



Purification of lithium hydroxide by ion-exchange processes for application in nuclear reactors

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1. Introduction

Lithium has applications in the nuclear energy, pharmaceutical, automotive areas. In the last decades, it has been increasingly visible the rising lithium demand in the international market. About 40% of lithium production is used in batteries, 15% correspond to automotive batteries. By 2020 automotive batteries are projected to require about five times as much lithium as in 2016 [1,2].

Lithium is the lightest metal in periodic table with two stable isotopes lithium-6 (Li-6) (7,52%) and lithium-7 (Li-7) (92,47%). It's found in several hard rock types, notably spodumene, and in brines, hence it is often mined in salt lakes, particularly in South America.

In nuclear area, lithium 7 has an important use due to transparency to neutrons. The 99.95% Li-7 hydroxide is use in Pressurized Water Reactor (PWR) as an additive primary coolant, for maintaining water chemistry, counteracting the corrosive effects of boric acid (used as neutron absorber) and minimizing corrosion in steam generators of PWRs. It is also used in the manufacture of chemical reagents and as a basic component for preparation of nuclear grade ion-exchange membranes, which are used in PWR coolant water treatment facilities. The purification is a necessary step that aims to improve the quality of the initial product, increasing the purity of lithium (> 99%). This work aims to purify lithium hydroxide monohydrate (LiOH.H₂O), with purity 99.6%. The impurities present are sodium and calcium. To obtain the purification and separation of impurities, an ion exchange process with a cationic resin was used and the determination of lithium, sodium and calcium was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) [3].

2. Methodology

For the purification of lithium hydroxide, the materials, reagents, equipment and method used in the procedure are listed below [4,5].

2.1 Materials, reagents and equipment

The materials, reagents and equipment used in the procedure were glass column (height x diameter), 20 x 2 cm; 50 mL centrifuge tubes in polypropylene; 50 mL glass beaker; long stem glass funnel of approximately

50 mL capacity; filter paper, slow filtering; nitric acid, HNO₃, 65%, Merck Millipore; methanol, MeOH, Merck Millipore; lithium hydroxide monohydrate (LiOH.H₂O), 99,6%; strong acid cationic resin AG-50W-X8, Bio-rad Labs. INC.; Inductively Coupled Plasma Optical Emission Spectrometry, ICP-OES, Spectro Flame M120, Modula, Spectro Analytical Instruments; peristaltic pump, model Lab N3, Shenchen; pHmeter, model PHS-3BW, Bante Instruments; magnetic stirrer, Quimis; heating plate, Eletolab and analytical balance OHAUS Pioneer IDT 7.

2.2 Methods

The steps of purification method are ion exchange procedure, following filtration, evaporation and reconstitution of the samples. Initially, for the procedure, the column was coupled to a peristaltic pump, and packed with the resin in water and a lithium solution was prepared from the lithium hydroxide monohydrate powder. For the ion exchange procedure, at first, the resin was conditioning with a solution of HNO₃, MeOH and water. Then, the lithium solution was add and the aliquots was collected in centrifuge tubes. Then, the elution solution was added to remove the lithium retained in the resin. The ion exchange conditions are shown in the Table 1.

Table 1: Conditions of ion exchange procedure for lithium purification.

Parameters	Value
Column dimensions, cm (h x d)	20 x 2
Lithium solution volume (mL)	40
pH	3
Flow rate (mL min ⁻¹)	3.00
Conditioning solution	0.2 mol L ⁻¹ HNO ₃ in water
Eluent volume (mL)	1100
Elution solution	0.5 mol L ⁻¹ HNO ₃ in 80% MeOH / 20% H ₂ O (v/v)

The Figure 1 shows the experimental system.



Figure 1: Experimental system of lithium purification.

The aliquot with MeOH was first filter and brought to the heating plate at 80 °C to evaporate the MeOH. Then was again filter to ensure a clear aliquot to the initial volume in order, not damage the analytical equipment. For the determination of lithium, sodium and calcium in the aliquots, analyzes were performed by ICP-OES and from this it was possible to verify the data and compare what method would apply to the purification of LiOH.

3. Results and Discussion

In this study, a methodology was developed to separate lithium from other impurities present in $\text{LiOH}\cdot\text{H}_2\text{O}$, such as sodium (Na) and calcium (Ca). For this, the ion exchange process was used, in which it was possible to observe the separation of lithium and sodium, mainly. The concentration of calcium in the sample is low. The chromatogram is shown in Figure 2, it is possible to observe the separation of the Li and Na.

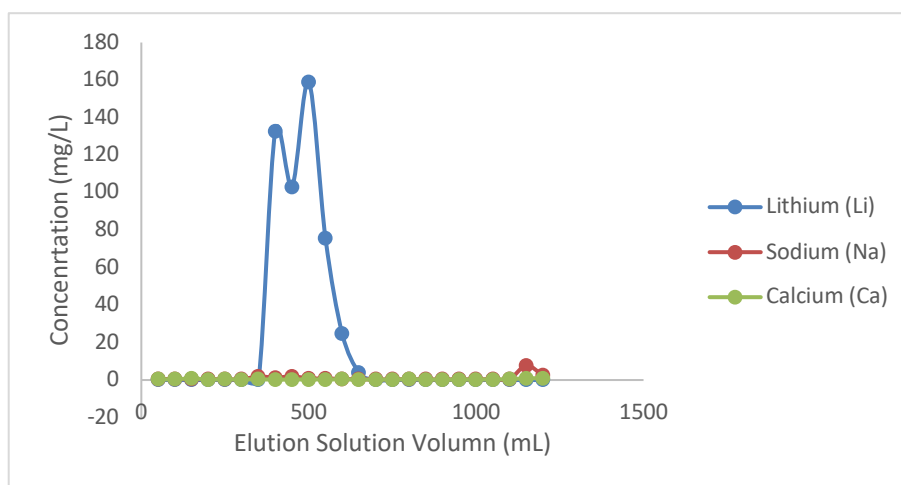


Figure 2: Chromatogram of Li and Na separation by ICP-OES.

From the methodology, the purity of lithium determinate was 96.93%. This recovery can be explained by the strong adsorption of lithium in the column.

4. Conclusions

The lithium and sodium exhibit similar behavior when presents in aqueous solution, a satisfactory separation was obtained through the ion exchange. The lithium's purity obtained was 96.93%. However, for the application in the nuclear activities, the purity must be over 99%. To evaluate which condition impact, more in the ion exchange, other tests evaluating as pH, acid concentration, resin volumn, flow rate and the quantity of organic content will be investigate.

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