Process optimization and leaching kinetics of zinc and manganese metals from zinc-carbon and alkaline spent batteries using citric acid reagent

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Abstract. Zn-Carbon and Alkaline spent batteries contains heavy metals, such as zinc and manganese, which can causes environmental problem if not handled properly. Usually the recovery of these metals were done by leaching method using strong acid, but the use of strong acids as leaching reagents can be harmful to the environment. This paper concerns the recovery of Zn and Mn metals from Zn-C and alkaline spent batteries using citric acid as the environmental friendly leaching reagent. The leaching conditions using citric acid were optimized and the leaching kinetics of Zn and Mn in citric acid solution was investigated. The leaching of 89.62% Zn and 63.26% Mn was achieved with 1.5 M citric acid, 90°C temperature, and 90 minutes stirring time. Kinetics data for the dissolution of Zn showed the best fit to chemical control shrinking core model, while the diffusion controlled model was suitable for the dissolution of Mn kinetics data. The activation energy of 6.12 and 1.73 kcal/mol was acquired for the leaching of Zn and Mn in the temperature range 60°C-90°C.

1. Introduction

Zinc-carbon and alkaline batteries are used in many electronic objects that small quantities of power are required, such as remote control, radios, and watches. Usually, they run out rapidly, producing huge quantity of spent batteries and increasing the environmental problem due to the metallic content, being considered as hazardous waste [1]. Zn-C and Alkaline batteries have the same electrode metal elements, Zn as anodes and Mn as cathodes, so often called as Zn-Mn batteries. Zn content is about 12-28% and Mn content is 26-45% of the total batteries powder mass [2]. It is necessary to recover Zn and Mn metals from these spent batteries to maintain the raw materials and to protect the environment.

Leaching is one of method to extract the metal content from the spent batteries with a liquid solvent or reagent to dissolve the metal in it. Strong acids, such as sulfuric acid, nitric acid, and hydrochloric acid, were often used as leaching reagents, but these acids can release toxic gases like Cl₂, SO₃, and NOₓ during the leach process and the waste acid solution after leaching is a threat for environment [3]. Replacing the leaching reagent with more environmentally friendly reagent, like organic acid, can reduce the problem for environment because organic acid more soluble in water and the waste from the leaching process with organic acid is considered more easily to processed.

Citric acid is an organic acid that classified as weak acid, but was often used as a leaching reagent among other organic acid. Citric acid was once used for leaching from low grade oxide ores and able to extract 82% of Zn metal [4]. Citric acid had been also used to recover Li and Co metal from Li-Ion batteries waste [5] and recover Pb, Cu, Zn metals on contaminated soil of plant waste [6]. In this
study, the citric acid is used as leaching reagent for recovery the Zn and Mn metal from Zn-Mn spent batteries. The leaching condition is optimized to get the maximum percentage of leaching. The optimum leaching conditions in this study were determined based on three leaching parameters: leaching reagent concentration, temperature, and stirring time.

The leaching kinetics is also investigated in this paper using the variations of temperature and stirring time data. The leaching kinetics are performed to know the rate model of leaching process and to determine the mechanism of leaching. The leaching kinetics of Zn metal in ammonium chloride solution has been studied and showed that the diffusion model was the best kinetic model for this process [7], while chemical reaction model was the suitable leaching kinetics model for Mn metal in sulfur dioxide solution [8]. As the leaching kinetics of Zn and Mn has not been well studied, the objective of this present work is to assess the suitable leaching kinetics models of Zn and Mn metals in citric acid solution.

2. Experimental

2.1. Materials and reagents

The spent Zn-C and alkaline batteries were collected from the local sources. The leaching reagents used in this work were citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) used as reducing agent. All solutions were prepared in distilled water and all reagents were analytical grade from Merck.

2.2. Battery dismantling and metal characterization

The spent batteries from several manufactures were manually dismantled. The black powder was a mixture of the cathodic (manganese oxides and graphite) and the anodic (zinc oxides and electrolyte solution). Dismantling products such as plastic film, ferrous scraps and paper pieces were separated. The battery powder then crushed and mashed to expand the surface area and make to increase leaching efficiency. After that, the battery powder was sieved to uniform the size of sample particles. The initial metals content of the powder were characterized using Atomic Absorption Spectroscopy (AAS, spectrometer SpectrAA 200-Varian) in order to evaluate the percentages of Zn and Mn metals.

2.3. Leaching of metals

All leaching experiments were carried out in a 250 mL Pyrex glass reactor with a thermometer to control the temperature and placed at hot plate stirrer to heat up the solution. The reactor was closed to reduce the loss of water by evaporation. A measured amount of battery powder and reagent leaching solution were added to reactor and allowed to reach thermal equilibrium, with agitation provide by the magnetic stirrer at 500 rpm for entire duration of the leaching and 1/20 solid-to-liquid ratio (S/L). All the leach liquor after leaching process were analyzed by AAS (spectrometer SpectrAA 200-Varian) to determine the total amount of zinc and manganese metals after the process.

3. Result and Discussion

3.1. Effect of acid concentration on leaching

The concentration of leaching reagent were varied 0.5 M, 1 M, 1.5 M and 2 M with leaching temperature 80°C and 120 minutes stirring time. The leaching efficiency results from the calculation of AAS analysis in leaching with various concentration of citric acid can be seen in Figure 1.

![Figure 1. Effect of citric acid concentration on leaching efficiency](image-url)
From Figure 1, it can be concluded that the greater concentration of citric acid lead to the greater leaching efficiency of Zn or Mn metals. The concentration that produces the maximum leaching percentage from all variation is 2M. The previous research mentioned that the leaching efficiency of metals using citric acid would have a certain optimum point at a certain concentration. As the citric acid concentration was higher and already surpassed the optimum point, there would be a decrease in leaching efficiency [9]. Contrast to the use of strong acids (such as sulfuric acid), which in tandem with increasing concentrations, the leaching efficiency will continue to increase to the constant limit [10]. Zinc and manganese metals originally in the form of powdered solids and tires bound to oxidants might be leached or dissolved due to the binding event with anions of citric acid. When the citric acid concentration increased, the ability and amount of citric acid anion formation also increases, thus it increasing the leaching efficiency of Zn and Mn metals.

Citric acid has 3 carboxyl groups in every one molecule and when dissociation occur one mol of citric acid in water, theoretically 3 mol H\(^+\) will be formed as shown in these following equations [9].

\[
\begin{align*}
C_6H_8O_7 \rightleftharpoons C_6H_7O_7^- + H^+, & \quad K_{a1} = 7.4 \times 10^{-4} \\
C_6H_7O_7^- \rightleftharpoons C_6H_6O_7^{2-} + H^+, & \quad K_{a2} = 1.7 \times 10^{-5} \\
C_6H_6O_7^{2-} \rightleftharpoons C_6H_5O_7^{3-} + H^+, & \quad K_{a3} = 4 \times 10^{-7}
\end{align*}
\]

The equations above show that the dissociation of citric acid yields 3 \(K_a\) values. This proved that citric acid is classified as a good organic acid in the leaching process because it could maintain the content of hydrogen ions (H\(^+\)) remain high. The dissociation reaction of citric acid is a reversible reaction, so it must have an equilibrium state. The formation reaction of zinc citrate and manganese citrate can be accelerated when the concentration of hydrogen ions increases, so zinc and manganese ions could bind to the anions of citric acid more.

Based on Figure 1, the increase of leaching efficiency from concentration 1.5 M to 2 M is not significant, it is because the concentration of formed \(H^+\) ions has started to saturated. The dissociation form of citric acid which is a reversible reaction (equation 1 to 3) causes when the citric acid concentration is increased further, the equilibrium will shift to the left. When the equilibrium shifts to the left, it will lead to reduced \(H^+\) ions formed that will reduce the leaching efficiency. Based on that, the optimum concentration for leaching using citric acid in this study is 1.5 M, because the increase of leaching percentage above 1.5 M isn’t effective anymore.

3.2. Effect of temperature on leaching

Temperature of leaching is the important parameters to get the high efficiency of recovery. In general, organic acids require higher temperature than strong acids to more ionized, because the high temperature can help to break the \(H^+\) chains that were bound to weak acids. In this study with citric acid, the temperature varied was 60°C, 70°C, 80°C, and 90°C with 1.5 M citric acid and stirring time 120 minutes. The results of the leaching efficiency with varying temperature can be seen in Figure 2.

![Figure 2. Effect of temperature on leaching efficiency](image)

In the graph on Figure 2 shows that the higher temperature of leaching causes the greater percentage of leaching Zn and Mn metals. The highest leaching percentage was at 90°C with leaching efficiency of Zn reach 87.87% and Mn 57.87%. The high temperature allows a reaction to occur faster because there are collisions between molecules that move more quickly in the compound. High
collision rate will make the higher kinetic energy. The relationship between the reaction rate and temperature was determined by the Arrhenius equation with activation energy factor. Activation energy is the energy that must be absorbed in the system from the environment to react and its value is influenced by temperature. From this study with temperature variation, it can be concluded that the optimum temperature for leaching of Zn and Mn metals from Zn-Mn spent batteries is 90°C.

3.3. Effect of time reaction on leaching

In the leaching process, it takes a certain time for citric acid to completely dissolve the zinc and manganese metal that present in the Zn-Mn batteries powder. The time that varied in this study was 30, 60, 90, and 120 minutes with 1.5 M citric acid and in operating temperature 90°C. The results of leaching efficiency with varying stirring time can be seen in Figure 3.

![Figure 3. Effect of stirring time on leaching efficiency](image)

Based on the graph in Figure 3, it can be seen that there is an increase of leaching efficiency up to 90 minutes, but the increase of leaching percentage is not significant when heading to 120 minutes. The increase of contact time between citric acid and Zn-Mn batteries powder causes more H+ ions of citric acid that are dissociate and form zinc citrate and manganese citrate compound, so the percentage of leaching Zn and Mn metals were getting bigger. However, the amount of dissociated H+ ions from citric acid will be difficult to increase when it has reached its saturation point, so that longer stirring time will not have a significant effect on the leaching efficiency and tend to be constant when it reaches its optimum time. At this variation of stirring time, it is concluded that the maximum stirring time for leaching of Zn and Mn metals from Zn-Mn batteries is 90 minutes with leaching efficiency of Zn 89.62% and Mn 63.26%. This result is the optimum leaching result with optimized some leaching parameters: citrate acid concentration 1.5 M, temperature 90°C, and stirring time 90 minutes.

3.4. Kinetics of leaching

More data on temperature and stirring time variations are needed to evaluate the kinetics of leaching. Citric acid was used as leaching reagent with concentration 1.5 M at fixed stirring speed and solid-liquid ration. On the previous experiment, we found that the optimum time for leaching of Zn and Mn metals with citric acid from Zn-Mn spent batteries was 90 minutes, then the time variation for kinetic study was only done until the optimum time. In order to determine the kinetic parameters and rate controlling step of leaching process, the popular shrinking core model was utilized [11]. In the solid-liquid reaction system, the reaction may be usually controlled by chemical reaction at the surface of the material or diffusion through the product layer [12]. If the reaction is controlled by diffusion through the product layer, it will have an integrated rate equation as follows [13]

\[
1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_d t \tag{4}
\]

If the reaction is controlled by chemical reaction on surface, integrated rate equation as follows [13],

\[
1 - (1 - X)^{\frac{1}{3}} = k_c t \tag{5}
\]

where \(X\) is the fraction reacted, \(k_d\) is the kinetic parameter for diffusion control, \(k_c\) is the kinetic parameter for chemical reaction control, and \(t\) is the reaction time (min). To analyze the kinetics of the leaching, data were fitted against both models and reaction time. The higher graphic linearity that
formed by the data with the shrinking model showing the more suitable shrinking model for the leaching process. The high linearity can be seen from $R^2$ value calculated based on the existing graph and showed the smaller data deviation that occurs. The plot of the data of leaching Zn with chemical reaction model can be seen in Figure 4(a), while the diffusion model can be seen in Figure 4(b).

If the graphs in Figure 4(a) and Figure 4(b) are compared, then the leaching of Zn profile which has higher linearity is chemical reaction on the surface model. It can be seen from the average of $R^2$ value of chemical reaction model that is bigger than the $R^2$ value of diffusion model. So, the leaching of Zn with citric acid from Zn-Mn spent batteries is controlled by chemical reaction on the surface. This model is also suitable for leaching of Ni metal from NiCd spent battery using sulfuric acid [14] and also suitable for leaching some metals that contained in Ni-MH spent battery [13].

The plot of the data of leaching Mn with chemical reaction model and diffusion model can be seen in Figure 5.

Based on Figure 5, the more suitable kinetic model for the leaching of Mn with citric acid from Zn-Mn spent batteries is the diffusion through the product layer, seen from the higher average $R^2$ values. For the activation energy calculation, leaching kinetic of Zn metal using the chemical reaction model, while Mn metal using the diffusion model.

The calculation to evaluate activation energy was using Arrhenius equation which has been adapted to linear line equation as follows.

$$\ln(k) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T}$$

where $A$ is the frequency factor, $E_a$ is the activation energy of the reaction, $R$ is the universal gas constant, $T$ is the absolute temperature, and $k$ is the reaction constant for the suitable kinetic model. The activation energy was calculated using the gradient of the linear regression of the equation of the
line between $ln \ (k)$ and $1/T$. The graph for leaching of Zn metal using chemical reaction model and diffusion model can be seen in Figure 6.

![Figure 6. Arrhenius plot for leaching of (a) Zn and (b) Mn metal](image)

Based on Figure 6(a), the calculated activation energy for Zn metal is 25.59 kJ/mol (6.12 kcal/mol), while the calculated activation energy for Mn metal based on Figure 6(b) is 7.22 kJ/mol (1.73 kcal/mol). The control process in the leaching kinetics have been characterized by the magnitude of activation energy, typically, $E_a = 1 - 3$ kcal/mol denoted diffusion controlled and higher for chemical control kinetics [14]. The activation energy of Zn in this study already in the activation energy range for chemical reaction on the surface, so as the activation energy of Mn in this study that also already in the range of activation energy for diffusion through the product layer, so it can be concluded that the choice of kinetic model for leaching of Zn and Mn metals is correct.

4. Conclusion
The optimum condition for leaching of Zn and Mn metals from zinc-carbon and alkaline spent batteries using citric acid as leaching regent are 1.5 M for citric acid concentration, at temperature 90°C, with stirring time 90 minutes. It can recover until 89.62% of Zn and 63.26% of Mn. The kinetic study show that the leaching kinetic of Zn metal from citric acid solution controlled by chemical reaction on the surface with the activation energy 6.12 kcal/mol and the leaching kinetic of Mn metal controlled by diffusion through the product layer with the activation energy 1.73 kcal/mol.

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