

Sorption of Perrhenate Ions by a New Anion Exchanger Based on an Oligomer of Epichlorohydrin and 4-vinylpyridine

A. Pidakhmet^{1*}, E.E. Ergozhin², T.K. Chalov² and A.I. Nikitina²

¹Kazakh-British technical university, 59 Tole Bi Str., 050000, Almaty, Kazakhstan

²JSC "A.B. Bekturov Institute of Chemical Sciences", 106, Sh. Ualikhanov Str., 050010, Almaty, Kazakhstan

Abstract

In this study, oligomer epichlorohydrine (OECH) was crosslinked with 4-vinylpyridin (VP) present initiator of peroxide benzoyl (BP). The resulting anionite (OECH-VP) was characterized by scanning electron microscopy (SEM) and tested for perrhenate ions sorption. 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 HCl solution and the sorption of perrhenate ions was studied. The influence of the concentration and pH of the model ammonium perrhenate solutions, contact time on the sorption activity of new anion exchangers (ECHO-VP) to perrhenate ions were studied. When studying the concentration effect of NH₄ReO₄ on the sorption of perrhenate ions by anionite ECHO-VP, the recovery degree at the content of 0.1-0.7 g/L of rhenium remained virtually unchanged and varied between 91- and 92%. When increasing the concentration of rhenium up to 1.02 g/L, the recovery degree (A) is reduced to 86%. The time to reach the equilibrium between the anion exchanger ECHO-VP and the solution of NH₄ReO₄, containing 0.94 g/L of rhenium and having a pH of 5.1 is 6 hours. Thus in the first 15 minutes 81% perrhenate ions are recovered. Structure of the surface anionite before and after sorption of rhenium ions were studied by electronic microscopy method. The results revealed that the anionite ECHO-VP has a folded surface with a developed system of macropores and the size of macropores was found to vary between 0.70-1.76 mc, and individual pores reach 2.59 mc. It was established that ion exchanger based on oligomers of epichlorohydrin and 4-vinylpyridine have better sorption properties for rhenium (VII) ions that a wide range of commercial sorbents. It was found that the sorption capacity and the extent of new anion extracting the perrhenate ions and reach their maximum values are respectively 371.6 mg-Re/g and 99% at pH 5.1.

Introduction

At the present time, there is a worldwide trend of rapid growth in consumption of rhenium by expanding its use in superalloys used in space technology, as well as in the manufacture of platinum-rhenium catalysts for high-octane gasoline production [1]. Rhenium is widely used in alloys with tungsten, molybdenum, nickel, cobalt, chromium, dramatically improving their properties and making them particularly heat resistant. These alloys are also used for manufacturing elastic elements, having high strength and vibration resistance, electronics, electrical engineering and instrumentation. Promising areas of application for rhenium-containing

catalysts are hydrocracking processes, manufacture of filters-neutralizers car exhaust converters. In this regard, the need for rhenium is growing.

Rhenium is a typical scattered element. Rhenium does not have own minerals, and it is produced simultaneously in the complex processing of copper, lead, uranium, molybdenum concentrates, ore tailings and waste waters, where its content ranges from fractions to tens of milligrams per liter [2-4]. Low rhenium content in the feed causes the difficulty of obtaining it. Improvement of existing technological schemes and creating new efficient processes associated rhenium from non-traditional raw materials is an important issue. The hydrometallurgical processing of polymetallic rhenium containing raw material

* Corresponding author. E-mail: pidahmet_aidyn@mail.ru

is recovered by ion exchange [1, 5]. Therefore of great scientific and practical importance is the creation of ion-exchange resins with improved absorption properties with respect to the perrhenate ions.

In this study, we synthesized and characterized of anionit based on epichlorohydrin oligomer (ECHO) and 4-vinylpyridine (VP).

Experimental

Reagents and Materials

Epichlorohydrin (ECH) (99%, empirical formula C_3H_5ClO , Mw $92.52 \text{ g}\cdot\text{mol}^{-1}$, density 1.183 g/ml at $25 \text{ }^\circ\text{C}$, boiling point $115\text{-}117 \text{ }^\circ\text{C}$, melting point $-57 \text{ }^\circ\text{C}$, refractive index $n_{20/D} 1.438$ Sigma-Aldrich, Germany).

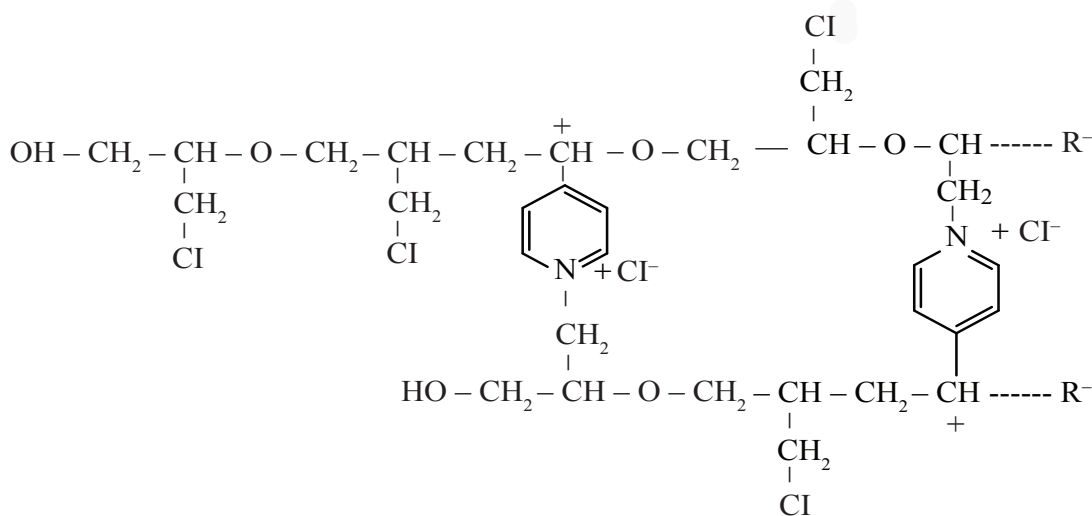
4-vinylpyridine (VP) (95%, Empirical formula C_7H_7N , Mw $105.14 \text{ g}\cdot\text{mol}^{-1}$, density 0.975 g/ml at $25 \text{ }^\circ\text{C}$, boiling point $62\text{-}65 \text{ }^\circ\text{C}$, refractive index $n_{20/D} 1.549$ Sigma-Aldrich, Germany).

Benzoyl peroxide (BP) (Linear formula $(C_6H_5CO)_2O_2$, Mw $242.23 \text{ g}\cdot\text{mol}^{-1}$).

Ammonium perrhenate NH_4ReO_4 (Aldrich, Germany).

Epichlorohydrin oligomer (ECHO) was obtained in the presence of the M-14 catalyst, activated aluminosilicate ($H^+ + Al^{3+}$), taken in an amount of 1% of the monomer weight. The reaction mixture was heated for 2 h at $30\text{-}50 \text{ }^\circ\text{C}$ and for 5-6 h at $60\text{-}80 \text{ }^\circ\text{C}$ 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-vinylpyridine (VP) in the presence of 0.1-0.5 wt.% benzoyl peroxide at $80 \text{ }^\circ\text{C}$ for 5 hours in a weight ratio ECHO:VP equal to 10:4. Then the reaction mixture is cured at $120 \text{ }^\circ\text{C}$ for 16 hours. 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:



Study of the Sorption of Perrhenate Ions by Anionites ECHO-VP

Sorption of perrhenate anionite ECHO-VP in OH- form (grain size 0.5-1 mm) was studied in static conditions at a ratio of sorbent: solution 1:400, at room temperature of $20 \pm 2 \text{ }^\circ\text{C}$, varying the concentration of rhenium in the solution NH_4ReO_4 from 0.102 to 1.024 g/L and a pH range of 1.2 to 6.2 with 0.1 N solution H_2SO_4 . Contact time of sorbent with solution is from 15 minutes to 7 days.

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 0.5 N H_2SO_4 solution on the recovery in Re^{7+} ($E_{1/2} = -0.50 \text{ V}$). The polarogram was filmed on a polarograph universal PU-1 cell thermostated at $25 \pm 0.5 \text{ }^\circ\text{C}$ using a dropping mercury electrode. Oxygen from the test solutions was removed by blowing argon for 5 minutes. A saturated calomel electrode was used as reference electrode.

The structure of the surface anion before and after the sorption of rhenium was examined by electron microscopy scanning electron microscope JSM 6510LA (JEOL, Japan) at a resolution of the microscope of $30 \text{ \AA}\cdot\text{cm}^{-1}$.

Results and Discussion

Effect of Concentration

Sorption of perrhenate ions by anionite ECHO-VP was performed from model solutions of ammonium perrhenate, which is normally used in industrial applications in the production of rhenium and its products [6, 7]. When studying the concentration effect of NH_4ReO_4 on the sorption of perrhenate ions by anionite ECHO-VP, the recovery degree at the content of 0.1-0.7 g/L of rhenium remained virtually unchanged and varied between 91 and 92% (Fig. 1). When increasing the concentration of rhenium up to 1.02 g/L, the recovery degree (A) is reduced to 86%.

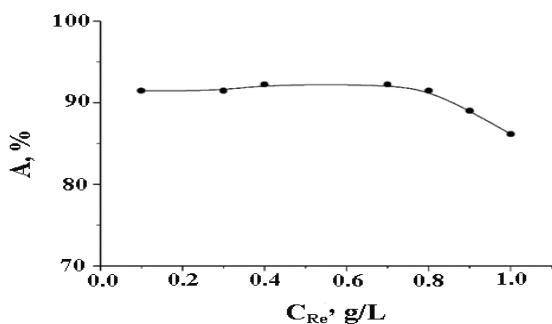


Fig. 1. The degree of recovery of perrhenate ions on ECHO-VP anion exchanger as function of the concentration of NH_4ReO_4 solution. The contact duration is 7 days.

As it is seen from Fig. 2, increasing the content of rhenium in the solution of NH_4ReO_4 , the SC of the anion exchanger increases, reaching 352.8 mg/g during the recovery of perrhenate ions from a solution containing 1.02 g/L of rhenium (pH 6.2).

It is shown [7] that increasing the concentration of the external solution lead to increasing the amount of metal ions that penetrate into the polymer skeleton, while the speed of penetration of exchanging ions in the deeper layer of the sorbent also increases.

When removing the perrhenate ions from a solution of NH_4ReO_4 , containing 0.1 g/L of rhenium anion exchanger ECHO-VP is equal to 37.2 mg of Re/g. Under similar conditions, industrial medium and low-basic anion condensation type EDE-10P, AN-2F and macroreticular adsorbents polymerization of AN-21, AN-22 have a lower absorbency and recovers 18.9: 20.5: 25.5 and 28.3 mg of Re/g respectively [8]. When the concentration of the stock solution is 0.5 g/L of rhenium, industrial highly basic gel anionite AMP and a porous anion AM-2b have similar sorption properties and reaches a SC of 47 mg of Re/g [9]. Anionite ECHO-VP perrhenate when removing ions from a solution of NH_4ReO_4

with the same content of rhenium has a higher absorbency and SC, equal to 216.8 mg of Re/g.

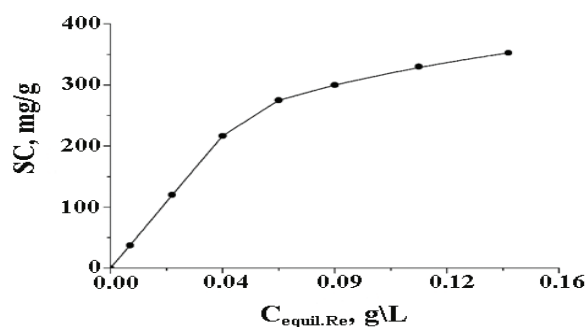
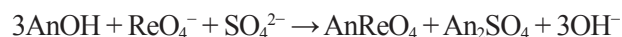


Fig. 2. Sorption isotherms of perrhenate ions on ECHO-VP anion exchanger. The contact duration is 7 days.

Effect of pH

The effect of the acidity of the solution on the sorption of perrhenate ions by anionite ECHO-VP is of particular interest, since the processing of copper and polymetallic ores produces rhenium-containing sulfuric acid solutions. As it is seen from Fig. 3, in the pH range 1.8-6.2 this effect is minimal. At pH 5.1 the SC and the degree of recovery of the ECHO-VP anion exchanger reach maximum values of 371.6 mg of Re/g and 99%, respectively. It is known [1] that in neutral, acidic and alkaline solutions rhenium is in the form of a simple monovalent anion ReO_4^- . The sorption of perrhenate ion anion exchanger in the OH-form can be schematically represented as follows:



By varying the pH the capacity is influenced by factors such as changes in the degree of protonation of the amino groups and the competitive adsorption of anions of acidic residues. These reasons seem to cause the reduction of anionite ECHO-VP at pH 6.2 (by reducing the degree of protonation of the amine) and pH 1.2 (by competitive adsorption of ions SO_4^{2-}).

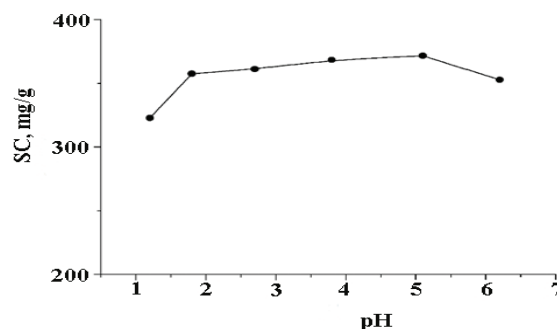


Fig. 3. Influence of acidity NH_4ReO_4 ($C_{\text{Re}} = 0.94 \text{ g/L}$) on the sorption of perrhenate ions with ECHO-VP anion exchanger, contact duration is 7 days.

Effect of time

It follows from Fig. 4 that the time to reach the equilibrium between the anion exchanger ECHO-VP and the solution of NH_4ReO_4 , containing 0.94 g/L of rhenium and having a pH of 5.1 is 6 hours. Thus in the first 15 minutes 81% perrhenate ions are recovered. Equilibrium sorption on the anion derived from lignin oligomer epichlorohydrin and 2-vinylpyridine was determined for 12 hours [1], for hot on anion exchangers AMP and AM-2b for 30 min [9]. The duration of establishing equilibrium in an anionite-solution system by an industrial anion exchanger AN-21 \times 16 depends on the degree of cross-linking and, consequently, resin with a DVB Content from 2 to 20% varies from 2 to 77 hours [1].

When studying the sorption of rhenium ions from a solution of ammonium perrhenate, containing 0.01 mol/dm³ of rhenium at pH 5.45-5.85 found that the capacities of the AN-21 anion exchanger gel structure is 49.2-81.1 mg/g [10]. SC of anion exchange of lignin-based oligomer of epichlorohydrin and 2-vinylpyridine is 111.6 mg of Re/g [1]. SC of synthesized anion exchanger ECHO-VP is much higher and is 371.6 mg of Re/g.

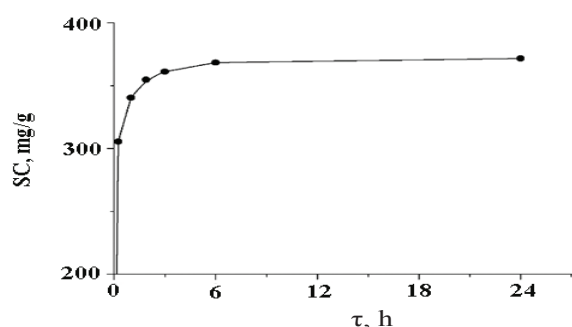


Fig. 4. Sorption capacity SC of ECHO-VP anion exchanger for perrhenate ions as function of the contact duration in the NH_4ReO_4 solution ($C_{\text{Re}} = 0.94$ g/L, pH 5.1).

The high sorption properties of the anion exchanger ECHO-VP are apparently due to the microstructure of its surface. Pictures taken from electron microscopy (Fig. 5) show that the anionite ECHO-VP has a folded surface with a well developed system of macropores.

As it can be seen from Fig. 5b,c, the size of pores is in the range of 0.70-1.76 μm , and the individual pores reach 2.59 μm . The large pore size helps to absorb the large ReO_4^- ions, with an ionic radius of 0.28 nm [11]. The surface layer of the anion exchanger ECHO-VP contains 5.91-17.11% rhenium.

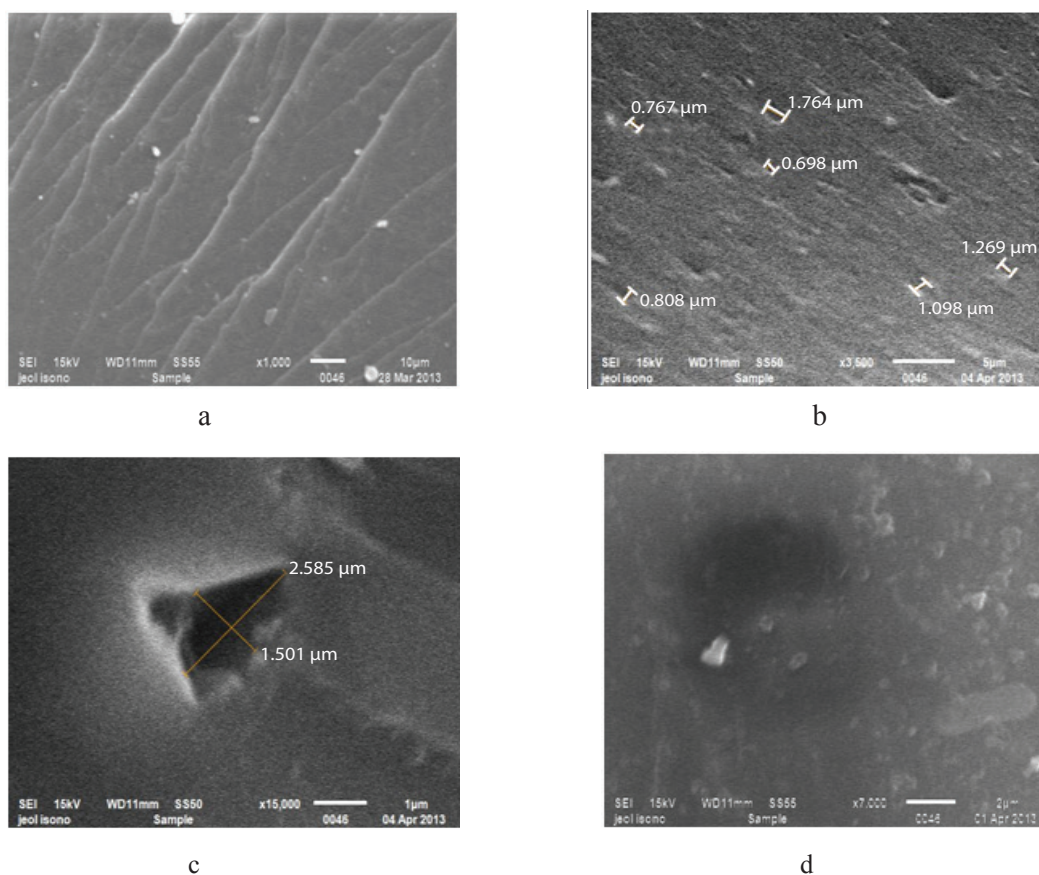


Fig. 5. The microstructure of the surface anion exchanger ECHO-VP before (a, b, c) after (d) sorption of perrhenate ions.

Conclusions

The sorption activity of new anion exchangers based on oligomers of epichlorohydrin and 4-vinylpyridine towards perrhenate ions was studied, looking into the dependency on the concentration and pH of the model ammonium perrhenate solutions and the contact time. It was established that it has a high sorption and good kinetic properties with respect to the perrhenate ions when extracting rhenium from the individual solutions. It was found that at a pH of 5.1 the SC and the degree of recovery of the ECHO-VP anion exchanger reach maximum values of 371.6 mg of Re/g and 99% respectively.

References

1. I.D. Troshkina, A.M. Serbin, Z.N. Khaing, O.N. Ushanova, Ju.V. Demin, A.M. Chekmarev. Corbcionnoe izvlechenie renija iz sernokislyh rastvorov aminosoderzhashhimi impregnatami [Sorption extraction of rhenium from sulfuric acid solutions of amine-impregnate]. Corbcionnye i hromatograficheskie processy, 6 (2006) 1022-1027.
2. V.A. Peganov, T.V. Molchanova, K.M. Smirnov. Sorbcionnye processy v tehnologii gidrometalurgicheskoj pererabotki molibdenitovyh koncentratov [Sorption processes in technology hydrometallurgical processing molybdenum concentrates]. Cvetnye metally, 12 (2010) 56-59.
3. V.P. Volkov, N.M. Meshherjakov, N.V. Nikitin, M.A. Mihajlenko. Promyshlennyj opyt sorbcionnogo izvlechenija renija iz oborotnyh rastvorov podzemnogo vyshhelachivaniya urana [Industrial experience of sorption of rhenium from circulating fluids underground leaching of uranium]. Cvetnye metally, 7 (2012) 64-66.
4. Z.S. Abisheva, A.N. Zagorodnjaja, V.N. Timofeev, L.A. Myltykbaeva. Intensifikacija desorbicii renija iz anionita AMP, nasyshhenogo iz promyshlennogo uransoderzhashhego rastvora podzemnogo vyshhelachivaniya polijelementnyh rud [Intensification of desorption of rhenium from the anion exchanger AMP, saturated solution of industrial in-situ leaching of uranium-containing ores polyelement]. Cvetnye metally, 10 (2012) 78-82.
5. N.N. Chopabaeva, E.E. Ergozhin, A.T. Tasmagambet, A.I. Nikitina. Sorbcija perrhenatov novymi ligninovymi anionoobmennikami [Sorption of perrhenate ions new lignin anion exchangers]. Himija tverdogo topliva, 2 (2009) 43-47.
6. V.G. Pareckij, A.D. Besser, Je.I. Gedgagov Puti povyshenija proizvodstva renija iz rudnogo i tehnogenogo syr'ja [Ways to increase the production of rhenium from ore and technogenic materials]. Cvetnye metally, 10 (2008) 17-21.
7. A.A. Palant, A.M. Levin, Je.F. Brjukvin, Ahmetov. Poluchenie koncentrirovannyh rastvorov renievoj kisloty jelektrodializom [Preparation of the concentrated electro dialysis perrhenic acid solutions]. Cvetnye metally, 11 (2010) 62-64.
8. E.E. Ergozhin, N.A. Bektenov, A.M. Akimbaeva. Polijelektrolity na osnove glicidilmetakrilata i ego sopolimerov [Polyelectrolytes based on glycidylmethacrylate and its copolymer]. Almaty: JeVERO, (2004):271.
9. Patent 2405845 RF. Sposob sorbcii ionov renija (VII) iz vodnogo rastvora [Way of sorption of rhenium (VII) ions from water Solution]. L.A. Voropanova, F.A. Gatiyeva. zajavl. 21.01.2009; opubl. 27.07.2010.
10. A.N. Zagorodnjaja, Z.S. Abisheva, A.S. Shari-pova, S.Je. Sadykanova, V.V. Bobrova. Vlijanie struktury anionitov na sorbciju renija i urana iz individual'nyh rastvorov i ih sovmestnogo prisutstvija [The influence of the structure of ion exchangers on the sorption of rhenium and uranium from individual solutions and their joint presence]. Nauki o zemle, 6 (2011) 42-47.
11. A.A. Blohin, A.A. Amosov, Ju.V. Murashkin, S.A. Evdoshenko, M.A. Mihajlenko, N.V. Nikitin. Sorbcija renija (VII) na gelevykh i makroporistykh anionitah razlichnoj osnovnosti iz rastvorov mineral'nyh kislot i ih ammonijnyh solej [Sorption of rhenium (VII) on the gel and macroporous anion exchangers of various basicity of solutions of mineral acids and ammonium salts]. Zhurn. prikl. himii, 9 (2005): 1436-1439.

Received 6 August 2013