Artificial wastewater treatment from recycling process of LiFePO₄ (LFP) batteries using activated carbon

L Prasakti*, A Prasetya, R M S D Suryohendrasworo and S N S H Puteri
Department of Chemical Engineering, Gadjah Mada University, Yogyakarta, Indonesia.
*Corresponding author’s e-mail: aguspras@ugm.ac.id

Abstract. In 2025, the demand of Li-ion batteries is estimated to reach 400,000 tons. A strategic effort is needed especially in the battery industry to realize sustainable use of Li-ion batteries. Spent batteries are being recycled using hydrometallurgical process to collect the lithium. This purifying process consists of leaching and precipitation which results in finding of lithium and sodium ions in the wastewater. To use water efficiently, wastewater is projected to be reused in the hydrometallurgical process. In order to do that, metal ions must be reduced from water to meet quality standards. In this experiment, granular activated carbon (GAC) and activated carbon block (CTO) were used as the adsorbent in a 30 minutes semi-continuous system. Samples were taken at 5, 10, 20, and 30 minutes at room temperature. Based on the result, granular activated carbon’s highest percentage of removal were 11.71% for lithium and 19.51% for sodium, and activated carbon block’s highest percentage of removal were 10.33% for lithium and 14.65% for sodium. It is observed from this experiment that the capacity of both adsorbents to remove lithium and sodium ions decreased after 20 minutes.

1. Introduction
Lithium ion battery or also known as Li-ion is a type of battery that is currently widely applied to electronic equipments, especially those that require recharging. With the increasing need for electronic equipments, including electric cars [1], Li-ion battery production is expected to increase. A lithium-ion battery with a LiFePO₄ cathode or better known as lithium iron phosphate (LFP) has a theoretical energy density of 550 Wh/kg, which is higher than commercial LiCoO₂ cathode cells [2], is a potential lithium ion battery for electric vehicles. By 2025, it is estimated that the demand for Li-ion batteries will reach 400,000 tons [3]. In Indonesia, the supply of lithium batteries is currently fulfilled entirely from imports. This is because Indonesia does not have lithium reserves.

Lithium metal itself is one of the rare metals, and its availability on earth is only 0.0017% [4]. Hence, a strategic effort is needed to realize sustainable use of Li-ion batteries. After the life cycle of the Li-ion battery ends, the Li-ion battery will be reprocessed to take the important metals contained in the cathode, especially lithium.

In general, the recycle process was done using hydrometallurgy methods which consisted of leaching and precipitation processes [5,6]. A previous study was conducted and high purity lithium (in the form of 99% lithium phosphate) was successfully obtained from spent LFP batteries. However, the purifying process produced wastewater containing various metals from LFP batteries’ cathodes, one of it was Li. The precipitation process was repeated three times and used NaOH as precipitant. This process resulted in high concentration of Na in the wastewater. The concentration of Na itself must be reduced before disposed to the environment.
Cathode powder leaching process requires a large amount of water. The amount of wastewater will still increase from the repeated precipitation process. In order to use water efficiently, wastewater generated from recycling process is projected to be reused in the hydrometallurgical process. In attempt to do that, metal ions must be reduced from waters to maximized its quality. Existing method, which is reverse osmosis is a highly effective method for removing sodium, but there is a lot amount of water wasted by the process, making it impractical to remove sodium from wastewater.

Activated carbon has been previously used to decrease particles from the aqueous solution, contaminated wastewater, common water sources, and dye [7–10]. The broad application of activated carbon in water treatment is primarily due to its generally low cost compared to other adsorbents, wide accessibility, high performance in adsorption processes, and surface reactivity [11]. This adsorbent offers great flexibility and adaptability to adjust its physical and chemical properties, thus opening the possibility of preparing materials with custom-made characteristics [12,13].

Activated carbons are among the effective adsorbents since of their great sorption capacity. It can be recovered by thermal desorption of the adsorbed substances or by fluid stage extraction within the case of soluble adsorbed species, although the previous method isn't very environment friendly and leads to the fractional mass loss of the adsorbent [14].

It has come to the authors’ notice that there is no experiment yet regarding this recycled LFP batteries’ wastewater treatment. An appropriate wastewater treatment system is needed to go side by side with the growing battery industry. Hence, in this study, granular activated carbon and activated carbon block (CTO) were evaluated to remove Li and Na ions in the artificial wastewater to find out whether they effective enough. The aim of this study is to find the right method and process to treat wastewater from recycled LFP batteries. The result obtained from this experiment is wished to be developed for a continuous wastewater treatment of recycled LFP batteries.

2. Materials and Methods

2.1 Materials
Artificial wastewater from LFP batteries recycling process has been made according to calculation conducted by Battery Recycling Team of Universitas Gadjah Mada. Other materials include granular activated carbon (GAC 933 RO, Aquazone), activated carbon block (CTO-10CL, Kolon), lithium hydroxide (LiOH, purity >98%, Merck), sodium hydroxide (NaOH pellets, Merck), and distilled water.

2.2 Artificial wastewater generation
Artificial wastewater was made to resemble the data collected from the LFP recycling process conducted by Electric Vehicle Team Gadjah Mada University. Artificial wastewater contained Li and Na ions with concentrations of 20 ppm and 70 ppm, respectively.

2.3 Adsorbent preparation
This experiment used granular activated carbon with series code GAC 933 RO Aquazone inserted inside 10 inch cartridge and activated carbon block CTO Kolon with series code CTO-10CL in the shape of 10 inch block column. The activated carbons were washed before being used by flushing them with distilled water to remove impurities or powder still contained on the surfaces.

2.4 Adsorption of artificial wastewater using semi-continuous method
Adsorption was done semi-continuously at room temperature (see Figure 1). The adsorption process was conducted in two methods, using granular activated carbon and the CTO activated carbon block as the adsorbent. Adsorption process carried out for 30 minutes with a flow rate range of 0.7 liter per minute and samples were taken at 5, 10, 20, and 30 minutes.
2.5 Data Analysis

*Inductively coupled plasma-optical emission spectrometer (ICP-OES)* Optima 8300 PerkinElmer was used to analyze the concentration of metal ions contained in the artificial wastewater solution that has passed the adsorption process. Removal percentage of metal ($R\%$) can be calculated using this equation:

$$R(\%) = \left(\frac{C_o - C_t}{C_o}\right) \times 100\%$$

where:

$C_o$ = initial ion concentration in solution (ppm)

$C_t$ = remaining ion concentration in solution after adsorption (ppm)

3. Results and Discussion

This experiment was carried out in semi-continuous method where the adsorbent was being passed by artificial wastewater for 30 minutes. Adsorbents’ effectiveness can then be obtained from their contact time with artificial wastewater. For 30 minutes, samples were taken on 5, 10, 20, and 30 minutes to evaluate the Li and Na ions concentration in effluent (Figure 2) and its removal effectiveness served Figure 3.

3.1 Comparison of adsorbent on the reduction of metal ions in artificial wastewater

From Figure 2, it can be seen that there was a decrease in lithium ions using either a granular activated carbon or using an activated carbon block. However, the trend shows that the two adsorbents had almost the same ability to adsorb lithium ions from artificial wastewater. After 20 minutes, lithium ions experienced an increase because both adsorbents had been saturated and therefore cannot adsorb more ion. The same trend can also be seen in Figure 3 where sodium ions also experienced a decrease when using granular activated carbon and activated carbon block. After 20 minutes, sodium ions experienced an increase using activated carbon block, meaning the adsorbent had been saturated, while the one using granular activated carbon experienced an increase at 30 minutes. It can be seen that at 20 minutes, sodium concentration using activated carbon block was higher than its initial concentration. This happened because sodium ions that had already bounded with activated carbon groups re-released itself from the active group to avoid interfering with the adsorption process or called desorption [15,16].
3.2 Effectivity of adsorbent based on contact time

It can be seen that the highest percent removal of lithium and sodium ions by granular activated carbon consecutively 11.71% and 19.51% were obtained at 20 minutes. Meanwhile, the highest percent removal of lithium and sodium ions by activated carbon block consecutively were 10.33% and 14.65% obtained at 10 and 20 minutes. This shows that the adsorption capacity of granular activated carbon and activated carbon block towards lithium ions were almost the same, and granular activated carbon had a higher adsorption capacity towards sodium than activated carbon block.

On the granular activated carbon, it was seen that at 30 minutes the percentage of removal for both lithium and sodium had decreased. This indicates that the adsorbent's ability to adsorb lithium and sodium ions had decreased or can be said to be saturated. This is in line with Figure 1 where there was no decrease in the concentration of lithium and sodium ions.

A different phenomenon happened to the activated carbon block adsorbent. This adsorbent experienced a decrease in the percentage of lithium and sodium at 30 and 20 minutes, respectively. This shows that the
adsorption capacity of activated carbon blocks on sodium metal ions was lower than granular activated carbon.

4. Conclusions
Based on the percent removal results, it can be said that granular activated carbon and activated carbon block had similar ability in reducing lithium, and granular activated carbon was more capable than activated carbon block in reducing sodium ions. However, the data also shows that the adsorption process had not been able to produce a significant metal removal percentage, which was in the range of 15-17% for Li and Na. Therefore, it is necessary to replace the filling material in the process column for the next trial to achieve higher metal removal percentage. It is also hoped that this artificial wastewater treatment can also show optimal results to be fully developed for a continuous wastewater treatment of recycled LFP batteries.

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