

УДК 543.05=66.081312+546.34

SORPTION OF LITHIUM IONS FROM AQUEOUS SOLUTIONS ON TRANSCARPATIAN CLINOPTILOLITE

L. Shevchuk^{1*}, V. Vasylechko^{1,2}, Ya. Kalychak¹

¹*Ivan Franko National University of Lviv,
Kyryla i Mefodiya Str., 6, 79005 Lviv, Ukraine;*

²*Lviv University of Trade and Economics,
Samchuka Str., 9, 79011 Lviv, Ukraine*

**e-mail: Liubomyr.Shevchuk@lnu.edu.ua*

The spectrophotometric method using thoron was optimized to determine the breakthrough point of lithium during its sorption on Transcarpathian clinoptilolite. The selectivity of this method towards zeolite cations was investigated. The results show that Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, and Fe³⁺ ions which are present in clinoptilolite do not interfere with Li⁺ determination in the analyzed model solutions.

The sorption properties of natural Transcarpathian clinoptilolite towards trace amounts of lithium in aqueous solutions were studied. The findings indicate that this natural aluminosilicate can be used as a sorbent in solid-phase extraction. The most effective sorption occurs from solutions at pH 6.5 using pre-fired at 350 °C clinoptilolite samples. Under optimal conditions, the sorption capacity of clinoptilolite towards lithium is 538 µg/g.

Keywords: sorption, solid phase extraction, lithium, natural clinoptilolite.

DOI: <https://doi.org/10.30970/vch.6601.137>

1. Introduction

Lithium is a typical alkali metal with a wide range of applications. Primarily, it is used in industry as a chemical power source in lithium-ion batteries, notably in electric vehicles [1–4]. Additionally, lithium is used in the production of specialized glass, ceramics, refrigerants, chemical reagents [5–9], and psychotropic drugs [10].

To meet the growing demand for lithium, an increment of production is necessary. Lithium is primarily extracted from natural sources, including ores (lepidolite, spodumene, petalite, amblygonite) [7], brine from salt lakes, seawater, and geothermal waters [5]. Lithium extraction from aqueous sources is generally more environmentally sustainable and cost-effective compared to mineral extraction. However, the range of selective methods for determining trace amounts of lithium remains relatively limited. Given the low concentrations of lithium in natural waters and most industrial solutions, developing efficient methods for concentrating lithium and recovery is essential.

In lithium analytical chemistry, various types of sorbents are utilized for sorption. For instance, manganese oxide with a spinel structure is commonly employed for the efficient extraction of lithium from seawater and brine. Manganese oxide-based materials exhibit high selectivity for lithium and significant adsorption capacity in a weakly alkaline environment (pH of seawater ~8), in the presence of alkali and alkaline earth metal ions [5, 7, 11–17].

Additionally, specially designed resins, aluminum composites, and inorganic ion exchangers [7, 18], as well as synthesized sorbents based on tin, antimony, dioxides based on titanium and zirconium [19], mixed oxides of titanium, and iron, titanium and chromium, arsenate of titanium and magnesium and thorium [20], along with synthetic zeolites [1, 21, 22], can also effectively serve this purpose.

Natural zeolites are effective sorbents for alkali metals in aqueous solutions [23–26]; however, their sorption properties towards lithium remain poorly studied. The processes of Li^+ cation sorption (via ion exchange) on natural phillipsite and its Na-form have been investigated. It was found that Li^+ in the phillipsite matrix is coordinated with two structural oxygen atoms and two water molecules [27]. The authors of [23] studied ion exchange equilibria involving Li^+ ions on Na-forms of clinoptilolite. It was shown that the sodium form of clinoptilolite, a sodium-potassium mineral in its natural state, exhibits increased selectivity for Li^+ cations. Acid-modified clinoptilolite has been used to extract Li^+ ions from aqueous solutions of its salts (LiCl , LiNO_3 , CH_3COOLi) [24]. Polish scientists [1] studied the sorption properties of Transcarpathian clinoptilolite toward high concentrations of Li^+ (10 mg/ml) under static conditions. It was found that clinoptilolite sorbs Li^+ ions most effectively from neutral solutions. The possibility of using natural clinoptilolite in combination with polyacrylic acid for lithium extraction from geothermal water has also been demonstrated.

The goal of our research is to investigate the sorption properties of natural Transcarpathian clinoptilolite to trace amounts of lithium in aqueous solutions and to explore the potential of using this natural aluminosilicate as a sorbent in solid-phase extraction.

2. Materials and experimental procedures

The clinoptilolite employed was from the deposit near the village of Sokyrnytsa in the Ukrainian Transcarpathian region. Analysis showed that the main component was present to the extent of 85–90 %. The specific surface area of this clinoptilolite has already been established as 59.0 m^2 [28]. The chemical composition of this zeolite in the oxide form was found to be (in %): SiO_2 , 67.29; TiO_2 , 0.26; Al_2O_3 , 12.32; Fe_2O_3 , 1.26; FeO , 0.25; MgO , 0.99; CaO , 3.01; Na_2O , 0.66; K_2O , 2.76; H_2O , 10.90 [29].

All solutions were prepared using double distilled water and high-purity reagents.

A standard Li(I) salt solution with $C_{\text{Li(I)}} = 1.0 \text{ mg/ml}$ was prepared by dissolving a portion of lithium sulfate in water. A working solution of Li(I) with $C_{\text{Li(I)}} = 0.5 \text{ }\mu\text{g/ml}$ was prepared by diluting the standard.

The pH of Li(I) solutions was adjusted to the desired value by adding 0.1 M NaOH and 0.1 M H_2SO_4 solutions. The pH was monitored using a pH meter 150 M with a silver chloride reference electrode, accurate to $\pm 0.05 \text{ pH units}$.

The sorption properties of clinoptilolite for Li(I) ions were studied under dynamic conditions in solid-phase extraction mode. A peristaltic pump was used to pass the Li(I) solution through a concentrating cartridge filled with the sorbent at a flow rate of 3 ml/min. The sorbent had a granule diameter of 0.200–0.315 mm. The research method under dynamic conditions is described in detail in [30].

Most of the existing spectrophotometric methods lack the analytical characteristics required to accurately determine the lithium breakthrough point. One of the most sensitive methods for lithium determination is the spectrophotometric method using thoron, which enables the detection of this rare alkali metal at concentrations as low as $0.05 \text{ }\mu\text{g/ml}$ [31, 32].

However, when studying the sorption properties of clinoptilolite under dynamic conditions, the method used to determine the breakthrough point must be selective for zeolite cations Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , and Fe^{3+} ions, as these ions can leach from the zeolite matrix and interfere with the analytical signal. Therefore, the selectivity of lithium determination using thoron was investigated towards alkali and alkaline earth metal cations, and Al^{3+} and Fe^{3+} cations. During these studies, the concentration of interfering metal ions gradually was changed until a relative error of Li^+ determination did not exceed 10 %, based on the optical density value. The results of the selectivity study are presented in the table.

Maximum permissible concentrations of excess foreign metal ions for spectrophotometric determination of Li(I) using Thoron ($T_{\text{Li(I)}} = 0.2 \text{ } \mu\text{g/ml}$, $T_{\text{Thoron}} = 560 \text{ } \mu\text{g/ml}$, $l = 1.0 \text{ cm}$, $\lambda_{\text{max}} = 490 \text{ nm}$, $\omega_{2\text{-propanone}} = 70 \text{ vol } \%$)

Metal ion	$C_{\text{Me}}/C_{\text{Li}}$	Metal ion	$C_{\text{Me}}/C_{\text{Li}}$	Metal ion	$C_{\text{Me}}/C_{\text{Li}}$
Na^+	20	Mg^{2+}	30	Al^{3+}	30
K^+	20	Ca^{2+}	20	Fe^{3+}	15

The obtained results show that Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , and Fe^{3+} ions, which are present in clinoptilolite, do not interfere with the determination of Li^+ in the analyzed model solutions. Since the permissible concentrations of these ions in the mother liquors obtained during the sorption of Li^+ ions do not exceed the values presented in the table, the highly sensitive spectrophotometric method for lithium determination can be used to determine the breakthrough point of this alkali metal.

Li(I) determination method

In a 25 ml flask, add 0.5 ml of a 20 % potassium hydroxide solution, 17.5 ml of propanone, 0.7 ml of a 0.2 % thoron solution, and the Li(I) solution. Bring the volume to 25 ml with water. Measure the optical density of the solution at $\lambda_{\text{max}} = 490 \text{ nm}$ against a reference solution (path length = 1.0 cm) using a ULAB-102 spectrophotometer. For selectivity studies, add standard solutions of Li(I) and a foreign metal ion to achieve the desired concentration of the foreign metal ion, and bring the volume to 25 ml with water.

3. Results and discussion

The results of the study on the sorption of Li(I) ions onto clinoptilolite in solutions of varying acidity are presented in Fig. 1.

The results demonstrate that Li^+ ion sorption occurs in the pH range from weakly acidic, neutral, and weakly alkaline conditions, with the maximum sorption capacity being achieved at pH 6.5. A noticeable increase in the sorption efficiency of clinoptilolite is observed with an increasing pH of weakly acidic solutions. This trend is closely correlated with the noticeable increase in the negative zeta potential of Transcarpathian clinoptilolite with an increasing pH of weakly acidic suspensions of this natural aluminosilicate [33].

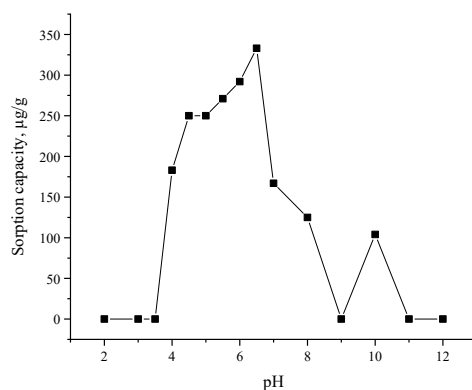
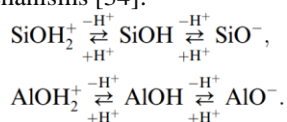


Fig. 1. The dependence of the sorption capacity of natural clinoptilolite on the pH of the Li(I) salt solution ($C_{\text{Li(I)}}$ = 0.5 µg/g; clinoptilolite grain diameter 0.200–0.315 mm)

The surface charge of zeolites is usually the result of protonation or deprotonation of hydroxyl groups, since pH controls the surface charge of the particle, and, therefore, the zeta potential, through such mechanisms [34]:



It is known that the surface OH-groups of clinoptilolite are sorption-active centers of metal ions [26, 28, 33, 35–40]. Usually, metal cations are sorbed more efficiently from solutions in which the dissociation of hydroxyl groups occurs with the elimination of H^+ on the surface of the mineral grains. However, the zeta potential of zeolites depends not only on the pH but also on the ionic strength of the suspension and the Al content in the framework [34, 35]. Increasing the concentration of Al atoms shifts the isoelectric point to lower pH values, which is explained by the higher acidity of Al [34]. Another possible explanation for this effect is that the bridging hydroxyl groups (Si-OH-Al) on the zeolite surface can be easily deprotonated with the formation of Si-O^- in a wide pH range, which makes the surface more negatively charged. Decreasing the Si/Al ratio counteracts the protonation of silanol groups in acidic solutions, leading to an isoelectric point shift to lower pH values [34]. In the pH range from 2 to 13, the clinoptilolite surface remains negatively charged due to the dissociation of hydroxyl groups [35]. Therefore, clinoptilolite can sorb metal ions even in a solution with a low pH value. Since Transcarpathian clinoptilolite belongs to the calcium low-silicon variety of clinoptilolites ($\text{Si/Al} = 4.4$) [26], in which the Al content is relatively higher compared to high-silicon varieties of clinoptilolite, the sorption of cations of individual metals, including Li^+ cations, on this domestic natural zeolite can occur in solutions with increased acidity. The authors [1] also attribute the increased sorption capacity of Transcarpathian clinoptilolite towards Li^+ ions under static conditions in weakly acidic and neutral solutions, with increasing pH, to the increase in the content of negatively charged groups on the zeolite surface.

Figure 1 shows that the sorption capacity of clinoptilolite decreases in neutral and weak alkaline solutions with increasing pH. According to [33], the negative zeta potential of Transcarpathian clinoptilolite remains practically unchanged in neutral and weakly alkaline solutions. However, in weakly alkaline and alkaline solutions, compound LiOH is formed.

Since lithium hydroxide ($K_b = 6.8 \cdot 10^{-1}$, $pK_b = 0.17$) is a weaker base compared to hydroxides of other alkali metals, a significant portion of lithium exists in the undissociated molecular form, LiOH , in alkaline solutions. Given that the coordination number of Li^+ ions is 4, hydrated $\text{Li}(\text{H}_2\text{O})_4^+$ cations predominate in weakly acidic solutions. This means that at the same total concentration of dissolved lithium, the fraction of lithium in the ionic form is significantly lower in alkaline solutions compared to acidic solutions. It is known [1, 23–25, 27] that the sorption of Li(I) by natural zeolites occurs via a cation exchange mechanism. In alkaline solutions, a significant portion of Li(I) exists in the molecular form of LiOH , which cannot be sorbed by ion exchange, likely leading to a decrease in the sorption efficiency of clinoptilolite for Li(I) in solutions with $\text{pH} > 7$.

Thus, it is clear that Li(I) sorption occurs within a narrow pH range in weakly acidic solutions, with the maximum sorption capacity achieved at pH 6.5. Therefore, for further studies, a Li(I) solution with pH 6.5 was used.

The sorption properties of Transcarpathian clinoptilolite are significantly influenced by its preliminary thermal treatment [28, 33, 35–38]. Therefore, clinoptilolite samples, washed with distilled water, were subjected to thermal treatment for 2.5 hours at various temperatures. After cooling in a desiccator, their sorption capacities towards Li(I) were determined under dynamic conditions. The results are presented in Fig. 2.

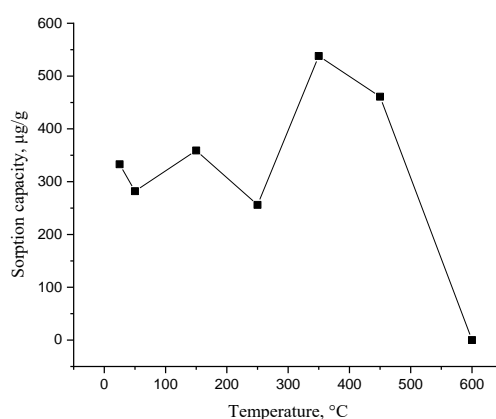


Fig 2. The dependence of the sorption capacity of clinoptilolite on the temperature of the previous treatment ($C_{\text{Li(I)}}$ = 0.5 µg/g; pH 6.5; diameter of sorbent grains – 0.200–0.310 mm)

Figure 2 demonstrates that clinoptilolite samples pre-calcined at 350 °C exhibit the highest sorption capacity for Li^+ ions, reaching 538 µg/g. We attribute this to the fact that samples of Transcarpathian clinoptilolite calcined at this temperature have the highest specific surface area (86 m²/g) [38]. A slight change in the sorption capacity is observed for clinoptilolite samples calcined in the low-temperature region. In the process of thermal desorption of water from the surface of Transcarpathian clinoptilolite during low-temperature calcination, three stages are distinguished [37].

The first stage involves the removal (evaporation) of the surface film of liquid water. The temperature range of this stage is limited to temperatures ≤ 100 °C. In this range, a small fraction of moisture bound to the zeolite is released (within 1–2 %). The second stage, whose temperature range is 80 (100)–180 °C, makes a decisive contribution to the thermal desorption process. This stage is associated with the removal of capillary-bound water from mesopores and capillaries. At this stage, 73–75 % of zeolite water is released.

The third stage of the thermal desorption process, which corresponds to the temperature range $> 180\text{ }^{\circ}\text{C}$, is associated with the removal of water adsorbed with active centers of the zeolite surface [37]. During dehydration, cations of the clinoptilolite exchange complex migrate along cationic positions and, probably, also affect the sorption properties of the zeolite [40].

We attribute the decrease in the sorption capacity of clinoptilolite calcined at temperatures $\geq 400\text{ }^{\circ}\text{C}$ not only to the decrease in its specific surface area but also to the processes of amorphization of this zeolite. At such temperatures, the natural form of Transcarpathian clinoptilolite begins to amorphize [35]. The lack of Li(I) sorption by clinoptilolite samples calcined at $600\text{ }^{\circ}\text{C}$ is probably due to both the amorphization of the zeolite and the processes of deep surface dehydroxylation at such high temperatures, as mentioned in [35].

4. Conclusions

The method of determining the slip moment for assessing the sorption properties of Transcarpathian clinoptilolite for Li(I) was optimized, and its selectivity was studied.

The sorption properties of natural Transcarpathian clinoptilolite for trace amounts of lithium in aqueous solutions were investigated and it was found that this natural aluminosilicate can be used as a sorbent in the solid-phase extraction method. The most effective sorption occurs at pH 6.5 and a pre-calcination temperature of zeolite $350\text{ }^{\circ}\text{C}$ and is $538\text{ }\mu\text{g/g}$.

Si(IV) не впливає на ефективність сорбції Sc(III). Це свідчить про те, що з таких розчинів можна концентрувати і вилучати слідові кількості Sc(III) і, відповідно, розділяти Sc(III) та Si(IV). За вищих вмістів Si(IV) в розчинах унеможлиблювався процес фіксації моменту проскакування Sc(III).

-
1. Wiśniewska M., Fijałkowska G., Ostolska I. et al. Investigations of the possibility of lithium acquisition from geothermal water using natural and synthetic zeolites applying poly(acrylic acid) // J. Cleaner Prod. 2018. Vol. 195. P. 821–830. DOI: <https://doi.org/10.1016/j.jclepro.2018.05.287>
 2. Molenda J. Lithium-ion batteries – State of art Novel phospho-olivine cathode materials // Mater. Sci.-Pol. 2006. Vol. 24. P. 61–67.
 3. Bruce P. G., Scrosati B., Tarascon J.-M. Nanomaterials for Rechargeable Lithium Batteries // Angew. Chem. 2008. Vol. 47. P. 2930–2946. DOI: <https://doi.org/10.1002/anie.200702505>
 4. Languang L., Xuebing H., Jianqiu L., Jianfeng H. et al. A review on the key issues for lithium-ion battery management in electric vehicles // J. Power Sources. 2013. Vol. 226. P. 272–288. DOI: <https://doi.org/10.1016/j.jpowsour.2012.10.060>
 5. Samadiy M., Deng T. Lithium Recovery from Water Resources by Ion Exchange and Sorption Method // J. Chem. Soc. Pak. 2021. Vol. 43, No. 04. P. 406–416. DOI: <https://doi.org/10.52568/000585>
 6. Guo G.-C., Wang D., Wei X.-L. First-principles study of phosphorene and graphene heterostructure as anode materials for rechargeable Li batteries // J. Phys. Chem. Lett. 2015. Vol. 6, Iss. 24. P. 1–16. DOI: <https://doi.org/10.1021/acs.jpclett.5b02513>

7. Swain B. Recovery and recycling of lithium: a review // *Sep. Purif. Technol.* 2017. Vol. 172. P. 388–403. DOI: <https://doi.org/10.1016/j.seppur.2016.08.031>
8. Meshram P., Pandey B. D., Abhilash. Perspective of availability and sustainable recycling prospects of metals in rechargeable – A resource overview // *Resour. Policy.* 2019. Vol. 60. P. 9–22. DOI: <https://doi.org/10.1016/j.resourpol.2018.11.015>
9. U. S. Geological Survey (USGS). Mineral commodity summaries 2024. P. 110. DOI: <https://doi.org/10.3133/mcs2024>
10. Arustamian O., Tkachishin V., Kondratiuk V. The use of lithium salts in medicine and symptoms of the poisoning with them // *Emergency Medicine.* 2018. No. 1.88. P. 30–36 (in Ukrainian). DOI: <https://doi.org/10.22141/2224-0586.1.88.2018.124966>
11. Umeno A., Miyai Y., Takagi N. et al. Preparation and adsorptive properties of membrane-type adsorbents for lithium recovery from seawater // *Ind. Eng. Chem. Res.* 2002. Vol. 41, Iss.17. P. 4281–4287. DOI: <https://doi.org/10.1021/ie010847j>
12. Yoshizuka K., Kitajou A., Holba M. et al. Selective recovery of lithium from seawater using a novel MnO₂ type adsorbent III–benchmark evaluation // *Ars Separatoria Acta.* 2006. Vol. 4. P. 78–85.
13. Kitajou A., Suzuki T., Nishihama S. et al. Selective recovery of lithium from seawater using a novel MnO₂ type adsorbent II – enhancement of lithium ion selectivity of the adsorbent // *Ars Separatoria Acta.* 2003. Vol. 2. P. 97–106.
14. Ooi K., Miyami Y., Katoh S. et al. Topotactic Li⁺ insertion to λ -MnO₂ in the aqueous phase // *Langmuir.* 1989. Vol. 5, Iss. 1. P. 150–157.
15. Ooi K., Miyai Y., Sakakihara J. Mechanism of Li⁺ insertion in spinel-type manganese oxide. Redox and ion-exchange reactions // *Langmuir.* 1991. Vol. 7. P. 1167–1171.
16. Yoshizuka K., Fukui K., Inoue K. Selective recovery of lithium from seawater using a novel MnO₂ type adsorbent // *Ars Separatoria Acta.* 2002. Vol. 1. P. 79–86.
17. Chaban M., Dzyazko Y., Bystryk O. Materials based on titanium and manganese oxides for selective recovery of lithium from water sources // *Ukr. Chem. J.* 2019. Vol. 85, No. 2. P. 88–100. DOI: <https://doi.org/10.33609/0041-6045.85.2.2019.88.2019.88-100>
18. Bukowsky H., Uhlemann E., Steinborn D. The recovery of pure lithium chloride from “brines” containing higher contents of calcium chloride and magnesium chloride // *Hydrometallurgy.* 1991. Vol. 27, Iss. 3. P. 317–325. DOI: [https://doi.org/10.1016/0304-386X\(91\)90056-R](https://doi.org/10.1016/0304-386X(91)90056-R)
19. Alberti G., Massucci M. A. Crystalline insoluble acid salts of tetravalent metals–IX: Thorium arsenate, a new inorganic ion exchanger specific for lithium // *J. Inorg Nucl. Chem.* 1970. Vol. 32. P. 1719–1727. DOI: [https://doi.org/10.1016/0022-1902\(70\)80662-5](https://doi.org/10.1016/0022-1902(70)80662-5)
20. Marinsky J. A., Marcus Y. Ion Exchange and Solvent Extraction: A Series of Advances. Taylor & Francis, 1995. 472 p.
21. Navarrete-Casas R., Navarrete-Guijosa A., Valenzuela-Calahorra C. et al. Study of lithium ion exchange by two synthetic zeolites: Kinetics and equilibrium // *J. Colloid Interface Sci.* 2007. Vol. 306, Iss. 2. P. 345–353. DOI: <https://doi.org/10.1016/j.jcis.2006.10.002>
22. Kayiran S., Darkrim F., Gicquel A. et al. Hydrogen adsorption in lithium exchanged Na A zeolites. In: A. Galarneau, F. Di Renzo, F. Fajula, J. Védrine (Eds.) / *Studies in surface science and catalysis. Zeolites and Mesoporous Materials Pave the Dawn of the 21st Century.* Elsevier Science BV. Amsterdam, 2001. Vol. 135.

23. Tarasevich Yu. I., Kardasheva M. V., Polyakov V. E. Ion-exchange equilibria on clinoptilolite // Journal of Water Chemistry and Technology. 1996. Vol. 18, No. 4. P. 346–352.
24. Pat. WO2010018418A1 (Croatia). Formulation based on micronized clinoptilolite as therapeutic agent providing highly bioavailable silicon / Lelas A., Cepanac I. 12.08.2008, publ. 18.02.2010.
25. Armbruster T. Clinoptilolite-heulandite: applications and basic research. In: A. Galarneau, F. Di Renzo, F. Fajula, J. Viedrine (Eds.) / Studies in surface science and catalysis. Zeolites and Mesoporous Materials Pave the Dawn of the 21st Century. Elsevier Science BV. Amsterdam, 2001. Vol. 135. P. 13–27.
26. Tarasevich Yu. I. Surface Phenomena on Dispersed Materials. Kyiv: Naukova Dumka, 2011. 390 p.
27. Gualtieri A. F. The structure of Li-phillipsite. In: A. Galarneau, F. Di Renzo, F. Fajula, J. Viedrine (Eds.) / Studies in surface science and catalysis. Zeolites and Mesoporous Materials Pave the Dawn of the 21st Century. Elsevier Science BV. Amsterdam. 2001. Vol. 135. 8 p.
28. Vasylechko V. O., Gryshchouk G. V., Lebedynets L. O. et al. Adsorption of Copper on Transcarpathian Clinoptilolite // Adsorp. Sci. Technol. 1999. Vol. 17, No. 2. P. 125–134. DOI: <https://doi.org/10.1177/026361749901700206>
29. Tarasevich Yu. I., Polyakov V. E., Penchov V. Z. et al. Ion-exchange qualities and structural features of clinoptilolites of various deposits // Khim. Techol. Vody. 1991. Vol. 13, No. 2. P. 132–140.
30. Vasylechko V. O., Gryshchouk G. V., Kuz'ma Yu. B. et al. Adsorption of Copper on acid-modified Thanscarpathion Mordenite // Adsorp. Sci. Technol. 1996. Vol. 14, No. 5. P. 267–277. DOI: <https://doi.org/10.1177/02636174960140050>
31. Thomason P. F. Spectrophotometric Determination of Lithium // Anal. Chem. 1956. Vol. 28, Iss. 10. P. 1527–1530.
32. Shevchuk L., Kostiv O., Vasylechko V., Kalychak Ya. Research on the selectivity of the method for determining the breakthrough point for evaluating the adsorption properties of Transcarpathian clinoptilolite regarding Li(I) Kyiv Conference on Analytical Chemistry: Modern Trends 2024. Lviv, 2024. 16–18 October. P. 101.
33. Slota E., Vasylechko V., Patsay I. et al. The use of H-form clinoptilolite to preconcentrate trace amounts of Nd(III) from aqueous solution under dynamic conditions // Micropor. Mesopor. Mater. 2022. Vol. 333. 111739. DOI: <https://doi.org/10.1016/j.micromeso.2022.111739>
34. Kuzniatsova T., Kim Y., Shqau K. et al. Zeta potential measurements of zeolite Y: Application in homogeneous deposition of particle coatings // Micropor. Mesopor. Mater. 2007. Vol. 103, Iss. 1–3. P. 102–107. DOI: <https://doi.org/10.1016/j.micromeso.2007.01.042>
35. Vasylechko V. O., Gryshchouk G. V., Kuz'ma Yu. B. et al. Adsorption of cadmium on acid-modified transcarpathian clinoptilolite // Micropor. Mesopor. Mater. 2003. Vol. 60, Iss. 1–3. P. 183–196.
36. Vasylechko V., Gryshchouk G., Bielikova A., Kuz'ma Yu. Adsorption of Cr(III) on Transcarpathian clinoptilolite // Visnyk Lviv Univ. Ser. Chem. 2005. Iss. 46. P. 148–156 (in Ukrainian).

37. Zakordonskiy V., Vasylechko V., Stashchuk P., Gryschouk G. Thermal desorption of water and adsorption properties of Transcarpathian zeolites // Visnyk Lviv Univ. Ser. Chem. 2004. Iss. 44. P. 247–256.
38. Vasylechko V. O., Gryschouk G. V., Zakordonskiy V. P. et. al. Sorption of terbium on Transcarpatian clinoptilolite // Micropor. Mesopor. Mat. 2013. Vol. 167. P. 155–161.
39. Argun M. Use of clinoptilolite for the removal of nickel ions from water: Kinetics and thermodynamics // J. Hazard. Mater. 2008. Vol. 150, Iss. 3. P. 587–595.
DOI: <https://doi.org/10.1016/j.jhazmat.2007.05.008>
40. Tsitsishvili G. V., Andronikashvili T. G., Kirov G. R. et. al. Natural Zeolites. Chichester: Ellis Horwood, 1991. 297 p.

СОРБЦІЯ ІОНІВ ЛІТІУ З ВОДНИХ РОЗЧИНІВ НА ЗАКАРПАТСЬКОМУ КЛИНОПТИЛОЛІТІ

Л. Шевчук^{1*}, В. Василечко^{1,2}, Я. Каличак

¹Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія, 6, 79005 Львів, Україна;

²Львівський торговельно-економічний університет,
вул. Самчука, 9, 79011 Львів, Україна
*e-mail: Liubomyr.Shevchuk@lnu.edu.ua

Одержання літію з водних ресурсів є екологічно й економічно доцільнішим, якщо порівнювати з мінералами. Однак існує обмежена кількість селективних методів визначення слідових кількостей літію. Оскільки в природних водах та більшості технологічних розчинах літій міститься у незначних кількостях, актуальним є розроблення методів концентрування та вилучення цього металу.

Оптимізовано спектрофотометричну методику з використанням торону для визначення моменту проскакування літію під час його сорбції на закарпатському клиноптилоліті.

Досліджено селективність цієї методики стосовно катіонів, що можуть вимиватися з цеолітної матриці і, відповідно, впливати на аналітичний сигнал. Результати свідчать, що іони Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , які містяться у клиноптилоліті, не заважають визначенню Li^+ в аналізованих модельних розчинах.

Вивчено сорбційні властивості природного закарпатського клиноптилоліту щодо слідових кількостей літію у водних розчинах та з'ясовано, що цей природний алюмосилікат можна використовувати як сорбент у методі твердофазової екстракції. Найефективніше сорбція відбувається з розчинів за pH 6,5 зразками клиноптилоліту, попередньо прожареними за температури 350 °C. За оптимальних умов сорбційна ємність клиноптилоліту стовно літію становить 538 мг/г.

Ключові слова: сорбція, твердофазова екстракція, літій, природний клиноптилоліт.

Стаття надійшла до редколегії 01.11.2024
Прийнята до друку 21.01.2025