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STUDY OF IRON AND CALCIUM REMOVAL ON MANGANESE SULFATE PRECURSORS FOR BATTERY CATHODE RAW MATERIAL APPLICATIONS

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Abstract

Global battery sales are expected to reach $310.8 billion in 2027, up 14.1% from 2020. 95% of the world's batteries are lead-acid, lithium-ion, or nickel-based. One of the most popular batteries on the global market is lithium-ion, which uses MnSO4 powder as its cathode raw material. Manganese sulfate-based lithium-ion batteries can be made using Indonesian resources, specifically manganese ore from Trenggalek. Trenggalek manganese ore is of poor quality and contains impurities, primarily Fe and Ca. To produce 98% powder manganese sulfate, the solution is prepared, reduced with briquette charcoal, leached, precipitated, carbonated, and crystallised. NH_4OH *reagent is used to remove Fe through precipitation, and the carbonatation process is employed to eliminate Ca, resulting in 97.237% purity of manganese sulfate powder product. This outcome is achieved under precipitation process conditions of [*NH_4OH *2M], T = 80 °C, pH = 4, t =180 minutes, while carbonatation process conditions are T=50 °C, t = 120 minutes.*

Keywords: *Lithium-ion batteries, iron recipitation, carbonatation, manganese sulphate*

1. INTRODUCTION

Batteries are the technology used for energy storage. Climate change is transitioning from fossil fuels to sustainable energy solutions, including batteries and bioenergy [1]. Analysis by the McKinsey Battery Insights team projects that the entire lithium-ion (Li-ion) battery chain, from mining through recycling, could grow by over 30 percent annually from 2022 to 2030. Batteries for mobility applications, such as EVs (electric vehicles), will account for the vast bulk of demand in 2030, about 4,300 GWh, an unsurprising trend, seeing that mobility is growing rapidly. This is largely driven by three major drivers: a regulatory shift toward sustainability, increased consumer demand for greener technologies, and emission-reduction targets [2].

With its potential in Indonesia, manganese sulfate powder can be utilized as a raw material for lithium-ion battery cathodes. Manganese sulfate powder is considered more efficient than

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manganese dioxide as a raw material for cathodes because the cations in the produced powder can store energy in the battery, resulting in better battery life than manganese dioxide as a cathode material [3]. The increasing global demand for manganese from many sectors that use manganese as a primary or supporting material for a product has led to very rapid and varied production of manganese [4].

The potential of manganese ore in Indonesia can be maximized as raw material for lithium-ion battery cathodes to fill the global battery market, which is one of the contributions in this era. The world's total reserves amount to 1.3 billion tons, and Indonesia's manganese ore reserves are 49.6 million tons according to the OEC (observatory of economic complexity). Although it only has a small portion of manganese reserves, its quality ranks as the best number one in the world. Manganese ore is an important mineral used as a raw material or alloying element in the manufacturing process of various products, including manganese as a raw material for lithium battery cathodes. In Trenggalek manganese ore, there are several main impurities, such as Ca and Fe, which pose a problem because the desired product for manganese sulfate powder production requires a purity of 98%, according to ISO 9001 and SNI 23625:2021 standards.

To obtain $MnSO_4$ from Trenggalek manganese ore, the process begins with leaching the Mn ore using H_2SO_4, followed by precipitation and carbonation, each intended to remove Fe and Ca, respectively. In the iron precipitation process in this study, the NH_4OH reagent is used, which is known to easily precipitate iron and other elements, with less than 5% [5]. The reactions occurring during the Fe precipitation process are explained in equations 1-3 [6][7][8].

$$\mathrm{MnO\,(s) + H_2SO_4\,(aq) \rightarrow MnSO_4\,(aq) + H_2O\,(aq)} \ldots\ldots (1)$$

$$\mathrm{MnSO_4\,(aq) + \mathbf{2}\,NH_4OH\,(aq) \rightarrow Mn(OH)_2\,(s) + (NH_4)_2SO_4\,(aq)} \ldots\ldots (2)$$

$$\mathrm{FeSO_4\,(aq) + 2\,NH_4OH\,(aq) \rightarrow Fe(OH)_2\,(s) + (NH_4)_2SO_4\,(aq)} \ldots\ldots (3)$$

A carbonatation process is carried out during the precipitation or removal of Ca. The result of the Ca precipitate obtained from carbonatation is $CaCO_3$. The carbonatation process is a solution saturation process by flowing CO_2 gas into the solution at a certain temperature and a fixed discharge [9]. The reaction will occur when the carbonatation process is carried out [10]-[12].

$$\mathrm{CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)} \ldots\ldots (4)$$

$$\mathrm{H_2CO_3(aq) \rightleftharpoons H{+}(aq) + HCO_3{-}(aq)} \ldots\ldots (5)$$

$$\mathrm{H^+(aq) + HCO_3^-(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)} \ldots (6)$$

$$\mathrm{Ca^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) + 2H_2O(l)} \ldots\ldots (7)$$

2. MATERIALS AND METHODS

Manganese ore was ground into a size of -80# +100# and then mixed with briquette charcoal of the same size, which is used as a reducer. The ratio between manganese ore and briquette charcoal is 4:1. It was then calcined at a temperature of 800 °C in a muffle furnace for 2 hours. The resulting calcination product is then quenched. Next, a leaching process is conducted to extract manganese ore using 4M H_2SO_4 at 70 °C for 1.5 hours. The precipitation process to remove Fe is carried out using 4M NH_4OH at 80 °C with variations in pH and time on the pregnant leach solution. The best precipitation result undergoes a process of removing Ca by carbonatation using CO_2 gas passed through the solution with variations in temperature and time. The solution then crystallized to convert into manganese sulfate powder.

3. RESULTS AND DISCUSSION

The results of XRF (x-ray fluorescence) analysis of Trenggalek manganese ore samples can be seen in Table 1.

Table 1. XRF analysis of manganese ore from Trenggalek

Element	Compound	Wt.%
Ca	CaO	36,50
Mn	MnO_2	33,10
Si	SiO_2	1,20
Fe	Fe_2O_3	0,80
Mg	MgO	0,10
Al	Al_2O_3	0,40
More	...	27,9

Table 1 shows that many other impurities are still found in Trenggalek manganese ore, even if the impurity content exceeds the Mn element.

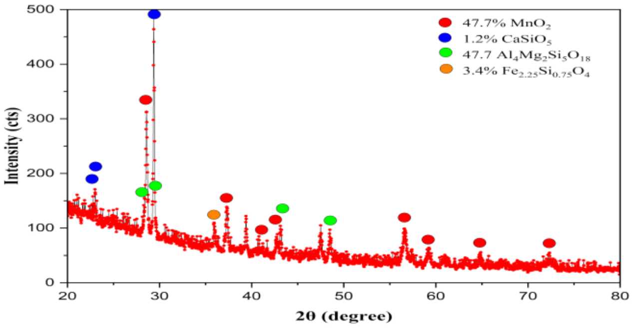


Figure 1. XRD analysis for manganese ore

With less than 35%, Manganese ore is categorized as low-grade manganese ore. Figure 1 presents the XRD (x-ray diffraction) analysis for the manganese ore. The XRD analysis in Fig. 1 was performed in the 20-80º range. Four compounds were identified: MnO_2, $CaSiO_5$, $Al_4Mg_2Si_5O_{18}$, and $Fe_2.25Si0.75O_4$. The main compound detected is MnO_2, with an intensity of 47.7% in the XRD analysis. MnO_2 is scattered at several points or peaks in the XRD analysis results. MnO_2 is the primary compound to be processed in producing manganese sulfate ($MnSO_4$) precursor as a raw material for lithium battery cathodes.

The briquette charcoal used as a reductant in this research was analyzed proximate using ASTM D3172 - ASTM D3175 standards. Table 2 presents the proximate analysis for the charcoal briquettes used in this study.

Table 2. Proximate analysis for charcoal briquettes

Parameter	**Test results (%)**
Moisture	19
Volatile Matter	5
Ash	41
Fixed Carbon	35

In addition to the charcoal briquettes, the composition of the manganese ore reduction was analyzed using XRF, as shown in Table 3.

Table 3. XRF analysis for the composition of manganese ore reduction

Element	**Compound**	**Wt.%**
Ca	CaO	53.06
Mn	MnO_2	36.74
Si	SiO_2	7.41
Sn	SnO_2	0.05
More		2.74

As in Table 3, the concentration of CaO reaches a peak of 53.06%, which indicates the CaO-rich phase as a matrix constituent. All the remaining elements were purified and removed as the samples were carried out for refining. These processes increased the purity of Mn from 33.1% to 36.74% and Ca from 36.5% to 53.06%. Briquette charcoal can be used as a reducer because it can convert the valence state of Mn^{4+} to Mn^{2+}, as Mn^{2+} is more readily leached by acid than Mn^{4+}. Using briquette charcoal as a reducing agent causes the conversion of Mn^{4+} to Mn^{2+} and increases the manganese ore content.

The leaching process of manganese ore is carried out under acidic conditions using sulfuric acid (H_2SO_4) at a concentration of 4 M at 70 °C for 90 minutes with a stirring speed of 350 rpm. Table 5 shows the results of the ICP-OES (inductively coupled plasma-optical emission spectroscopy) analysis of the manganese ore leaching with a 10x dilution.

Table 4 shows that the Mn content in the PLS (pregnant leach solution) increases after the leaching process up to 17777 ppm.

Table 4. ICP-OES analysis for pregnant leach solution

Element	**ppm**	**Element**	**ppm**
Mn	17777	Na	204
Al	1662	K	101
Fe	743	Ti	49
Mg	286	Sn	46
Ca	220	Si	40

Precipitation is carried out on a 20 mL filtrate of the PLS by adding reagent [NH_4OH 2M] at a temperature of 70 °C with variations in pH and time. The pH variations used are 4, 6, 8, 10, and 12, while the time variations used are 60 minutes, 120 minutes, and 180 minutes. The percentage removal of Fe is obtained from the following formula.

$$Removal\ (\%) = \frac{Initial\ Element\ Level\ (ppm) - Final\ Element\ Level\ (ppm)}{Initial\ Element\ Level\ (ppm)} x100$$

This formula quantifies the efficiency of Fe removal under different conditions.

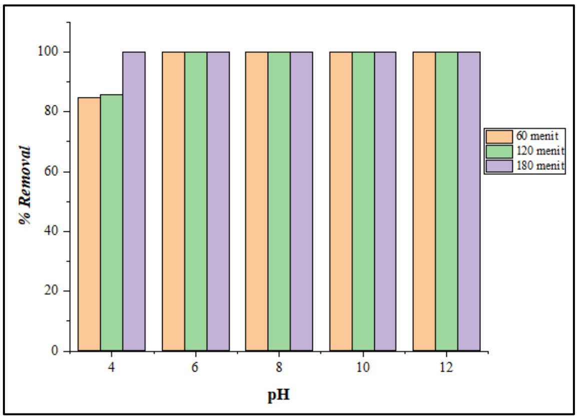


Figure 2. Effect of pH variations on percent Fe removal

Figure 2 illustrates the effect of pH variations on the percentage of Fe removal.

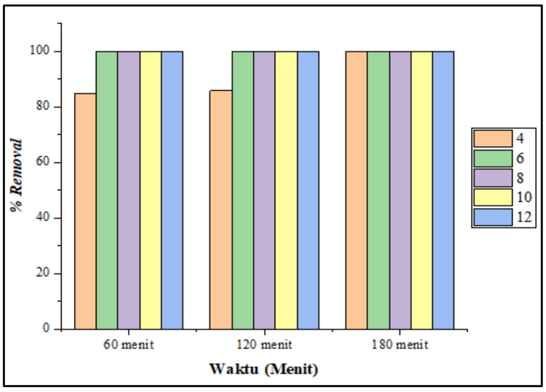


Figure 3. Effect of time variations on percent Fe removal

The higher the pH, the greater the Fe that can be removed. This happens because Fe can precipitate in the pH range of 1 - 2.5, producing Fe^{3+} ion precipitates, while in the pH range of 6.5 - 8.5, producing F^{2+} ion precipitates, referring to the Monhemius diagram [13]. The smaller the concentration of Fe^{3+} ions, the higher concentration of OH^- ions is needed, and increasing the concentration of OH^- can be done by increasing the pH of the solution [14]. To further investigate the influence of other variables, Fig. 3 illustrates the effect of time variations on the percentage of Fe removal. The highest condition in the Fe precipitation process is at pH 4, with a precipitation process of 180 minutes, which is 100%, with the remaining Mn content in the filtrate of 6.129 ppm, the highest level compared to other variable conditions. The time used affects the maximum precipitate results because the time used in the precipitation process can cause the process to occur optimally between the PLS sample and the precipitation agent, namely NH_4OH [15].

Table 5. ICP-OES analysis for the filtrate before and after the Fe precipitation

Element	Before the precipitation process of Fe (ppm)	After the precipitation process of Fe (ppm)
Al	1.662	209
Ca	220	117
Fe	743	0
K	101	19.3
Mg	286	20
Mg	286	20
Mn	17.777	6.13
Na	204	38.2
Si	40	35.7
Sn	46	28.3

Table 5 shows that several elements are missing in the filtrate that precipitate in the residue during the Fe precipitation process using NH_4OH.

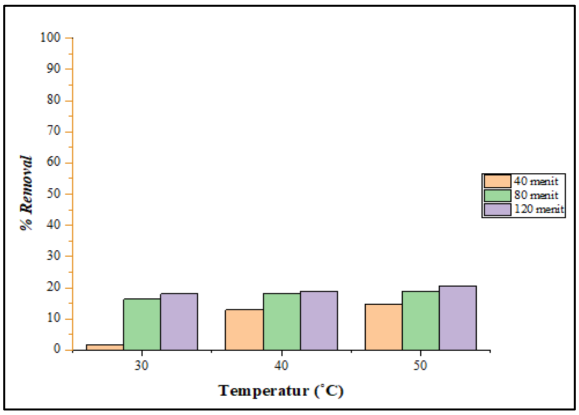


Figure 4. Effect of temperature on Ca precipitation

This occurs because using NH_4OH as a precipitation reagent is not selective in precipitating Fe. The carbonatation process was carried out by flowing CO_2 gas with a discharge of 5 L/min to the best filtrate sample of Fe precipitation results using NH_4OH as much as 100 mL with an agitation speed of 200 rpm. Time variations are 40 minutes, 80 minutes, and 120 minutes. At the same time, the temperature variations are 30, 40, and 50 °C. As shown in Fig. 4, the temperature used in the carbonatation process significantly affects the precipitation of Ca. The temperature used in the carbonatation process affects the precipitation of Ca. Figure 4 illustrates that the higher the temperature, the greater the percentage of Ca precipitation.

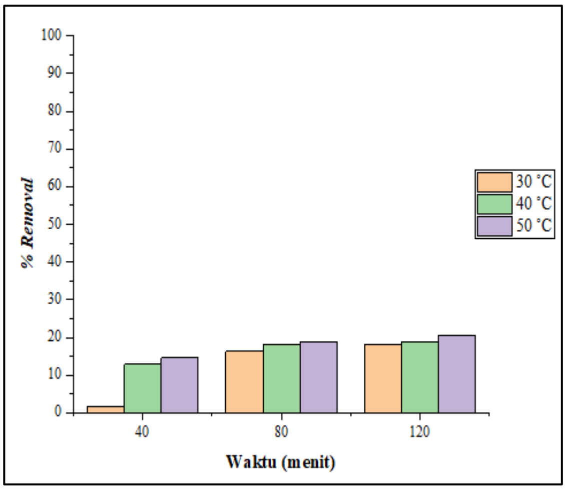


Figure 5. Effect of time on Ca precipitation

This is because, at higher temperatures, the reaction between calcium and CO_2 to form calcium carbonate occurs more easily[16]. In addition to temperature, Fig. 5 illustrates the effect of time on Ca precipitation.

(a) (b)

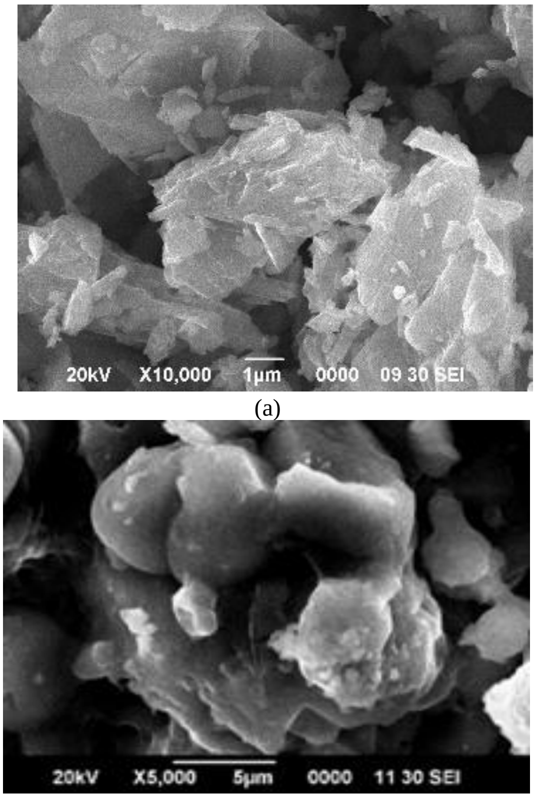
Figure 6. (a) Crystallization process, and (b) Product after crystallization

In this study, the longer the time used, the more Ca can be deposited; this happens because the CO_2 gas that reacts with the filtrate sample will form more calcium carbonate, and the longer the temperature used, the more calcium carbonate will be formed. The best conditions in this study were 120 minutes and 50 °C with 20.51% Ca precipitation [16]. Following the precipitation phase, the crystallization process is depicted in Fig. 6. Figure 6(a) shows the crystallization process, while Figure 6(b) presents the product after crystallization. Table 6 presents the XRF analysis for the manganese sulfate product. The composition details in this table highlight the significant elements and compounds present in the product.

Table 6. XRF analysis for manganese sulfate product

Element	Compound	Wt.%
S	SO_3	70.457
Mn	MnO	26.78
P	P_2O_5	0.823
Ca	CaO	0.683
Al	Al_2O_3	0.647
K	K_2O	0.361
Si	SiO_2	0.131
Cu	CuO	0.06
Ni	NiO	0.03
Zn	ZnO	0.0186
V	V_2O_5	0.0074
Br	Br	0.002
Total		100

The purity of the powdered manganese sulfate product is 97.237%. Typically, the usage requirement for powdered manganese sulfate as a raw material for lithium battery cathodes is 98%.



(b)

Figure 7. (a) SEM analysis of manganese ore, (b) SEM analysis of the manganese sulfate product

Figures 7(a) and 7(b) display the morphology of both the manganese ore and the manganese sulfate product. Figure 7(a) Trenggalek manganese ore is in the form of rough tetragonal crystals; this form (MnO_2 or pyrolusite) is caused by elements that form metallic gray manganese oxide compounds is the morphological form of manganese ore before a process is carried out. Meanwhile, Figure 7(b) is the morphology of the manganese sulfate powder product after undergoing several processes, where the surface is smoother than before the process.

4. CONCLUSION

The quality of manganese sulfate ($MnSO_4$) powder products is 97.237%. The optimal conditions for the Fe precipitation procedure employing the NH_4OH reagent are pH 4 for 180 minutes and 100% Fe elimination. The optimal temperature for Ca precipitation in carbonatation is 50 ºC for 120 minutes, resulting in a 20.51% Ca removal rate.

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