather efficiently. At a specific consumption of regeneration solution of 3.5 cm^3/cm^3, the degree of copper desorption from the cationite DOWEX MAC-3 reaches 92.37 %, from the cationite KU-2-8 – 91.68 %.

Thus, a limiting factor for the application of ion exchange during concentration of copper ions from diluted solutions is a low efficiency of sorption. Sorption efficiency does not depend on the form of ionite, nor on the presence of hardness ions, and is determined only by the concentration of copper ions in the solution.

Based on the known information about high efficiency of filters with combined action during deep deionization, we studied the processes of extraction of copper ions from water using a mixture of the cationite KU-2-8 in the acidic form and the anionite AV-17-8 in the basic form (Fig. 5).
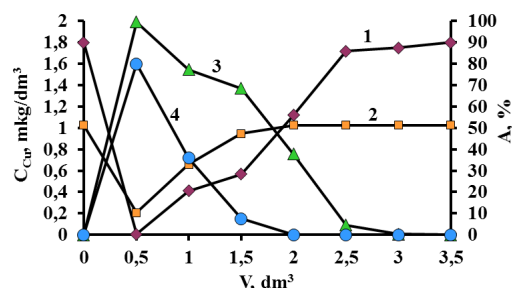

Fig. 5. Dependence of concentration (1; 2) and degree of extraction (3; 4) of copper ions from water on the volume of solutions with a concentration of 1.800 mkg/dm^3 (1; 3) and 1.025 mkg/dm^3 (2; 4) passed through the filters of combined action with a volume of the cationite KU-2-8 in the H$^+$-form and the anionite AV-17-8 in the OH$^-$-form, cm^3: 30:40 (1; 3); 20:30 (2; 4)

Fig. 5 shows that at concentration of copper ions at the level of approximately 1–2 mkg/dm^3, only the first samples demonstrate a substantial decrease in the content of copper ions in water. Only in one sample, the copper ion concentration decreases to 0.007 mkg/dm^3 ($7.0 \cdot 10^{-6}$ mg/dm^3). In this case, the efficiency of extraction of copper ions largely depends on the volume of the filtering load. The best results were obtained at a loading volume of 70 cm^3, compared to the loading with a volume of 50 cm^3. However, for the first case, there is a sharp decrease in the degree of extraction of copper ions with an increase in the volume of filtrate. Thus, when filtering 0.5 dm^3 of the solution, a degree of copper ions extraction achieves 99.61 %, at 1.0 dm^3 – 77.22 %, at 2.0 dm^3 – 37.78 %, and at 3.0 dm^3 – 0.28 % only. Explaining such a sharp reduction in the capacity of ionites only by the microaddition of hardness ions and carbonates in distilled water is impossible because the real capacity of ionites is much higher on the number of ions in water. In addition, similar results were obtained also when using a solution of copper ions in the bidistilled water (Table 1).

In this case, residual concentration of copper in the solution depends only on the volume of ion-exchange material and maximally decreases to $5.3 \cdot 10^{-5}$ mg/dm^3.

When extracting ions of metals from standards solutions, their concentration reaching tens of mg/dm^3, they differ little by selectivity. In the strongly diluted solutions, the

picture changes dramatically. Thus, under typical conditions, the selectivity of cationites for copper ions is slightly higher than the selectivity for the hardness ions and, to a certain degree, is lower than the selectivity for lead ions. In the case of strongly diluted solutions, at concentrations lower than $1 \cdot 10^{-4}$ mg/dm³, copper ions vpractically do not sorb. Under the same conditions, the degree of extraction of lead ions reaches 99.9–100 % and almost does not decrease with increasing volume of filtrate (Table 2).

Table 1

Dependence of concentration of copper ions after filtration of the solution of copper sulphate ($[Cu^{2+}]$=0.1444 mg/dm³) in bidistilled water, a volume of 1 dm³, on the loading volume of filter with combined action

V_{KU-2-8}, cm³ H⁺-form	$V_{AB-17-8}$, cm³ OH⁻-form	$[Cu^{2+}]$, mg/dm³
20	20	$1.6 \cdot 10^{-3}$
30	40	$2.1 \cdot 10^{-4}$
40	60	$5.3 \cdot 10^{-5}$

Thus, at a concentration of lead ions of 214.5 mkg/dm³, when separating 5.0 dm³ of the filtrate (V_i=20 cm³), flashing of lead ions is observed at the level of 6–12 mkg/dm³ and is within an error of the analysis [12]. At a starting concentration of lead ions of 0.026 mkg/dm³ ($2.6 \cdot 10^{-5}$ mkg/dm³), the flashing of lead amounts to 1.1–1.8 mkg/dm³ and is also within an error of the analysis. Even better results are obtained when using the cationite KU-2-8 in the Na⁺-form (Fig. 6).

In the given case, at starting concentration 111 mg/dm³, the content of lead ions in the first sample of filtrate reaches 0.756 mkg/dm³ (the degree of extraction is 99.30 %) and further decreases to $(5–6) \cdot 10^{-3}$ mkg/dm³ with increasing volume of the filtrate to 4.0–4.5 dm³ when the volume of ionite is only 10 cm³. The degree of extraction in this case rises to 99.99 %.
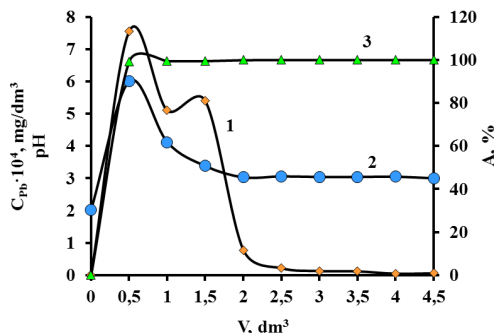

Fig. 6. Dependence of concentration of lead ions (1), pH of the medium (2), and the degree of extraction of lead ions (3) on the volume of lead nitrate solution ($[Pb^{2+}]$=0.111 mg/dm³) in distilled water passed through the cationite KU-2-8 in the Na⁺-form (V_i=10 cm³) (EDC=50 mg/dm³)

A slightly larger flashing of lead ions in the first samples is due to the fact that cationite is primarily in the Na⁺-form. Standard lead solution contains an excess of acid. This is the reason for lowering pH of the model solution to 2.03–2.05 at a concentration of lead ions of approximately 0.1 mg/dm³. That is why, when filtering the given solution, cationite partially transforms from the Na⁺-form to the H⁺-form.

It is due to this that as the amount of ionite in the H⁺-form increases, the sorption capacity of cationite for lead ions grows.

In any case the degree of extraction of lead amounts to 99.3–99.9 %, which makes it possible to capture the lead almost completely from a diluted solution.

When studying the desorption of lead ions from a weak-acid cationite, we found an interesting feature (Fig. 7).

Despite a very small amount of the sorbed lead on cationite of 0.0062–53.600 mg/dm³, when using the 2M solutions of HCl, desorption efficiency increases with decreasing mass of the sorbed lead.

Table 2

Dependence of residual concentration and the degree of extraction (A) of lead ions, pH of the medium on volume of the solution of lead nitrate in distilled water, passed through the cationite DOWEX MAC-3 (V_i=20 cm³) in the Na⁺-form

V_{sol}, dm³	$[Pb^{2+}] \cdot 10^3$, mkg/dm³				pH				A, %			
1	2	3*	4	5	6	7*	8	9	10	11*	12	13
0	$214.5 \cdot 10^3$	$1.11 \cdot 10^3$	340	26	2.2	2.0	2.1	2.0	–	–	–	–
0.5	9.0	0	0	0	9.3	7.7	9.6	8.5	99.9	100	100	100
1.0	8.0	0	0	0	9.2	8.4	9.2	9.5	99.9	100	100	100
1.5	12.0	0	0	0	9.3	8.4	8.7	9.3	99.9	100	100	100
2.0	7.0	0	27	1.1	9.3	7.2	9.2	9.1	99.9	100	96.5	94.2
2.5	6.5	$1.7 \cdot 10^2$	12	1.2	9.2	7.4	8.9	9.1	99.9	99.8	94.7	95.4
3.0	6.2	$2.7 \cdot 10^3$	18	1.5	9.1	7.1	9.3	9.3	99.9	97.5	95.6	95.8
3.5	6.0	$3.3 \cdot 10^3$	15	1.3	9.3	6.9	8.9	9.3	99.9	98.3	92.9	95.3
4.0	6.0	$1.9 \cdot 10^3$	24	1.5	9.2	7.4	8.8	8.9	99.9	97.0	93.3	95.0
4.5	6.0	$2.7 \cdot 10^2$	23	1.8	9.2	7.1	–	9.2	99.9	98.3	–	93.1
5.0	6.0	–	–	1.8	9.2	–	–	8.8	99.9	–	–	93.1
$m_{c.i.}$, mg	1.072	0.497	$13 \cdot 10^{-4}$	$12 \cdot 10^{-5}$	–	–	–	–	–	–	–	–
EDC, mg/dm³	53.6	49.7	$65 \cdot 10^{-3}$	$62 \cdot 10^{-4}$	–	–	–	–	–	–	–	–

Note: * – volume of ionite (V_i) 10 cm³

If, in the course of a decrease in the mass of sorbed lead from 53.6 mg/dm^3 to 4.97 mg/dm^3 the degree of desorption at a specific consumption of the solution of acid of 5 cm^3/cm^3 grows from 57 to 71 %, then at a mass of the sorbed lead of 0.065 mg/dm^3 the degree of desorption rises to 97 % under the same conditions, and at a mass of the sorbed lead of 0.0062 mg/dm^3 – up to 99 %.
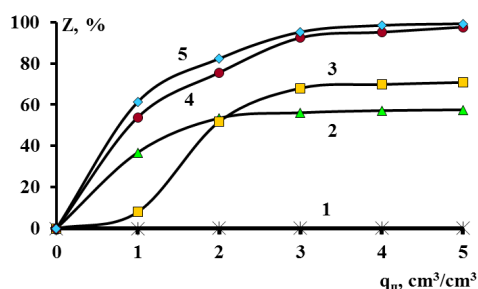

Fig. 7. Dependence of the degree of lead ion desorption from the cationites KU-2-8 (1) and DOWEX MAC-3 (2; 3; 4; 5) on specific consumption of the 2M HCl solution (cm^3/cm^3) at a mass of the sorbed ions (mg) per 20 cm^3 of ionite: 1.00 (1); 1.072 (2); 0.994 (3); 0.0013 (4); 0.000124 (5)

Desorption of lead ions from the strong-acid cationite when using the 2M solution of HCl at a mass of the sorbed ions of 50 mg/dm^3 almost did not occur. This suggests a fairly high selectivity of cationite with sulfonate groups for lead ions.

6. Discussion of results of the extraction of copper and lead cations using an ion-exchange method from strongly diluted solutions

Any method of water purification is characterized by a specific range of the concentration of pollutants at which applying this method yields the most effective results. For the ion exchange, such ion concentration is approximately 1–200 mg/dm^3. However, under certain conditions, when modifying the method, these limits of concentrations can be significantly expanded. Thus, when using weak-acid cationites, it is possible to achieve high efficiency in the softening of salt water with a sodium chloride concentration greater than 100 g/dm^3 [15]. When using filters of combined action, it is possible to achieve deep deionization of water at starting concentrations of ions below 0.1 mg/dm^3. However, the processes of ion-exchange extraction of the ions of heavy metals from solutions with concentrations at the levels of 0.1–10 mg/dm^3 have not been studied sufficiently.

When using strong- and weak-acid cationites in the volumes when capacity is significantly greater than the quantity of ion moles in the passed-through solutions, efficiency of the ion sorption is determined only by the concentration of copper ions in water. In this case, the processes of sorption are little affected by the concentration of hardness ions, pH of the medium, the time of contact between water and ionite. Sorption to a certain degree depends on the form of ionite – it is reduced during transition from the H$^+$-form to the Na$^+$-form. This is associated with the higher selectivity of ionite for sodium ions compared with protons. In any case when copper ion concentrations are below 0.1 mg/dm^3, their sorption does not take place on weak-acid cationites and at

concentrations at the level of 1 mg/dm^3 on the strong-acid cationite KU-2-8. In this case, desorption of copper ions from cationites when using the 2M solution of HCL proceeds quite effectively.

When using filters of combined action, copper ion concentration in the solution can be reduced to 0.053 mg/dm^3.

It is obvious that satisfactory results in the concentration of strongly diluted solutions of copper ions can be obtained at the concentrations of copper ions to 1 mkg/dm^3. In this case, the concentration of copper ions in regeneration solutions increases to 1–20 mg/dm^3, that is, by 3–4 orders of magnitude. When using filters of combined action, copper can be extracted from solutions with concentration to 0.1 mg/dm^3 by increasing concentration in the regeneration solution in comparison with the starting solution by 4–5 orders of magnitude. In the case of extracting copper ions from water, the main factor is mostly the selectivity of ionite, which depends on the charge of ions and the radius of hydration shell.

In the case of lead ions, the main factor is the formation of slightly soluble complexes of lead ions with carboxylic and sulfonate groups. It is through this that the almost complete removal of lead on the strong- and weak-acid cationites is achieved, regardless of the concentration of starting solutions, even when they reach a few mkg/dm^3. It is due to this that even at insignificant amounts of the sorbed lead ions on a low-base cationite the degree of their desorption is low when using the 2M solution of HCl. Only at a mass of the sorbed lead at the level of a few mkg per 1 dm^3 of ionite, the degree of desorption amounts to 97–99 % at a specific consumption of regeneration solution of 5 cm^3/cm^3.

In the case of sulfonate groups in a strong-acid cationite, lead ions form so stable complexes with ionite that lead almost completely is extracted at the concentrations lower than 0.1 mg/dm^3. In this case, during regeneration of cationite by the 2M solution of HCl, the degree of lead desorption of lead is below 0.27 % at a specific consumption of the solution of acid of 5 cm^3/cm^3 of ionite.

Given these results, we may argue that weak-acid cationites will be effective when concentrating lead from the superdiluted solutions using the stages of sorption and desorption. It is better to use strong-acid cationites when removing lead ions from water.

7. Conclusions

1. We investigated the processes of sorption and desorption of copper ions on strong- and weak-acid cationites from strongly diluted solutions. It is shown that under conditions when the capacity of cationites is exhausted by not larger than 50 %, the sorption of copper ions from tap and distilled water mainly depends on the concentration of copper ions in water. On the strong-acid cationites, copper almost does not sorb from the solutions with a concentration of copper ions ≤1 mkg/dm^3; on the weak-acid cationites from the solutions with a concentration ≤0.1 mkg/dm^3. It is shown that the depth of deionization of copper sulphate solutions on the filters of combined action depends on the concentration of solutions and the ratio of volumes of the solutions and ionite. Minimum concentration of copper ions after the filters of combined action reaches 10^{-2} mkg/dm^3.

2. It is established that lead ions are effectively removed from the superdiluted aqueous solutions at concentrations

less than 1 mkg/dm³. The sorption of lead ions proceeds better on the strong-acid cationites. When using the 2M solutions of HCl, the degree of their desorption from a weak-acid cationite increases with decreasing mass of the sorbed lead. At a mass of the sorbed lead of 0.0062 mg/dm³, the degree of extraction reaches 99 %, while desorption almost does not occur from a strong-acid cationite at a mass of the sorbed ions of 50 mg/dm³.

3. Given the efficiency of sorption and desorption of copper and lead ions, it is shown that weak-acid cationites enable effective concentration of lead ions from the superdiluted solutions. They could be used in the processes of sample preparation when determining the content of lead in water at its trace concentrations. The application of cationites for copper ion concentration is appropriate at its minimal concentrations of 1.01–1.00 mg/dm³.

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