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Research article

Effect of the acid treatment conditions of kaolinite on etheramine adsorption: A comparative analysis using chemometric tools

Paulo Vitor Brandão Leal [a, b], Zuy Maria Magriotis [c, *], Priscila Ferreira de Sales [d], Rísia Magriotis Papini [e], Paulo Roberto de Magalhães Viana [e]

[a] Colegiado do Bacharelado em Ciências e Tecnologia da Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39.440-000, Janaúba, MG, Brazil
[b] Departamento de Química, Universidade Federal de Lavras, 37200-000, Lavras, MG, Brazil
[c] Departamento de Engenharia, Universidade Federal de Lavras, 37200-000, Lavras, MG, Brazil
[d] Instituto Federal de Educação Ciência e Tecnologia de Minas Gerais - Campus Bambuí, 38900-000, Bambui, MG, Brazil
[e] Departamento de Engenharia de Minas, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil

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ABSTRACT

The present work evaluated the effect of the acid treatment conditions of natural kaolinite (NK) regarding its efficiency in removing etheramine. The treatment was conducted using sulfuric acid at the concentrations of 1 mol L^{-1} (KA-01), 2 mol L^{-1} (KA-02) and 5 mol L^{-1} (KA-05) at 85 °C. The obtained adsorbents were characterized by X-ray fluorescence, X-ray diffraction, N_2 adsorption/desorption isotherms, zeta potential analysis and infrared spectroscopy. The Response Surface Method was used to optimize adsorption parameters (initial concentration of etheramine, adsorbent mass and pH of the solution). The results, described by means of a central composite design, were adjusted to the quadratic model. Results revealed that the adsorption was more efficient at the etheramine concentration of 400 mg L^{-1}, pH 10 and adsorbent mass of 0.1 g for NK and 0.2 g for KA-01, KA-02 and KA-05. The sample KA-02 presented a significant increase of etheramine removal compared to the NK sample. The adsorption kinetics conducted under optimized conditions showed that the system reached the equilibrium in approximately 30 min. The kinetic data were better adjusted to the pseudo-second order model. The isotherm data revealed that the Sips model was the most adequate one. The calculation of E_{ads} allowed to infer that the mechanism for etheramine removal in all the evaluated samples was chemisorption. The reuse tests showed that, after four uses, the efficiency of adsorbents in removing etheramine did not suffer significant modifications, which makes the use of kaolinite to treat effluents from the reverse flotation of iron ore feasible.

1. Introduction

In the past years, the mining activity has led to studies on its sustainability due to the concern about environmental and social issues that surround this industry in the world. These studies have been increasingly focused on the need for a modern mining model inserted in a more sustainable context in which annual reports of companies relate not only their financial results, but also their performance regarding the sustainable use of resources (Mudd, 2010). In this sense, the use of water resources stands out once, during the mining process, the activities linked to ore beneficiation consume an expressive amount of water. Among such activities, flotation is the most widely used step for ore concentration, which consumes approximately 5 m^3 h^{-1} of water per ton of processed ore. Moreover, it uses different chemical reagents to make the process feasible (Magriotis et al., 2010).

Flotation is the most effective solution, from both a technological and economical point of view, for the beneficiation of iron ore. Research on this method started in 1931 demonstrating that reverse cationic flotation is an efficient method for the beneficiation of oxidized iron ore. Flotation may also be applied to reduce the silica content in magnetite concentrate (Filippov et al., 2014). Despite the high applicability to the industry of iron ore, it is verified that this ore beneficiation step presents some problems associated with the great metal waste and high costs of amine

* Corresponding author.
E-mail addresses: paulo.leal@ufvjm.edu.br (P.V.B. Leal), zuy@deg.ufla.br (Z.M. Magriotis), priscila.sales@ifmg.edu.br (P.F. Sales), risia@demin.ufmg.br (R.M. Papini), pviana@demin.ufmg.br (P.R.M. Viana).

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collectors (Ma et al., 2011). It is important to highlight that the etheramine applied as cationic collector in the process of reverse flotation of iron ore is discarded in tailings dams, which requires the search for alternatives to recover this reagent (Araújo et al., 2010).

The degradation of etheramine, a reagent used in the reverse flotation of iron ore, occurs by the action of microorganisms, which happens in approximately 28 days. However, with the continuous process of sedimentation, this degradation may be insufficient leading to the contamination of watercourse. This reagent is corrosive, very toxic to aquatic organisms and has a high value of chemical oxygen demand (Magriotis et al., 2010). This fact shows the importance to reuse part of this reagent because of economical or environmental aspects. Therefore, adsorption can be an interesting alternative for the treatment of this effluent.

Adsorption has been considered one of the most efficient and economical processes for the removal of pollutants from water, which stands out due to its low cost and operational limits (Poonkuzhali et al., 2014). Among a great variety of adsorbents that can be used, clay minerals have been used as an alternative to make adsorption feasible for different processes.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is defined as a clay-mineral type 1:1, consisting of two basic units. The first consists of an octahedral layer composed by oxygen atoms and hydroxyl groups in a compact way, in which atoms of aluminum, iron and magnesium are arranged in this coordination. The second is called tetrahedral unit of silica in which the silicon atom in the center is equidistant from four oxygen atoms or possibly hydroxyls (Morsy et al., 2014).

Clay minerals are low-cost, abundant and generally safe materials for environmental applications due to the possibility of having different characteristics such as high porosity, surface charge and surface functional groups. They can be used as adsorbents, filters, flocculators and carbon stabilizers. Moreover, their physicochemical and mechanical properties allow structural, textural and chemical changes, which makes them good adsorbents and carriers of organic compounds (Perez et al., 2014; Yuan et al., 2013).

During acid activation, exchangeable cations of the clay are replaced by H^+ ions from the acid, causing partial modifications to the crystalline structure of the acidified material. The effect of such modification contributes to the increase in surface acidity, surface area and porosity. The material resulting from the acid treatment consists of one part of the starting mineral and the other of a porous, protonated and hydrated amorphous silica phase with a three-dimensional cross-linked structure (Ugochukwu et al., 2014); (Komadel and Madejová, 2012).

There are two ways one can investigate the effect of a large number of variables. The most commonly used method involves the variation of one variable, while keeping the other variables constant, until all variables have been studied. This methodology has two disadvantages: first, a large number of experiments are required, and second, it is likely that the combined effect of two or more variables may not be identified (Frontistis et al., 2017). One way to avoid these flaws is to consider a statistical approach with an experimental design.

Chemometric tools have been frequently applied to methods to optimize analysis as they reduce the number of required experiments, among other advantages that result in a lower consumption of reagents and duration of experiments These tools allow the simultaneous study of several control parameters and the development of mathematical models to evaluate the relevance and significance of the studied parameters. Furthermore, they facilitate the evaluation of interactions among parameters. There are two types of variables in multivariate projects: (i) qualitative and quantitative responses and (ii) factors, which can be selected by fractional or complete factorials to obtain results of significant effects over the analytical response (Tarley et al., 2009; Asadollahzadeh et al., 2014).

The optimization through the factorial design and response surface analysis is largely applicable. For adsorption, the application of a statistical experimental design may increase product yield and reduce the variability, costs and duration of the process (Chatterjee et al., 2012). Therefore, research has been conducted in order to combine factorial design and response surface to optimize the removal of contaminants of distinct classes that include dies (Chatterjee et al., 2012; Ravikumar et al., 2006; Sales et al., 2013; Singh et al., 2011) and heavy metals (Garg et al., 2008; Kavalathy et al., 2009).

In this context, the present work aimed to investigate the influence of chemical treatment on the adsorption capacity of etheramine by kaolinite using the Response Surface approach for the optimization of parameters of the adsorption process (initial concentration of adsorbate, adsorbent mass and pH of solution).

2. Materials and methods

2.1. Adsorbate

For the tests of adsorption, solutions of amine Flotigan EDA - etheramine acetate with dodecyl radical neutralized at 30% (Clariant) - from a storage solution with concentration of 2 g L^{-1} were prepared.

2.2. Adsorbent

The *in natura* kaolinite used as adsorbent and matrix for the chemical treatments was provided by Mineradora Química e Minérios from the city of Ijaci in the state of Minas Gerais, Brazil. For the adsorption tests, kaolinite was crushed and sieved through a 0.42 mm mesh (35 Tyler).

2.3. Modification of kaolinite by acid treatment

The acid treatments were performed with solutions of sulfuric acid at different concentrations (1 mol L^{-1}, 2 mol L^{-1} and 5 mol L^{-1}) under reflux at 85 °C and agitation, for 3 h. After the treatment, the samples were filtered with deionized water until neutral pH and dried in a lab oven at 100 °C for 2 h. The samples KA-01, KA-02 and KA-05 were crushed and sieved through a 0.42 mm mesh (35 Tyler).

2.4. Characterization of adsorbents

The chemical composition of the adsorbents was determined by X-ray fluorescence (Phillips CUBIX 3600). The XRD analyses were conducted in a spectrophotometer, model Philips PW1710, using CuKα_1 radiation with scan of 4° and 9° (2θ) and scan rate of 0.6°θ s^{-1}. The specific surface area of adsorbents was determined through the measurement of adsorption and desorption of nitrogen at −196 °C with the Brunauer-Emmett-Teller method (BET) in a Micrometrics ASAP 2020. To determine the zeta potential, suspensions of the adsorbent (particle size < 37 μm) were deposited/conditioned in bottles at 22 °C during 2 h at pH from 2 to 12 with a solution of 2 mmol L^{-1} of sodium nitrate as supporting electrolyte. The measurements of potentials were conducted in a Zeta Meter model ZM3-DG, in which the applied tension ranged from 75 to 200 mV. The infrared spectra were obtained from an ATR analysis (Attenuated Total Reflectance) with an interval from 4000 to 400 cm^{-1}, resolution of 4 cm^{-1} and 64 scans in a Bruker Vertex70V series spectrometer.