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Leaching of Metals from Waste Silver Oxide-Zinc Button Cell Batteries by *Aspergillus niger*

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Abstract: Leaching of metals from waste button cell batteries was explored in this study. *Aspergillus niger* spent medium was used for metal leaching to avoid toxicity of metals toward microbial cells. Process parameters including time, temperature, shaking speed, and volume of the spent medium were optimized. We obtained 100% leaching of zinc and silver in six hours at 60 °C and 100 rpm using 15 mL spent medium. The use of spent medium supported the indirect leaching process. The organic acid produced by fungi acts as a lixiviant, aiding the metal leaching in this process.

Keywords: button cell batteries; silver; Zinc; *Aspergillus niger*; culture supernatant; two-step bioleaching

1. Introduction

The trend of miniaturization of various products and devices has led to the wide use of button cell batteries. Considering their operating longevity, small size, as well as high capacity per unit mass, they are used to power many portable electronic devices like wristwatches, calculators, toys, hearing aids, and medical devices [1]. These disposable batteries turn into waste after their life is over and long storage results in inactivation of these batteries [2].

Heavy metals present in such batteries entail severe environmental and health risks if improperly disposed; hence, recycling these batteries is crucial. Although these batteries are hazardous when disposed of in nature, they are rich repositories of valuable metals. Thus, recycling of waste batteries is advantageous to protect the environment and to recover valuable metals. Conventional techniques, such as pyro- and hydrometallurgy, are used to extract metals from these wastes [1,2]. Although these methods are fast and efficient, they require high energy and emit toxic gases and chemicals, so these processes are expensive and cause secondary pollution [3]. There is a need to develop an eco-friendly and sustainable process to recycle waste button cell batteries. Bioleaching is a process that uses microorganisms to recover metals. This process operates under mild conditions. It reduces the energy and material consumption, which makes the process eco-friendly [4–6]. *Aspergillus niger* was selected to leach metals from button cell batteries, since fungi are more advantageous compared to bacteria in the bioleaching process. They can grow at high pH, produce lixivants, like organic acids that chelate metal ions, and stimulate the rate of metal leaching [7]. In this study, the spent medium bioleaching process was used. For industrial applications, bioleaching by the spent medium is desirable to achieve high leaching efficiency [8]. Generally, spent medium bioleaching is preferable owing to the independent lixiviant generation and separate chemical process that allows individual process optimization of each step, resulting in maximum productivity. So, the spent medium process was utilized in the current investigation to recover silver from spent button cell batteries.

2. Materials and Methods

2.1. Materials

Chemicals were procured from Sigma Aldrich (St. Louis, MO, USA). The solutions were prepared using deionized water. The waste button cell batteries were obtained from a local market. The powder, containing silver (Ag), zinc (Zn), and mercury (Hg), was collected by manually dismantling waste button cell batteries. The powder was dried at 60 °C before experiments.

2.2. Determination of Metal Content of Waste Button Cell Battery Powder

The aqua regia method was used for the digestion of waste button cell battery powder. The digested solution was filtered using a 0.45 µm membrane filter and diluted before determining its metal content using an inductively-coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer, Waltham, MA, USA). Table 1 shows the metal content of the waste button cell battery powder.

Table 1. The metal content of button cell battery.

Metal	Metal Content (mg/g)
Zn	290 ± 0.82
Ag	35.86 ± 0.31
Hg	6.30 ± 0.06
Fe	0.02 ± 0.001

2.3. Microorganism Used and Spent Medium Collection

A. niger, obtained from the Food Industry Research and Development Institute (FIRDI), Hsinchu, Taiwan, was grown on sucrose medium. The media included sucrose (100 g), NaNO₃ (1.5 g), KH₂PO₄ (0.5 g), MgSO₄·7H₂O (0.025 g), KCl (0.025 g), and yeast extract (1.6 g) per liter of glass-distilled water [9]. *A. niger* was grown at 30 °C and 120 rpm for 10 days. The fungus produced only citric acid using sucrose as reported earlier [10]. Considering the earlier results, the spent medium in this study was collected after incubating *A. niger* at 25 °C and 120 rpm for 10 days. The spent medium had a citric acid concentration of 20 g/L and pH 1.97 [10]. The spent medium was filtered through a 0.22 µm filter before the experiments.

2.4. Various Physicochemical Parameters

To study the effect of time, 0.10 g waste battery powder was added to 100 mL spent medium in a 250 mL flask and incubated 30 °C and 150 rpm. The samples were collected in 2 h increments up to 8 h and were sent for metal analysis.

The waste battery powder (0.10 g) was added to 100 mL spent medium in a 250 mL flask. The temperature was varied from 30 to 60 °C to examine the effect of temperature on metal leaching.

The effect of shaking speed on leaching of metals was studied by adding spent battery powder (0.10 g) in 100 mL spent medium in 250 mL flasks at 60 °C and varying the shaking speed from 0 to 150 rpm for the leaching experiment. Samples were collected from the flasks after leaching the solution for 8 h.

The varying volumes of spent medium from 5 to 20 mL in a 50 mL flask were employed for the study. We added 0.10 g waste battery powder and flasks were placed at 60 °C and 150 rpm. Samples were collected from the flasks after leaching the solution for 8 h.

2.5. Analytical Methods

The metal concentrations in the leaching solutions were analyzed with a Kontron S-35, inductively coupled plasma optical emission spectrometry (ICP-OES). The experiments were run in triplicates.

3. Results and Discussion

3.1. Leaching of Metals from Button Cell Battery Powder

The increasing amount of battery waste and the presence of hazardous and precious metals has raised environmental and economic concerns. We report the use of microorganisms as an eco-friendly and sustainable approach for the metal reclamation from the battery waste. The process described here involves the use of microbial culture supernatant, which is the most preferable method from an industrial application viewpoint. The bioleaching potential of *A. niger* is well known and is credited with organic acids production, mainly citric acid, which acts as lixiviants for metal recovery.

3.2. Various Physicochemical Parameters

The *A. niger* spent medium was used to explore the leaching of metals from button cell batteries. Figure 1 shows the pattern of metal leaching at different time intervals. In the first four hours, only 27% of Ag was leached, while 64% of Zn was leached. The elevation in leaching of metals was observed with an increase in incubation time up to six hours. No significant effect was noted on leaching of metals by further incubating for eight hours. Around 80% Zn and 41% Ag were leached after six hours of incubation. These results indicate that citric acid effectively solubilized Zn from waste button cell batteries. Citric acid was reported to play a key role in the recovery of Zn from Zn-Mn batteries [3]. The leaching of Hg was not satisfactory. Only 2% leaching was achieved using *A. niger* spent medium for six hours (Figure 1).

Similar results were observed by Sathaiyan et al. [2] and Aktas [1]. They required 50 and 60 min for dissolution of Ag, respectively. In their studies, they used a high concentration of nitric acid. The present results are favorable as compared to those of Sathaiyan et al. [2] and Aktas [1] since *A. niger* spent medium contain citric acid has less impact on the environment.

The temperature influenced the leaching results as depicted in Figure 2. Studies were carried out at varying temperatures ranging from 20 to 60 °C. At lower temperatures (30 °C) only around 80, 41, and 2% leaching was observed for Zn, Ag, and Hg, respectively. Increases in incubation temperature favored the metal leaching. The 100% leaching of Zn and Ag were achieved at 60 °C. Around 11% Hg was leached at 60 °C. Thus, 60 °C was found to be the optimum temperature for silver extraction and was therefore employed in all subsequent experiments. Aktas [1] remarked on the influence of temperature in the silver dissolution from spent button cells. Yoo et al. [11] obtained the similar results indicating elevated effective dissolution of Ag and Cu from solders at higher temperatures.

Leaching of metals from waste battery powder using *A. niger* spent medium was evaluated by varying shaking speed from 50 to 200 rpm. Higher leaching of metals was detected as the shaking speed increased, resulting in 100% extraction of Zn and Ag at 100 rpm (Figure 3). Further increases in shaking speed to 150 rpm decreased the metal leaching efficiency. Yoo et al. [11] proposed that higher shaking speeds keep the mineral particles suspended in the solution. Therefore, a higher shaking speed is essential for effective particle suspension in the solution [12]. Aktas [1] reported a similar observation suggesting the impact of diffusion-controlled kinetic factors on the dissolution of Ag.

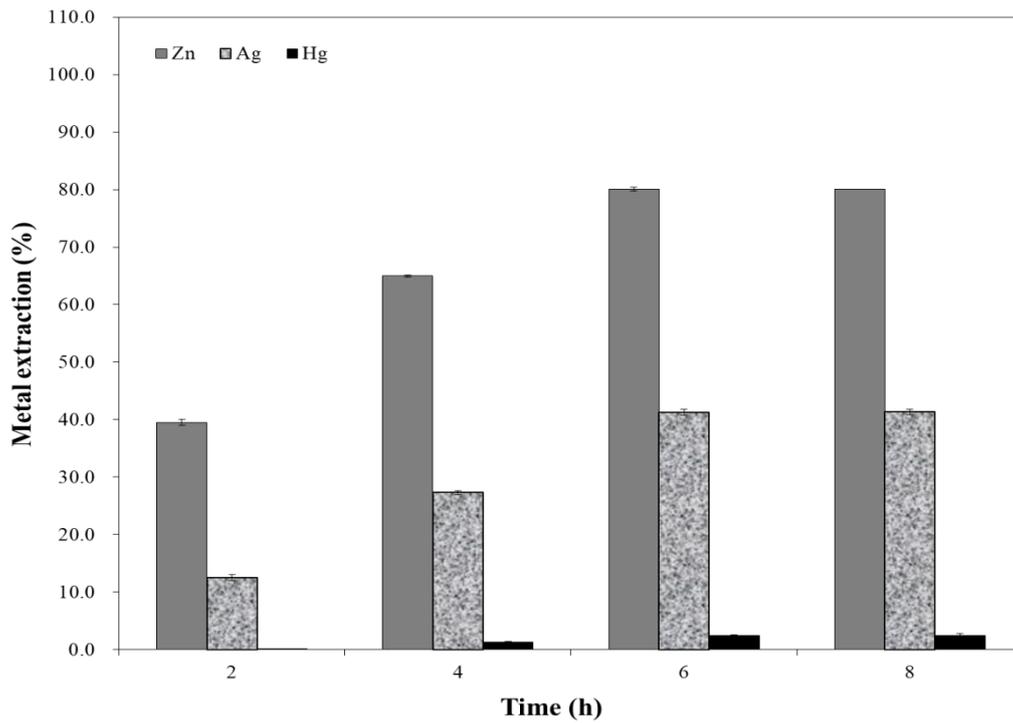


Figure 1. Evaluation of time period for leaching of metals using 100 mL *A. niger* spent medium at 30 °C and 150 rpm.

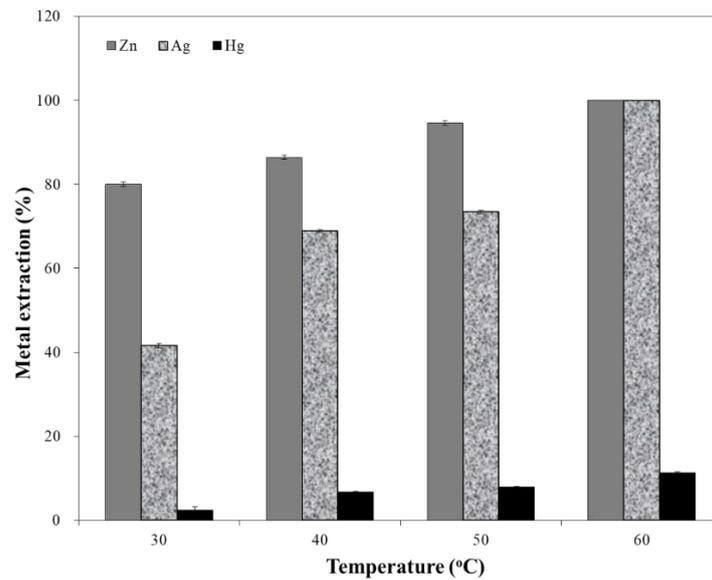


Figure 2. Effect of temperature on metal leaching using 100 mL *A. niger* spent medium after six hours of incubation and 150 rpm.

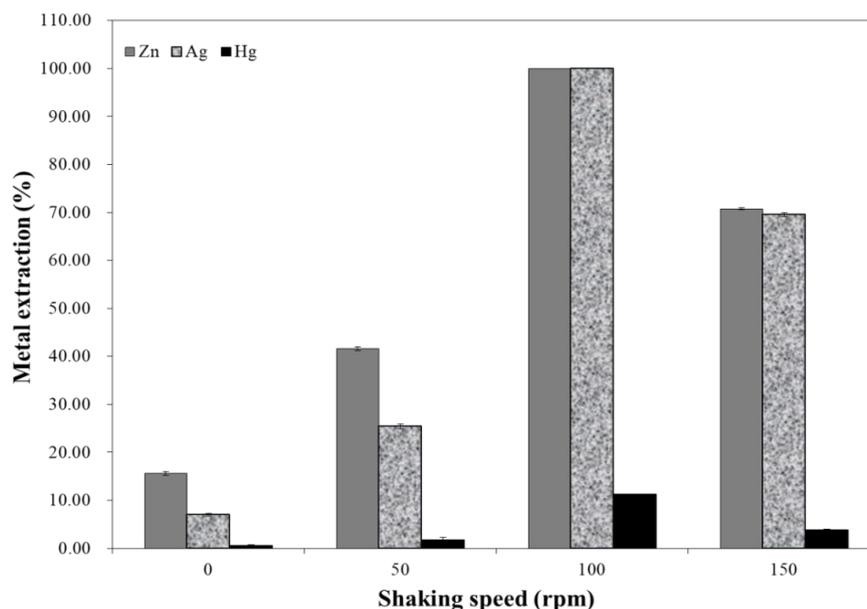


Figure 3. Effect of shaking speed on metal leaching using 100 mL *A. niger* spent medium after six hours of incubation at 60 °C.

The volume of spent medium also influenced the leaching of metals, resulting in higher leaching efficiency with an increase in volume up to 15 mL (Figure 4). Further increase in volume had no positive effect on metal leaching. The substantial volume of the spent medium assisted the transport of the ionic product from spent powder. However, this effect was saturated above 15 mL [13]. These outcomes suggest that the *A. niger* spent medium is an effective leaching agent for recovery of Zn and Ag from spent button cell batteries.

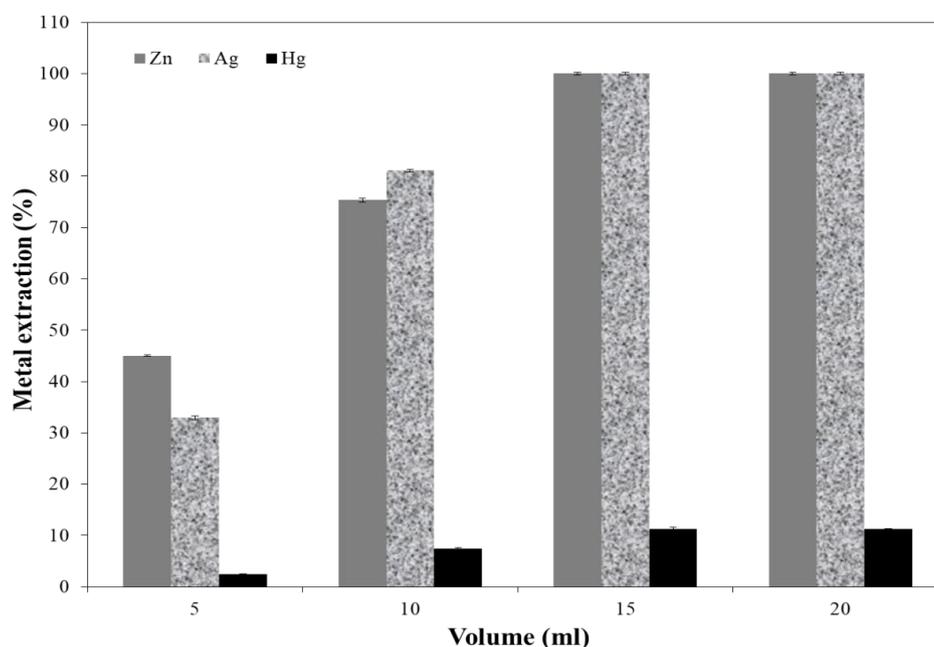


Figure 4. Effect of *A. niger* spent medium volume on leaching of metals after six hours of incubation at 60 °C and 100 rpm.

Table 2 compares the current and earlier studies by our group. In a previous study, the spent culture medium of *Acidithiobacillus ferrooxidans* was used to leach Ag from button cell batteries [6]. As silver is toxic to microbial cells, in the previous study, *Acidithiobacillus ferrooxidans* was grown in

growth medium for the production of Fe^{3+} . Then, the spent culture medium containing Fe^{3+} was used for the leaching process. Aktas [1] suggested that during power generation using button cell batteries, silver oxide is reduced to metallic silver and zinc metal is converted to zinc oxide. The overall reaction can be given as follows [1,14]:

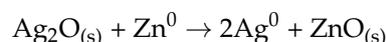


Table 2. A comparisons between current and earlier studies for recovery of metals from spent silver oxide-zinc button cell batteries.

Reference	Micro-Organism Used	Metal Recovery (%)		Time Required (h)
		Ag	Zn	
Jadhav and Hocheng [6]	<i>Acidithiobacillus ferrooxidans</i>	100	NA	1
Jadhav et al. (Present study)	<i>Aspergillus niger</i>	100	100	6

The bioleaching process using *Acidithiobacillus ferrooxidans* is based on oxidizing potential of Fe^{3+} . The zinc metal cannot be leached using *Acidithiobacillus ferrooxidans*, since the zinc present in button cell batteries is already in the oxidized form. The Fe^{3+} produced by *Acidithiobacillus ferrooxidans* can only solubilise the reduced metallic silver from button cell batteries. Although silver recovery required much less time compared to this study, the drawback of using *At. ferrooxidans* is that it was not able to leach Zn. To overcome this problem *A. niger*, a bioleaching system based on organic acid production, was used in this study.

4. Conclusions

In the present study, a spent medium bioleaching process was employed to leach Zn and Ag from spent button cell batteries. Findings indicated 100% leaching of Zn and Ag was achieved using 15 mL *A. niger* culture supernatant with a six hour incubation period at 60 °C and 100 rpm. These results suggest that an environmentally-friendly process can be developed for leaching metals from button cell batteries using *A. niger* culture supernatant.

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