Anion exchange removal of Al^{3+} from Li$^+$-Al^{3+} aqueous solution (originating from lithium recovery from brine)

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Abstract: The purpose of this study is to separate aluminum(III) ion from an aqueous solution containing Li$^+$ at 25°C. Al^{3+} was transferred into [Al(C$_2$O$_4$)$_3$]$^{3-}$ by means of complexation and removed by an anion exchange resin. This resin was anionic type Amberlite IRA 402 regenerated by sodium chloride. Hence, a theoretical study based on speciation diagrams was carried out to determine the best pH domain for separation. The complexation of aluminum ions by ammonium oxalate was studied. The motar ratio of Ox/Al and pH was investigated. Optimum values of these factors were found to be 3 and 4 respectively. In this case, the remaining lithium is 98.5%.

Keywords: Anionic exchange resin; speciation diagrams; lithium remaining; aluminum; ammonium oxalate.

Introduction

As the lightest metal in the periodic table, lithium is widely found in trace amounts in most rocks, soils and natural waters. It is electrochemically reactive and has a low thermal expansion coefficient. It has also the highest specific heat of the solid elements. Some lithium compounds also possess flat viscosity/temperature ratios[1].

During the 1980s, the technology of recovering lithium ions from salt brines was successfully applied in industrial processes. Salt Lake brines have overtaken the place of solid minerals as the main source for recovering lithium ions over the world[2,3].

Since the typical composition of brines differs, researchers have developed many technologies for lithium recovery, including organic solvents extraction[4], ions exchange extraction[5], precipitation[3], adsorption by acid and sodium Amberlite[6,7], extraction using supported liquid membranes[8], nanofiltration method[9], adsorption on novel nanocrystal MnO$_2$[2,10], and so forth, from lithium-containing brines.

Economically speaking, recovering lithium from brine with a high Mg/Li ratio has been a worldwide problem, which seriously restricts the extraction and processing of lithium. Researchers have managed to employ various methods to deal with it[1,11-17].

The above techniques are justified considering that the mass ratio between lithium content in such a brine and total dissolved salts, is about 6×10^{-5}. Thus to make the recovery of these lithium traces easier, it would be convenient to keep this element in a new matrix which brings back the ratio (Li/new matrix salt) to a higher value. On that basis and with respect to many published results[12], Li trapping by fresh prepared Al hydroxide was adopted.

After that, a solid/liquid separation was conducted in order to recover a solid phase enclosing the major part of initial lithium in the brine. Subsequently the solid phase relatively concentrated in lithium was dissolved in order to prepare a new solution containing especially Li^+ and Al^{3+}. Such solution will be treated again in order to form a pure Li^+ final solution. Hence anion exchange technique was chosen for the above purpose. Indeed, this technique has been widely used for metal ion separation since the pioneering work of Riley and Taylor[18]. The success of ion exchange resins was mainly due to their high specificity and sorption strength for metal ions that are complexed with the active groups they present. For this purpose, a theoretical study based on the speciation diagrams was performed to identify the pH domain making such separation easy.

Finally, the objective of the present paper is to separate lithium ion from an aqueous solution containing a mixture of Al^{3+} and Li^+ by anion exchange resin after aluminum complexation.

Experimental Section

The included reagents are: lithium chloride (+99% ROTH), sodium chloride (99% SIGMA-ALDRICH), aluminum chloride hexahydrate (+99% Prolabo), ammonium oxalate monohydrate (99% MERCK), hydrochloric acid (37% Prolabo) and anionic exchange resin Amberlite IRA-402. Lithium and aluminum were determined using Vario-6 atomic absorption spectrometer. Apparent pH was measured using a 691 Metrohm pH-meter. Chloride concentration was measured by potentiometric analysis using Titrino DMS 716 and a silver nitrate solution (0.1N). Powder X-ray diffraction (XRD) analysis was carried out to identify the phase of the materials using PHILIPS PW 3040generator.

The complexation of aluminum with oxalate was carried out by first introducing Al^{3+} into the solution containing Li^+, then Al^{3+} was complexed using the ammonium oxalate at the same time using a strong base or acid solution to vary pH.

The maximum of lithium trapping was achieved at molar ratio Al/Li = 5^{12}. The molar ratio for Ox/Al was fixed at 3 as reported in the remainder of this work (see Figure 1).

The experimental protocol consists of adding 2.98 g of $(NH_4)_2C_2O_4.H_2O$ to 39 mL of Al^{3+} (0.18M) and 5 mL of Li^+ (0.28M). pH values were varied between 3 and 10 usinghydrochloric acid or sodium hydroxide (2M). The resulting mixtures undergo a solid/liquid separation using a centrifugation step followed by a membrane filtration (ϕ 50 mm, 0.2 μm). Then, filtrates were chemically analyzed using an atomic absorption spectrometer (For Li^+: $\lambda Li^+ = 670,8$ nm, flame: C_2H_2/Air, standard: 0.5, 1, 2, 4 and 5 ppm. For Al^{3+}: $\lambda Al^{3+} = 309,3$ nm, flame: N_2O/C_2H_2, standard: 10, 20, 40, 50 and 100 ppm).

Prior to use, the resin Amberlite IRA402 was regenerated with NaCl solution (1M) and rinsed with ultra-pure water. The exchange capacity is defined as the total number of ionizable groups expressed in millimoles per gram of dry resin.

Potentiometric titration was used to determine chloride concentration released by a well-defined mass of resin. In this case, chloride concentration was 0.03 molL^{-1} and the anionic exchange capacity of the Amberlite IRA-402 was 1.5 mmol g^{-1}dry resin.

Results and Discussion

Lithium trapping from highly concentrated solutions using aluminum hydroxide as an adsorbent was studied[19]. It is reported that the maximal lithium retention using aluminum

hydroxide gel is 95%. That procedure leads to a two-component system (Li^+/Al^{3+}) which should be separated in order to form a pure Li^+ final solution. For this purpose the use of exchange ion resin is adopted. However the solution contains two ions under cationic form which leads to the idea of changing the positive charge of Al into a negative charge by complexing it. The use of $C_2O_4^{2-}$ is approved.

Visual MINTEQ version 2.61 software was used to establish the chemical species present in the Al-Ox system. Such diagram is helpful to predict the behavior of formation and dissolution of chemical species in considered pH conditions and consequently their possible separation.

The variation of aluminum complex $[Al(C_2O_4)_3]^{3-}$ during pH variation in the range (0-4) is represented in Figure 1. After testing several molar ratios Ox/Al (1-5) it was found that 3 is the best molar ratio because aluminum is present at 100% anionic form $[Al(C_2O_4)_3]^{3-}$ from pH 3.5.
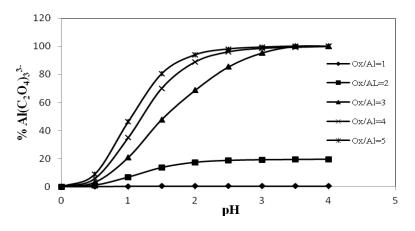

Figure 1. Percentage of $[Al(C_2O_4)_3]^{3-}$ versus pH for different molar ratios Ox/Al

Figure 2 shows the effect of pH on the precipitation of lithium and aluminum by means of ammonium oxalate at molar ratios Al/Li = 5 and Ox/Al = 3. It is established that a pH increase above pH 7 favours precipitation of lithium and aluminum. Maximum precipitation of lithium and aluminum is obtained at pH = 9, wherein only 15% aluminum and 34% of lithium remain in solution. Almost 100% of lithium and aluminum remained in the solution at a pH less than 4. Therefore, it is interesting to know the distribution of lithium and aluminum ions in this pH range (<4). To this end, a theoretical study based on the speciation diagrams of all species was made to specify the pH favouring the separation.
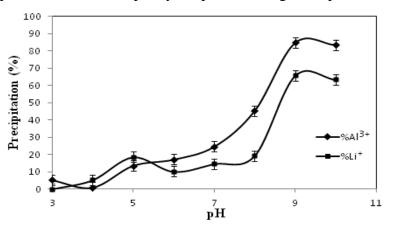

Figure 2. pH effect on the degree of precipitation of lithium and aluminum by means of ammonium oxalate

As indicated by Figure 2 the addition of oxalate causes the simultaneous precipitation of aluminum and lithium at different pH > 4. XRD pattern (Figure 3) confirms the precipitate of aluminum as aluminum oxalate and aluminum hydroxide.
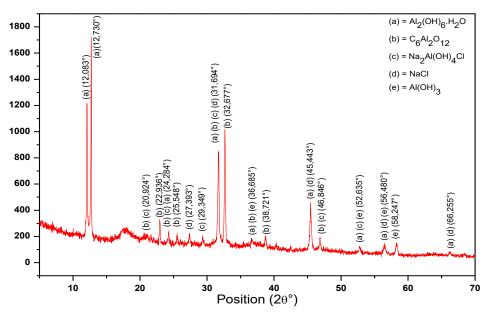

Figure 3. XRD patterns for the precipitate formed at pH = 9

Speciation diagram of aluminum is represented in Figure 4. The result of modeling is obtained for solutions mixture at molar ratios Al/Li = 5 and Ox/Al = 3 at different pH values (0-4). Figure 4 shows in the range of pH 0-4 five ionic species of aluminum (Al^{3+}, $[AlH(C_2O_4)]^{2+}$, $[Al(C_2O_4)_3]^{3-}$, $[Al(C_2O_4)_2]^-$ and $[Al(C_2O_4)]^+$). The above ionic species have maximum pH respectively at 0, 0,4, 1 and 0.5.

It should be noted that aluminum is present almost 100% as anionic form $[Al(C_2O_4)_3]^{3-}$ at pH = 4. On the other hand the analysis of speciation diagram of lithium shows the predominance of Li^+ which has a stable variation for pH between 0 and 4.

From these results, the pH value which effects the separation between the considered ions is 4 because in this value, the aluminum is present as anionic form $[Al(C_2O_4)_3]^{3-}$ and lithium as cationic form Li^+.

Thus, the use of Amberlite IRA-402 (anion exchange resin) allows the uptake of aluminum complex $[Al(C_2O_4)_3]^{3-}$ and the rejection of cationic lithium form (Li^+).
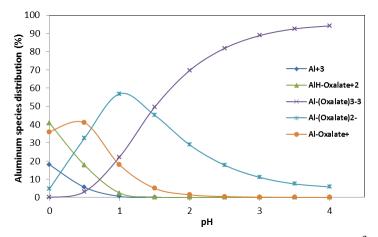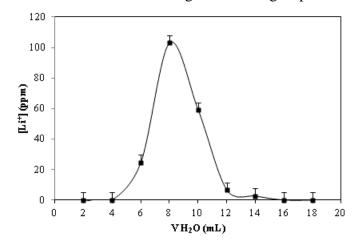

Figure 4. Aluminum species repartition as function of pH values. $[Al^{3+}] = 0.14$ mol L^{-1}
$[(C_2O_4)^{2-}] = 0.42$ molL^{-1}

Table 1. Soluble organic Al and Li species and formation constants (log form) used for Al and Li speciation with visual Minteq.

Species	log K	Source
$[Al(C_2O_4)_2]^-$	13.41	20
$[Al(C_2O_4)_3]^{3-}$	17.09	20
$[AlH(C_2O_4)]^{2+}$	7.46	20
$[Al(C_2O_4)]^+$	7.73	20
LiCl(aq)	-0.16	21

Washing volume of Amberlite IRA 402 was also performed in order to reject lithium ions contained in the resin coating solution. During this process, lithium ions were rejected with a constant flow of ultra-pure water. The evolution of Li^+ concentration according to added H_2O volume is reported in Figure 5. This figure shows that all lithium is released after the addition of 16 ml H_2O. The mass balance for the loading and washing steps is determined in Table 2.

Figure 5. Lithium washing curve during Li^+/Al^{3+} separation by Amberlite IRA402 (bed volume BV=20mL, bed volume capacity = 1mvalBV^{-1}, flow rate = 4mLmin^{-1})

Table 2. Mass balance for lithium washing process.

V $_{H2O}$(mL)	2	4	6	8	10	12	14	16	18
C_i(ppm)	0	0	24.6	103.1	59.1	6.6	2.6	0	0
Li^+ (mg)*	0	0	0.0492	0.2062	0.1182	0.0132	0.0052	0	0
Li^+_{in} (mg)**	0.4000								
Li^+_{out}(mg)***	0.3920								

Li^+ (mg) = C_i. Vi (C_i= Li concentration of recovered volume V_i of washing solution (mg L^{-1}), V_i = 0.002L)
Li^+_{in} (mg) = 200 (mg L^{-1}) $\times$ 0.002 (L)
Li^+_{out} (mg) = $\sum C_i .V_{i =} \sum Li^+$

After resin preparation, lithium and aluminum concentrations were determined using an atomic absorption spectrometer. In our case, the sorption mechanism of $[Al(C_2O_4)_3]^{3-}$ complex by Amberlite IRA-402 may be described according to the reaction:

$$3\ R\text{-}N(CH_3)_3{}^+Cl^- + [Al\text{-}(C_2O_4)_3]^{3-} \longrightarrow [RN(CH_3)_3{}^+]_3[Al\text{-}(C_2O_4)_3{}^{3-}] + 3Cl^-$$

Lithium and aluminum concentration before and after resin separation is reported in Table3.In this case, the remaining lithium is 98.5%.

Table 3. Lithium and aluminum concentration before and after resin separation.

	Before resin separation	After resin separation
Al^{3+} (mg L^{-1})	3790.8	0
Li^+ (mg L^{-1})	200	197
Li^+ (mg)*	10	9.85

*Li^+(mg) = Li^+ (mg L^{-1}) $\times$ 0.05 (L)

Conclusion

This study clearly shows that the anionic exchange resin is suitable for removing aluminum from an aqueous solution containing Al^{3+} and Li^+. Aluminum ions complexation is done by ammonium oxalate. The molar ratio Ox/Al and pH is investigated. Optimum values of these factors are found to be 3 and 4 respectively. In this case, lithium remaining is 98.5%. Finally this study establishes the optimal conditions for Al^{3+} removal as follows: Al^{3+} complexation using oxalate ion at pH = 4, which provides an anionic species, which will be then retained by "Amberlite IRA 402" resin.

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