Biorecovery of metal sulfides from leachates obtained through zinc-carbon battery recycling

Retka J.[1,*], Uhrynowski W.[1], Yang Z.[1], Karczewska-Golec J.[1], Bajda T.[2], Debiec-Andrzejewska K.[1], Drewniak L.[1]

[1] Faculty of Biology, University of Warsaw, Miecznikowa 1, 02-096 Warsaw, Poland
[2] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Mickiewicza 30, 30-059 Cracow, Poland

*corresponding author: e-mail: jretka@biol.uw.edu.pl

Abstract
One of the most commonly used methods of recycling of spent zinc-carbon (alkaline) batteries is hydrometallurgical leaching with sulfuric acid. The technology is highly efficient and enables the recovery of the majority of deposited metals. Unfortunately, it also generates highly acidic wastewaters containing significant amounts of sulfates and metal ions, which have typically been considered off-balance material.
The aim of the study was to develop a biotechnology for the recovery of metals (in the form of sulfides), based on the activity of sulfate-reducing bacteria (SRB). SRB reduce sulfates to sulfides, which bind with metal ions to produce an insoluble precipitate. To maximize the efficiency of metal sulfide biorecovery by SRB, the acidic wastewaters were pretreated with sodium hydroxide and then with biogenic ammonia (produced by urea-degrading bacteria) to reach pH 5.0. Further alkalinity was generated during organic compound decomposition carried out by SRB in cultures containing appropriately diluted, pretreated leachates.
As a result of the proposed biotechnology, metal ions and sulfates, were almost completely removed from the leachate. This way new raw materials: metal sulfides and treated (industrial-quality) water with circumneutral pH were produced.
Keywords: zinc-carbon (alkaline) batteries, recycling, acidic leachate, sulfate reducing bacteria, metal sulfide

1. Introduction

Modern hydrometallurgical technologies tend to optimize production while minimizing waste. Depending on the raw materials and technology used, the leachate is an acidic or alkaline solution and can contain significant amounts of metals and metalloids. Several effective chemical methods are used, including neutralization, electrolysis, adsorption, ion exchange, membrane separation and photocatalysis to remove acidic wastewater from hydrometallurgical processes. Chemical neutralization seems to be economically attractive (Chen et al., 2009). Dosage of alkalis means that metals in wastewater can be removed by precipitation at different pH values in the form of (hydro)oxides.
Alternatively, in the case of effluents containing both metal ions and sulfates, the treatment can also be performed using biological methods based on the activity of SRB. They reduce sulfates to sulfides, which bind with metal ions to produce an insoluble precipitate. The generated metal sulfides are characterized by low solubility and thus high stability over a wide range of pH values. This enables the separation of sludge and its further use as a raw material in metallurgical processes.
Therefore, the aim of the study was to develop a novel, low-cost biotechnology for the recovery of metals from leachates obtained through alkaline battery recycling. SRB were used as the main driving force for the reduction of sulfates and subsequent bioprecipitation of metal sulfides.

2. Materials

In the experiments, industrial leachate from alkaline battery recycling plant were used. The effluent had low pH (0.5) and a high sulfate content (~130 g/l), as sulfuric acid had been used as a leaching agent. Despite the application of appropriate separation methods (electrolysis), the leachates still contained substantial amounts of heavy metals (Table 1), including iron, manganese, nickel, and zinc.

Table 1. Element concentration (mg/l) in the raw leachate used in this study.

Al	As	B	Ba	Ca	Cd	Co
62	<5	<3	<0.3	167	61.3	42.1
Cr	Cu	Fe	K	Li	Mg	Mn
2.0	70.4	247	4036	4	39	18294
Mo	Na	Ni	P	Pb	SiO_2	Sr
<0.9	249	409	<15	<3	96	1.8
Ti	V	Zn				
1.1	<2	36049				

< below the limit of detection

3. Results

Although SRB are active under both acidic and (slightly) alkaline conditions, to facilitate effective sulfate reduction, the pH should be set between 5 and 8 (Liu et al., 2018). For economic reasons, and because the SRB activity itself leads to an increase in the pH of the culture, the pre-treatment procedure only aimed at reaching pH 5. According to the solubility tables, at this pH, precipitation of iron can be expected while other metals should still remain in the solution.

Increasing the pH of the leachate was performed with NaOH, and NH_3(aq) solutions that are commonly exploited in industrial settings due to their low price among chemical reagents. As a source of ammonia, biogenic NH_3 (further referred to as B-NH_3) produced by ureolytic (urea-degrading) bacteria and contained in the post-culture medium was used.

For the production of B-NH_3 we used nine urease-synthesizing bacterial strains, which converted urea into ammonia. For 1% B-NH_3, the precipitate emerged at pH 2.5. However, up to pH 5.0 sediment productivities in leachates pretreated with 1% B-NH_3 were low. In NaOH pretreated leachates, more dissociated free hydroxyls that aggregate impurities were generated during the titration process. The hydroxyls might have immediately reacted with ions in the leachate resulting in co-precipitation of oxides and hydroxides with not only Fe but also SO_4^{2-} and cations, such as Zn^{2+}, in the form of complex compounds, including jarosite and schwertmannite (Bigham et al., 1996).

Among tested variants, the use of NaOH to reach pH 3.5 and biogenic NH_3 in the 3.5-5 pH range was the most optimal method of raw leachate pretreatment. The biological pre-treatment stage is likely to increase the concentration of beneficial growth supplements (especially nitrogen compounds and vitamins) needed in further biological treatment.

However, following the pre-treatment substantial amounts of zinc and manganese still remained in the obtained leachate, resulting in its high toxicity. Thus, a series of SRB cultures were carried out on appropriately diluted pre-treated leachates. After 21 days of incubation under optimal growth conditions, significant (>80%) reduction in sulfate concentration and formation of a black precipitate were observed in culture variants that initially contained not more than 125, 225 and 1500 mg/L of Mn^{2+}, Zn^{2+} and SO_4^{2-} ions, respectively. It was proved that over 99% reduction in sulfate concentration and substantial removal of manganese (>84%) and zinc ions (>99%) from the liquid phase of the cultures. What is more, SRB cultivation increased pH of the cultures to approximately 7.3. The observed pH increase proves that SRB are capable of complete neutralization of the pretreated (pH 5.0) leachates. In the light of these natural SRB capabilities, the use of chemical reagents to further increase the pH from 5.0 to 7.0 is unnecessary and uneconomic.

The bioprecipitation productivity in SRB cultures carried out on media with the additon of 1.25% of the pre-treated leachates was approx. 1.3 g (dry weight) per 1 l of culture. It contained up to 10% of Mn^{2+} and 12.5% of Zn^{2+} by weight. The parameters summarizing the pH changes and concentrations of selected metal ion after subsequent stages of the treatment process are presented in Table 2.

Table 2. Metal concentration and pH changes during the (pre)treatment. Raw leachate was treated with the following agents: 40% NaOH (to reach pH 3.5), ureolytic bacteria post-culture medium containing biogenic ammonia (to reach pH 5.0), and sulfate reducing bacteria (to reach pH 7.25).

	Raw effluent	Stage I		Stage II
Treatment	—	Chem. (NaOH)	Biol. (B-NH_3)	Biol. (SRB)
pH	0.48	3.5	5.0	7.25
Fe (mg/l)	247	2.93	0.00	0.00
Zn (mg/l)	36049	31019	26960	0.03
Mn (mg/l)	18294	15426	11409	11.37

Abbreviations: Biol – biological; Chem. - chemical

4. Conclusions

To conclude, the results confirmed that combined biological and chemical treatment of acidic leachate is a solid alternative to purely chemical neutralization methods. The use of bacteria increases the pH of the leachate as well as remove metal and sulfate ions from it, is cost-effective and environmentally friendly.

The study also confirmed the potential of sulfate reducing bacteria to precipitate metal sulfides, leading to the production of both industrial-quality water and valuable raw materials for metallurgical industry. Laboratory analyses have shown promising results, indicating that combined biological and chemical treatment of hydrometallurgical wastewater can be effective.

References

Bigham, J. M., Schwertmann, U., Traina, S. J., Winland, R. L., Wolf, M., (1996), Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta*, **60(12)**, 2111-2121.

Chen, Q., Luo, Z., Hills, C., Xue, G., Tyrer, M., (2009), Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide. *Water Research*, **43(10)**, 2605-2614.

Liu, Z. H., Yin, H., Lin, Z., Dang, Z., (2018), Sulfate-reducing bacteria in anaerobic bioprocesses: basic properties of pure isolates, molecular quantification, and controlling strategies. *Environmental Technology Reviews*, **7(1)**, 46-72.