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Sorption Of Rare Metal Ions by Ionite Based on Diglycidyl Thiourea and Various Amines

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Abstracts: The article studies the process of sorption of molybdenum and vanadium ions on anion exchangers obtained on the basis of thiourea, epichlorohydrin and various amines. Various amines (urea, guanidine, melamine, polyethylene polyamine, ethylenediamine, etc.) are used as substances containing ionic groups. The regularities of ion exchange and the main properties of the tested anionites are given, the influence of the pH of the medium and interfering ions in the process of sorption of molybdenum and vanadium ions are studied. For vanadium, the use of empirical partition relations and of an extended Freundlich equation were tested, with promising results. The objective of this paper is to investigate the use of the pH dependent Freundlich model of Gustafsson et al., for describing vanadate(V) sorption to 26 mineral soils (all having less than 12% organic C), and to discuss the possible use of the model for risk assessments. The kinetic curves of the sorption process, the values of the diffusion coefficients for the initial periods of molybdenum sorption are given. In particular, the distribution coefficient of the radiotracers of ^{99}Mo and ^{131}I as homologs of Sg and Ts using the surface modification of chabazite was investigated as liquid-solid system in the present study. The kinetics of molybdenum sorption was carried out under static conditions from an ammonium molybdate solution with a concentration of 1 g/L for molybdenum ions and at pH 4.5–5. Under the same conditions, molybdenum ions are sorbed much faster by the DGT + M anion exchanger in comparison with AN-2F anion exchangers, in which the diffusion coefficient is much lower. The static exchange capacity (SEC) was determined in industrial solutions in the presence of mineral acids (hydrochloric, sulfuric and nitric), usually contained in them. The obtained kinetic equilibrium parameters of the tested anion exchangers were compared with those of industrial polycondensation anion exchangers, such as AN-2F and AN-1.

Keywords: Ion Exchanger, Sorption, Molybdenum, Vanadium, Radiotracers, Chabazite, Kinetic Curves, Process, Concentration, Diffusion.

1. INTRODUCTION

Industrialization and technological developments have important roles in the daily life of people as well as causing of environmental problems. Presence of the metal ions in the environment is very useful for human beings and living organisms while they cause a health problem when high concentrations of these metals directly or indirectly contact with humans, animals, underground water sources and agricultural areas.

Molybdenum is considered as a key micronutrient for some living organisms and one of the biologically active transition element due to its vital role in enzymatic redox reactions as well as its specific geochemical behavior [1]. It is a bioessential element and the presence of molybdenum in water samples is of great interest from chemical and environmental points of view [2]. The decay product of Mo-99, Tc-99m, is the workhorse isotope in nuclear medicine for diagnostic imaging. Tc-99m is used for the detection of disease and for the study of organ structure and function. Tc-99m is especially useful for nuclear medicine procedures because it can be chemically incorporated into small molecule ligands and proteins that concentrate in specific organs or tissues when injected into the body. The fast-growing utilization of molybdenum in the anthropogenic activities illustrates the potential for a lot of toxic discharges into the ecosystem. Molybdenum commonly presents principally in the hexavalent oxidation state, Mo(VI) and molybdate (MoO_4^{-2}) ions [3]. Molybdate oxoanions are water soluble and cause an environmental problem if their concentration exceeds 5 ppm [4]. Pollution of groundwater by molybdate anions represents a serious issue in the field of drinking water obtained from wells [5].

Excited and advanced studies on nuclear chemistry are directed to discover and identify the chemical properties of superheavy elements (SHEs). All elements of atomic number ≥ 104 are called SHEs [6]. SHEs are synthesized by accelerators in heavy-ion-induced nuclear reactions [7]. The chemical studies of SHEs are big challenged due to

SHEs experiments must be chemically performed on a “one-atom-at-atom” scale because of extremely low production rates of atoms and the shortlived (few seconds) of these nuclides. Preparation of these kinds of experiments is required a lot of expense and preliminary investigations. Therefore, the development of new chemical systems applicable in fast kinetic experiments usually the lighter homologs was used as model experiments of SHEs [6–10]. Seaborgium (Sg) and tennessine (Ts) are located in the periodic table in groups 6 and 17 as Mo and I, respectively. In our previous work, the extraction and sorption behavior of carrier-free ^{99}Mo as a homolog of Sg using ionic liquids [6] and impregnated resin with trioctylamine (BR-TOA) [7] were investigated. In this regards, the distribution coefficient of the radiotracers of ^{99}Mo and ^{131}I as homologs of Sg and Ts using the surface modification of chabazite was investigated as liquid-solid system in the present study.The largest producers of molybdenum separate the isolated metal from copper compounds using selective flotation [11].

Vanadium is a transition metal that, being ubiquitously distributed in soil, crude oil, water and air, also found roles in biological systems and is an essential element in most living beings. There are also several groups of organisms which accumulate vanadium, employing it in their biological processes. Vanadium being a biological relevant element, it is not surprising that many vanadium based therapeutic drugs have been proposed for the treatment of several types of diseases. Namely, vanadium compounds, in particular organic derivatives, have been proposed for the treatment of diabetes, of cancer and of diseases caused by parasites.The recovery of vanadium is more complicated and employs a vanadium-bearing slug from steel manufacturing or the removal of extremely small vanadium levels from copper-containing concentrates [12]. In both cases, multiple solvent extraction methods are been applied [13,11]. However, when the concentrations of the materials that are being recovered are low, the approach is not sufficient. Moreover, applying these procedures carries the risk of losing the precious resources in the substantial levels of wastes that are also produced [11] . According to Syed [14], in this a situation, the only economically viable method for achieving a satisfactory extraction degree is the application of ion-exchange sorbents bearing selective ligands. Over the last several years, multiple polymeric materials are been applied for the sorption and recovery of molybdenum and vanadium. The successful application of modified poly(ethyleneimine) supports containing ammonium, carboxymethyl or phosphonomethyl groups [15], iminodiacetic chelating resins [16] and D2EHPA-immobilized Amberlite XAD-4 resin [17] have been reported. Further applications indicate that commercially available ion-exchange suspension copolymers, such as Amberlite IRA904 [18] and Dowex 1-x8 [19], are suitable for preconcentration of molybdenum and vanadium. In addition, modified silica polyamine composites (SPC) made from silanized amorphous nanoporous silica gel and polyamines have been employed for the selective oxyanion removal to achieve a higher selectivity towards tungsten than molybdate [20]. Styrene/divinylbenzene-based resins (i.e., Amberlite IRA-400 and Amberlite IRA-743 (see Fig 1)) bearing quaternary ammonium and N-methyl-D-glucamine functionalities exhibit the ability to effectively retain oxyanions, such as borates [21,22], chromates [23] and arsenic [24,25]. The current study aims to investigate the suitability of Amberlite IRA400 and Amberlite IRA-743 resins for sorption of molybdenum and vanadium oxyanions from their single-component aqueous solutions.

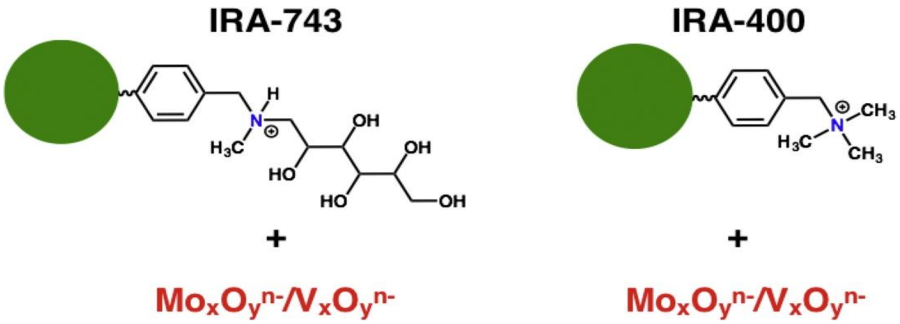

Fig 1. Structure of Amberlite IRA-400 and Amberlite IRA-743

The sorption kinetics as well as the environment pH at which the polymers exhibited the best performance were investigated. In addition, equilibrium studies were performed different temperatures. Finally, the reusability of the ion-exchange resins was investigated for repeated sorption and desorption cycles.

The iron oxide nanoparticles are increasingly applied for heavy metals removal from wastewaters since they exhibit excellent adsorption properties and can be easily separated using magnetic field [25-27]. Their drawbacks like small particle size, excessive pressure drops and coaggregation observed in flow-through systems could be avoided by supporting magnetite nanoparticles on polymers. Magnetic polymer microspheres combining a polymer and inorganic magnetic nanoparticles have been successfully used as carriers for enzyme immobilization, protein purification [28], separation of toxic and radioactive pollutants [29], etc. Glycidyl methacrylate (GMA) based copolymers have versatile applications due to the presence of epoxy groups which offers numerous functionalization possibilities in mild reaction conditions. Amino-functionalized macroporous crosslinked copolymers of GMA and ethylene glycol dimethacrylate (EGDMA), PGME, prepared by suspension copolymerization in the shape of regular beads and specific pore size [30] have been utilized as matrix for enzyme attachment [31], sorbents for removal of textile dyes [32], radionuclides [33], precious and heavy metals, etc. [34-36].

In industry, when processing non-ferrous metals and their satellites, when selective processes are required in order to concentrate or separate the target components, anion exchange is especially effective if the metal ions are in the form of anionic complexes. Among these metals, an important place is occupied by molybdenum, rhenium, tungsten, vanadium, etc. [37]. In the literature there are a significant number of publications devoted to the study of the features of separation, separation of molybdenum and its purification from impurities using anionites of various structures. [38].

The polycondensation reaction opens up wide possibilities for the synthesis of ion-exchange polymers. When obtaining anion-exchange polymers of this type, the process of formation of the spatial structure and the introduction of ionogenic groups proceed in one stage. Various amines (urea, guanidine, melamine, polyethylene polyamine, ethylenediamine, etc.) are used as substances containing ionic groups. [39,40].

There are different approaches to the development of models for simulation of metal binding in soils. One is to use process-oriented surface complexation models [41,42,43]. However, although these models provide insights to the mechanisms involved, they are difficult to set up for soils due to the large number of parameters that need to be estimated. Another approach is to use empirical isotherm equations. Although they are not process-oriented they can still be useful for predicting anion sorption as they require less input. For vanadium, the use of empirical partition relations [44] and of an extended Freundlich equation [45] were tested, with promising results. The Freundlich model can also be extended with a term accounting for the influence of pH, which is often the most important parameter that governs metal sorption in soils [46]. We recently showed a new way to include such a pH term for describing SO_4^{-2} adsorption to soils [47]. An important prerequisite for the use of a Freundlich model is that only one type of adsorption process is important. In the case of vanadium, the model is not likely to perform well if both vanadium(IV) complexation to organic matter and vanadate(V) sorption to Fe and Al hydrous oxides are significant. Therefore it may be hypothesized that the Freundlich models may work in mineral soils in which vanadate(V) sorption may be the predominant process. The objective of this paper is to investigate the use of the pH dependent Freundlich model of Gustafsson et al. [47] for describing vanadate(V) sorption to 26 mineral soils (all having less than 12% organic C), and to discuss the possible use of the model for risk assessments. To investigate the hypothesis that adsorbed vanadate(V) was the predominant reaction product, vanadium Kedge XANES spectroscopy was performed for three of the soils, which were different concerning pH, content of Fe and Al hydrous oxides, and texture.

2. MATERIALS AND METHODS

At present, it is important to study the physicochemical and mechanical properties of ion-exchange polymers, which make it possible to determine the fields of application, advantages and disadvantages of the synthesized anionites. On the other hand, physicochemical studies of ion exchangers make it possible to determine ways of modifying some properties of anionites.

Despite a significant number of studies devoted to the ion-exchange method for the extraction and separation of metals, solving this problem continues to be a top priority for the hydrometallurgical industry. In the Republic of

Uzbekistan, the number of branches of the national economy that use ion-exchange polymers is increasing annually. Until now, ion exchangers are imported into Uzbekistan from abroad, the use of which affects the cost of products. In addition, most of the imported ion exchangers, especially of the polycondensation type, have low indicators of such properties as chemical heat resistance, mechanical strength, and others, which limits the possibilities and scope of their application.

For this purpose, we carried out a study of the physicochemical and mechanical properties of the obtained ion-exchange polymers.

In this regard, it was of interest to study the sorption of molybdenum on the obtained by us anion exchanger DGT+PEPA (diglycidylthiocarbamide and polyethylenepolyamine) DGT+M (diglycidylthiocarbamide and melamine), DGT+HPAN (diglycidylthiocarbamide and hydrolyzed polyacrylonitrile) which contains polycrystalline groups in its structure. [48].

The study of the kinetics of the sorption process makes it possible to reveal the mechanism of sorption, which, in turn, will make it possible to choose the optimal parameters for conducting the ion-exchange process. The kinetics of molybdenum sorption by the anion exchanger DGT+PEPA, DGT+M, DGT+HPAN and the industrial anion exchanger AN-2F was carried out under static conditions from an ammonium molybdate solution with a concentration of 1 g/L for molybdenum ions and at pH 4.5–5. Anionites were used in Cl^-- form.

The contact time of the anion exchangers with the solution ranged from 5 minutes to 2 days. The results of sorption of molybdenum for a time from 0.5 to 2 days remain practically the same. In this case, the static exchange capacity (SEC) of the molybdate ion for 0.5 days on the DGT + PEPA anion exchanger was 282 mg/g, DGT + M 275 mg/g, DGT + HPAN 278 mg/g, on the AN-2F anion exchanger, 262mg/g. To quantitatively characterize the equilibrium distribution of molybdenum between the phases of the anionite and the solution, the distribution coefficients K_d were calculated using the formula [49].

$$K_d = \frac{\mathrm{M}_{ex}}{\mathrm{M}_s} \qquad (1)$$

M_{ex} - concentration of molybdenum in anion exchanger, mg/l;

M_{or} - equilibrium concentration of molybdenum in solution, mg/ml;

3. RESULTS

The distribution coefficient for the DGT + M anion exchanger was 413 mg/l, and for the AN-2F anion exchanger, 389 mg/l. The data obtained indicate that the anion exchangers DGT + PEPA, DGT + M, and DGT + HPAN have a higher sorption capacity in relation to molybdenum ions as compared to the AN-2F anion exchanger. The distribution coefficients clearly characterize the sorption and selectivity of anionites. This value is a measure of the affinity of the tested anionites for molybdenum and shows the degree of selectivity under specific research conditions.

In order to establish the mechanism of sorption of molybdenum, we used the known time dependences of the ion exchange rate $\lg(1-F) = K_1\tau$ for film and $F = K_2\tau^{1/2}$ for gel kinetics, where F is the relative content of sorbed molybdenum in the anion exchanger (the degree to which ion-exchange equilibrium is reached) [50]. The study was carried out under static conditions with the ratio of the liquid phase of the ammonium molybdate solution to the solid phase - anionite 1000: 1.

The F value was determined by the equation:

$$F = \frac{M_\tau}{M_\infty} \qquad (2)$$

M_τ - sorbed molybdenum for time τ, mg.

M_∞ - sorbed molybdenum at equilibrium

Based on the experimental and calculated data, kinetic curves were constructed (Fig. 2-4) and table. 1.

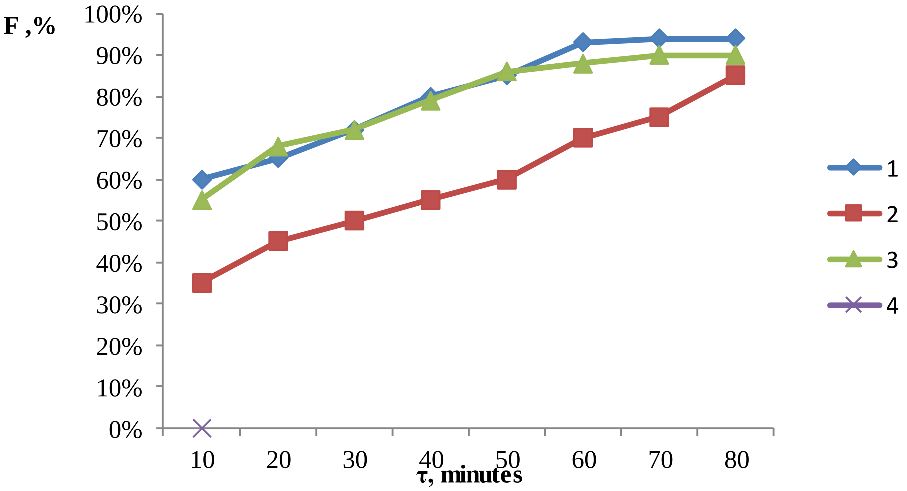

Fig. 2. Molybdenum absorption rate: 1 - anion exchanger DGT + M; 2 - anion exchanger DGT + PEPA; 3 - anion exchanger DGT + HPAN; 4 - anion exchanger AN-2F.

When constructing a graph from the data obtained, it was found that for the dependence of lg (l – F) on τ, the experimental points do not fit on a straight line. Apparently, the internal diffusion mechanism of kinetics has a dominant effect on the sorption rate.

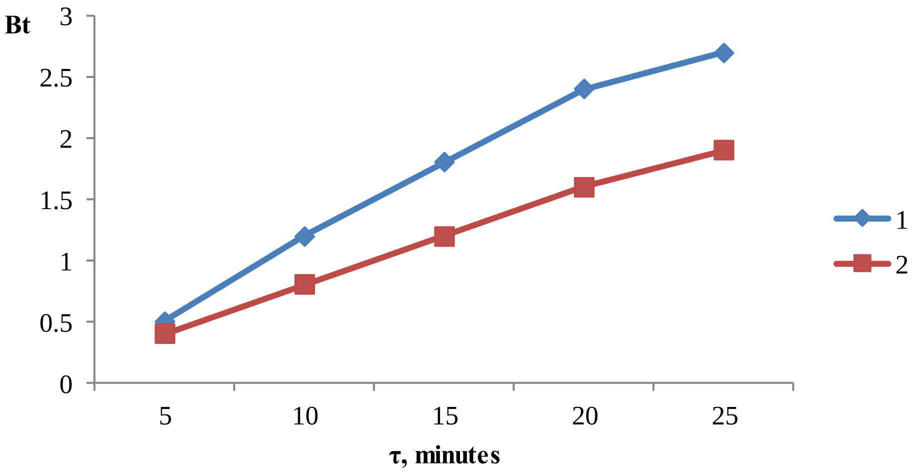

Fig. 3. Graph of diffusion of sorption of ions: 1 - anion exchanger DGT+M; 2 - anion exchanger DGT + PEPA; 3 - anion exchanger DGT + HPAN; 4 - anion exchanger AN-2F.

The limiting effect of gel kinetics can also be judged by the linear dependence in the coordinates $F - \sqrt{\tau}$, when F<0.4 (Fig. 3) and according to the dependence curves $B_t - \tau$ for the whole process, where, in the first approximation, all points fit on a straight line (Fig. 3.).

The diffusion coefficient was determined by the formula:

$$\overline{D} = \frac{B_t \cdot r^2}{\tau \cdot n^2} \qquad (3)$$

Where: B_t - dimensionless quantity, which we find from tabular data as a function of F.

$\overline{D}$ - diffusion coefficient, cm^2/sec;

τ - contact time of solution with anionites, sec .;

r - radius of anionite grain in a swollen state, cm;

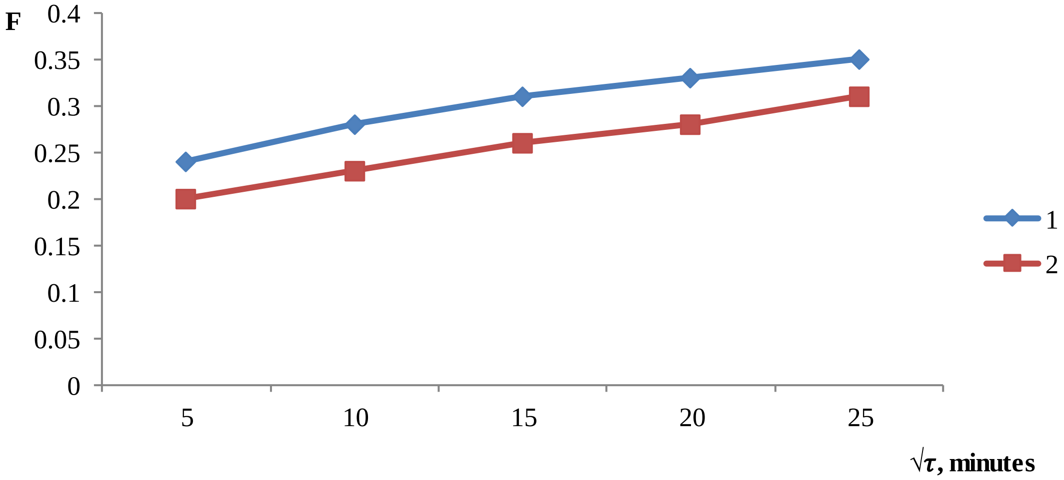

Fig. 4. Graph of diffusion absorption of molybdenum ions: 1 - anion exchanger DGT + M; 2-anion exchanger DGT + PEPA; 3-anion exchanger DGT + HPAN; 4-anion exchanger AN-2F.

The calculated values of the diffusion coefficients of molybdenum (Fig. 4.) after 1 hour of contact of the ion exchanger with the solution are for DGT + M anion exchangers – 5,7·10^{-3} cm^2/sec and for AN-2F – 3,9·10^{-3} cm^2/sec.

The table shows the values of the diffusion coefficients $\overline{D}$ for the initial periods of sorption of molybdenum, when the degree of saturation F of the anion exchanger with molybdenum is not more than 0.5.

Table 1. Kinetics of sorption of molybdenum on anion exchangers

Anionite	F	$\overline{D} \cdot 10^8, \mathrm{cm}^2/\mathrm{sec}$	τ, min
DGT + M	0,09	0,64	5
	0,10	0,57	10
	0,19	0,85	15
	0,25	0,77	35
	0,31	0,74	50
	0,34	0,67	60
AN-2F	0,23	0,85	30
	0,28	0,83	60
	0,37	0,72	120

The data in the table show that at the initial moments of sorption, the diffusion coefficients practically do not remain constant. Despite the fact that the anion exchanger DGT + M surpasses the industrial anion exchanger AN-2F in sorption rate, the kinetics of molybdenum sorption for the tested anion exchangers as a whole is slow, the sorption process is limited by internal diffusion. The slow rate of sorption of molybdenum is apparently explained by its ionic state and steric factors.

Under the same conditions, molybdenum ions are sorbed much faster by the DGT + M anion exchanger in comparison with AN-2F anion exchangers, in which the diffusion coefficient is much lower.

For weakly basic anion exchangers obtained by the polycondensation of melamine, epichlorohydrin and thiourea - (DGT + M), guanidine, epichlorohydrin and thiourea - (DGT + HPAN), studies were carried out of individual regularities of ion exchange, which could serve as the basis for the physicochemical characteristics of the tested anionites. [48].

Of the main chemical properties of ion exchangers, the ion exchange capacity, which characterizes ion exchangers in order to assess their operational properties, is of great practical importance [51]. Its value mainly depends on the number of ionogenic groups of the ion exchanger, the degree of their dissociation, as well as on the nature and concentration of the exchanged ions.

The static exchange capacity (SEC) was determined in industrial solutions in the presence of mineral acids (hydrochloric, sulfuric and nitric), usually contained in them. The obtained kinetic equilibrium parameters of the tested anion exchangers were compared with those of industrial polycondensation anion exchangers, such as AN-2F and AN-1 [52]. Table 2. The main physical and chemical properties of the tested anionites are presented.

Table 2. Basic properties of the tested anionites

Anionites	Bulk weight, g/ml	Mechanical strength,%	Specific volume of the swollen anionite in the OH^- form, ml/g	SEC 0.1 N solution, mg-eq/l		
				H_2SO_4	HNO_3	HCl
DGT + M	0,65	99,1	2,5	7-7,5	4,6	9,5
AN-2F	0,5	-	3,1	6	-	6,2

The studies were carried out depending on the ionic form of the anionite, the pH of the medium, the presence of competing ions, etc. For comparison, we used the industrial anionite AN – 2F, which is recommended for the extraction of molybdenum from industrial solutions, and the anionite FA –C, which is selective to molybdenum ions [53]. The sorption of molybdenum was carried out under static conditions, the anionites were tested in OH^-, SO_4^-, Cl^- - forms, the initial solutions of ammonium molybdate had a pH in the range from 4 to 5. The sorption of molybdenum was carried out both from pure solutions of ammonium molybdate (C_{out}=1g/l) and in the presence of competing sulfate ions $(C_{Na_2SO_4} = 1N)$. Table 3. shows the data on the sorption of molybdenum by anion exchangers.

Table 3. Sorption of molybdenum by the tested anion exchangers

Anionites	**Absorbed molybdenum from pure solutions, mg/g**	**Partition coefficient mg/l**	**Absorbed molybdenum in the presence of 1 n solution Na_2SO_4, mg/g**
DGT+M in OH^-- form in SO_4^-- form in Cl^-- form	201 245 230	374	168 202 175
FA-C in OH^-- form in SO_4^-- form in Cl^-- form	78 115 68	212	60 60 60
AN-2F in Cl^-- form	230	320	62

Comparison of data on the sorption of molybdenum on the tested anion exchangers in $OH^-, SO_4{}^{2-}, Cl^-$ - forms shows that in the cases $OH^-,\ Cl^-$ - forms, the sorption of molybdenum is somewhat suppressed by sulfate ions, while in $SO_4{}^{2-}$- form this phenomenon is absent.

Analysis of the table. 3. shows that the anion exchanger DGT + M has a high selectivity to molybdenum, which is almost the same during sorption, both from pure solutions of ammonium molybdate and in the presence of competing ions. Anionite FA-S is somewhat inferior to the anionite AN-2F in sorption of molybdenum from pure solutions, however, in the presence of competing ions, it has the same sorption capacity.

The influence of the pH of the medium on the sorption of molybdenum was investigated in the range of pH = 1-10. The specified pH value was reached by adding sulfuric acid and ammonium hydroxide. Table 4. presents the results, where the data for the AN-2F anionite are given for comparison.

Table 4. Sorption of molybdenum by anion exchangers and dependence on the pH of the medium

Anionites	pH of the medium	Sorption of molybdenum from ammonium molybdate solution (C = 1 g / l),%
DGT+M in OH^-- form	2,2 3,8 5,1 8,2 9,6	72 88 74 38 25
AN-2F in OH^-- form	2,2 4,2 6,1 8,1 10	38 54 39 20 8,0

From the data in Table 4. it can be seen that the maximum value of molybdenum sorption is observed at pH 4–6.5. From a practical point of view, an important indicator of ion-exchange polymers is the rate at which equilibrium is reached - the kinetics of sorption.

When choosing an ion exchanger for the sorption extraction of any metal, along with other factors, its kinetic properties are of great importance. In relation to vanadium, in the literature there is a delayed kinetics of sorption by strongly basic anion exchangers in salt form [54]. Therefore, it is of interest to obtain data on the rate of vanadium sorption by the named anionites DGT+PEPA, DGT+M, and DGT+HPAN in the hydroxyl form.

The main task of the work was to elucidate the limiting stage that determines the vanadium absorption rate. These stages can be external diffusion, internal diffusion and ion exchange (chemical) interaction. The results of sorption work are shown in Figure 5. In coordinates, the content of vanadium in the resin is time.

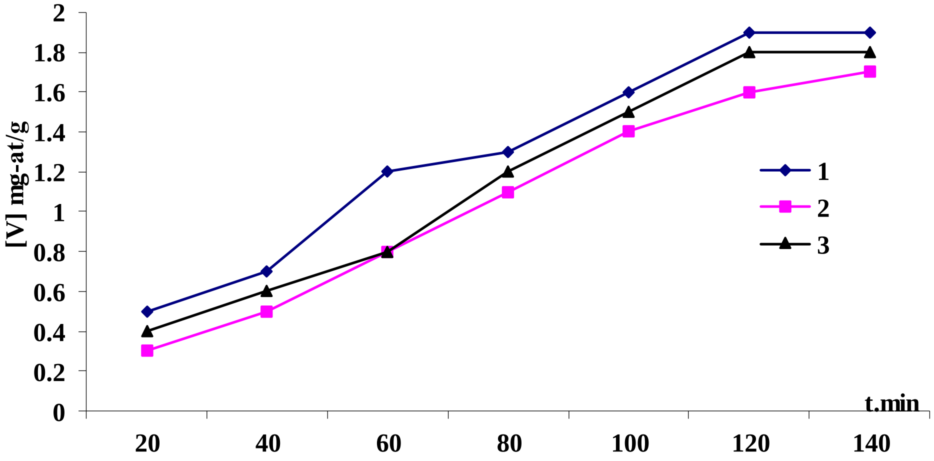

Fig. 5. Dependence of vanadium sorption by the anion exchangers DGT+PEPA(1), DGT+M (2) and DGT + HPAN (3) in the hydroxyl form on the duration of stirring.

From the figure it can be concluded that the rate of vanadium sorption by these anion exchangers decreases in the order DGT+PEPA> DGT+M> DGT+HPAN.

Calculation of the coefficients of the functions that determine the external and internal diffusion shows that the value of the internal diffusion rate coefficient is less than the value of the external diffusion coefficient (Table 5.). Hence, a preliminary conclusion can be drawn that the rate of absorption of vanadium by anion exchangers has a large internal diffusion.

***Table 5*. The coefficients of the rates of external and internal diffusion, calculated from the experimental data.**

Anionites	External diffusion rate coefficients $K \cdot 10^2$ sec^{-1}	Internal diffusion rate coefficients $B \cdot 10^2$ sec^{-1}
DGT+PEPA	1,75±0,46	4,85±1,7
DGT+M	1,79±0,35	5,13±1,45
DGT+HPAN	1,56±0,58	3,92±1,03

In addition to these coefficients, the determining factor can be assessed using kinetic curves in coordinates $\ln(1-F) = \varphi(t)$ and $F = \varphi(\sqrt{t})$. The curves plotted based on the results of the work are shown in Figures 6 and 7.

Figure 6 shows that the kinetics of vanadium sorption by ion exchangers DGT+PEPA, DGT+M and DGT+G in the hydroxyl form is not determined by either external diffusion or chemical interaction, since the curves are not straight lines.

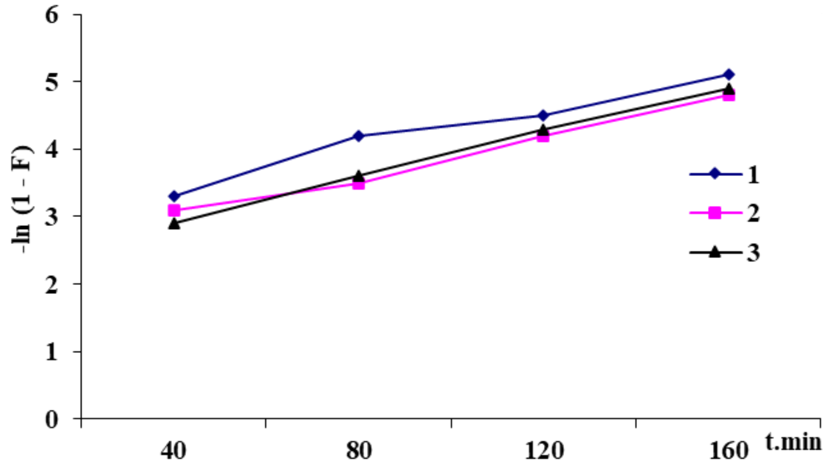

Fig 6. Kinetic curves of vanadium sorption by anion exchangers DGT + PEPA (1), DGT + M (2) and DGT + HPAN (3) in the coordinates of the equation $\ln(1-F) = \varphi(t)$

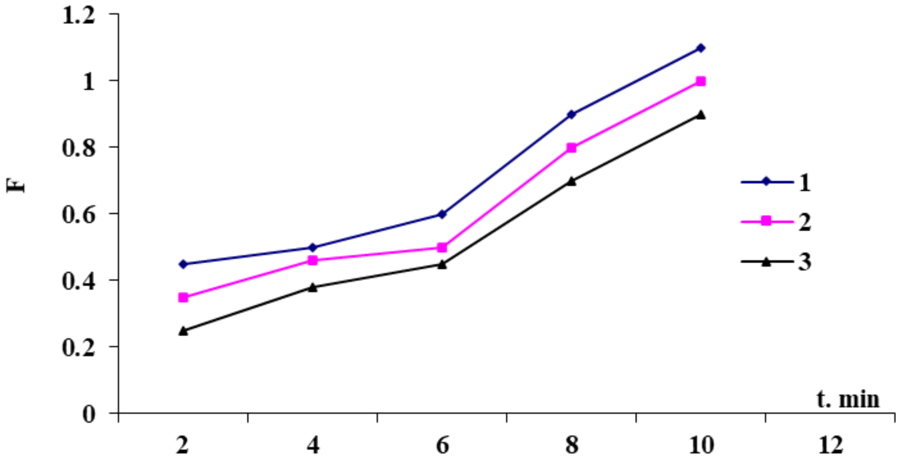

Fig 7. Kinetic curves of vanadium sorption by anion exchangers DGT + PEPA (1), DGT + M (2) and DGT + HPAN (3) in the coordinates of the equation $F = \varphi(\sqrt{t})$

Figure 7 shows the kinetics of vanadium sorption by the anion exchangers DGT + PEPA, DGT + M, and DGT + HPAN. In the case of gel kinetics (internal diffusion), the dependence of F on $\sqrt{t}$ should be expressed by a curve that, for small values of t, has a straight course and then bends. This is the case in our case (Figure 7), which confirms the preliminary conclusion drawn on the basis of table number 5.

The vanadium sorption process is described by the diffusion equation for a spherical shape:

$$\frac{dqr}{dt} = D\frac{d^2qr}{dx^2} \qquad (4)$$

If the value of the diffusion coefficient D, calculated for different times of contact of the ion exchanger with the solution, is constant, then it can be argued that the rate of absorption of ions is indeed limited by internal diffusion.

To calculate the diffusion coefficient, you can use the ready-made tabular data of the dependence B_t of F and the equation:

$$D = \frac{B_t \cdot r^2}{t \cdot \pi^2} \qquad (5)$$

We calculated the diffusion coefficients of vanadium in the anion exchangers DGT + PEPA, DGT + M and DGT + HPAN in the hydroxyl form, which are, respectively, $1{,}71 \cdot 10^{-6}$; $1{,}42 \cdot 10^{-6}$; and $9{,}66 \cdot 10^{-8}$; cm^2/sec. Using the found diffusion coefficients for the named anion exchangers with a particle size of 0.25 - 0.5 mm, the maximum time required to establish equilibrium between the solution and the ion exchanger under these conditions was calculated. It is 7.24 hours for DGT+PEPA ion exchanger, 8.42 hours for DGT+M ion exchanger and 8.8 hours for DGT+HPAN.

To carry out experiments on desorption of vanadium, depending on the mixing time, a solution of 0.2 n sodium hydroxide was used, considering that this concentration is sufficient for desorption of vanadium from the anionites DGT+PEPA, DGT+M and DGT+HPAN. The experiments were carried out under the same conditions as in the study of the sorption rates. The results of experiments and calculations are shown in Figure 8.

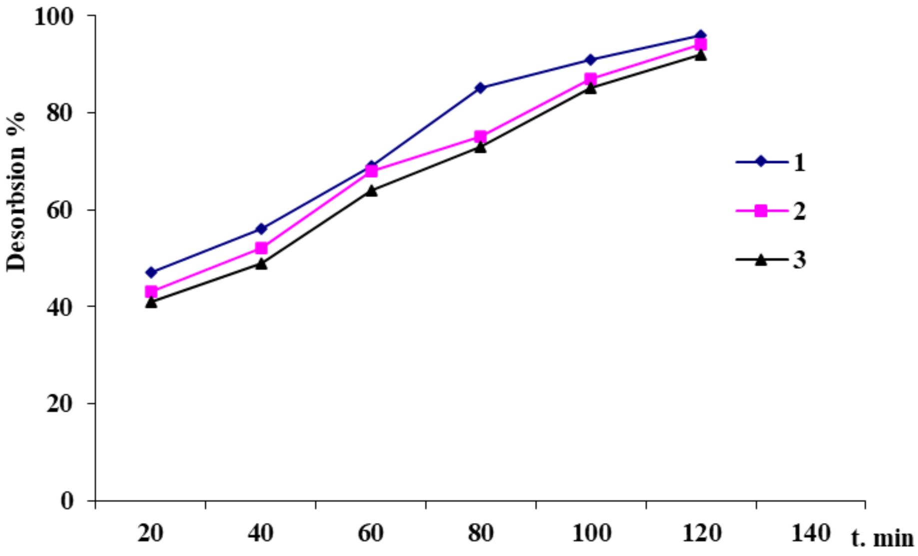

Fig 8. Dependence of desorption of vanadium from anion exchangers DGT+PEPA (1), DGT+M (2) and DGT+HPAN (3) on the duration of stirring.

The figure shows that the desorption rate is quite high, most of the vanadium is desorbed in the first 10 minutes of mixing. By selecting the conditions, especially the speed of stirring the solution, it is possible to achieve 100% desorption of vanadium.

To determine the limiting stage of desorption, the rate coefficients of internal and external diffusion were calculated and curves were plotted in coordinates $\ln(1-F) = \varphi(t)$ and $F = \varphi(\sqrt{t})$, as described above. It turned out that the rate of desorption is not limited by either external or internal diffusion. The process is also not in the mixed diffusion region, since the free term of the equation

$$y = a + bx, \qquad (6)$$

$$where\ y = \ln(1-F), x = t$$

does not meet the specified limit of 0 to -0.49. Only the application of the equation of bimolecular chemical reaction gave a more or less constant rate constant:

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (7)$$

$$from\ where\ \ k = \frac{1}{t}\cdot\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} \qquad (8)$$

The rate constant K was found to be equal for DGT + PEPA (4,4±1)·10^{-3}, DGT+M (5,2±1)·10^{-3}, and DGT+HPAN (6,8±2)·10^{-3}. Thus, it can be concluded that the rate of desorption of vanadium is controlled by a bimolecular chemical reaction and decreases with decreasing vanadium concentration in the resins.

DISCUSSION AND CONCLUSION

The sorption of ions of molybdenum and vanadium was studied on the obtained anion exchangers, depending on the pH-medium, the ionic form of the ion exchanger, the concentration of the studied ions, the presence of competing ions, etc. It was established using potentiometric titration that the cations of molybdenum, vanadium and other nonferrous metals are absorbed by the anion exchangers mainly due to complexation and partly due to the formation of hydroxides.

The sorption and selective characteristics of the anion exchanger obtained on the basis of thiourea, epichlorohydrin in the presence of melamine (DGT+M) with respect to molybdenum ions were investigated depending on the pH medium, the ratio of the solid phase to the liquid, ionic form of the ion exchanger, the concentration of the solutions under study, and the presence of competing sulfate ions. The kinetics of the absorption of molybdenum ions have been investigated.

It was found that the intradiffusion mechanism of kinetics has a dominant effect on the sorption rate. The optimal conditions for the absorption of molybdenum ions by the DGT+M anionite were found and the possibility of using this anionite in the sorption of molybdenum ions in hydrometallurgy was shown.

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