Synthesis and Characterization of Modified Resins and Their Selective Sorption Towards Rhenium from Binary (Re & Mo) Solutions

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ABSTRACT: *Three amine-functionalized resins were prepared by suspension polymerization of vinyl-benzyl chloride, divinylbenzene, and subsequent amination process. The effect of chain length and cyclic amine on the performance of resins was investigated in a multicomponent system (Re & Mo). Different amines were used in the investigation. Different analyses such as Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FT-IR) spectroscopy, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Kiejdahl's and Volhard's methods were used to characterize the synthesized resins. The synthesized resins then were assayed in a batch mode using binary solutions of Re(VII) and Mo to evaluate their efficiency in the selective sorption of rhenium ions. Among all investigated resins, resin C revealed better separation properties in acidic solution (pH=1) with the highest sorption capacity up to 46.4 mg Re/g and a distribution coefficient of 870 that is more attributed to a steric barrier created against the polymeric molybdenum ions that are larger than objective ions in the studied system.*

KEYWORDS: *Amine-functionalized resins; Re-Mo binary system; Selective sorption.*

INTRODUCTION

In recent years, due to the lack of high-grade deposits, an increasing effort has been devoted to the recovery of precious metals from waste solutions and any secondary sources with low content of the desired metals. Rhenium is one of the most precious and noble metals in nature. It is widely used in high-end technologies, i.e., metallurgy, chemical, and petrochemical industries [1-3] for its unique physical and chemical properties, such as refractoriness, plasticity, high density, corrosion resistance, and catalytic activity. Rhenium, due to having close similarities with Mo in terms of chemical properties and ionic radius, the ionic radius of Re^{4+} and Mo^{4+} are 0.72 Å and 0.70 Å, respectively, usually occurs with molybdenum-bearing ores. That can raise serious problems in the separation of rhenium and molybdenum processes. They compete with each other, and finally, it causes to decrease in rhenium loading [4]. Rhenium is also present in solutions produced by copper heap leaching and underground uranium ore leaching process [5,6].

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In these solutions, the rhenium concentration has been detected to be relatively low, 0.1, and 0.25-0.25 ppm, respectively. The price spikes ($2,900 per kg, Metal Bulletin, February 2020), along with the large volume of the pregnant leach solutions (PLS), make it necessary to make an earnest attempt to prepare an efficient extractant for selective recovering of Re ions from multicomponent dilute solutions.

At a wide pH range, rhenium is present in solutions as perrhenate anions (ReO_4^-) (Fig. 1), and like the other monovalent anions, these ions have a strong affinity to anion exchange resins [5]. Therefore, the preferred industrial process of rhenium recovery is the ion-exchange method. At low pH values, similar to those in rhenium industrial bear solutions, the rhenium ion sorption can be accomplished by the direct protonation of resin through the following reactions [7]:

$$\mathrm{R-NH_2 + H_2SO_4 \rightarrow R-NH_3^+ + HSO_4^-} \qquad (1)$$

$$\mathrm{R-NH_3^+ + \ ReO_4^- \rightarrow \ R-NH_3ReO_4} \qquad (2)$$

Where $R\text{-}NH_2$ represents the polymer resin and the functional group.

Ion-exchangers are polymeric materials with selective functional groups and chelating resins that have been used for many years in laboratories and have been allowed to apply in sorption technology for the recovery of valuable metals, such as Au, Pt, Pd, U [9,10], Mo [11], Cs [12], Cr [13], Th [14] and Re [15,16]. Since the choice of the resin matrix and type of ligands attached to the polymer plays an essential role in achieving selectivity and making a resin for the specific conditions of a particular process, a variety of functional groups with a selective behavior toward desired metals have been utilized [17-19].

A comprehensive survey of the literature on the synthesis, modification, and sorption of perrhenate ions shows very few numbers of research studies have been conducted to synthesize and improve resins for rhenium recovery [20-22]. In general, these studies had indicated that strongly basic anion exchangers absorb rhenium and molybdenum almost equally while weakly basic anion exchangers are more selective to mentioned ions than to molybdenum. In one study, the separation of Re and Mo ions was conducted using cyclic amine groups anion exchangers from bearing solutions [21]. It was most likely attributed to the fact that the cyclic functional groups are creating a steric barrier to the polymeric molybdenum ions larger than the objective ions. The produced resins with a high cross-linking agent (14-16%) have a rigid and tight structure, which makes the molybdenum polyanions (MoO42–, Mo7O246–, Mo8O264–) inaccessible to the functional groups due to size differences between involved ions [21]. These resins are known as gel-type or microporous ion exchangers that can act as a sieve. The diffusion of molybdenum molecules to inner active sites was restricted by these resins whiles perrhenate ions can still infiltrate into the matrix without restrictions [6].

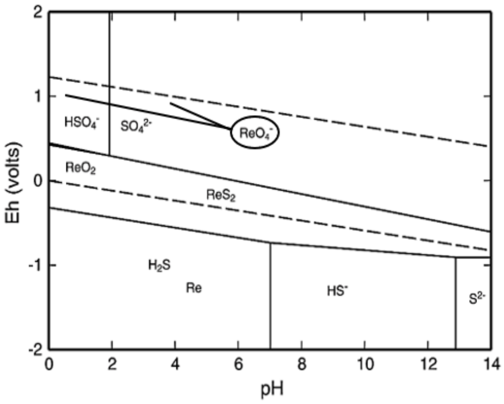

Fig. 1: Eh–pH diagram for Re–S–H_2O system (25 °C, 1 bar, ∑S = 10−1, and ∑Re = 10−6) [8].

The objective of this work is to evaluate the effects of three amine-functionalized resins on selective sorption of Re from a binary system (Re & Mo). It is noteworthy that this work has been carried out for the first time for the application in hydrometallurgy processes. The resins were prepared via suspension polymerization of VBC-DVB and subsequent amination, and then the selective adsorption of synthesized resins from multicomponent acidic solutions containing Re and Mo was assessed.

EXPERIMENTAL SECTION

Reagents and instruments

Vinyl benzyl chloride (VBC, Acros Organics, 90%) was used after purification. DVB purchased from Merck, was extracted with a 10% (w/w) sodium hydroxide solution to remove the inhibitor and then was washed with deionized water until neutralization. The initiator, Azo-bis-isobutyronitrile (AIBN) from Fluka, was used as received without any purification. Dimethylformamide (DMF), absolute acetone, and n-hexane were from Merck. Rhenium and Molybdenum standard stock solutions were prepared by dissolving NH_4ReO_4 (Aldrich) and $(NH_4)_6Mo_7O_{24}.4H_2O$ (Aldrich), respectively, in deionized water. The surface and cross-section morphologies of the resins were examined using the Philips XL30 model SEM. FT-IR spectra of the resins in KBr pellets were recorded by Bruker Tensor 27. The concentrations of metal ions in solutions were determined using ICP-OES (Optima 7300 DV Perkin Elmer).

All other reagents were of analytical grade, and they were used without further purification.

Polymerization and modification

VBC/DVB polymeric resins were prepared by the suspension polymerization method. A mixture of VBC and divinylbenzene was poured into a 250 mL three-neck glass reactor equipped with a mechanical stirrer, a reflux condenser, and a thermometer and then AIBN was added as radical initiator. Polymerization was carried out in the presence of a hexane as inert diluents. Subsequently, the resulting resin was filtered and was washed with deionized water and then with absolute acetone. The beads were dried under vacuum at 50 °C for 24 h. The morphology (surface and cross-section) and particle size distribution of polymer beads are illustrated in Fig. 2 and Table 1. The surface was very smooth, and the cross-section of the bead was porous with a pore size of about 10 µm, which was induced by removing hexane. These pores made microchannels to facilitate the penetration of the solution to the active sites. Particle size distribution is mono-modal and narrow so that over 85% of beads are in the range of 300 to 710 µm.

Three sets of product resins (3 g each) with a particle size in the range of 500 – 1180 µm were selected for the amination process. To introduce amine groups into polymer beads, they were swollen solvent and then were reacted with excess to the chlorine content in the polymer. Three resins A, B, and C were produced according this procedure. After the amination process, the resins were filtrated and were washed with cold and hot water and then with 1M HCl, water, and 1M NaOH three times to remove the Cl^- ions.

Methods of analysis

Regain of water was measured by centrifuging of 1 g of polymer swollen in water for 5 min at 3000 rpm. After vacuum drying at 80 °C for 24 h, the polymer was weighted, and the water regain calculated as below equation:

$$W = (m_w - m_d) / m_d \tag{3}$$

where m_w is the weight of the wet polymer after centrifugation (in a glass vial with a fritted glass bottom), and m_d is the weight of the dry polymer.

Content analysis of nitrogen and chlorine was measured by Kjeldahl's [23] and Volhard's methods, respectively [19]. In Kjeldahl's process, the resin sample (about 250 mg) was mineralized in the concentrated

Table 1: The particle size distribution of synthesized beads.

Particle size (µm)	Retained on sieve (%)
1400	1.2
1180	3.2
1000	4
850	4
710	26
500	42
300	18.6
210	0.7
-210	0.3

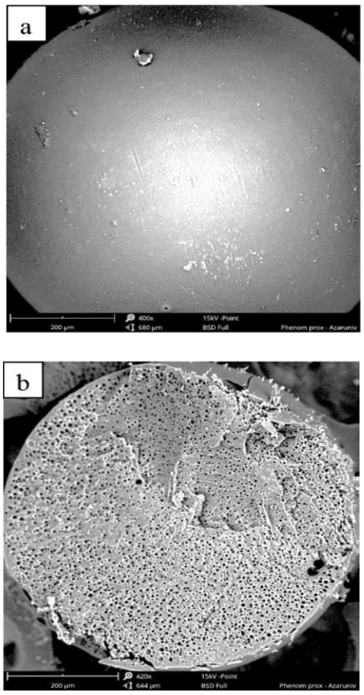

Fig. 2: Scanning electron micrograph of the VBC/DVB copolymer (a) surface, (b) cross-section.

sulphuric acid. The result is an ammonium sulfate solution. An excess base (NaOH) was added to the acid digestion mixture to convert NH_4^+ to NH_3, followed by boiling and condensation of the ammonia NH_3 gas in a receiving solution. The amount of nitrogen in the sample was measured via direct acid-base titration and a strong acid of known concentration (HCl). The chlorine content (Volhard's methods) was measured by burning about 20 mg of the dry polymer sample in oxygen in a flask containing 3% hydrogen peroxide solution.

Metal sorption

The adsorption experiments were carried out under batch/static conditions with conical flasks (150 mL). The amount of adsorbed metal ions on the resin were determined from the initial and final ion concentration in the solution. All equilibrium adsorption experiments were conducted at 290 K. The pH of the investigated solutions was adjusted to one by adding sulfuric acid, and the value held constant throughout the studied temperature. Since in industrial bearing solutions, Mo is present in a much higher concentration than Re, so, in the current study, the concentrations of Re and Mo were simulated comparable to real conditions and the procedure for equilibrium experiments involved with the rhenium ions concentrations of 100 mg/l and Mo concentration of 500 mg/l. A 50 mL of prepared solutions in series of flasks was mixed with a known amount of resins, about 0.05 gr. The resins were swelled in deionized water for eight hours before adding to the flasks. It is noteworthy that when resin swells, the pore size of the resin increases, and therefore the diffusion rates are increased. This phenomenon affects the solvent uptake and also the solvent activity in the resin. Polar solvents are better swelling agents than nonpolar solvents due to stronger interactions between the solvent and the ions and ionic and polar groups of the resin. The flasks were kept in a shaker equipped with a thermostat at a speed of 180 rpm for 10 h. The capacity of adsorbed metal was calculated from the mass balance equation as follows:

$$q_e = \frac{C_0 - C_e}{W} V \tag{4}$$

where C_0 is the initial concentration of ions in solution (mg/L), C_e stands for the equilibrium concentration measured after adsorption (mg/L); V is the total volume of solution (L), and W is the weight of the dry resin (g) [24].

Table 2: Water gain and N content of resins before and after the amination process.

Sample	Water regain (g/g)	N (mmol/g)
Copolymer	0.29	
Resin A	1.61	3.73
Resin B	1.32	3.81
Resin C	1.76	3.89

The distribution coefficient of metals (K) was calculated as the ratio of the amount of metal adsorbed by 1 g of resin and the amount of metal remaining in 1 mL of the solution after sorption [25].

RESULTS AND DISCUSSION

Resins modification

In this research, three new anion exchange polymers were prepared by suspension polymerization. The copolymers were modified to be used to separate perrhenate anions from the molybdenum ions. The copolymerization of vinyl benzyl chloride with divinylbenzene was carried out to obtain cross-linked polymers. The extent of substitution was investigated by chlorine analysis before and after the amination process. The chlorine content of starting copolymer was 3.95 mmol/g and later reduced to zero, which means the amine groups completely reacted with chloromethyl groups of the copolymer. The results of water gain and N content of resins before and after the amination process are shown in Table 2. As seen from data, in general, the amine-modified resins have higher, about five times, water content than the unmodified copolymer of VBC and DVB. Also, the N content of the resins increased, which confirmed the complete amination of the copolymer.

Resins Characterization

The structures of all modified resins were investigated by the FT-IR spectroscopy and were compared with VBC/DVB copolymer to depict the substitution of chloromethyl groups by amines. FT-IR spectra of the copolymer, resin A, B, and C are shown in Fig. 3. The disappearance of the chloromethyl groups stretch vibration at wavenumbers of 673 cm^{-1} and 1260 cm^{-1} along with the appearance of the new peak at 1050 cm^{-1}, which ascribed to the stretching vibration of the C–N bond [26], confirmed the successful amination of copolymers.

Table 3: Re and Mo uptake from binary solution.

Resin	Sorption		K		β
	Re (mg/g)	Mo (mg/g)	Re	Mo	Re
Dowex 21K	32.4	68	479.3	157.4	3.0
Purolite A170	40.7	67	686.3	154.7	4.4
A	21.9	20	280.4	41.7	6.7
B	30	0	428.6	0.0	….
C	46.4	46	870.5	100.9	8.6

K is the distribution coefficient, and β is the separation factor.

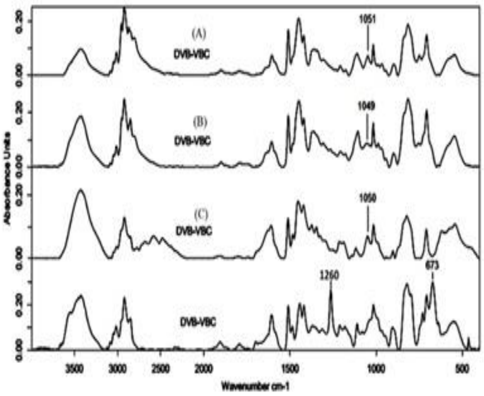

Fig. 3: The FT-IR spectra of the copolymer VBC/DVB and the resins A, B, C.

The resins in swollen forms were used to examine the perrhenate ions separation from molybdenum ions in acidic solutions under the conditions presented in the experimental section. The results shown in Table 3 reveal that the resin C shows the highest distribution coefficients and sorption capacity towards perrhenate ions. The reason is attributed to the structure of resin. Resin B did not interact with molybdenum.

The increase in base strength creates a steric hindrance to the amine group for the molybdenum polyanions binding and so they partially were sorbed only by surface functional groups [21,27]. Molybdenum polyanions ($Mo_8O_{26}^{4-}$, $Mo_7O_{24}^{6-}$) are known that generally form in acidic solutions (1<pH<5) and are substantially larger than perrhenate ions [21,28].

The separation factor (β) was used to the characterization of the selectivity of investigated resins. It was expressed as the ratio of the distribution coefficient of two metal ions (Re & Mo). As presented in Table 4, the selectivity of rhenium was calculated in the following order, B>C>A>. However, it should be pointed out that the distribution coefficient of the resin C is more than twice the resin B. So, the resin C seems to be more advisable adsorbent for application in hydrometallurgical or Re/Mo separation procedures. The adsorption of two commercial anionic resins, including the Dowex 21K resin, a strong base/gel-type with quaternary amine functional groups, and the Purolite A170 resin, a weak base complex amine /macroporous-type, were also evaluated and the results are shown in Table 3. Not only the resin C is effective than resin A and B, but it is also better than the commercial ones.

CONCLUSIONS

Three ion-exchange resins with different amine functional groups were synthesized. The obtained polymers then were characterized and tested for their sorption capabilities of perrhenate ions from Re/Mo binary solutions. Different characterization methods were used to be more detailed on the evaluation of newly obtained resins' affinity toward rhenium ions. The results showed that the structure of amine has an essential role in the sorption of target ions. The most efficient one was resin C and maximum separation factor (β), 8.6 which made the resin better than the two common commercial resins. The results also showed that by modifying the amine groups, the amount of Re ions absorbed increased, while the sorption of rival ions (Mo) shifted down.

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