Int. J. Chem. Sci.: 13(2), 2015, 990-996
ISSN 0972-768X
www.sadgurupublications.com

THE ANION EXCHANGE RESIN BASED ON DIGLYCIDYL BENZYLAMINE AND POLYETHYLENIMINE TO EXTRACT PERRENATE IONS

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ABSTRACT

Sorption new perrhenate anion ion on the diglycidyl benzylamine and polyethyleneimine was studied. The influence of the concentration and pH of model solutions of ammonium perrhenate, and the time of their contact with the ion exchanger at its absorption capacity were observed. It was found that the adsorption capacity of the anion exchanger for removing ions from solution ReO_4^- (NH_4ReO_4) containing 1.02 g/L of rhenium was 373.6 mg of Re/g.

Key words: Anionites, Benzylamine, Aniline, Polyamines, Sorption, Rhenium.

INTRODUCTION

Rhenium is one of the rarest elements in Earth's crust with an average concentration of 1 ppb; other sources quote the number of 0.5 ppb making it the 77th most abundant element in Earth's crust[1,2]. Rhenium is probably not found free in nature (its possible natural occurrence is uncertain), but occurs in amounts up to 0.2% in the mineral molybdenite (which is primarily molybdenum disulfide), the major commercial source, although single molybdenite samples with up to 1.88% have been found[1,3].

Commercial rhenium is extracted from molybdenum roaster-flue gas obtained from copper-sulfide ores. Some molybdenum ores contain 0.001% to 0.2% rhenium[1-4]. Rhenium (VII) oxide and perrhenic acid readily dissolve in water; they are leached from flue dusts and gasses and extracted by precipitating with potassium or ammonium chloride as the

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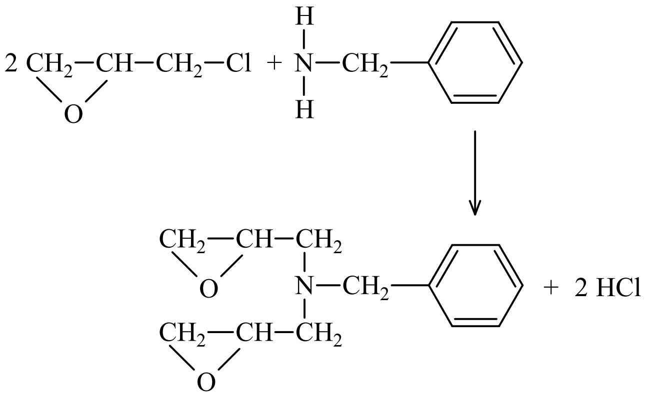
perrhenate salts, and purified by recrystallization[1,5]. Total world production is between 40 and 50 tons/year.

Sorption methods are the most simple, less expensive, well-managed and energetically favorable process, characterized by the absence of secondary pollution[6]. They consistently and increasingly widely used in different industries, technologies, research and chemical analysis, including analytical chemistry of rhenium and to obtain it[7,8]. Therefore, the creation of associated sorbents for extraction of rhenium from the rhenium-containing raw materials is an important issue.

Anion based diglycidyl benzylamine and polyethyleneimine (PEI) was synthesized in two steps. First of epichlorohydrin (ECH) and benzylamine (BA) was obtained diglycidyl benzylamine having high reactivity due to the presence in it of a busy cycle α-oxide, according to the **Scheme 1**.

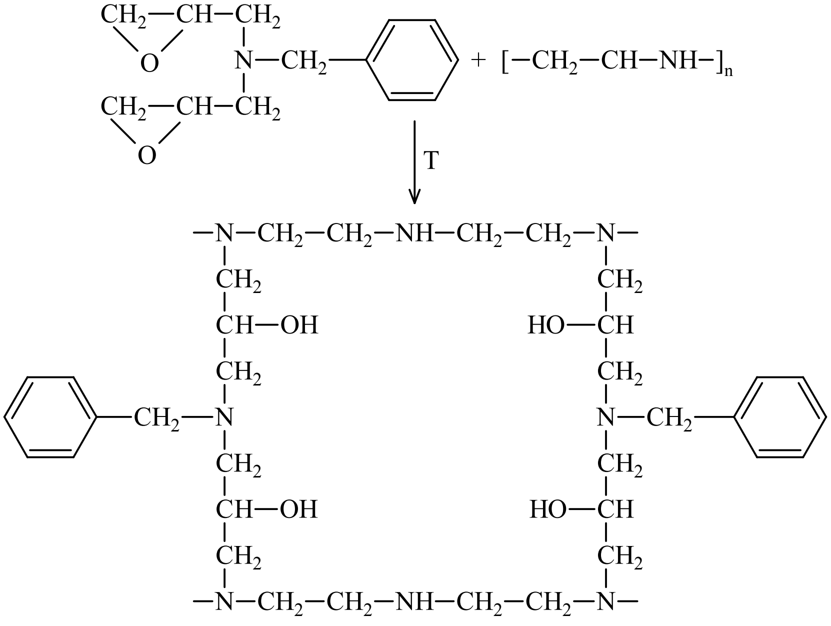


Scheme 1

Used for the synthesis of a soluble anion PEI with a large number of amino groups. Amination diglycidyl benzylamine was carried out in dimethylformamide medium, the use of which will prevent local overheating due to the exothermic effect opening of the epoxide groups, according to the **Scheme 2**.

In the interaction of the BA, ECG with PEI is a sequential nucleophilic addition of the amino groups with epoxy groups. As a result, a new multi-functional macroreticular anion exchange resin BA-ECH-PEI static exchange capacity (SEC) in 0.1 N HCl solution of 7.76 meq/g. Study its sorption capacity with respect to the ions of rare metals is of scientific interest to identify possible areas of practical application of the anion exchanger.

The purpose of the work is studying sorption ReO_4^- ions by anion exchanger BA-ECH-PEI.



Scheme 2

EXPERIMENTAL

Sorption of ReO_4^- ions by BA-ECH-PEI anionites in the OH form (grain size 0.5-1 mm) was studied in static conditions at sorbent to solution ratio equal to 1:400, room temperature 20 ± 2°C, by varying concentration of rhenium in NH_4ReO_4 solution between 0.102 and 1.024 g/L and changing their acidity between pH 1.2 and 6.2 adding 0.1 N of H_2SO_4 or NaOH solution. Duration of sorbent contact with the solutions was between 15 minutes and 7 days. For the preparation of model solutions used NH_4ReO_4 salt production company «ALDRICH» (the USA).

Sorption capacity (SC) was calculated from the difference between the initial and the equilibrium concentration of the solutions, which were determined by classical polarography on a background of 0.5 N H_2SO_4 on the waves recovery ReO_4^- ($E_{1/2}$ = – 0.5 V). Polarographic curves were recorded on a universal polarograph PU-1 in cell thermostated at 25 ± 0,5°C using a dropping mercury electrode. Oxygen was removed from the solutions analyzed by blowing argon for 5 mins. As reference electrode a saturated calomel electrode serving.

RESULTS AND DISCUSSION

Investigation of the effect of solution concentration on sorption properties NH_4ReO_4 anion BA-ECH-PEI showed that ions ReO_4^- are almost completely absorbed from solutions containing 0.1-0.7 g/L of rhenium, the degree of removal (A) constitutes 96-97% (Fig. 1). When the concentration of the rhenium to 1.02 g/L, it decreases slightly, reaching 90%.

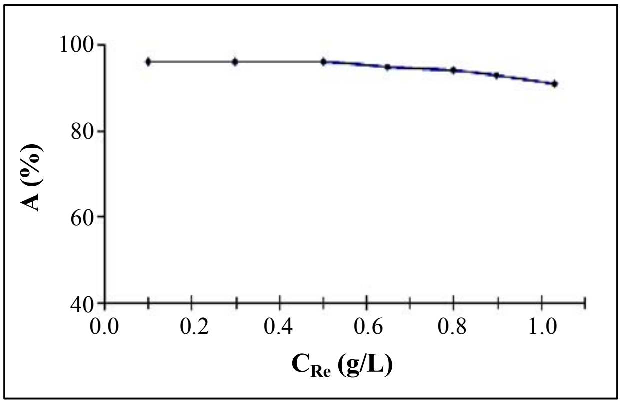


Fig. 1: The degree of extraction of perrhenate anion ion BA-ECH-PEI concentration solutions NH_4ReO_4. Time of contact is 7 days

Fig. 2, which shows the sorption isotherm rhenium ions anion BA-ECH-PEI implies that its SC increases with increasing content of the solution and extracting NH_4ReO_4 perrhenate ions from a solution containing 1.02 g/L of rhenium and having a pH of 6.2 equals 370.4 mg/g.

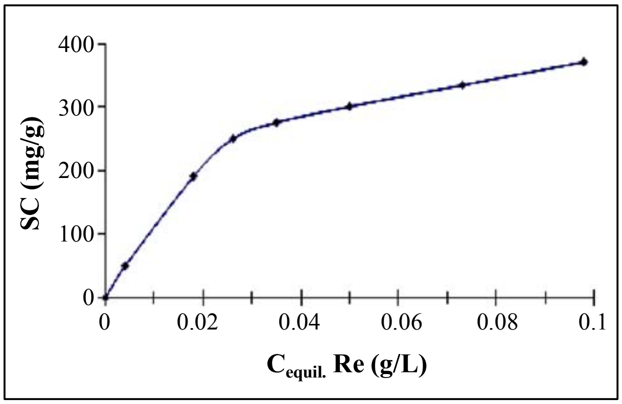


Fig. 2: Sorption isotherms of perrhenate ions by anionite BA-ECH-PEI. Time of contact is 7 days

Fig. 3 shows that in the pH range of 1.2-6.2 pH solution NH_4ReO_4, which varies by adding 0.1 N solution of H_2SO_4, has no significant effect on the sorption of perrhenate anion ion BA-ECH-PEI. This is probably due to the lack of competitive sorption of acid anions, as the ionic radius ReO_4^- ion larger than the radius of the anion SO_4^-, and the charge is correspondingly less.

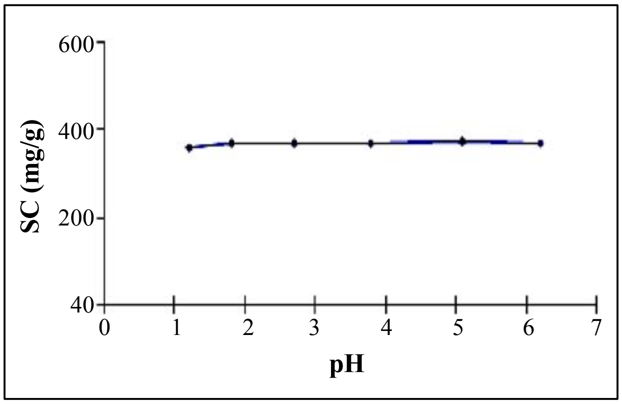


Fig. 3: Impact of acidity of NH_4ReO_4 (C_{Re} = 2.1 g/L) solutions on sorption of rhenium ions by anionites BA-ECH-PEI. Time of contact is 7 days

It is known, that the selectivity to the anion exchangers anions is higher, the larger the size of the anion is less than the charge and thereby its lower hydration[9]. Having a low charge, larger and less hydrated anions under the influence of the structure of water more easily displaced by a phase of the anion exchanger, in which water is less ordered structure, and form ion pairs there with hydrophobic cations-functional groups of anion exchangers. Therefore, single-shot, larger and less hydrated anion ReO_4^- should sorbed more selective than the ion SO_4^-. The maximum absorption of ions ReO_4^- observed at pH 5.1. The degree of extraction and SC anion exchanger BA-ECH-PEI, up respectively, 99.5% and 373.6 mg/g.

Fig. 4 shows the kinetic curve of sorption of ReO_4^- anion BA-ECH-PEI. The equilibrium between it and a solution containing 0.94 g/L of rhenium and having a pH of 5.1, occurs within 2 hrs. However, it should be noted that after 15 mins absorption of rhenium ions is 94%.

The authors of that synthesized from lignin, ECH and PEI oligomer ion exchanger containing predominantly NH_2-, NH-groups, similar to those obtained by us anionites BA-ECH-PEI fuller extracts perrhenate ions in environments close to neutral (pH 5-6)[10]. Full sorption equilibrium is established in the first ion exchanger for 2 hr, and SC is 232.8 mg/g, that is 1.6 times smaller than that of the BA-ECH-PEI. Industrial anion exchanger AN-

21x16 ReO_4^- when removing ions from a solution containing 0.93 g/L of rhenium has an even lower capacity equal to 34.3 mg/g[11].

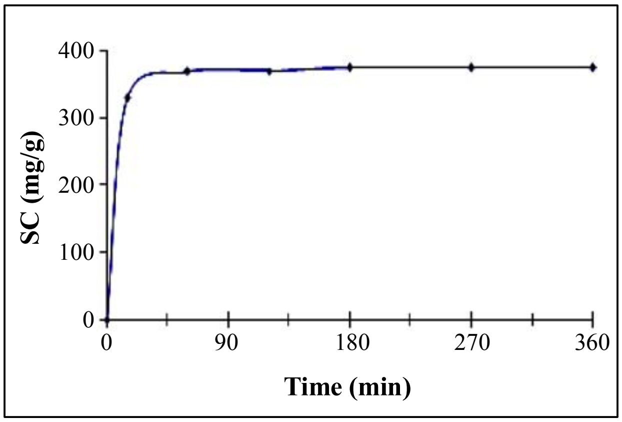


Fig. 4: Dependence ReO_4^- anion ion sorption BA-ECH-PEI on the duration of its contact with a solution of NH_4ReO_4 (C_{Re} = 0,94 g/l, pH = 5,1).

SC anion copolymer of glycidyl methacrylate and 3-propylene glycol diacrylate and when removed from the PEI solution containing 0.1 g/L of rhenium is 30 mg/g[12]. Under similar conditions, the capacity of the anion exchanger BA-ECH-PEI reaches 39.2 mg/g. Industrial anion exchangers EDE-10P, AN-2 F, AN-21, AN-22 have an even lower absorbency and recovered 18.9; 20.5; 25.5 and 28.3 mg of Re/g[12].

CONCLUSION

The novel anion exchanger BA-ECH-PEI has a high sorption and kinetic properties with respect to the perrhenate ions and its use is promising for efficient retrieval of technological solutions formed in the processing of raw rhenium.

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Revised : 15.03.2015 *Accepted : 17.03.2015*