



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



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ARTICLE INFO

Article history:

Received 5 February 2013

Received in revised form

6 May 2013

Accepted 9 May 2013

Available online 26 June 2013

Keywords:

Kaolinite

Etheramine

Chemical treatment

Thermal treatment

Chemometric tools

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 m³ 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 tonnes leading to a total amine consumption of approximately 15,000–20,000 tonnes 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 (Ptáček 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 (Estareles 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 $90 \text{ }^\circ\text{C}$ 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 $100 \text{ }^\circ\text{C}$ 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 $25 \text{ }^\circ\text{C}$. 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 $60 \text{ }^\circ\text{C}$ 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 ($25 \text{ }^\circ\text{C}$) to $750 \text{ }^\circ\text{C}$, with a heating rate of $30 \text{ }^\circ\text{C min}^{-1}$. After undergoing calcination, the sample was placed in a stove at $100 \text{ }^\circ\text{C}$ 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 $30 \text{ }^\circ\text{C}$ – $1000 \text{ }^\circ\text{C}$, in an atmosphere of synthetic air, at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. 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 $\text{CuK}\alpha_1$ radiation with scanning from 4° to 90° with sweep speed corresponding to $0.6^\circ \text{ min}^{-1}$. 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 $37 \text{ }\mu\text{m}$, were sedimented/conditioned at a temperature of $22 \text{ }^\circ\text{C}$ for 2 h, at the selected pH, in 250 mL measuring cylinders with the addition of a $2.0 \times 10^{-3} \text{ mol L}^{-1}$ 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 $25 \text{ }^\circ\text{C}$ 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

(BET) method. The analyses were carried out by a Micromeritics ASAP 2020 device. The infrared spectroscopy with Fourier transformation (FTIR) was carried out using pellets of KBr (300 mg of KBr to 3 mg of sample) in the range 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . The analyses were carried out using Digilab Excalibur equipment, series FTS 3000. With the aim of comparing the characterized samples subjected to chemical (acid and peroxide) treatments and thermal treatment, chemometric analyses were carried out using the GUI Octave program.

2.3. Influence of physico-chemical parameters on adsorption

For the adsorption tests, 10 mL aliquots of etheramine solution were placed in contact with an appropriate mass of adsorbent material, in which the systems were maintained at ambient temperature (25 ± 1 °C) on an orbital shaker (100 rpm). The final concentration of etheramine was determined using the bromocresol green method (Magriotis et al., 2010). Aliquots were analyzed by UV–vis spectroscopy (Femto, model 800 XI UV–vis spectrometer) at 410 nm. The percentage of etheramine removed was calculated by the following equation:

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

where C_0 and C_t are the initial and at time t concentrations of etheramine (mg L^{-1}), respectively.

To determine the equilibrium time a monitored 12-h analysis was carried out. For this, 10 mL of etheramine solution at an initial concentration of 200 mg L^{-1} adjusted to pH 10, by the addition of potassium hydroxide solution 0.1 mol L^{-1} , was placed in contact with 0.1 g of adsorbent. To establish the influence of the initial concentration, solutions at concentrations corresponding to 100, 200 and 400 mg L^{-1} were used. For this, an adsorbent mass/adsorbate volume ratio of 1:100 (0.1 g of adsorbent) was used. To study the influence of adsorbent mass/adsorbate volume ratio (1:50, 1:100 and 1:200), 0.2; 0.1 and 0.05 g of adsorbent, respectively, were placed in contact with 10 mL of etheramine solution, adjusted to pH 10. The last parameter analyzed was the influence of pH. A solution of etheramine was prepared at an optimized initial etheramine concentration, adjusted to pH: 4, 7, 10 and 12, using acetic acid or potassium hydroxide solution 0.1 mol L^{-1} . All experiments were carried out in duplicate, to confirm the reproducibility of the results.

2.4. Adsorption isotherms

The isotherms of adsorption were constructed using the optimized parameters. For this, solutions of adsorbate at concentrations in the range 10–1000 mg L^{-1} were prepared. The quantity of etheramine adsorbed by a mass of kaolinite at equilibrium was determined from the equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where Q_e (mg g^{-1}) is the quantity of etheramine adsorbed by the mass of kaolinite at equilibrium, C_0 and C_e are the initial and at equilibrium concentrations of etheramine (mg L^{-1}) respectively, V is the volume of the solution (L) and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of the adsorbents

TG/DTA measurements were carried out in order to assess the thermal stability of natural kaolinite as well as to define the

conditions for carrying out thermal treatment. Kaolinite showed a loss of mass of approximately 14% in the temperature range between 400 and 600 °C probably due to the loss of water molecules and impurities that were retained on the surface of the material. DTA analysis showed an endothermic peak at around 500 °C may be associated with the process of dehydroxylation of kaolinite (Fernandez et al., 2011; Cheng et al., 2010). From the results obtained, the temperature of 750 °C was defined for carrying out the thermal treatment of the natural material, seeing that at this temperature the kaolinite is already modified and it is thus desirable to examine the influence of its structure on the etheramine adsorption process.

The chemical compositions of the kaolinite samples are shown in Table 1. It can be seen that, of the treatments used, the most effective in modifying the chemical composition of the starting material was the acid treatment. The modifications caused by the treatments to the chemical composition of kaolinite were compared using algorithms obtained from the development of chemometric tools. By application of the pre-processing of the data obtained by XRF an analysis was carried out using seven variables (seven constituent oxides), obtaining the principal components (PC). With the results emerging from the information stored by principal components 1 and 2 (PC1 and PC2), correlation analyses were carried out between the samples evaluating their chemical compositions. The results are shown in Fig. 1A and B. When principal components analysis (PCA) is applied to establish the effect of treatments on the chemical composition of the kaolinite sample, it can be seen that according to principal component 1 (PC1), which retains 75.98% of the information, the sample that underwent acid treatment is markedly different from the others, appearing as it does in the right-central area of the scores graphic. Thus it can be stated that acid treatment is shown to be effective in changing the chemical composition of the starting material for altering the majority constituents of clay minerals: silica and alumina (Dudkin, 2010). During the acid leaching process, the process of dealumination occurs, leading to the formation of an amorphous material with high silica content. This fact can be proven through the correlation between the graphics of scores (Fig. 1A) and weights (Fig. 1B), which shows that in the area of acid treatment, the preponderant characteristic obtained by the weights graphic is silica content. This change in chemical composition could further be linked to the elimination of mineral impurities or even the greater solubility of octahedral cations in comparison to silica (Dudkin, 2010). In accordance with the results arising from the analysis of the values of the auto scale constituents of the samples, a dendrogram was obtained in which the samples were set out on the x axis and the similarity index on the y axis. The samples were then included according to their proximity and the results obtained are shown in Fig. 1C. From the results presented in Fig. 1C, it can be seen, from the proximity of samples compared by chemical composition, that those showing the greatest mutual similarity are the ones subjected to peroxide treatment and thermal treatment, both of which are similar to the sample of natural kaolinite. In this

Table 1
Chemical composition of kaolinites samples.

Constituent	KN (%)	KA (%)	KP (%)	KT (%)
SiO ₂	52.75	60.2	52.84	52.67
Al ₂ O ₃	43.13	36.41	43.30	43.58
Fe ₂ O ₃	3.05	2.42	3.11	2.90
CaO	0	0.08	0.01	0.02
MgO	0.46	0.25	0.20	0.25
Na ₂ O	0.09	0.11	0.09	0.09
K ₂ O	0.52	0.53	0.44	0.49

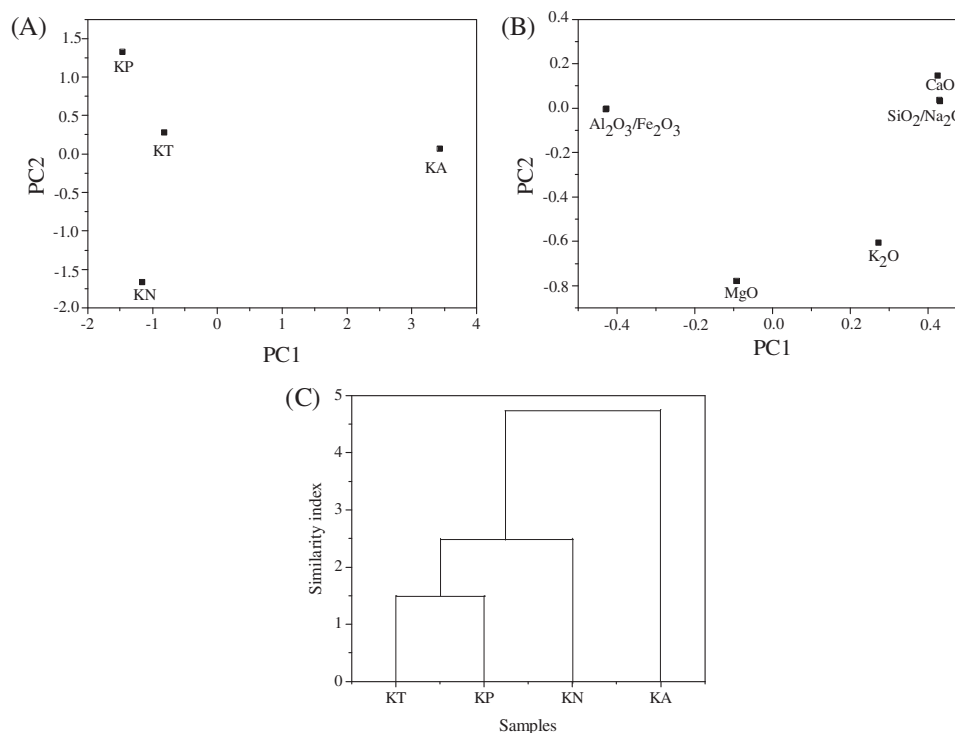


Fig. 1. Scores graph (A), weight graph (B) and dendrogram (C) for the chemical composition of the samples.

group, the sample that appears most comparable with natural kaolinite is the one treated with peroxide, which in turn corroborates reports in the literature that affirm the efficacy of this treatment for removal of organic material supposedly contained on the surface of the clay mineral, without any other significant effect on the chemical composition of the sample (Melo et al., 2010). On the other hand it is seen from Fig. 1C that the acid treatment was the one that most modified the starting material, exhibiting a lesser similarity to the data set analyzed.

Zeta potential (Fig. 2), in general, shows the same tendency, with a reversal of charge from positive to negative, with the increase in pH. In an acid medium, the positive surface charge may be associated with the adsorption of H⁺ ions in centers of negative charge, whilst in a basic medium, increase in negative charge of the kaolinite surface is observed due to the process of adsorption of hydroxyl ions at centers of positive charge or to the mechanism of deprotonation of hydroxyl groups present at the surface (Alkan et al., 2008). It can be seen that the treatments caused changes with regard to the isoelectric point (IEP), which may be associated with the change in chemical composition resulting from the treatments.

The results of the acidity tests (Table 2) suggest that the chemical and thermal treatments are responsible for change in the surface properties of the adsorbent material. As was observed, the acid leaching significantly increased the acidity of the starting material, which may be attributed to the substitution of exchangeable cations for protons and the dissolution of octahedral aluminum cations, creating Lewis acid sites in the structure (Bhattacharyya and Gupta, 2006). On the other hand, a diminution of acidity of the sample subjected to thermal treatment has been attributed to the removal of Brönsted acid sites which are generally represented by the proton H⁺ bonded to the oxygen atom present at the surface of the constituent oxides of clay minerals (Al–OH). In this way, the removal of OH groups alters the acidity of the starting material (Fernandez et al., 2011; Sand and Comer, 1954). The drastic

reduction in acidity for the sample subjected to treatment with peroxide may be related to the formation of surface “peroxo” groups or to the reduction of organic material, possibly containing acid surface groups. It can also be seen from Table 2 that of the treatments used, only the acid treatment was able to increase the surface area, which possibly is associated with effects of acid leaching, such as: disaggregation of clay particles and elimination of impurities (Panda et al., 2010). The diminution in surface area of kaolinite when subjected to thermal treatment may be related to the collapse of the crystalline structure during the calcination process (Michot et al., 2008). The reduction in surface area for the sample subjected to treatment with peroxide may be associated with the action of that in reducing the quantity of organic material (Melo et al., 2010).

In the light of the results that emerged from the analyses of IEP, acidity and S_{BET} (Table 2), two-dimensional graphics were constructed in which the first two principal components which retains 91.53% of the information. The principal components analysis (PCA) results are shown in Fig. 3A and B. Analyzing Fig. 3A and considering the results coming from PC1, which holds 66.12% of the information, it can be seen that the sample subjected to acid treatment stands out from the others by possessing significantly higher acidity values (Fig. 3B), consistent with the experimental results. In addition, the position of the peroxide and thermal treatments in the right-hand area of the scores graphic, opposite the high-acidity area on the weights graphic shows that such treatments reduced the acidity of the natural material. From PC2, which holds 25.41% of the information, it can be verified by analysis of the graphics of scores (Fig. 3A) and weights (Fig. 3B) that natural kaolinite differs from all the treated samples because of its high IEP, provided that it keeps its chemical composition unaltered. Further, the greater area for the sample submitted to acid treatment is proven, given that, for the weights graphic, this surface quality is found in the upper part of the graphic, which is compatible with the

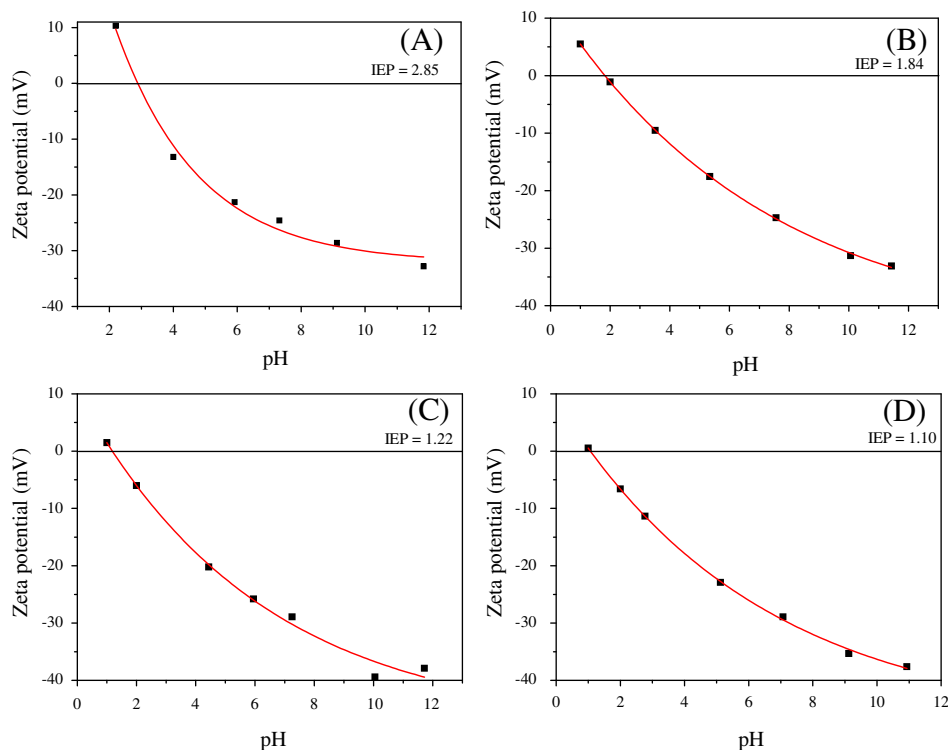


Fig. 2. Zeta potential of KN (A), KA (B), KT (C) and KP (D).

position of the sample on the scores graphic. Such results are seen to be coherent when HPA is carried out, as seen in Fig. 3C, which shows the dendrogram constructed from the data provided by Table 2. Analysis of Fig. 3C shows a greater similarity between the samples submitted to thermal and peroxide treatments, which is consistent with the index of similarity shown in the principal components analysis. Thus, with the aims of validating the chemometrics results and identifying the constituent phases of the samples, as well as constituent functional groups of the samples KN, KA, KP and KT, XRD and FTIR analyses, respectively, were carried out.

The XRD spectra are shown in Fig. 4. It can be seen that the chemical treatments maintained the structure of kaolinite intact. The disappearance of the quartz and kaolinite peaks seen in Fig. 4C shows the efficiency of thermal treatment in the destructuring of the starting material, with a consequent loss of crystallinity. Moreover, the peaks identified at 20° (4.46 Å) and 25° (3.5 Å) which refer to the structure of disordered kaolinite (Wang et al., 2010) show that the natural material passed through a transformation process.

The FTIR spectra (Fig. 5) show a broadening and diminution of the bands situated between 3700 and 3200 cm^{-1} for the samples KA and KP, indicative of a possible distortion of the octahedral layers which make up its structure (Makó et al., 2006). However, for the KT sample, the disappearance of the 3696 and 3619 cm^{-1} bands, attributed to the vibrations of OH groups, and of the 914 cm^{-1} band,

referring to the Al–OH stretchings of the structure of gibbsite which makes up the kaolinite, puts calcination into effect as the treatment responsible for the withdrawal of hydroxyl groups from the starting material, in which an alternation is noted in the geometry of the gibbsite sheets with a change in the coordination index of the aluminum, from octahedral to tetrahedral (Makó et al., 2006). Meanwhile, the appearance of the band at 817 cm^{-1} indicates change to the structure, given that the band at around 800 cm^{-1} is characteristic of the vibration of the Al–O bond as regards the structure of metakaolinite (Cristóbal et al., 2009).

3.2. Adsorption assays

3.2.1. Influence of type of treatment on equilibrium time

Kinetic studies of adsorption were carried out using the kaolinite subjected to chemical and thermal treatments, in order to establish the time in which the adsorbent/adsorbate system reached equilibrium. The equilibrium time for KA and KP was reached in 30 min, whilst for the KT sample equilibrium was reached in 6 h. Calcination causes the transformation of kaolinite into metakaolinite. The disorganized structure of metakaolinite hinders the interactions between the adsorbent material surface and the adsorbate molecules causing increase in equilibrium time. All subsequent experiments were, therefore, conducted for a maximum period of 1 h for KA and KP samples and 8 h for KT sample.

3.2.2. Influence of initial etheramine concentration

The influence of the initial etheramine concentration on adsorption is shown in Fig. 6. For KA and KT samples, it can be seen that adsorption proved most efficient for the initial etheramine concentration corresponding to 200 mg L^{-1} . For the three samples there was an increase in the rate of etheramine removal, when the initial concentration is increased from 100 mg L^{-1} – 200 mg L^{-1} , a

Table 2

Parameters of the IEP, acidity and (S_{BET}) obtained for kaolinities samples.

Sample	IEP	Acidity (mmol g^{-1})	S_{BET} ($\text{m}^2\text{ g}^{-1}$)
KN	2.85	0.85	34.32
KA	1.84	0.91	72.27
KP	1.10	0.33	25.83
KT	1.22	0.77	27.55

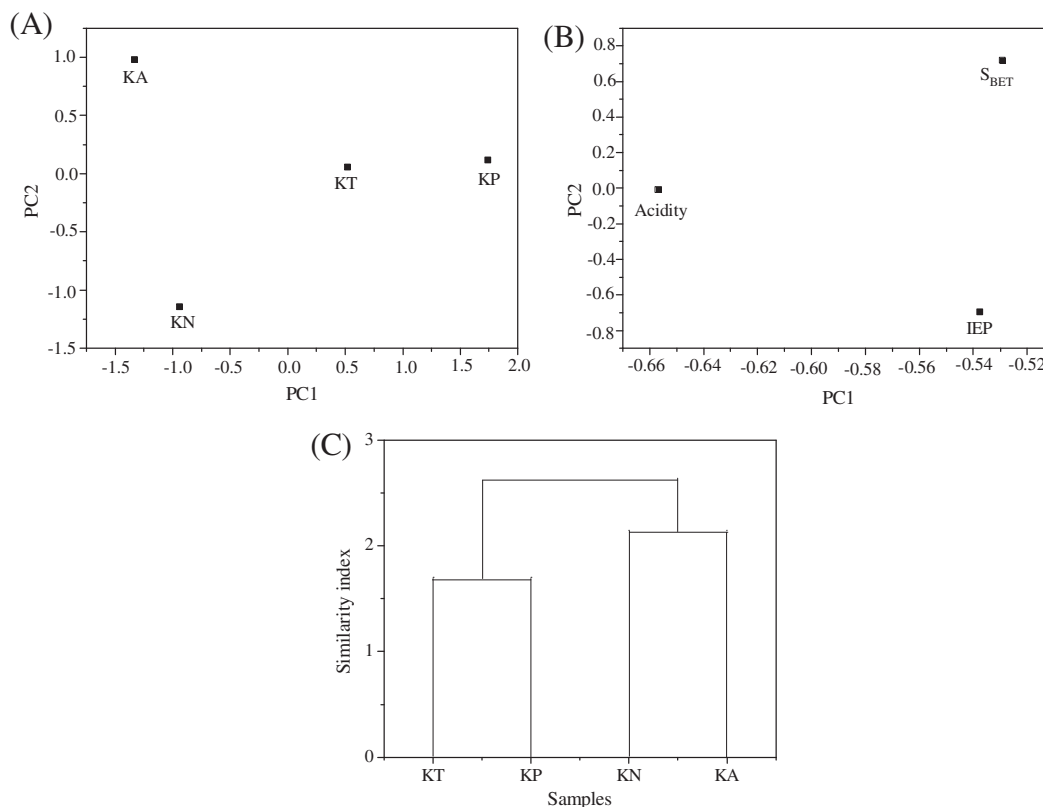


Fig. 3. Scores graph (A), weight graph (B) and dendrogram (C) related to surface properties of the samples.

phenomenon attributed to the existence of a larger amount of adsorbate molecules interacting with the surface of adsorbent material. For the KA and KT when the initial etheramine concentration is increased from 200 mg L⁻¹–400 mg L⁻¹ there was a decrease of percentage of etheramine removal, although there was an increase of the actual amount of etheramine adsorbed per unit mass of adsorbent. In this case, the increase in initial etheramine concentration provides an important increase in driving force that overcomes the mass transfer resistance of etheramine between the aqueous and solid phases. For KP, it was found that the quantities of etheramine removed when the initial concentrations were of 200 and 400 mg L⁻¹ were similar. This is possibly associated with the effect of treatment with peroxide that eliminates the organic matter by oxidation increasing the active sites. For the analysis of subsequent parameters, the optimized concentrations of etheramine were of 200 mg L⁻¹ for KA and KT and of 400 mg L⁻¹ for KP.

3.2.3. Influence of the adsorbent mass/adsorbate volume ratio

Once the initial concentration of etheramine had been optimized, the effect of the quantity of adsorbent upon the process was assessed. To do so, aliquots of the same volume of adsorbate (10 mL) were placed in contact with different quantities of adsorbent material, thereby obtaining ratios with distinct proportions, 1:50, 1:100 and 1:200, corresponding to 0.2; 0.1 and 0.05 g of adsorbent, respectively. The results obtained are shown at Fig. 7. For the KA sample it can be seen that, at the ratios corresponding to 1:100 and 1:200, there was proximity of quantity of contaminant removed. However, it is shown that, at ratio 1:50, the quantity of etheramine adsorbed was greater. When the adsorption was carried out using KT as adsorbent, proximity was found between the percentage quantities removed at the ratios of 1:50 and 1:100. However, it is found that, for KP sample, the three ratios show

similar efficiencies as regards removal of the contaminant. In this case the adsorption process may be governed principally by the capacity of the molecules of adsorbate to migrate sufficiently toward the surface. This being the case, the 1:50, 1:100 and 1:200 ratios were defined as the most appropriate for the continuation of the study for KA, KT and KP, respectively.

3.2.4. Influence of pH

The influence of pH on adsorption is shown in Fig. 8. The results show that pH is a parameter that influences the removal of the contaminant, because it affects the form of the etheramine molecules in solution and the surface charge of the adsorbents. At pH around 8.5, the concentration of etheramine in ionic form approximates to 100%, whilst for pH above 11.5 it is the concentration of the molecular form that has this value. Equilibrium between the ionic and molecular forms occurs at pH near 10.5 (Leja, 1982). When the etheramine molecule is near the surface of the kaolinite, the oxygen atoms of groups Si–O⁻ and Al–O⁻, present on the surface of the kaolinite, attract the hydrogen of group NH₂, forming hydrogen bonds. In an acid medium, these bonds are less likely to occur, since the adsorption of H⁺ ions at the centers of negative charge diminishes the electrostatic interactions that cover the surface of the adsorbent material with molecules of etheramine, in ionic form NH₂⁺ (Zhao et al., 2003). In this way, it was shown that, for all the adsorbents used, the removal process appeared inferior at pH 4. In basic pH, apart from the electrostatic mechanism, it is believed that adsorption by hydrogen bonding also occurs, which covers the Si–OH and Al–OH sites exposed on the edge-plane of the adsorbent material (Hussain et al., 1996). In this way, it was verified that the adsorption was better at pH 10 for the KA and KP kaolinite samples. At this pH value, apart from the material possessing negative charge that favors interaction through electrostatic mechanisms, there is equilibrium

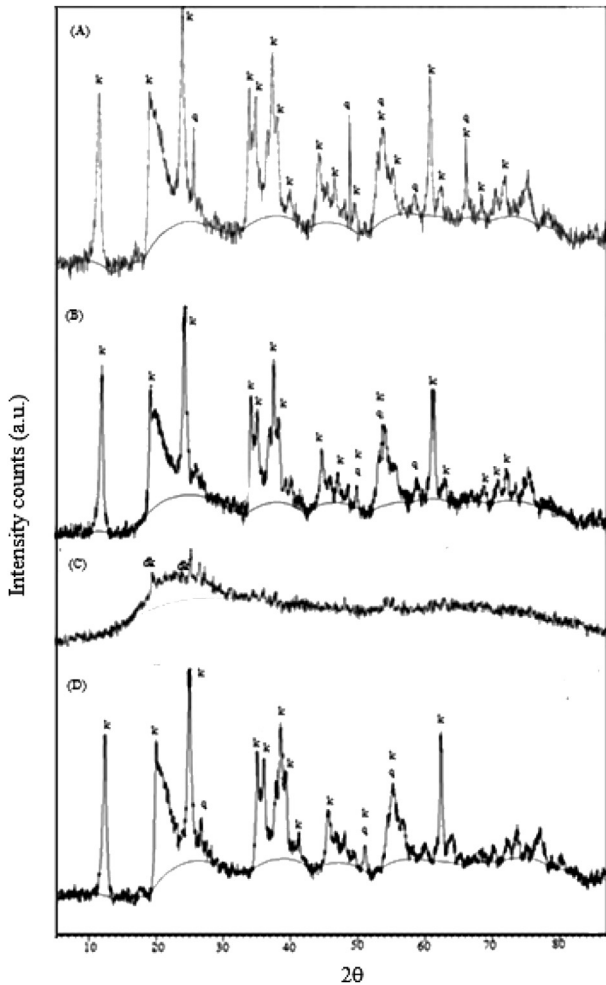


Fig. 4. XRD of the KN (A), KA (B), KT (C) and KP (D): k = kaolinite; q = quartz; dk = disordered kaolinite.

between the ionic and molecular forms of the etheramine molecules, which may be associated with the formation of an ionic-molecular complex that boosts the adsorptive process (Smith, 1963). However, it was found that pH value 10 was not ideal for the KT kaolinite. The explanation for this result may be related to the fact that this kaolinite showed a modified structure, which could be of influence in the interactions with the molecules of adsorbate and affect the

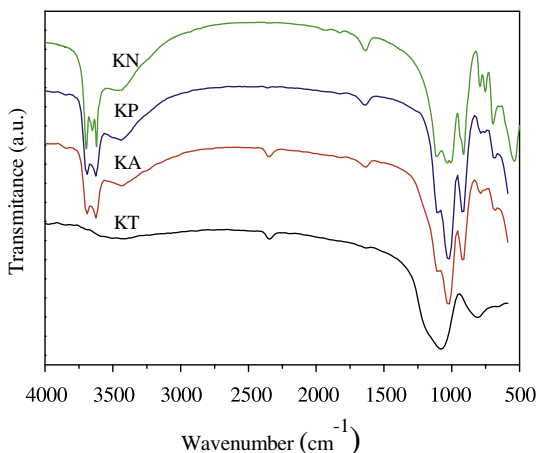


Fig. 5. FTIR spectra of KN, KA, KT and KP.

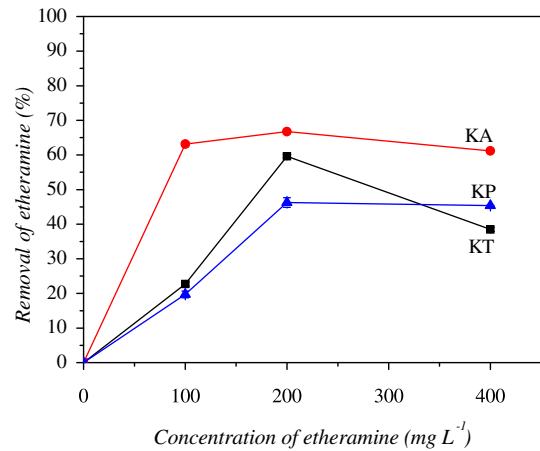


Fig. 6. Influence of the initial concentration on the adsorption.

optimization of this parameter, with better removal observed at pH 7. In accordance with the results presented, it may be inferred that the etheramine adsorption process on prepared adsorbents is governed as much by electrostatic forces as by the formation of multi-layers, maintained by hydrogen bonds. To continue the adsorption study, pH 10 was used for the samples subjected to chemical treatments, whilst for that subjected to thermal treatment, the optimized pH was 7. Such results suggest that the chemical treatments are the most appropriate, because the flotation process is carried out at pH 10, making these adsorbents useable in the industrial sphere.

3.2.5. Kinetic study of etheramine adsorption

As can be seen from the analysis of the influence of parameters upon the kinetics of adsorption, the optimal conditions present significant changes when the material subjected to chemical and thermal treatments is compared. Therefore, it becomes necessary to analyze the results of the kinetic study of adsorption taking into account the quantity of etheramine removed per mass of optimized adsorbent (Q). The kinetic study of adsorption is useful for explaining the mechanisms of adsorption. The experimental data were analyzed using kinetic models of pseudo-first (Lagergren, 1898), pseudo-second order (Ho and McKay, 1999) and intra-particle diffusion (Weber and Morris, 1963) represented mathematically by their respective non-linear equations:

$$Q = Q_e(1 - e^{-k_1 t}) \quad (3)$$

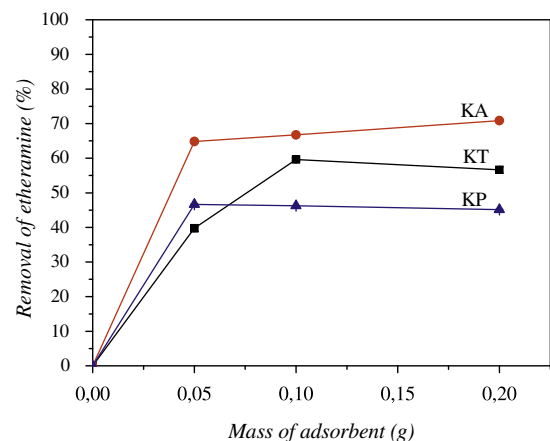


Fig. 7. Influence of the weight of adsorbent on the adsorption.

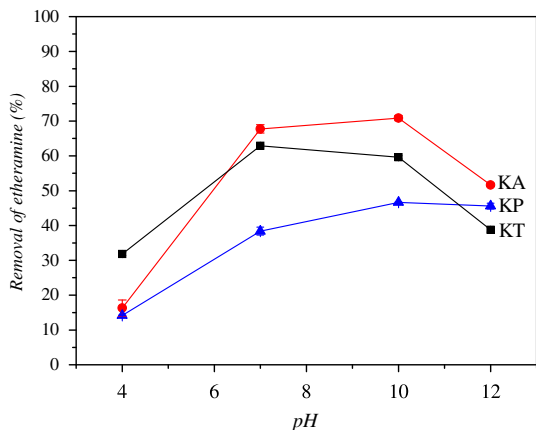


Fig. 8. Influence of pH on the adsorption.

$$Q = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \tag{4}$$

$$Q = k_d t^{1/2} + C \tag{5}$$

where Q is the amount of adsorbate (mg g^{-1}) adsorbed at time t (min), Q_e is the amount of adsorbate (mg g^{-1}) adsorbed at equilibrium, k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) and k_d ($\text{mg g}^{-1} \text{min}^{-1/2}$) are, respectively, the pseudo first-order, second-order and intraparticle diffusion ($\text{mg g}^{-1} \text{min}^{-1/2}$) rate constants and C (mg g^{-1}) is the thickness of the diffusion layers.

According to intraparticle diffusion model, intraparticle diffusion is the rate controlling step if the plot of Q vs. $t^{1/2}$ is linear and pass through the origin (Weber and Morris, 1963). If the plot does not pass through the origin, this is indicative of some degree of boundary layer control and that the intraparticle diffusion is not the only rate limiting step but also other kinetics models may control the rate of adsorption.

The results obtained (Table 3) show that the kinetic of adsorption adequately fitted the pseudo-second-order model for the treated kaolinite samples KA and KP. This result can also be verified in the work that used natural kaolinite (Magriotis et al., 2010). The results suggest that the limiting stage in the rate of adsorption is adsorption at the surface, which is dependent on availability of the adsorption sites; as well as pointing toward the chemical nature of the adsorbate–adsorbent interactions. On the other hand, it was found that the adsorption of etheramine by thermally treated kaolinite followed the kinetic model of pseudo-first-order, suggesting that the structure of the adsorbent significantly influenced the kinetic of adsorption.

3.2.6. Adsorption isotherm

The isotherms of adsorption were evaluated using the models of Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) which are represented, respectively, by the non-linear equations:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$Q_e = K_F C_e^{1/n_F} \tag{7}$$

where Q_e is the amount of etheramine adsorbed (mg g^{-1}) at equilibrium, Q_m is the maximum adsorption capacity of a monolayer (mg g^{-1}), K_L is the Langmuir constant (L mg^{-1}), C_e is the concentration of dye at equilibrium (mg L^{-1}), K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) is

Table 3 Kinetic parameters for adsorption of etheramine onto kaolinites.

	KA	KT	KP	KN ^a
Q_{exp} (mg g^{-1})	7.088	12.463	32.874	16.01
<i>Pseudo-first-order</i>				
Q_e (mg g^{-1})	7.088	12.795	36.260	16.02
k_1 (min^{-1})	1.5390	0.1109	0.1425	0.2130
R	0.9998	0.9783	0.9788	0.9997
Standard error	0.0667	1.0892	2.9567	0.1542
<i>Pseudo-second-order</i>				
Q_e (mg g^{-1})	7.119	14.045	40.4402	16.27
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	2.5307	0.0111	0.0051	0.0694
R	0.9998	0.9572	0.9918	0.9999
Standard error	0.0601	1.5221	1.8457	0.0859
<i>Intraparticle diffusion</i>				
k_d ($\text{mg g}^{-1} \text{min}^{-1/2}$)	0.7410	0.5139	4.5676	1.2955
C (mg g^{-1})	2.6896	6.2109	7.7400	5.4440
R	0.7420	0.6116	0.9289	0.7877
Standard error	2.1690	4.1590	5.3504	4.0611

^a Magriotis et al., 2010.

the Freundlich constant relating to the relative capacity of adsorption (mg g^{-1}) and n_F is a constant relating to the intensity of adsorption.

It is seen from Table 4 that although there may be proximity of the correlation coefficients for the two isotherm models assessed, it is found that the adsorption of etheramine was better fitted to the Langmuir model for the three adsorbents used. The results are similar when working with the natural material (Magriotis et al., 2010). The etheramine adsorption capacities of KA, KT and KP, were 27, 29 and 59 mg g^{-1} , respectively, while the natural material showed a value of 34 mg g^{-1} (Magriotis et al., 2010). The lesser quantity of etheramine removed by the kaolinite subjected to acid treatment may be due to the partial dissolution of the clay mineral (Cristóbal et al., 2009). The thermal treatment also showed less efficacy in the removal of etheramine, when compared to the natural material. The withdrawal of OH groups from the clay layers, accompanied by movements of cations within the octahedral layers, is the principal cause of the reduction in adsorptive capacity (Cristóbal et al., 2010). Of the treatments used, it is seen that the chemical treatment with peroxide was the most efficient for etheramine removal, seeing that the adsorptive capacity was shown to be significantly higher. This fact is related to the effect of peroxide in the removal of organic matter at the surface of the adsorbent material, which brings about the separation of the constituent layers of the kaolinite, so guaranteeing greater accessibility for the molecules of adsorbate.

Table 4 Langmuir and Freundlich isotherm parameters.

	KA	KP	KT	KN ^a
$Q_m(\text{exp})$ (mg g^{-1})	27	59	29	34
<i>Langmuir</i>				
Q_m (mg g^{-1})	33.09	69.40	34.12	35.96
K_L (L mg^{-1})	0.0078	0.0079	0.0106	0.0137
R_L	0.837–0.060 ^b	0.835–0.058 ^b	0.790–0.054 ^b	0.422–0.018 ^c
R	0.9748	0.9903	0.9763	0.9838
Standard error	3.0803	4.4437	3.4205	2.8021
<i>Freundlich</i>				
K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	2.594	6.627	3.491	12.28
n_F	2.856	3.132	3.120	3.879
R	0.9013	0.9282	0.9227	0.9396
Standard error	5.9790	11.8984	6.0956	5.3525

^a Magriotis et al., 2010.

^b $C_0 = 25$ and 2000 mg L^{-1} .

^c $C_0 = 100$ and 4000 mg L^{-1} .

The favorability and feasibility of adsorption process can be determined by the separation factor or equilibrium factor (R_L) in the analysis of data by Langmuir isotherm. It defined by Hall et al. (1966):

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). All the R_L values calculated using Eq. (8) lies between 0 and 1 (Table 4) indicating that etheramine adsorption on the kaolinites samples is favorable.

4. Conclusions

The XRF and hierarchical components analyses revealed that the acid treatment was the most effective in changing the chemical composition. Meanwhile, the zeta potential, S_{BET} and acidity indicated thermal treatment as the most effective in modifying the properties of kaolinite, which can be validated through the use of PCA, HCA, XRD and FTIR. This modification of the starting material ended up having an unfavorable effect on the equilibrium time in the adsorption process. The structure of kaolinite exercised an important influence on the interaction of the system. The proposed treatments produced modifications to the starting material which affected the adsorption process. The adsorbent treated chemically with peroxide would be the most appropriate, since it succeeded in removing the greatest quantity of etheramine, in comparison with the natural material. The chemical treatment with peroxide can be the most applicable for clay minerals, given that it acts only in the removal of organic matter, without, however, altering their chemical composition and structure.

Acknowledgments

To CAPES and to FAPEMIG for financial support. To LGRQ/UFLA where this work was conducted. To NUCAT/PEQ/COPPE for the analyses of adsorption/desorption of N_2 . To Intercement Brasil S.A for the XRF analysis.

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