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Metallic ions catalysis for improving bioleaching yield of Zn and Mn from spent Zn-Mn batteries at high pulp density of 10%

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HIGHLIGHTS

- Metallic ions exhibited different catalytic activity towards bioleaching of ZMBs.
- 0.8 g/L Cu^{2+} catalytic bioleaching greatly enhanced mobilization of both Zn and Mn.
- A possible intermediate $CuMn_2O_4$ accounted for efficient Cu^{2+} catalytic bioleaching.
- Generation of $KFe_3(SO_4)_2(OH)_6$ stoped further bioleaching of hetaerolite.
- Chemical reaction controlled model fitted best for Cu^{2+} catalytic bioleaching.

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ABSTRACT

Bioleaching of spent batteries was often conducted at pulp density of 1.0% or lower. In this work, metallic ions catalytic bioleaching was used for release Zn and Mn from spent ZMBs at 10% of pulp density. The results showed only Cu^{2+} improved mobilization of Zn and Mn from the spent batteries among tested four metallic ions. When Cu^{2+} content increased from 0 to 0.8 g/L, the maximum release efficiency elevated from 47.7% to 62.5% for Zn and from 30.9% to 62.4% for Mn, respectively. The Cu^{2+} catalysis boosted bioleaching of resistant hetaerolite through forming a possible intermediate $CuMn_2O_4$ which was subject to be attacked by Fe^{3+} based on a cycle of Fe^{3+}/Fe^{2+}. However, poor growth of cells, formation of $KFe_3(SO_4)_2(OH)_6$ and its possible blockage between cells and energy matters destroyed the cycle of Fe^{3+}/Fe^{2+}, stopping bioleaching of hetaerolite. The chemical reaction controlled model fitted best for describing Cu^{2+} catalytic bioleaching of spent ZMBs.

1. Introduction

Zn–Mn batteries (ZMBs), including alkaline and zinc–carbon batteries, are extensively used in radios, recorders, toys, remote controls, watches, calculators, cameras, and in many other objects where small quantities of power are required [1]. As non-rechargeable primary cells, consumption of ZMBs is far more than that of secondary ones such as lithium ion batteries. Nowsdays, annual consumption of ZMBs is estimated to reach 40 billion units worldwide [2]. Accordingly, equivalent quantity of spent ZMBs is generated, which poses a serious threat to ecosystem and human health due to their toxicity, abundance and permanence in the environment [3]. On the other hand, the spent ZMBs are regard as second resources owing to very high content of 12–28% for Zn and 26–45% for Mn, which have been listed as strategic metals by many countries when facing the rising demand and limited natural resources supply [1,4]. Therefore, recycling processes for the spent ZMBs should be developed to achieve environment protection as well as effective utilization of secondary resources.

In recent years, great efforts have been focused on extraction of valuable metals Zn and Mn from the spent ZMBs [1]. Hydrometallurgical techniques are the most widely applied for the purpose, which use various strong acids such as H_2SO_4 as working media assisted by H_2O_2 or SO_2 as reducing agents [5]. Lately, application of organic matters such as glucose, sucrose, glycerine, ascorbic acid, citric acid, oxalic acid and formic acid as reductants to replace the strong acids to meet green chemistry [6–8], but an increased cost is expected. In mining industry, bio-hydrometallurgical processes (bioleaching) have been gradually replacing hydrometallurgical ones to extract target metals from low-grade ores due to their environment friendliness, low cost and few industrial requirements [9–13]. Recently, bioleaching technology has been attracting

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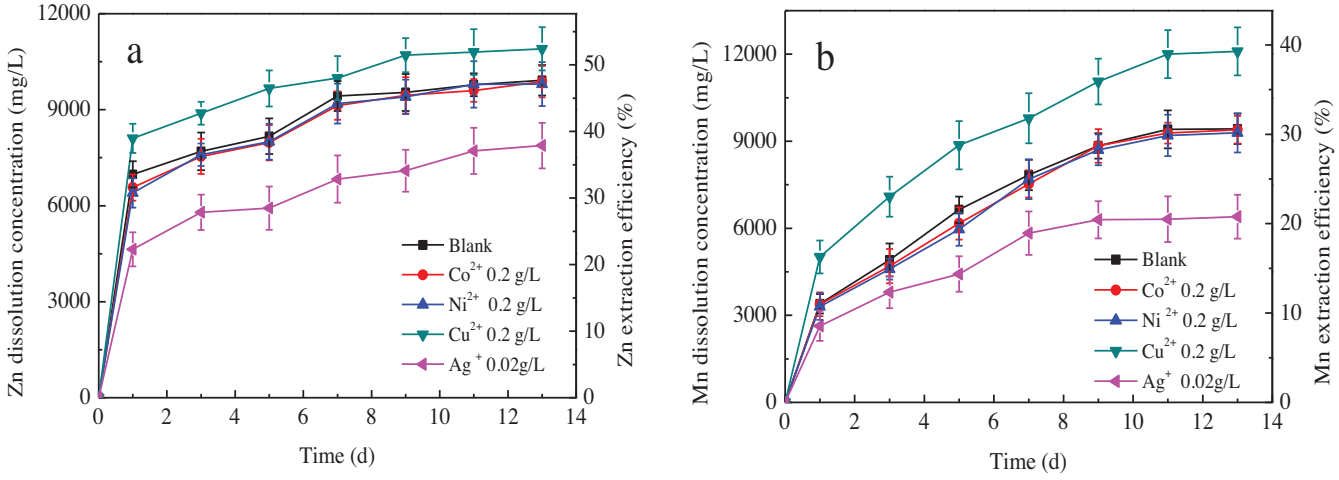

Fig. 1. Zn (a) and Mn (b) leached from the spent Zn–Mn batteries as a function of incubation time by bioleaching in the presence of various catalytic metallic ions.

growing concerns in recovery of valuable metals Co, Li, Ni, Cd, Zn, Mn from various spent batteries such as Ni–Cd batteries, lithium-ion batteries, ZMBs as the secondary resources [2,14–17], displaying a prosperous future.

In bio-hydrometallurgy/bioleaching, pulp density (i.e., ratio of solid materials weight to volume of bioleaching media) is a vital parameter which greatly affects design of bioreactor and consumption of media [18–22]. An increase in pulp density from 1% to 10% (w/v) means a sharp reduction of 90% in both volume of bioleaching media and size of bioreactor for treating per weight of solid materials, resulting in a huge decline of operation cost. In bio-hydrometallurgy of low-grade ores, pulp density is generally 10% or higher because the ores are mainly reduced sulfides ores which do not contain alkaline matter or toxic compounds. In contrast, the spent batteries always contain high concentration of alkaline matter or toxic compounds as oxides or hydroxides which greatly harm growth and activity of leaching cells. As a result, the pulp density was often only 1% or lower in bioleaching of the spent batteries [14–16,23], meaning that a significant quantity of media and a great volume of reactor were required [2]. The drawbacks of bioleaching cast a shadow on its well-established good reputation of saving energy, environment friendliness and high safety and hereby limit its commercial application in tackling spent batteries.

In bio-hydrometallurgy aiming at reduced sulfides ores, in order to deal with slow kinetics of metals dissolution, accession of catalytic metallic ions such as Cu^{2+}, Bi^{3+}, Hg^{2+}, Ag^{+} and Co^{2+} was an efficient way to accelerate electron transfer of bioleaching process and thus improve extraction performance [24–28]. Addition of 1.27 g/L Cu^{2+} as catalyst greatly enhanced Zn dissolution from sphalerite concentrate by bioleaching, and Zn extraction yield elevated from 52% to 88% [25]. Cu extraction yield from chalcopyrite concentrate by mixed cultures increased around 3-fold over the control experiment without Ag^{+}, indicating important role of Ag^{+} as catalyst in bioleaching process [28]. Lately, Cu^{2+} and Ag^{+} as catalysts also attracted attentions to improve bioleaching performance of spent batteries at pulp density of 1%. Almost all cobalt (99.9%) was bioleached from $LiCoO_2$ after 6 days in the presence of Cu^{2+}, while 43.1% of Co dissolution was obtained after 10 days without Cu^{2+} [28]. Ag^{+} at 0.02 g/L also displayed an evident enhancement on bioleaching performance of Co from $LiCoO_2$, and its release yield rose from 43.1% to 98.4% [29]. Except for the spent lithium ions cathode material $LiCoO_2$, however, there was no any report available regarding catalytic bioleaching of any other spent batteries by metallic ions despite very poor bioleaching performance at higher pulp density due to alkaline matter or toxic compounds.

Considering the huge amount of spent ZMBs and high concentration of both Zn and Mn in them, recovery of Zn and Mn from the spent ZMBs becomes a hot subject worldwide. Nearly 100% of Zn recovery and 89% of Mn recovery were achieved at pulp density of 4% by bioleaching through conditions optimization, but bioleaching of ZMBs still faced great challenge at high pulp density of 10% due to low efficiency. In this work, catalytic bioleaching was used

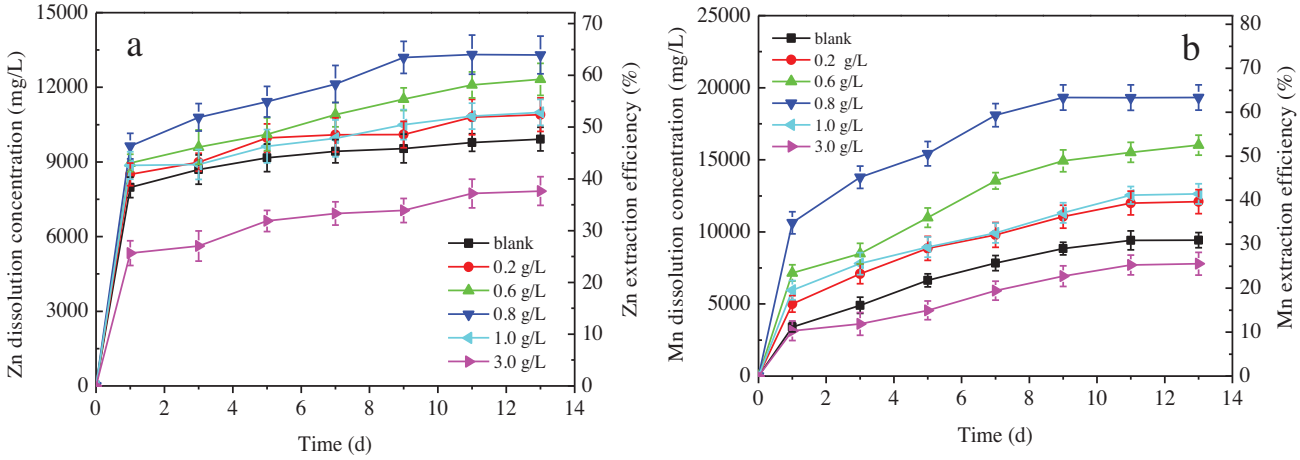

Fig. 2. Zn (a) and Mn (b) leached from the spent Zn–Mn batteries as a function of incubation time by Cu^{2+} catalytic bioleaching under varied concentrations of Cu^{2+}.