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Lithium extraction from geothermal waters; a case study of Ömer-Gecek (Afyonkarahisar) geothermal area

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Abstract: Lithium (Li) is the lightest metal, has unique physicochemical properties and is the main component of lithium-ion batteries. Rechargeable lithium-ion batteries play a very important role in maximizing the performance of electric devices and vehicles. It is predicted that the metal and mineral demand for lithium-ion batteries will increase 56 times by 2050. In order to meet the increasing demand, in addition to known methods, lithium recovery from geothermal waters has become a very popular research subject. There are abundant geothermal water resources in the world, especially in Turkey and in Afyonkarahisar. The aim of this study is to produce an adsorbent for the retention of lithium in geothermal waters and to remove lithium ions from geothermal water with the help of this adsorbent. Geothermal samples for lithium enrichment were obtained from Ömer-Gecek (Afyonkarahisar), where hosts geothermal resources with low-medium enthalpy containing 3.5 mg/L Li. In this context, an inorganic adsorbent was developed by using $MnCO_3$, LiOH and sodium silicate. The characterization and performance parameters of the adsorbent were investigated. As a result of adsorption experiments in fixed bed column, we can perform calculations based on a ton of adsorbent in a column with natural water feed rate of 1.63 t/h. The outcome is 236.7 g of Li, which is equivalent to 2519.6 g of Li_2CO_3 in 41.6 h. Our findings show that the adsorbent developed in our study can be used to retain Li^+ from geothermal waters.

Key words: Lithium, geothermal, adsorption, Ömer-Gecek, Afyonkarahisar

1. Introduction

Lithium (Li) is the lightest metal and lithium and its products are widely used in glass, catalysts, aluminium production, rubber synthesis, pharmaceuticals, and Li-ion batteries due to its unique physicochemical properties (Zante et al., 2019; Swain, 2017; Wang et al., 2020). Lithium is mainly derived from different geological resources, e.g., minerals such as spodumene and lepidolite, clays such as hectorite, salt lakes, and underground brine reservoirs (Xu et al., 2016; An et al., 2012; Barbosa et al., 2014; Zante et al., 2019; Wang et al., 2020). Brine reservoirs contain 66% of global lithium reserves and lithium is contained in salt waters, lakes, salars, oilfield and geothermal brines (Bauer, 2000; Mohr et al., 2012).

Geothermal brines are potentially significant sources of valuable minerals and metals including lithium (Li), caesium (Cs), and rubidium (Rb), precious metals such as gold (Au), platinum (Pt), palladium (Pd), and silver (Ag), and rare earth metals (Brown and Simmons, 2003; Bourcier et al., 2005; Lo et al., 2014). The reservoir parameters such as composition of host rocks, chemical composition of fluid, temperature, pressure and pH during fluid and rock mass interaction are important factors determining chemical composition of geothermal fluids (Bakane, 2013). Lithium is often enriched in geothermal fluids due to their high saline composition. Lithium production from geothermal fluids has come to the forefront compared to other sources in respect to low production cost, providing environmentally friendly solutions and low carbon emissions.

Turkey is located in the Alpine-Himalayan orogenic belt and has rich geothermal resources due to favourable geological conditions. There are approximately 1000 geothermal and mineral water sources in Turkey. The temperature of 170 geothermal resources is higher than 40 °C. In terms of location, 78% of geothermal areas are located in Western Anatolia, 9% in Central Anatolia, 7% in Marmara region, 5% in Eastern Anatolia and 1% in other regions. Of Turkey's geothermal resources, 90% are low and medium temperature and these resources are suitable for direct

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applications (heating, thermal tourism, various industrial applications, etc.). Additionally, 10% of geothermal resources in Turkey are suitable for indirect applications such as electric power generation (MTA, 2021). Afyonkarahisar is one of the most important geothermal fields in Western Anatolia, together with Denizli, Aydın, Çanakkale, İzmir and Kütahya. Geothermal resources in Afyonkarahisar are distributed in Ömer-Gecek, Gazlıgöl, Sandıklı, Heybeli, Bayatçık, İscehisar, Salar and İhsaniye provinces (Başaran et al., 2020; Yıldız et al., 2020; Karaoğlu, 2021).

Rechargeable lithium-ion batteries play a very important role in maximizing the performance of electric devices and vehicles. In the European Commission's Action Plan on Critical Raw Materials, it is predicted that the demand for lithium will increase 56 times by 2050 (EC, 2020). For this reason, studies about the exploration, extraction and production of lithium resources from the earth's crust have gained importance. The lithium concentration of geothermal fluids varies between 0.10 and 58.66 mg/L. Lepidolite mineral in pegmatite and nepheline syenite, clays in boron deposits and saline lake basins are other lithium resources in Turkey and there are studies about the recovery of lithium from these resources (Gülez et al., 2019; Çelebi, 2019; Eser, 2019; Üçerler, 2020).

Many physical and chemical extraction methods were developed for selective recovery of Li^+ from seawater or brines. These include absorption and then extraction into solutions, precipitation, electrodialysis, evaporation, and membrane separation methods (Yanagase et al., 1982; Rothbaum and Buisson, 1986; An et al., 2012; Kim, 2008; Mesram et al., 2014; Mroczek et al., 2015; Çetiner et al., 2015; Yanar, 2015; Bunani, 2017; Recepoğlu et al., 2017a,b; Çelik et al., 2018; Çetiner, 2018; Zhao et al., 2019; Lawagon et al., 2019; Wang et al., 2020; Çermikli, 2020; Xu et al., 2021; Çifci and Meriç Pagano, 2021a). Promising results were obtained for the recovery of lithium by the adsorption method using inorganic and bioadsorbents (Kitajou et al., 2003; Zandevakili et al., 2014; Çifci and Meriç Pagano, 2021b).

This study was carried out with the aim of producing an adsorbent for the retention of lithium in geothermal waters and removing lithium ions from geothermal water with the help of the prepared adsorbent. Geothermal waters for lithium retention studies were obtained from the low-medium enthalpy Ömer-Gecek area (Afyonkarahisar). In this context, an inorganic adsorbent was produced by using $MnCO_3$, LiOH, and sodium silicate. The characterization and performance parameters (adsorption capacity, rate etc.) were investigated.

2. Materials and methods

2.1. Ömer-Gecek geothermal area (ÖGG)

Based on geological properties and tectonic structure, the geothermal areas in Afyonkarahisar are distributed in Ömer-Gecek, Gazlıgöl, Sandıklı, Heybeli, Bayatçık, İscehisar, Salar and İhsaniye provinces (Figure 1).

Afyon metamorphic rocks are the basement rocks of the geothermal system in Afyonkarahisar. Palaeozoic marble and quartzite are the reservoirs and the Cenozoic units are the cap rocks. Recharge is mainly meteoric and it involves surface and underground waters infiltrating into the basin. Precipitation falling onto the high sections of the Afyon-Akşehir graben, percolate into the reservoir rocks along major faults and fracture zones and they are heated at depth and ascend to the surface by convection. The water temperatures of Afyonkarahisar geothermal areas vary between 30–128 °C and the electrical conductivities (EC) are between 350 and 7820 µs/cm. The chemical compositions of these different areas have different types depending on their temperatures, depths and reservoir rocks. Based on the Piper diagram (Figure 2), Ömer-Gecek and Bayatcık waters have Na-Cl type, Sandıklı waters are at the boundary with Na-Ca-SO_4-HCO_3 type, Heybeli waters have mixed type with Na-Ca-HCO_3-SO_4, İhsaniye, İscehisar and Gazlıgöl waters are in the Na-HCO_3 area and the lowest temperature Salar waters are Ca-HCO_3 type.

Due to the ease of access to the site, the high production rate of geothermal waters, the support provided by AFJET Corporation, and the lithium content of the waters in area, we focused on the ÖGG province. Geothermal fluid of 700 t/h is obtained from 30 wells drilled in the ÖGG region and produced fluids are used for electricity generation, residential/greenhouse heating and thermal tourism. The lithium concentrations of the waters in the region reach 3.5 ppm (Table 1).

2.2. Adsorbent production

In our study, we aimed to develop an Mn-based inorganic adsorbent sensitive to Li^+-ions. We planned that the adsorbent should be produced at approximate ratio of 1/1 mole (Demirkapı, 2019; Yıldız et al., 2019). The mixture of $MnCO_3$ and LiOH was heated at 450 °C for 5 h in order to remove the CO in $MnCO_3$ and to obtain MnO_2 (Sabry et al., 1986; Yoshizuka et al., 2002; Wang et al., 2006; Tian et al., 2010) (Figure 3a).

The inorganic adsorbent was prepared with sodium silicate (Na_2OxSiO_2) as binding agent to shape the adsorbent powder into a cylinder block with high physical strength and abrasion resistance to overcome possible process conditions such as mixing and stirring at various pH levels and elevated temperatures (Chung et al., 2014). To prepare the binder, 72% pure sodium silicate was diluted and added to the Li-Mn mixture at 19.00%, 24.00%, and 30.00% by weight (Figure 3b) (Demirkapı, 2019; Yıldız et al., 2019). The formed paste of Li-Mn and sodium silicate was shaped to 0.3 × 0.4 cm and allowed to dry (Figure 3c). Finally, the product durability was increased by heat treatment at 650 °C for 4 h (Figure 3d).

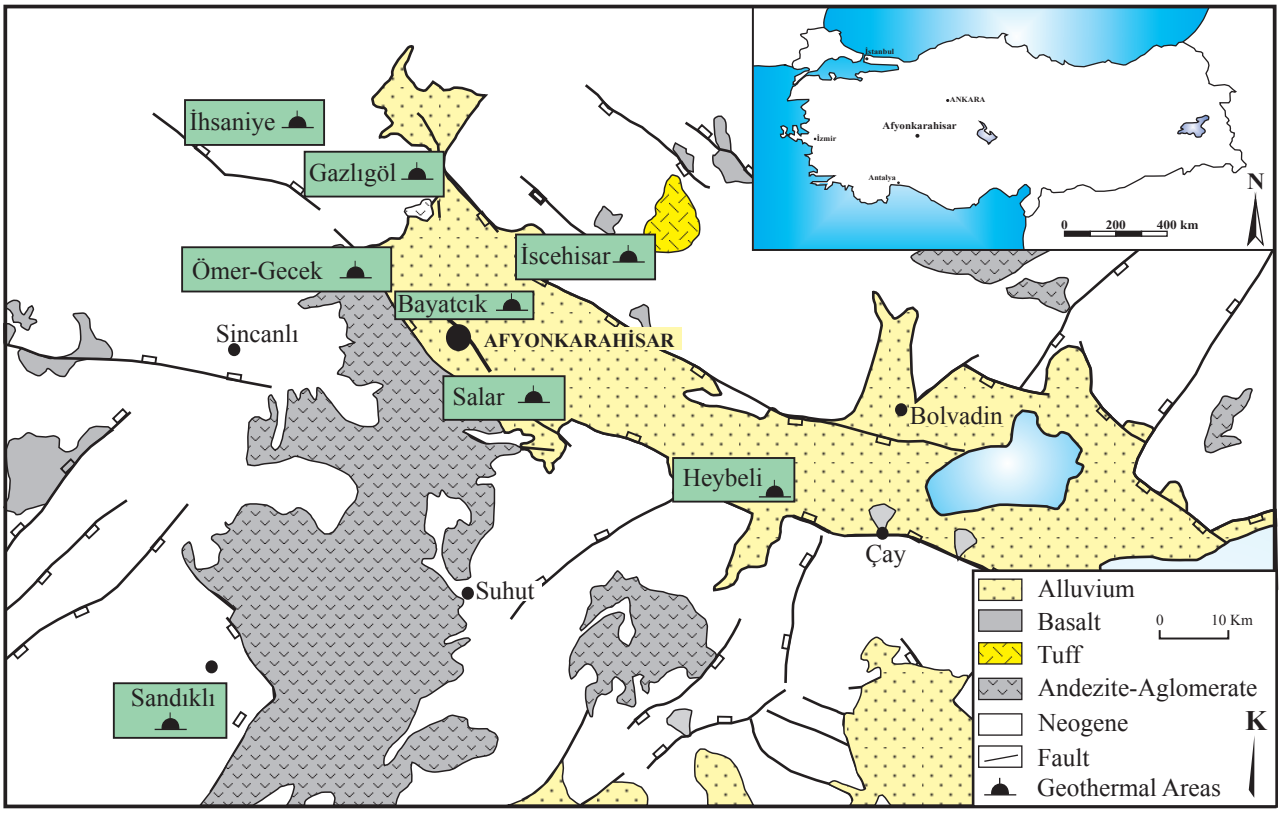

Figure 1. The distribution of geothermal areas in the Afyon-Akşehir graben system (modified from Gürsoy et al., 2003).

The adsorbent was then washed with HCl to remove the lithium content. In this way, a porous and spongy adsorbent with empty spaces suitable for the diameter of lithium ions was obtained.

2.3. Adsorbent characterization

X-ray diffraction (XRD), scanning electron microscope (SEM) and BET surface area analyses were performed on the adsorbent for mineralogical, morphological and physical characterizations. The qualitative mineralogical analysis was conducted by using a Shimadzu XRD-6000 model diffractometer (Ni filter, Cukα radiation and a scanning speed of 2 °/min). The semiquantitative analysis for mineral type, crystal structure and sizes were calculated with the accompanying Brooker EVA software. Morphological and microchemical analyses were performed using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS). Before SEM analysis, freshly broken surface samples were coated with carbon and examined using a Jeol-6400 Scanning Electron Microscope. BET surface area analysis was carried out with Quantachrome Nova 2200 model analyser.

2.4. Performance tests of adsorbent

Li ion retention performance of the adsorbents prepared with constant solid ratio (0.25 g/100 cc) and mixing time (24 h) and different amounts of binder (19wt.%, 24wt.%, and 30wt.%) were investigated in solutions with different initial Li^+ concentrations (1, 2, 5, 10 and 50 ppm). The best performing composition was detected with adsorption rate experiments (at 30, 60, 180, 480, and 1440 min) and this was used in an adsorption column to define the required parameters. All experiments were performed at room temperature and pH was adjusted to 5.5–6.0.

Actual performances of the adsorbent beads were revealed by feeding the Li^+ content of artificial solution (2.5 ppm) and geothermal water (3.5 ppm) from the ÖGG area to the identical adsorption columns (3 cm diameter, 30 cm length) with the same experimental parameters (feed rate of 1 cc/min, for 1620 min) for comparison.

3. Results

3.1. Adsorbent characterization

XRD analysis was performed on the adsorbent before and after acid treatment to determine the changes in the crystal structure that enable selective Li^+ adsorption. In the X-ray diffraction graph of the adsorbent, compatible peaks with $Li_{1.4}Mn_{1.7}O_4$ at 74.6% and $(Li_{0.989}Mn_{0.011})$ $(Li_{0.060}Mn_{1.940})O_4$ at 13.4% were determined with cubic crystal structure according to Brooker EVA software (Noerochim et al., 2015; Demirkapı, 2019; Yıldız et al., 2019) (Figure 4a).

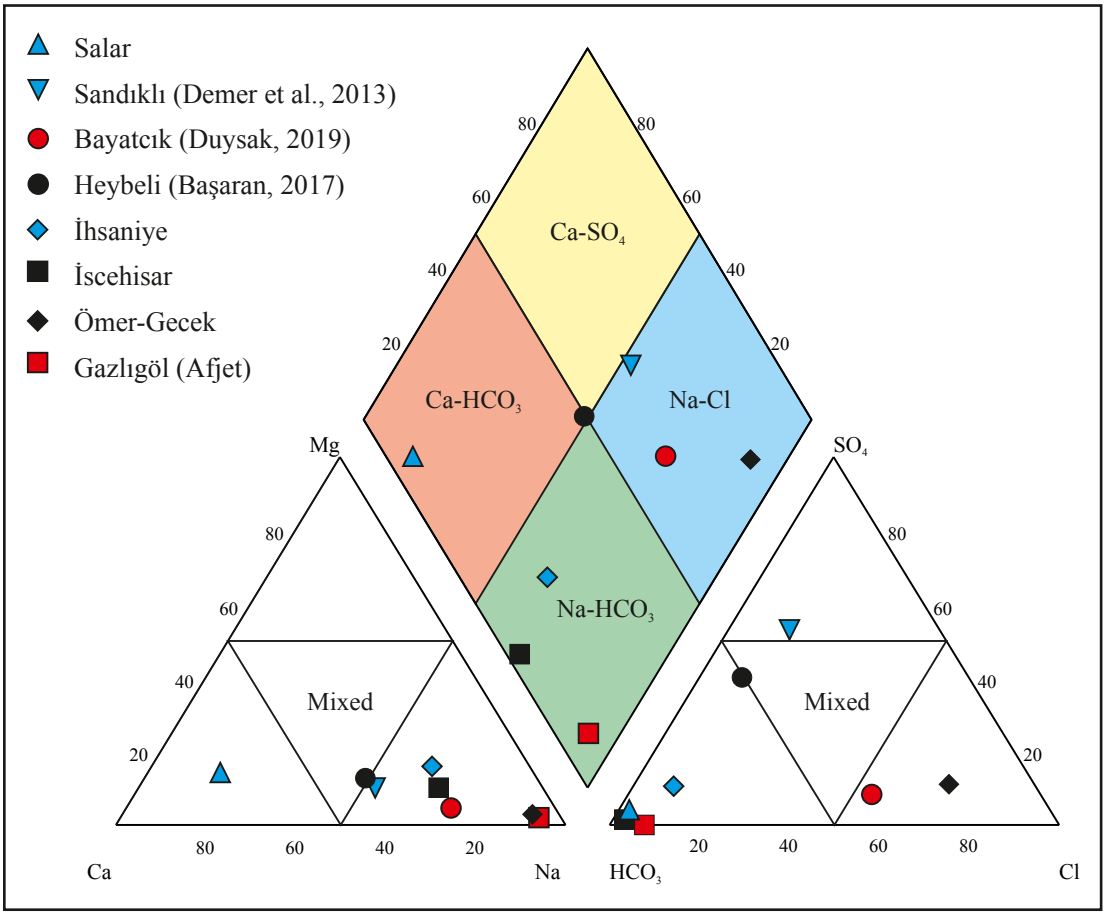

Figure 2. The piper diagram of Afyonkarahisar geothermal waters.

Table 1. The results of geochemical analysis of geothermal fluids from ÖGG province (Yıldız et al., 2011).

		OZ2	**Y2**	**AF21**	**AF20**	**AS1**	**KO**	**HA**	**AF25**
T	(°C)	59	44	81	90	51	41	42	-
EC	(µs/cm)	5740	702	7460	6790	471	2840	4420	-
B	ppb	6414	7380	22	9045	881	4223	5192	-
Li	*ppb*	*1890*	*1957*	*1290*	*2383*	*2239*	*1018*	*1300*	*3500*
Mg	ppm	18.7	41.2	21.7	20.5	20.8	58.4	58.4	-
Mn	Ppb	20.4	272.4	16.8	14.1	54.7	307.8	126.4	-
Na	ppm	1300.2	1538.9	5.4	1762.4	1750	542.1	868.6	-
Si	Ppb	42661	32183	12947	59814	58547	66679	67662	-

After acid treatment, new structures emerged; due to ion exchange between Li^+ and H^+, the crystal formula changed to 75.38% $H_{1.10}Li_{0.08}Mn_{1.73}O_{4.05}$, 12.29% $Li_{0.115}MnO_2$, 12.33% $(Li_{0.04}Mn_{0.035})Mn_{1.965}$ O_4. Crystal size calculated from the first peak is approximately 336.5 Å which changed to 321.8 Å after acid treatment. A right shift was observed in the XRD peaks of acidified samples due to the shrinkage of the spinel cage structure and the formation of lithium manganese oxides with cubic structure after the release of the lithium ion replaced by hydrogen (Figures 4b and 5). Accordingly, the cubic crystal size 8.226 Å was reduced to 8.0787 Å. The undesired minerals with minor quantities were formed by binder composition and impurities from crucible surfaces.

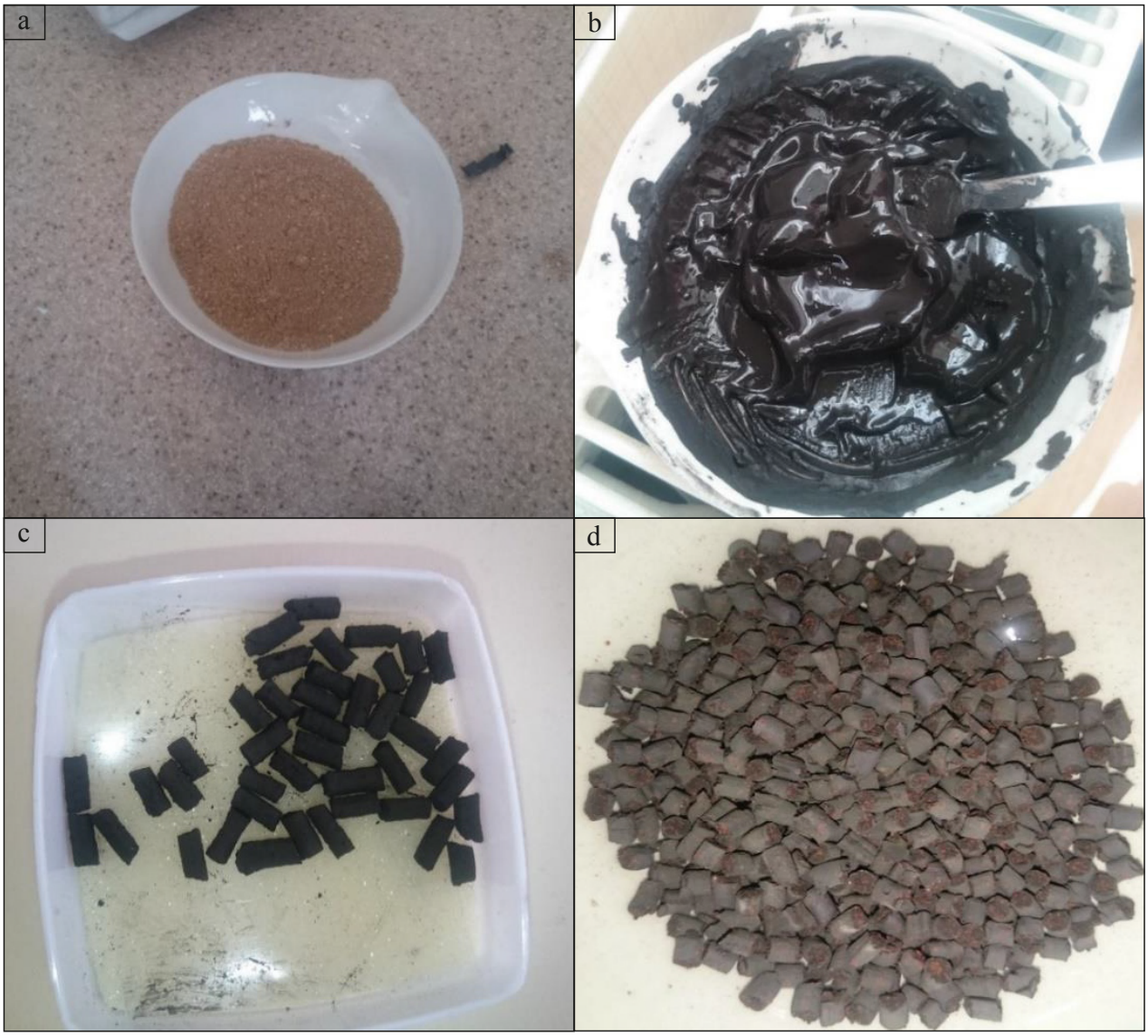

Figure 3. The production stages of adsorbent, (a): Li-Mn mixture are prepared by 1/1 molar ratio, (b): pasty mixture, (c): sized and dried mixture and (d): the heated mixture at 650 °C.

In the SEM investigations, it is remarkable that the adsorbent has different sizes of pores in its surface morphology (Figure 6). The diameter of the smallest pores varied between 41.23 and 114.0 μm and the diameter of the largest pores varied between 152.3 and 240.8 μm. When the EDS spectra of points 1 and 2 are examined, the Mn content of the pores decreased compared to the matrix, whereas the Si ratio increased (Figure 7).

The adsorbent BET surface area was measured as 53.140 m^2/g, the pore volume as 0.022 cc/g and the pore size as 1.838 Å. These results are similar to the BET analysis results of an adsorbent with $Li_{1.33}Mn_{1.67}O_4$ composition (LMA1 sample after acid treatment, 46.97 m^2/g) studied by Wang et al. (2009).

3.2. Determination of adsorbent ability

The adsorbents produced with different binder ratios were tested with Li solution prepared containing 1, 2, 5, 10 and 50 ppm. The adsorption curve in Figure 8 was created to compare the adsorption capacity obtained as a result of the 24-h experiment. The sample containing 19.00% sodium silicate binder (A) could not maintain its structural integrity and crumbled. Since the adsorption capability of the adsorbent containing 24.00% binder (B) is lower than the 30.00% sample (C), it was not chosen (Figure 8).

After the acid treatment, material A mainly scattered and 10% of material A was preserved and retained structural integrity. After acid activation, 90% of material B physically preserved its structure. However, material

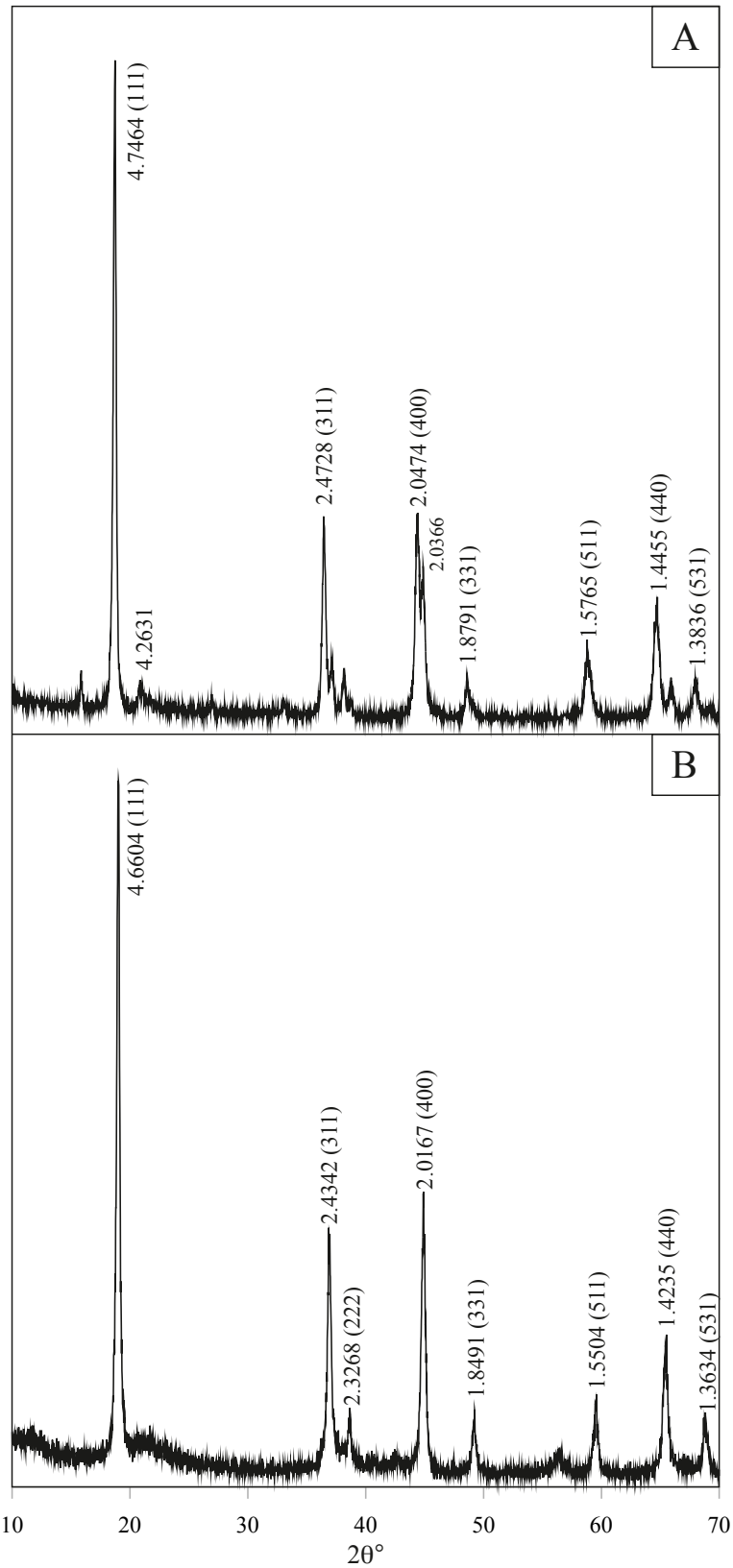

Figure 4. XRD graphics of adsorbent; (a): before acid treatment, (b): after acid treatment.

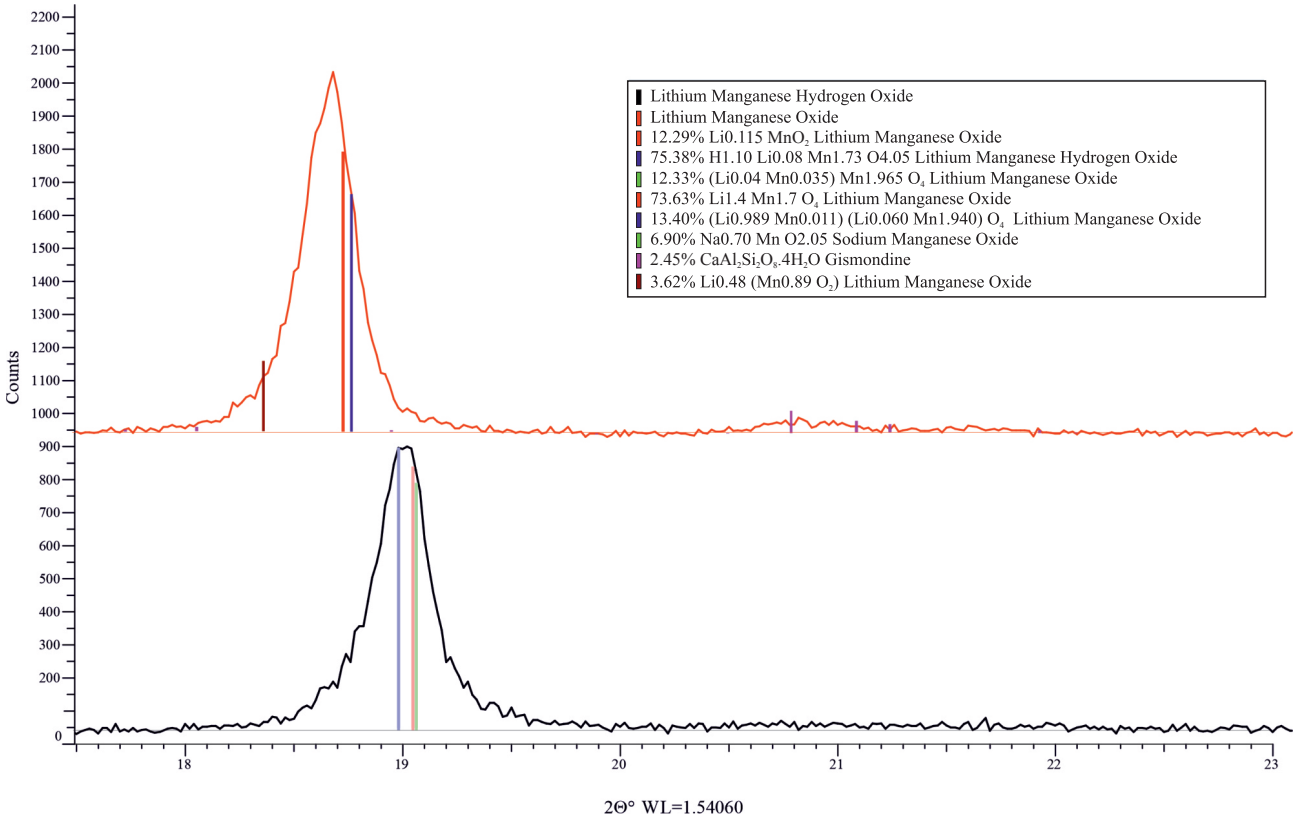

Figure 5. The shift of the first XRD peak due to acid treatment.

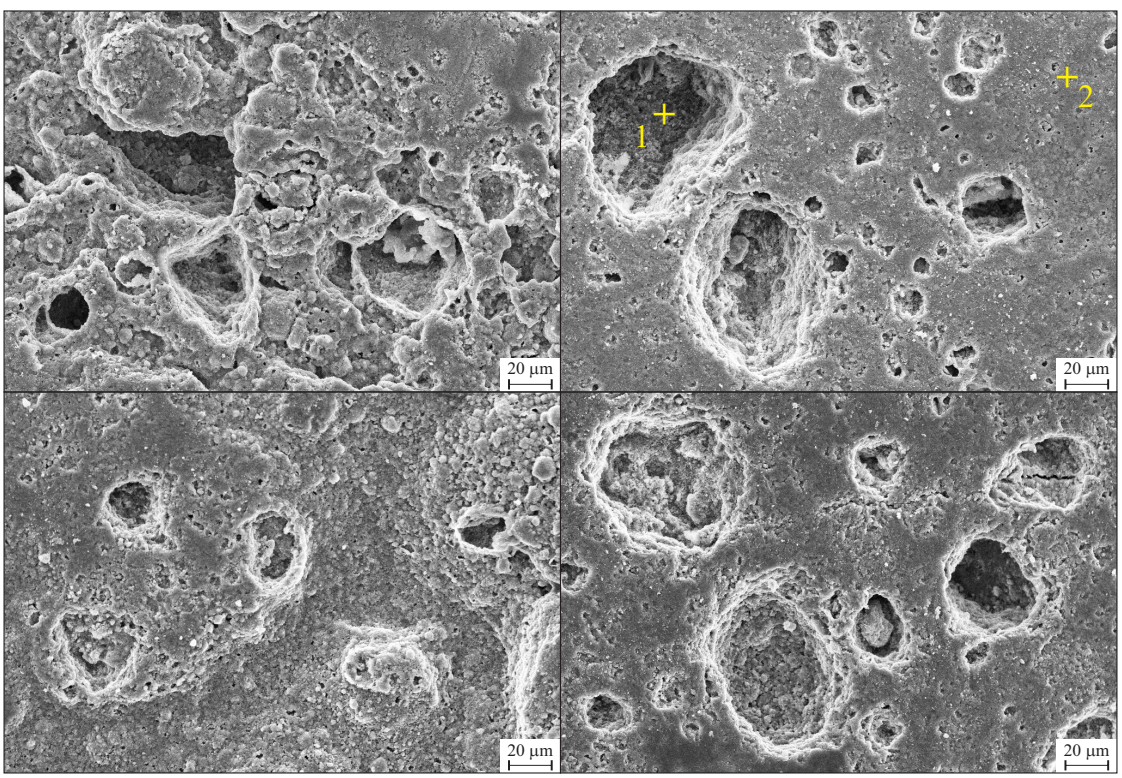

Figure 6. Scanning electron microscope images of produced adsorbent.

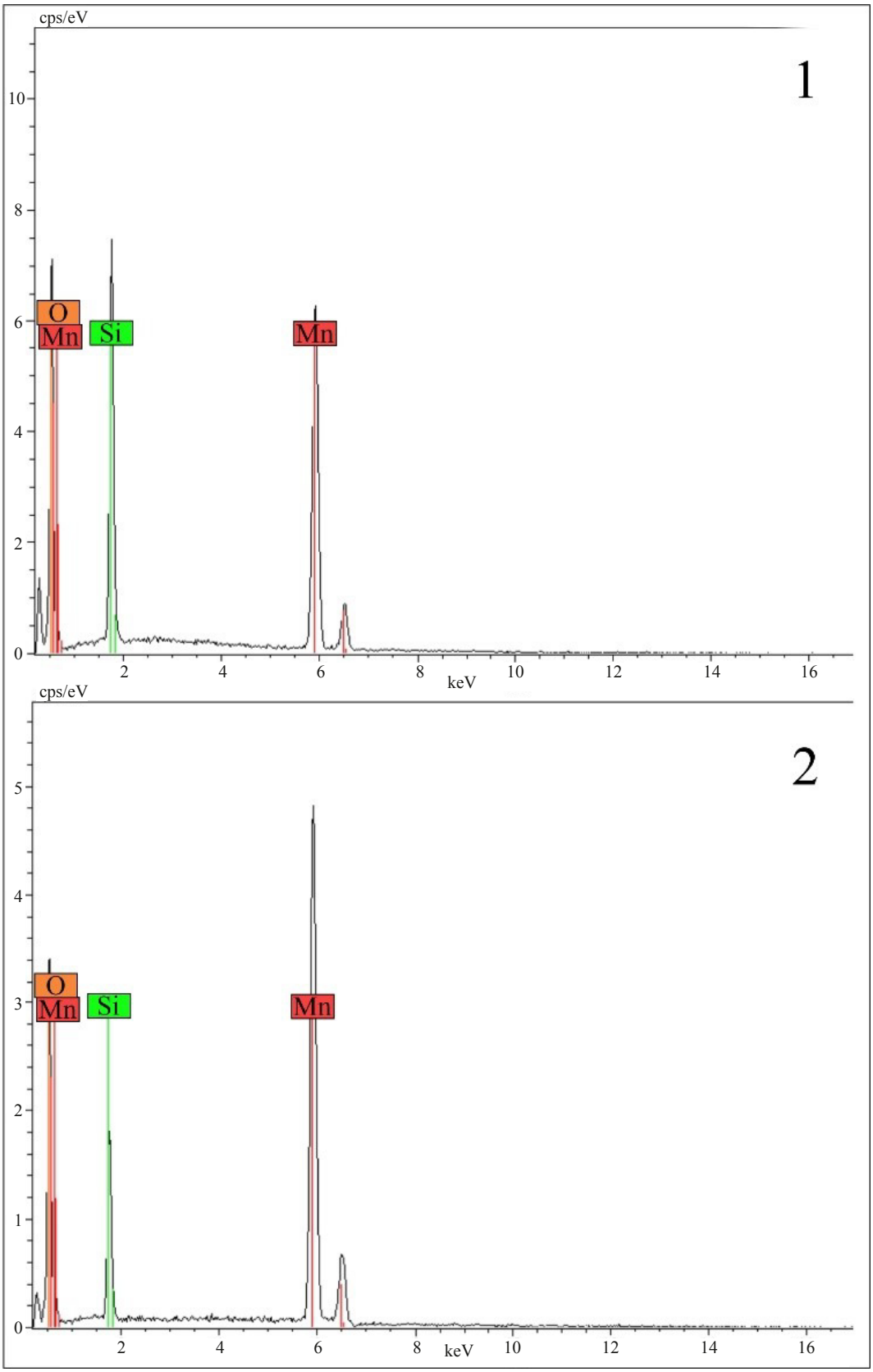

Figure 7. The EDS spectra of adsorbents.

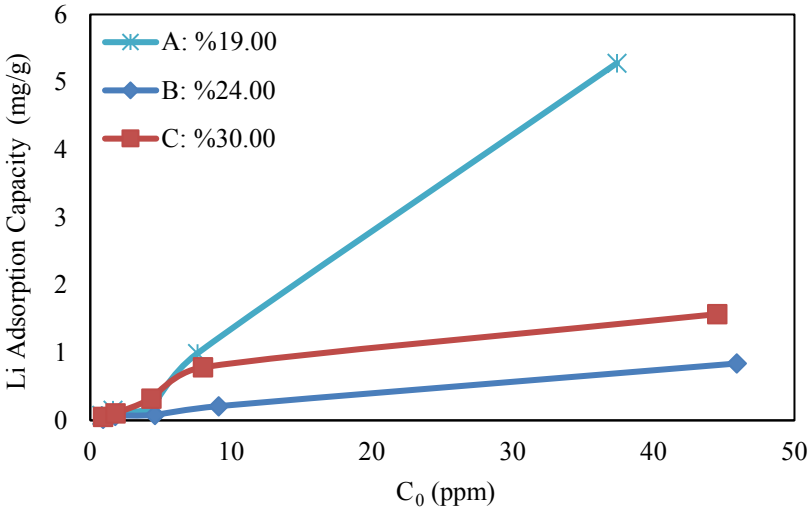

Figure 8. The lithium adsorption curves at different binder ratios.

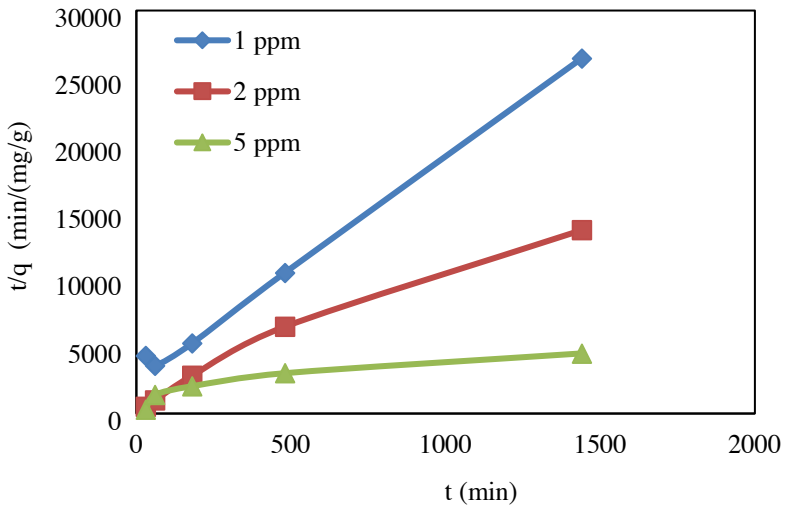

Figure 9. The graphic of adsorption rates versus time at different initial Li^+ concentrations.

C did not deform and preserved its initial physical properties. The difference between material B and C is that material B consists of a hard core after acid treatment. For this reason, it was determined that material B has lower holding capacity than C.

3.3. Determination of adsorption rate

After the end of structural adsorption capacity tests, the experiments were performed with material C. Here by keeping the initial Li^+ ion concentrations close to natural geothermal water content, tests were performed at 1, 2 and 5 ppm initial concentration by varying the time. The results were converted into the pseudo second order kinetic model to verify the coefficients for the following adsorption column experiments (Figure 9; Table 2).

$$\frac{t}{q_t} = \frac{1}{k} + \frac{1}{q_c} t$$

where *t*: time (min), *k*: sorption rate constant (g/mg/min), q_t: material adsorbed with time, q_c: amount of material adsorbed at equilibrium (mg/g), *t: coefficient* (mg/g).

3.4. Column experiments

In column experiments, the adsorption capabilities of the adsorbent were examined with artificial Li solution at 2 ppm with original water samples taken from the AF-25 geothermal drill well. The column feed rate, adsorbent amount in the column and the intervals of collecting filtrate samples were defined according to rate experiments. The adsorption efficiency of the adsorbent beads was tested in

Table 2. Determination of kinetic model constants and R^2 values.

Concentration	1/k	1/qc	R^2
1 ppm	2876	16.27	0.9963
2 ppm	877.22	9.1502	0.9807
5 ppm	1148.3	2.4908	0.846

a dynamic system and evaluated with breakthrough curves plotted for normalized Li^+ concentrations (C/C_o) versus bed volume (BV) as time constant. Here when (C/C_o) = 1, the column is full of Li ions and can no longer adsorb anymore, and (C/C_o) = 0.1 defines an efficient adsorption operation as 10% of the feed Li ions start to leak at the end of the column. In real world applications, the feed would be directed to a fresh column while the previous one would be sent to the regeneration unit for Li-ion concentrate retention (Figure 10). The height/diameter (H/D) ratio of the prepared column was around 15.

For BV calculations, the equations below were utilized (Özdemir and Turan, 2007);

$$BV = \frac{V_F}{V_R} = \frac{Qxt}{V_R}$$

The BV value per hour is defined as;

$$\frac{BV}{h} = \frac{Qxt}{V_R}$$

Empty bed contact time (EBCT) is calculated as;

$$EBCT = \frac{V_R}{Q}$$

Adsorption time (t);

$$t = \frac{V_F}{Q} = BVxEBCT$$

where V_F is the total volume of water passing through adsorption process (cm^3), V_R is constant bed volume (cm^3), C_o is feed Li^+ ion concentration (ppm), C is Li^+ ion concentration at the exit (ppm), EBCT is empty bed contact time (min), Q is feed rate (cm^3/s) and t is adsorption time (Özdemir and Turan, 2007).

As the feed rate is constant, the BV intervals are the same for both experiments. As there is a slight difference in the normalized adsorption values, we reached 10% cut-off rate earlier with natural geothermal water because the natural water Li ion content was measured as 3.5 ppm after the experiment. EBCT was calculated as 25.61 min for the artificial sample and efficient operation period (t) was 28.17 h. While for geothermal water, EBCT is the same but efficient operation (t) time was calculated as 26.04 h. Here, we can perform a scale-up calculation according to the above data for a ton of absorbent in a column with geothermal sample water feed rate of 1.63 t/h, a total of 236.7 g of Li ion equivalent will be collected as 2519.6 g of Li_2CO_3 in 41.6 h. As the average geothermal water capacity of AFJET Corporation facility is 900 t/h with approximately 3.5 ppm Li^+, it has the potential for Li_2CO_3 annual production of 294.46 t or roughly 25% capacity to fulfil the required annual supplement of 1200 t for Turkey. These values were calculated to give a brief idea of how important the geothermal facilities are as natural lithium resources. More exact evaluations require further studies including lithium release efficiency of the adsorbent with crystallization and purification of lithium product, which is being examined in ongoing industrial research by the authors.

4. Discussion

Lepidolite minerals in magmatic rocks, clays in boron deposits, active (Tuz Lake, Acıgöl and Van Lake) and dried lake basins and geothermal resources are most important lithium resources in Turkey (Akgök and Şahiner, 2017). Geothermal resources in Turkey contain highly soluble minerals and metals due to their geological characteristics. Exploration studies showed that lithium concentration reaches a maximum of 68 ppm in geothermal resources in our country (Gülez et al., 2019). The geological parameters such as the structure and composition of the reservoir rock, composition and circulation time of the geothermal fluid, type of recovered material (fluid, sludge and scale) and type of valuable metal (Si, Li, etc.) in geothermal systems are effective for the determination of lithium recovery methods from geothermal sources (Bourcier et al., 2005).

Several extraction methods were applied for retention of lithium from geological sources. Evaporative crystallization (Stamp et al., 2012), coprecipitation (Kenjiro et al., 1983), solvent extraction (Seeley and Baldwin, 1976) and adsorption (Chitrakar et al., 2000) are the most well-known extraction methods (Weng et al., 2020). Adsorption methods have advantages such as cost-effective for extraction of lithium from brine (high chemical stability, and high Li^+ uptake capacity) and being environmentally friendly (low toxicity) (Ooi et al., 1987; Chitrakar et al., 2000; Zang, et al., 2007; Zang, et al., 2009).

Li-Mn spinel adsorbents have superior lithium selectivity, high lithium adsorption capacities, and excellent regeneration performance, so there are many studies about their adsorption capacity and crystal structure (Wang, et. al. 2006; 2009; Tian et al., 2010). There are several studies about patents (Chung et al., 2008; 2014) for producing adsorbents in the form of beads and practical adsorption. There are several studies about adsorption with Mn-Li spinels from the sea (Yoshizuka et. al., 2002), lake waters, underground waters from oil beds and geothermal reserves

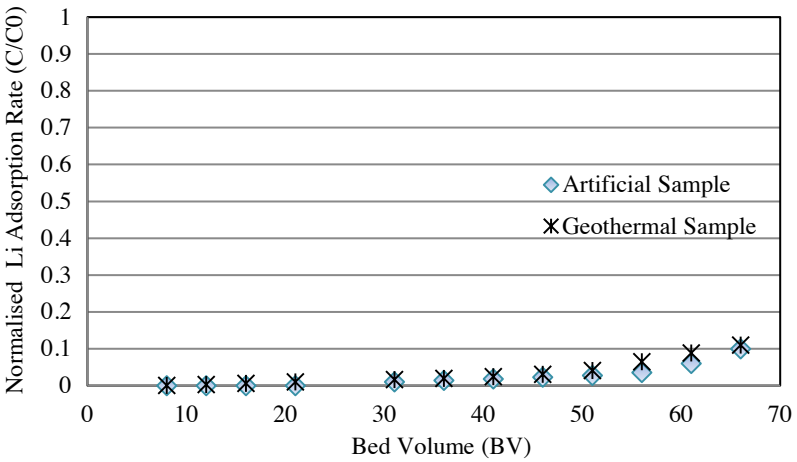

Figure 10. Comparison of Li adsorption performance in a column with artificial and natural geothermal water feed.

(Yanagase, 1982). At the end, we may conclude that Mn-Li spinels with various elemental rates can be produced with the desired binder at necessary bead size for applications. The adsorbents may not be optimum until they are tested with the original Li^+-ion source because nature delivers water with unique ionic composition at any location and environment.

5. Conclusion

Li ion selective beads of well-known Mn-Li spinels were prepared in the geometrical form of cylinders with diameters and length of 3 and 4 mm respectively. The beads, naturally dried overnight, were placed in crucibles and heated for sintering with Na-silicate at 650 °C for the best shape for adsorption media. The Na-Cl type Ömer-Gecek geothermal waters with Li+ values up to 3.5 ppm were used for column tests. The optimum adsorption time was determined by examining the adsorbent amount, lithium amount, feeding time and column volume parameters. According to fixed bed adsorption column parameter scale-up equations (*EBCT*, *BV* and *t*), with a feed of 1.63 tonnes/hour of geothermal water, 236.7 g of Li^+ ion can be collected, equivalent to 2519.6 g Li_2CO_3 in a period of 41.6 h.

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