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Research paper

Designing and optimization of separation process of iron impurities from kaolin by oxalic acid in bench-scale stirred-tank reactor

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ABSTRACT

Kaolin leaching by oxalic acid in a bench-scale stirred-tank reactor using response surface methodology and face centered central composite design based on three variables: oxalic acid concentration (X_1: 0.1–0.3 M), temperature (X_2: 30–80 °C) and duration of the leaching test (X_3: 2–4 days) was investigated. The experimental data obtained were fitted to a second-order polynomial equation using multiple regression analysis by Design-Expert 7 software and were analyzed by analysis of variance (ANOVA). According to ANOVA, all factors (X_1, X_2 and X_3) influenced the response (dissolved iron concentration) and a positive regression coefficient of variables suggested an increase in dissolved iron concentration with an increase in oxalic acid concentration, temperature and time of leaching but there was not any interaction between them. The 3-D response surface plot and the contour plot derived from the mathematical model were applied to determine the optimal conditions. The optimum leaching conditions for maximum dissolved iron concentration were found to be oxalic acid concentration of 0.21 M, temperature of 77 °C and duration of the leaching test of 4 days. After the washing stage of kaolin, in those experiments that pH was above 4, iron oxalate precipitate was formed and the percentage of residual iron in the sample after leaching was higher than expected. In general, the minimum amount of residual iron in the kaolin was 0.75% (w/w) that was obtained in tests where the oxalic acid concentration, temperature, time of the leaching and pH of final solution were 0.3 M, 30 °C, 2 days and 3, respectively.

1. Introduction

Kaolin is one of the most important industrial clay minerals. It is comprised predominantly of the mineral kaolinite, a hydrated aluminum silicate. Kaolinite is a common clay mineral but the relatively pure and commercially useable deposits are few in number (Murray, 2006). Kaolin is used in industries such as pottery, paint, plastics, paper, cements, pharmaceuticals and cosmetics (Gámiz et al., 2005). Mostly due to their low cost, easy availability and non-toxicity, kaolin can be used as adsorbents in pollution control processes such as of heavy metal ions, organic pollutants such as dyes and pesticides in water purification treatments. Kaolin has also been tested for drug adsorption and controlled release as well as supports for enzyme catalysts (Castellano et al., 2010).

Kaolinite has physical and chemical properties which make it useful in a great number of applications (Murray, 2006). The whiteness is one of the most important factors in determining the application and economic value of kaolinite. In general, the most deleterious impurities for the whiteness of kaolin are iron oxide and titanium oxide minerals (Chandrasekhar and Ramaswamy, 2006; Xia et al., 2012). Iron is present mainly in the following minerals: goethite, hematite, magnetite, pyrite and ilmenite (Bertolino et al., 2010). To reach the specification required by the market, it is necessary to eliminate impurities from kaolin, mainly iron impurities, through beneficiation processes (Santos et al., 2012). These processes generally included magnetic separation, froth flotation, selective flocculation, and size separation by hydrocyclones and leaching (He et al., 2011). Among these methods, leaching is the most effective approach, using primarily sulfur dioxide, sodium dithionite or thiourea and commercial organic acids. Oxalic acid is found to be the most promising organic acid because of its acid strength, good complexing characteristics and high reducing power (Ambikadevi and Lalithambika, 2000). Using oxalic acid, the dissolved iron can be precipitated from the leach solution as iron (II) oxalate dihydrate, which can be represented as a useful potential feedstock for added-value products (Du et al., 2011). Oxalic acid can be produced both by chemical and fermentative processes. Due to increasing demand in hydrometallurgy and for wider applications in other processes, production of oxalic acid from a cheap carbon source by fermentation appears more attractive as an eco-friendly, non-hazardous microbial process yielding this acid at a lower cost. Among the varieties of fungi producing oxalic acid, *Aspergillus niger* is the organism of choice for its efficient productivity (Mandal and Banerjee, 2005).

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Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes in which a response of interest is influenced by several variables and the objective is to optimize this response. RSM has an important application in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables, alone or in combination, on the processes (Baş and Boyac, 2007).

Several studies have evaluated the kaolin processing by different methods (Guo et al., 2010; Tuncuk et al., 2013; Zegeye et al., 2013) especially with oxalic acid and oxalic acid-producing strains of *A. niger*, to reduce its iron impurities and increase its quality (De Mesquita et al., 1996; Raghavan et al., 1997; Taxiarchou et al., 1997; Ambikadevi and Lalithambika, 2000; Cameselle et al., 2003; Mulligan et al., 2004; Calderon et al., 2005; González and Ruiz, 2006; Lee et al., 2007; Du et al., 2011; He et al., 2011; Martínez-Luévanos et al., 2011; Xia et al., 2012). In the previous studies (Hosseini et al., 2007; Aghaie et al., 2009), firstly, bioleaching of iron from a highly contaminated kaolin sample using two different strains of *A. niger* was carried out on laboratory scale 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. Secondly, *A. niger* isolated from a pistachio shell was applied to remove iron impurities from an Iranian kaolin sample. In order to study the effects of initial pH, sucrose and spore concentration on oxalic and citric acid production, and consequently iron dissolution, response surface methodology based on a five-level, three-variable central composite design of experiments was employed. In these studies, the highest iron removal was 67.4% (w/w).

So far, most of the reported research has been performed on a laboratory scale. For instance, in Musiał's et al. (2011) work, the process of kaolin bleaching involved an oxalic-acid-enriched, fermented medium from the cultivation of *A. niger* XP, the carbon and energy source being biodiesel-derived waste composed of glycerol and fatty acids. This is a novel method of utilizing a waste by-product of the biofuel industry. Oxalic acid was produced during submerged batch culture in a bioreactor. Leaching tests were performed in a thermostated 2-liter glass vessel. In addition, Zegeye et al. (2013), Martínez-Luévanos et al. (2011), He et al. (2011) and Cameselle et al. (2003), conducted their experiments in small scaled flasks.

Therefore, it is necessary to identify the important factors that influence the performance of both of the iron leaching from kaolin by oxalic acid and biological production of oxalic acid processes in large-scale systems.

The stirred tank reactor can be considered the basic chemical reactor; modeling on a larger scale than the conventional laboratory flask. Reactors can economically handle moderate volumes of material, but they allow for a close control of the variables involved, rendering significantly better performances (Acevedo, 2000).

Tank sizes range from a few liters to several thousand liters. They are used for homogeneous and heterogeneous liquid–liquid and liquid–gas reactions and for reactions that involve freely suspended solids, which are held in suspension by agitation. As the degree of agitation is under the designers' control, stirred tank reactors are particularly suitable for reactions where good mass transfer or heat transfer is required. They are operated as batch reactors or continuous reactors (Nanda and Pharm, 2008). Since results obtained in the bench-scaled reactor can be extrapolated, with slight correction, to the real situation they will help show whether kaolin leaching by oxalic acid is possible under acceptable conditions. In the present study, after designing the experiments by Design-Expert7 software, leaching of iron from a kaolin sample [3.07% (w/w) Fe_2O_3] was carried out using oxalic acid in a bench-scale stirred-tank reactor. The effects of oxalic acid concentration, temperature, and time on the iron removal extent were investigated by employing a central composite design.

2. Materials and methods

2.1. Kaolin sample

A kaolin sample containing 3.07% (w/w) Fe_2O_3 with the particle size of 80% under 7.93 μm (d_{80} = 7.93 μm) was provided by Madan Goharan Company, Isfahan, Iran. The chemical and mineralogical compositions of the sample were obtained by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively (Tables 1 and 2).

2.2. Analysis methods

In order to determine the kaolin composition, and specially its iron contents, XRF and XRD analyses were performed on an ARL 8410 instrument, tube anode: Rah, and 60 kV. In addition, kaolin samples, in an X-ray diffraction apparatus, model EQUINOX 3000 produced by INEL, France, were exposed to Cu-Kα1 radiation (wavelength used = 1.540598 Å). Powder X-ray diffraction must be done with fine-grained samples. Therefore, a fine-grained sample was prepared by sieving or grinding it in a mortar and pestle. The sample is then put into the middle of the well of the sample holder and pressed flat with a glass slide. Several pressings are usually necessary, in between cleaning off powder from around the well. It is important that the top of the sample be coplanar with the top of the sample holder. In addition, XRD examination was carried out with a range of $0° < 2\theta > 180°$, step size: 0.030, scanning speed: 15°/min, counting time: 10 min and slit width: 20 mm.

To determine the kaolin particle size distribution, particle size analysis was performed on a Fritsch Particle Sizer "Analysette 22". Dissolved iron concentration and residual iron concentration of kaolin after leaching by oxalic acid (Merck product) and three washing steps were measured by Atomic absorption/flame emission spectrophotometer SHIMADZU model AA-6800.

2.3. Leaching tests in stirred tank reactor

In this study, a stirred tank reactor made of glass with a working volume of 3 l was used. The set up of the reactor is shown in Fig. 1. The main column consisted of an internal tube of 10 cm internal diameter and 50 cm height, an external tube of 13 cm internal diameter and 50 cm height. Hot air generated by two electric elements embedded inside a tank was blown by the blower into the space between the two tubes so that the temperature of reactor contents was increased. The desired temperature in each test was attained by using a thermostat and a thermometer mounted on the reactor. When the reactor reached the desired temperature, elements and blower were turned off by the thermostat. In the reactor, agitation with a speed of 100 rpm was achieved by an electric motor and double blade agitator. In each leaching experiment, the stirred tank reactor was fed with 2.5 l slurry of 10% solid content and oxalic acid. The pH of slurry was adjusted to 2.5–3 using dilute NH_4OH.

2.4. Design of experiments

Response Surface Methodology (RSM) consists of a group of mathematical and statistical techniques that are based on a fit of empirical models to the experimental data obtained in relation to the experimental design. Toward this objective, linear or square polynomial function is employed to describe the system studied and, consequently, to explore (modeling and displaying) experimental conditions until its optimization. Some stages in the application of RSM as an optimization

Table 1
Chemical composition of the kaolin clay sample.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	TiO_2	SO_3	L.O.I.
Amount (%)	55.80	25.60	3.07	0.38	0.42	0.57	0.42	0.78	2.21	9.26