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Recovery of Scandium from Chloride Media Using the Novel Ion Exchange Resin

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Abstract -This study focused on separation and recovery of scandium from chloride solution using the new synthesized ion exchange resin. The resin containing glycol amic acid groups shows the possibility to recover scandium from chloride aqueous solutions. At pH 1, the adsorption selectivity of scandium can be obtained among the others metals. The kinetic adsorption of scandium by the resin was found slowly, and contact time 24 hours was chosen as a suitable time in this study. The elution of scandium from the loaded resin could be completed with 2 M HCl solution at 80 °C. The close process will be established based on the optimum parameters which are obtained throughout this investigation, and that process can be applied in metal extraction processing for recovery of scandium and the other rare earth metals using the novel ion exchange resin.

Keywords: Scandium(III); Rare earth metals; Adsorption; Resin;

1. Introduction

Scandium is known as one of rare earth elements, which has been used in metal halide lamp, electronics, strengthen alloy, aerospace, airplane construction, catalyst ceramics, etc. Extraction and separation of scandium from the ores are difficult therefore, scandium is expensive and its application in industry has been limited (Xu et al., 2013). Pyrometallurgy is a suitable technology for recovery of scandium from its ore containing high scandium content. However, the high energy consumption and environmental pollution are considered to make this technology to be less attractive. Hydrometallurgical technology is an alternative method to the traditional pyrometallurgy for recovery of metals from primary and secondary sources because of its advantages such as low capital cost with suitability for small scale application, reduced environmental degradation and high metal recoveries (Tuncuck et al., 2012). In hydrometallurgy, leaching is a fundamental process using lixiviants such as acids (sulfuric, hydrochloric, nitric acid), cyanide, thiosulfate or alkaline solutions, to dissolve desired metals (Jadhay and Hocheng, 2012). There are several techniques to separate and recover the rare earth metals from aqueous media such as precipitation, solvent extraction, adsorption and ion exchange resin, etc. Goto and his research group have developed extractants containing glycol amic acid group which are selective for extraction of rare earth metals, and the works have been published in several patents and scientific journals (Goto et al., 2013; Kubota et al., 2011; Sasaki et al., 2013; Shimojo et al., 2014; Yang et al., 2013). In that investigations, the extractants containing the glycol amic acid showed effectively and selectively extraction of rare earth metals from the mixture of diversity of metals. However, the disadvantages of solvent extraction have been pointed out such as the loss of extractant, phase separation, third phase formation, etc. (Nguyen et al., 2013). The recovery of rare earth metals from aqueous solutions using resin has been investigated by many researchers (Chao et al., 1981; Gasser and Aly, 2013; Korovin and Shestak, 2009), but there are no adsorbent containing the special functional groups for selective adsorption of rare earth metals in practical use. Therefore, the new idea is generated to develop the adsorbent containing glycol amic acid group for recovery of rare earth metals. The Japanese company has synthesized successfully the resin containing the glycol amic acid, which is used in this study to explore the possibility in separation and recovery

of the rare earth metals from aqueous chloride solution. The adsorption between metals and resin is investigated to find out the appropriate adsorption behavior.

2. Experimental

2.1. Materials

In order to carry out the adsorption studies, the synthetic solutions containing scandium, cerium, lanthanum and aluminum of 20, 750, 300 and 2000 mg/L were prepared similarly to the composition of the chloride solution generating in the rare earth extraction processing of monazite, by dissolving metals chloride in de-ionized water. The chemicals viz. scandium, cerium, lanthanum, aluminum chloride, hydrochloric and sulfuric acid, etc. were laboratory grade reagents. The resin was provided by the Japanese company, was used throughout this study.

2.2. Methods

The experimental studies for the adsorption and elution of the metals using the resin were performed in batch test. The batch experiments were carried out using a conical flask in a shaking water bath under atmospheric conditions using the resin.

The percentage adsorption was calculated using the following equation:

Adsorption(%) =
$$\frac{(C_o - C_t)}{C_o} \times 100$$
 (1)

Where C_o is the initial concentration of metal in the feed and C_t is concentration of metal in raffinate at time t (mg/L).

The metal content of the samples was analyzed by Inductive Coupled Plasma (ICP-OES, SPECTRO, Germany) to determine scandium and other metals concentration in the solutions before and after contacting with resin beads.

3. Results and Discussion

3. 1. Effect of Solution Ph on Adsorption of Scandium

The experiments were carried out with 0.1 g resin and 100 mL of synthetic solutions in various pH range. Fig. 1 indicated that adsorption of scandium increases from pH 0 till pH 2, and at pH 1 the selectivity adsorption of resin for scandium was obtained among other metals Ce, La, Al.

The reason to explain the selectivity behavior is come from the radius pore of resin and ionic radius of metal species. The ionic radius of scandium (7.4 nm) is known as the smallest among the rare earth elements. This factor allows ionic scandium can enter inside the resin and react with functional groups. For cerium and lanthanum, their ionic radius are bigger than pore size of resin (radius 8.51 nm), therefore they could not penetrate inside resin.

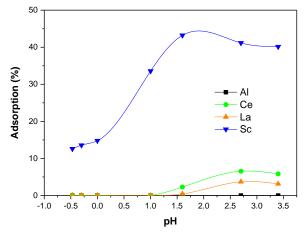


Fig. 1. Effect of pH on adsorption of metals using the resin

The other thing is the dissociation of resin. The resin is weak cation exchanger because it contains carboxylic acid functional groups which are less active at low pH. The dissociation of the resin in aqueous solution can be expressed:

$$R-NH-COCH_2-OCH_2-COOH \quad \rightleftharpoons \quad R-NH-COCH_2-OCH_2-COO^- + H^+$$
(2)

Equation (2) indicates that when pH decreases (acidity increases), the equilibria tends to shift to right side to form un-dissociated resin. Thus, the adsorption capacity of resin for metals is decreasing as less dissociated functional groups.

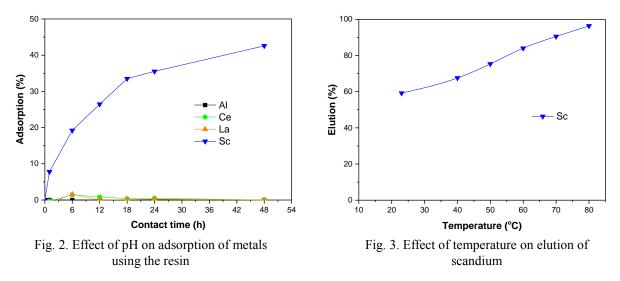
The adsorption reaction between scandium and resin is proposed as follows:

$R-NH-COCH_2-OCH_2-COO^- + Sc \rightleftharpoons (R-NH-COCH_2-OCH_2-COO)_3Sc + 3H^+$ (3)

When pH increases, the dissociation of resin is increasing, and the existence of species Sc^{+3} , Ce^{+3} , La^{+3} are dominant, therefore the adsorption efficiency increases.

3. 2. Effect of Contact Time

The effect of contact time on the adsorption of scandium(III) by the resin was studied using 0.1 g of resin and 100 mL of synthetic solutions (liquid/solid, A/R: 1000 (v/w)) in different stoppered flasks with varying time from 1 to 48 hours. The adsorption of scandium(III) on resin was found to be increased with increasing time. The result in Fig. 2 shows that the adsorption of scandium on the resin was slow, and the equilibria can be obtained after longer time (more than 48 hours). Therefore, contact time 24 hours was chosen as a suitable time in this investigation.



3. 4. Elution Of Scandium(III) In Batch Experiment

For the elution of scandium from the loaded resin was carried out in the batch test. The Sc loaded resins (7.27 mg Sc/g resin) was eluted by HCl in different concentration. The results obtained to indicate that the percentage elution of scandium increases with increasing concentration of HCl until 2M, and decrease when increase HCl above 2 M. Therefore, concentration of HCl at 2 M was selected for recovery of scandium from the loaded resin throughout this study. The elution mechanism of scandium by HCl eluent might be described as following equation:

$$(R-NH-COCH_2-OCH_2-COO)_3Sc + 3H^+ \rightleftharpoons 3R-NH-COCH_2-OCH_2-COOH + Sc$$
(4)

With the purpose to increase the elution efficiency of scandium from loaded resin, the experiments were carried out with 2 M HCl concentration at different temperature. Fig. 3 depicted that the elution efficiency of scandium increase in increasing temperature, and elution can be completed at temperature 80 $^{\circ}$ C.

4. Conclusions

The resin was found to adsorb effectively and selectively scandium(III) at pH 1, and the adsorption selectivity of the resin for scandium among the mixture is suggested from the pore size of the resin beads. The kinetic adsorption of scandium by the resin is slow, and contact time 24 hours was chosen as a suitable time in this study. Scandium loaded on the resin can be eluted completely by 2 M HCl eluent at temperature 80 $^{\circ}$ C.

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