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SORPTION AND ION EXCHANGE PROCESSES

Sorption Purification of Sodium Molybdate Solutions to Remove Vanadium(V) Impurity

A. I. Afanas'ev[a], A. A. Blokhin[a]*, Yu. V. Murashkin[a], and M. A. Mikhaylenko[b]

[a] *St. Petersburg State Technological Institute (Technical University), Moskovskii pr. 26, St. Petersburg, 198013 Russia*
[b] *Representative Office of Purolite Ltd. in Russia, ul. Lusinovskaya 36, Moscow, 115093 Russia*
**e-mail: blokhin@list.ru*

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Abstract—Possibility of performing deep purification of concentrated sodium molybdate solutions to remove vanadium(V) impurity by selective sorption of vanadium(V) from the solutions with fixed pH values on a strong base anion exchange resin Purolite A500/2788 was demonstrated.

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Owing to its high melting point, heat resistance, mechanical strength, and other useful properties, molybdenum is widely used in various fields of modern science and technology. Admixtures of various elements adversely affect the properties of molybdenum and its compounds. Most of impurities find way into molybdenum compounds from starting raw materials. An important secondary source of molybdenum raw materials are spent catalysts for hydroprocessing of raw oil. Spent catalysts, as a rule, contain vanadium commonly present in oil and captured by the catalysts. When molybdenum is recovered from spent catalysts, vanadium passes into molybdate solutions. The properties of molybdenum(VI) and vanadium(V) are close and these elements tend to form mixed polyanions containing both the components [1]. Therefore, purification of molybdate solutions to remove vanadium meets severe difficulties. The classical way to purify ammonium molybdate solutions to remove vanadium via precipitation of the poorly soluble ammonium metavanadate fails to provide a deep purification of solutions to remove this impurity even when the optimal parameters of the process are observed. According to [2], the residual content of vanadium(V) in the resulting crystals of ammonium paramolybdate cannot be reduced to below 0.05 wt %. In addition, this method can only be used for purification of ammonium molybdate solutions, being inapplicable in the case of sodium molybdate.

One of the most effective and selective methods for separation and purification of inorganic substances is the ion-exchange sorption. There have been publications devoted to recovery of impurity amounts of vanadium(V) from solutions with comparatively high molybdenum(VI) concentrations of 60–90 g L^{-1} by the ion-exchange sorption method [3–6]. In two of these [3, 4], it was shown that a selective extraction of vanadium(V) from ammonium molybdate solutions is possible after the solution pH is brought to 6.9–7.2 by sorption on a strongly base anion exchange resin, followed by desorption with a 6 M solution of hydrochloric acid. In two others [5, 6], this was done via sorption of vanadium(V) from ammonium molybdate solutions with pH 74–8.2 on chelating resins containing as functional groups either iminodiacetate groups or amino phosphonic acid groups, or simultaneously pyridine groups and primary amino groups, with the subsequent desorption of vanadium(V) with an ammonia solution [4]. The data presented in these reports demonstrate, on the whole, a high efficiency of the suggested methods for sorption purification of ammonium molybdate solutions by sorption of vanadium(V) impurity: the vanadium concentration in the purified solutions decreases from 0.3–0.4 to 0.01 g L^{-1} of V_2O_5. However, these data cannot be used to fully assess the potential of the ion-exchange method for purification of molybdate solutions to remove vanadium(V). First, these data refer only to purification of ammonium molybdate solutions, but not to sodium molybdate. Second, experiments were performed on solutions with molybdenum concentration of 60–90 g L^{-1}, whereas in real solutions, the concentration of molybdenum(VI) may reach values of 150 g L^{-1} and more. In addition, the suggestion to perform desorption of vanadium from a strongly base anion exchange resin with a solution with high concentration of hydrochloric acid cannot be considered as appropriate.

The goal of our study was to examine the sorption of vanadium(V) under static and dynamic conditions from concentrated sodium molybdate solutions on anion exchangers with various basicities.

EXPERIMENTAL

Taking into account the tendency of vanadium(V) to form polyanions in solutions, we tested macroporous anion exchangers: strongly base anion exchange resin Purolite A500/2788 and weakly base anion exchange resins Purolite A111 with tertiary amino groups and Purolite S984 with secondary and primary amino groups (A500, A111, and S984, respectively). The first two of these are synthesized on the styrene matrix, and the third, on the acrylate matrix. The weakly basic anion exchangers were preliminarily converted to the protonated (sulfate) form.

The experiments in which the sorption and desorption of vanadium was examined were performed under static and dynamic conditions. In the first case, the ratio between the weighed portion of the ion exchanger (grams in terms of the mass of the dry ion exchanger) and the volume of the solution brought in contact with the ion exchanger (mL) was 1 : 100, and the time of contact under agitation in MemmertONE 14 shaker, 46–48 h. It was found preliminarily that this contact duration is more than sufficient for the equilibrium to be attained. After this time elapsed, the solutions were separated from the anion exchange resins and composition of the former was analyzed. The change in the vanadium concentration was used to calculate, with the weighed portion of the anion exchanger and the solution volume taken into account, the weight capacity of the anion exchangers [mg of vanadium(V) g^{-1} dry anion exchanger], which were then recalculated to the volume capacity [mg of vanadium(V) mL^{-1} swollen ion exchanger] with consideration for the sp. vol. of ion exchangers. In the experiment performed under dynamic conditions, we used a column packed with 20 mL of the anion exchanger at H : D = 12 : 1. The rate at which the solution was passed through the column was 0.75–1.0 sp. vol. h^{-1}. Vanadium(V) was introduced into the working solutions in the form of a sodium vanadate solution produced by dissolution of vanadium(V) in a dilute sodium hydroxide solution.

The content of vanadium and molybdenum in the solutions was determined by photocolorimetric analytical methods: the content of vanadium, by measuring the optical absorption of phosphovanadate tungstic heteropoly acid [7], and that of molybdenum, by measuring the optical absorption of the complex of molybdenum(VI) with the rhodanide ion [8]. The pH values of the solutions were determined with a universal electrode on a pH-410 ion meter.

RESULTS AND DISCUSSION

The state of molybdenum(VI) and vanadium(V) in solutions is determined by their pH values and also by their concentration, and primarily by the concentration of the macrocomponent, molybdenum. Therefore, in the initial stage of the study we examined the influence exerted by the pH value of sodium molybdate solutions at four different molybdenum concentrations: 50, 100, 125, and 150 g L^{-1} on the sorption of vanadium at a constant initial concentration of this element of 1.0 g L^{-1}. A part of the results obtained in these experiments is presented in Fig. 1.

It follows from Fig. 1 that all the three anion exchangers show the ability to sorb vanadium(V) from molybdenum-containing solutions, and do so in a comparatively narrow range of pH values. The run of the dependences of the vanadium(V) distribution coefficients on the acidity of sodium molybdate solutions in the sorption on both strongly and weakly basic anion exchangers is the same and has a dome-shaped form. On passing from the neutral to the weakly alkaline region, the vanadium(V) distribution coefficients sharply grow, reach the maximum values, and then decrease as the solution pH increases further. The positions of the maxima in the dependences of the vanadium(V) distribution coefficients on the solution pH scale depend in the sorption on anion exchangers on the concentration of sodium molybdate in the solutions and shift to the alkaline region by 0.4 pH units: from pH ~7.2 to pH ~7.6 as the molybdenum(VI) concentration increases from 50 to 150 g L^{-1}. With consideration for the available data on the state of molybdenum(VI) and vanadium(V) in solutions [1], a possible reason for the

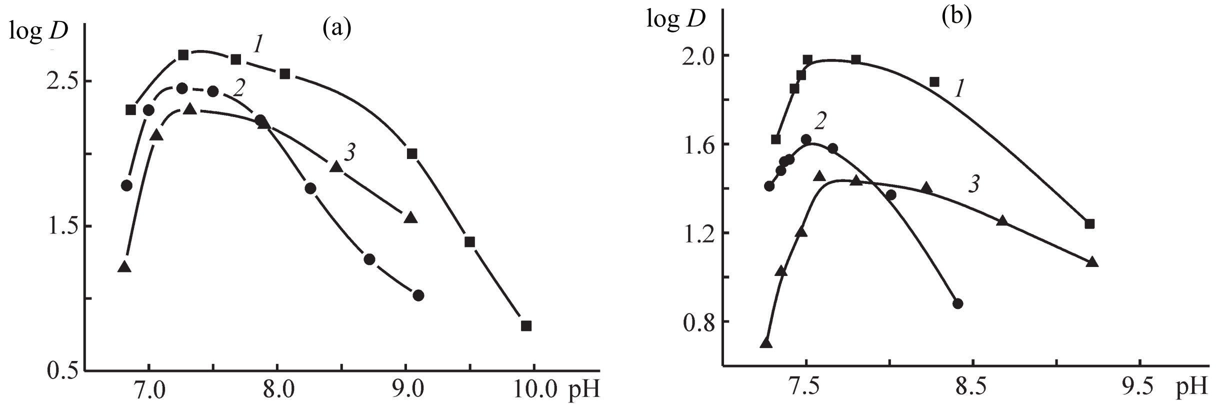

Fig. 1. Dependence of the vanadium(V) distribution coefficients *D* on the pH value of Na_2MoO_4 solutions with molybdenum(VI) concentrations of (a) 50 and (b) 150 g L^{-1} and vanadium(V) concentration of 1.0 g L^{-1} in sorption on anion exchangers (*1*) A500, (*2*) A111, and (*3*) S984.

ascending run of the left-hand part of the plots describing the dependence of the vanadium(V) sorption of the pH value of sodium molybdate solutions is that vanadium(V) starts to be converted to the polymeric form as the alkaline solutions are acidified to pH < 10, and the fraction of vanadium(V) in the form of polymeric anions grows under the same conditions. At pH values corresponding to the maximum distribution coefficients of vanadium(V), it is present in solutions predominantly in the form of $V_3O_9^{3-}$ and, possibly, $V_4O_{12}^{4-}$ ions [1, 9]. Under these conditions, the macrocomponent, molybdenum(VI), is also present in solutions as a monomeric molybdate ion MoO_4^{2-}, and the increased selectivity of macroporous anion exchangers to polymeric anions, compared with those of the monomeric type, is well known [10]. Molybdenum(VI) starts to be converted into the polymeric molybdate ion $Mo_7O_{24}^{6-}$ only upon acidification of the solutions to pH ~7.2 at molybdenum(VI) concentration in solution of 50 g L^{-1} or at pH ~7.5 at its concentration in solution of 150 g L^{-1} [11]. Thus, the transition of molybdenum(VI) to the form of the heptamolybdate anion $Mo_7O_{24}^{6-}$ capable of competing with polyvanadate ions and the formation of mixed vanadium-molybdenum polyanions, which, similarly to the mixed tungsten-molybdenum polyanions, start to be formed at pH values corresponding the onset of the conversion of molybdenum(VI) to the heptamolybdate ion [11], should be considered the reason why the vanadium(V) distribution coefficients on anion exchangers decrease upon acidification of the solutions to pH below the optimal values. The run of the dependence of the sorption of vanadium(V) sorption on weakly basic anion exchangers on the pH value of sodium molybdate solutions is also superimposed by the effect in which the degree of protonation of their functional groups decreases upon an increase in the solution pH.

Additionally, we obtained the dependence of the capacity of A500 anion exchanger for the macrocomponent, molybdenum(VI), on the pH value of the sodium molybdate solution (Fig. 2). These data were obtained by analysis of the desorbates upon desorption of molybdenum from an anion exchanger washed with water with a solution containing 1 M NaOH and 1 M $NaNO_3$.

It can be seen in Fig. 2 that, indeed, the capacity of the strongly basic A500 anion exchanger for molybdenum(VI) sharply grows as the solution is acidified to pH < 7.5, and, after this value is reached, it starts to be converted to the polymeric form.

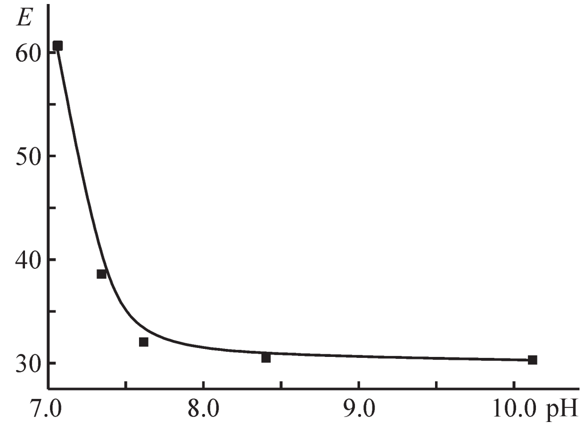

Fig. 2. Dependence of the capacity of A500 anion exchanger for molybdenum(VI) on the solution pH with initial molybdenum(VI) concentration of 150 g L^{-1}. (*E*) Volume capacity of the anion exchanger for molybdenum(VI) [mg molybdenum(VI) per mL swollen anion exchanger].

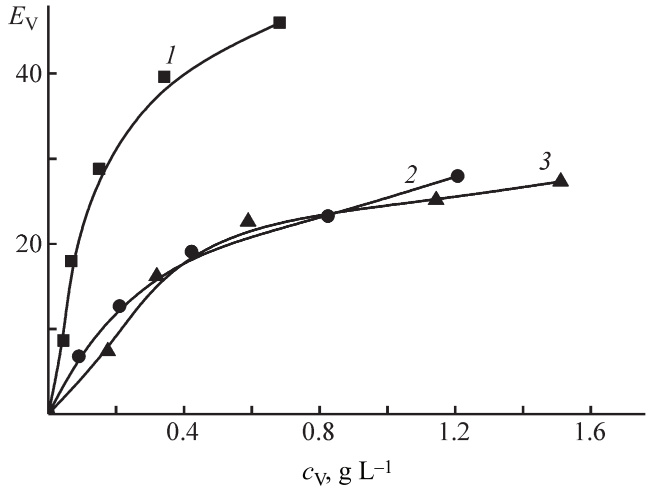

Fig. 3. Sorption isotherms of vanadium(V) on anion exchangers (*1*) A500, (*2*) A111, and (*3*) S984 from a sodium molybdate solution with molybdenum(VI) concentration of 150 g L^{-1}. (E_V) Volume capacity of the anion exchanger for vanadium(V) [mg vanadium(V) per mL swollen anion exchanger] and (c_V) vanadium(V) concentration in the equilibrium solution.

To choose the sorbent for purification of sodium molybdate solutions to remove vanadium(V) on a more reasonable basis, we obtained sorption isotherms of this element from a solution with molybdenum(VI) concentration of 150 g L^{-1} at the nearly optimal equilibrium pH values of 7.6 ± 0.2 (Fig. 3).

As follows from Fig. 3, the strongly basic anion exchanger A500 strongly surpasses the weakly basic anion exchangers A111 and S984 in the capacity for vanadium(V) in the whole range of its equilibrium concentrations.

A study of the desorption of vanadium(V) from A500, A111, and S984 anion exchangers demonstrated that, while vanadium(V) is rather fully desorbed from weakly basic anion exchanger with sodium or ammonia hydroxide solutions, vanadium(V) can only be desorbed from the strongly basic anion exchanger with solutions containing mixtures of sodium or ammonium hydroxide and nitrate or sodium or ammonium chloride.

In conclusion, we performed an experiment on purification of a sodium molybdate solution to remove vanadium(V) on A500 anion exchanger under dynamic solutions. In the experiment, a sodium molybdate solution with molybdenum(VI) and vanadium(V) concentrations of, respectively, 150 and 1.0 g L^{-1} was passed through a column packed with A500 anion exchanger. On being saturated with vanadium(V), the anion exchanger was washed with distilled water. Then, vanadium(V) and molybdenum(VI) were desorbed with a solution containing 1 M NaOH and 1 M $NaNO_3$. The results obtained are presented in Fig. 4 and in the table.

It can be seen in Fig. 4 that a nearly full absorption of vanadium(V) is observed for the first 20 sp. vol. of the solution passed through the column, with its concentration in the solution not exceeding 0.01 g L^{-1}. As the solution is passed further, the vanadium(V) concentration at the column outlet starts to gradually increase. A clearly pronounced breakthrough of vanadium(V) occurred on passing about 40 sp. vol. the solution. The sorbed vanadium(V) was nearly fully eluted with 5 sp. vol. of a solution of mixed sodium hydroxide and nitrate (see

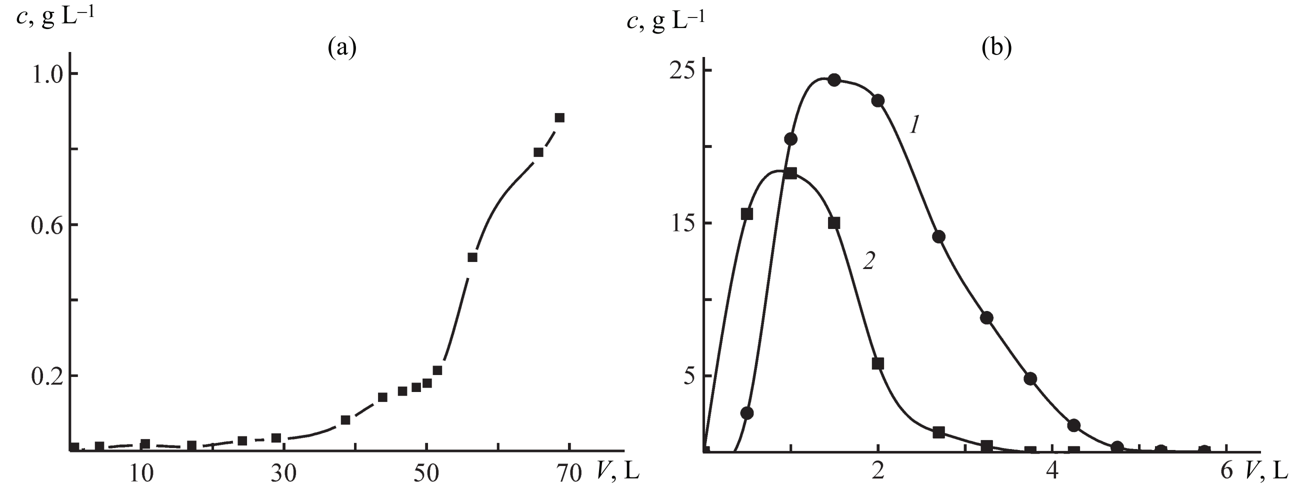

Fig. 4. Elution curves for (a) sorption of vanadium(V) on A500 anion exchanger and (b) desorption of (*1*) vanadium(V) and (*2*) molybdenum(VI). (*c*) Concentration of vanadium(V) in solution at the column outlet and (*V*) volume of the solution passed through the column (specific volume, i.e., the volume of the solution related to the anion exchanger volume in the column).

Summarized data on sorption and desorption of vanadium(V) and molybdenum(VI)

Sorption of vanadium(V), mg mL^{-1}	Desorption of		Distribution coefficients D of V(V) and Mo(VI)
	vanadium(V)	molybdenum(VI)	
55.8	28.9	54.6	270

table). In the course of sorption–desorption, vanadium(V) strongly concentrated in the desorbate. The concentration of vanadium(V) in the averaged eluate (11.6 g L^{-1}) exceeds its concentration in the starting solution by more than an order of magnitude. The capacity of the anion exchanger for the macrocomponent, molybdenum(VI), was 28.9 mg mL^{-1} ion exchanger according to the desorption data. Thus, the ratio between the amounts of vanadium(V) and molybdenum(VI) contained in the combined desorbate was 1.9, whereas in the starting solution, this ratio was 0.007. It is found on this basis that the separation coefficient of vanadium(V) and molybdenum(VI) in the sorption on A500 anion exchanger reaches a value of 270. The total amount of molybdenum(VI) in the solution passed until the breakthrough of vanadium(V) was 150 40 = 6000 mg of oxygen per 1 mL of the ion exchanger. Consequently the loss of molybdenum(VI) with the desorbate is 0.5% relative to the amount of purified sodium molybdate in terms of molybdenum.

CONCLUSIONS

(1) It was found in a study of the sorption of vanadium(V) from sodium molybdate solutions on a strongly basic anion exchanger Purolite A500/2788 and weakly basic anion exchangers Purolite A111 and Purolite S984 that the run of the dependences of the vanadium(V) distribution coefficients on solution pH in sorption on all the anion exchangers has a dome-like shape and the pH values corresponding to the maximum absorption of vanadium(V) are determined by the concentration of the macrocomponent, sodium molybdate, in solutions and are shifted into the alkaline region, from pH ~7.2 to pH ~7.6, upon an increase in the molybdenum(VI) concentration from 50 to 150 g L^{-1}.

(2) It was shown that the strongly basic anion exchanger Purolite A500/2788 strongly surpasses the weakly basic anion exchangers in the capacity for vanadium(V) in the whole range of its equilibrium concentrations from a concentrated sodium molybdate solution with pH ~7.6.

(3) It was found that a deep removal of vanadium(V) is achieved in the purification of a concentrated sodium molybdate solution to remove vanadium on the strongly basic anion exchanger Purolite A500/2788. In this case the separation coefficient of vanadium(V) and molybdenum(VI) is as large as 270. The vanadium(V) being sorbed is nearly fully eluted from the anion exchanger with 5 sp. vol. of a solution of mixed sodium nitrate and sodium hydroxide.

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