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Study of chemical and thermal treatment of kaolinite and its influence on the removal of contaminants from mining effluents

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ABSTRACT

The effects of chemical and thermal treatments on the structure of kaolinite were examined, as well as the influence of those changes upon the removal of etheramine, a cationic collector used in the processing of iron ore. The materials were characterized using XRD, XRF, specific surface area (S_{BET}), FTIR, zeta potential and a test for determination of acid sites. The effects of the treatments on the structure of kaolinite were evaluated using chemometric tools developed from principal components analysis algorithms and hierarchical components analysis. The parameters evaluated in the kinetic study of adsorption were contact time, initial concentration of etheramine, quantity of adsorbent and pH. The adsorption of etheramine in the samples subjected to chemical treatments could be explained by a pseudo-second order model, whilst for the sample subjected to thermal treatment, better fit was with the pseudo-first order model. With regard to adsorption isotherms, it was shown that for the three adsorbents used, adsorption followed the Langmuir model. The maximum quantities adsorbed were 27 mg g^{-1}, 29 mg g^{-1} and 59 mg g^{-1}, respectively, for the samples subjected to acid, thermal and peroxide treatments. The treatment with peroxide was found to be the most suitable for removal of etheramine.

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1. Introduction

In the 21st century, environmental pollution is one of the principal threats to all living beings. Among the different types of pollution, the degradation of water resources is especially noteworthy and constitutes one of the greatest problems of current times (Nandi et al., 2008).

Among the main industries that contribute to the environmental pollution, like the chemical, textile, food industries, pulp and paper, the mining-metallurgical industry plays a major role. Although mining is indispensable for the proper development of our society and is of economic benefit to the country, mining activity can have harmful environmental consequences arising from the increasing use of reagents intended to secure greater efficiencies in mineral processing.

The mining process can be divided in the mine operations, blasting and transporting the crude ore, and the beneficiation process. Flotation is the most commonly used process for concentrating minerals and it uses a considerable amount of water; on average 5 m^3 h^{-1} per tonne of mineral processed (Magriotis et al., 2012; Ciminelli and Barbosa, 2008). Flotation plants can be found throughout the world and the flotation process is responsible for obtaining the most part of all metals produced in the world. The concentration of iron-ore is usually done by means of reverse flotation using etheramine acetate as cationic collector (Araújo et al., 2005). The world iron ore production in 2010 reached 2.2 billion tones leading to a total amine consumption of approximately 15,000–20,000 tones per year (Magriotis et al., 2010).

Etheramines are corrosive, toxic to aquatic organisms, and have a high Chemical Oxygen Demand (COD) value. Although they are considered biodegradable, the degradation of etheramines takes place over approximately 28 days. Even so, the silting-up of ore tailings dams and the possible overflow from them via the spillway

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may make the residence-time of the etheramines in the tailing dams insufficient for their degradation, which is a risk to the environment (Araújo et al., 2010; Magriotis et al., 2010).

Thus processes have emerged that seek to minimize the environmental impacts and regularize secondary pollutants, such as photocatalytic degradation processes, biological degradation, precipitation, coagulation, membrane separation processes, chemical oxidation, electrochemical techniques. Among these, adsorption is coming to the fore, and is of notable importance to the mineral industry, given that it has appropriate characteristics of ease of operation and economic viability (Karaoglu et al., 2010).

The search for adsorbents that combine satisfactory properties and are at the same time eco-friendly is gaining importance, whilst cost is always an additional parameter when working at the industrial level (Bhattacharyya and Gupta, 2009; Gupta and Suhas, 2009). From among a vast quantity of adsorbents that might be used, clay minerals are being singled out as having ready availability and a notably lower price, when compared to other materials that have been used (Ptácek et al., 2011; Karaoglu et al., 2010; Bhattacharyya and Gupta, 2009; Lin and Juang, 2009).

Kaolinite, a phyllosilicate of type 1:1, would appear to be a promising adsorbent, as it is chemically inert at pH values between 4 and 9, is low-priced and easily available. The presence of a permanent negative charge means that kaolinite could be used for the removal of positively charged compounds, such as, in this case, etheramine in ionic form (Karaoglu et al., 2010; Cristóbal et al., 2009).

The efficiency of clay minerals in adsorption processes can be enhanced through structural modifications obtained by intercalation, pillarization, chemical and thermal treatments (Panda et al., 2010). In the application of treatments, the current tendencies seek to produce purer materials with greater specific areas, making them more competitive and attractive for industrial use. Among the treatments used, chemical treatments (carried out with acid or peroxide) and thermal treatments are prominent.

The acid treatments consist of leaching the clay samples in solutions of inorganic acid, promoting the disaggregation of the clay particles and the elimination of impurities. As a result of these changes, the treated materials have an increase in acidity, surface area and pore-diameter (Panda et al., 2010). The treatment with peroxide is responsible for the elimination of organic matter, without, however, altering its chemical composition (Melo et al., 2010). The thermal treatments consist of calcining the clays in order to make them thermally stable materials. The changes brought about depend on the degree of disorder of the crystalline structure and on the rate of heating (Michot et al., 2008). Chemical and thermal treatments can cause profound changes in the starting sample, and the use of multivariate statistics is fundamentally important in determining their influence upon the structural properties of the clay mineral.

Once used, the algorithms developed retain a considerable amount of information expressing interrelationships that exist between the variables, thereby making possible the identification of similarity between the samples (Boruvka et al., 2005; Webster, 2001). Of particular note among these algorithms are hierarchical component analysis (HCA) and principal components analysis (PCA), classified as exploratory because they do not take into account the identity of the samples. Chemometric tools are being used, for example, in analysis of drinking water (Estarelles et al., 2001), analysis of the physical characteristics of activated sludge from water treatment systems (Tomita et al., 2002) and monitoring of residual water in treatment works (Aguado and Rosen, 2008), among others.

In this context, the aim of this work was to investigate the effect of chemical (acid and peroxide) treatments and thermal treatment on the structure of kaolinite through the use of characterization techniques and computational tools, as well as to verify the influence of these treatments upon the removal of etheramine, a reagent used in mineral processing.

2. Experimental

2.1. Adsorbate

The adsorption tests were carried out using the amine Flotigam EDA (Clariant) as adsorbate: etheramine acetate with dodecyl radical, neutralized at 30%. The solutions of etheramines used in the experiments were diluted from a 2 g L^{-1} solution.

2.1.1. Adsorbents treatments

The natural kaolinite (KN) was provided by Mineradora Química e Minérios of Ijaci, Minas Gerais state, southeast Brazil. The sample was subjected to chemical (acid and peroxide) treatments and thermal treatment.

2.1.2. Adsorbents treatments

The acid treatment was carried out with hydrochloric acid solution 6 mol L^{-1}, for 3 h, at a temperature of 90 °C under reflux and shaking. The solid/liquid ratio was 1 g of kaolinite per 30 mL of acid solution. After treatment, the sample was washed with type II water until pH neutral and dried at 100 °C for 24 h. The sample was macerated and sieved (sieve 0.425 mm − Tyler series), resulting in sample KA. The peroxide treatment was carried out with hydrogen peroxide (35% v/v) for 3 h at a temperature of 25 °C. The solid/liquid ratio was 45 g of kaolinite per 1000 mL of peroxide. The sample was washed in type II water until pH neutral and dried at 60 °C for 12 h. The sample was macerated and sieved (sieve 0.425 mm − Tyler series), resulting in sample KP. The thermal treatment was carried out in a muffle oven for 5 h. The sample was heated from ambient temperature (25 °C) to 750 °C, with a heating rate of 30 °C min^{-1}. After undergoing calcination, the sample was placed in a stove at 100 °C and afterward in a desiccator until it reached ambient temperature. The sample was macerated and sieved (sieve 0.425 mm − Tyler series), resulting in sample KT.

2.2. Characterization of the adsorbents

To determine the temperature of calcination, the sample was subjected to thermal analysis. The material was heated to temperatures in the range 30 °C–1000 °C, in an atmosphere of synthetic air, at a heating rate of 10 °C min^{-1}. The analyses were carried out with a Shimadzu DTG-60AH thermomechanic analyzer. The chemical compositions of the adsorbents were determined by x-ray fluorescence (XRF) (Phillips CUBIX 3600). The analyses of x-ray diffraction (XRD) were carried out with a Phillips model PW 1710 spectrometer using CuKα_1 radiation with scanning from 4° to 90° with sweep speed corresponding to 0.6° min^{-1}. The zeta potential of the kaolinites was measured using a Zeta Meter 3.0+, model ZM3-D-G (Zeta Meter Inc). The suspensions of adsorbents, ground beforehand to below 37 μm, were sedimented/conditioned at a temperature of 22 °C for 2 h, at the selected pH, in 250 mL measuring cylinders with the addition of a 2.0×10^{-3} mol L^{-1} solution of $NaNO_3$, used as an indifferent electrolyte. The applied tension was varied at an interval of 75–200 mV. 20 measurements were carried out to arrive at a representative average measured potential. Acidity was determined using 0.1 g of the adsorbents and 20 mL of potassium hydroxide solution (0.01 mol L^{-1}). The system was maintained at 25 °C on an orbital shaker (50 rpm) for 3 h, followed by titration with hydrochloric acid solution (0.01 mol L^{-1}). Specific surface area (S_{BET}) was determined through adsorption/desorption of nitrogen (77 K) using the Brunauer–Emmet–Teller