Ion-Selective Deposition of Manganese Sulphate Solution from Trenggalek Manganese Ore by Active Carbon and Sodium Hydroxide

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Abstract. One of the steps in manganese dioxide manufacturing process for battery industry is a purification process of lithium manganese sulphate solution. The elimination of impurities such as iron removal is important in hydrometallurgical processes. Therefore, this paper present the purification results of manganese sulphate solution by removing impurities using a selective deposition method, namely activated carbon adsorption and NaOH. The experimental results showed that the optimum condition of adsorption process occurs on the addition of 5 g adsorbent and the addition of 10 ml NaOH 1 N, processing time of 30 minutes and the best is the activated carbon adsorption of Japan. Because the absolute requirement of the cathode material of lithium ion manganese are free of titanium then of local wood charcoal is good enough in terms of eliminating ions Ti is equal to 70.88%.

1. Introduction

The development of battery technology has grown rapidly especially development of lithium-based battery since it has many advantages such as having light weight, large current density and quickly and easily replenished [1]. Rechargeable lithium ion battery has been commercially available in recent years. Lithium ion battery is used for component in computing, entertainment and telecommunications equipment needed to enrich the information especially mobile society. Among several choices of battery cathode materials, LiMn$_2$O$_4$ is an attractive candidate for a positive electrode for rechargeable lithium batteries because it is cheap, environmentally friendly and stable at low temperatures compared to other cathode materials [2]. However, these materials have problems in severe capacity fading during charge-discharge cycles. Many studies have concurred that capacity fading caused by various factors such as Jahn-Teller distortion, unstable reaction of two phases, the slow solubility of manganese into the electrolyte, instability lattice and particle size distribution [3]. Therefore, in the manufacture of lithium batteries, manganese oxide needed more pure than the manganese dioxide used for metal-based dry battery zinc-carbon and alkaline-based. One of the requirements for lithium manganese dioxide is free of Ti ion that can decrease lithium battery voltage.

The elimination of impurities such as iron is one of the main concerns in hydrometallurgical processes. One common technique used to remove impurities is precipitation. Precipitation of impurities can be done through the formation of metal hydroxides by raising the pH of the leaching solution. Some precipitations can be done by adding solution of calcium oxide (CaO), magnesium oxide (MgO) or caustic soda (NaOH) as the precipitator (Esmaeili et al., 2005) [4]. Natharma, 1987,
reported that iron impurities could be removed through the formation of iron hydroxide by raising the pH of the sulfuric acid which is used as leaching solution with calcium oxide (CaO) [5]. Calcium oxide (CaO) is preferred over other alkalies because of its abundant availability and inexpensive. The addition of magnesium oxide (MgO) and caustic soda (NaOH) are also often used for pH adjustment although more expensive than calcium oxide around two or five times [6]. When pH is adjusted, the alkaline reagent will form colloid hence the amount of solids after leaching will be slightly decrease because of the formation of metal hydroxides of impurities. The use of reagents such as MgO and NaOH with high costs should be consideration given to the amount of loss of value of the metal during the solid-liquid separation and the cost involved in the recovery process. The elimination of iron with the addition of CaO, MgO and NaOH to raise the pH of the acid solution was studied by John Jamieson, in 1995 [7]. Studies indicated that in sulfate solution, the use of calcium oxide and magnesium oxide produce multiple phase ferrihydrite. However, the formation of gypsum inhibited filterability with the addition of calcium oxide. pH adjustment with the addition of caustic soda (NaOH) produced smooth goethite crystals with slow filtration.

In the process of purification of manganese sulphate, pink manganese sulphate solution still has some impurities such as ions Ti, Fe, Cu and other metal ions. Manganese oxide that is used for battery industries required purity especially it should be free from titanium, copper and heavy metals since it might affect the performance of lithium manganese cathode in battery.

2. Experimental

2.1. Materials and reagents
In this study, the raw material was manganese sulphate solution from the leaching process of manganese ore that were reduced by activated carbon. Manganese ore was from Sukarame, Trenggalek which contains silica 48.73% by weight and an iron (III) oxide 3.77% by weight. XRF result is shown in below table :

| No. | Oxides                  | wt % |
|-----|-------------------------|------|
| 1   | Manganese ( MnO₂ )      | 46.03|
| 2   | Silica ( SiO₂ )         | 48.73|
| 3   | Iron (III) Oxide ( Fe₂O₃ ) | 3.77 |
| 4   | Calcium ( CaO )         | 1.10 |
| 5   | Barium ( BaO )          | 0.46 |
| 6   | Magnesium ( MgO )       | 0.00 |
| 7   | Phosphor ( P₂O₅ )       | 0.56 |

Adsorption process was conducted using activated carbon. Solution of manganese sulfate that were absorbed having almost saturated concentration that resulted from the process of leaching manganese ore that has been reduced by activated carbon.

2.2. Experimental Methods
Adsorption process was carried out in batch vessel using a 250-ml erlenmeyer with hot plate and magnetic stirrer. Manganese sulphate was taken from sulfuric acid leaching process result of reducted manganese ore from Trenggalek. Manganese sulphate was filtered to separate the dirt and the presence of dissolved crystals. 100 ml clear-pink manganese sulphate solution with pH 1 was taken and poured into a 250-ml erlenmeyer. Sodium hydroxide with concentration 1 N was added and mixture was stirred,
pH of mixture was measured and precipitation that obtained was observed. Activated carbon was added into the mixture and stirred and immediately the time when adding activated carbon was recorded. After the adsorption process, the solution was filtrated then pH was measured. Filtrate was diluted 10 times for analyzing ion Fe, Ti and Cu and diluted 200 times for analyzing ion Mn. Concentration measurement of Fe, Ti, Cu and Mn was conducted by ICP (Inductively Coupled Plasma).

3. Results and discussion

3.1. Effect of NaOH Concentration

In this research, the adsorption was performed by activated carbon from Japan for NaOH concentration variable experiment and reaction time experiment.

3.1.1 The addition of 5 ml of 1 N NaOH solution

As shown in Fig. 1, the addition of 1 N NaOH with a concentration of about 5 ml per 100 ml solution of manganese sulphate drastically decreased the concentration of Fe and Cu ions in 10 g activated carbon. Concentration of Ti did not decrease, which means it could be concluded that the adsorption process of Ti was not running. Concentration of Ti rose later in the addition of 10 g of activated carbon starts to decline, but the decrease was not significant.

![Figure 1. Graph of the relationship between the addition of activated carbon to the concentration of ions Fe, Cu and Ti on the addition of 5 ml of 1 N NaOH](image)

From these results it can be seen that the optimum adsorption of Fe and Cu were in the addition of 10 g of activated carbon where the concentration of Fe and Cu ions drastically reduced from about 2-2.5 ppm to 0.5 ppm. Addition of 20 g activated carbon decreased concentrations of Cu / Fe from 0.5 ppm to 0.4 ppm.

3.1.2 The addition of 10 ml of 1 N NaOH solution

Fig. 2 shows addition of NaOH increase the adsorption of Fe while adsorption of Cu was almost constant. Similarly, increment of addition NaOH from 5 ml to 10 ml did not give significant effect on Ti adsorption. From the experimental results shown that the addition of NaOH from 5 ml to 10 ml, the addition of 5 g activated carbon is able to adsorb Fe until the concentration is about 0.3 ppm. Meanwhile with the addition of NaOH only 5 ml were able to adsorb about 0.3 ppm of activated carbon required four times more that to 20 g.

The addition of NaOH which is just 5 ml per 100 ml solution of manganese sulfate activated carbon be able to save a quarter are from 20 g to about 5 g. By looking at these results the optimum
activated carbon adsorption process on the addition of 1 N NaOH 10 mL and 5 g of activated carbon per 100 ml solution of manganese sulfate processed.

![Graph of the relationship between the addition of activated carbon to the concentration of ions Fe, Ti and Cu in the addition of 10 ml of 1 N NaOH](image)

**Figure 2.** Graph of the relationship between the addition of activated carbon to the concentration of ions Fe, Ti and Cu in the addition of 10 ml of 1 N NaOH

### 3.2. Effect of Reaction Time

#### 3.2.1 Adsorption Optimization

Optimal condition was reached on the addition of 5 ml of NaOH 1 N for 100 ml solution of manganese sulfate. The active carbon adsorption process was first carried out for 30 minutes. Therefore experiment to determine the optimum processing time was needed by varying the adsorption process from 15 to 90 minutes using 15 minutes interval. Fig. 3 shows that optimum processing time for Fe and Cu ion adsorption was 30 minutes and for Ti ion was 45 minutes. Extending the processing time much further will resolve in the detachment of Fe, Cu and Ti ion in the solution fluctuatively.

![Active carbon adsorption processing time vs. ion concentration of Fe, Cu, and Ti in the addition of 5 g of active carbon and 10 ml of NaOH 1 N](image)

**Figure 3.** Active carbon adsorption processing time vs. ion concentration of Fe, Cu, and Ti in the addition of 5 g of active carbon and 10 ml of NaOH 1 N

#### 3.2.3 Manganese Residual

Measurement of manganese residual concentration was carried out to see the effect of processing time to the reduction of manganese. There were some concentration of manganese that was carried inside the active carbon. Fig. 4 shows that the initial concentration of manganese was 42 g/l and then drop to 38 g/l in the first 15 minutes. The increase of processing time did not result in the significant manganese reduction, only 4.5% to the initial concentration. From this result, we conclude that the optimum adsorption processing time was 30 minutes.
3.3. Effect of Type Absorbent

After optimal processing time was obtained then the selection of active carbon was carried out. There were 3 species of active carbon that was compared, active carbon from Philippine (which is usually used in Gold mine adsorption process), active carbon from Japan, commercially available active carbon (Merck, Germany and Brataco, Indonesia), Indonesian locally produced active carbon, and wood charcoal for manganese reduction process.

Fig. 5 shows that Fe ion was adsorbed 89.74% using Japan made active carbon and 81.13% using local active carbon. The lowest adsorption was using Brataco and Merck active carbon resulting 61.70% and 75.14% adsorption respectively. For Cu ion adsorption the best result was obtained using Philippine made active carbon and wood charcoal with adsorption percentage 44.49% and 40.33% respectively. Wood charcoal resulted in 70.88% and the Japan made active carbon resulted in 44.54% adsorption on Ti ion, while others resulted in 0% adsorption.

Overall the adsorption using wood charcoal was resulted in a high percentage of adsorption for all Fe, Cu, and Ti ion 74.83%, 40.33%, and 70.88% respectively. Therefore the application of wood charcoal in the reduction process would directly adsorbed the Fe, Cu, and Ti ion and the use of wood charcoal in the pilot plant need not to be replaced.

3.4. Surface Imaging of Active Carbon

From the experiment we can conclude the Japan made carbon active have the highest adsorption than other active carbon. The result from wood charcoal also showed a high percentage of adsorption. Fig.
6 shows the SEM imaging at the surface of Japan made active carbon and wood charcoal. The SEM imaging shows that both Japan active carbon and wood charcoal are porous, but the Japanese active carbon is more solid and smooth than the wood charcoal so that the adsorption of wood charcoal is higher than the others. Despite resulting in lower percentage of adsorption, the wood charcoal application in the reduction process is giving more advantage in terms impurities elimination, so that the more expensive active carbon would not be needed and lowered the cost for the leaching process.

![SEM imaging](image)

**Figure 6.** SEM imaging of (a) wood charcoal and (b) Japanese made active carbon

4. Conclusion

Optimum adsorption process was reached for 5g carbon active and 10 ml of NaOH addition per 100 ml of solution with processing time of 30 minutes. Best result for Fe ion adsorption was using Japanese active carbon. Adsorption of Cu ion was best obtained using Philippines active carbon, and the best result for Ti ion adsorption was using wood charcoal. As required that the content of Titanium should be minimum for the material of manganese lithium catode, then the best active carbon to be used is from wood charcoal.

Acknowledgment

The authors would like to acknowledge Dr. Bambang Prihandoko dan Indonesian Consortium of Lithium Battery for their support, so this research can be conducted and presented.

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