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Research paper

Kinetic modeling of the bioleaching process of iron removal from kaolin

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ABSTRACT

A kinetic model was developed to assess the influence of batch cultivation of *Aspergillus niger* on the bioleaching of iron from kaolin. A simple model was proposed using the logistic equation for growth, and the Luedeking–Piret equations for iron removal, acid formation and sucrose consumption. The performance of the model was compared against that obtained by the empirically experimental data. The model provides a reasonable description for each parameter during the growth phase. The experimental results also suggest that the product formation depends upon both the instantaneous biomass concentration, and growth rate.

1. Introduction

Weathering of rocks generates large volumes of clays including kaolins, and quartz sands, as well as other minerals, especially iron and titanium oxides. Kaolin is an economically important raw material often used in a wide variety of ceramic applications, from high quality tableware and sanitary ware to electrical porcelain, tiles and glasses. However, Fe oxyhydroxides are also usually present, rendering some kaolins unusable for commercial applications due to insufficient whiteness. Hence kaolins need to be beneficiated by removal of mineral impurities, mica constituents and other iron-bearing minerals before their use in some of the above-mentioned purposes. Although physicochemical procedures, such as magnetic separation and flotation, could be used for beneficiation of kaolin, they are expensive. On the other hand, biological methods are cheaper and have less adverse environmental impact (Štyriaková and Štyriak, 2000). Optimum results have been obtained by the microbially produced organic acids, especially oxalic acid (Kawatra and Natarajan, 2001). At ambient conditions, the highest iron-leaching activity was observed with the culture media filtrate from an oxalic acid producing *Aspergillus niger* strain (Mandal and Banerjee, 2004) *A. niger* produces three organic acids: gluconate, citrate, and oxalate (Magnuson and Lasure, 2004). Oxalic acid is the most promising because of its acid strength, good complexing characteristics and high reducing power, compared to other organic acids (Lee et al., 2006). It functions: i) by direct attack of H^+ ions, which removes iron from the kaolin; and ii) by formation of a stable complex, which, in a following step can be easily removed (Cameselle et al., 1998). Biological processes for iron removal have also been evaluated based on the use of *A. niger*. Cameselle et al. (1998) studied the capacity of two strains of *A. niger* to remove iron from a Fe-rich kaolin and compared "in situ" and "two stage" bioleaching techniques. Mandal and Banerjee (2004) evaluated the iron-dissolution rate equations from clay using oxalic acid or *A. niger* culture filtrate with respect to temperature, pH, solids concentration and oxalic acid concentration. Hosseini et al. (2007) investigated the effects of strain type, pulp density, and time of clay addition on the iron removal from a Fe-rich kaolin by employing a 2^3 full factorial design.

Generally, kinetic models are experimentally derived and fit the cultivation data reasonably well (Kiviharju et al., 2007). In most environmental applications of biological systems, biokinetic models describing the rates of substrate utilization and biomass accumulation are useful for understanding the mechanisms resulting to microbial growth (Ahn et al., 2005). Fermentation models are normally divided into structured models that take into account some basic aspects of cell structure, function, and composition, and in unstructured models; however, only cell mass is employed to describe the biological system (Zand et al., 2004). The easiest technique for kinetic modeling is the application of an unstructured kinetic model.

In a previous study (Aghaie et al., 2009), a response surface methodology, and central composite design were applied to optimize the bioleaching of iron from a kaolin sample by *A. niger* isolated from pistachio shell. Therefore, in order to expand our knowledge on this process, more detailed experiments were performed and kinetic models for the microbial growth, product formation and substrate uptake were obtained.

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2. Materials and methods

2.1. Microorganism and culture conditions

A. niger was originally isolated from pistachio shell. The medium utilized for growth was composed of malt extract, 30 g/l, meat peptone, 3 g/l and agar, 15 g/l, at pH 5.6. The culture was kept for 7 days at 30 °C in this medium to obtain sufficient numbers of spores. For fermentation, a medium with the following composition was used: sucrose, 30 g/l; NH_4NO_3, 0.45 g/l; KH_2PO_4, 0.1 g/l; $MgSO_4 \cdot 7H_2O$, 0.3 g/l; $FeSO_4 \cdot 7H_2O$, 10^{-4} g/l; $ZnSO_4 \cdot 7H_2O$, 25×10^{-5} g/l (Cameselle et al., 1998).

2.2. Kaolin sample

The kaolin sample with $d_{80} = 4.4$ μm was supplied by Mehrkhak Company, Tehran, Iran from a deposit located in Damghan, Semnan province, Iran, containing 2.19% w/w Fe_2O_3. The chemical and mineralogical composition of the sample is presented in Tables 1 and 2.

2.3. Bioleaching experiments

The initial pH, and sucrose and spore concentration of the bioleaching experiments were set to 2.5, 30 g/l, and 87×10^7 spores/l, respectively. The sterile solution (0.1% w/w Tween80 and 0.9% w/w NaCl) was used to recover the spores from a 7-day agar slant (Cameselle et al., 1998). Subsequently, the spores were counted using a microscope. Bioleaching experiments were carried out in 500-ml Erlenmeyer flasks containing 100-ml of culture medium at 30 °C and 160 rpm on a rotary shaker for 35 days. Also, 3 g of kaolin was added to the culture media at the beginning of the experiments. Bioleaching experiments were performed in duplicate culture and the averaged value of the measurements was calculated.

2.4. Analytical methods

The concentration of biomass was calculated from the cell dry weight, which was determined by a gravimetric method. The biomass suspension was centrifuged, washed several times with distilled water and dried to a constant weight at 90 °C. The liquid filtrate was used for analysis. Dissolved iron concentration was determined by the 1,10-phenanthroline method (Jeffery et al., 1989). Sugar was estimated colorimetrically according to Nelson (1944), and Somogyi (1952), after hydrolysis of the spent media. Oxalic acid concentration was estimated by $KMnO_4$ titration (Jeffery et al., 1989).

3. Kinetic models

Different kinetic equations were fitted to the cultivation data using Matlab 7.4 software. The equation used for growth estimation was logistic equation. For substrate consumption, and product formation, Luedeking–Piret equations were applied. The models employ rate parameters of biomass (X), iron, oxalic and citric concentrations (P) and substrate concentration (S) to describe the bioleaching process.

3.1. Microbial growth

When microbial cells were incubated into a batch culture containing fresh culture media, an increase in cell concentration was observed. It is common to use cell dry weight to measure cell concentration. The simplest relation describes exponential growth as an unstructured model. Microbial cell growth is an autocatalytic reaction, in which the growth rate is proportional to the cell concentration initially present in the media. The batch system is a closed system, which would only maintain cell viability for a limited time, and the growth cycle changes progressively from one phase to another in the remaining media and environmental conditions. The logistic equation leads to a lag phase, an exponential initial growth rate and a stationary population of concentration (X_m). Often the birth rate decreases as the population itself increases, due to the increased substrate consumption, and subsequent lack of carbon source (Najafpour, 2007).

The logistic equation is a substrate independent model. It can finely describe the inhibition of biomass on growth, which exists in many batch fermentations (Liu et al., 2003). The logistic equation can be described as follows:

$$dX/dt = \mu_m X(1 - X/X_m) \tag{1}$$

where μ_m is the maximum specific growth rate (1/day) and X_m is the maximum attainable biomass concentration (g dry cell weight/l). Integration of Eq. (1) using $X = X_0$ ($t = 0$) gives a sigmoid variation of X as a function of t which may represent both an exponential and stationary phase (Eq. (2)):

$$X = \frac{X_0 \, e^{\mu_m t}}{1 - (X_0/X_m)(1 - e^{\mu_m t})}. \tag{2}$$

3.2. Product formation

The relationship between biomass and the product for the bioleaching process by *A. niger* could be simulated by the Luedeking–Piret model (Liu et al., 2003):

$$dP/dt = \alpha dX/dt + \beta X \tag{3}$$

where α is the growth-associated formation coefficient of product, while β is non-growth-associated formation coefficient of product.

This model was originally proposed for describing the lactic acid production by *Lactobacillus delbrucckii* (Luedeking and Piret, 1959). The first term of Eq. (3), i.e., $\alpha \cdot dX/dt$, is referred to as the growth-associated formation rate of product and implies that the growing cells yield the product in constant proportion of their growth. Non-growth associated product formation term (βX) shows that all the microorganisms yield the product in a constant proportion of their concentration, regardless of the growth phase (Mu et al., 2006).

Eq. (3) can also be written as follows:

$$dP = \alpha dX + \beta X dt. \tag{4}$$

Table 2
Mineralogical composition of the clay sample.

Major phase	Minor phase
Kaolinite [$Al_2O_3 \cdot SiO_2$]	Quartz [SiO_2] Iron sulfate [$FeSO_4$] (trace) Illite [$KAl_3Si_3AlO_{10}(OH)_2$] Goethite [FeO(OH)] (trace)

Table 1
Main chemical composition of the clay sample.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	TiO_2	MnO	P_2O_5
Amount (%)	56.380	23.570	2.190	0.130	0.190	2.720	0.500	2.662	0.001	0.108