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Chemical separation of Li from Na⁺ and K⁺ ions using ion exchange resin (AG 50W-X8)

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ABSTRACT

An ion-exchange method has been developed for separation of Li from alkali elements (Na and K). A column of AG 50W-X8 cation-exchange resin was found appropriate to separate lithium from the solution. In 0.1 M HCl solution sodium and potassium ions were completely stripped and lithium ions was passed from the column without any adsorption. All determinations of ions were performed by Atomic Absorption Spectroscopy. Separation and recovery efficiency was found was 99.24%.

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KEYWORDS

Lithium;
Chemical separation;
Ion exchange;
Alkali Ions;
AG 50W-X8 resin.

1. INTRODUCTION

Lithium is the first element from the alkaline group in the Periodic Table. It has the highest negative electrode potential and is stable only in non-aqueous electrolytes. The lithium-ion battery was "born" in 1991 and grew rapidly as the power source of choice for portable electronic devices, especially wireless telephones and laptop computers, during the past 16 years. Today, the modern world cannot be described without considering lithium-ion batteries^[1]. The search for lithium selective reagents has intensified over the past several years duo to industrial and clinical needs^[2]. Also widely used as catalysts, electrode materials in Li/MnO₂ batteries^[3]. Lithium salts are widely used in the treatment of psychiatric Disorders^[4].

Separation of Li⁺ from other alkali ions is very interest and important. There are different purification methods such as solvent extraction with TOPO ligand^[5], crown ether^[6], adsorption of Li on MnO₂ nano-crys-

tal^[3] and ion exchange. Abe et al. recovered lithium from seawater and hydrothermal water by titanium (IV) antimonate synthetic inorganic cation exchanger^[7]. There is a similar report about separation of lithium from other alkali elements. Strelow et al. separated lithium from sodium, beryllium and other elements by cation-exchange chromatography in nitric acid-methanol^[8]. At this reference, first, lithium and other ions in 0.1 M nitric acid 50% methanol were adsorbed on the AG 50W-X8 Resin and then, eluted by different volumes of 1 M nitric acid. In this work, we improved the previous method^[8] by use of HCl solution and some changes in the procedure. Ion-exchange chromatography is one of the methods commonly employed because there is no limitation in the volume of the sample. Furthermore it is an effective way for separating solute particles and also capable of extracting positively charged ions^[9].

In this work, ion exchange chromatography (negative chromatography) method was used for purification of Li. In this method, lithium ion is not adsorbed on the

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AG 50W-X8 cation-exchange resin while the main impurities Na and K were completely adsorbed. To separate lithium from impurities, different concentrations of HCl, HCl/methanol and HCl/ethanol on AG 50W-X8 cation-exchange resins were used. 0.1M hydrochloric acid was obtained as the most adequate solvent to separate lithium from other elements.

2. EXPERIMENTAL

2.1. Materials

All chemicals were analytical grade and used without further purification. Water was double distilled and AG 50W-X8 (H⁺, 200-400 mesh, Bio-Rad) was used. Borosilicate glass column with 20 cm length and 2 cm diameter with sinter glass plate at the bottom was used. AAS (Atomic Absorption Spectroscopy, Varian Spectra AA-200, Swaziland) was used for analyzing the samples.

2.2. Methods

2.2.1. Preparation of samples

The compounds (LiCl, NaCl and KCl) were weighted by digital weighing machine precisely then they were solved in distilled water or HCl completely. The solution was evaporated to near dryness and several drops of concentrated hydrochloric acid were added to the residue and were evaporated again and dried. This process was repeated several times until the solution was converted to chloride form. Then residue was adjusted with different concentrations (0.05, 0.1, 0.15 M and 3 M) HCl, also /methanol and HCl/ethanol.

2.2.2. Ion exchange chromatography

First the Borosilicate glass column with 20 cm length and 2 cm diameter with sinter glass plate at the bottom was packed with 20 g of AG 50W-X8 (200-400 mesh, H⁺ form) cation-exchange resin and treated with 0.1M HCl solution (150 ml). The 0.1M HCl solution containing Li, Na and K (80 ml) was loaded onto the column, and then the column was washed with 520 ml 0.1 M HCl solution. Li passed; Na and K were adsorbed on the resin. To assure that lithium was eluted completely, last drops were tested by a platinum wire on flame. Nonexistence of a violet flame shows that Li has been came out completely from the cation-exchange resin.

The effect of HCl molarities on the elements adsorption on the resin was investigated by varying the HCl concentration.

To reuse the resin, the impurities were eluted with 3 M HCl. The loading solutions and the eluted one were analyzed by AAS. Detection limit of Atomic Absorption Spectroscopy (AAS) for the elements are in ppm levels.

2.2.3. Calculations

The recovery percentage (separation yield; R.P%) was determined by (eq. 1):

$$\%R.P = \frac{C_i}{C_e} \times 100 \quad (1)$$

Where C_i and C_e are the concentrations of ions in the loaded and eluted solution from the resin, respectively. The distribution coefficient, K_d was determined by eq. 2:

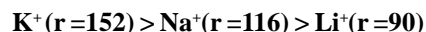
$$K_d = \frac{C_i - C_e}{C_e} \times \frac{v}{m} \quad (2)$$

Where v is the volume of the solution in ml (600 ml) and m is the mass of the resin in gram (20 g). The absorption percentage A% was calculated from K_d as:

$$\%A = \frac{100K_d}{K_d + \frac{v}{m}} \quad (3)$$

3. RESULT AND DISCUSSION

Ionic radius of K⁺ and Na⁺ are more than Li⁺ radius. While cation radius enhances, cation volume increases too, so for the solvolysis and complex formation requires more concentration of Cl⁻.



As a result, 0.1 M HCl is not sufficient for K⁺ and Na⁺ stable complex formation and the solvolysis with the negative ligand (Cl⁻). Hence, these ions are replaced with H⁺ (RSO₃H) and adsorbed on strong cation exchange resin as following (eq. 4):



Here is R: resin lattice, M⁺: Cation in, H⁺: proton, r: on resin, s: in solution. According to above mention lithium in 0.1 M HCl and sodium in 0.5 M HCl and potassium in 1 M HCl form stable anion complex, and pass without any adsorption and should be maximum recovery. The solution containing Li was passed through

TABLE 1: Comparison separation yield in different HCl concentrations

HCl concentration	Li separation yield %	Na separation yield %	K separation yield %
0.05	0.25	6.86	5.21
0.10	99.24	2.27	2.11
0.15	79.30	78.7	1.15
0.30	71.40	79.75	57.78
0.50	70.60	98.66	78.31
0.70	68.60	77.64	66.29
0.90	67.20	78.60	66.67
1.00	65.20	81.60	97.62
1.50	60.80	80.80	67.06
2.00	59.70	80.82	67.07
2.50	58.50	80.83	67.08
3.00	57.30	80.85	67.08

TABLE 2: Log K_d and A% in different HCl concentrations for Li, Na and K

HCl concentration	Li		Na		K	
	Log Kd	A%	Log Kd	A%	Log Kd	A%
0.05	4.093	99.75	2.610	93.14	2.737	94.79
0.1	-0.636	0.76	3.111	97.73	3.145	97.89
0.15	0.894	20.7	0.909	21.3	3.412	98.85
0.3	1.080	28.6	0.882	20.25	3.341	42.22
0.5	1.095	29.4	-0.389	1.34	0.920	21.69
0.7	1.137	31.4	0.937	22.36	1.183	33.71
0.9	1.165	32.8	0.911	21.4	1.176	33.33
1	1.204	34.8	0.833	18.4	-0.136	2.38
1.5	1.287	39.2	0.851	19.2	1.169	32.94
2	1.303	40.3	0.849	19.18	1.161	32.93
2.5	1.328	41.5	0.846	19.17	1.176	32.92
3	1.350	42.7	0.842	19.15	1.169	32.91

the resin, LiCl was eluted too and other unwanted ions were adsorbed.

In the present work, Alkali metal impurities such as Na and K were separated from Li using a 20 g cation-exchange resin (AG 50W-X8) with 0.1 M hydrochloric acid. To remove the retained lithium was eluted with 0.1 M hydrochloride.

3.1. The influence of HCl on ions adsorption on resin

A key parameter for designing a process for industrial leachates is the effect of the HCl acid concentration. The recovery of Li (from a 200 Li mgL⁻¹ solution) was tested for HCl concentrations between 0.05 and 3 M. Results of separation yield versus HCl concentration were summarized in TABLE 1. TABLE 2 shows the adsorption percentages (A%) and Log K_d (distribution coefficient) for the given experimental conditions. The distribution coefficients (K_d) and ions adsorption

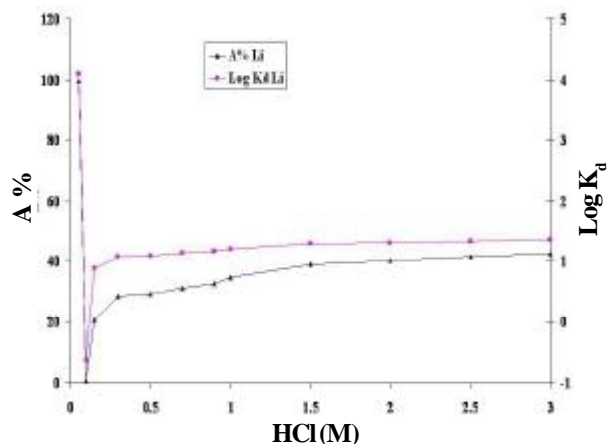


Figure 1: The influence of HCl concentration on Li adsorption

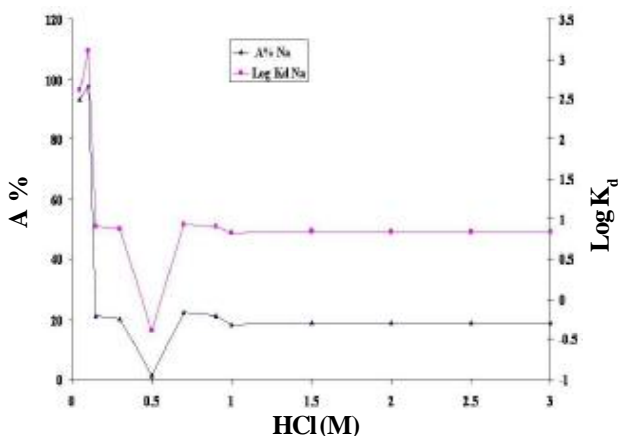


Figure 2: The influence of HCl concentration on Na adsorption

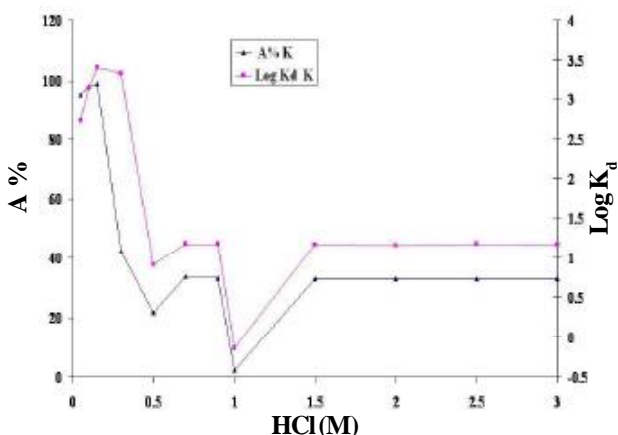


Figure 3: The influence of HCl concentration on K adsorption

percentages (A%) were determined for the cation exchange resin and shown as A%, Log K_d in figures 1-3

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TABLE 3: The influence of HCl+MeOH 80% concentration on element adsorption

Element	HCl+MeOH 80% concentration[M]	Separation yield[%]	K _d	A%
Li	0.1	0.2	15180	99.8
	0.5	67	14.78	33
	1	60.54	19.55	39.46
Na	0.1	3.21	905	96.79
	0.5	12.3	213.8	87.7
	1	35.04	55.61	64.96
K	0.1	1.72	1710	98.28
	0.5	2.22	1320	97.78
	1	1.25	2370	98.75

TABLE 4: The influence of HCl+EtOH 80% concentration on element adsorption

Element	HCl+EtOH 80% concentration[M]	Separation yield[%]	K _d	A%
Li	0.1	0.88	3375	99.12
	0.5	48.9	31.37	51.1
	1	54.5	25.02	45.5
Na	0.1	1.74	1690	98.26
	0.5	4.44	645	95.56
	1	22.5	103.3	77.5
K	0.1	0.94	3150	99.06
	0.5	2.27	1290	97.73
	1	3.45	840	96.55

TABLE 5: The influence of 0.1M HCl+MeOH 40% on element adsorption

0.1M HCl MeOH 40%	Separation yield[%]	K _d	A%
Li	48.65	31.67	51.35
Na	14.1	183.3	85.9
K	1.18	2520	98.82

as a function of HCl concentrations. With attention to TABLES 1 and 2, lithium has maximum adsorption in 0.05 M HCl concentration. Lithium stable anion complex was not formed because of low HCl concentration and reaction progress in reverse direction (production Li⁺ cation). Li⁺ cation was replaced with H⁺ (RSO₃H) on strong cation exchange resin. In 0.1 M HCl, the reaction is irreverent in direction very stable anion complex formation and LiCl leaves without any adsorption with maximum recovery, and absorption percentage and Log K_d decrease severely. In figure 1 lithium behavior is observable perfectly. TABLE 2 shows that sodium adsorption increase from 0.05 until 0.1 and maximum adsorption is in 0.1M HCl. In fact amount of Cl⁻ is not sufficient for Na stable anion complex formation, so Na stable anion complex was not convened. Na⁺ cation was replaced H⁺ (RSO₃H) and was adsorbed on the resin until 0.5 M HCl. In this con-

centration amount of Cl⁻ is sufficient for Na stable anion complex formation. So reaction was irreverent in direction very stable anion complex formation, all of the Na⁺ was convert stable anion complex. It was exited without any adsorption. Increasing HCl concentration, the reaction was reversed and a small quantity of it was adsorbed and a large quantity was excreted. In figure 2 sodium behavior is observable completely. The results in TABLES 1 and 2 shows that potassium has the same treatment of sodium but the maximum adsorption is in 0.15 M HCl. K⁺ cation was replaced H⁺ (RSO₃H) and adsorbed on resin until 1 M HCl. In figure 3 potassium behavior is observable completely.

In TABLE 3 the influence of HCl+MeOH80% molarity on the elements adsorption was investigated. According to other investigations, we expect maximum recovery for lithium but, Li recovery percentage maximum was achieved 60.54% in 1M HCl and 35.04 % of Na were extracted along Li. From data of recovery percentage in TABLE 4 it appears that ethanol behavior is similar that methanol. Li and Na recovery percentage maximum were achieved 54.50% and 22.50% in 1M HCl, respectively. In TABLE 5 the effectual of 0.1MHCl+MeOH40% molarity on the elements adsorption was contemplated. In this concentration all of the ions adsorbed completely and Li recovery percentage was achieved 48.65%. So alcohols among HCl reduce lithium separation yield and recovery percentage severely.

One would prefer the sulphonated polystyrene resin in case where large amount of sodium and more strongly remained ions are present, because this resin has larger capacities and operates with a sufficiently large separation factor. The AG 50W-X8 cation-exchange resin shows higher efficiency in the separation of lithium from other elements in comparison to other such as Bio-Rex 40 resin^[10] and Duolite C-3 resin^[11].

Strelow^[8] separated lithium from sodium, beryllium by cation-exchange chromatography in HNO₃ (1M)-CH₃OH (80%). At first all of ions adsorbed with HNO₃ (0.1M)-CH₃OH (50%) on AG 50W-X8 cation-exchange resin then eluted lithium with 500 ml HNO₃ (1M)-CH₃OH (80%) from cation-exchange chromatography column.

In this work, lithium was separated from Na and K by AG 50W-X8 cation-exchange in HCl (0.1 M) alone

TABLE 6: Comparison between positive chromatography and negative chromatography

Kind of chromatography	HCl molarity	Separation yield %	K_d	A%
Positive	0.05	0.25	12390	99.75
	0.1	75.85	9.55	24.15
Negative	0.05	0.25	12390	99.75
	0.1	99.24	0.231	0.76

(free alcohols). First lithium is adsorbed with 0.05 M HCl completely and then lithium is eluted with 0.1 M HCl (positive chromatography); the recovery percentage Li was achieved 75.85% as shown in TABLE 6. Considering the obtained results in TBALLES 1 and 2 were indicating that 0.1 M HCl is the most suitable concentration for separating of lithium from other. In this concentration the impurities such as Na and K were adsorbed on the resin and Li was eluted from the resin (negative chromatography). The chemical purification of Li in the final solution which measured by AAS was 3.89 ppm and separation yield of Li was 99.24 % and K_d was 0.231 and A% was 0.76%.

4. CONCLUSION

AG 50W-X8 cation-exchange resin (negative chromatography method) is excellent and a very efficient for selective separation of milligram as well as microgram amount of Li from practically all other elements such as solution containing Na and K. The recovery percentage is 99.24% using a concentration of 0.1 M HCl solution. The method is accurate technique for the separation of lithium from alkali impurities.

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