Available online at www.sciencedirect.com
ScienceDirect
Applied Clay Science 37 (2007) 251–257
Applied Clay Science
www.elsevier.com/locate/clay

Bioleaching of iron from highly contaminated Kaolin clay by *Aspergillus niger*

M.R. Hosseini [a], M. Pazouki [b,*], M. Ranjbar [a], M. Habibian [c]

[a] *Department of Mineral Processing, Engineering Faculty, Shahid Bahonar University, Kerman, Iran*
[b] *Department of Energy, Materials and Energy Research Center, MeshkinDasht, Karaj, Iran*
[c] *Department of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran*

Received 18 July 2006; received in revised form 23 January 2007; accepted 26 January 2007
Available online 2 February 2007

Abstract

Kaolin is a clay mineral that has a wide application in the industry specially, in paper, ceramic, and porcelain manufacturing. One of the most important factors that affects the value of this raw material is its brightness. Unfortunately, with the iron oxides deposit on mineral particles during kaolin formation, much of this clay has become unusable for industries. So, several chemical methods have been applied in mineral processing plants to reduce these contaminants, but finding a more sustainable approach like biological methods have always attracted a great attention. In this work bioleaching of iron from a highly contaminated kaolin sample was carried out using two different strains of *Aspergillus niger*, and the effects of strain type, pulp density, and time of clay addition on the iron removal were investigated by employing a 2^3 full factorial design. Finally, it is concluded that strain type has the most significant effect on the response; also, the highest removal extent was 42.8% that was obtained by using the strain isolated from pistachio shell, and at the pulp density of 20 g/l when the clay was added at the beginning of the experiments.

Keywords: Kaolin; Bioleaching; *Aspergillus niger*; Iron removal

1. Introduction

Kaolin clay is a hydrous alumino silicate ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) (Asmatulu, 2002), and an essential resource in porcelain and ceramic manufacturing (Ryu et al., 1995; Styriakova and Styriak, 2000), production of paper, pigments, and fillers. Clay is formed by the mechanical and chemical breakdown of rocks; also, depending on the atmospheric and geological condition of deposition, as well as the degree of alteration of the clay, iron (hydr)oxides (usually Fe^{3+} forms) are commonly precipitated or adsorbed to the clay surfaces or admixed as a separate phase (Murad, 1987; Stucki et al., 1988) that make much of the kaolin unusable for commercial application due to insufficient whiteness (Styriakova and Styriak, 2000), and the reduction of refractoriness of products (Lee et al., 2002). So, for the reasons mentioned above, the quality of kaolin is measured in terms of iron content (Lee et al., 2002).

Some researchers have developed different physical and chemical techniques (and recently microbiological) with the purpose of removing the ferric iron present as oxide or hydrated oxide in the clay. These techniques generally include magnetic separation, froth flotation, selective flocculation, size separation by hydrocyclones, and leaching (Styriakova and Styriak, 2000; Lee et al.,

* Corresponding author. Tel.: +98 261 6208943; fax: +98 261 6201888.
E-mail address: mpazouki@merc.ac.ir (M. Pazouki).

0169-1317/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2007.01.010

2002). However, the removal efficiency of iron is low because the iron in kaolin may be tightly adsorbed or it may be in a complexed form (Lee et al., 2002) that is not easily separated by the first four methods. Most of the industries have employed potent chemical reductants such as dithionite or hydrazine to remove iron impurities but these chemicals are not the cause of iron reduction in nature (Kostka et al., 1999); also, removal of only the poorly crystalline or more readily soluble iron oxide phases can be carried out using various methods such as ammonium oxalate or dilute HCl extractions (Stucki et al., 1988). Complete separation or removal of iron oxide phases by chemical means without in some way altering the remaining phase is unlikely (Manceau et al., 2000). Furthermore, the clay structure collapses during reduction in response to the reduction of structural Fe (Kostka et al., 1999); also, chemical methods have high operating costs and environmental impacts.

Field observations and laboratory experiments demonstrate that microbes can accelerate aluminum silicate mineral weathering reactions in direct contact with mineral surfaces, by producing organic and inorganic acids, creating metal-complex ligands, changing redox condition or mediating formation of secondary mineral phase (Styriakova and Styriak, 2000). Therefore, microorganisms which oxidize or reduce iron should be considered as a new and alternative method to remove iron impurities from kaolin (Lee et al., 2002). Microbial leaching is thought to be less energy-intensive than high temperature chemical processes and requires low capital and operating costs (Ryu et al., 1995), and causes less environmental problems (Mulligan et al., 2004).

In this work, the ability of two strains of *Aspergillus niger* to remove iron (hydr)oxides from a highly contaminated kaolin, and influence of some effective parameters on removal efficiency is studied.

2. Materials and methods

2.1. Kaolin sample

Kaolin sample with the particle size of 90% under 9.32 μm (d_{90}=9.32 μm) was supplied by Mehrkhak Company, Tehran, Iran from a deposit located in Damghan, Semnan Province, Iran that is unsuitable for using in ceramic body in sanitary ware manufacturing, because of its high content of iron oxides (11% Fe_2O_3).

2.2. Microorganisms and culture media

Two different strains of *A. niger* were used in the experiments. One *A. niger* NCIM 548 that was kindly provided by Dept. of Chem. Eng., IIT Madras, India, and the other was originally isolated from pistachio shell.

A solid media (malt extract, 30 g/l; meat peptone, 3 g/l and agar, 15 g/l, at pH 5.6) was employed for the growth and maintenance of the microorganism at 30 °C. A synthetic media (Cameselle et al., 2003) containing sucrose, 120 g/l; NH_4NO_3, 450 mg/l; KH_2PO_4, 100 mg/l; $MgSO_4{\cdot}7H_2O$, 300 mg/l; $FeSO_4{\cdot}7H_2O$, 0.1 mg/l; $ZnSO_4{\cdot}7H_2O$, 0.25 mg/l was employed as culture media.

2.3. Bioleaching of mineral samples

Fungal spores were suspended from a 7-day agar slant in a sterile solution (0.1% Tween80, and 0.9% NaCl) and enumerated by a microscope. Bioleaching experiments were carried out in 500-ml Erlenmeyer flasks containing 100 ml of culture media inoculated at a concentration of 10^6 spores/ml, and incubated at 30 °C, and 160 rpm on a rotary shaker. Amounts of 2 and 6 g of kaolin were added to the culture media in the beginning of the cultivation and on the third day. All experiments were performed in duplicate, and the average of the results reported, were with 2% deviation.

2.4. Methods of analysis

In order to determine the kaolin composition, and specially its iron contents, XRF analysis was done by ARL 8410 instrument, tube anode: Rh, and 60 kV (Table 1). Also, to determine kaolin particle size, particle size analysis made by Fritsch Particle Sizer "Analysette 22".

To analyze the amount of removable iron by a leaching process, iron was extracted from the kaolin by heating it for 15 to 20 min in 6 N HCl (Lee et al., 2002), and then total iron content was determined by the 1,10-phenanthroline method (Jeffery et al., 1989).

To register the changes in pH value, and dissolved iron concentration, sampling was done in determined intervals. Then the solid phase was separated, and the pH value of the liquor was measured by Metrohm pH meter model 744; also dissolved iron concentration was measured by the 1,10-phenanthroline method (Jeffery et al., 1989).

To calculate the removal percent of the iron, the measured dissolved iron concentration in the cultured media was divided

Table 1
Chemical composition of the clay sample

Component	P_2O_5	MnO	TiO_2	MgO	K_2O	Na_2O	CaO	Fe_2O_3	AL_2O_3	SiO_2
Percent	0.105	0.001	2.729	0.45	2.19	0.19	0.09	11.11	25.82	44.78