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Bioleaching of valuable elements from red mud using autochthonous biomass

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Abstract. Red mud (RM) is the main residue produced by the alkaline extraction of aluminum from bauxite, and it contains valuable metals (e.g., iron, aluminum, titanium, silicon). Aim of this research was to investigate the biologically induced leaching of valuable elements from RM using autochthonous biomass, in order to simultaneously reduce RM polluting potential and extract metals for their subsequent recovery. Such approach is challenging, since high alkalinity and pH, as well as the absence of sulphides, constrain the use of traditional bio-hydrometallurgical techniques. Bioleaching tests were performed at different temperatures (22°C, 28°C) and solid to liquid ratios (S/L: 2%, 5%), using a leaching medium containing glucose, yeast extract and ethanol. The best results were achieved at 28°C and S/L ratio of 5%: pH rapidly dropped from 9.7 to 6.25 and remained constant till the end of the test. Metal concentrations in the liquid phase were 2%-Fe, 8%-Al and 1%-Ti. As expected, iron was less available to leaching at such pH, as it was mostly present as hematite in RM. Abiotic contribution to metals leaching was negligible. Results are promising, and further investigations are needed to favor pH drop to lower values, with a consequent increase in metals bioleaching.

Keywords: bioleaching, circular economy, metals recovery, red mud.

1. Introduction

Aluminum is one of the most important light metals, commonly present in nature as oxide (Alumina, Al_2O_3), in a mineral known as bauxite (Qu et al., 2019). The alkaline extraction of alumina from bauxite is called Bayer process, which is based on caustic soda (NaOH) to chemically dissolve the bauxite compounds and to extract the aluminum oxide (Ghorbani at al., 2008). The bauxite residue produced from this process is called red mud (RM). Nowadays, about 95% of alumina is extracted from bauxite ores, and 90% of it is extracted by the Bayer process (Vakilchap at al., 2016). The RM contains the substances originally present into the bauxite (e.g., Al, Fe, Ti, Si, etc.) and the minerals originated during the Bayer process (Ghorbani et al., 2008). Due to its composition, RM is defined as a ‘‘polymetallic raw material’’ or an ‘‘artificial ore’’ (Qu et al., 2015).

RM is largely studied because of its potentially dangerous impact on the environment. It can cause soil contamination, surface freshwater and groundwater pollution, and even seawater contamination due to fine particles suspension (Vakilchap et al., 2016). Failure of dams has already caused the release of metals in the environment. In 2010, a red mud lake released one million cubic meters of liquid in Ajka (Hungary), causing the death of several people (Qu & Lian, 2013).

The recently updated critical raw materials (CRM) list (EIT, 2021) defines as “strategic materials” those used in digital applications and linked to energy storage, for instance Cu, Al, Ni and Fe. Europe is lately using 23% of the world’s mine production while only producing 2-3% of it. In this light, Europe’s aim is to shift from linear to circular economy, fostering sustainable development (EIT, 2021; ERA-MIN, 2013). This translates in moving toward a “zero waste” economy, as stated by several opportunities such as the UN Agenda 2030 goals (UN Sustainable Development Goals, SDG, 2021). Hence, exploiting new “unconventional” deposits like RM represents a key step toward industrial competitiveness (EIT, 2021).

A way to recover valuable substances in RM is to leach metals into solution. The chemical extraction using different types of acids, such as sulfuric, nitric and hydrochloric acids, has been largely used and studied (Qu et al., 2019). An alternative treatment could be bio-hydrometallurgy, which exploits the metabolism of one or more microorganisms to achieve the leaching of metals from solid wastes, ores or minerals (Jain & Sharma, 2004; Sethurajan et al., 2018).

The bio-hydrometallurgical process can be defined as relatively inexpensive and environmentally friendly, since it requires low energy supply and very low or no chemical dosage (Jain & Sharma, 2004; Lee & Pandey, 2012; Qu et al., 2013). In particular, bioleaching is applied to low grades ores and rocks, but also to mining and industrial wastes containing metals, and to sewage sludge (Jain & Sharma, 2004).

The most studied topic in bioleaching field is the sulphide bioleaching mediated by chemoautotrophic microorganisms such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. However, these bacteria are not suitable for metals recovery from RM due to the absence of sulfur in bauxite residues and their high alkalinity (Vachon et al.,1994).

Microbial extraction of metals from non sulphidic ores has been less studied. Non sulphidic ores can be leached using metabolites produced by heterotrophic bacteria and fungi (Jain & Sharma, 2004). Fungi were widely studied (Ghorbani et al., 2008; Qu et al., 2015, 2013; Vakilchap et al., 2016) to extract metals from RM, whilst less attention has been paid to bacteria so far (Qu et al., 2019; Vachon et al., 1994), due to the harsh environment provided by RM: in previous studies (Ghorbani et al., 2008; Qu et al., 2015, 2019; Qu & Lian, 2013; Vakilchap et al., 2016), a selected biomass was inoculated into sterilized RM to investigate the bioleaching of metals.

Based on the hypothesis that biomass can adapt and survive in such a harsh environment, the aim of this research was to evaluate the biological activity and bioleaching potential of autochthonous biomass in RM, in the perspective of process application in engineered systems. Among several metals contained in RM, the fate of Fe, Al and Ti was investigated, due to their well-recognized economic importance.

2. Materials and Methods

2.1. Red Mud

Red mud produced by the Bayer process was collected from a storage site in Europe, and characterized in terms of pH, electric conductivity (EC), acid neutralization capacity (ANC), content of metals and mineral composition.

2.2. Bioleaching experiments

The experiments were carried out in batch mode, using 500 ml glass bottles. For the bioleaching tests, RM was not de-hydrated in order to preserve the autochthonous biomass possibly colonizing the system. Leaching medium (400 ml) consisting of 30 g/l of ethyl alcohol 96%, 10 g/l of glucose, and 10 g/l of yeast extract, according to Qu et al. (2019), was added into each bottle. Different solid to liquid (S/L) ratios were used: 2% and 5% (w/v). Each solid concentration was tested with two different temperatures (22°C and 28°C), for a total of four experimental conditions. The different temperatures are associated to room temperature and to an optimal temperature for mesophilic microorganisms, that is usually employed for bioleaching experimentations, also with RM (Qu et al., 2019). Each test was carried out in duplicate. The tests lasted about 31 days, during which the slurry was stirred at 120 rpm. In order to avoid oxygen limitation, the batches were aerated for three hours once a week. The abiotic control was performed under the same conditions of batch experiments, with the addition of $HgCl_2$ (2 g/L).

2.3 Analytical methods

To determine EC and pH, dry RM (100 g) was added to 500 ml distilled water for 16 h (Qu & Lian, 2013). RM chemical composition was analyzed by ICP-OES (PerkinElmer 7000 Optima) after a total digestion according to EPA method 3052. Mineralogical composition was determined by XRD, using a Rigaku GegerFlex D-Max diffractometer with a Cu Kα anode operating at 30 kV and 30 mA. The diffraction patterns were collected at angular range of 4 to 70°, with a step size of 0.02°.

The ANC was assessed by mixing several subsamples of dry RM with distilled water containing pre-selected amounts of acid (HNO_3) at a L/S=10 l/kg and stirring the suspension for 48 h (UNI CEN/TS 15364).

At regular intervals (i.e., twice per week), 15 ml samples were taken from the bottles and centrifuged at 5000 rpm for 15 minutes to eliminate the solid part. The supernatant was filtered at 0.45 µm and used to evaluate pH and metals concentration (ICP-OES). Metals extraction efficiency was calculated according to the following equation:

$$Extraction\ [\%] = \frac{Metal\ in\ leachate\ [mg]}{Metal\ in\ RM\ [mg]} \cdot 100$$

3. Results and discussion

The average pH, EC and $ANC_{4.5}$ of RM were respectively 10.5, 20.8 mS/cm and 4.4 mmol H^+/g. The high pH is explained by high content of the several alkaline elements.

Table 1 shows the concentrations of some chemical elements in RM.

Table 1. Chemical composition of RM

Elements	%	Elements	%
Fe	19.6 ± 0.8	K	0.02 ± 0.01
Al	3.0 ± 0.2	Na	4.67 ± 0.01
Mg	0.03 ± 0.01	Ti	3.45 ± 0.07
Ca	2.08 ± 0.04	Si	1.80 ± 0.02

In all the experiments, pH decreased very quickly (days 0-7), and it remained basically stable in the neutral range till the end of the tests. The decrease in pH can be reasonably attributed to microbial activity, since the abiotic control did not show any pH variation. Table 2 shows the initial and the lowest pH values achieved during the treatment for each batch configuration.

Figure 1 shows the pH trend observed during batch test #D, in which the best results were achieved in terms of pH decrease. The pH values observed in our study are higher in comparison to others reported in literature (Ghorbani et al., 2008; Qu et al., 2015, 2019; Qu & Lian, 2013; Vakilchap et al., 2016), in which a strictly acid environment was achieved using selected cultures.

Table 2. Initial and lowest pH values measured in batch tests

Batch test # (T, S/L)	Initial pH	Lowest pH
A (22 °C, 2%)	9.52	7.25
B (28 °C, 2%)	9.50	6.51
C (22 °C, 5%)	9.70	7.08
D (28 °C, 5%)	9.70	6.25

One reason for such difference might be ascribed to the lowest biomass concentration, since no inoculum was added in our study, combined with the higher ANC of the RM, compared to other studies (Qu et al., 2019; Qu & Lian, 2013).

The best results were achieved at 28 °C, thus confirming the temperatures indicated by Qu et al. (2019) as optimal for mesophilic metabolisms (28-30 °C). As for the effect of the L/S ratio, higher amounts of solids in the reactors led to lower pH values, likely due to the higher initial content of biomass in the system.

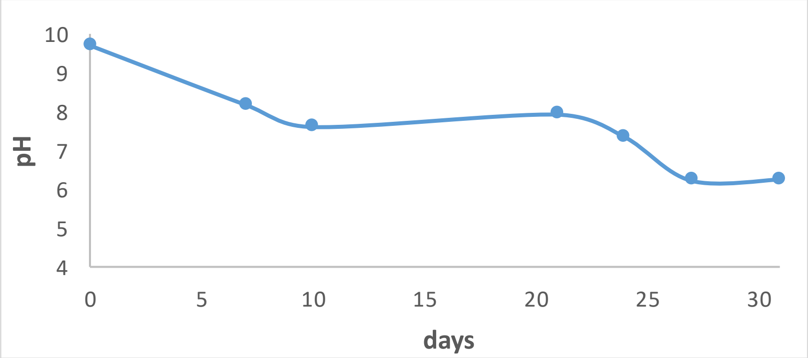

Figure 1. pH trend of batch test #D

The highest extraction of metals, as shown in Table 3, is to be attributed to the lowest pH values achieved in batch test #D.

Table 3. Average extraction efficiencies achieved in batch experiments

Batch test (T, S/L)	Fe [%]	Al [%]	Ti [%]
A (22 °C, 2%)	0.40	1.40	0.52
B (28 °C, 2%)	0.12	2.00	0.68
C (22 °C, 5%)	0.10	2.62	0.70
D (28 °C, 5%)	1.77	8.25	0.90

The observed extraction efficiencies were lower than those achieved in previous studies using pure cultures of *Acetobacter* and *Aspergillus niger* (Qu et al., 2019; Vakilchap et al., 2016). Such lower extraction efficiency can be ascribed to the absence of any inoculum in our tests. The biomass already presents in RM was able to produce metabolites that could leach some metals: the results achieved at the end of test #D are the starting point to switch to semi-continuous operation, in the perspective of process scale-up. Moreover, the identification of autochthonous microbial communities actually involved in the bioleaching may drive the selection of possible biomass inocula and the choice of a specifically tailored leaching medium, thus fostering biomass enrichment with consequent decrease in pH.

Despite the higher content of iron than aluminum in RM, a greater Al extraction efficiency was achieved, likely due to RM mineralogical composition. As shown in Figure 2, the main mineralogical components of untreated RM were Hematite (Fe_2O_3), Calcite ($CaCO_3$), Sodalite ($KNa_3Al_3Cl(SiO_4)_3$), Rutile (TiO_2) and Weddellite ($Ca(C_2O_4)$-$2(H_2O)$), and the mineralogical composition is compatible with its chemical composition for major elements (Table 1).

Comparison between the XRD analyses of untreated and treated RM shows a similar composition, but with a clear decrease in almost all peak intensities, consistent with a likely decrease in concentrations following the bioleaching treatment. An exception to this trend is Weddellite, whose peak intensity significantly increased after the bioleaching process. The process released aluminum more than iron, this might be due to more insoluble iron components contained in RM such as hematite. This mineral phase needs a more acidic environment to be leached.

4. Conclusion

In this study, the possibility to exploit the activity of autochthonous biomass to achieve bioleaching of valuable metals from RM was successfully assessed.

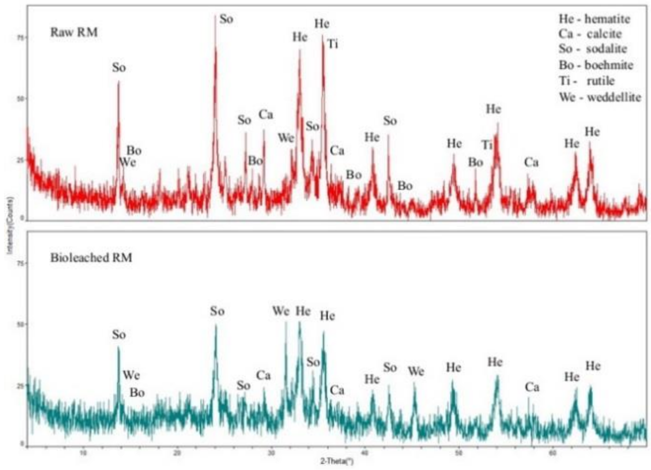

Figure 2. XRD Analyses of raw and bioleached RM

Despite the harsh environment, pH dropped from alkaline to neutral values in all the conditions tested. High S/L ratio and temperature were proved to enhance pH drop and consequent metals release in the liquid phase. All the elements of interest (i.e., Fe, Al, Ti) were released, and the highest extraction efficiency was achieved for Al. Results are promising, and further investigation is needed in order to foster pH decrease and strengthen acidic conditions, thus maximizing metals release.

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