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달성 鑛山에서 採取한 混合 호산성 균주를 利用한 폐리튬 밧데리의 바이오 浸出[†]

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Bio-dissolution of waste of lithium battery industries using mixed acidophilic microorganisms isolated from Dalsung mine[†]

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요 약

혼합 호산성 박테리아를 이용하여 리튬이온 밧데리 산업 폐기물로부터 코발트와 리튬의 침출을 연구하였다. 혼합 호산성 박테리아의 성장기질은 단체 황 및 2가 철이온으로 구성되어 있으며 미생물에 의한 금속의 침출은 폐기물에 존재하는 금속과 황산이온의 양자 반응 때문에 일어난다. 본 연구에서 12일간 미생물 침출반응시 고상 폐기물중 코발트의 80%, 리튬의 20%가 용해되었으며 고액비가 높을수록 금속의 독성으로 인하여 미생물의 성장은 억제된다. 단체 황의 농도가 높을 조건에서는 일부 황 분말이 용해되지 않으며 금속의 침출속도는 황의 증가에 따라 감소한다.

주제어 : 호산성 균주, 폐리튬밧데리, 미생물 침출, 성장, 달성광산

Abstract

Mixed acidophilic bacteria were approached for leaching of cobalt and lithium from wastes of lithium ion battery industries. The growth substrates for the mixed mesophilic bacteria are elemental sulfur and ferrous ion. Bioleaching of the metal was due to the protonic action of sulfate ion on the metals present in the waste. It was investigated that bioleaching of cobalt was faster than lithium. Bacterial action could leach out about 80 % of cobalt and 20 % of lithium from the solid wastes within 12 days of the experimental period. Higher solid/liquid ratio was found to be detrimental for bacterial growth due to the toxic nature of the metals. At high elemental sulfur concentration, the sulfur powder was observed to be in undissolved form and hence the leaching rate also decreased with increase of sulfur amount.

Key words: Acidophilic microorganism, Lithium battery waste, Bioleaching, Growth, Dalsung Mine

1. Introduction

In the present scenario, it is important to protect our environmental resources in a global scale and the development of various advanced technologies is necessary. It is now accepted that much greater concern must be exercised over environmental issues in the mining of ores and in the extraction of metals. There is also a need to develop more efficient processes that will allow the use of lower-grade ores and new processes to deal with ores and industrial wastes that can not be handled by conventional technology. The recovery of metals from low grade

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ores, minerals and more specifically various wastes is a part of biotechnology[1] because microbiological leaching can be used to recover valuable metals from various industrial wastes and detoxify them for environmental safe deposition[2].

In recent years there has been an increasing global interest in interactions of heavy metals within microorganism[3]. The pollution of the environment with heavy metals has led to the selection of heavy metal resistant microorganisms in the soil and water of industrial regions. In many cases, resistance to heavy metal encoded on plasmid and that can be used for the creation of novel microbial strains[4,5].

Many industries produce hazardous byproducts in their working cycles. The world production of wastes is constantly increasing, specifically in the industrialized countries. Each year a large number of electric and electronic wastes namely, spent batteries, printed circuit board are being generated from various industries. Besides, wastes from petroleum industries are also playing important role to create hazardous environment by producing highly toxic metals.

Production of spent lithium-ion secondary batteries (LIBs) is increasing world-wide and 10% of market share is in Korea. In the case of LIBs valuable metals such as cobalt and lithium can be recycled[6,7]. During preparation of LIBs a surplus amount of wastes remains and cobalt and lithium like metals are rich in these waste. Hydrometallurgical techniques are being applied to recover metals from spent waste of LIBs. Application of biohydrometallurgical process, specifically bioleaching, would be a challenge over the conventional technologies due to the cost effective and technical feasibility of the former[8-11].

Bioleaching is the process in which microorganisms catalyze the dissolution of metals from rock minerals and ores. Microorganisms include chemolitho-autotrophic, acidophilic and iron and sulfur oxidizing bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*. These organisms use CO_2 as sole carbon source and ferrous and reduced inorganic sulfur compounds as the energy source[12]. *Thiobacilli* can grow and produce sulfuric acid using elemental sulfur as energy source with oxygen as the terminal electron acceptor.

The present work was carried out to recover valuable metals like cobalt and lithium from the solid wastes using both pure and mixed culture of microorganisms. The experimental studies were done using elemental sulfur and Fe^{2+} as the energy sources for the bacteria.

2. Materials And Methods

All the reagents used in the experiment are analytical grade (AR) unless otherwise stated, and all aqueous solutions were prepared by using de-ionized water.

2.1. Bacteria

Mine drain water sample was collected from Dalsung Tungsten-Copper abandoned mine, Daegu, South-East of Korea. The pH of the sample was measured to be 2.85~3.2. The sample was considered to harbor mixed acidophilic microorganisms in it. The mine water was then enriched in 9K medium[13] with elemental sulfur (10 g/L) as the sole energy source to obtain mixed sulfur oxidizing bacteria. The growth of bacteria was observed by measuring the cell number and pH change in the medium. To obtain the bacteria the medium was filtered and the un-dissolved elemental sulfur was separated and washed out the attached bacteria from sulfur powder repeatedly.

2.2. Adaptation of bacteria

To adapt the bacteria with solid waste powder, mixed sulfur oxidizing bacteria were applied. The medium prepared for the adaptation study contained the mineral salt solution along with elemental sulfur (10 g/L) as the energy source. The concentration of solid wastes during adaptation was varied from 1 g/L to 10 g/L. Free bacteria concentration in the solution was regularly observed by using the Neuber counting chamber which contains 25 squares each of 0.01 mm^2. Adaptation was carried out by transferring the subculture to fresh media with a higher concentration of LIBs. The decrease in pH of the solution indicated bacterial growth and the suspended mixed bacterial population were found to be at least 4.0×10^8 cells/mL.

2.3. Characterization of solid wastes of LIBs

In the present study, the solid wastes of LIBs were collected from Recycling R&D Centre of KIGAM, ground and sieved to obtain the mesh size of ~106 μm. This powder was characterized by XRD (Rigaku X-Ray Diffractometer, Rigaku, Japan) and the $LiCoO_2$ phase was clearly viewed (Fig. 1). The specific surface area of the cathode LIBs sample was determined by a BET method (Micromeritics, Tristar 3000, Unit 1) and found to be 3.26 m^2/g. The mean particle size was determined with a particle size analyzer (Malvern Mastersizer 2000, Version 2.00) and found to be d(0.5) = 8.3 μm.

2.4. Bioleaching study

Bioleaching studies were carried out in 300 mL conical flasks containing 100 mL of an iron free 9K medium with an initial pH of 2.5. To the prepared medium, elemental sulfur of 10 g/L was added as the energy source. Aseptically, the adapted bacteria culture of 4.0×10^8 cells/mL were inoculated into the medium after adding solid waste powder. The flasks were incubated in a shaking incubator at 30°C and 200 rpm. Sterile controls were performed using filter-sterilized medium at an initial pH of 2.5 with 10 g/L of elemental sulfur. Experiments varying different leaching conditions such as; solid/liquid ratio (w/v) and concentration of elemental sulfur were carried out.

2.5. Analytical determinations

The pH of each experiment was measured throughout the experimental course using a glass electrode (Thermo Electro Corporation, Orion 720+). Culture samples (1.5 mL) were taken periodically, transferred to microfuge tubes (1.5 mL) and centrifuged at 12,000 rpm for 10 minutes. Losses from solution were compensated by adding distilled water. Cobalt and lithium concentrations in the solution were determined after centrifugation using an Atomic Absorption Spectrophotometer (Varian SpectrAA-400). Samples were diluted to the appropriate concentration range with distilled water and measured in triplicate.

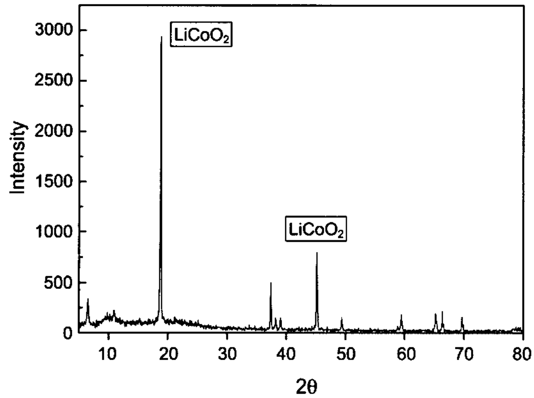

Fig. 1. XRD pattern of the solid wastes of LIBs.

3. Results and Discussion

3.1. Metal solubilization by bacteria

An initial series of experiments were carried out to study the behavior of the microbial strain in the solid wastes of LIBs having no energy source such as sulfide, sulfur or iron for the microbial growth. The preliminary results are presented in Fig. 2, and 3 where data shows the percentage of Co and Li leached into the solution, at solid/liquid (w/v) ratio of 5 g/L. Each experiment showed high dissolution of cobalt into the leaching medium compared to lithium. From the results, microbial activity is confirmed during leaching experiments. Where inocula were present with energy sources such as elemental sulfur only, dissolution of both lithium and cobalt increased. In the presence of bacteria, cobalt leaching was found to be 80% whereas it was 11% in the absence of cells i.e. the blank experiment.

Microbial activity during the waste dissolution experiments was confirmed by measuring the pH change of the leaching solutions and blanks during the experimental period. In the presence of bacteria and sulfur the pH of the solution decreased from 2.5 to 1.7 due to production of sulfuric acid by the oxidative activity of bacteria. Whereas in blank experiment, pH

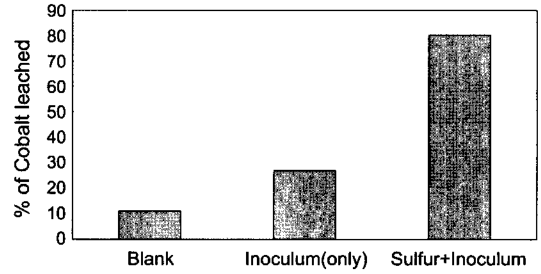

Fig. 2. Cobalt leaching at different experimental conditions. (time = 12 days, initial pH = 2.5, elemental sulfur = 10 g/L)

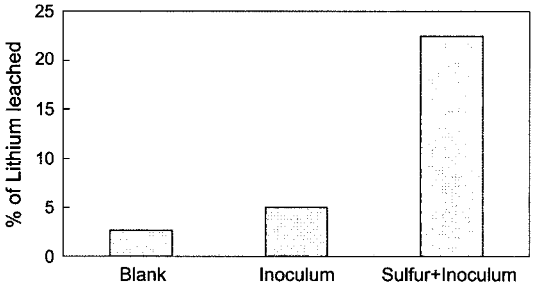

Fig. 3. Lithium leaching at different experimental conditions. (time = 12 days, initial pH = 2.5, elemental sulfur = 10 g/L)

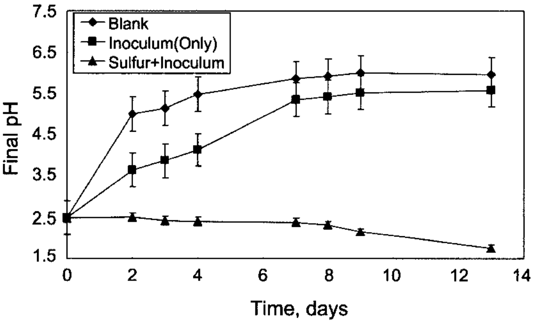

Fig. 4. Final pH of the solution at different experimental conditions. (time = 12 days, initial pH = 2.5, elemental sulfur = 10 g/L)

of the solution increased from 2.5 to 6.0, which may be due to the presence of oxide phases in the waste sample (Fig. 4). On the other hand, in absence of energy sources such as sulfur, no cell growth was observed leading to a low metal solubilization (27% of cobalt). In this case, pH values initially increased and remained constant at 5.5.

These results signified that the elemental sulfur in nutrient medium is oxidized to sulfuric acid as the activity of the microorganisms. The major reaction takes place here is the protonic attack of SO_4^{-2} ion on LIBs by following mechanism:

$$S^0 + O_2 + H_2O \rightarrow H_2SO_3 \qquad (1)$$

$$H_2SO_3 + \frac{1}{2}O_2 \rightarrow H_2SO_4 \qquad (2)$$

The soluble H_2SO_3 is considered as the key intermediate of the oxidation. The bacteria attach onto sulfur particles and grow with the oxidation of sulfur. The sulfuric acid is released into the solution as the metabolic products. This highly acidic medium did help in mobilization of the metals into the solution. Due to high solubility nature of cobalt, it dissolves faster than lithium during the leaching process. So, in further results, leaching of cobalt has been prioritized looking at its high dissolution rate.

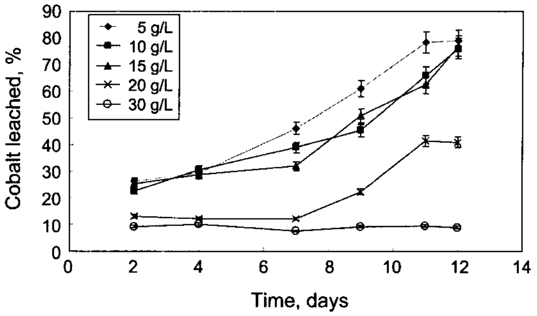

Fig. 5. Cobalt leaching at different concentration of solid waste.(time = 12 days, elemental sulfur = 15 g/L, bacteria = 4×10^8 cells/mL)

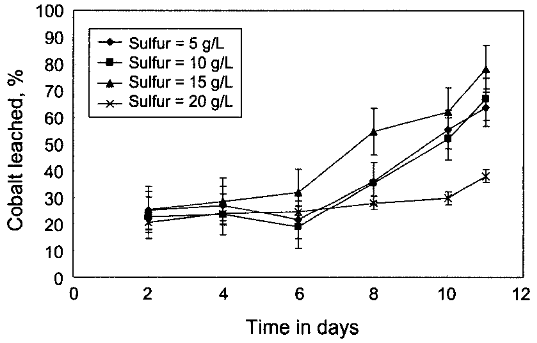

Fig. 6. Cobalt leaching at different concentration of elemental sulfur. (solid waste concentration = 15g/L, initial pH = 2.5, bacteria = 4×10^8 cells/mL)

3.2. Effect of solid/liquid (w/v) ratio

Bacterial dissolution of cobalt from the solid wastes of LIBs was carried out at different concentration of the solid waste powder varying from 5 g/L to 30 g/L, at 15 g/L of elemental sulfur concentration. The leaching result is shown in the Fig. 5. The extraction of cobalt was favored from 5 g/L to 15 g/L of solid loading and beyond this concentration the leaching of cobalt was found to be in decreasing trend. At 5 g/L of solid waste concentration, cobalt dissolution was about

79% whereas at 30 g/L it was about 9% within the time period of 12 days. It seems that higher concentration of solid wastes pose some toxic effect on bacterial growth and the adapted bacteria can limit their activity up to 15 g/L of solid/liquid ratio. At higher solid/liquid ratio, the solid elemental sulfur was observed to be in insoluble status due to inactiveness of cells. Earlier, Tuovinen *et al.*[14)] reported that cobalt was the most toxic cation among other heavy metals on the growth of *A. ferrooxidans* on an elemental sulfur medium. So, when the solid/liquid ratio was increased, the metal concentration in the LIBs increased simultaneously, and hence, the cell growth was arrested by the toxic nature of the metals.

3.3. Effect of elemental sulfur amount

Varying elemental sulfur amount from 5 g/L to 20 g/L at solid loading of 15 g/L, cobalt leaching was conducted (Fig. 6). With increase of elemental sulfur amount the leaching % of cobalt increased, however, it was limited up to 15 g/L of elemental sulfur. At 20 g/L of elemental sulfur concentration, the cobalt leaching was decreased. This may be due to the hydrophobic nature of elemental sulfur which was found to be in un-dissolved state at 20 g/L concentration within the stipulated leaching period. But, the leaching rate increased from 63% to 78% when elemental sulfur concentration increased from 5 g/L to 15 g/L. The bacteria were able to find enormous surface area to attach with the elemental sulfur and hence, the oxidation of sulfur was faster. The oxidation of sulfur could be visible by its wetting and well dispersion in the medium.

4. Conclusion

Bioleaching of cobalt from the solid wastes of lithium ion battery industry using mixed acidophilic bacteria has promising approach. Bacteria isolated from the Dalsung mine water that harbors mixed acidophilic culture, helped in leaching of the valuable metal like cobalt from the cathode waste of the battery. These bacteria could grow well while elemental sulfur was incorporated in the medium and thus sulfur oxidizing bacteria from the mine water were applied for the bioleaching test. Results revealed that the mixed acidophilic culture produced sulfuric acid by the oxidation of elemental sulfur to leach metals indirectly from the waste battery powder. Leaching of cobalt was faster than lithium in this investigation. From the experimental data, it could be concluded that about 80 % of cobalt and 20 % of lithium leached out from the solid wastes of LIBs within 12 days of the experimental period. The results were also compared with control or blank experiment where the leaching of cobalt was extensively less in absence of bacteria.

Application of mixed culture implies that the process can be industrially feasible instead of pure culture. To obtain more efficient leaching rate these mixed culture need to be adapted with higher concentration of battery waste powder. As a whole, this study infers that the mine drainage water can be utilized to isolate suitable microbial strain for the metal recovery from waste materials or sulfide minerals which can be ecologically sustainable.

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