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Issue VII, November 2024

e-ISSN 2707-9481

ISBN 978-601-80473-3-6

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<https://doi.org/10.31643/2024.10>

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Study of acid treatment of lithium-manganese precursors

Abstract: Lithium production in Kazakhstan could be strategically important for the country as there has been a growing demand for this metal for the production of lithium-ion batteries, which are widely used in electric vehicles, portable devices and for storing energy from renewable sources. In addition, Kazakhstan is actively developing its lithium industry and is looking for ways to make the most efficient use of its lithium resources to support global energy. The use of highly selective sorbents can play a decisive role in the development of lithium-containing natural resources. The paper presents the results of research on acid treatment. X-ray phase analysis showed that the obtained manganese dioxide sorbent has a cubic crystal lattice structure.

Keywords: acid treatment, lithium-manganese precursors, hydrochloric acid, X-ray diffraction analysis, sorbent.

Introduction

Lithium is a light alkali metal with high ductility. Due to its outstanding chemical characteristics, including excellent electrical conductivity and low density, it is widely used in various industries (Tarascon, 2010; Kenzhaliyev et al., 2021; Ablakatov, et al., 2023; Abdulvaliyev et al., 2025).

Lithium is characterised by a wide variety of compounds that are required for many applications. Also, lithium has a wide range of industrial applications. It plays a key role in the production of glass and ceramics, is used in pharmaceuticals and nuclear power, and finds use in the creation of alloys for the aerospace industry. However, the most well-known use of lithium is in the production of lithium batteries, which are found in mobile phones, laptops, electric cars and other lithium-ion battery-powered devices (Bai et al., 2020; Ul'tarakova et al., 2021; Ablakatov et al., 2022; Balaram et al., 2024).

Lithium-ion batteries (Li-ion) are a type of battery that uses lithium ions as the main element for storing and transferring electrical energy. As mentioned above, they are widely used in modern devices such as smartphones, laptops, electric cars and portable electronics due to their high energy capacity, and low self-discharge (Gao et al., 2023; Nandihalli, 2024).

These features make lithium-ion batteries one of the most sought-after and efficient batteries, especially for mobile devices and electric vehicles.

The growing global demand for lithium stimulates research and development of technological solutions for processing lithium-containing hydromineral raw materials, including associated formation brines (Alera et al., 2024; Xin et al., 2016).

Recently, lithium-ion sieve (LIS) technology has become one of the most promising technologies for lithium extraction from petroleum brines. LIS provide highly selective extraction of lithium from complex solutions with a high content of associated components. In general, LIS is divided into two types depending on their chemical composition: lithium-manganese oxide (LMO) and lithium-titanium oxide (LTO) (Quanmin et al., 2024; Joshua et al., 2022; Stringfellow & Dobson, 2021).

Manganese oxide-based lithium ion oxides are currently the most popular selective sorbents. In previous studies, the conditions for the preparation of lithium-manganese precursor having the composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ were studied. To clarify and obtain additional information, it is of great interest to study the acid treatment of lithium-manganese precursors.

Research Methods

Analysis methods: the quantitative content of basic elements in precursors were determined on an atomic emission spectrometer with inductively coupled plasma Optima 8300DV (Perkin Elmer Inc., Waltham, MA, USA). X-ray phase analysis (XRD) was carried out on a diffractometer D8 ADVANCE "BRUKER AXS GmbH", (Karlsruhe, Germany) radiation $\text{Cu-K}\alpha$, database PDF-2 International Center for Diffraction Data ICDD (Swarthmore, PA, USA).

Experimental procedure: precursors were poured with the required amount of dilute hydrochloric acid solution according to the experimental procedure for acid treatment. The process was performed at a given temperature and contact time under stirring in a 3 dm^3 sealed thermostated cell equipped with a VELP Scientifica LS F201A0151 mechanical stirrer (Usmate Velate, Italy), providing a fixed speed. Constant temperature was maintained using an Aizkraukles TW 2.02 water bath thermostat (ELMI, Riga, Latvia).

Research Results

Acid treatment was carried out to remove lithium from the lithium-manganese precursor and to obtain a sorbent. At removal of lithium from the precursor, at the same time in the structure of the resulting sorbent, there should remain free vacant cells, very small in size, which during sorption can be occupied only by lithium, or replacement of lithium by a hydrogen atom capable of exchange for a lithium atom.

The effects of temperature, precursor-to-acid weight ratio and duration on acid treatment were studied.

The influence of process temperature was studied under the following conditions: temperature 30, 40, 50, 60 °C; HCl concentration 0.5 M; duration 12 h; ratio of sorbent mass to acid solution volume (S:L) = 1:800. The results of the studies are given in Figure 1.

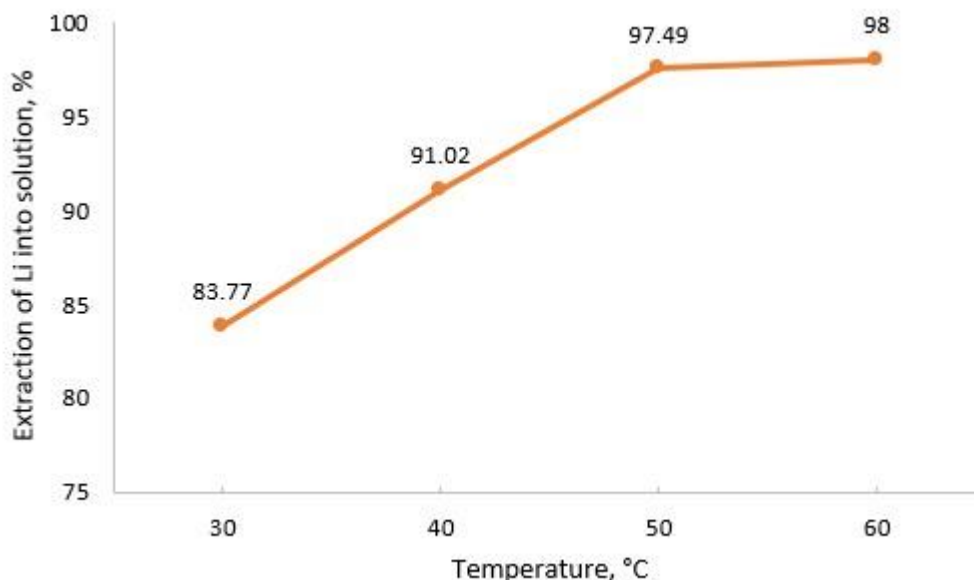


Figure 1. Effect of temperature on acid treatment of precursor

The obtained research results show that with increasing process temperature lithium extraction into solution increases, at temperature 40 °C lithium extraction reaches above 91 %. Losses of manganese in the whole temperature range under study are ~12.5-14 %. The most preferable temperatures are 40 °C, at which lithium extraction is 91 %, manganese losses are 12.95 %.

Study of the influence of precursor mass to acid volume ratio. The studies were carried out under the following conditions: temperature 40 °C; HCl concentration 0.5 M; duration 12 h; sorbent mass to acid solution volume ratio (S:L) = 1:600; 1:700; 1:800; 1:900. The results of the studies are given in Figure 2.

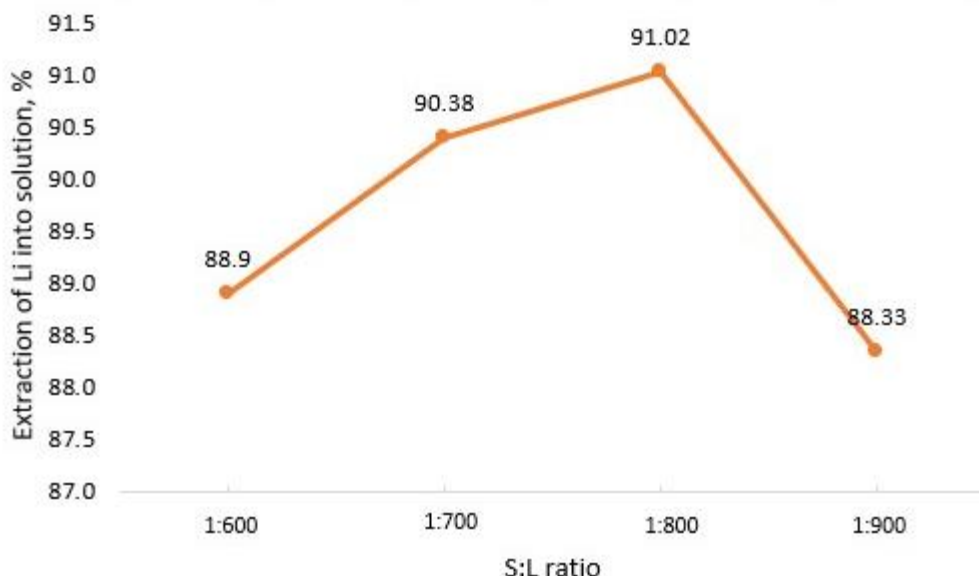


Figure 2. Effect of S:L ratio on acid treatment of precursor

The results of experiments show that at S:L ratios 1:700 and 1:800 lithium extraction becomes maximum and makes ~90-91 %, at the same time manganese losses are in the range of 12,28-12,95 %. On this basis, the most acceptable are S:L ratios of 1:700 and 1:800.

The influence of duration of acid treatment was studied under the following conditions: temperature 40 °C; HCl concentration 0.5 M; S:L ratio = 1:800; duration 2, 6, 12, 18 and 24 hours. The obtained results are given in Figure 3.

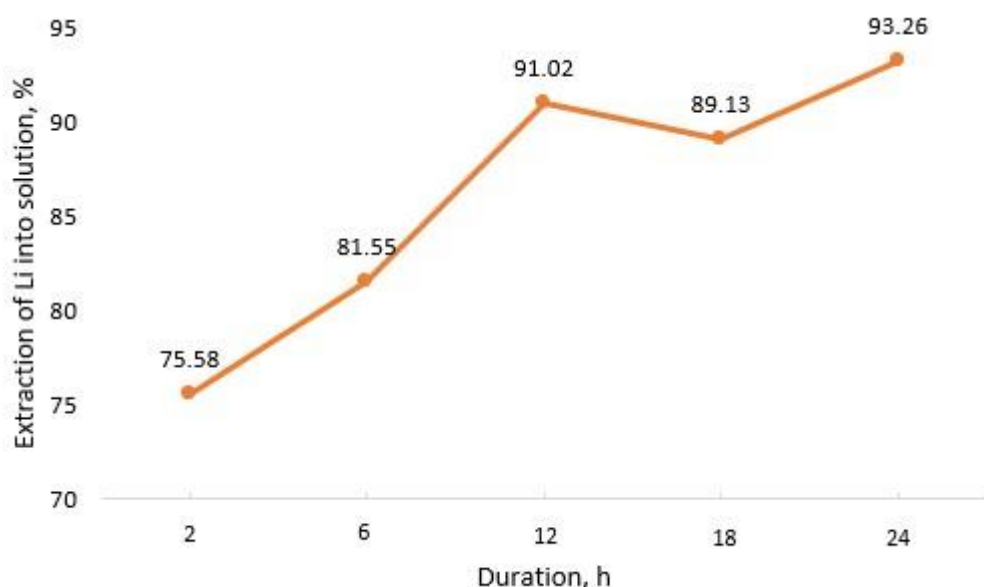


Figure 3. Effect of Process Duration on acid treatment of Precursor

Increasing the duration of acid treatment leads to an increase in the degree of lithium transfer into the solution. At 12 h and more the recovery reaches ~90 % and more, at that throughout the studied values of duration of the process manganese losses practically do not change. From the obtained data the most preferable duration of 24 h, at which the lithium recovery above 93 % is achieved.

X-ray phase analysis of the obtained sorbent presented in Figure 4. shows that it consists of manganese dioxide monophase with cubic crystal lattice structure.

Thus, the results of the conducted studies of acid treatment showed that the most acceptable conditions of the process are temperature 40 °C, HCl concentration 0.5 M; S:L ratio = 1:700 and 1:800 and

duration of 24 h. In this case, the lithium extraction into solution from the precursor can reach ~93 %, and the lithium content in the sorbent is 0.277 %.

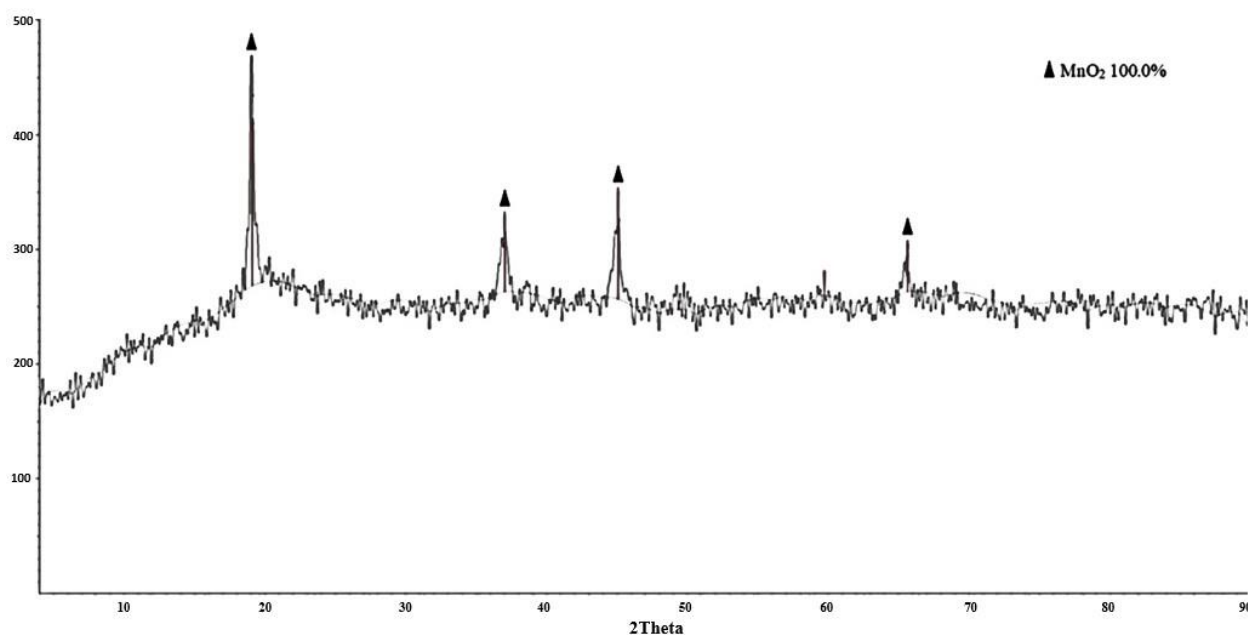


Figure 4. Diffractogram of the obtained sorbent

Thus, the results of the conducted studies of acid treatment showed that the most acceptable conditions of the process are temperature 40 °C, HCl concentration 0.5 M; S:L ratio = 1:700 and 1:800 and duration 24 h. In this case, the lithium extraction into solution from the precursor can reach ~93 %, and the lithium content in the sorbent is 0.277 %.

Conclusions

The obtained research results show that acid treatment of precursor is preferably carried out under the following conditions: temperature 40-50 °C, HCl concentration 0.5 M; S:L ratio = 1:700 and 1:800 and duration of 24 hours. In this case, the lithium extraction into solution from the precursor can reach ~93-97 %.

CRedit author statement: **Z. Karshyga:** Supervision, Conceptualization, Visualization, Methodology. **A.Yersaiynova:** Data curation, Writing draft preparation, Reviewing and Editing, Investigation. **A.Yessengazyev:** Validation. **B. Orynabayev:** Software.

Acknowledgement. This work was supported by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, grant number No BR18574018.

Cite this article: Yersaiynova A.A., Yessengazyev A.M., Karshyga, Z.B., Orynabayev B.M. (2024). Study of acid treatment of lithium-manganese precursors. *Challenges of Science*. Issue VII, pp. 71-75. <https://doi.org/10.31643/2024.10>

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