Selection of organic acid leaching reagent for recovery of zinc and manganese from zinc-carbon and alkaline spent batteries

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Abstract. Zinc-carbon and alkaline batteries are often used in electronic equipment that requires small quantities of power. The waste from these batteries contains valuable metals, such as zinc and manganese, that are needed in many industries and can pollute the environment if not treated properly. This paper concerns the recovery of zinc and manganese metals from zinc-carbon and alkaline spent batteries with leaching method and using organic acid as the environmental friendly leaching reagent. Three different organic acids, namely citric acid, malic acid and aspartic acid, were used as leaching reagents and compared with sulfuric acid as non-organic acid reagents that often used for leaching. The presence of hydrogen peroxide as manganese reducers was investigated for both organic and non-organic leaching reagents. The result showed that citric acid can recover 64.37% Zinc and 51.32% Manganese, while malic acid and aspartic acid could recover less than these. Hydrogen peroxide gave the significant effect for leaching manganese with non-organic acid, but not with organic acid.

1. Introduction
Zn-C and Alkaline batteries are primary batteries that often found in the market because of its wide use in various electronic devices and the price is quite affordable. Zn-C and Alkaline batteries have the same electrode metal elements, Zn as anodes and Mn as cathodes, so often called Zn-Mn batteries, differ only in the type of electrolyte used. It is estimated that about 40 billion of Zn-Mn batteries are run out rapidly and thrown away, producing huge quantity of spent batteries which represent major environmental and health threat due to toxic metals such as Zn and Mn [1]. The Zn content are about 12-28% and the Mn content reaches 26-45% of the total powder mass in Zn-Mn batteries [2]. Zn and Mn metals are also a valuable metal in industrial world and have been listed as strategic metals by many countries due to the increasing use of these metals with increasingly limited natural resources [3]. Because of the dangers for the environment and the importance of Zn and Mn metals for life, so it is necessary to recover the Zn and Mn metals, especially from the considerable amount of waste batteries in the world.

Leaching is a solid-liquid extraction method in which the process of separating solid metal waste was mixed with leaching reagent, a liquid solvent to dissolve the metal in it. The commonly used leaching reagents are strong acids such as sulfuric acid, nitric acid and hydrochloric acid. However, the use of strong acids as leaching reagents can release toxic gases like Cl₂, SO₃, and NOₓ during the leach and the waste acid solution after leaching is a threat to the environment [4]. Reduced adverse effects of the leaching process can be done by replacing the leaching reagent with a more environmentally friendly reagent, which is organic acid because it is more soluble in water and the waste from the leaching process with organic acid is considered more easily processed.
This study was conducted to determine the effectiveness of organic acids as environmentally friendly leaching reagent in the process of leaching zinc and manganese from Zn-C and alkaline spent batteries. The organic acids that used were citric acid, malic acid, and aspartic acid. The three organic acids were selected because of their characteristics including easy natural degradation and the absence of toxic gases in the reaction process, and because of previous reports of other metal leaching processes. In the previous study, leaching on zinc from low grade oxide ores using citric acid was able to extract 82% of Zn metal [5]. Whereas malic acid and aspartic acid had been used as leaching reagents of Li-On batteries and could recover until 90% Co, 100% Li for malic acid and 60% Co, 60% Li for aspartic acid [6].

This study also examined the use of hydrogen peroxide as a manganese reducing agent in the leaching process with organic acids and non-organic acids. The low dissolved Mn element in sulfuric acid caused by the solubility of manganese oxide such as Mn$_2$O$_3$ and Mn$_3$O$_4$ in sulfuric acid is partial because the produced of MnO$_2$ is difficult to dissolve on strong acids [7]. The MnO$_2$ compound is most stable manganese oxide with oxidation number 4+, so an additional reducing agent is required to reduce manganese oxide number to be more easily dissolved in the leaching process. Based on previous research, hydrogen peroxide gave a quite effective result and cheaper than other reducing agents, so it was often used as manganese reducing agent [8].

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 consisted of citric acid, malic acid, and aspartic acid as organic acid, then sulfuric acid as non-organic acid, and hydrogen peroxide as reducing agent. All solutions were prepared in distilled water and all reagents were analytical grade (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 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS, Jeol JSM-6510LA) and Atomic Absorption Spectroscopy (AAS, spectrometer SpectrAA 200-Varian) in order see the characteristic of the powder and to evaluate the percentages of zinc and manganese 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 2 M 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. The leaching operation conditions were made equally to facilitate comparison of the leaching efficiency of each different leaching reagent and the same amount of hydrogen peroxide were added as the reducing agent. The solid-to-liquid ratio (S/L) that used was 1/20 with operating temperature 80°C (353 K) and 3 hours reaction time. All the leach liquor after leaching process were analyzed by AAS (Atomic Absorption Spectroscopy) to determine the total amount of zinc and manganese metals after the process.
3. Result and Discussion

3.1. Characterization of spent battery powder

The powder of Zn-C and Alkaline spent batteries mixture was tested with SEM-EDX and AAS. The SEM-EDX test is performed to determine the morphology and the elements that contained in the initial sample. While the AAS test is performed to determine the amount of concentration zinc and manganese quantitatively as the basis for calculating the percentage of leaching efficiency. The SEM and EDS test results can be seen in Figure 1 and Figure 2.

Figure 1. SEM result of Zn-C and alkaline batteries powder

Figure 2. EDS result of Zn-C and alkaline batteries powder

Figure 1 show the SEM image, which reveals the fine nature of powder was identified as irregular and agglomerated. The EDS spectrum in Figure 2 shows the metals contained in Zn-Mn batteries powder are zinc, manganese, and aluminum. In addition, there are also elements of carbon and oxygen detected in the EDS test. This result is in accordance with the research conducted by I De Michelis et al. in 2007 [9] for the metal content of a mixture of Zn-C and Alkaline batteries. The AAS test results can be seen in Table 1.

Table 1. Zn and Mn content of Zn-C and alkaline batteries powder

| Element     | Content (%) | Unit conversion (mg/g sample) |
|-------------|-------------|-------------------------------|
| Zinc        | 14.52       | 145.20                        |
| Manganese   | 22.66       | 226.60                        |

According to Table 1, the concentrations of zinc and manganese metal elements are 14.52% and 22.66% respectively. This result is close to the results of research conducted by De Michelis et al.[7] for
the zinc content of the Zn-C and Alkaline battery mixture, which is about 15.46% by weight and the results of research by Peng et al. [9] for the manganese content of Zn-C batteries, which is about 26.3% by weight. The previous research had shown that there were four main compounds contained in Zn-Mn battery waste, namely ZnO, MnO, Mn₂O₃, and Mn₃O₄ [2].

3.2. Leaching efficiency with organic acid reagent

There were three organic acid leaching reagents varied in this study, namely aspartic acid, malic acid, and citric acid, and also conducted leaching with non-organic acid, sulfuric acid. These four acids were compared their ability to dissolve the Zn and Mn metals from Zn-Mn batteries powders. The leaching process was carried out using these reagents at temperature 80°C, leaching time 180 minutes, ratio solid/liquid 1/20, and obtained percentage leaching as seen in Table 2.

Table 2. Zn and Mn content in leach liquor and the leaching efficiency

| Leaching Reagent | AAS Results (ppm) | Leaching Efficiency (%) |
|------------------|-------------------|-------------------------|
|                  | Zn                | Mn                      | Zn | Mn |
| Aspartic acid    | 3081.46           | 2941.97                 | 42.44 | 25.97 |
| Malic acid       | 4511.69           | 5332.98                 | 62.14 | 47.07 |
| Citric acid      | 4673.43           | 5814.34                 | 64.37 | 51.32 |
| Sulfuric acid    | 6601.10           | 4850.92                 | 90.92 | 42.81 |

Figure 3. Comparison of leaching efficiency for each leaching reagent

Based on Table 2 and bar graph in Figure 3, the largest percentage of leaching for zinc and manganese metal among organic acid reagent is citric acid which is 64.37% for Zn metal, and 51.32% for Mn metal. The results of leaching by using malic acid for Zn and Mn metals showed almost the same value, although the value is still below citric acid. The lowest leaching result was shown by the use of aspartic acid as reagent, only 42.44% for Zn metal and 25.97% for Mn metal.

The factor affecting the percentage of leaching is the level of acidity (pH) of each organic acid used. Each of the organic acid was prepared into the solution form with a concentration of 2 Molar then measured the acidity level using pH-meter with several repetitions. The result is citric acid having the lowest pH, ranging from 1.1 -1.3. While malic acid has a pH ranging from 1.2-1.5 and aspartic acid pH ranges from 1.5-1.7. So, the highest acidity levels is citric acid, followed by malic acid, and the lowest acidity is aspartic acid. Based on the result of leaching percentage and acidity level, it can be concluded that the higher acidity used, the higher leaching percentage can be reached for Zn and Mn metals. This is consistent with the research of Li Li et al. in 2013 [6], that the reagent acidity level can affect the solubility of metals in the leaching process.

Sulfuric acid as a non-organic acid comparative variable yields leaching percentage of Zn 90.92% and Mn 42.81%. Compared to organic acids, non-organic acids give better results in dissolving Zn metal but show poor results for dissolving Mn metal. High percentage of leaching Zn because the sulfuric acid is a strong acid that permits the perfect ionization, so that the Zn elements that contained in a batteries
powder will be more easily dissolved in sulfuric acid than in organic acids. Leaching reaction of Zn and Mn metals in sulfuric acid solution can be seen in the following equation [7].

\[
\begin{align*}
ZnO + H_2SO_4 & \rightarrow ZnSO_4 + H_2O \\
MnO + H_2SO_4 & \rightarrow MnSO_4 + H_2O \\
Mn_2O_3 + H_2SO_4 & \rightarrow MnSO_4 + MnO + H_2O \\
Mn_3O_4 + 2H_2SO_4 & \rightarrow 2MnSO_4 + MnO_2 + 2H_2O
\end{align*}
\]

The low dissolved of Mn element in sulfuric acid caused by the solubility of manganese oxide such as Mn$_2$O$_3$ and Mn$_3$O$_4$ in sulfuric acid is partial because it produces an insoluble MnO$_2$ compound in sulfuric acid [7]. The MnO$_2$ compound is the most stable manganese oxide with oxidation number 4+, so an additional reducing agent is required to reduce the manganese oxide number to be more easily dissolved in the leaching process.

3.3. Effect of H$_2$O$_2$ on leaching

The addition of H$_2$O$_2$ solution aims to increase the solubility of manganese in the reagents used. To increase the solubility of the manganese elements, it is necessary to add reducing agent, one of which is H$_2$O$_2$ solution. The graphs in Figure 4 and Figure 5 illustrate the effect of adding H$_2$O$_2$ solutions to the leaching process by using sulfuric acid reagents as non-organic acids and citric acid reagents as organic acids.

![Figure 4](image1.png)  
**Figure 4.** Effect of H$_2$O$_2$ on leaching Zn metals

![Figure 5](image2.png)  
**Figure 5.** Effect of H$_2$O$_2$ on leaching Zn metals

In the Figure 4 and Figure 5, it is shown that the addition of H$_2$O$_2$ solution increases the percentage leaching of Mn and Zn metals on the sulfuric acid and citric acid reagents, but the most significant effect is seen in the percentage leaching of Mn metal in sulfuric acid, from 42.81% to 91.75%. This is because hydrogen peroxide can help reduce the Mn metal oxide number in the MnO$_2$ compound to dissolve it in sulfuric acid. The reduction reaction occurring in the MnO$_2$ compound can be seen in equation 5.

\[
MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O
\]
The MnO$_2$ compound is the most stable manganese oxide, so to lower the oxidation number need reducing agents that have a lower redox energy potential than the decomposition basic reaction of the compound, which is 16.82 at 85°C. Hydrogen peroxide has 8.93 redox energy potential at 85°C, so it is possible to become the reducing agent of MnO$_2$ compound. The effect of adding H$_2$O$_2$ solution is not very significant on the leaching of Mn metal by using citric acid, from 51.32% to 56.90%. The reason is the citric acid is an organic weak acid that having a lower energy potential than the decomposition reaction of the MnO$_2$ compound, so that it has been able to reduce the compound even without the aid of hydrogen peroxide, consequently the addition of H$_2$O$_2$ has no significant effect in reducing the MnO$_2$ compound. However, the percentage leaching of Mn metal using citric acid is still very small compared to sulfuric acid when H$_2$O$_2$ is added because citric acid is a weak acid that could not be fully ionized, so that the amount of H$^+$ ions that can bind to the metal oxide is less than that of sulfuric acid as the strong acids.

The addition of hydrogen peroxide can also increase the percentage leaching of Zn metal although not significantly. The addition of H$_2$O$_2$ to sulfuric acid has increase the percentage leaching of Zn metal from 90.92% to 95.11%, whereas in citric acid there was an increase of leaching percentage of Zn metal from 64.37% to 77.64%. This is because hydrogen peroxide is a weak acid that releases H$^+$ ions that help bind the metal oxides, so that the percentage leaching of Zn metal can increase.

4. Conclusion

Initial metal content of the mixture Zn-C and Alkaline spent batteries powder is 14.52% wt for Zn and Mn metal is 22.56% wt. Leaching reagent of organic acid showing best leaching result for Zn and Mn metal in Zn-Mn spent batteries is citric acid with 64.37% leaching percentage for Zn metal, and 51.32% for Mn metal. Addition of H$_2$O$_2$ solution give the significant effect for leaching of Mn metal using sulfuric acid, with 48.94% leaching percentage increase, but didn’t give significant effect on leaching of Mn using citric acid.

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