



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 m³ 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 isomorphous 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 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 $\text{Cu K}\alpha_1$ radiation scanning from 4° to $90^\circ 2\theta$. In order to determine zeta potentials, suspensions of adsorbents (particle size $< 37 \mu\text{m}$) 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 $298 \pm 1 \text{ K}$ 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:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

in which, C_0 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

Table 2
Textural analysis of the adsorbents.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pores		Average pore diameter	
		Area ($\text{m}^2 \text{g}^{-1}$)	Volume ($\text{cm}^3 \text{g}^{-1}$)	BET	BJH
				(\AA)	(\AA)
Kaolinite	34.3	40.7	0.2183	245.3	213.1
Activated carbon	643.5	130.1	0.1137	22.2	35.0
H-BEA	641.6	300.3	0.7758	57.2	103.3

from 15 min to 24 h, at pH 10.0, with an initial concentration of etheramine of 200 mg L^{-1} and 100 mg of adsorbent. The influence of initial concentration of adsorbate (100, 200 and 400 mg L^{-1} of etheramine) was studied, as were the influences of adsorbent dosage (50, 100 and 200 mg of adsorbent) and of pH (4.0, 7.0, 10.0 and 12.0) on the removal of etheramine by kaolinite and activated carbon. The tests with the H-BEA adsorbent were carried out in the optimized conditions during the kaolinite and activated carbon experiments. All such adsorption experiments were performed in triplicate.

The adsorbents were tested for their re-use. After adsorption at optimized conditions, the solution was filtered and the adsorbent (kaolinite or activated carbon) were subjected to washing with type II water (1 g of the adsorbent and 20 mL of water) at 60°C for 2 h, filtered, dried in an oven for 16 h and re-used in the experiments of etheramine adsorption. This procedure was repeated three times. The etheramine removal efficiencies of the washed adsorbents were compared with those samples subjected only to oven drying (100°C) for 16 h.

2.4. Adsorption isotherms

The adsorption isotherms of the three different adsorbents were determined with etheramine in the concentration range 0 to 4000 mg L^{-1} and the remaining parameters at their optimized values. The amount of etheramine adsorbed per unit mass of adsorbent was determined from:

$$Q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

in which Q_e is the amount of etheramine adsorbed per unit mass of adsorbent (mg g^{-1}), C_o is the initial concentration of etheramine (mg L^{-1}), C_e is the concentration of etheramine (mg L^{-1}) at equilibrium, m is the mass of adsorbent (g) and V is the volume of solution (L). All experiments were conducted in triplicate.

2.5. Chi-square analysis

To identify a suitable isotherm and kinetics model for the sorption of etheramine on kaolinite, activated carbon and H-BEA, non-linear chi squared (χ^2) analysis was carried out as follows:

$$\chi^2 = \sum \left(\frac{(Q_{\text{exp}} - Q_{\text{calc}})^2}{Q_{\text{calc}}} \right) \quad (3)$$

where Q_{exp} is the experimental data of the adsorption capacities and Q_{calc} is the adsorption capacities obtained by calculating from the model. If χ^2 is a small number, the data from the model are similar to the experimental data, whereas if χ^2 is a larger number, they differ.

3. Results and discussion

3.1. Adsorbents characteristics

The textural analyses of kaolinite, activated carbon and H-BEA are shown in Table 2. The kaolinite showed the lowest specific surface area and larger pore diameter, conversely, the activated carbon had the highest specific surface area and smaller pore diameter. H-BEA showed a specific surface area value close the activated carbon, but with larger pore diameter.

The XRD spectrum of the kaolinite (Fig. 1) shows a minor presence of quartz. Studies carried out with three different samples of kaolinite showed that small differences in chemical and mineralogical composition do not cause significant changes in the zeta potential or in the adsorption process (Magriotis et al., 2010).

The electrokinetic behavior of adsorbent materials in solution is one of their most important properties. The zeta potential of kaolinite and activated carbon (Fig. 2A and B respectively) became more negative when the pH increased indicating that the two materials are stabilized due to their higher negative charge. This behavior is attributed to the adsorption of OH^- ions in the surface centers of positive charge of kaolinite or the deprotonation of the surface hydroxyl groups. The negative charge decreasing when the pH decreases is attributed to H^+ adsorption in the positive centers of charge (Alkan et al., 2005). The activated carbon presents several functional groups on its surface. The increase in the activated carbon negative charge has been attributed to the dissociation of carboxylic groups occurring between pH 2 and pH 6 (Chingombe et al., 2005). The H-BEA (Fig. 2C) showed a negative surface charge in almost all the studied pH range.

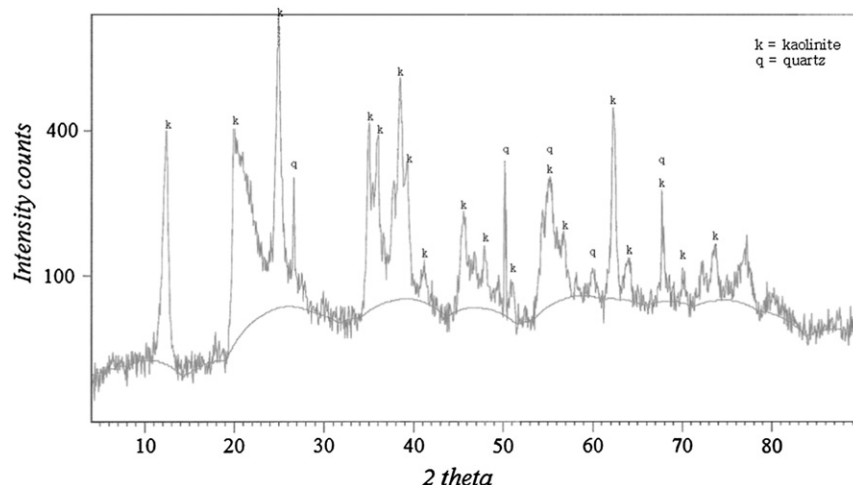


Fig. 1. Powder XRD of the kaolinite sample.

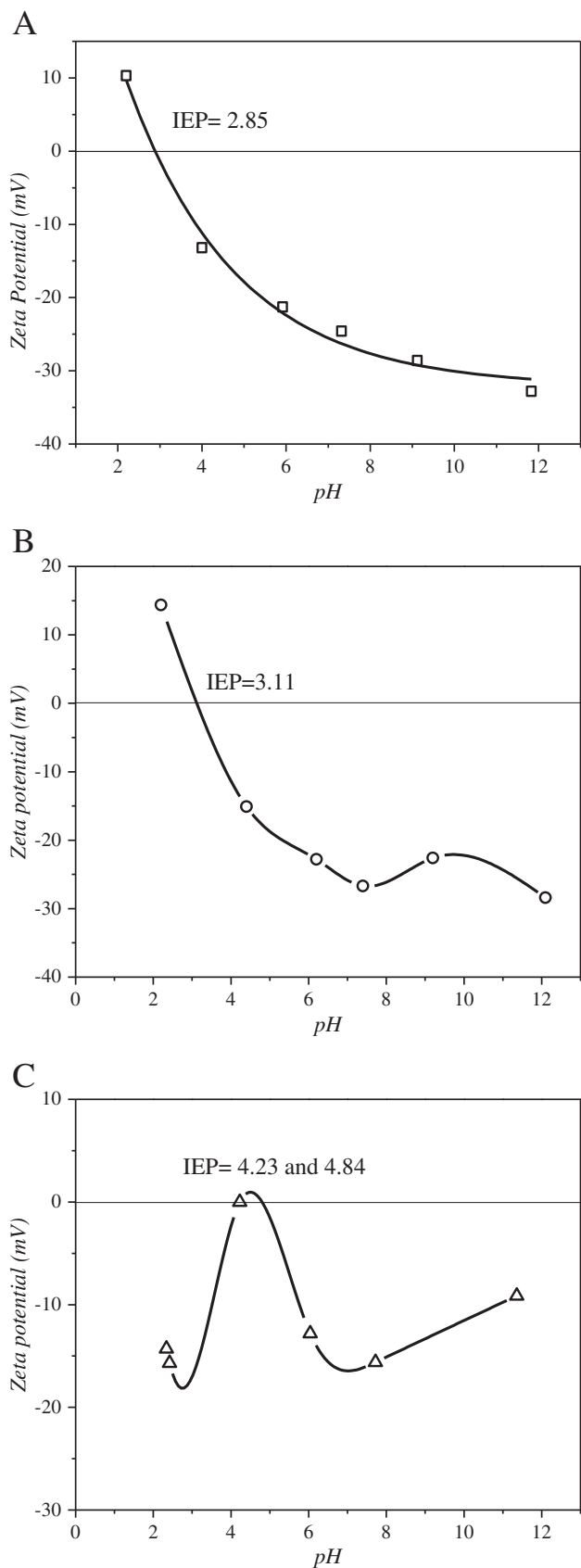


Fig. 2. Influence of pH on the zeta potential of kaolinite (A), activated carbon (B) and BEA (C).

3.2. Influence of physicochemical parameters on the adsorption of etheramine by kaolinite and activated carbon

All experiments were conducted for a maximum period of 2 h; a period which proved to be sufficient to attain equilibrium (Fig. 3). The influence of the initial concentration of adsorbate on adsorption was studied by varying the initial etheramine solution concentration of 100, 200 and 400 mg L⁻¹, maintaining contact time of 2 h, 100 mg of adsorbent and pH 10. The results are shown in Fig. 4. Elevation of the initial concentration of etheramine from 100 to 200 mg L⁻¹ increased adsorption significantly and the efficiency of removal of etheramine improved from 50 to 80% in kaolinite and 93 to 96% in activated carbon. In this case, the increase in concentration of etheramine may accelerate the diffusion of the adsorbate molecules on the adsorption sites of the adsorbent, as a result of the increased driving force of the concentration gradient. However, further increase in the initial concentration of adsorbate (400 mg L⁻¹) had no significant effect on removal, a phenomenon related to decrease in the availability of adsorption sites due to the saturation of surfaces of the adsorbents, thereby making the removal constant (Özer et al., 2007). Hence the optimal initial concentration of etheramine in the solution was established at 200 mg L⁻¹.

The influence of the dosage of adsorbent on the removal of etheramine was studied by varying the amount of adsorbent of 50, 100 and 200 mg, contact time of 2 h, maintaining initial etheramine concentration of 200 mg L⁻¹ and pH 10. The results are shown in Fig. 5. When the value changed from 50 mg to 100 mg of adsorbent, the efficiency of removal of etheramine increased from 64 to 80% in kaolinite and 80 to 96% in activated carbon, a result that can be explained by the enlargement of the surface area of adsorbent. A further increase in the ratio to 200 mg of adsorbent did not alter the efficiency of adsorption, which remained at 79% and 90% in kaolinite and activated carbon, respectively. Thus, dosage of adsorbent of 100 mg was considered optimal for adsorption because it was not only very efficient, but also resulted in a smaller consumption of adsorbents.

In an adsorption study pH is an important parameter since it can cause modifications in the adsorbent surface charge and provoke the adsorbate ionization in such a way as to favor or hinder the process. The influence of the pH on the removal of etheramine was studied by varying the pH through 4.0, 7.0, 10.0 and 12.0, maintaining contact time of 2 h, initial etheramine concentration of 200 mg L⁻¹ and amount of adsorbent of 100 mg. The results presented in Fig. 6 show that adsorption was strongly influenced by pH. The adsorption efficiency on the etheramine removal was superior at pH 10 for the two adsorbents (80% and 96% for kaolinite and activated carbon respectively) and

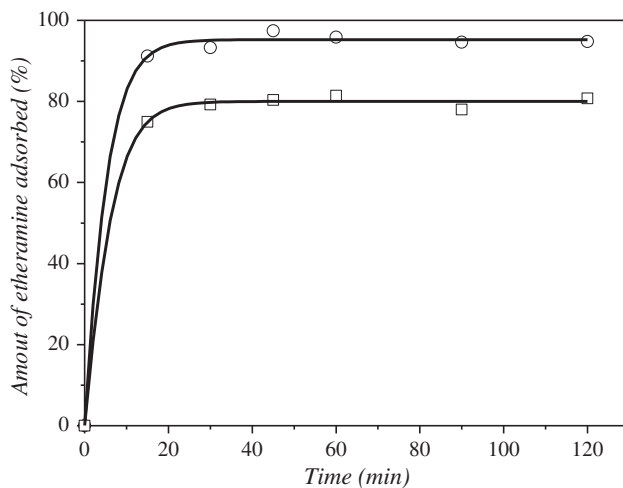


Fig. 3. Influence of contact time on the removal of etheramine by kaolinite (□) and activated carbon (○).

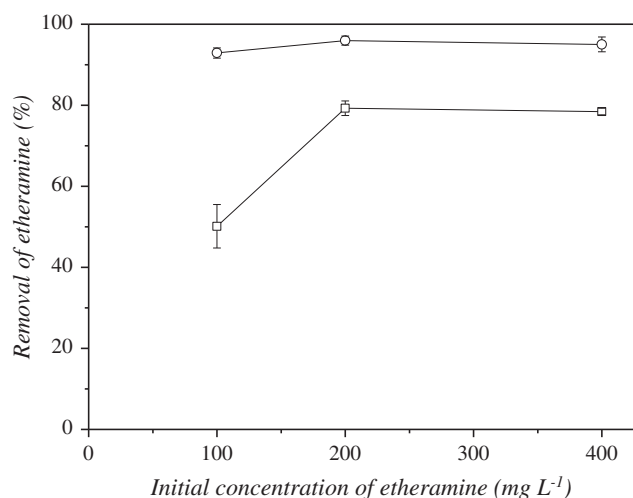


Fig. 4. Influence of the initial concentration of etheramine on adsorption by kaolinite (□) and activated carbon (○).

decreased at pH 7 (58% and 90%) as well as at pH = 12 (56% and 87%). The removal efficiency at pH 4 was lower for kaolinite (34%) and showed a limited influence during adsorption using activated carbon (87%). The pH has a great influence in the etheramine adsorption since in acid medium it favors the dissociated form and in alkaline medium the molecular form. For pH values around 9.0 the cation concentration is about 100% and the same situation occurs with the molecular form at pH values above 11.5. For pH values around 10 the amine is 50% in the ionic form and 50% in the molecular form (Leja, 1982).

Etheramine adsorption on the kaolinite surface occurs primarily due to electrostatic interaction forces between the etheramine ionic form and the kaolinite surface. When pH = 4 and pH = 7 the amine is 100% in the ionic form and therefore the adsorption process is electrostatic interaction. When pH = 4 the kaolinite surface has a small negative charge. An increase to pH 7 makes the kaolinite surface charge more negative, favoring the adsorption process. When pH = 12 the amine is 100% in the molecular form and kaolinite has a large negative surface charge. In this situation the adsorption process occurs probably due to colloidal precipitation of etheramine on the kaolinite surface. However, the adsorption process needs more detailed studies to clearly establish the effective adsorption mechanism. The largest adsorption in pH =

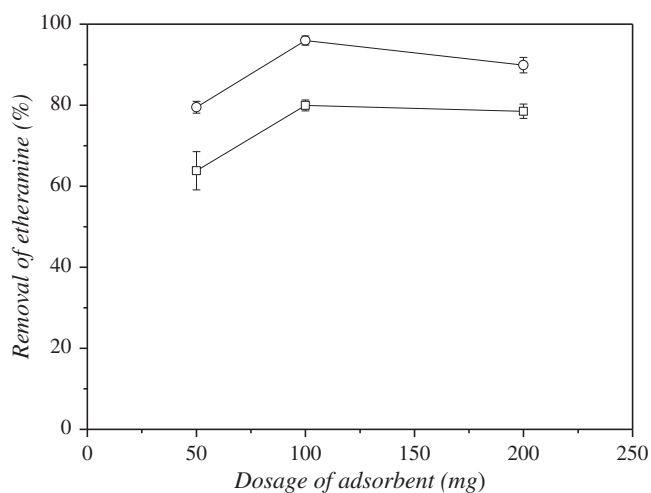


Fig. 5. Influence of the dosage of adsorbent on the adsorption of etheramine by kaolinite (□) and activated carbon (○).

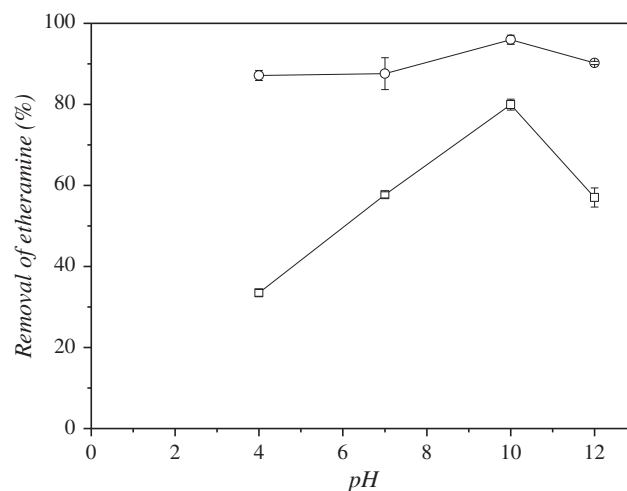


Fig. 6. Influence of pH on the adsorption of etheramine by kaolinite (□) and activated carbon (○).

10 is due to the simultaneous occurrence of the ionic and molecular forms of amine permitting the formation of ionic-molecular complexes that are more active on the surface of the kaolinite (Magriotis et al., 2013; Smith, 1963). The results indicate that the etheramine adsorption on the kaolinite surface relates to the extent of etheramine dissociation in the solution and also to the kaolinite surface charge.

Adsorption when using activated carbon is strongly influenced by the surface area and has a minor influence from the surface charge. The efficiencies of removal of etheramine by kaolinite, activated carbon and H-BEA were compared using the optimized parameters, namely, pH 10.0, initial concentration of adsorbate of 200 mg L⁻¹, dosage of adsorbent of 100 mg and a contact time of 2 h. The efficiencies of removal of etheramine by kaolinite, activated carbon and H-BEA were 80% (16 mg g⁻¹), 96% (19,2 mg g⁻¹) and 98% (19,6 mg g⁻¹), respectively (Fig. 7). The similarity of etheramine adsorption efficiency for the activated carbon and H-BEA can be explained by the similarity of the surface area results achieved for the two adsorbents.

The regeneration of the adsorbent is an important factor in the economic viability of their use. The results of re-use tests of kaolinite and activated carbon are shown in Table 3. The washing of the adsorbent liberated nearly all the adsorption sites. Kaolinite showed a small loss of efficiency only after the 3rd re-use, while for the activated carbon this

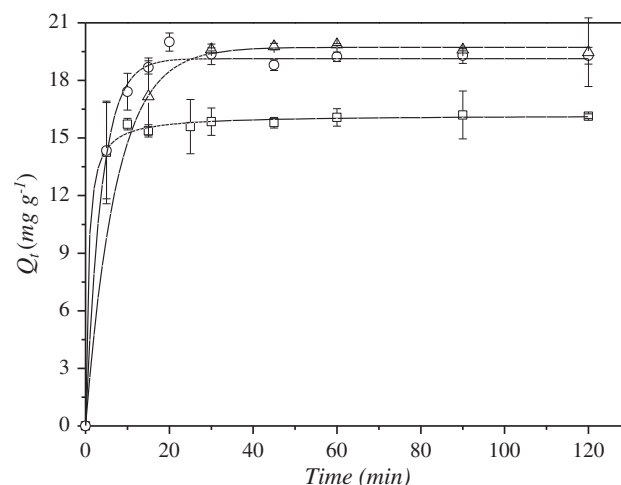


Fig. 7. Amount of etheramine removed by kaolinite (□), activated carbon (○) and BEA (Δ).

Table 3
Loss of etheramine removal efficiency of the used adsorbents.

Adsorbent	Loss of etheramine removal efficiency (%)					
	Used adsorbent			Washed adsorbent		
	1 st reuse	2 nd reuse	3 rd reuse	1 st reuse	2 nd reuse	3 rd reuse
Kaolinite	23	27	27	0	0	1.1
Activated carbon	2.3	13	21	1.5	1.4	1.5

small loss of efficiency was observed from the 1st re-use. These results show that the adsorbents may be regenerated by washing. Furthermore, the adsorbate desorbed during the step of regeneration can be re-used in the flotation process, making the process economically viable.

3.3. Adsorption isotherm

Solutions with different initial concentrations from 0 to 4000 mg L⁻¹ were prepared with the objective of analyzing the adsorption isotherms. The tests were performed using optimal parameters. The isotherms results showing the etheramine adsorption on kaolinite, activated carbon and H-BEA are depicted in Fig. 8.

The maximum experimentally obtained for the monolayer (Q_m) was approximately 33.5 mg g⁻¹ for the kaolinite, 65.5 mg g⁻¹ for the activated carbon and 80.8 mg g⁻¹ for the H-BEA. However, comparing the amount adsorbed for the monolayer formation and the available specific surface area of the adsorbent (Table 4) kaolinite is the most efficient adsorbent.

The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models were both tested for equilibrium description. The Langmuir isotherm has been frequently used in the adsorption of organic compounds solutions on clays, carbon and zeolites (Abu-Lail et al., 2010; El-Naas et al., 2010; Unuabonah et al., 2008; Zhang et al., 2009). The Langmuir isotherm is the simplest isotherm model and considers a monolayer adsorption onto a uniform surface that contains a finite number of active sites, uniform adsorption energy and no transmigration of sorbate in the plane of the surface. It can be represented by the following equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

in which Q_m is the capacity of monolayer adsorption (mg g⁻¹), and K_L is the Langmuir equilibrium constant (L mg⁻¹).

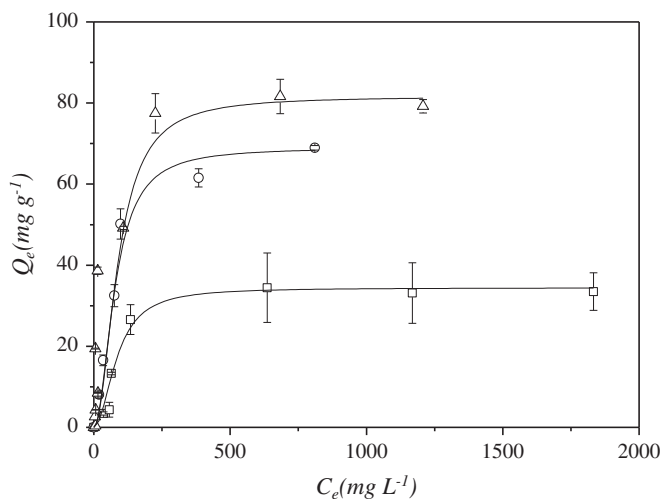


Fig. 8. Adsorption isotherms of etheramine on kaolinite (□), activated carbon (○) and BEA (Δ).

Table 4
Comparison between adsorbents according to the quantity required for the monolayer formation and the available specific surface area.

Parameter	Kaolinite	Activated Carbon	H-BEA
S_{BET} (m ² g ⁻¹)	34.3	643.5	641.6
Q_m (mg g ⁻¹)	33.5	65.5	80.8
Q_{ms} (mg m ⁻²)	0.9761	0.1018	0.1060

The Langmuir isotherm presents some problems since it conceptualizes the independence of the adsorbed molecules, and surface uniformity. The Freundlich isotherm attempts to remove the limitations of the Langmuir isotherm since it considers that adsorption occurs on heterogeneous surfaces and deals with the influence of the adsorbate/adsorbent interactions.

$$Q_e = K_F C_e^{1/n_F} \quad (5)$$

in which K_F is the Freundlich constant indicating the relative adsorption capacity of the adsorbent (mg^{1-1/n} g⁻¹ L^{1/n}), and $1/n_F$ is a constant indicating the adsorption intensity.

The experimental data were tested in the Langmuir and Freundlich isotherms. The results are presented in Table 5. The Langmuir isotherm was consistent to represent the etheramine adsorption on the three adsorbents.

3.4. Adsorption kinetics

Adsorption kinetic curves are often useful for explaining the mechanisms of adsorption. The models most used to investigate the mechanism of sorption, characteristic constants of sorption were the pseudo-first order of Lagergren (Lagergren, 1898) and pseudo-second order kinetics of Ho and Mckay (Ho and Mckay, 1998).

The kinetics of adsorption by the three different adsorbents were investigated using the conditions previously optimized. First-order kinetics was represented by the model proposed by Lagergren (Lagergren, 1898):

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad (6)$$

in which Q_e and Q_t (mg g⁻¹) are the adsorption capacities at equilibrium and at time t , respectively, k_1 is the rate constant of pseudo-first order adsorption (min⁻¹).

Second-order kinetics was represented by the model proposed by Ho and Mckay (Ho and Mckay, 1998):

$$Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \quad (7)$$

Table 5
Comparison between adsorbents according to the Langmuir and Freundlich adsorption models.

Isotherm	Kaolinite	Activated carbon	H-BEA
<i>Langmuir</i>			
Q_m	35.96	78.08	86.71
K_L	0.01370	0.0107	0.0180
R	0.9838	0.9908	0.9872
χ^2	1.444	5.754	21.54
<i>Freundlich</i>			
K_F	12.22	6.696	10.22
n_F	3.879	2.778	3.217
R	0.9396	0.9721	0.9609
χ^2	6.284	16.34	48.77

Table 6
Comparison between adsorbents according to pseudo first- and second-order kinetic and intraparticle diffusion models.

Model	Kaolinite	Activated carbon	H-BEA
Experimental Q_e (mg g ⁻¹)	16.01	19.29	19.67
<i>Pseudo First order</i>			
k_1 (min ⁻¹)	0.4553	0.2675	0.1376
Q_e (mg g ⁻¹)	15.87	19.13	19.72
R	0.9988	0.9993	0.9997
χ^2	0.0335	0.01167	0.008278
<i>Second order</i>			
k_2 (mg g ⁻¹ min ⁻¹)	0.0995	0.0304	0.0208
Q_e (mg g ⁻¹)	16.19	19.18	20.40
R	0.9992	0.9974	0.9980
χ^2	0.0241	0.3158	0.06777
<i>Intraparticle diffusion</i>			
k_{id} (mg g ⁻¹ min ^{-0.5})	0.9503	1.2583	1.6139
C_{id} (mg g ⁻¹)	8.059	9.3244	6.2958
R	0.6399	0.7093	0.8051
χ^2	6.312	6.780	4.532

in which Q_e and Q_t (mg g⁻¹) are the adsorption capacities at equilibrium and at time t , respectively, k_2 is the rate constant of pseudo-second order adsorption (g mg⁻¹ min⁻¹).

The adsorption process of the adsorbate molecules from the bulk liquid phase onto the adsorbent surface may proceed in three steps: (1) mass transfer of the adsorbate molecules across the external boundary layer; (2) intraparticle diffusion within the pores of the adsorbent and (3) adsorption at a site on the surface. Prediction of the rate-limiting step is an important factor to be considered in adsorption process. However, the pseudo first and pseudo second order models cannot give information or evaluate the contribution of intraparticle diffusion to the adsorption mechanism. The intraparticle diffusion model proposed by Weber and Morris (1963) is given by the equation:

$$Q_t = k_{id}t^{0.5} + C_{id} \quad (8)$$

where k_{id} (mg g⁻¹ min^{-0.5}) is the intraparticle diffusion rate constant and C_{id} is associated with the boundary layer thickness.

The values obtained by applying pseudo-first and pseudo-second order kinetic and intraparticle diffusion models to the adsorption of etheramine by kaolinite, activated carbon and H-BEA are presented in Table 6. The etheramine removal by kaolinite is better described by a pseudo second-order kinetics controlled by the interaction among the molecules of etheramine and the functional groups at the kaolinite surface. In addition, the etheramine adsorption by activated carbon and H-BEA can be better fitted by a pseudo first-order model with less dependence on adsorbate/adsorbent interaction. The results suggest that the influence of the interaction 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 its adsorption on activated carbon and H-BEA which present a larger specific surface area and smaller pore size. For the activated carbon and H-BEA, which presented pseudo-first-order kinetics, it can be observed in Fig. 7 that equilibrium was reached faster by activated carbon that showed the highest rate constant.

4. Conclusions

Considering the adsorption kinetics it was possible to determine that the optimal adsorption parameters were: initial concentration of 200 mg L⁻¹, adsorbent dosage of 100 mg/10 mL of etheramine solution, pH = 10 and equilibrium time lower than 2 h.

The adsorption under optimal conditions is effective and shows a removal percentage close to 80%, 96% and 98% for kaolinite, activated carbon and H-BEA respectively. The discrepancy for the kaolinite adsorption

values compared to the other adsorbents can be explained by the modest surface area presented by kaolinite (34.3 m²g⁻¹) in relation to the areas of activated carbon (643.4 m²g⁻¹) and H-BEA (641.6 m²g⁻¹).

The adsorption isotherms demonstrated that the largest etheramine quantity adsorbed per unit of adsorbent (Q_m) was attained with the H-BEA (80.8 mg g⁻¹), followed by the activated carbon (65.5 mg g⁻¹) and the kaolinite (33.5 mg g⁻¹). However, comparing the amount adsorbed for completing the monolayer and the specific surface area of the adsorbent it can be concluded that kaolinite is the most efficient adsorbent.

The etheramine adsorption on kaolinite was strongly influenced by pH whilst in the activated carbon and H-BEA the pH showed a weak influence, most probably due to their larger specific surface area.

The etheramine adsorption on the three adsorbents was better resolved by the Langmuir model and follows a pseudo second order mechanism for kaolinite while the etheramine adsorption on activated carbon and H-BEA follow a pseudo first-order model mechanism. The results suggest that the influence of the interaction adsorbate/adsorbent was more important for the adsorption of etheramine on kaolinite, which has a smaller specific surface area and larger pore size.

The adsorbents may be regenerated by washing. Washed kaolinite showed 1.1% loss of efficiency after the third re-use, while the washed activated carbon showed 1.5% after the first re-use.

Kaolinite appears to be a promising adsorbent since it has a low acquisition price which makes it more viable for use in an industrial process, compared to activated carbon and H-BEA. The adsorbent's utilization for the removal of etheramines from wastewaters of the iron ore reverse flotation process has great potential. It can be an important step in the mining companies' search for sustainability measures related to water consumption and the environmental impacts generated by the effluent's disposal.

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