Biological treatment of wastewater produced during recycling of spent lithium primary battery

Kyoungkeun Yoo *, Shun-Myung Shin, Dong-Hyo Yang, Jeong-Soo Sohn

Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Gwahang-no 92, Yuseong-gu, Daejeon 305-350, Republic of Korea

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A B S T R A C T
Wastewater produced during recycling of spent lithium primary battery was biologically treated with Acidithiobacillus ferrooxidans to decrease the pH and metal concentration. Since the wastewater contains high concentrations of Cr, Ni, and Li, the effects of these metals on the bacterial activity in a 9 K medium were also investigated. Samples of the medium with different metal concentrations were treated, and the oxidation ratio of Fe²⁺ ions was measured to examine the activity of bacteria. In the treatment of simulated wastewater, the presence of Cr and Ni ions with concentrations of 8000 g m⁻³ and 13,000 g m⁻³, respectively, did not inhibit the bacterial activity, whereas the oxidation ratio of Fe²⁺ ions was observed to be low in the medium when Li ion was present with a concentration at 5000 g m⁻³. This observation suggested that at this concentration, Li ion suppressed the bacterial activity. In the case of treatment of real wastewater containing Cr, Ni, and Li, the oxidation ratio of Fe²⁺ to Fe³⁺ was observed to be low while the Fe concentration and pH decreased to 21,633 g m⁻³ and 1.8, respectively. Thus, the wastewater produced during the recycling of spent lithium primary batteries can be effectively treated biologically for re-circulating in the recycling process.

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1. Introduction

For over thirty years, lithium primary batteries have been known for their useful properties such as long shelf life, constant voltage output, wide operating temperature range, and low self-discharge (Pistoia et al., 2001). The batteries are used in various fields such as IT, medical, and military. The global primary lithium battery market was estimated to be worth $820.6 million in 2003 and it is expected to increase to $11,355.3 million in 2010 (http://www.frost.com, Frost & Sullivan). However, when the batteries are heated to high temperatures, charged, pierced, over-discharged, or short-circuited, they explode because of two reasons: lithium reacts violently with water or air, and components such as elemental sulphur and organic electrolytes are flammable. Even a spent lithium primary battery contains unreacted lithium; thus, it is difficult to recycle spent lithium primary batteries. Toxco, an environmental firm in Southern California, has developed a lithium recycling process for all kinds of lithium batteries, wherein the batteries are crushed after freezing with liquid argon or liquid nitrogen. However, this process is costly because of the requirement of extremely low temperatures (Pistoia et al., 2001; Yoo et al., 2008).

A recycling process (Fig. 1) for spent lithium primary batteries has been proposed by Yoo et al. (2008). The process prevents the batteries from exploding and recovers valuable materials such as acrylonitrile-butadiene-styrene (ABS) resin, polyvinyl chloride (PVC) resin, nickel, and stainless steel. In the process, Li in the battery is oxidized to Li⁺ in the step, “Stabilizing the battery cells with acid solution”, before the battery is crushed, to prevent the battery from exploding during the crushing process. In this paper, this oxidation is termed ‘stabilization of the battery’. The stabilized battery does not explode when it is crushed. The oxidation of Li metal can be achieved by dipping the batteries in sulphuric acid, which dissolves the external casing of the battery and then reacts with Li. In Yoo’s study, the effects of temperature and reaction time on the stabilization of the batteries were investigated for examining the possibility of increasing the recovery ratio of valuable metals from the batteries and accelerating the stabilization of the batteries. The authors reported that the batteries were stabilized at 35 ºC and 50 ºC for 3 days and 1 day, respectively. However, in a pilot-scale test at 35 ºC involving the use of a two-ton battery, 5% of the battery exploded after the 3 days stabilization. This indicates that a battery should be stabilized for more than 6 days to ensure the safety of the process (not published). The wastewater generated in the process contains high concentrations of Fe, Cr, Ni, and Li (Yoo et al., 2008). If the cost of wastewater treatment is high, it could affect the feasibility of the process. One way of reducing the cost is to re-circulate the wastewater in the recycling process. Therefore, the pH and metal concentration should be decreased to dissolve the external case.
It is well known that Acidithiobacillus ferrooxidans obtains energy by oxidizing different inorganic substances such as ferrous sulphate (Daoud and Karamanev, 2006). The bacteria oxidize Fe$^{2+}$ and cause the precipitation of the ions in the form of jarosite minerals.

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$

$$\text{M}^+ + 3\text{Fe}^{3+} + 2\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{OH})_6 + 8\text{H}^+$$

Here, M$^+$ represents a monovalent ion such as K$^+$, Na$^+$, NH$_4^+$, or Ag$^+$. The oxidizing ability of the bacteria is found to be useful for the removal of Fe ions from wastewater. Furthermore, the bacteria have been researched for use in the recovery, removal, and reduction of metals such as Cr, Ni, and Li from wastewater, soil, sediment, and minerals.

The bacteria have been used to reduce Cr(VI) to Cr(III) in wastewater (Allegretti et al., 2006; Cabrera et al., 2007; Quinterana et al., 2001; Sisti et al., 1996) and to leach Cr from sewage and wastewater sludge (Couillard and Chartier, 1991; Drogui et al., 2005a,b; Gu and Wong, 2004a,b; Kim et al., 2005; Tyagi et al., 1993; Wong and Gu, 2004, 2008), fly ash (Brombacher et al., 1998), a contaminated and Wong, 2004a,b; Kim et al., 2005; Tyagi et al., 1993; Wong and ter sludge (Couillard and Chartier, 1991; Drogui et al., 2005a,b; Gu 2001; Sisti et al., 1996) and to leach Cr from sewage and wastewater (Allegretti et al., 2006; Cabrera et al., 2007; QuiIntana et al., 2006). The extent of inhibition varies with the bacterial strain and growth conditions (Baillet et al., 1998; Cabrera et al., 2008), and activated sediment (Kaštánek et al., 1994). Simate and Ndlovu, (2008) investigated bacterial leaching of nickel laterites using Ac. ferrooxidans (ATCC 19859) was obtained from EWHA University, Seoul. The organism was cultured in a 9 K medium (Silverman and Lundgren, 1959) with an initial pH of 2.0; the medium contained 44.22 g of FeSO$_4$$\cdot$$7$H$_2$O, 3 g of (NH$_4$)$_2$SO$_4$, 0.5 g of K$_2$HPO$_4$, 0.5 g of MgSO$_4$$\cdot$$7$H$_2$O, 0.1 g of KCl, and 0.01 g of Ca(NO$_3$)$_2$ in 1000 cm$^3$ of 0.01 kmol m$^{-3}$ H$_2$SO$_4$. All reagents used in this study were of reagent-grade. Cells were harvested at late logarithmic phase when the culture pH was about 1.3, were re-suspended in an iron-free 9 K medium, and were used as inocula in the biological treatment test. The wastewater produced in the lithium primary battery recycling process was obtained from a pilot plant of Korea Recycling Company. The composition and pH of the wastewater are given in Table 1.

2. Materials and methods

2.1  Materials

A pure culture of A. ferrooxidans (ATCC 19859) was obtained from EWHA University, Seoul. The organism was cultured in a 9 K medium (Silverman and Lundgren, 1959) with an initial pH of 2.0; the medium contained 44.22 g of FeSO$_4$$\cdot$$7$H$_2$O, 3 g of (NH$_4$)$_2$SO$_4$, 0.5 g of K$_2$HPO$_4$, 0.5 g of MgSO$_4$$\cdot$$7$H$_2$O, 0.1 g of KCl, and 0.01 g of Ca(NO$_3$)$_2$ in 1000 cm$^3$ of 0.01 kmol m$^{-3}$ H$_2$SO$_4$. All reagents used in this study were of reagent-grade. Cells were harvested at late logarithmic phase when the culture pH was about 1.3, were re-suspended in an iron-free 9 K medium, and were used as inocula in the biological treatment test.

The wastewater produced in the lithium primary battery recycling process was obtained from a pilot plant of Korea Recycling Company. The composition and pH of the wastewater are given in Table 1.

2.2  Biological treatment of wastewater

Two kinds of wastewater samples were prepared. Simulated wastewater samples were prepared by adding reagent-grade Cr$_2$O$_3$, NiSO$_4$$\cdot$$6$H$_2$O, or Li$_2$SO$_4$$\cdot$$H_2$O to a 9 K medium. The real wastewater samples were prepared using the wastewater obtained from Korea Recycling Company. The composition of the prepared wastewater samples is shown in Table 2, where ‘iron-free 9 K medium concentrated 10 times’ indicates a solution containing 30 g of (NH$_4$)$_2$SO$_4$, 5 g of K$_2$HPO$_4$, 5 g of MgSO$_4$$\cdot$$7$H$_2$O, 1 g of KCl, and 0.1 g of Ca(NO$_3$)$_2$ in 1000 cm$^3$ of 0.01 kmol m$^{-3}$ H$_2$SO$_4$. The initial pH of all the wastewater samples was adjusted to 2 adding 1 kmol m$^{-3}$ H$_2$SO$_4$. The wastewater samples were filtered with a 0.2 $\mu$m membrane filter; subsequently, 100 cm$^3$ of each sample was taken in a 250 cm$^3$ Erlenmeyer flask. An amount of 1 cm$^3$ of the bacterial culture (2 $\times$ 10$^8$ cells cm$^{-3}$) was introduced in the wastewater samples, and the flasks were capped with Si sponge stoppers for preventing contamination by other bacteria.

Table 1

<table>
<thead>
<tr>
<th>pH and concentrations of Fe, Cr, Ni, and Li in the wastewater.</th>
<th>WW (ml)</th>
<th>WW (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (−) Fe (g m$^{-3}$) Cr (g m$^{-3}$) Ni (g m$^{-3}$) Li (g m$^{-3}$)</td>
<td>2.1</td>
<td>44920</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Composition of wastewater samples.</th>
<th>90 vol.% WW (ml)</th>
<th>10 vol.% WW (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-free 9 K medium concentrated 10 times</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Wastewater in Table 1</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>Deionized and distilled water</td>
<td>–</td>
<td>80</td>
</tr>
<tr>
<td>1 kmol m$^{-3}$ H$_2$SO$_4$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

WW: wastewater.
while ensuring aeration. All flasks were set in a rotary flask shaker and were shaken at 35 °C and 180 rpm. In every biological treatment test, 9 K mediums with and without the bacteria were tested together for comparison: The 9 K medium with the bacteria was used to compare results in the solutions with and without the metal ions such as Cr, Ni, and Li, and the 9 K medium without the bacteria, termed ‘control’, was also tested to facilitate comparison between the results with and without the addition of the bacteria.

2.3. Stabilization test on the spent lithium primary battery using treated wastewater

After the 90 vol.% wastewater (Table 2) was biologically treated, the treated wastewater was used for stabilization test. The initial pH of the treated wastewater was adjusted to 0.3 adding sulphuric acid, and 200 cm3 of the solution and three cells of a spent battery (Bobbin type, BA6853 K, Vitzrocell Co., Ltd.) were introduced in a 500 cm3 Erlenmeyer flask. The flask was set in a shaking bath (Bobbin type, BA6853 K, Vitzrocell Co., Ltd.) were introduced in a 500 cm3 Erlenmeyer flask. The flask was set in a shaking bath and agitation at 35 °C and 100 rpm for 6 days. The solutions were sampled everyday to measure the pH and the concentrations of Fe, Cr, Ni, and Li. After the experiment was terminated, the batteries were collected and dried at 80 °C overnight. The dried batteries were crushed to examine whether the batteries were exploded or not.

2.4. Analytical methods

For measuring the pH, metal concentrations, and Fe3+ concentration, samples of the solutions were extracted at the desired times and were filtered with a 0.2 µm membrane filter. The filtrates were diluted with 0.1 kmol m−3 nitric acid, and the concentrations of metals such as Fe, Cr, Ni, and Li were analyzed with an AAAnalyst 400 atomic absorption spectrometer (Perkin–Elmer, Germany) and a JY-38 Plus inductively coupled plasma atomic emission spectrometer (Labmat, Australia). The detection limits for Fe, Cr, Ni, and Li were 1 × 10−3 g m−3, 2 × 10−1 g m−3, 5 × 10−2 g m−3, and 6 × 10−2 g m−3.

The ferric sulphosalicylate method (Karamanev et al., 2002) was used to analyze the ferric ion concentration. The method involves the use of a UV-1601PC UV–visible spectrophotometer (Shimadzu Co., Japan) for the colorimetric measurement of a red-coloured ferrous ferric sulphosalicylate complex. This complex was prepared by adding agent-grade 5-sulphosalicylic acid dehydrate. The absorbance of the complex was measured at 505 nm.

After the experiment was terminated, the precipitate formed was collected and dried at 105 °C overnight. The dried precipitate was characterized using a Ru-200B X-ray diffractometer (Rigaku, Japan). The X-ray diffraction data were collected using Cu Kα radiation (accelerating voltage: 30 kV; current: 40 mA), a scan speed of 8°/min, and an angle range of 10–70°/2θ; a step scanning method was used.

3. Results and discussion

As shown in Table 1, the wastewater analyzed contained metals such as Fe, Cr, Ni, and Li. The effects of the metals on the activity of A. ferrooxidans were investigated using simulated wastewater samples containing Cr, Ni, and Li.

Figs. 2 and 3 show the pH values of the solutions as a function of time. In Fig. 2, the pH increases and then decreases with an increase in time; however, the control pH does not show such a trend. In Fig. 3, the pH increases slowly in the solution containing an Li concentration of more than 5000 g m−3 and in the control, while it shows an increase and a subsequent decrease in the solution containing 2000 g m−3 of Li and the 9 K medium; the variation in the pH is slow in the solution with 2000 g m−3 of Li. As can be
metals. The oxidation ratio of Fe²⁺ was obtained using the following equations:

\[ \text{Ox} = \frac{[\text{Fe}^{2+}]_i - [\text{Fe}^{3+}]_i}{[\text{Fe}^{2+}]_i} \times 100 \]  

Here, \([i]\) and \([i]_o\) represent the concentration and initial concentration of species \(i\), \(\text{Fe}_{\text{total}}\) denotes the total concentration of Fe, and \(R_{\text{ox}}\) represents the oxidation ratio of the Fe²⁺ ions. The concentration of Fe²⁺ ions was obtained from the difference between the total Fe concentration and the Fe³⁺ ion concentration, as shown in Eq. (3).

Figs. 8 and 9 show the oxidation ratio of Fe²⁺ ions as a function of time. In Fig. 8, the oxidation ratios in the Cr and Ni solutions and 9 K medium increase rapidly to 99% in 5 days, whereas the oxidation ratio in the control solution increases gradually to 20% in 11 days. In Fig. 9, the oxidation ratio of the Fe²⁺ ions increases at a lower rate in the solutions containing Li as compared to that of the 9 K medium. The ratio increases to 99% in 7 days in the solution with 2000 g m⁻³ of Li, while it increases to 25% and 24% in the solutions with 5000 and 8000 g m⁻³ of Li, respectively, in 11 days.

In the solutions containing Cr and Ni ions, the oxidation ratio of Fe²⁺ shows almost the same behavior as that in the 9 K medium. Previous studies have reported that the inhibition effects of Cr are observed when the metal concentration is in the range 39–3900 g m⁻³. Fig. 8 shows that the bacterial activity is unaffected at Cr concentrations in the range 950–8000 g m⁻³; the figure also

Fig. 6. XRD result of the precipitate in the solution with 2000 g m⁻³ Li (J: jarosite).

Fig. 7. Removal ratios of Ni ion.

Fig. 8. Oxidation ratios of Fe²⁺ in the solutions with Cr and Ni ions.

Fig. 9. Oxidation ratios of Fe²⁺ in the solutions with Li ions.

Fig. 10. pH variations in the wastewater solutions as a function of time.
The pH variation is a result of the oxidation of Fe\(^{2+}\). As discussed above, the pH increases with time (Fig. 11), it does not decrease in the control. The Fe concentration and pH increased rapidly after 2 days, while the concentrations of Cr and Li increased gradually. This result suggested that the biological treatment decreased the Fe\(^{2+}\) oxidation activity of \(A.\) ferrooxidans significantly.

As seen in Table 1, the wastewater contains 11,560 g m\(^{-3}\) of Cr, 1153 g m\(^{-3}\) of Ni, and 6250 g m\(^{-3}\) of Li. Because these metal concentrations could suppress the bacterial activity during wastewater treatment, 90 vol.% and 10 vol.% wastewater solutions are prepared; the composition of these solutions is presented in Table 2. Figs. 10–12 show the pH, Fe concentration, and the oxidation ratio of Fe\(^{2+}\) ions. In Fig. 10, the pH is observed to first increase and then decrease, and the variation in the pH is more rapid in the 90 vol.% wastewater than in the 9 K medium; the increase and decrease in the pH are not observed in the case of the control. As discussed above, the pH variation is a result of the oxidation of Fe\(^{2+}\) ions. Because the initial Fe concentration is higher in the 90 vol.% wastewater than in the 9 K medium, in the 90 vol.% wastewater, the amount of oxidized Fe\(^{3+}\) ions is greater, and the variation of pH is more rapid. While the Fe concentration in the wastewater decreases with time (Fig. 11), it does not decrease in the control. These results indicate that Fe ions were oxidized and precipitated in the wastewater solutions according to Eqs. (1) and (2).

Fig. 12 shows the variation in the oxidation ratio of Fe\(^{2+}\) with time. The oxidation ratio increases to 99.7%, 99.8%, and 66.5% in 11 days in the 9 K medium, 10 vol.% wastewater, and 90 vol.% wastewater, respectively. The low oxidation ratio in the 90 vol.% wastewater probably results from the high initial Fe concentration and the high concentration of metals such as Cr and Li. However, though the 90 vol.% wastewater contains 5500 g m\(^{-3}\) of Li, the inhibition effect is not significant compared to that seen in Fig. 9. The inhibition effect has been found to vary with the bacterial strain and growth conditions (Baillet et al., 1998; Cabrera et al., 2005a,b). Since the batteries contain other constituents such as organic electrolytes and additives, there would be minor amounts of other elements in the wastewater extracted from the batteries, but the effects of the constituents could not be determined because it was difficult to identify these constituents. Although a weak inhibition effect is observed in the 90 vol.% wastewater, the Fe concentration and pH decrease to 21,633 g m\(^{-3}\) and 1.8, respectively.

The stabilization test was performed on a lithium primary battery using the wastewater treated above to examine the possibility of circulating the treated wastewater. Fig. 13 shows the pH and metal concentrations during the test as a function of time. The Fe concentration and pH increased rapidly after 2 days, while the concentrations of Cr and Li increased gradually. This result suggested that the stainless steel case of the battery was dissolved completely though the wastewater treated contains high concentrations of Cr and Li ions. Furthermore, the increases in the pH and Fe concentration showed a trend very similar to that in the stabilization test performed on pure 0.5 kmol m\(^{-3}\) \(\text{H}_2\text{SO}_4\) (Yoo et al., 2008). When the batteries stabilized for 6 days were crushed, there was no explosion. This result indicated that the batteries were successfully stabilized with the treated wastewater. Therefore, as can be seen in Fig. 1, wastewater could be re-circulated in the recycling process by the biological treatment. Further study should be required to recover or remove the metal ions like Cr, Li, and Ni, because the metal ions would be concentrated through re-circulating the wastewater.

Generally, acidic wastewater with metal ions is treated by neutralization methods using a basic reagent such as NaOH. Because a low pH and a low metal concentration are required to re-circulate the wastewater in the process shown in Fig. 1, the substantial addition of acids may be required in the neutralization methods. The results discussed above indicate that the biological treatment decreases the pH as well as Fe concentration, which implies a saving in terms of the amount of reagent that would otherwise be required to decrease the pH of the solution. The slow kinetics of biological processes have restricted the use of biological treatment. However, in the recycling process, considering that it takes more than 6 days to stabilize the primary lithium battery, the wastewater treatment process would not significantly increase the total time taken by the recycling process. Consequently, wastewater treated by the bacteria can be re-circulated in the recycling process.

4. Conclusions

Wastewater produced during a lithium primary battery recycling process is treated using \(A.\) ferrooxidans, and the treated water is re-circulated in the process. In the treatment of the simulated wastewater, it is found that the bacteria can grow in solutions with high metal concentrations such as 8000 g m\(^{-3}\) of Cr and 13,000 g m\(^{-3}\) of Ni, but a Li concentration of 5000 g m\(^{-3}\) in a pure 9 K medium significantly suppresses the Fe\(^{2+}\) oxidation activity of
the bacteria. In the case of a 90 vol.% real wastewater solution, although a low Fe oxidation ratio is observed, the pH and Fe concentration decrease to 1.8 and 21,633 g m⁻³, respectively. This result suggests that wastewater treated by the bacteria can be reused in the recycling process.

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References

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