

Lithium content in pool water and boron compounds in Kırka

Bekir Sıtkı Çevrimli¹, Şükrü Kalaycı^{1*}

¹Chemical Technology Department, Vocational School of Technical Sciences, Gazi University, Ankara, Turkey
Corresponding Author: skalayci@gazi.edu.tr

ABSTRACT

Lithium compounds play an extremely important role in the production of lithium-ion batteries. Lithium ions in wastewater and amorphous boron compounds of Kırka Boron Plant, where Turkey's important boron mine is extracted, were determined. Lithium ions from wastewater and boron compounds were recovered by using an absorbent containing redox type spinel LiMn_2O_4 . The pH value of the solution and the concentration of the absorbent were investigated as suitable working conditions for the determination of lithium ions. Appropriate pH value was determined as 9.85 and absorbent value as 10 g L^{-1} . The ICP-OES device and light with a wavelength of 670.8 nm were used to measure the lithium ions concentrations. The analytical performance of the system has been improved by performing extensive optimization of various factors. The linear range and LOD/LOQ of the optimized method were found to be $7.3 \pm 1.1 \text{ mg L}^{-1}$ and $1.24 \pm 0.11 \text{ mg L}^{-1}$, respectively. The accuracy/applicability of the presented method was verified using samples of wastewater from Kırka Boron pools and solids accumulated at the bottom. Lithium concentration in wastewater was measured as $168.5 \pm 2.4 \text{ mg L}^{-1}$ as the average of 10 measurements at 95% confidence level, and $285.6 \pm 3.7 \text{ mg L}^{-1}$ in boron compounds.

KEYWORDS; Lithium ions, Boron compounds, Pool water, Absorbent, ICP-OES.

Date of Submission: 02-11-2025

Date of acceptance: 11-11-2025

I. INTRODUCTION

Lithium is an important mineral in batteries produced as an environmentally friendly and sustainable new energy source. Especially today, the increase in electric vehicle production has made it more attractive. In particular, its strong electroactivity has come to the fore [1]. It increases the demand for exploration and extraction of resources to obtain lithium [2].

There are many studies to investigate lithium in nature. In these studies, lithium is present in both low and high concentrations in natural samples. Lithium analysis was performed in underground, lake, river and sea waters in different parts of the world and lithium values between 0-1000 ppm were found [3-8].

Studies have shown that the amount of lithium depends on soil, climate and water factors. It was determined that the amount of lithium was affected by the structure of the soil, climatic conditions and groundwater [9-12]. There are also studies on the use of lithium in the medical field. The negative effects of excessive lithium on human and living health have been examined in detail [13-17].

Lithium extraction, especially from salt water, is an extremely economical method. Significant progress has been made in the recovery of lithium from salt water samples [18-21]. In these studies, solvent extraction, ion sieve adsorption, electrochemical approaches and membrane separation methods were used. In salt systems, due to the changing amounts of cations and anions, ionic salts such as chloride, sulphate and carbonate can be formed. The change in composition leads to the selected processes and the difficulty of the process.

In this study, lithium minerals in pool water and amorphous compounds in Eskişehir Kırka Bor extraction facilities were collected using a column. The characterization process of the absorbent used in this column was performed. Lithium determination in these samples was measured using ICP-OES. It was determined that the amount of lithium was high. It was investigated whether this lithium could be used in energy production.

II. MATERIAL AND METHODS

Materials and methods

In the experiments, analytical purity LiCl salt was used. The required amount was weighed and 1000 mg/L stock solutions were prepared for each. Sortarius brand deionized water was used in the preparation of the solutions. Clay containing natural talc from Kulp district of Diyarbakir was used as adsorbent.

The amount of lithium in boron pool water and its amorphous compounds was analyzed using the Pelkin Elmer brand ICP-OES 7300 DV device. To compare the results, the same samples were also analyzed using Jenway brand Flame Emission Spectroscopy.

Preparation of the column

Clay brought from Diyarbakir is used as absorbent. The chemical content of the clay used as an adsorbent in the study; 63.4 % SiO_2 , 0.2 % Al_2O_3 , 0.2 % CaO , 3.3 % Fe_2O_3 , 26.4 % MgO , ≤ 1.0 % K_2O , ≤ 0.1 % Na_2O , ≤ 0.8 % TiO_2 , ≤ 0.1 % P_2O_5 , ≤ 0.1 % MnO and 5.30 % A.Za determined as a result of XRF analysis methods and is given in Figure 1. A 30 cm long column filled with clay was used to separate lithium.

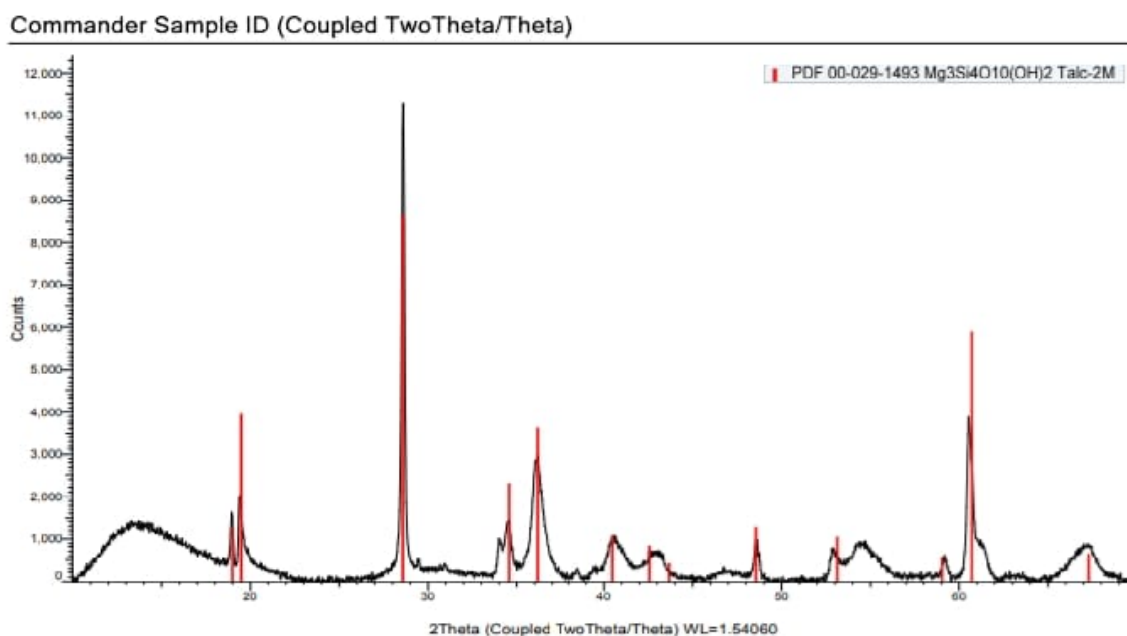


Figure 1. XRD graph of clay absorbent.

Preparation of amorphous compounds and pool water

Approximately 100 g of the amorphous compound that appeared transparent was weighed. The crystals were crushed and turned into powder. 10 g of these crystals were weighed accurately and taken into an Erlenmeyer flask. 250 mL of deionized water was added. This was heated to approximately 200 °C on a magnetic stirrer. The dissolving process at this temperature lasted 6 hours. The mixture became completely soluble and was cooled. This solution was filtered through a column filled with clay. This filtrate was used for lithium analyses. The same procedure was done for the pool water sample.

III. RESULTS VIEW

Analysis parameters with ICP-OES

Lithium solutions of 25, 50, 100 mg/L were prepared daily using deionized water from the stock 1000 mg/L solution of lithium. Deionized water was used as the blank solution. Lithium analysis was performed with the ICP-OES device at a wavelength of 670.8 nm. LOD and LQD values of the method were calculated. The values are given in Table 1.

$[\text{Li}^+]$: mg/L	LOD: mg/L	LQD: mg/L	R^2
0-100	7.3 ± 1.1	1.24 ± 0.11 mg	0.9985

Table 1. Lithium analysis parameters with ICP-OES method

Validation values of the method

Validation values of this method were examined. For this purpose, standard lithium solutions were measured with ICP-OES. The added and found values were compared and % recovery values were calculated. The results are given in Table 2. When the values were examined, it was determined that the validation values of the method were high.

Lithium added: mg/L	Lithium found: mg/L	% Recovery
5.0	4.9	98
27.0	26.8	99
150.0	149.6	100
500.0	492.5	99

Table 2. Validation values of the method**Selectivity of clay absorbent in lithium recovery**

Langmuir Isotherm equation [22] was used to determine the absorption balance of the clay sample used as absorbent. Absorption parameters were measured and given in Table 3. According to these values, the clay sample was found to have high absorption values for lithium recovery.

T (°K)	q _m (mg/g)	K _L (×10 ² L/mg)	R _L	R ²
298	882.34	4.76	0.246	0.982
308	959.61	6.01	0.197	0.991
318	964.45	6.25	0.184	0.996

Table 3. Langmuir parameters on Lithium absorption of clay absorbent at different temperatures.

Lithium recovery surfaces in water samples were measured using different absorbents and the values are given in Table 4. According to these results, it was understood that the clay sample could be used as an absorbent in lithium analysis.

Absorbent	Sample	Li recovery	Reference
Manganese oxide	Seawater	98.3	23
Fly ash	Water	95.0	24
Sorbents based on aluminum compounds	Brines	96.5	25
Clay	Pool water and boron compounds	97.6	This work

Table 4. Comparison of lithium recoveries using different absorbents.**Lithium content in amor compounds and pool water**

The amount of lithium in the amorphous compounds and pool water brought from Eskişehir Kırka Bor facilities and passed through the column was measured using both ICP-OES and Flame Emission Spectroscopy (AES). The results were calculated as the average of 4 measurements with a 95% confidence level. The values are given in Table 5. t and F tests were applied to compare the results of both methods. According to the data obtained, it was seen that the analysis results and the values found in both methods were compatible with each other.

Sample	ICP-OES	AES	t-test (t _{critical} =3.18)	F-test (F _{critical} =9.60)
Amorphous compounds	84.6 ± 1.7	87.1 ± 2.5	1.85	3.26
Pool water	37.2 ± 1.1	40.5 ± 1.8	2.36	5.67

IV. CONCLUSION

Amorphous compounds and pool water brought from Eskişehir Kırka Bor facilities were made soluble. Then, lithium mineral was collected by passing through a column filled with clay. Lithium content was measured in these samples using ICP-OES. It was determined that the results were consistent with the values measured with Flame Emission Spectroscopy. It was seen that the amount of lithium was high in these samples. It was understood

that the lithium here could be used in battery preparation. It was emphasized that it would be an important source for lithium.

The amorphous boron compound and pool water extracted from boron facilities were used only to obtain boron. With this study, it was measured that the amount of lithium detected in the excess compound and pool water was high. This study showed that the use of this compound or the lithium found in pool water is important in lithium battery production.

REFERENCE

- [1]. Swain B, Recovery and recycling of lithium: a review. *Sep. Purif. Technol.*, 2016; 172:388-403. Doi.org/10.1016/j.seppur.2016.08.031
- [2]. Paranthaman MP, Li L, Luo J, Hoke T, Ucar H, Moyer BA, Harrison S. Recovery of lithium from geothermal brine with lithium-aluminum layered double hydroxide chloride sorbents. *Environ. Sci. Technol.*, 2017; 51:13481-86. Doi.org/10.1021/acs.est.7b03464
- [3]. Junn-Hsing G, Chia-Lian T. Determination of Low-level Lithium in Environmental Water Samples by Neutron Activation. *Appl. Radiat. Isot.*, 1995; 46(4):211-15. Doi.org/10.1016/0969-8043(94)00118-J
- [4]. Munk L, Jochens H, Jennigs M, Bradley D, Hynek S, Godfrey L. Geochemistry of lithium-rich brines in Clayton Valley, Nevada, USA. 11 th SGA Biennial Meeting Let's Talk Ore Deposits. 26-29th September 2011 Antofagasta, Chile.
- [5]. Kapusta ND, Mossaheb N, Etzersdorfer E, Hlavin G, Thau K, Willeit M, Praschak-Rieder N, Sonneck G, Leithner-Dziubas K. Lithium in drinking water and suicide mortality. *The British Journal of Psychiatry*, 2011; 198:346–50. doi: 10.1192/bjp.bp.110.091041
- [6]. Figueroa L, Barton S, Schull W, Razmilic B, Zumaeta O, Young A, Kamiya Y, Hoskins J, Ilgren E. Environmental Lithium Exposure in the North of Chile—I. Natural Water Sources. *Biol Trace Elem Res.* 2012; 149:280–90. Doi:10.1007/s12011-012-9417-6
- [7]. Liaugaudaitė V, Mickuviene N, Raskauskiene N, Naginiene R, Sher L. Lithium levels in the public drinking water supply and risk of suicide: A pilot study. *Journal of Trace Elements in Medicine and Biology*, 2017; 43:197–01. Doi.org/10.1016/j.jtemb.2017.03.009
- [8]. Kong F, Yang Y, Luo X, Sha Z, Wang J, Ma Y, Ling Z, He B, Liu W. Deep hydrothermal and hallow groundwater borne lithium and boron loadings to a mega brine lake in Qinghai Tibet Plateau based on multi-tracer models. *Journal of Hydrology*, 2021; 598:126313-18. Doi.org/10.1016/j.jhydrol.2021.126313
- [9]. Godfrey LV, Chan LH, Alonso RN, Lowenstein TK, McDonough WF, Houston J, Li J, Bobst A, Jordan TE. The role of climate in the accumulation of lithium-rich brine in the Central Andes. *Applied Geochemistry*, 2013; 38:92–02. Doi.org/10.1016/j.apgeochem.2013.09.002
- [10]. Isfahani RN, Fazeli A, Bigham S, Moghaddam S. Physics of lithium bromide (LiBr) solution dewatering through vapor venting membranes. *International Journal of Multiphase Flow*, 2014; 58:27–8. Doi.org/10.1016/j.ijmultiphaseflow.2013.08.005
- [11]. Puranen A, Tejlund P, Granfors M, Schrire D, Josefsson B, Bengtsson B. Lithium and boron analysis by LA-ICP-MS results from a bowed PWR rod with contact. *EPJ Nuclear Sci. Technol.*, 2017; 3:2-6. Doi.org/10.1051/epjn/2016042
- [12]. Kowalczyk E, Givélet L, Amlund H, Sloth JJ, Hansen M. Risk assessment of rare earth elements, antimony, barium, boron, lithium, tellurium, thallium and vanadium in teas. *EU-FOR A Journal*, 31 January 2012. Doi.org/10.2903/j.efsa.2022.e200410
- [13]. Cetin I, Nalbantcilar MT, Tosun K, Nazik A. How Trace Element Levels of Public Drinking Water Affect Body Composition in Turkey. *Biol Trace Elem Res.*, 2017; 175:263–70. Doi.org/10.1007/s12011-016-0779-z
- [14]. Kot FS. On the rubidium and lithium content and availability in the sub-arid south-eastern Mediterranean: potential health implications. *Environ Geochem Health*, 2018; 40:1841–51. Doi.org/10.1007/s10653-018-0134-8
- [15]. Izsak B, Hidvegi A, Balint L, Malnasi T, Vargha M, Pandics M, Rihmer Z, Dome P. Investigation of the association between lithium levels in drinking water and suicide mortality in Hungary. *Journal of Affective Disorders*, 2022; 298:540–7. Doi.org/10.1016/j.jad.2021.11.041
- [16]. Lombard MA, Brown EE, Saftner DM, Arienzo MM, Fuller-Thomson E, Brown CJ, Ayotte JD. Estimating Lithium Concentrations in Groundwater Used as Drinking Water for the Conterminous United States. *Environ. Sci. Technol.*, 2024; 58:1255-64. Doi.org/10.1021/acs.est.3c03315
- [17]. Aragona F, Cicero N, Nava V, Piccione G, Giannetto C, Fazio F. Blood and hoof biodistribution of some trace element (Lithium, Copper, Zinc, Strontium and Lead) in horse from two different areas of Sicily. *Journal of Trace Elements in Medicine and Biology*, 2024; 82:127378-82. Doi.org/10.1016/j.jtemb.2023.127378.
- [18]. Razmjou A, Asadnia M, Hosseini E, Korayem AH, Chen V. Design principles of ion selective nanostructured membranes for the extraction of lithium ions. *Nat. Commun.*, 2019; 10 (1): 1-15. Doi.org/10.1038/s41467-019-13648-7.
- [19]. Li X, Mo Y, Qing W, Shao S, Tang CY, Li J. Membrane-based technologies for lithium recovery from water lithium resources: a review. *J. Membr. Sci.*, 2019; 591: 117317-117341. Doi.org/10.1016/j.memsci.2019.117317.
- [20]. Zhao X, Yang H, Wang Y, Sha Z. Review on the electrochemical extraction of lithium from seawater/brine. *J. Electroanal. Chem.*, 2019; 850: 113389-113393. Doi.org/10.1016/j.jelechem.2019.113389.
- [21]. Liu G, Zhao X, Ghahreman A. Novel approaches for lithium extraction from salt-lake brines: a review. *Hydrometallurgy*, 2019; 187: 81-100. Doi.org/10.1016/j.hydromet.2019.05.005.
- [22]. Vasiliu S, Bunia I, Racovita S, Neagu V. Adsorption of cefotaxime sodium salt on polymer coated ion exchange resin microparticles: Kinetics, equilibrium and thermodynamic studies. *Carbohydrate Polymers*, 2011; 85(2): 376-387. Doi.org/10.1016/j.carbpol.2011.02.039.
- [23]. Wajima T, Munakata K, Uda T. Adsorption behavior of lithium from seawater using manganese oxide adsorbent. *Plasma and Fusion Research*, 2012; 7:2405021-2405024. Doi.org/10.1585/pfr.7.2405021.
- [24]. Xu Z, Wang X, Sun S. Performance of a synthetic resin for lithium adsorption in waste liquid of extracting aluminum from fly-ash. *Chinese Journal of Chemical Engineering*, 2022; 44: 115-123. Doi.org/10.1016/j.cjche.2021.03.036.
- [25]. Boroumand Y, Razmjou A. Adsorption-type aluminium-based direct lithium extraction: The effect of heat, salinity and lithium content. *Desalination*, 2024; 577: 117406-114410. Doi.org/10.1016/j.desal.2024.117406.