Lithium and Calcium recovery by activated carbon from coconut shell char

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Abstract. Spent rechargeable batteries and electronic waste become a future challenge. The precious metal inside should be recovered for pursuing a circular economy society. Here, lithium phosphate battery has been dismantled and leached the cathodes by acidic solution to produce metal solutions. The metal content will be separated by a simple adsorption mechanism using activated charcoal. Coconut shell char has been activated by KOH in several temperature settings and then tested to adsorb lithium and calcium ions in the leaching solution. The capacity of adsorption and selectivity between the ions were investigated. The adsorption capacity is strongly related to the activation temperature and KOH/char ratio. Higher activation temperature and agent ratio tend to provide better-activated carbon for metal ion adsorption. It is found that Li ions have lower affinity toward the surface of carbon especially in low concentration than Ca ions.

1. Introduction
Lithium-ion batteries (LIB) are popular batteries used as a power source because of their energy density. At present, the LIB is estimated to constitute 37% of the market for rechargeable resources. Batteries constitute 39% of overall lithium usages. The prospect of an electric vehicle in the future that is increasingly apparent automatically increases the need for LIB in a larger size. Light vehicles that use electric hybrid systems, hybrids and electric hybrid plug-ins will need a lightweight battery.

Meanwhile, many other industries such as ceramics, rocket propellant, nuclear, pharmaceutical, lubricants, vitamin A production, and the synthesis of organic compounds also require lithium compounds. Lithium mining from salt or ore in the future cannot meet market demand so that lithium mining from wastewater sources and seawater starts to be pursued [1].

Bioleaching is another method used in lithium recovery efforts. Spodumene, a source of lithium, is a mineral that is difficult to be processed and requires a high-temperature treatment. This is clearly not profitable from an industrial perspective. The role of microorganisms is interesting to use because it requires lower energy, but a longer time required. The microorganisms such as Penicillium purpurogenum, Aspergillus niger, and Rhodoterula rubra has been observed for this application.

The absorption of lithium through electro-sorption has also been investigated. Cathodic polarization increases sorption, while, conductivity and pH variations are easily optimized to recover lithium electrochemically [2]. In his research, the simple adsorption via activated coconut shell char with KOH...
activator will be observed. It is expected that activated carbon with KOH at a certain temperature and chemical ratio will be able to provide high lithium adsorption. Since the activating method provides important surface properties and structure of carbon to be used for selected purposes [3].

2. Methods

2.1. Activated carbon preparation
Coconut shell charcoal is crushed and sieved using a standard sieve to get particle size between 10 and 14 mesh. Then, a mixture of KOH and charcoal powder with weight ratio of KOH/char at 0.5: 1, 1: 1, and 1.5: 1 is prepared. All three samples were activated at 600 °C to study the effect of the activating agent ratio. For the effect of activation temperature study, the equal ratio of activator and charcoal was used. Activation temperature variations are 500 °C, 600 °C, and 700 °C using a horizontal tube furnace under nitrogen flow and heating rate of 20 °C/min. All six samples were washed using distilled water until the pH was near neutral, then filtered and dried. Samples were characterized through analysis using Fourier Transform Infrared Spectroscopy (FTIR) and also the Surface Area Analyzer. Activated carbon sample identification is summarized in Table 1.

| ID    | KOH/Char ratio | Heat Treatment Temp., °C |
|-------|----------------|--------------------------|
| C500/1| 1:1            | 500                      |
| C600/1| 1:1            | 600                      |
| C700/1| 1:1            | 700                      |
| C600/0.5| 0.5:1       | 600                      |
| C600/1.5| 1.5:1       | 600                      |

2.2. Activated carbon adsorption
LiFePO4 battery leachate solution was prepared by soaking cathode layer with sulfuric acids. After leaching, the Fe ion was separated from the solution by precipitation using Ca(OH)2. Thus, inside the solution remain Li and Ca as the major ions. In taking the batch adsorption data, the weight of charcoal added to 50 mL solution was varied from 1 to 15 gram inside Erlenmeyer flasks. Then the mixture is then shaken using a shaker bath for 1 day at room temperature. The concentration of the solution after adsorption was analyzed using ICP-EAS (Perkin Elmer).

3. Results and Discussion
FTIR analysis was carried out to identify functional groups on the carbon surface. In Figure 1, we can see the absorption bands owned by coconut shell charcoal and activated char at wavenumbers around 3448.72 cm⁻¹ (OH), 2924 cm⁻¹ (CH₃), and 1600 cm⁻¹ (C = O). At an increase in temperature, it can be seen as a shift in absorption wavenumbers. KOH activator also seems to cause a shift in absorption wavenumbers. It can be said that there is no new functional group that appears by the activation method. All the peaks come from the origin of char but in the lower intensity for the activated ones.

For the intensity of the peaks, the temperature of activation plays an important role in reducing the intensity. Higher temperature will create carbon with less functional groups. The highest activation temperature sample (C700/1) shows almost flat spectra. Meanwhile, for KOH ration the effect is minor. The increase of the ratio from 0.5 to 1.5 seems does not give any impact on the chemical properties of the samples since the three spectra are similar (C600/0.5 to C600/1.5).

For porosity characterization, the results are provided in Table 2. It is clearly seen that the raw char has very small porosity. Then, the increase of treatment temperature to 600 °C does not significantly increase the surface area, while, for the highest temperature the surface area starts to improve rapidly. It can be assigned that the carbon is very hard and solid that is not easy to be activated. Meanwhile, for
KOH ratio, using low ratio of 0.5 did not alter so much the char while for the highest ratio the porosity is increase significantly. It can be concluded that only two samples (C700/1 and C600/1.5) can be considered as activated carbon. In other words, the activation can be achieved by increasing the temperature higher than 600 °C or using more KOH at lower temperature.

Table 2. Porosity profile of the chars

| ID      | BET Surface area, m²/g | Pore volume x100, cc/g | BJH Pore average diameter, Å |
|---------|------------------------|------------------------|------------------------------|
| Raw char | 0.7                    | 0.7                    | 26.5                         |
| C500/1  | 12                     | 1.2                    | 26.6                         |
| C600/1  | 71.5                   | 7                      | 26.8                         |
| C700/1  | 502                    | 30.5                   | 26.9                         |
| C600/0.5| 21.5                   | 2.2                    | 26.9                         |
| C600/1.5| 226.8                  | 15                     | 27.1                         |

Figure 1. FTIR analysis results from coconut shell charcoal

In Figure 2, it can be seen that the lithium adsorption isotherm of carbon with different activation temperatures (500 °C, 600 °C, and 700 °C) and activated agent ratio (0.5, 1.0 and 1.5). It appears that the adsorption capacity is relatively low in lower concentration. It indicates that Li-ion has low affinity toward the carbon surface. The increase of the capacity in high concentration has a positive correlation with the porosity. The larger surface area of carbon tends to adsorb Li-ion more. In IUPAC classification of isotherm, this isotherm is considered as type III isotherm which is typical for non-porous or macroporous adsorbent. Thus, the lithium ions seem does not attach inside the micropores but rather than outer and large pores surfaces. The low affinity of carbon toward Li-ions also has been reported elsewhere [4,5]. Low interaction between carbon atoms in the surface of char and Li ions in the solution
could be due to the low atomic mass of the ions. The interatomic potential interaction suggests that the force has a positive correlation with the atomic mass of the interacting atoms as well as the distance among the atoms.

Figure 2. Adsorption isotherm of Lithium ions

Figure 3 shows the adsorption isotherm for Ca ions. In general, the isotherms are different from Li-ion, the isotherm represent type I or II of the IUPAC classification. The small shoulder in lower solution concentration can be a hint for monolayer adsorption saturation of micropore filling of Ca ions. It indicates a relatively strong interaction between pore surface and Ca ions. The low porosity of carbon (C600/05) still represents the type III isotherm since there is no significant micropore that can be filled by Ca ions instead of the outer surface and macropores.

Figure 3. Adsorption isotherm of Calcium ions
4. Conclusions
The method of activation strongly related to the porosity development of the char that will lead to adsorption characteristics. The prepared activated carbon has different behaviour in adsorbing Li and Ca ions. Li-ions tend to be less attracted to the pores of carbon. In low concentration, Ca ion will be absorbed larger than Li-ions while in the concentrated solution, the capacity is relatively similar.

5. References
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