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Lithium Recovery Using Hydrogen Manganese Oxide Adsorbent Derived from Spinel Lithium Manganese Oxide

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Abstract

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method. The synthesized adsorbent was characterized using Scanning Electron Microscopy to identify its physical characteristics and surface morphology. The adsorption capacity toward lithium solution was performed through an ion exchange process, and the adsorption values were determined using Atomic Absorption Spectroscopy (AAS). The synthesized HMO has a high lithium adsorption capacity for lithium-ion, 23 mg/g and 10 mg/g for desorption. The optimum uptake capacity of HMn_2O_4 is 44% of the initial values (52 ppm) © 2023 Universitas after 120 minutes of contact time. The synthesized hydrogen manganese oxide adsorbent could be used in commercial-scale lithium recovery.

Keywords: *adsorbent; brine; hydrogen manganese oxide; lithium; recovery*

Abstrak

Pemulihan Litium Menggunakan Adsorben Hidrogen Mangan Oksida Berasal dari Spinel Litium Mangan Oksida. Pengambilan lithium dari air garam (brine) baru-baru ini menarik banyak perhatian yang dengan seiring meningkatnya permintaan industri, khususnya untuk aplikasi penyimpanan energi, seperti baterai. Pengambilan lithium dari brine dilakukan dengan menggunakan adsorben jenis hidrogen mangan oksida. Adsorben hidrogen mangan oksida atau HMn₂O₄ (HMO) berasal dari spinel lithium mangan oksida (LMO), yang disintesis dari prekursor LiOH dan MnO₂ melalui metode refluks. Adsorben hasil sintesis ini kemudian dikarakterisasi menggunakan teknik Scanning Electron Microscopy (SEM) untuk mengidentifikasi karakteristik fisik dan morfologi permukaannya. Pengujian kapasitas adsorben untuk dapat mengadsorpsi lithium dalam larutan, dilakukan menggunakan metoda pertukaran ion. Nilai lithium yang teradsorpsi ditentukan dengan menggunakan metoda Spektroskopi Serapan Atom (AAS). Dari hasil penelitian didapatkan bahwa HMO yang disintesis memiliki kapasitas adsorpsi lithium yang tinggi yaitu 23 mg/g, kapasitas desorpsi 10 mg/g. Kapasitas adsorpsi optimum dari HMn₂O₄ hasil sintesis adalah 44%, setelah proses adsorpsi dilakukan selama 120 menit. Adsorben hidrogen mangan oksida (HMn₂O₄) yang disintesis memiliki potensi untuk dapat dimanfaatkan guna mengambil lithium dari brine dalam skala besar.

Lithium recovery from brine recently attracted significant attention due to increasing industrial demand for energy storage, such as batteries. The lithium recovery from lithium

brine was investigated using hydrogen manganese oxide adsorbent. The hydrogen

manganese oxide adsorbent HMn_2O_4 (HMO) is derived from the spinel lithium manganese oxide (LMO), which is synthesized from LiOH and MnO_2 precursor through the reflux

Kata kunci: adsorben; brine; hydrogen mangan oksida; lithium; perolehan



INTRODUCTION

In recent years, there has been a substantial increase in demand for lithium (Li) as a cathode material for lithium-ion batteries (LIBs), driven predominantly by the rapid expansion of the electric vehicle industry [1]. Geothermal and seawater are promising sources of lithium in the future to supply the global demand for electric vehicles, where lithium is the crucial component [2]. Some reports showed that the geothermal brine contains lithium that could be recovered. Brine from geothermal possesses a lithium concentration of about 40-60 ppm [3]. This study shows that geothermal brine can be utilized as an alternative to lithium sources. Ion exchange, solvent extraction, co-precipitation, and adsorption are methods for recovering lithium from brines [4].

World consumption is predicted that by the year 2025, lithium carbonate will be around 160,000 tons per year [5]. Almost two thirds of the world's lithium is produced from brine sources. Obtaining a ton of lithium is estimated, and a half million brine is required [6]. Lithium reserves are estimated at 14 million tons, and most of them are stored in seawater, salt-lake brine, geothermal brine, and lithium ore. Geothermal brine, seawater, and solid lithium contained in lithium ore [7]

The adsorption method is the most effective technique among all the methods for recovering metal ions from liquid sources, such as lithium recovery from geothermal brine. This method has advantages over others due to its low cost and environmentally friendly. The Li-ion sieve-type metal oxide adsorbents, such as hydrogen manganese oxide (HMO) from LMO, have been intensively studied due to their excellent stability and selectivity for Li ions recovery through adsorption [8]. Many works have been reported on preparing lithium manganese oxides (LMO), such as LiMn₂O₄, to recover lithium from liquid brine sources. Lithium manganese oxides have a three-dimensional spinel structure to provide the insertion of lithium ions with reversible reactions in liquid media. This material shows good selectivity to lithium-ion and low toxicity and chemical stability, which is compatible with applications for lithium-ion recovery from brine. The formation of adsorbent is conducted by acid treatment, in which Li+ is substituted by H+ to form HMO through the ion exchange process and maintaining the spinel structure. Hence, this HMO has high selectivity to lithium as a solid adsorbent. It was reported by Xu et al. that the substitution of the manganese site with lithium in the spinel structure affects the lithium uptake in the adsorption process [9]. Chitrakar's group [9] reported that the hydrogen lithium adsorbent (H_{1.6}Mn_{1.6}O₄) derived from Li_{1.6}Mn_{1.6}O₄

showed the highest lithium uptake compared to $LiMn_2O_4$ [9]. This study examined lithium-ion recovery from geothermal brines using contained powder HMO adsorbent. The study examined the impact of contact time on the adsorption-desorption of the adsorbent during the recovery of Li⁺ ion.

MATERIALS AND METHOD Materials

Lithium hydroxide (LiOH), manganese (II) oxide (MnO₂), LiCl, and sulfuric acid were obtained from Sigma-Aldrich and used as received.

Preparation of LMO and HMO

The LMO and HMO were synthesized using the reflux method described by Chitrakar's group [9]. In the reflux method, 5 g of MnO_2 was mixed with 100 mL of a 4 M LiOH solution and boiled at 120 °C for 8 h. The precipitate was filtered, washed with deionized water, and dried at 70 °C for 3 h. The obtained product (LiMnO₂) was then heated at 400 °C for 4 h in the air to get Li_{1.6}Mn_{1.6}O₄. The Li⁺ extraction was carried out batchwise by stirring 1.5 g of material with 2 L of a 0.5 M HCl solution for one day to form H_{1.6}Mn_{1.6}O₄. The acid-treated materials were filtered and washed with deionized water and air dried. The finished product was used to adsorb lithium ions from the samples.

Characterization and Analysis

The morphology of the granulated LMO was examined using a scanning electron microscope (SEM). The amount of Li⁺ recovered was analyzed by Atomic adsorption spectroscopy (AAS).

RESULT AND DISCUSSION

Adsorbent Characterization

SEM analysis was conducted to analyze the morphology of the synthesized LMO. **Figure 1** shows the SEM results of the LiMn₂O₄ synthesized using a reflux method at the temperature of 120 °C. The images of LMO under SEM with 1,000x, 10,000x, and 30,000x magnification illustrate that the granules of the compound are irregular and non-uniform and show smooth surfaces.

The surface of these particles does not appear to have the expected pores at higher magnification (30,000x). These expected pores are vital for the adsorption, where the highly porous surface will help the adsorption process. Unfortunately, the surface area of the synthesized LMO was not measured. However, the images showed spherical micro-sized aggregates on the surface, which is expected to increase the surface area.



Figure 1. LMO images using SEM at different magnifications (a) 1,000x, (b) 10,000x, and (c) 30,000x.

Conversion of LMO into HMO

The LMO (LiMn₂O₄) was first converted into HMO (HMn₂O₄) by assisting with HCl before use to recover lithium from brine. A total of 1 gram of dry LiMn₂O₄ was placed in a tea bag, as shown in **Figure 2**, to prevent adsorbent loss during the exchange process (acid treatment) between Li⁺ and H⁺.



Figure 2. (a) LMO in the tea bag (b) Acid treatment process between Li⁺ and H⁺

The acid treatment process was carried out by dipping $LiMn_2O_4$ into a solution of 0.5 M HCl. This process was carried out within 24 hours so that the ion exchange occurs between Li^+ ions within the $LiMn_2O_4$ with H^+ ions in the HCl solution, as shown in **Figure 3**. The reaction that happened is as follows:

LiMn₂O₄+HCl→HMn₂O₄+LiCl

Adsorption and Desorption Adsorption

 Table 1. Lithium-ion adsorption by HMO at various times

Time (min)	Remaining Li in sol. (mg/L)	Li+ adsorbed (mg/L)	Adsorption Efficiency (%)
30	48	4	7.7
60	44	8	15
90	30	22	42
120	29	23	44
150	32	20	38
180	32	20	38

Note: Initial Li⁺ concentration is 52 mg/L

The HMn_2O_4 (HMO) was then applied for Li-ion adsorption. The HMO was first placed into a container of 1 liter of Li⁺ solution with an initial concentration of 52 ppm. This Li⁺ solution was stirred using a magnetic stirrer to circulate the solution in order for adsorption and ion exchange process to take place. The adsorption process was carried out by varying the contact time between 30-180 minutes with 30 minutes intervals. The result is presented in **Table 1**, and it is illustrated in **Figure 3**.

Table 1 shows that the maximum Li uptake is 23 mg/g adsorbent, and the optimum contact time is 120 min. Further stirring, the Li uptake decreases to 20 mg/L and stabilizes at this number, this might be due to the equilibrium being shifted to the solution site, and the desorption occurred.



Figure 3. Lithium-ion adsorption by HMO at various times.

The initial lithium concentration was set at 52 mg/L and measured using Atomic Absorption Spectroscopy (AAS). This Li-ion was mimicked using LiCl salt solution as a model compound. Figure 3 shows that the Li^+ adsorption by HMO to form LiMO increased slowly up to the equilibrium level, which is 44% after 120 min stirring. On further stirring, the adsorption slightly decreased to 38% at 150 min and stabilized at the same value at 180 min stirring. This can be summarized that the optimum stirring time or contact time is 120 min. Up to this point, the adsorption achieved an equilibrium condition where there was no further stirring required. The results indicated that the Li adsorption capacity of the synthesized HMO compound was limited at 23 mg/g adsorbent, as explained in Table 1. However, this adsorption capacity is considered very high, and it has the opportunity to be upscaled.

Desorption

Figure 4 shows the amounts of Li released from the LiMO during the desorption process at various time. The desorption is to liberate Li ions from LiMO (LiMn₂O₄) through the ion exchange mechanism where H^+ exchanges the Li⁺ from LiMO by immersing LiMO in HCl solution so that Li⁺ forms LiCl. This desorption process is the opposite of adsorption, where the LiMO (HMn₂O₄) is converted to HMO (HMn₂O₄), and it can be reused for the following adsorption. The desorption process was also carried out by varying the time, which is shown in **Table 2**.

 Table 2. Desorption of Li⁺ from LiMO at various times.

Time (min)	Remaining Li ⁺ (mg/L)	Desorbed Li ⁺ (mg/L)	Desorption Efficiency (%)
30	21.8	1.2	5.2
60	21.5	1.5	6.5
90	21	2	8.7
120	20	3	13.0
150	20	3	13.0
180	20.5	2.5	10.9

Note: Initial Li⁺ concentration for desorption was 23 mg/L $\,$



Figure 4. Lithium-ion desorption by LiMO at various times.

Figure 4 shows that the desorption efficiency was increased from 5.2% in the first 30 minutes to 13% after 120 minutes of stirring, and the equilibrium was reached at this point. Further stirring to 180 min resulted in a slight decrease in the desorption to 10.9%. The phenomena are similar to the adsorption process in which the efficiency reaches the optimum at 120 min.

CONCLUSION

This study shows that the stirring time affects the yield of lithium recovered from brine. The lithium adsorption yields 23 mg/g uptake and the efficiency at 44%. This result is very high compared to most reported study. However, in the desorption process

the lithium recovered is far from the expected value which is 3 mg/g or 13% efficiency. Both adsorption and desorption process achieved optimum value at 120 min stirring and reached equilibrium after this point. The summary of this study revealed that the method (reflux method) can be upscale to recover lithium from brine using hydrogen manganese oxide adsorbent. The adsorbent was synthesized successfully using simple technique and it worked very well to recover the lithium via ion-exchange mechanism.

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