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SORPTION OF VANADIUM (V) AND CHROMIUM (VI) IONS BY ANION EXCHANGER BASED ON AN OLIGOMERS OF EPICHLOROHYDRIN AND 4-VINYLPYRIDINE

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ABSTRACT

The new macropore anion exchange resin was synthesized by polycondensation of epichlorohydrin oligomer and 4-vinylpyridine, the static exchange capacity (SEC) of which is equal to 6.75 mg-equiv g^{-1} in 0.1 M HCI solution and the sorption of vanadium (V) and chromium (VI) ions were studied. The influence of the concentration and pH of the model solutions of ammonium metavanadate and potassium dichromate, contact time on the sorption activity of new anion exchangers ECHO-VP to vanadium (V) and chromium (VI) ions were investigated. Structure of the surface anion exchanger was studied by electronic microscopy method.

Key words: Anion exchanger, Oligomer of epichlorohydrin, 4-vinylpyridine, Ammonium metavanadate and Potassium dichromate, Sorption, Vanadium (V) and Chromium (VI) ions, Sorption capacity.

INTRODUCTION

Due to the rapid development of industry, the problem of rational use of natural mineral resources acquires new features[1]. This trend necessitates the development of effective processes suitable for the extraction of valuable components from significant volumes of poor solutions. In addition, many industrial effluents are a source of water pollution with toxic metals that dictates the need for appropriate cleaning methods. These elements, which extraction from aqueous media has a great scientific and practical interest include vanadium and chromium.

At present time is to increase the current production, reducing costs and improving quality of vanadium compounds[2]. These problems can be solved by introducing in

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hydrometallurgy vanadium sorption processes. Therefore, an important task is the creation of advanced ion exchange resins for the extraction of vanadium ions(V) from solutions, cleaning it from waste water to sanitary norms and obtain the V_2O_5 is a high purity.

Technology of inorganic compounds of hexavalent chromium based on processing of chromic iron by methods of alkaline oxidizing roasting with followed leaching water[3]. Slurry, containing 10% chromium ottoretrieve is sent to the slurry tank hydraulic transport, which are used in a large amount of water current, which is washed with a compound of Cr (VI). In this process, accumulate unutilized waste water containing from 3-5 to 20-30 g/L of Cr_2O_3. Cleaning them from ions Cr (VI) will not only solve a number of environmental problems, but also to prevent the loss of expensive chromium compounds, which in return will increase the production of its efficiency and reduce consumption of fresh water due to its recycling use[4]. Therefore the actual is also the synthesis of ion exchangers with improved properties for the sorption of Cr (VI).

In this study, we synthesized and characterized new macro porous anion exchanger based on anoligomer of epichlorohydrin and 4–vinylpyridine of OECH-VP and the static exchange capacity (SEC) of OECH-VP, which is equal to 6.75 mg-equiv g^{-1} in 0.1 M HCI solution.

EXPERIMENTAL

Reagents and materials

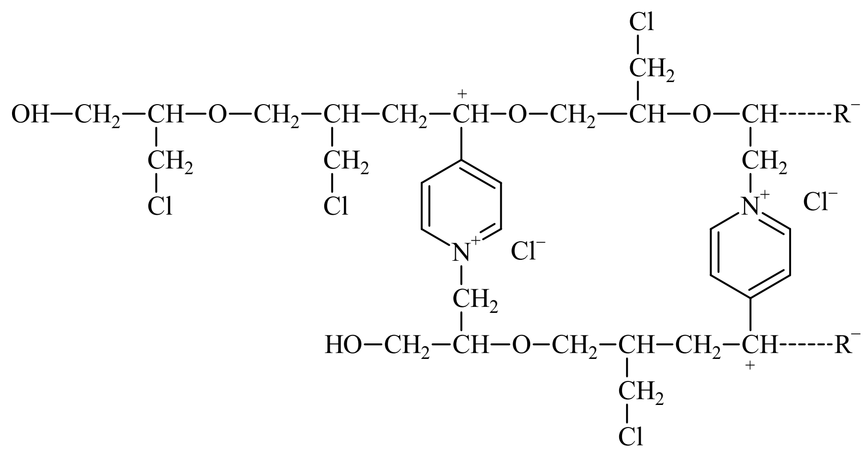
Epichlorohydrin (ECH) (99%, Empirical formula C_3H_5ClO, Mw 92.52 g mol^{-1}, density 1.183 g/mL at 25°C, boiling point 115-117°C, melting point -57°C, refractive index n20/D 1.438 Sigma-Aldrich, Germany).

4-vinylpyridyne (VP) (95%, Empirical formula C_7H_7N, Mw 105.14 g mol^{-1}, density 0.975 g/mL at 25°C, boiling point 62-65°C, refractive index n20/D 1.549 Sigma-Aldrich, Germany).

Benzoyl peroxide (BP) (Linear formula $(C_6H_6CO)_2O_2$, Mw 242.23 g mol^{-1}).

Epichlorohydrin oligomer (ECHO) was obtained in the presence of the M-14 catalyst, activated alumino silicate ($H^+ + Al^{3+}$), taken in an amount of 1% of the monomer weight. The reaction mixture was heated for 2 h at 30-50°C and for 5-6 h at 60-80°C with stirring at a constant rate and then cooled down. The reaction product was dissolved in benzene, precipitated with water-ethanol mixture (2:1), and filtered off. The resulting viscous brown product was dried at room temperature under vacuum to constant weight.

Anion exchange resin was synthesized in an optimal condition by polycondensation of epichlorohydrin oligomer (ECHO) and 4-vinylyridine (VP) in the presence of 0.1-0.5 wt.% benzoyl peroxide at 80°C for 5 hrs in a weight ratio ECHO: VP equal to 10:4. Then the reaction mixture is cured at 120°C for 16 hrs. It was then ground to give a particle size of 0.5-1.0 mm. As a result, a new anion exchanger ECHO-4VP was synthesized. The spatial structure of the anion exchanger resin:



The methods of the sorption of vanadium (V) and chromium (VI) ions by anion exchanger OECH-VP

Sorption of VO_3^- and $Cr_2O_7^{2-}$ ions by anion exchanger OECH-VP in OH^- form (grain size 0.5-1 mm) were studied in static conditions at a ratio of sorbent: solution 1:400, at room temperature of 20 ± 2°C, varying the concentration of vanadium in the solution NH_4VO_3 from 0.19 to 2.037 g/L and a pH range of 1.7 to 6.6 and the concentration of chromium in the solution $K_2Cr_2O_7$ from 0.205 to 2.106 g/L and a pH range of 1.1 to 5.6 with 0.05 M solution of H_2SO_4 or 0.1 M NaOH. Contact time of sorbent with solution is from 15 mins to 7 days. For the preparation of model solutions used salt of NH_4VO_3 and $K_2Cr_2O_7$ qualification "h.ch."

Sorption capacity (SC) was calculated from the difference between the initial and equilibrium concentration of the solution, which was determined by the method of classical polarography against 0.1 M HCI solution on the recovery in VO_3^- ($E_{1/2}$ = −0.85V) and against 0.1 M KOH solution on the recovery in $Cr_2O_7^{2-}$ ($E_{1/2}$ = −1.17 V). The polarogram was filmed on a polarographniversal PU-1 cell thermostated at 25 ± 0.5°C using a dropping mercury electrode. Oxygen from the test solutions was removed by blowing argon for 5 min. A saturated calomel electrode was used as reference electrode.

The structure of the surface anion exchanger was examined by scanning electron microscope JSM 6510LA (JEOL, Japan) at a resolution of the microscope of 30 Å · cm^{-1}.

RESULTS AND DISCUSSION

Removal of salts of vanadium and chromium from natural waters and technological solution shampered by the variety of oxidation degree of these elements[5,6]. Their ionic state has a significant effect concentration and acidity of solutions. Depending on the extent of oxidation is vanadium or chromiumin solution and facing researcher tasks using various anion and cation exchange resins. To determine the optimum parameters of the process of sorption of polyvalent metal ions has been studied extracts anion exchanger capacity OEHC-VP-I with respect to the ions of vanadium (V) and chromium (VI), and depending on the concentration and pH of model solution and the duration contact of the anionite-solution (Fig. 1-3).

As seen from Fig. 1, the extraction of vanadium (V) and chromium (VI) ions from solutions, containing upto 0.2 g/L of metals, they are absorbed by the anion exchanger OEHC-VP-Ito the same extent. An increase in their concentration in the solutions of NH_4VO_3 and $K_2Cr_2O_7$ exceeding 0.2 g/L of chromium ions(VI) recovered better than the ions of vanadium (V). If in the range pH of 1.1-5.1 the SC of anion exchanger OEHC-VP-Ion the chromium ions (VI) are not dependent on the acidity of the solutions $K_2Cr_2O_7$ (Fig. 2), its sorption activity with respect to the ions of vanadium (V) rises with increasing pH solutions of NH_4VO_3, reaching a maximum value 203.6 mg/g at pH 6.6. Ions of chromium (VI) at pH 1.1-5.1 absorbed anion exchanger OEHC-VP better than ions of vanadium (V).

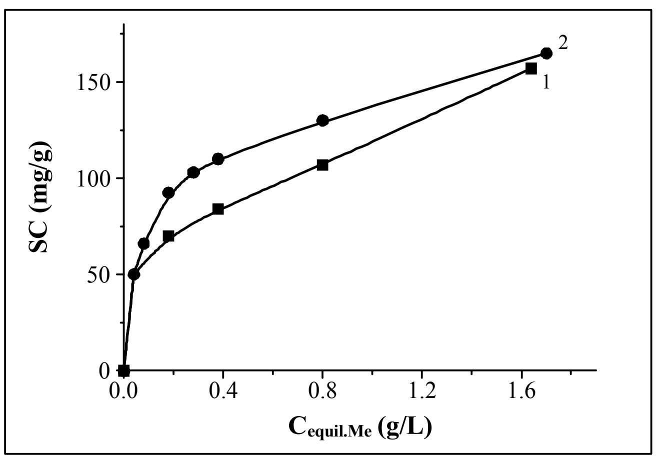


Fig. 1: Sorption isotherms of VO_3^- (1) and $Cr_2O_7^{2-}$ (2) ions by anion exchanger OECH-VP, the contact time 7 days

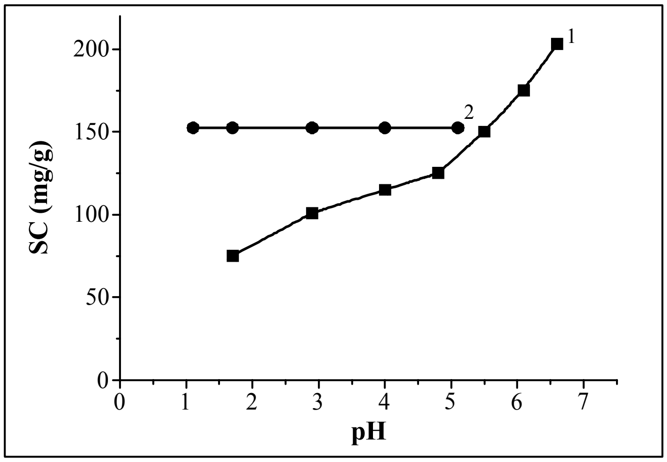


Fig. 2: Dependence the sorption of VO_3^- (1) and$Cr_2O_7^{2-}$(2) ions by anion exchanger OECH-VP from the acidic solution of NH_4VO_3 (C_v = 1.92 g/L) and $K_2Cr_2O_7$(C_{Cr} = 2.08 g/L), the duration of contact time 7 day

From Fig. 3, where the kinetic curves of sorption of vanadium (V) and chromium (VI), it follows that the equilibrium state between the anion exchanger OECH-VP and solutions of $K_2Cr_2O_7$ (pH 1.2, C_{Cr} = 2.08 g/L) is installed respectively for 3 hand 1 h. Hence the synthesized ion exchanger has high kinetic properties.

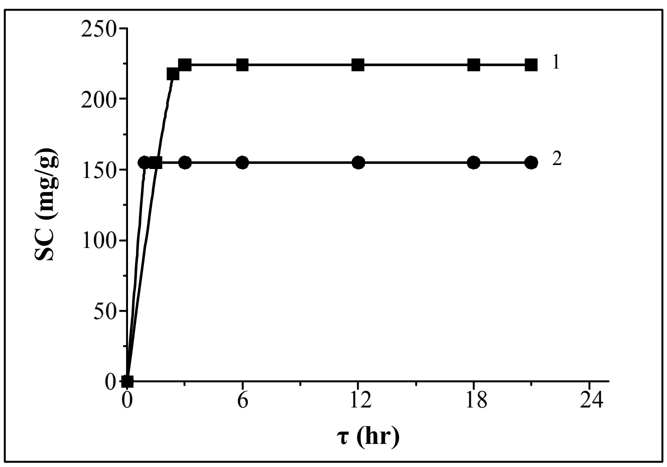


Fig. 3: Kinetic curves of sorption of vanadium (1) and Cr (2) ions by anion exchanger of OECH-VP-I

In terms of V_2O_5 the exchange capacity of the anion exchanger OECH-VP is 363.46 mg/g, i.e. slightly lower than the commercial anion exchanger EDE-10P

(400 mgV_2O_5/g)[7]. Established[8] that the ion exchanger in the OH^- form does not remove ions $Cr_2O_7^{2-}$, and SC of industrial anion exchangers AN-28 and AB-17 x 8 on ions of Cr(VI), respectively equal to 116 and 130 mg/g[9] (for we synthesized anion exchanger of OECH-VP-I –166,4 mg/g).

It is known that the topological structure given by the chemical structure of the initial monomers and the synthesis conditions plays an important role in shaping the properties of cross-linked polymer[10]. The affinity to the anion exchange resins of complexing metal ions depends on their porosity and electron donating capability of the functional groups[11]. Fig. 3 shows the surface morphology of the anion-exchanger OECH-VI-I. These electrons microscopic analysis showed the anion exchanger at OECH-VI-I it is presented in the form of straight folds.

The anion exchanger has a developed system of macropores. As seen from Fig. 3, their sizes OECH-VI are within 0.698-1.764 microns, and the individual poresreach 2.585 microns. Consequently, high sorption capacity of the anion exchanger OECH-VI apparently due to its surface a microstructure more precisely and greater porosity.

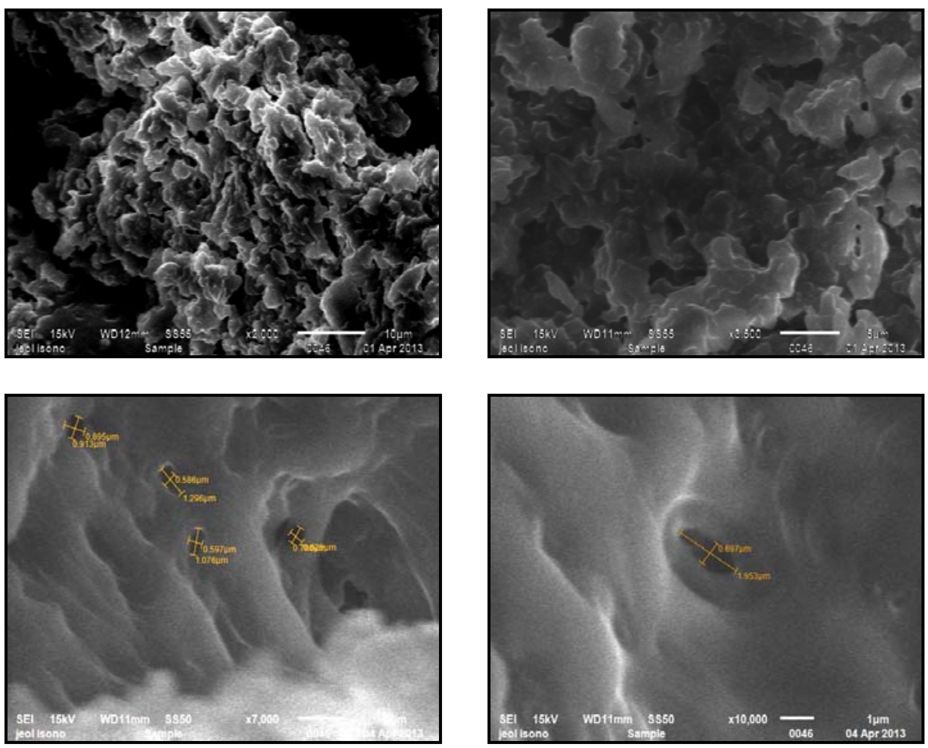


Fig. 3: Micro structure surface of anion exchanger OECH-VI-I

Thus, comparatively high sorption and kinetic properties of the anion exchanger of OECH-VP can recommend it to extract the polyvalent metal ions of vanadium (V) and chromium (VI).

CONCLUSION

The sorption activity of new anion exchangers based on oligomers of epichlorohydrin and 4-vinylpyridine towards vanadium (V) and chromium (VI) ions were studied, looking into the dependency on the concentration and pH of the model solutions of ammonium metavanadate and potassium dichromate, and the contact time. It was established that it has a high sorption and good kinetic properties with respect to the vanadium (V) and chromium (VI) ions when extracting vanadium and chromium from the individual solutions. It was found that at a pH of 6.6 the SC of the ECHO-VP anion exchanger reaches maximum values of 203.6 V/g and 166.4 Cr/g, respectively.

REFERENCES

1. V. G. Berezjuk, O. V. Evptjuhova, O. B. Dubrovina and A. M. Kaiemov, Some Properties Floated Compounds Vanadium, Chromium and Manganese, J. App. Chem., **56(10)**, 2240-2244 (1983).
2. N. I. Razuvaeva, B. A. Muhitdinova, A. I. Nikitina, E. E. Ergozhin, A. O. Bajkonurova and G. A. Usolceva, Study of Sorption of Vanadium, Copper, Lead and Zinc Allyl Redox Polymers, J. Chem., Kazakhstan, **No. 2**, 5-10 (2009).
3. A. Sarsenov, Environmental Security and Resource During Processing of Chromiteore and Borate, Almaty, 233 (2000).
4. K. B. Lebedov, E. I. Kazancev, V. M. Rozmanov, V. S. Paholkov and V. A. Chemezov, Ion Exchangers in Non-ferrous Metallurgy, Metallurgy, 352 (1975).
5. A. I. Nikitina, G. A. Tolegen, S. A. Shoinbekova, B. A. Muhitdinova and E. E. Ergozhin, Polarographic Sorption Study of Vanadium Ion Shomo-and Copolymers Based on Vinyl Redox Polymers, J. Chem., Kazakhstan, **No. 4**, 44-52 (2006).
6. S. L. Sleksiva, S. N. Bolotin and T. G. Cjupko, Study of the Sorption of Chromium(VI) by Ion Exchange Materials and Sorbents, J. App. Chem., **80(3)**, 378-380 (2007).
7. B. E. Begenova, Sorption Properties of Ion-Exchange Resins Based on Glycidyl Derivatives of Aromatic Compounds and Polyamines, J. Chem., Kazakhstan, **4**, 76-81 (2007).

8. E. A. Shejnina and K. M. Saldadze, Removal of Heavy Metal Impurities Brine Electrolysis with a Mercury Cathode using Ion Exchangers, AN SSSR, 153-159 (1963).

9. G. P. Vishnevskaja, R. Sh. Safin and E. N. Frolova, State of Cr^{3+} Ions in the Sulfo-and Sulfo Phenol Containing Cation Exchanger KU-2 and KU-1 According to the EPR, J. Phys. Chem., 2225-2228 (1996).

10. V. I. Irzhak, B. A. Rozenberg and N. S. Enikolopjan, Cross-linked Polymers (Synthesis, Structure, Properties), 248 (1979).

11. K. M. Saldadze and V. D. Kopylova-Valova, Complexingion Exchangers (Complexes), 336 (1980).

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