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Comparative Study on Lithium Recovery with Ion-Selective Adsorbents and Extractants: Results of Multi-Stage Screening Test with the Use of Brine Simulated Solutions with Increasing Complexity

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Abstract: Oil (and natural gas) field brines can be considered promising sources of lithium for the sustainable supply of a growing market. To date, many materials have been developed for direct lithium recovery from brines, but most often these materials have been tested under various conditions, what makes it impossible to compare them. The aim of this research is to provide knowledge that would enable the comparison and selection of effective sorbents for different types of brines. For this purpose, an eight-step experimental protocol was employed. The recovery tests started with a pure lithium solution (300 mg/kg), and then other salts were gradually added, resulting in a brine containing Li⁺ (220 mg/kg), Na⁺ (7.21 wt%), Ca²⁺ (3.0 wt%) and Mg²⁺ (1000 mg/kg). For selected cases, the effect of pH was also investigated. Fifty materials (including ion exchange resins, organophosphate extractants, mineral adsorbents) were examined, for which the distribution coefficient and lithium recovery were determined. Moreover, for the most promising materials, lithium over magnesium selectivity and lithium ion capacity were determined. Only γ -Al₂O₃, TiO₂ and MnO_x-based powders keep their effectiveness in ultra-high salinity ranges and in the presence of high concentrations of Ca²⁺ and Mg²⁺ in alkaline solution.

Keywords: lithium; lithium recovery; oil field brine; lithium-selective material; adsorbent; extractant; sorption; multi-stage screening test; testing protocol

1. Introduction

Lithium production from domestic resources has drawn much attention in the European Union (EU) due to geopolitical and economic reasons. The development of e-mobility stimulates the growing demand for lithium, and its shortages may hinder the global energy transition [1]. The price of battery-grade lithium carbonate spiked from USD 10,000–18,000 per ton in previous years up to USD 75,000 per ton in December 2022 [2]. At the same time, many experts forecast that the electric vehicle (EV) market is expected to maintain steady growth for the next few years [1]. According to the REPowerEU policy announced by the EU in 2022 [3], the current use of fossil fuels is only temporary. The long-term goal announced in this program is to accelerate the diversification of energy sources and the decarbonization of industry and transport. A manifestation of this is the announcement of an increase in expenditure on the development of new technologies for the extraction and processing of critical raw materials, including lithium: "The 2023–2024 work programme for Cluster4 sets out a range of funding opportunities concerning CRMs, for instance in the call on resilient value chains (e.g., to improve technologies for extraction and processing of CRMs). It has a total indicative budget worth €213 million" [4]. The



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). above-mentioned position of the EU indicates an increase in demand for new technologies for obtaining critical materials, including new technologies for lithium recovery. In short-term perspectives, the total lithium consumption would increase from 93 kilotons in 2021 to 220–288 kilotons by 2025 [5]. To meet the goals of the Paris Agreement in 2040, at least 40 times the amount of lithium is needed (compared to 2020) [6]. The World Economic Forum estimates that global transport needs 2 billion electrical vehicles to achieve net zero-emission transport and raises questions concerning lithium demand and resources, which motivates the search for new lithium resources, and this concern especially affects Europe [7].

Despite the relative global abundance of lithium, its commercial sources are of three types: hard rock deposits, brines and clay minerals which constitute 19%, 78% and 3% of the total resources, respectively [8]. Identified lithium resources are about 89 million tons (Mt) and distributed as follows: Bolivia 21 Mt (brines and salars), Argentina 19 Mt (brines and salars), Chile 9.8 Mt (brines and salars), USA 9.1 Mt (brines), Australia 7.3 Mt (hard deposits), China 5.1 Mt (hard deposits and brine) [9]. According to the International Energy Agency, Chinese companies account for around 60% of the global lithium chemical supply [10] and China's leadership in battery cell manufacturing is of concern to Western countries. In 2020, the European Commission identified lithium as crucial to the EU's economy and added it to the Critical Raw Materials list [11]. Currently, according to the European Commission report, the major global supplier of lithium is Chile with a 44% share in the market. Moreover, Chile is the main supplier of lithium materials for the European Union with a 78% share [11]. Worldwide (in 2022), there are eight full-scale facilities which produce lithium from continental brines. Four of them are located in South America in the so-called Lithium Triangle (Salar de Atacama 1 and 2 (Chile) and Salar del Hombre Muerto and Salar de Olaroz (Argentina)). Other important extraction facilities are Clayton Valley in the USA and Lake Zabayu (or Zabuye), Dongtai Salt Lake and Xitai Salt Lake in China. Deposits of lithium are also found in Bolivia (Salar de Uyuni). Lithium is produced using conventional solar evaporation/crystallization technology at all of the above-mentioned facilities. Salar de Atacama 1 and 2 are the largest production facilities in the world (121190 tons of lithium carbonate equivalent per year) and have the greatest experience in recovering lithium on an industrial scale. Nevertheless, since the 2000s, the environmental impact of solar evaporation technology has been discussed and there has been a growing interest in reducing its environmental impact [12]. Therefore, there is a need to develop novel technologies for direct lithium extraction as well as (due to the growing lithium market) to search for unconventional sources of lithium. Due to limited data concerning the environmental impact of the lithium production using different technologies, a life cycle assessment of the fully developed technology will be needed in the future for decision makers prior to investing in a full-scale facility [12]. Distribution of lithium resources is very uneven and only 1-2% of worldwide lithium is produced in the European Union [13]. There are a few confirmed pegmatite deposits in Europe, including Portugal (Barroso-Alvao, Guarda-Goncalo) [14], Spain (Extremadura region) [15], the Czech Republic (Cinovec) [16], France, Austria (Wolfsberg), Finland and Germany [8]. In the USA only one lithium mine operates today (Albemarle's Silver Peak in southwestern Nevada) [17]. To become self-reliant in terms of lithium supplies, both the USA and the EU should develop lithium extraction from geothermal brines and oil field waters.

Intensive work is underway to recover lithium from hypersaline geothermal fluids in the Salton Sea area in California, where 600,000 tons of lithium carbonate could potentially be produced annually (raw material: geothermal brine; [Li] = 202 mg/kg; technology: inorganic sorbents) [18,19]. Within the European Geothermal Lithium Brine (EuGeLi) project [20], pilot-scale tests were conducted in 2021 at the Rittershoffen geothermal power plant (northern Alsace (raw material: geothermal brine; [Li] = not made publicly available; technology: sorbents)) [21]. The most promising sources of lithium are oil field brines due to the higher lithium concentration than in geothermal brines or in seawater. The average lithium concentration in seawater is 0.17 mg/L, and although various technologies

have been tested to recover lithium from this source, it is unprofitable [22,23]. The average lithium concentration in the Salton Sea geothermal brine is 202 mg/L, but other geothermal fluids in the USA contain 0.5–30 mg/kg of lithium [24]. Sanjuan et al. [25] identified six geothermal systems in Europe with lithium concentrations greater than 125 mg/L. Reported lithium concentrations in oil field brines are in the following ranges: 50–572 mg/L for the Smackover Formation in the Gulf of Mexico, 132–333 mg/L in Texas Cretaceous reservoirs and 100–288 mg/L in North Dakota Devonian formations [26,27]. Moreover, in the case of oil field brines, industrial infrastructure is usually located at the mining site (capital expenditure (CAPEX) will be lower than for green field investment). The oil field brine is under high pressure which is beneficial because less energy is required to pump the brine through the sorbent bed. Another advantage is that the post-process brine can be reinjected into the formation, so the environmental impact will probably be lower in comparison to the solar evaporation technology [12,28,29], but precise assessment will only be possible after assessing the full technology using life cycle assessment. However, the use of oil field brine as a source of lithium has several constraints. First of all, the concentrations of other ions hindering the recovery of lithium are also high. Typical ranges of sodium, potassium, calcium, magnesium and lithium ions in oil field (gas field) brines are 10-204,302 mg/L, 1-5490 mg/L, 1-83,950 mg/L, 1-25,340 mg/L and 0-611 mg/L, respectively [30] (for comparison of the composition of conventional sources of lithium: continental brine from Atacama Chile: $[Na^+] = 6.5-9.1$ wt%; $[K^+] = 1.79-3.13$ wt%; $[Ca^{2+}]$ = 245-530 mg/kg; $[Mg^{2+}] = 0.93-1.30 \text{ wt}$; Li⁺ = 1500-2420 mg/kg [27]). Conventional solar evaporation/crystallization technology allows for concentration of lithium from 2000 mg/L to 6 wt%, so it will be a hard task to apply this technology to brine with lower lithium concentrations (50-350 mg/kg) [24]. Therefore, the most important thing is to find a sorbent or extractant which allows lithium separation from complex brines and exhibits high selectivity towards lithium in such a complex solution. In the literature, there are many examples of lithium-selective molecular sieves (based on manganese oxides, titanium oxides and aluminum hydroxide) [24,31–33], extractants (crown ethers, organophosphates, multi-component extractants) [24,34,35], as well as other materials (resins loaded with aluminum hydroxides [36,37], zeolites [38,39], molecular imprinted polymers [40,41]). The experience of research teams in recent years is well summarized in many comprehensive reviews (e.g., [24]) that are readily available, so we will not describe it in detail. However, such materials are often tested under different and incomparable conditions.

Taking into account above-described economic and political background (from a regional European Union point of view) and including the current state of lithium separation technology, it can be assumed that there is a need to develop novel processes in the area of direct lithium separation as well as trials to apply known lithium recovery methods to novel resources such as oil field brines. The main aim of our study is to present benchmark data for several promising materials (according to the literature) and for products available on the market used to separate lithium from complex brines simulating oil field brines. This is the first step to develop and check the feasibility of lithium recovery from oil field (and gas field) brines.

Baudino et al. [42] highlighted the need for a systematic research methodology in which various materials for lithium recovery will be tested and reported in a standardized manner. Our paper is also the answer to this postulate. We propose an eight-stage experimental protocol to test lithium recovery from oil field brines. In the first stage, sorbents and extractants are introduced into the artificial brine containing only Li⁺ in a concentration of 300 mg/kg. Sodium, magnesium and calcium are then added to this solution in various concentrations, resulting in the final stage of testing a brine containing: 220 mg/kg of Li⁺, 7.21 wt% of Na⁺, 3 wt% of Ca²⁺ and 1000 mg/kg of Mg⁺. Applying this test protocol, 50 different materials (commercially available ion exchange resins, adsorbents and extractants as well as sorbents synthesized (Table A1) or modified by us) for lithium recovery were tested.

This study is mainly considered within the framework of raw materials and tasks in the territory of the European Union, therefore the research methodology including brine composition and Li-selective materials selection was adjusted accordingly. It is commonly known that the presence of magnesium ions interferes most with the recovery of lithium. The magnitude of the influence of various ions can be described by the following series: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. We decided to perform a multi-stage screening test with the use of eight brine simulating solutions with increasing complexity of the composition to check effects of additions of subsequent ions to the solution. The possible effect of the presence of cesium and rubidium ions was ignored due to the low (0.1-50 mg/kg) concentration of these elements, and the weak effect of potassium ions was also omitted. A detailed description of the influence of individual ions on lithium recovery is included in the Results section and discussed both in the light of literature data and our own research. Due to the possible influence of pH, we also performed tests for brines after pH correction (to pH 9). As a result of the test, we obtained the values of the distribution coefficient (K_d) of lithium ions. K_d was used as a success criterion due to the simplicity of determination and its usefulness. First of all, the distribution coefficient describes the affinity of sorbent/extractant for lithium ions in different matrixes. High affinity for lithium is a prerequisite for the practical application of a given sorbent/extractant. The $K_d > 3$ criterion is the minimum criterion that can be accepted for a given sorbent to be subjected to further testing, but it is too small to use such a sorbent practically. Nevertheless, the purpose of this research is also to explore new materials that have not been considered to date. A weak success criterion allows us not to miss new, potentially interesting materials. We also believe that our results can be a guide for the development of new lithium-selective materials.

2. Materials and Methods

2.1. Materials

2.1.1. Commercially Available Extractants and Adsorbents

AmberLite MAC-3 H (MAC3), Lewatit MonoPlus SP112, Lewatit TP260, Amber-Lite HPR1200 H (HPR 1200H), AmberLite IRC120 H (IRC 120H), phenylphosphonic acid (PhPO(OH)₂), trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (CYPHOSIL 104), trioctylphosphine oxide (TOPO), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTA), reduced graphene oxide (RGO), silica gel for column chromatography 60 A (Silica 60 Å), activated aluminum oxide, basic Brockmann I (γ -Al₂O₃), halloysite nanoclay (halloysite), kaolinite, silica mesoporous SBA-15 (SBA-15), zirconium(IV) hydroxide (Zr(OH)₄) and ethyl/butyl phosphonic acid silica (SiO₂-Et/Bu-PO(OH)₂) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Purolite CT169, Purolite C100 and Puromet MTS9500 were provided by Purolite. Bis(2-ethylhexyl) phosphate (D2EHPA), tri-n-butyl phosphate (TBP), tritolyl phosphate (TCP), zeolite beta ammonium form (β -zeolite) and zeolite ZSM-5 ammonium form (ZSM-5) were purchased from Alfa Aesar (Haverhill, MA, USA). (2-Ethylhexyl)phosphonic acid mono-2-ethylhexyl ester (mono-D2EHPA) was purchased from TCI Chemicals (Tokyo, Japan). Norit SX2 R activated carbon was purchased from Pol-Aura (Warsaw, Poland). Cellulose, phosphate (Selectacel[®] phosphate) (CellPhos) was purchased from Polysciences (Warrington, PA, USA). Links to the product data sheets of commercially available resin, adsorbents and extractants are provided in Appendix B.

2.1.2. Chemicals for Synthesis

Analytical grade chemicals were used for the synthesis of adsorbents. Manganese(II) acetate tetrahydrate, phosphoric acid, nitric acid, lithium carbonate, hydrochloric acid and formaldehyde solution (36 wt%) were purchased from Pol-Aura. Zirconium carbonate basic hydrate and titanium(IV) oxide sulfate sulfuric acid hydrate were purchased from Alfa Aesar. Titanium(IV) oxide, anatase and rutile, (3-aminopropyl)triethoxysilane (APTES), hypophosphorous acid solution (50 wt%), aminotris(methylenephosphonic acid) (50 wt% aqueous solution), toluene (SeccoSolvTM) and methanol were purchased from Sigma-Aldrich.

2.2. Sorbent Synthesis

2.2.1. Synthesis of Zirconium Phosphates and Mixed Zirconium and Titanium Phosphate

Zirconium phosphate sorbents (ZrP1, ZrP2, ZrP3, ZrP4, ZrP5 and ZrTiP) were prepared by a precipitation method according to the following procedure. First, 66.60 g of zirconium carbonate basic hydrate (or 41.32 g of zirconium carbonate basic hydrate and 30.00 g of titanium(IV) oxide sulfate sulfuric acid hydrate in the case of ZrTiP) was reacted with 70 cm³ of 65 wt% nitric acid, then a freshly prepared solution of zirconium nitrate (or mixture of zirconium and titanium) was diluted with 1 M nitric acid (in the case of ZrP6, 4.5 times the amount of nitric acid solution was used than in the case of other sorbents, while in the case of ZrP5, no dilution was used). To the clear solution of zirconium (or zirconium and titanium) nitrate, phosphoric acid (42.5 wt%) was gradually added with constant stirring to obtain the assumed molar ratios P:Zr (or P:(Zr + Ti) in the case of ZrTiP) of approximately 1 for ZrP1, 2 for ZrP2, ZrP5, ZrP6 and ZrTiP, 10 for ZrP3 and 0.5 for ZrP4. The white precipitate formed was left in mother liquor for 48 h for aging. In the next step, the zirconium phosphate was separated by centrifugation and washed with deionized water until the pH of the wash water was about 4. The obtained material was dried in air at 102 °C for 24 h and then ground down to the desired particle size.

2.2.2. Synthesis of Zirconium Phosphonates and Mixed Zirconium and Titanium Phosphonate

Zirconium phosphonate sorbents (Zr-ATPMP1, Zr-ATMP2, Zr-ATMP3, Zr-ATMP4, Zr-ATMP5 and ZrTi-ATMP) were prepared by a precipitation method. In our work, the following procedure was used. First, 66.60 g of zirconium carbonate basic hydrate (or 95.90 g of zirconium carbonate basic hydrate and 32.0 g of titanium(IV) oxide sulfate sulfuric acid hydrate in the case of ZrTi-ATMP) was reacted with 70 cm³ of 65 wt% nitric acid, then a freshly prepared solution of zirconium nitrate (or mixture of zirconium and titanium) was diluted with 1 M nitric acid. To the clear solution of zirconium (or zirconium and titanium) nitrate, aqueous aminotris(methylenephosphonic acid) (50 wt%) was added dropwise with constant stirring to obtain the assumed molar ratios P:Zr (or P:(Zr + Ti) in the case of ZrTi-ATMP) of approximately 100 for Zr-ATMP1, 6.5 for Zr-ATMP2, 12.5 for Zr-ATMP3, 25 for Zr-ATMP4, 50 for Zr-ATMP5 and 2.5 for ZrTi-ATMP. The resulting suspension was stirred for 1 h and then allowed to stand for 48 h. In the next stage, the precipitate formed was separated by centrifugation and washed with deionized water several times. Centrifugation and washing were carried out until the supernatant reached pH 3. The obtained material was dried in air at 102 °C for 24 h and then ground down to the desired particle size.

2.2.3. Synthesis of Manganese Oxide-Based Adsorbents

Manganese oxide-based adsorbents (LIS10, LIS11 and LIS12) were prepared as follows: appropriate amounts of manganese(II) acetate tetrahydrate (40.0 g for LIS10, 20.0 g for LIS11, 5.0 g for LIS12) and lithium carbonate (132.7 g for LIS10, 132.7 g for LIS11, 70.0 g for LIS12) were ground and transferred to an alumina crucible and calcinated in air (ramp from room temp. 1 °C/min; isothermal calcination at 400 °C for 4 h, slow free cooling for 8 h). The assumed Li:Mn molar ratios were 2.0 for LIS10, 1.0 for LIS11 and 0.5 for LIS12. The obtained materials were pickled with hydrochloric acid and, in the first stage, 1 L of deionized water and 10 g of 35 wt% hydrochloric acid were added to approximately 10.0 g of sorbent, the mixture was stirred for 3 h and then it was left overnight. The clear lithium chloride solution was decanted. Next, a portion of dilute hydrochloric acid (0.01 M) was added to the sorbent, mixed, left overnight and thereafter the solution was lower than 20 mg/kg. In the final step, lithium-free wet material was mixed with 1 L of deionized water and left overnight, then the solution was decanted and wet sorbent was dried at 40 °C for 72 h.

2.2.4. Synthesis of Titanium Oxide-Based Adsorbents

Titanium oxide-based adsorbents (LIS1, LIS2, LIS3, LIS4, LIS5) were prepared according to the following procedure. Appropriate amounts of titanium oxide rutile or anatase (46.0 g of anatase for LIS1, 46.0 g of rutile for LIS2, 20.0 g of anatase for LIS3, 20.0 g of anatase for LIS4, 20.8 g of anatase for LIS5) and lithium carbonate (50.0 g for LIS1 and LIS2, 37.1 g for LIS3, 9.9 g for LIS4, 19.2 g for LIS5) were ground and transferred to an alumina crucible and calcinated in air (ramp from room temp. 2 °C/min; isothermal calcination at 700 °C for 4 h (500 °C for LIS5), slow free cooling for 8 h). The assumed Li:Ti molar ratios were 2.5 for LIS1 and LIS2, 4.3 for LIS3, 1.1 for LIS4 and 2.0 for LIS5. The prepared materials were pickled with hydrochloric acid and, in the first step, 1 L of deionized water and 10 g of 35 wt% hydrochloric acid were added to approximately 10.0 g of sorbent, the mixture was stirred for 3 h and then it was left overnight. The clear lithium chloride solution was decanted. Next, a portion of dilute hydrochloric acid (0.01 M) was added to the sorbent, mixed, left overnight and thereafter the solution was decanted. The operation was repeated until lithium concentration in the solution was lower than 20 mg/kg. In the final stage, lithium-free wet material was mixed with 1 L of deionized water and left overnight, then the solution was decanted and wet sorbent was dried at 40 °C for 72 h.

2.2.5. Preparation of Silica Modified by Aminophosphonate Groups

The modification of silica with aminophosphonate groups was performed as follows: 10 g of silica gel for column chromatography 60 Å was dried at 120 °C for 6 h under vacuum and subsequently reacted with 250 mL of dried toluene and 20 g of APTES under nitrogen. The reaction mixture was refluxed for 24 h. Afterward, the APTES-modified silica gel was separated by filtration, rinsed with toluene and methanol and dried under vacuum. In the next step, 30 mL of glacial acetic acid was added to the APTES-modified silica gel, followed by the addition of 50 mL of H₃PO₂ solution (50 wt%) and 20 mL of formaldehyde solution (36 wt%). The reaction mixture was stirred at room temperature for 3 days. Thereafter, the obtained modified silica (SiO₂-APTES-CH₂-PO(OH)₂) was separated by filtration, rinsed with methanol and dried at 40 °C for 6 h under vacuum.

2.3. Analytical Method

The concentrations of lithium and magnesium were determined by flow injection atomic absorption spectrometry (FI-AAS) using the calibration curve method. Measurements were carried out on an AAnalyst 100 Atomic Absorption Spectrometer by PerkinElmer. In order to take into account the influence of the matrix, standard solutions for calibration curves were prepared, containing sodium and calcium chloride in concentrations reflecting the composition of the matrix (for each stage of the screening tests). Each analysis was repeated five times, and the mean value was taken as the result.

2.4. Screening Test Procedure

An eight-stage procedure was used to select the most effective sorbents/extractants. In the first stage, recovery of lithium was examined using pure lithium chloride solution (300 mg/kg). The distribution coefficients (K_d) of lithium ions determined under the conditions described below were used as the success criterion. If K_d > 3, the sorbent/extractant passed to the second stage, otherwise the test was repeated with a pure lithium solution at pH 9 (pH of the solution mixed with the sorbent was corrected using diluted NaOH solution). If K_d (at pH 9) > 3, the sorbent/extractant passed to the second stage, otherwise the sorbent/extractant was rejected from subsequent tests. The above-described procedure was repeated in successive steps using K_d (or K_d pH 9) > 3 as the acceptance criterion. Recovery of lithium from sodium chloride solutions (at different concentrations of NaCl) in 2–4 stages was studied. The effect of calcium chloride addition was studied in stages 5 and 6, while the effect of magnesium chloride addition was studied in stages 7 and 8. The compositions of the solutions used at the various stages of the screening tests are presented in Table 1.

Stage Number	Li ⁺ [mg/kg]	Na ⁺ [wt%]	Ca ²⁺ [wt%]	Mg ²⁺ [mg/kg]
1	300	0	0	0
2	300	0.10	0	0
3	297	1.00	0	0
4	240	7.86	0	0
5	240	7.86	0.1	0
6	220	7.21	3.0	0
7	220	7.21	3.0	300
8	220	7.21	3.0	1000

Table 1. The composition of the solution used at a given stage of screening tests.

2.5. Lithium Recovery Tests (for Each Stage of Screening Test)

Lithium recovery tests were performed as follows: 1.00 g of the appropriate sorbent (or 1.00 g of the appropriate extractant diluted with an organic solvent 1:1 (wt/wt)) was mixed with 10.00 g of a solution with the appropriate concentration of Li^+ , Na^+ , Ca^{2+} and Mg^{2+} as described for each stage of the screening tests in Table 1. The mixtures were shaken at room temperature for 24 h. After a given time of contact, the sorbent/extractant was removed from the mixtures by filtration or centrifugation. The clear solution after sorption was diluted 100-fold and analyzed by FI-AAS. For each sorbent, the sorption experiment was carried out twice, and the average value was taken as the result.

The values of the distribution coefficient (K_d) of lithium ions were calculated according to Equation (1):

$$K_d = \frac{(C_{0_Li} - C_{e_Li}) \cdot \left(\frac{m_{sol}}{m_{sorb}}\right)}{C_{e_Li}} \tag{1}$$

where C_{0_Li} (mg/kg) and C_{e_Li} (mg/kg) are the initial and the equilibrium concentration of lithium, m_{sol} (g) and m_{sorb} (g) are the mass of solution and sorbent used in sorption experiment.

The values of recovery of lithium ions R_{Li} (%) were calculated according to Equation (2):

$$R_{Li} = \frac{(C_{0_Li} - C_{e_Li})}{C_{0_Li}} \cdot 100\%$$
(2)

The values of R_{Li} for all tested materials are included in Appendix A (see Table A2).

2.6. Determination of Maximum Lithium Capacity Values for Selected Cases

The lithium ion recovery tests were repeated using increasing masses of the appropriate lithium ion solution (10.00, 20.00, 40.00, 70.00 g, etc.) and the values of the lithium ion sorption capacity (q_e) were calculated according to Equation (3):

$$q_e = \frac{(C_{0_Li} - C_{e_Li}) \cdot m_{sol}}{m_{sorb}}$$
(3)

The maximum sorption capacities of lithium ions for the tested materials were determined on the basis of the collected data (q_e) according to Equation (4):

$$q_{e_max} = \lim_{\substack{\frac{m_{sol}}{m_{sorb}} \to \infty}} q_e \tag{4}$$

For selected cases, the selectivity values of lithium ion recovery over magnesium ion recovery ($\beta_{Li/Mg}$) were calculated according to Equation (5):

$$\beta_{Li/Mg} = \frac{(C_{0_Li} - C_{e_Li}) \cdot (C_{e_Mg})}{(C_{0_Mg} - C_{e_Mg}) \cdot (C_{e_Li})}$$
(5)

where C_{0_Mg} (mg/kg) and C_{e_Mg} (mg/kg) are the initial and the equilibrium concentration of magnesium.

3. Results and Discussion

3.1. Effect of Brine Composition on Performance of Lithium Ion-Selective Materials—Results from Multi-Stage Screening Test

The cost-effective and environmentally friendly technology of lithium recovery from oil (and natural gas) field brines is a difficult and complex task, as was mentioned in the Introduction. Currently, our research group is evaluating the feasibility of developing such a technology [43]. One of the first tasks in our project is an extensive search for cheap or easy to produce (or commercially available) materials with high affinity for lithium (based on literature data, i.a., [24]) that could operate in such a complex environment as oil field brine. In order to obtain a wide spectrum of tested sorbents and extractants, we tried to select several representatives from different groups of materials (including ion exchange resins, extractants and inorganic sorbents). In our opinion, performing screening tests on a diverse group of materials provides a better understanding of the possibilities of selection of a promising material for recovery of lithium from oil field brines than focusing on a single initially selected (based on the literature data) group and performing a more comprehensive study. We have noticed that in the literature, lithium recovery studies are most often carried out on pure lithium solutions or lithium-enriched seawater, so a simple review of the literature does not allow us to select the material best suited for our application. Moreover, the comparison of literature results is difficult due to the different test conditions used in the studies. We decided to perform an eight-stage screening test for the preliminary evaluation of the materials taken from various groups (ion exchange resins, inorganic sorbents, extractants, etc.). Batch adsorption/extraction experiments were performed under constant and comparable conditions at each stage of the test. The effect of the brine composition (concentration of Li⁺, Na⁺, Ca²⁺ and Mg²⁺ ions) on the distribution coefficients (K_d) of lithium ions is shown in Table 2. The distribution coefficient represents the experimentally measured lithium concentration ratios between the brine and sorbent (or extractant) phases. The greater the K_d value, the more lithium this material captures. The obtained results are varied and the progressive influence of the matrix on the sorption capacity can be seen. Based on the experimental data described above, we also calculated recovery of lithium (using Equation (2)) under the given test conditions, which are included in Appendix A (Table A2).

Sample Name	K _d 1 (K _d 1 pH 9)	K _d 2 (K _d 2 pH 9)	K _d 3 (K _d 3 pH 9)	K _d 4 (K _d 4 pH 9)	K _d 5 (K _d 5 pH 9)	K _d 6 (K _d 6 pH 9)	K _d 7 (K _d 7 pH 9)	K _d 8 (K _d 8 pH 9)
			Commercial	ly available res	sins			
MAC3	2 (22)	2 (176)	1 (2)	Х	Х	Х	Х	Х
Lewatit MonoPlus SP112	42	26	6	1 (1)	Х	Х	Х	Х
Purolite CT169	165	74	7	1 (2)	Х	Х	Х	Х
Purolite C100	69	41	5	1 (1)	Х	Х	Х	Х
Lewatit TP260	155	108	18	5	3 (4)	1 (1)	Х	Х
Puromet MTS9500	180	111	25	5	5	1 (1)	Х	Х
HPR 1200H	64	33	2 (2)	Х	Х	Х	Х	Х
IRC 120H	72	40	2 (2)	Х	Х	Х	Х	Х

Table 2. Influence of brine composition on the distribution coefficients (K_d) of lithium ions—results from a multi-stage screening procedure.

Sample Name	K _d 1 (K _d 1 pH 9)	K _d 2 (K _d 2 pH 9)	K _d 3 (K _d 3 pH 9)	K _d 4 (K _d 4 pH 9)	K _d 5 (K _d 5 pH 9)	K _d 6 (K _d 6 pH 9)	K _d 7 (K _d 7 pH 9)	K _d 8 (K _d 8 pH 9)
		Comme	cially available	e organophospł	nate extractants			
D2EHPA	3	1 (3)	Х	Х	Х	Х	Х	Х
TBP	1 (2)	Х	Х	Х	Х	Х	Х	Х
TCP	2 (3)	X	X	X	X	X	X	X
PhPO(OH) ₂	2 (4)	5	2 (2)	X	X	X	X	X
mono- D2EHPA	1 (4)	5	1 (9)	X	X	X	X	X
TOPO	0(2)	5 Y	2 (2) X	X	X	X	X	X
	0 (2)	~ ~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		A damba	Х	Λ	Λ
 DTA	2	1 (2)			v	v	v	v
DIA	3	1 (3)		A la Carbon basa	A december to	Λ	Λ	Λ
N. : CV0 D	2 (2)			vie Carbon-base			N	
Norit SX2 R	2(2)	X	X	X	X	X	X	X
KGO	2 (2)	Commonsially	۸ بند مینواماداند.	^ 		^ 	Λ	Λ
	1 (2)	Commerciany			Zeomes) auson	N N	Ň	X
Silica 60 A	1 (2)	X	X 10	X	X	X	X	X 2 (0)
γ -Al ₂ O ₃	7	11	19	9	7	8	4	2 (8)
Halloysite	4	2 (4) V	2 (2) X	X	X	X	X	X
SBA-15	1 (3)	A 4	2(2)	A Y	A Y	A Y		A Y
Zr(OH)	0(1)	X	2 (2) X	X	X	X	X	X
B-zeolite	5	5	2(2)	x	X	X	x	X
ZSM-5	4	2 (3)	2 (2) X	X	X	X	X	X
		O	her commercia	llv available ad	sorbents			
CallPhas	0	5	2 (2)	v	v	v	v	v
SiO ₂ -Et/B ₁₁ -	9	5	2 (2)	Λ	Λ	Λ	Λ	Λ
PO(OH) ₂	11	15	3 (5)	1 (2)	Х	Х	Х	Х
		Man	ganese oxide-ba	sed adsorbents	s (prepared)			
LIS10	6	2 (>3000)	1 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)
LIS11	5	2 (>3000)	1 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (136)
LIS12	5	2 (>3000)	5	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (300)
	Z	irconium phos	phate and phos	phonate-based	adsorbents (pr	epared)		
ZrTiP	4	3 (4)	2 (23)	5	<1(1)	х	х	х
ZrP1	5	1 (4)	$\frac{1}{1}(13)$	2 (19)	<1 (3)	X	X	X
ZrP2	5	3 (4)	2 (19)	$\frac{1}{2}(12)$	<1 (3)	X	X	X
ZrP3	6	4	$\frac{2}{2}(4)$	$\frac{2}{2}(4)$	<1 (<1)	X	X	X
ZrP4	1 (2)	x	X	X	X	X	X	X
ZrP5	6	1 (76)	1 (11)	2 (4)	1 (5)	<1 (2)	Х	Х
ZrP6	5	3 (4)	1 (36)	4	<1 (3)	x	Х	Х
Zr-ATMP1	4	4	3 (2)	Х	x	Х	Х	Х
Zr-ATMP2	10	9	3 (2)	Х	Х	Х	Х	Х
Zr-ATMP3	11	10	3 (5)	2 (<1)	Х	Х	Х	Х
Zr-ATMP4	11	10	3 (2)	X	Х	Х	Х	Х
Zr-ATMP5	12	10	4	2 (<1)	Х	Х	Х	Х
ZrTi-ATMP	2 (2)	Х	Х	x	Х	Х	Х	Х
		Tita	nium oxide-bas	ed adsorbents	(prepared)			
LIS1	2 (10)	1 (4)	1 (4)	1 (12)	1 (2)	Х	Х	Х
LIS2	2 (5)	1 (2)	x	x́	x	Х	Х	Х
LIS3	3 (>3000)	2 (>3000)	<1 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)
LIS4	2 (>3000)	5	1 (>3000)	1 (>3000)	1 (>3000)	2 (>3000)	2 (>3000)	2 (>3000)
LIS5	4	1 (1)	X	X	X	X	X	X
			Other adso	rbents (prepare	ed)			
SiO ₂ -APTES-CH ₂ - PO(OH) ₂	9	5	4	2 (5)	<1 (2)	Х	Х	Х

Table 2. Cont.

3.2. Recovery of Lithium from Pure Lithium Solution

There are many materials that exhibit affinity for lithium ions in pure diluted solution (stage 1). Ion exchange resins with sulfonic (Purolite CT169, Purolite C100, HPR 1200H,

Lewatit MonoPlus SP112) as well as aminophosphonic (Lewatit TP260, Puromet MTS9500) surface functional groups exhibit the highest affinity at neutral pH. These resins allow the recovery of about 95% of lithium (see Table A2 in Appendix A). Arroyo et al. [44] report similar retention yields (>95%) for K2629 resin (modified with sulfonic acid) and TP207 and TP208 resins (modified with iminodiacetatic acid). Overall, resins of these types have a capacity of around 20–30 mg/g [45]. The ion exchange resin with carboxylate groups (MAC3) exhibits a moderate affinity for lithium only at pH 9 (approximately 10 times lower than resins with sulfonic and aminophosphonic groups).

Sorbents based on manganese oxide and titanium oxide show the highest affinity for lithium, but only in basic solution (pH 9). The extraordinary sorption capacity of Mn-based adsorbents has been reported elsewhere, both in pure lithium solutions and in various brines [46–48]. However, in the case of titanium-based sorbents, there is a higher sensitivity of sorption properties due to synthesis conditions.

Phosphate-based sorbents (zirconium phosphates and phosphonates, silica modified with phosphonic and aminophosphonic acid, cellulose phosphate) as well as organophosphate extractants exhibit moderate values of distribution coefficients. γ -Al₂O₃ also has a moderate affinity. It is commonly known that lithium–aluminum layered double hydroxide chloride sorbents are used as lithium-selective sorbents [49,50], but the application of bare γ -Al₂O₃ without any modifications is probably novel. Other mineral sorbents such as zeolites, natural clays, silica and mesoporous silica (SBA-15) and zirconium hydroxide have low affinity even in pure lithium solution. The studies of Belova et al. [51] and Wiśniewska et al. [39] show that even chemically modified zeolites are ineffective, with sorption capacity up to 5 mg/g. Carbon-based materials (RGO and activated carbon) have very low affinity and have been excluded from subsequent studies. In general, the carbonaceous materials may be used as a carbothermic reductant in thermal reduction processes to facilitate recovery of lithium from ternary cathode powder [52] but not as a sorbent for direct lithium extraction.

3.3. Sodium Ion Effect

The effect of the presence of sodium ions was observed during the second, third and fourth stages of the test. From the literature, it is known that ionic radius and dehydration energy of the cations are important factors when considering the affinity for the sorbent (ion exchange material)—typically, the affinity increases when decreasing the hydrated radii of cations [53,54] as well as when decreasing dehydration enthalpies (sequence similar to lyotropic sequence). The dehydration enthalpies of the individual ions (Li⁺, Na⁺, K⁺) are 578.1, 463.3 and 380.3 kJ/mol [55], respectively, while the hydrated radii of ions are Li⁺ = 340 pm, Na⁺ = 276 pm and K⁺ = 232 pm [54]. The values of hydrated radii of ions for alkali metals reported by various authors differ slightly [56], but these values prove that lithium sorption from monovalent ion solution may be hindered.

The affinity of resins with sulfonic functional groups virtually disappeared with an increasing concentration of sodium ions up to 7.21 wt%. This result is quite obvious, but there are some literature reports of attempts to use such sorbents. Resins with aminophosphonic functional groups are slightly more resistant and show low affinity for lithium even in 20% NaCl solution. The obtained results confirm previous findings of Fukuda [45] that commercial resins are not suitable for lithium extraction from a concentrated brine. To overcome this problem, typical anion exchange resins should be modified by contacting with aluminum compounds as described in the following patents [57,58]. The affinity for lithium in the case of the tested commercially available organophosphate extractants dropped to a value close to zero even at lower sodium concentrations. To improve the efficiency of organophosphate extractants, different co-extractants and diluents may be added [59,60]. The majority of zirconium phosphonates also stopped adsorbing lithium at about 1 wt% NaCl concentration. Zirconium phosphate show a moderate affinity for lithium even in 20% NaCl solution, but only in alkaline solution. The decreasing sorption of lithium is in this case related to the increasing amount of adsorbed sodium. Zirconium

phosphates prepared by Borgo et al. [53] exhibited ion exchange capacities of 0.05, 0.38 and 0.57 mmol/g for Li⁺, Na⁺ and K⁺, respectively. The authors observed that Na⁺ and K⁺ were completely retained in the column filled with ZrO₂/phosphate while Li⁺ was not kept at all. The predominance of Na⁺ with respect to Li⁺ and the high affinity of zirconium phosphates towards Na confirm the results of other works [56,61]. γ -Al₂O₃ has a slightly higher distribution coefficient in concentrated NaCl solutions. All of the manganese-based sorbents and two of titanium-based sorbents exhibit the highest affinity for lithium in alkaline solution and no deterioration of sorption properties was observed in these cases. The highest lithium ion capacity in the presence of 20 wt% NaCl solution is shown by manganese oxide-based material LIS10 (17.0 mg/g—see Table 3) which was synthesized at the highest Li/Mn molar ratio, equal to 2. Such results are in good agreement with those obtained by [19], where nanostructured lithium manganese oxide tested in a concentrated brine exhibited high selectivity over Na⁺ and Mg²⁺, and the lithium capacity was in the range of 11-16 mg/g. Two other MnO_x-based materials show a similar lithium ion capacity to the titanium oxide-based materials (5.2–6.8 mg/g), while γ -Al₂O₃ exhibits the lowest capacity (1.8 mg/g). It should be noted that in the case of both manganese and titanium oxide-based materials, the conditions of material synthesis have a crucial role.

Table 3. Lithium-ion capacity for sorbents selected on the basis of screening tests. Lithium ion capacity was measured in solutions typical for the last five stages of screening tests.

Sample	q _e [mg/g]								
Name	Stage 4 pH 9	Stage 5 pH 9	Stage 6 pH 9	Stage 7 pH 9	Stage 8 pH 9				
γ -Al ₂ O ₃	1.8	1.1	0.9	0.7	0.5				
LIS10	17.0	16.6	16.2	16.0	15.5				
LIS11	6.8	6.1	6.1	6.1	6.0				
LIS12	5.2	4.3	4.3	3.7	3.4				
LIS3	6.0	6.1	7.7	7.7	8.1				
LIS4	6.1	6.0	4.9	3.5	2.6				

3.4. Calcium Ion Effect

The negative impact of divalent ions on lithium recovery is often reported, despite the recovery method [24,62]. For resins with aminophosphonic functional groups as well as for zirconium phosphate and for silica functionalized with aminophosphonic groups, the affinity for lithium ions dropped to zero after the addition of calcium ions. It is known from the literature that calcium ions have an extremely high affinity for materials functionalized with phosphoric, phosphonic and aminophosphonic groups [63], therefore the application of any material with these kinds of functional groups will be ineffective in calcium-rich brines. Some compounds such as D2EHPA dissolved in *n*-dodecane are even suggested to be applied in the first stage to remove divalent metals, and then other extracting agents may recover up to 83% of lithium [64]. The selectivity of organophosphorus solvents themselves is low. In Japan, liquid–liquid extraction from geothermal waters is applied and lithium recovery is at the level of 50% while magnesium and calcium recoveries are almost 100% [65]. Ion exchange resins may be applied to purify a lithium extract containing divalent ions as described by Nishihama et al. [66], but here the strongly acidic cation exchange resin adsorbs Mg²⁺ and Ca²⁺ and lithium remains in the solution. Only γ -Al₂O₃ and manganese-based and titanium-based sorbents (at pH 9) are effective in lithium sorption in the presence of 3 wt% of calcium. However, the presence of calcium has some negative effects on the lithium ion capacity in the case of manganese-based sorbents. It should be noted that at neutral pH only γ -Al₂O₃ exhibits affinity for lithium, while in other cases pH correction is required. The presence of calcium has a highly negative effect on the lithium ion capacity in the case of γ -Al₂O₃ (reduction by 50% after addition of 3 wt% of Ca²⁺). Materials based on MnO_x are much more resistant to the influence of calcium—reduction only by 5–17% after addition of 3 wt% of Ca²⁺ (LIS10 is the most resistant material in this group). A study of Miyai et al. [67] confirms that manganese oxide

ion sieves are selective for lithium over both monovalent and divalent cations and the selectivity follows the sequence of $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Na^+ = K^+ << Li^+$ at pH 8. The lithium ion capacity for TiO₂-based material (LIS3) even increased after addition of 3 wt% of Ca²⁺, and for the second Ti-based material (LIS4) the capacity decreased by 20%.

3.5. Magnesium Ion Effect

Separation of Li⁺ and Mg²⁺ is difficult because both elements exhibit similar ionic hydration radii and chemical characteristics. For typical salt lake brines, the Mg^{2+/}Li⁺ ratio is usually unfavorable (6, 20 and 133 for Salar de Atacama in Chile, Uyuni in Bolivia and Great Salt Lake in USA, respectively [22,46]). Separation of lithium from divalent cations can be achieved by simple precipitation using various precipitants such as Ca(OH)₂, Na₂C₂O₄, Na₂CO₃, oxalic acid and NaOH [68,69]. Xu et al. [70] and Sun et al. [71] reviewed magnesium and lithium separation methods including precipitation, adsorption, solvent extraction, nanofiltration and electrochemical methods. According to the literature, the selective extraction of lithium over magnesium during one-step adsorption is difficult to achieve, hence another approach is applied in practice. The alkaline earth metals can be removed during the pretreatment stage and then the treated brine is passed through an ion exchange column to recover the lithium [72]. To sum up, the development of lithium (over magnesium)-selective sorbents suitable for direct lithium recovery from brines is a very attractive issue.

The distribution coefficient for γ -Al₂O₃ decreases from 8 to 2 with the addition of magnesium ions (final concentration of Mg²⁺ was 1000 mg/kg; approximately 5 times higher than lithium concentration). In the case of manganese-based sorbents, the distribution coefficient decreased instantly for two materials (LIS11, LIS12). The third Mn-based material (LIS10) retained its sorption properties. The titanium oxide-based materials (LIS3 and LIS4) also retained their high affinity for lithium. The lithium ion capacity calculated for the last five stages of screening tests is shown in Table 3.

The addition of magnesium to the brine negatively influences the lithium ion capacity for γ -Al₂O₃ (reduction by 44% compared to brine rich in calcium (3 wt% of Ca²⁺)). The reduction of lithium ion capacity for manganese-based materials is low (LIS10 and LIS11—reduction by 2–4%) or moderate (LIS12—reduction by 21%). In the case of titaniumbased materials, one material is resilient to the presence of magnesium ions (LIS3)—lithium ion capacity even increased by 5%—while for the other, the presence of magnesium resulted in a reduction of the capacity by 47% (LIS4). According to the literature, magnesium concentration is the most limiting factor for lithium recovery, therefore, for the most promising cases, we determined the selectivity factor for lithium over magnesium adsorption as shown in Table 4.

Sample	β _{Li/Mg}					
Name	Stage 7 pH 9	Stage 8 pH 9				
γ-Al ₂ O ₃	< 0.05	<0.05				
LIS10	>150	>150				
LIS11	>150	3.1				
LIS12	>150	0.6				
LIS3	>150	>150				

Table 4. Selectivity factor β between Li⁺ and Mg²⁺.

 γ -Al₂O₃ shows very low Li⁺/Mg²⁺ selectivity. Manganese-based materials exhibit high Li⁺/Mg²⁺ selectivity (>150) in the presence of 300 mg/kg of magnesium ions, but after increasing Mg²⁺ concentration (up to 1000 mg/kg) the selectivity for LIS11 and LIS12 significantly decreases, while for LIS10 no negative effect was observed. In the case of titanium oxide-based materials, only LIS3 exhibits high Li⁺/Mg²⁺ selectivity, while LIS4 has moderate Li⁺/Mg²⁺ selectivity. It should be noted that the selectivity results are consistent with the trends of changes in lithium ion capacities upon the increasing

magnesium concentration in the brine. The sorption properties of both manganese and titanium-based materials are sensitive to the synthesis conditions, which will be examined in depth in future studies. Nevertheless, only these two groups of materials have the potential to be used in the real lithium recovery technology.

4. Conclusions

Lithium recovery from oil field brines is a huge challenge due to the complex chemistry and high salinity of the brines. Sodium, calcium and magnesium have a strong negative impact on the final lithium recovery rates. The applied testing protocol allowed a critical comparison of examined materials used for lithium sorption and extraction. Based on the results obtained, some recommendations for different materials can be made and some general predictions can be expressed.

(1) The tested ion exchange resins may be suitable for lithium adsorption from lowsalinity brines such as seawater or geothermal brines, however, it is likely that the tested resins exhibit limited selectivity for lithium ions even in diluted solutions. Resins with aminophosphonic groups such as Puromet MTS9500 and Lewatit TP260 are more effective than those with sulphonic or carboxylic acid functional groups. The most important constraint is associated with the high affinity of aminophosphonic groups for calcium and magnesium.

(2) The application of organophosphate extractants is limited due to their moderate extraction efficiency. These compounds require the removal of divalent ions in the pretreatment step, which is their known drawback, but also the elevated sodium concentration hinders lithium sorption.

(3) Reduced graphene oxide (RGO) and Norit SX2 R activated carbon are completely unsuitable for lithium recovery. Other carbon-based materials (and nanomaterials) with carboxylic surface functional groups are likely to be ineffective as well.

(4) Mineral adsorbents, including zeolites and clays, may only be used for brines with low salinity (sodium concentration below 1 wt%). γ -Al₂O₃ shows high resistance to salinity. It can adsorb from pure LiCl solution (under test conditions) up to 87% of Li⁺, while from the concentrated brine it captures 66% of the lithium without any pH correction. The affinity of bare γ -Al₂O₃ for lithium has probably not been reported in the literature. Typical aluminum-based lithium-selective materials are layered double hydroxides (LiCl·2Al(OH)₃·xH₂O).

(5) Mn-based sorbents are superior to others and allow the recovery of 99% of lithium under test conditions, regardless of the composition of the brine. These materials are easy to obtain via simple calcination of manganese acetate and Li₂CO₃, followed by leaching of the lithium with HCl. The process presented in the current study is a simplification of the method described in the literature and should be easily scalable. Moreover, the synthesized manganese oxide-based materials are more robust to the synthesis conditions than the titanium oxide-based materials.

(6) Zr-based adsorbents (phosphates and phosphonates) have a moderate affinity for lithium. Increasing the pH only slightly improves their sorption capacity, but the high content of Mg^{2+} and Ca^{2+} in the brine excludes them from further applications, probably for the same reasons as in the case of aminophosphonic ion exchange resins.

(7) The method of preparation or the precursors used for the synthesis probably strongly influence the crystallographic structure of lithium titanium oxide ion sieves. Lithium can be more easily inserted into anatase-based materials (LIS3 and LIS4). At pH corrected to 9, more than 99% of lithium is adsorbed from each tested brine by anatase-based materials (LIS3 and LIS4).

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Appendix A

Table A1. Data on the synthesis and characteristics of the obtained sorbents.

	Zirconium Phosphate Sorbents									
Sorbent Name	Synthesis Method	Zr Source	P Source	P:Zr Molar Ratio in the Reaction Mixture	Sorbent Characteristics					
ZrP1 ZrP2				1:1 2:1	white, amorphous white, amorphous					
ZrP3	precipitation method;	zirconium carbonate	42.5 wt% phosphoric	10:1	white, crystalline					
ZrP4	temperature	with 65 wt% nitric acid	acid	0.5:1	white, amorphous					
ZrP5				2:1	white, crystalline					
ZrP6 ZrTiP				2:1 2:1 (P:(Zr + Ti))	white, amorphous white, amorphous					
		Zirconium	phosphonate sorbents							
Sorbent name	Synthesis method	Zr source	P source	P:Zr molar ratio in the reaction mixture	Sorbent characteristics					
Zr-ATMP1 Zr-ATMP2 Zr-ATMP3 Zr-ATMP4 Zr-ATMP5 ZrTi-ATMP	precipitation method; synthesis at room temperature	zirconium carbonate basic hydrate treated with 65 wt% nitric acid	50 wt% aminotris(methylenephos acid)	$\begin{array}{c} 100:1\\ 6.5:1\\ 12.5:1\\ 25:1\\ 50:1\\ 2.5:1 \end{array}$	white, amorphous white, amorphous white, amorphous white, amorphous white, amorphous light beige, amorphous					
		Manganese	oxide-based sorbents							
Sorbent name	Synthesis method	Mn source	Li source	Li:Mn molar ratio in the reaction mixture	Sorbent characteristics					
LIS10	solid state reaction; at	manganese(II) acetate	lithium carbonate	2:1	black, crystalline Li _{1.33} Mn _{1.67} O ₄					
LIS11 LIS12	400 C for 4 h	tenanyurate		1:1 0.5:1	Li _{1.33} Mn _{1.67} O ₄ black, crystalline Li _{1.33} Mn _{1.67} O ₄					
	Titanium oxide-based sorbents									
Sorbent name	Synthesis method	Ti source	Li source	Li:Ti molar ratio in the reaction mixture	Sorbent characteristics					
LIS1 LIS2 LIS3 LIS4 LIS5	solid state reaction; at 500–700 °C for 4 h	titanium oxide anatase titanium oxide rutile titanium oxide anatase titanium oxide anatase titanium oxide anatase	lithium carbonate	2.5:1 2.5:1 4.3:1 1.1:1 2.0:1	white, crystalline Li ₂ TiO ₃ white, crystalline Li ₂ TiO ₃					

Sample Name	R _{Li} 1 (R _{Li} 2 pH 9)	R _{Li} 2 (R _{Li} 2 pH 9)	R _{Li} 3 (R _{Li} 3 pH 9)	R _{Li} 4 (R _{Li} 4 pH 9)	R _{Li} 5 (R _{Li} 5 pH 9)	R _{Li} 6 (R _{Li} 6 pH 9)	R _{Li} 7 (R _{Li} 7 pH 9)	R _{Li} 8 (R _{Li} 8 pH 9)
			Commercia	lly available res	sins			
MAC3	16.6% (68.8%)	16.7% (94.6%)	9.1% (16.7%)	х	х	х	Х	х
Lewatit MonoPlus SP112	80.8%	72.2%	37.5%	9.1% (9.1%)	Х	Х	Х	Х
Purolite CT169	94.3%	88.1%	41.2%	9.1% (16.7%)	Х	Х	Х	Х
Purolite C100	87.3%	80.4%	33.3%	9.1% (9.1%)	X	X	Х	Х
Lewatit TP260	93.3%	91.5%	64.3%	33.3%	(28.6%)	9.1% (9.1%)	Х	Х
Puromet MTS9500	94.7%	91.7%	71.4%	33.3%	33.3%	9.1% (9.1%)	Х	Х
HPR 1200H	86.5%	76.7%	16.7% (16.7%)	Х	Х	Х	Х	Х
IRC 120H	87.8%	80.0%	16.7% (16.7%)	Х	Х	Х	Х	Х
		Comme	rcially available	e organophospl	nate extractants			
D2EHPA	23.1%	9.1% (23.1%)	Х	Х	Х	х	Х	Х
TBP	9.1% (16.7%)	Х	Х	Х	Х	Х	Х	Х
TCP	16.7% (23.1%)	Х	Х	Х	Х	Х	Х	Х
PhPO(OH) ₂	16.7% (28.6%)	33.3%	16.7% (16.7%)	Х	Х	Х	Х	Х
mono- D2EHPA	9.1% (28.6%)	33.3%	9.1% (47.4%)	Х	Х	Х	Х	Х
CYPHOSIL 104	37.5%	33.3%	16.7% (16.7%)	Х	Х	Х	Х	Х
ТОРО	0%(16.7%)	Х	Х	Х	Х	Х	Х	Х
		0	ther commercia	lly available ex	tractants			
BTA	23.1%	9.1% (23.1%)	Х	Х	Х	Х	Х	Х
		Comm	ercially availal	ole carbon-base	d adsorbents			
Norit SX2 R	16.7% (16.7%)	Х	Х	Х	Х	Х	Х	Х
RGO	16.7% (16.7%)	Х	Х	Х	Х	Х	Х	Х
		Commercially	y available min	eral (including	zeolites) adsor	bents		
Silica 60 Å	9.1% (16.7%)	Х	Х	Х	Х	Х	Х	Х
γ -Al ₂ O ₃	41.2%	52.4%	65.5%	47.4%	41.2%	44.4%	28.6%	16.7% (44.4%)
Halloysite	28.6%	16.7% (28.6%)	16.7% (16.7%)	Х	Х	Х	Х	Х
Kaolinite	9.1% (23.1%)	Х	Х	Х	Х	Х	Х	Х
SBA-15	33.3%	28.6%	16.7% (16.7%)	Х	Х	Х	Х	Х
Zr(OH) ₄	0% (9.1%)	Х	X	Х	Х	Х	Х	Х
β-zeolite	33.3%	33.3%	16.7% (16.7%)	Х	Х	Х	Х	Х
ZSM-5	28.6%	16.7% (23.1%)	Х	Х	Х	Х	Х	Х

Table A2. Influence of brine composition on the recovery of lithium ions (R_{Li}) —results from a multi-stage screening procedure.

Sample Name	R _{Li} 1 (R _{Li} 2 pH 9)	R _{Li} 2 (R _{Li} 2 pH 9)	R _{Li} 3 (R _{Li} 3 pH 9)	R _{Li} 4 (R _{Li} 4 pH 9)	R _{Li} 5 (R _{Li} 5 pH 9)	R _{Li} 6 (R _{Li} 6 pH 9)	R _{Li} 7 (R _{Li} 7 pH 9)	R _{Li} 8 (R _{Li} 8 pH 9)
		0	ther commercia	lly available ac	lsorbents			
CellPhos	47.4%	33.3%	16.7% (16.7%)	х	Х	х	х	х
SiO ₂ -Et/Bu- PO(OH) ₂	52.4%	60.0%	23.1% (33.3%)	9.1% (16.7%)	Х	Х	Х	Х
		Man	ganese oxide-ba	ased adsorbent	s (prepared)			
LIS10	37.5%	16.7% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)
LIS11	33.3%	16.7% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (93.2%)
LIS12	33.3%	16.7% (>99.7%)	33.3%	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (96.8%)
	7	Zirconium phos	phate and phos	phonate-based	l adsorbents (pr	epared)		
	20 (0)	23.1%	16.7%	22.20/	<9.1%	N/	X	X
ZrIiP	28.6%	(28.6%)	(69.7%)	33.3%	(9.1%)	Х	Х	Х
ZrP1	33.3%	9.1% (28.6%)	9.1% (56.5%)	16.7% (65.5%)	<9.1% (23.1%)	Х	х	Х
ZrP2	33.3%	23.1% (28.6%)	16.7% (65.5%)	16.7% (54.5%)	<9.1% (23.1%)	Х	Х	Х
ZrP3	37.5%	28.6%	(28.6%)	16.7% (28.6%)	<9.1% (<9.1%)	Х	Х	Х
ZrP4	(16.7%)	Х	Х	Х	Х	Х	Х	Х
ZrP5	37.5%	9.1% (88.4%)	9.1% (52.4%)	16.7% (28.6%)	9.1% (33.3%)	<9.1% (16.7%)	Х	Х
ZrP6	33.3%	23.1% (28.6%)	9.1% (78.3%)	28.6%	<9.1% (23.1%)	Х	Х	Х
Zr-ATMP1	28.6%	28.6%	23.1% (16.7%)	Х	Х	Х	Х	Х
Zr-ATMP2	50.0%	47.4%	23.1% (16.7%)	X	Х	Х	Х	Х
Zr-ATMP3	52.4%	50.0%	23.1% (33.3%)	16.7% (<9.1%)	Х	Х	Х	Х
Zr-ATMP4	52.4%	50.0%	23.1% (16.7%)	X	Х	Х	Х	Х
Zr-ATMP5	54.5%	50.0%	28.6%	(<9.1%)	Х	Х	Х	Х
ZrTi-ATMP	16.7% (16.7%)	Х	Х	Х	Х	Х	Х	Х
		Tita	nium oxide-bas	sed adsorbents	(prepared)			
LIS1	16.7% (50.0%)	9.1% (28.6%)	9.1% (28.6%)	9.1% (54.5%)	9.1% (16.7%)	Х	х	Х
LIS2	16.7% (33.3%)	9.1% (16.7%)	Х	Х	Х	Х	Х	Х
LIS3	23.1% (>99.7%)	16.7% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)
LIS4	16.7% (>99.7%)	33.3%	9.1% (>99.7%)	9.1% (>99.7%)	9.1% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)	16.7% (>99.7%)
LIS5	28.6%	9.1% (9.1%)	Х	Х	Х	Х	Х	Х
			Other adso	orbents (prepar	ed)			
SiO ₂ -APTES-CH ₂ - PO(OH) ₂	47.4%	33.3%	28.6%	16.7% (33.3%)	<9.1% (16.7%)	Х	Х	Х

Table A2. Cont.

Appendix B

Links to the product data sheets of tested resins, adsorbents and extractants available on the market (in parentheses are the abbreviations used in the article), accessed on 27 February 2023. AmberLite MAC-3 H (MAC3; https://www.dupont.com/content/dam/dupont/am er/us/en/water-solutions/public/documents/en/IER-AmberLite-MAC-3-H-PDS-45-D0 0846-en.pdf).

Lewatit MonoPlus SP112 (Lewatit MonoPlus SP112; https://lanxess.com/en/Product s-and-Brands/Products/l/LEWATIT--MonoPlus-SP-112).

Lewatit TP260 (Lewatit TP260; https://lanxess.com/en/Products-and-Brands/Products/l/LEWATIT--MonoPlus-TP-260).

AmberLite HPR1200 H (HPR 1200H; https://www.dupont.com/content/dam/dupon t/amer/us/en/water-solutions/public/documents/en/IER-AmberLite-HPR1200-H-PDS -45-D01221-en.pdf).

AmberLite IRC120 H (IRC 120H; https://www.dupont.com/content/dam/dupont/ amer/us/en/water-solutions/public/documents/en/IER-AmberLite-IRC120-H-PDS-45 -D01245-en.pdf).

Purolite CT169 (Purolite CT169; https://www.purolite.com/product-pdf/CT169.pdf). Purolite C100 (Purolite C100; https://www.purolite.com/product/pl/c100).

Puromet MTS9500 (Puromet MTS9500; https://www.purolite.com/pl/product-pdf/MTS9500.pdf).

Bis(2-ethylhexyl) phosphate (D2EHPA, https://www.alfa.com/en/catalog/017723/). Tri-n-butyl phosphate (TBP; https://www.alfa.com/en/catalog/A16084/).

Tritolyl phosphate (TCP, https://www.alfa.com/en/catalog/A17433/).

(2-Ethylhexyl)phosphonic acid mono-2-ethylhexyl ester (mono-D2EHPA; https://ww w.tcichemicals.com/US/en/p/M2871).

Phenylphosphonic acid (PhPO(OH)₂; https://www.sigmaaldrich.com/PL/pl/produ ct/aldrich/p29006?gclid=EAIaIQobChMIob_r5P_-_AIVpRJ7Ch1PWgFpEAAYASAAEgIE rvD_BwE&gclsrc=aw.ds).

Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (CYPHOSIL 104; https://www.sigmaaldrich.com/PL/pl/product/aldrich/28612).

Trioctylphosphine oxide (TOPO; https://www.sigmaaldrich.com/PL/pl/product/a ldrich/223301?gclid=EAIaIQobChMIq8Gmr4D_AIVAUaRBR2yPwuSEAAYASAAEgIQXf D_BwE&gclsrc=aw.ds).

4,4,4-Trifluoro-1-phenyl-1,3-butanedione (BTA, https://www.sigmaaldrich.com/PL/pl/product/aldrich/217042).

Activated carbon Norit SX2 R (Norit SX2 R; https://pol-aura.pl/wegiel-aktywny-nor it-sx-2-czda-7440-44-0-p-2062.html).

Reduced graphene oxide (RGO; https://www.sigmaaldrich.com/PL/pl/product/ald rich/777684?gclid=EAIaIQobChMI0ILQoIH__AIVpdlMAh2bvA2BEAAYASAAEgInovD_ BwE&gclsrc=aw.ds).

Silica gel for column chromatography 60 Å (Silica 60 Å; https://www.sigmaaldrich.c om/PL/pl/product/sial/89943).

Aluminum oxide activated, basic Brockmann I (γ-Al₂O₃; https://www.sigmaaldrich.c om/PL/pl/product/sigald/199443?gclid=EAIaIQobChMIuOGhqo_g-gIVk5GyCh1UKgc 6EAAYASAAEgK7sfD_BwE&gclsrc=aw.ds).

Halloysite nanoclay (halloysite; https://www.sigmaaldrich.com/PL/pl/product/ald rich/685445).

Kaolinite (kaolinite; https://www.sigmaaldrich.com/PL/pl/product/sial/03584).

Silica mesoporous SBA-15 (SBA-15; https://www.sigmaaldrich.com/PL/pl/product /aldrich/914614).

Zirconium(IV) hydroxide (Zr(OH)₄; https://www.sigmaaldrich.com/PL/pl/product /aldrich/464171?gclid=EAIaIQobChMI38Kd4I7g-gIVgEWRBR2ccQW4EAAYASAAEgIxnP D_BwE&gclsrc=aw.ds).

Zeolite beta muonium form (β-zeolite; https://www.alfa.com/en/catalog/045873/). Zolite ZSM-5 ammonium form (ZSM-5; https://www.alfa.com/en/catalog/045879/). Cellulose, phosphate (Selectacel[®] phosphate) (CellPhos; https://www.polysciences.c om/india/cellulose-phosphate-selectacel-phosphate).

Ethyl/butyl phosphonic acid silica (SiO₂-Et/Bu-PO(OH)₂, https://www.sigmaaldri ch.com/PL/pl/product/aldrich/744794).

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