Minerals Engineering 81 (2015) 1–4

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Leaching of valuable metals from red mud via batch and continuous processes by using fungi

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ARTICLE INFO

Article history:
Received 24 December 2014
Revised 16 July 2015
Accepted 24 July 2015
Available online 28 July 2015

Keywords:
Bioleaching
Red mud
Valuable metals
Aspergillus niger
Continuous bioleaching

ABSTRACT

Bioleaching of valuable metals (Ga, Ge, V, Sc, La, Eu, Yb) from red mud was examined. Batch and continuous leaching experiments were deployed by using the filamentous fungi, *Aspergillus niger*. The leaching results showed that there was a strong negative relation between biomass and pH value. In batch leaching test, the best leaching performance was achieved under spent medium process at 2% pulp density. And in continuous leaching test, the system can reach a steady state at high red mud pulp densities (10%) with a pH value below 3.0. Comparing to organic and inorganic acids leaching, the continuous leaching mode which produces organic acids through glycometabolism by using *A. niger* is cost effective in a laboratory scale.

1. Introduction

Red mud is a chemical waste generated by the alkaline extraction of Alumina from bauxite in the refinery. The global red mud storage is estimated to be over 2.7 billion tonnes nowadays, and still increasing rapidly (Klauber et al., 2011). Unfortunately, utilization of red mud is very difficult due to its alkalinity, salinity and radioactivity (Gräfe et al., 2011).

Red mud is regarded as a "polymetallic raw material" or an "artificial ore" with high amounts of valuable metals, e.g., gallium, germanium, vanadium and rare earth elements (REEs) (Klauber et al., 2011). Recovering these valuable metals from red mud is a potential choice to deal with the dilemma of natural ores shortage. Leaching metals from red mud into solution is the first step to recover them. Comparing to conventional chemical leaching process, bioleaching is generally considered as a "green technology" which can be applied to avoid the high cost and negative environmental impact (Santhiya and Ting, 2005).

Therefore, the objective of this study is to investigate the leaching of red mud by using *Aspergillus niger* which have a high organic acid production. Two different bioleaching mode—batch and continuous leaching were employed in the experiments, and the leaching ratios of Ga, Ge, V, Sc, La, Eu and Yb from red mud were determined.

2. Materials and methods

2.1. Red mud samples

The fresh red mud samples were collected from the bauxite residue storage area (26°41′N, 106°35′E) of Chinalco by using sterile laminated stainless steel containers. They were transported to the library, dried to constant weight in the oven at 80 °C, ground using a porcelain mortar and pestle and dry screened through 74 μm sieves.

2.2. Microorganisms

A. niger (ITS sequence GenBank accession JF909353), provided by the Research Center For Bio-Resource & Technology, Institute of Geochemistry, Chinese Academy of Sciences, was used in the bioleaching. *A. niger* were inoculated on potato dextrose agar (PDA) at 30 °C for 7 days. The mature conidia were washed off from the surface of the solid slant with a sterile solution of physiologic

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http://dx.doi.org/10.1016/j.mineng.2015.07.022
0892-6875/

saline (9 g/L NaCl). The number of spores was counted using a hemocytometer and adjusted to approximately 10^7 spores/mL.

2.3. Batch bioleaching in shake flask

2 mL of spore suspension was added to 100 mL of sucrose medium (autoclaved at 121 °C for 15 min) with the composition (g/L): sucrose 100; KNO_3 0.5; KH_2PO_4 0.5; yeast extract 2.0; peptone 2.0. Bioleaching experiments were conducted using 250 mL Erlenmeyer flasks containing 100 mL of sucrose medium in an orbital shaking incubator at 30 °C and 120 rpm. Three series of bioleaching processes were carried out: (i) incubating the fungi together with the red mud and medium (one-step process); (ii) pre-culturing *A. niger* for 3 days, then adding the red mud (two-step process); (iii) using cell-free spent medium after 10 days incubation of *A. niger* (spent medium process). Experiments were terminated when there were no obvious changes in the pH value. All experiments were run in triplicate.

2.4. Continuous bioleaching in stirred tank reactor

The continuous leaching were performed in a round-bottomed glass tank with 30 cm height and 30 cm diameter. The reactor was equipped with a pH and DO (Dissolved Oxygen) detector, a temperature controller, an air distributor, and a mechanical stirring device mounted on a rotating shaft. The feed made up of red mud slurry and sucrose medium solution was stored in a reservoir which was connected into the reactor by a peristaltic pump. Air was continuously injected into the liquid medium through the air distributor at the bottom of reactor. When the feed continuously flowed into the reactor, an equal volume of slurry was withdrawn at the exit by a suction tube. The reactor was charged with 12 L of liquid medium constantly.

2.5. Chemical leaching

Chemical leaching tests were conducted in 500 mL Erlenmeyer flasks at 30 °C, 120 rpm, solid-to-liquid ratio of 10, and leaching time of 120 h. The pH value of leachate was adjusted to 3.0 by using different kinds of acids.

2.6. Analytical methods

All the analytical methods were described in detail in our previous studies (Qu and Lian, 2013; Qu et al., 2013). The metals leaching percentage were calculated by material balance through the concentration in leachate divided by total concentration in shake flask or feed flow.

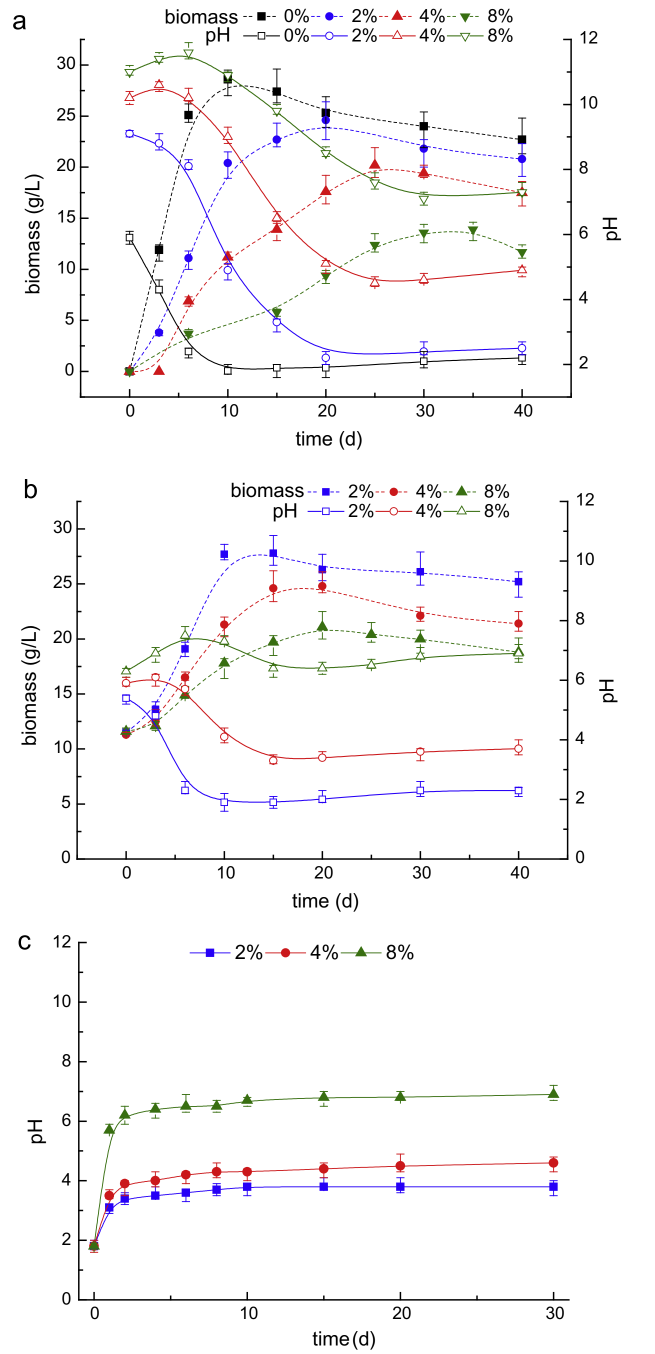

Fig. 1. Biomass and pH variation in function of time at different red mud pulp densities in batch tests under (a) one-step process, (b) two-step process, and (c) spent medium process.

3. Results and discussion

3.1. Element composition of red mud

The weight concentration of valuable metals in red mud (ppm): Ga (570); Ge (53); V (4220); Sc (158); La (416); Eu (110); Yb (28). La, Eu and Yb were chosen as the representatives of light, middle and heavy rare earth elements, respectively.

3.2. Batch bioleaching

The pH and biomass changes in batch leaching tests are shown in Fig. 1. There is a strong negative correlation between biomass and pH value. This indicates that the metabolic activities of the fungi play a crucial role in reducing pH value. It is well known that the acidification of leaching medium is due to the organic acids excreted by fungi (Klauber et al., 2011).

When increased the pulp densities of red mud, the biomass decreased, and the lag phase of fungal growth increased. This phenomenon indicates that red mud has a drastically adverse impact on fungal growth. Comparing to one-step process, *A. niger* had a better growth condition and organic production in two-step process.

Fig. 2 shows the leaching efficiency under different bioleaching processes and red mud pulp densities. With an increase in red mud pulp densities, the leaching efficiencies of all processes decreased. However, the decreasing tendencies were different. The spent

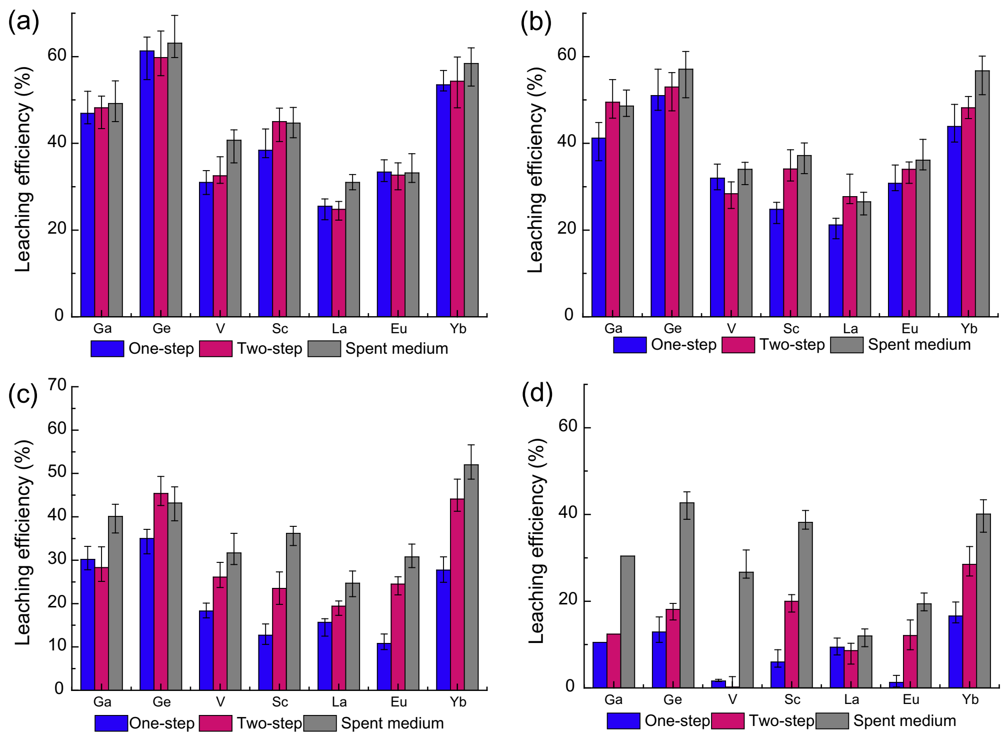

Fig. 2. Extraction efficiencies of valuable metals from red mud by using *Aspergillus niger* under various bioleaching processes in batch test at the pulp densities of: (a) 2% (w/v), (b) 4% (w/v), (c) 6% (w/v), and (d) 8% (w/v).

medium process showed the lowest decreasing tendency, while the one-step process showed the highest. The best leaching ratios were achieved under spent medium process at 2% pulp density, at about 63% of Ge, 59% of Yb, 50% of Ga, 44% of Sc, 40% of V, and over 30% of Eu and La.

The previous study believed that the valuable metals were worth to be recovered when a uniform total concentration exceeded 0.1% (Petropulu et al., 1996). In view of the elemental composition in our red mud sample, Ga, V, La, Sc, and Eu are worth to be recovered.

The high performance liquid chromatography tests showed that *A. niger* mainly secreted citric, oxalic and gluconic acid (data were not shown). With an increase of pulp densities, the production of both citric and gluconic acid decreased, while the oxalic acid slightly increased.

3.3. Continuous bioleaching

A discontinuous leaching stage is necessary for fungi to obtain a steady growth in the reactor. Therefore, a discontinuous stage was designed before continuous leaching. The sucrose medium with 2% (w/v) of red mud was feed into the reactor, and 200 mL of spore suspension was inoculated. The discontinuous leaching operating conditions: 30 °C; agitation rate of 300 rpm; air flow rate of 180 L/h. After 60 h of cultivation for *A. niger*, the pH value in the reactor decreased to the lowest point of 1.9, and the biomass reached the maximum of 23.1 g/L. Then the mode of operation was converted to the continuous bioleaching.

The initial experimental parameters of continuous leaching were the same as discontinuous leaching, but the residence time was set as 48 h. At the beginning of the continuous tests, the pH of solution increased, which indicated that the biomass in the reactor was diluted through the feeding of fresh liquid medium and the output of bioleached pulp. Subsequently the pH value was fluctuating until 4 days later and then constantly remain below 2.0. By this time, it was considered that *A. niger* was adapted to the continuous leaching mode and the organic acids production were stable. Under this condition the leaching percentages of metals were as follows: 54% of Ga, 60% of Ge, 37% of V, 45% of Sc, 27% of La, 30% of Eu and 62% of Yb.

When increased the red mud concentration to 10%, the pH of liquid medium in the reactor drastically increased. Therefore the experimental parameters were adjusted. After 15 days of running, the continuous leaching system was steady with a pH value below 3.0. The parameters were as follows: temperature of 30 °C; agitation rate of 250 rpm; air flow rate of 280 L/h; residence time of 96 h. The leaching percentages of metals were: 31% of Ga, 33% of Ge, 19% of V, 30% of Sc, 16% of La, 23% of Eu and 44% of Yb.

Based on our experiments results, prolonging residence time was beneficial to fungi growth at high red mud concentration. But when over 6 days, the positive effect was marginal. An excessive agitation rate can exert a negative effect on continuous leaching system. This is probably because that the violent shear force will smash the mycelium and restrain the fungal metabolism. However, moderate agitation is indispensable since it can homogenize the solid, liquid and gas phases in the reactor.

In order to survey the cost performance of continuous leaching by using fungi, it was compared with organic and inorganic acids leaching (Table 1). The pH value of all the chemical leaching tests was controlled at 3.0, for in accordance with that in continuous leaching. The data showed that the leaching efficiencies of organic acids were higher than that of inorganic acids, which is probably because the organic acids can increase the leaching ability through the chelation or complexation with metal ions.

The continuous leaching mode by using fungi had almost the same metal leaching efficiencies as citric acid leaching. But the estimated cost of continuous leaching was only half of that of citric acid leaching, and it was also lower than that of oxalic and HCl leaching. This result indicates that the continuous leaching mode which produces organic acids through glycometabolism by using

Table 1
Estimation cost to extract 1 ton of red mud by using fungi, inorganic and organic acids.

Leaching mode	Consumption	Metals leaching ratios from red mud (%)							Estimated cost[c] (¥)
		Ga	Ge	V	Sc	La	Eu	Yb	
Aspergillus niger[a]	1 t (sucrose)	31	33	19	30	16	23	44	2600
H_2SO_4[b]	110 L	13	12	5	12	3	10	7	1320
HCl[b]	338 L	17	14	10	9	5	11	22	4056
Oxalic acid	232 kg	24	24	19	16	8	18	34	3248
Citric acid	309 kg	33	30	17	27	16	25	41	4944

[a] In continuous leaching mode at 10% pulp density (operating parameters are shown in Section 3.3).
[b] Mass concentration of H_2SO_4 and HCl were 98% and 37% respectively.
[c] The prices of reagents were given by Fine Chemicals Store of Alibaba Group.

A. niger is cost effective in a laboratory scale. Though the agitation, aeration and other power consumption will increase the expenditure, the carbon resources sucrose can be substituted for organic wastes such as whey permeate, molasses and kitchen garbage, which will decrease the total cost.

However, this is only a preliminary study on continuous bioleaching of red mud. In view of the applied potentiality of continuous leaching by using fungi, deeper research need to be carried out.

Acknowledgements

This work was supported by the youth research funding of Luoyang Institute of Science and Technology, and funding of Education Department of Henan (15A180049).

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