Research paper

A comparative study for the removal of mining wastewater by kaolinite, activated carbon and beta zeolite

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ABSTRACT

The present work aimed to compare the use of kaolinite, activated carbon and beta zeolite in the removal of etheramine from water. It evaluated the influence of physical–chemical parameters on etheramine adsorption in the three adsorbent materials. The initial concentration of etheramine was 200 mg L^{-1} and the water/adsorbent ratio was 1:100; the adsorption was favorable at pH 10.0. The adsorption equilibrium was reached in 30 min and the removal efficiencies of etheramine for kaolinite, activated carbon and beta zeolite were 80%, 96% and 98%, respectively. The adsorption isotherms were determined under optimized conditions and in the concentration range of 0 to 4000 mg L^{-1}. The etheramine adsorbed per unit mass of adsorbent was 33.5 mg g^{-1}, 65.5 mg g^{-1} and 80.8 mg g^{-1} for kaolinite, activated carbon and beta zeolite, respectively. However, comparing the amount adsorbed for monolayer formation and the available specific surface area of the adsorbent, kaolinite is the most efficient adsorbent. The etheramine adsorption isotherms are better fitted to the Langmuir model. The adsorption kinetics of etheramine on kaolinite could be explained by a pseudo second-order model, while on activated carbon and beta zeolite by a pseudo-first-order model. The results suggest that the influence of the interaction of adsorbate/adsorbent is more important for the adsorption of etheramine on kaolinite, which has a smaller specific surface area and larger pore size, than it is for the activated carbon and beta zeolite which present a larger specific surface area and smaller pore size. The adsorbents may be regenerated by washing: kaolinite showed 1.1% of loss of efficiency after the third re-use, while the activated carbon showed 1.5% after the first re-use.

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1. Introduction

In recent years environmental degradation due to human activity has become more frequent leading to a critical situation. One of the great problems today is the contamination of water resources.

The present technology involved in mining operations and ore beneficiation has contributed significantly in this direction since enormous volumes of water are required throughout the process. The water used during ore processing also carries a variety of chemical products which are used mostly during the froth flotation process. Thus, the water economy during the production of iron ore is gaining special attention.

Mining is one of the basic sectors of the world-wide economy. World iron ore production in 2011 reached 2.9 billion tons (U.S.G.S., 2013) and the number of deposits with low iron content is continuously increasing, which forces the mining companies to increase the froth flotation process that is the most used method for iron ore beneficiation. Consequently it is important to study the volumes, origin, quality and recycling of the water used during mineral processing.

Reverse cationic flotation using etheramine acetate as the collector reagent is the most common beneficiation method for iron ore concentration (Araújo et al., 2005) and is one of the most water consuming stages during the mining process. Iron ore flotation usually shows a consumption of water close to 5 m^3 h^{-1} per ton of treated ore (Ciminelli and Barbosa, 2008) and produces an effluent containing large amount of etheramine.

Despite the fact that etheramine can degrade by microorganisms, this reagent is corrosive, very toxic for aquatic organisms and has a high chemical oxygen demand (COD) value. The degradation of etheramine occurs in approximately 28 days (Araújo et al., 2010; Magriotis et al., 2010) but the continuous filling of the dam pond as

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well as the eventual overflow through the spillway can make the retention time in the dam pond insufficient for etheramine degradation, leading to the contamination of water courses as well as underground waters.

The traditional effluent and recycled water treatment in mineral processing, involving only solid/liquid separation and pH control, is no longer enough. The techniques of ore beneficiation have been diversified to compensate the lowering of the iron content in the beneficiation plants' feedstock and to keep or improve the final market specifications. For this reason there is an increasing quantity of organic compounds being added to the existing content of contaminants in the mining wastewater. The study of adsorption as a method for the removal of reagents from mining wastewater acquires importance.

Adsorption with activated carbon is the most popular method currently used for adsorption since it has been the most efficient adsorbent for the adsorption of dyes, organic material in sewage and effluent organic compounds (Cabal et al., 2009; Gupta et al., 2011; Hsiu-Mei et al., 2009; Reffas et al., 2010). Activated carbon is generically defined as a carbonaceous material of considerable specific surface area. A more specific connotation for the term activated carbon is that of highly porous carbons produced by a carbon rich material through physical or chemical activation. It can be produced from a great variety of precursors and primarily from bituminous carbon, wood, turf, polymers and biomass (Rouquerol et al., 1999).

Among the different adsorbents that make ionic exchange, the zeolites are adequate, because they have a great capacity of cationic exchange and an affinity for heavy metals. The zeolites have three-dimensional structures consisting of silica and alumina tetrahedrons. Due to the great number of pores in the structure the zeolites are considered to be like molecular screens. Recent studies have shown the zeolites' ability for removing organic contaminants in water (Abu-Lail et al., 2010; Li et al., 2011; Salvestrini et al., 2010). The search for low cost materials to be used as adsorbents has been widely studied with the objective of re-using the effluent water, reducing pollution of water resources and decreasing water consumption.

Kaolinite is the most abundant phyllosilicate mineral found in highly weathered soils. It is type 1:1 clay originating from the alteration of Al-silicates and particularly the feldspars. Kaolinite consists of silica tetrahedron layers linked to alumina octahedron layers by means of hydrogen bonding between the tetrahedrons' basal oxygen and the hydroxyls from the octahedron layers. Due to isomorphic substitution of Si^{4+} by Al^{3+}, the tetrahedron layers present a small negative charge (Grim, 1962).

Kaolinite is widely used in the paper industry, refractory pigments and ceramics. Although kaolinite does not have a history of being marketed as an adsorbent it appears to be a mineral with suitable characteristics for to use in the environmental area (Lee and Kim, 2002; Li and Gallus, 2007; Nandi et al., 2009; Quintelas et al., 2010) and presents economic potential for use in removal of etheramines from reverse iron ore flotation tailings (Magriotis et al., 2010).

The aim of this work was to compare etheramine adsorption on the surfaces of kaolinite, activated carbon and beta zeolite. The investigation was centered on the evaluation of the process parameters such as pH, adsorbent dosage and etheramine initial concentration. The adsorption isotherms were adjusted to the models of Langmuir and Freundlich. Kinetic models of adsorption were used to analyze the kinetics and the etheramine adsorption mechanisms on the adsorbents.

2. Materials and methods

2.1. Adsorbate

The adsorbate was Flotigam EDA (Clariant, São Paulo, Brazil), an etheramine acetate containing a dodecyl radical and neutralized to 30% with acetic acid. It was prepared at various dilutions in the range 100-4000 mg L^{-1} from a stock solution containing 4 g L^{-1}.

2.2. Adsorbents

The kaolinite sample utilized in the present work is a natural kaolinite originated from the Ijaci region in Minas Gerais State, Brazil. The sample (Table 1) was kindly supplied by a local mine named "Mineradora Química e Minérios". The kaolinite was fragmented and passed through a 0.425 mm screen aperture and used in the tests without any prior treatment.

The beta zeolite (Table 1) was synthesized in Maringá State University in Paraná State, Brazil) and it was in the acid form H-BEA. The activated carbon was a commercial product named Cromoline.

The chemical compositions of the kaolinite and H-BEA were determined using a Philips (Almelo, Netherlands) model CUBIX 3600 X-ray fluorescence spectrometer. The specific surface areas of adsorbents were evaluated by measuring the adsorption and desorption of nitrogen at 77 K, according to the Brunauer, Emmett, Teller (BET) method, with the aid of a Micromeritics (Dublin, Ireland) model ASAP 2020 analyser. The powder XRD data were obtained in a Phillips spectrometer model PW 1710 using Cu Kα_1 radiation scanning from 4° to 90° 2θ. In order to determine zeta potentials, suspensions of adsorbents (particle size < 37 μm) were adjusted to an appropriate pH (in the range 2–12) and sedimented/conditioned for 2 h at 195 K in 250 mL conical flasks containing 2 mmol L^{-1} sodium nitrate solution as supporting electrolyte. Potentials were measured using a Zeta Meter (Staunton, VA, USA) System 3.0 + ZM3-D-G instrument: the applied tension varied between 75 and 200 mV, and zeta potentials were expressed as the mean value of 20 repetitions.

2.3. Influence of physicochemical parameters on adsorption

Batch-type experiments were carried out to determine the effects of physicochemical parameters on the efficiency of removal of etheramine by kaolinite and activated carbon. In each case, an appropriate amount of powdered adsorbent was added to 10 mL of etheramine solution, the pH was adjusted, by the addition of concentrated acetic acid or 0.1 mol L^{-1} potassium hydroxide as appropriate, and kept constant during the whole adsorption experiments. The resulting mixture was maintained at 298 ± 1 K on an orbital shaker (100 rpm). In order to determine the amount of etheramine remaining in solution, samples of the mixture were removed at appropriate intervals, filtered, and analyzed spectrometrically at 410 nm using bromocresol green methodology (Magriotis et al., 2010). The percentage removal (%R) of etheramine was calculated from the equation:

$$\%R = \frac{C_o - C_t}{C_o} x100 \qquad (1)$$

in which, C_o is the initial concentration of etheramine (mg L^{-1}) and C_t is the concentration of etheramine (mg L^{-1}) at time t.

Experiments to determine the equilibrium time were performed, with the contact time between adsorbent and adsorbate in the range

Table 1
Chemical composition of kaolinite and H-BEA.

Constituents	Concentration (%)	
	Kaolinite	H-BEA
SiO_2	45.75	73.40
Al_2O_3	37.41	7.25
Fe_2O_3	2.64	0.50
CaO	0.00	0.13
MgO	0.40	0.27
SO_3	0.00	0.00
Na_2O	0.08	0.06
K_2O	0.45	0.00
Loss on ignition	15.35	19.80