



Adsorption of etheramine on kaolinite: A cheap alternative for the treatment of mining effluents

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ABSTRACT

The results of laboratory experiments aimed at determining the influence of physicochemical parameters on the adsorption of etheramine (adsorbate) on white, pink and yellow kaolinites (adsorbent) are presented. The adsorption of etheramine was favoured at pH 10.0 under conditions where the initial concentration of etheramine was 200 mg l⁻¹ and the ratio of adsorbent to volume of etheramine solution was 1:100 g ml⁻¹. Equilibrium adsorption was attained within 30 min and the efficiencies of removal of etheramine by white, pink and yellow kaolinite were 77%, 80% and 69%, respectively. The adsorption isotherms of the kaolinites were determined under optimum conditions and with adsorbate in the concentration range of 0–4000 mg l⁻¹. The amounts of etheramine adsorbed per unit mass of adsorbent were 33.03, 34.32 and 23.11 mg g⁻¹ for white, pink and yellow kaolinites, respectively. The adsorption of etheramine on kaolinites was better fitted to the Langmuir rather than the Freundlich isotherm, and could be explained by a pseudo-second-order kinetic model. It is concluded that kaolinites offer significant potential in the treatment of effluents originating from the processing of lower grade iron ores by froth flotation.

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1. Introduction

Iron ore represents one of the most important mineral resources worldwide with an annual production of around three billion tonnes. As supplies of high-grade iron ore are becoming depleted, the application of mineral concentration processes to lower grade ores is attaining increasing importance. The most widely used concentration method involves inverse froth flotation with etheramine acetates as cationic collectors [1]. This procedure requires around 4 m³ of water per tonne of iron ore processed and produces an aqueous pulp that contains significant amounts of etheramine. Considering that etheramines are surface active agents they are widely used as wetting agents. The world consumption of etheramine during iron ore processing is estimated to be in the range of fifteen to twenty thousand tonnes per year or approximately 85 million US dollars. This material is corrosive, very toxic to aquatic organisms and has a high chemical oxygen demand (COD) value. Degradation of etheramine occurs in approximately 28 days. However with the silting of ore tailings dams, as well as possible tailings dams flows via spillways, the residence time of the etheramine in the tailing

dams becomes insufficient for its degradation. Thus it represents a potential source of contamination and a threat to the environment. Treatment of the water used in the flotation process is, therefore, critical for the mining industry, not only to prevent environmental damage but also in consideration of legal and economical implications.

Among the various methods of water treatment that are available, the adsorption of harmful residues in low cost materials has received considerable attention since it not only prevents environmental contamination but also permits the reutilisation of water with positive economical advantages [2,3]. Moreover, effluent recycling represents a positive step for companies that are genuinely concerned with environmental sustainability.

In this context, clay soils are inexpensive adsorbent materials that act as Lewis and Brönsted acids and offer large cation exchange capacities (CEC) in a layered structure that exhibits both chemical and mechanical stability [4]. Kaolinite, one of the most abundant minerals in soils and sediments, is characterised by a 1:1 dioctahedral phyllosilicate structure comprising tetrahedral layers of silica and octahedral layers of alumina linked by hydrogen bonds formed between the basal oxygen of the tetrahedrons and the hydroxyl groups of the octahedrons. The tetrahedral sheet presents a permanent weak negative charge owing to the isomorphous substitution of Si⁴⁺ by Al³⁺, whereas the octahedral sheet and the peripheral crystals present a pH-dependent variable charge arising from the protonation and deprotonation of the superficial hydroxyl groups

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Table 1
Chemical composition of adsorbents.

Constituents	Concentration (%)		
	White kaolinite	Pink kaolinite	Yellow kaolinite
SiO ₂	44.25	45.75	53.40
Al ₂ O ₃	37.08	37.41	28.70
Fe ₂ O ₃	2.39	2.64	2.77
CaO	0.02	0.00	0.03
MgO	0.41	0.40	0.37
Na ₂ O	0.08	0.08	0.08
K ₂ O	0.43	0.45	0.36
Loss on ignition	15.99	15.35	15.40

[5]. Since, soil particles, including those of kaolinite, are able to interact with the solid residues from industrial and domestic effluents released onto the terrestrial surface, the soil itself can function as a filter for human waste [6]. In this respect, kaolinite constitutes an important and economically viable adsorbent by virtue of the large quantities that are available globally and its excellent CEC properties [7].

Due to its extremely low cost, the clays have presented various industrial applications. The kaolinite is widely used in the ceramic, paint, pesticide, paper, cement, pharmaceutical, plastic and textile industries, among others. Besides these applications, the kaolinite has been used in the environmental area, with application in the treatment of industrial effluents, such as the removal of azo dyes [7–10], polymers [11] organic pollutants [12], heavy metals [13–19].

This paper reports the results of laboratory experiments relating to the adsorption of etheramine acetate onto different kaolinite types carried out with the aim of examining the possibility of applying such materials to the treatment of etheramine-containing effluents originating from iron ore mining. Kaolinite was selected as the adsorbent due its extremely low cost, various industrial applications including the treatment of industrial effluents and also its widespread natural occurrence.

2. Materials and methods

2.1. Adsorbate

The adsorbate was Flotigam EDA (Clariant, São Paulo, SP, Brazil), an etheramine acetate containing a dodecyl radical (Fig. 1) and neutralised to 30% with acetic acid, and 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 samples used in this investigation were natural Brazilian kaolinities obtained from Ijaci, Minas Gerais state, southeast of Brazil. Three different types of kaolinite, kindly provided by Mineradora Química e Minérios (Ijaci, MG, Brazil), were used as adsorbents (Table 1). The kaolinite was reduced to a powder, sieved thorough a 0.425 mm mesh (Tyler series) and used directly in the experiments without prior treatment.

The chemical compositions of the three kaolinite types were determined using a Phillips (Almelo, Netherlands) model CUBIX 3600 X-ray fluorescence spectrometer. Their specific surface areas 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. In order to determine zeta potentials, suspensions of kaolinite (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 mM 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 values of 20 repetitions. The morphological features of the samples were obtained from scanning electron microscopy (SEM) using a JEOL microscope (Tokyo, Japan) model JSM-5410. The powder XRD data were obtained in a Phillips spectrometer (Amsterdam, Netherlands) model PW 1710 using Cu Kα₁ radiation scanning from 4° to 90° 2θ at a scan rate of 6° 2θ s⁻¹.

2.3. Influence of physicochemical parameters on adsorption

Batch-type experiments were designed to determine the effects of physicochemical parameters on the efficiency of removal of etheramine by pink kaolinite. In each case, an appropriate amount of powdered kaolinite was added to 10 ml of etheramine solution, the pH was adjusted by the addition of concentrated acetic acid or 0.1 M potassium hydroxide as appropriate, and the resulting mixture was maintained at 298 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 0.5 ml aliquots transferred to separating funnels. Bromocresol green (0.5 ml of a solution containing 3 g l⁻¹) and 10 ml of chloroform were added to each funnel, the mixture was shaken for 5 min and then allowed to stand for a further 5 min. Aliquots of the yellow-coloured denser phase were removed and analysed spectrometrically at 410 nm. The percentage removal (%R) of etheramine was calculated from the equation:

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

where C₀ is the initial concentration of etheramine (mg l⁻¹) and C_t is the concentration of etheramine (mg l⁻¹) at time t.

The influence of contact times, in the range 15 min to 24 h, between adsorbent and adsorbate was determined at pH 10.0 with an initial concentration of etheramine of 200 mg l⁻¹ and an adsorbent to solution volume ratio of 1:100 (g ml⁻¹; corresponding to 0.1 g of pink kaolinite). In further experiments the contact time was limited to the range 15–120 min, whilst other variables (where appropriate) remained as indicated, in order to study the effects of initial concentration of adsorbate (100, 200 and 400 mg l⁻¹ of etheramine), adsorbent: solution volume ratio (1:50, 1:100 and 1:200 g ml⁻¹ corresponding to 0.2, 0.1 and 0.05 g of kaolinite, respectively) and pH (4.0, 7.0, 10.0 and 12.0) on the removal of etheramine by pink kaolinite. All such assays were performed in triplicate.

2.4. Adsorption isotherms

The adsorption isotherms of the three different types of kaolinities were determined with etheramine in the concentration range 0–4000 mg l⁻¹ and the remaining parameters at their optimised values. The amount of etheramine adsorbed per unit mass of kaolinite (q_e; mg g⁻¹) was determined from:

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

where 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.

The data obtained were fitted to the isotherm models of Langmuir [20]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

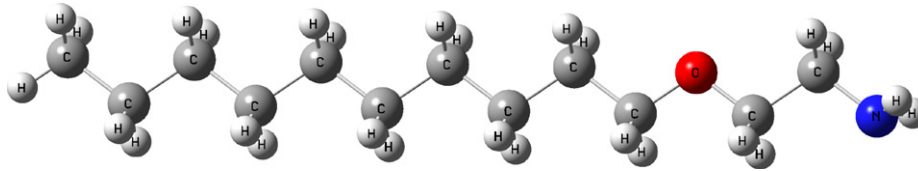


Fig. 1. Structure of etheramine.

where q_m is the capacity of monolayer adsorption (mg g^{-1}) and K_L is the Langmuir equilibrium constant, and of Freundlich [21]:

$$q_e = K_F C_e^{1/n_F} \quad (4)$$

where K_F is the Freundlich constant indicating the relative adsorption capacity of the adsorbent ($\text{mg}^{1-1/n} \text{kg}^{-1} \text{l}^{1/n}$), and $1/n_F$ is a constant indicating the adsorption intensity.

2.5. Kinetics of adsorption

The kinetics of adsorption by the three types of kaolinite was investigated using the conditions previously optimised. First-order kinetics was represented by the model proposed by Lagergren [22], namely:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

where 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}). Integration of this equation with boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ produces Eq. (6):

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \quad (6)$$

and Eq. (7):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

Pseudo-second-order kinetics was represented by the model proposed by Ho and Mackay [23], namely:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

where 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 ($\text{g mg}^{-1} \text{min}^{-1}$). Separating the variables in Eq. (8) and integrating for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (9)$$

This equation can be rearranged to:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (10)$$

2.6. Chi-square analysis

To identify a suitable isotherm and kinetics model for the sorption of etheramine on kaolinite this analysis has been carried out. In this study, a non-linear Chi-square test was used. The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from the models. The

equivalent mathematical statement is:

$$\chi^2 = \sum \left(\frac{(q_{\text{exp}} - q_{\text{calc}})^2}{q_{\text{calc}}} \right) \quad (11)$$

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 the data from the model are similar to the experimental data, χ^2 will be a small number, whilst if they differ; χ^2 will be a larger number.

3. Results and discussion

3.1. Characteristics of the kaolinite samples studied

The specific surface areas of white, pink and yellow kaolinite employed in the present study were 33.27, 34.32 and 30.95 $\text{m}^2 \text{g}^{-1}$, respectively. These values are somewhat greater than those previously reported for kaolinite samples, namely, 13.69 $\text{m}^2 \text{g}^{-1}$ [7] and 28.13 $\text{m}^2 \text{g}^{-1}$ [13].

The zeta potentials of white, pink and yellow kaolinite (Fig. 2) were higher at pH 10.0 (−28.46, −30.25 and −28.00 mV, respectively) than at pH 4.0 (−8.81, −13.20 and −9.15 mV, respectively), indicating that the materials are stabilised at alkaline pHs by the larger magnitude of the superficial negative charge. It has been shown that high pH increases the negative charges on the surface of minerals [24–28] and, for kaolinite, such behaviour may be attributed either to the adsorption of OH^- ions by the positive-charged centres or to the deprotonation of OH groups present on the surface of this material. The smaller negative charge present on kaolinite at low pHs may be explained by the adsorption of H^+ onto the negatively charged centres of the particles [28].

The SEM analysis showed that the three kaolinites exhibit similar morphology (Fig. 3). The individual grain size is about 150 μm (white and yellow kaolinite) and 200 μm (pink kaolinite) for the larger particles and 10 μm for the small.

The XRD spectra of the clays are given in Fig. 4. The yellow kaolinite shows the presence of quartz and mica, and kaolinite as main phase. The pink kaolinite shows a weak presence of quartz and the white kaolinite has a single phase kaolinite.

3.2. Influence of physicochemical parameters on the adsorption of etheramine by pink kaolinite

An initial experiment (data not shown) relating to the influence of contact time between adsorbate and adsorbent on the removal of etheramine by pink kaolinite was conducted over a 24 h period and revealed that equilibrium was attained within 30 min, at which point 80% of the etheramine was removed from solution. All subsequent experiments were, therefore, conducted for a maximum period of 2 h (Fig. 5).

The influence of the initial concentration of adsorbate on adsorption is shown in Fig. 6. 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%. However, further increase in the initial concentration of adsorbate (400 mg l^{-1}) had no significant effect on removal, pre-

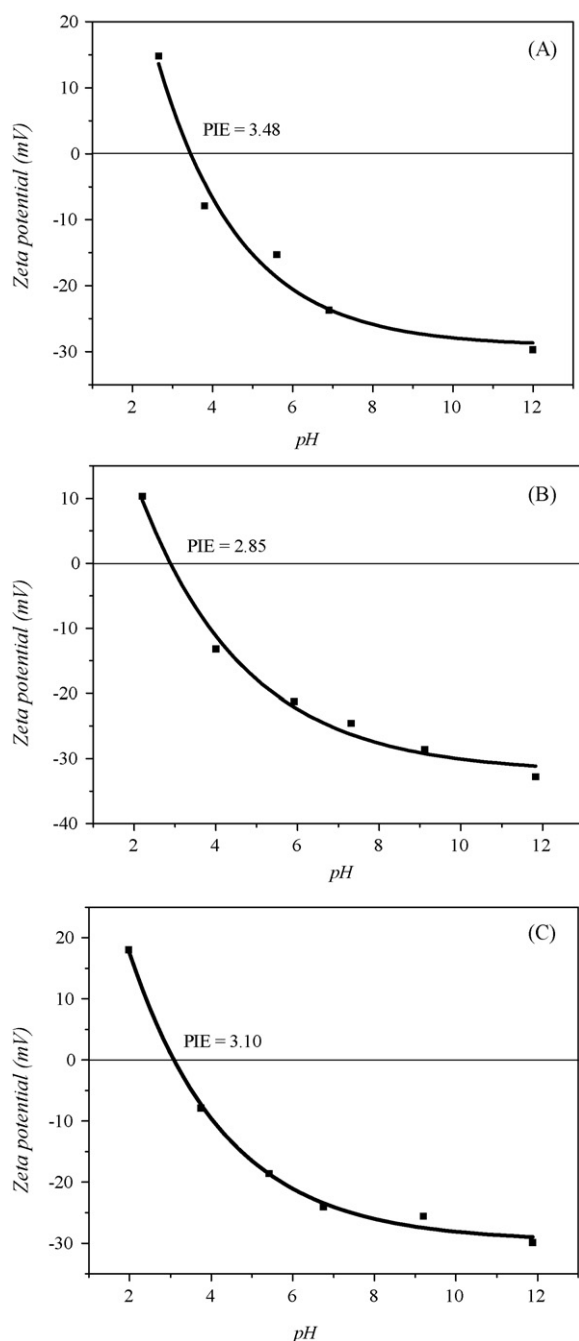


Fig. 2. Influence of pH on the zeta potential of white (A), pink (B) and yellow (C) kaolinite.

sumably because the kaolinite surface was already saturated with etheramine. Hence the optimal initial concentration of etheramine in the solution was established at 200 mg l^{-1} .

The influence of the ratio of the amount of adsorbent to the volume of adsorbate solution on the removal of etheramine is shown in Fig. 7. When the value changed from 1:200 (g ml^{-1} ; 0.05 g kaolinite) to 1:100 (g ml^{-1} ; 0.1 g kaolinite), the efficiency of removal of etheramine increased from 64% to 80%, a result that can be explained by the enlargement of the surface area of adsorbent. A further increase in the ratio to 1:200 (g ml^{-1} ; 0.2 g kaolinite) did not alter the efficiency of adsorption, which remained at 79%. Thus, a ratio of adsorbent to volume of 1:100 was considered optimal for adsorption because it was not only very efficient, but also resulted in a smaller consumption of kaolinite.

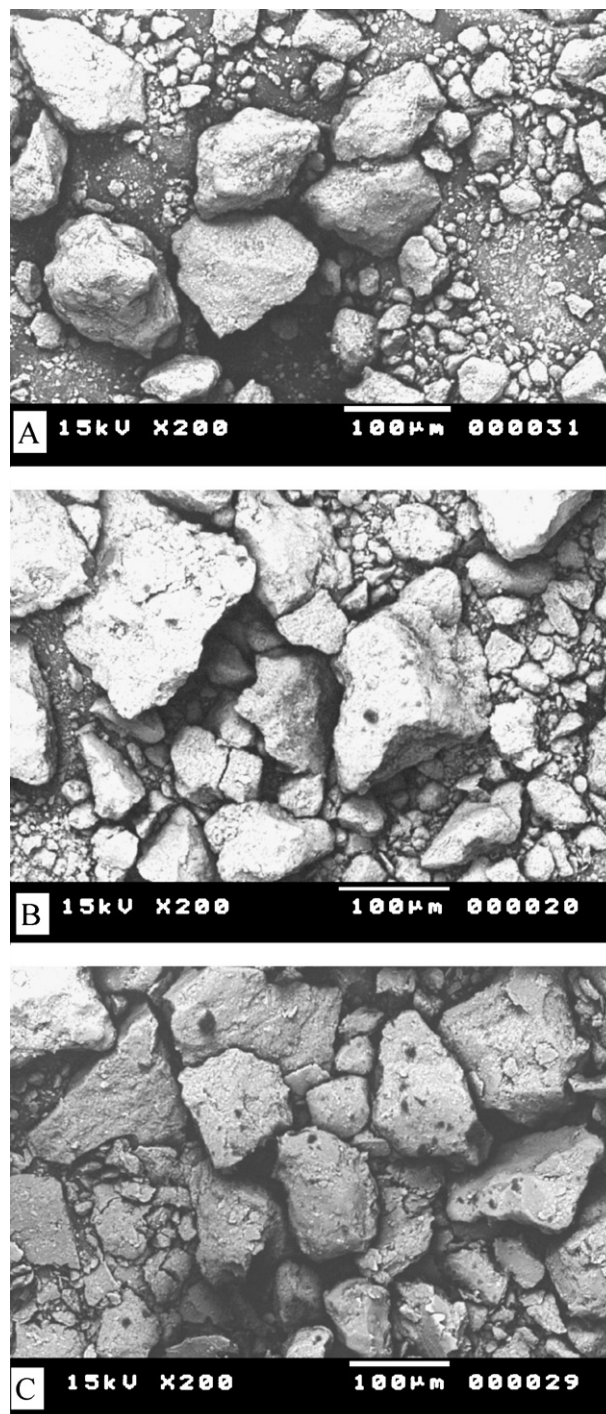


Fig. 3. SEM photomicrographs of white (A), pink (B) and yellow (C) kaolinite.

The results shown in Fig. 8 demonstrate that adsorption was greatly influenced by pH. The most efficient removal of etheramine (80%) was achieved at a pH of 10.0, but declined at pHs 7.0 and 12.0, respectively, to 58% and 56%, whilst at pH 4.0 just 34% of etheramine was removed. Adsorption of etheramine on kaolinite surface is particularly due to the forces of electrostatic interactions between the ionic form of etheramine and the surface of kaolinite. At pHs below 9.0, the etheramine cation is predominant (*ca.* 100%), whereas the non-dissociated form predominates at pHs above 11.5. At pH 10.0, 50% of the etheramine is ionised and 50% is in the molecular form [29]. With respect to kaolinite, at pH 4.0 the surface is slightly negative and there is a small electrostatic interaction with

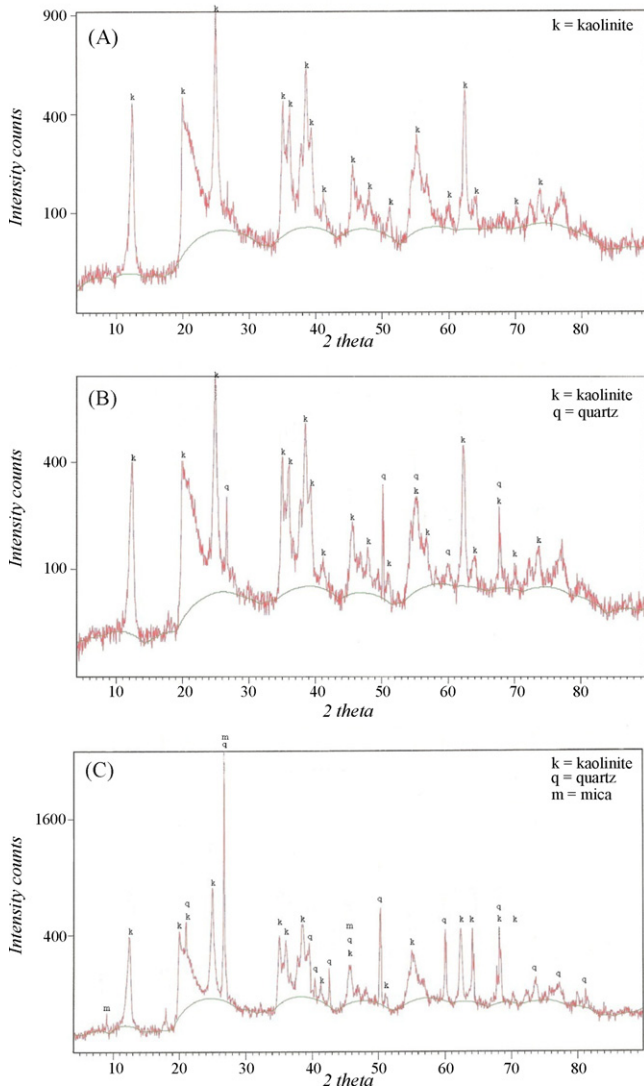


Fig. 4. Powder XRD of white (A), pink (B) and yellow (C) kaolinite.

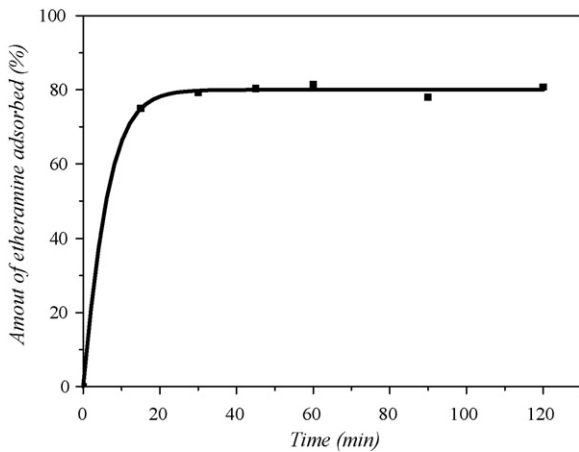


Fig. 5. Influence of contact time between pink kaolinite and etheramine on the amount of etheramine adsorbed (%).

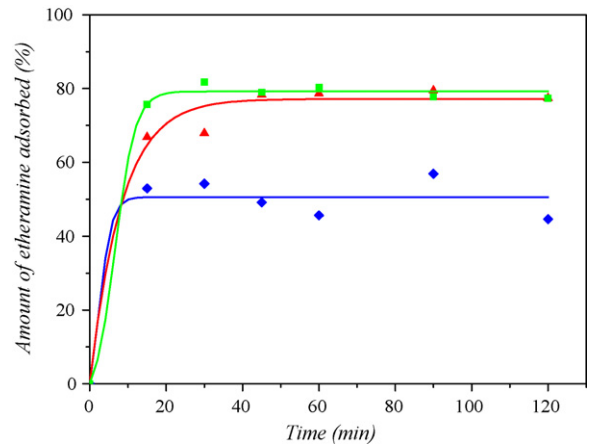


Fig. 6. Influence of the initial concentration of etheramine on adsorption by pink kaolinite: \blacklozenge 100 mg l⁻¹; \blacksquare 200 mg l⁻¹; \blacktriangle 400 mg l⁻¹.

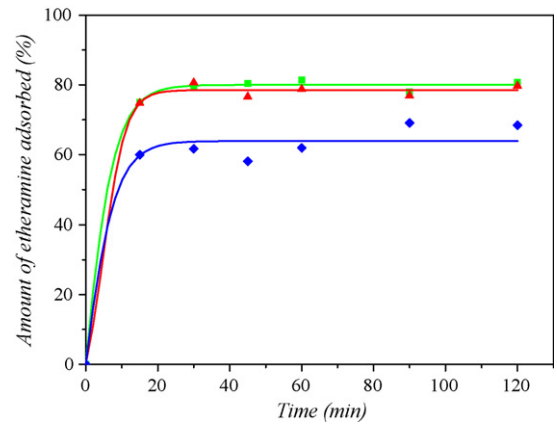


Fig. 7. Influence of the ratio of adsorbent to volume of etheramine solution (g ml⁻¹) on the adsorption of etheramine by pink kaolinite: \blacktriangle 1:50; \blacksquare 1:100 \blacklozenge 1:200.

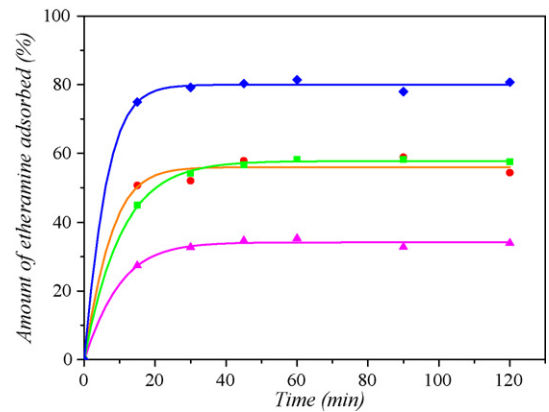


Fig. 8. Influence of pH on the adsorption of etheramine by pink kaolinite: \bullet 12.0; \blacklozenge 10.0; \blacksquare 7.0; \blacktriangle 4.0.

etheramine. As the pH increases, the surface of kaolinite becomes more negative and electrostatic attraction increases, hence facilitating adsorption. This process is favoured at pH 10.0 probably due to ionic and molecular forms of etheramine occurring simultaneously, allowing the formation of ionic-molecular complexes that are more active on the kaolinite surface [30]. When pH 12.0 is attained, however, 100% of the etheramine is in the molecular form and the kaolinite surface presents a strong negative charge.

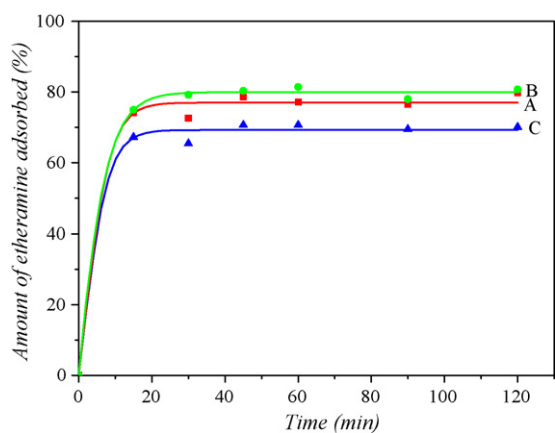


Fig. 9. Removal of etheramine by white (A), pink (B) and yellow (C) kaolinite.

Under such circumstances, adsorption probably occurs as a result of colloidal precipitation of the etheramine on the kaolinite, but the exact mechanism of adsorption at highly alkaline pH values is still unclear. It is concluded that the adsorption of etheramine on the surface of kaolinite depends not only on the degree of dissociation of the former in solution but also on the amount of negative charge on the surface of the latter.

3.3. Efficiency of removal of etheramine

The efficiencies of removal of etheramine by the kaolinites were compared using the optimised parameters, namely, pH 10.0, ratio of adsorbent to volume of solution of 1:100 (g ml^{-1} ; 0.1 g kaolinite) and a contact time of 120 min. The efficiencies of removal of etheramine by white, pink and yellow kaolinite were 77%, 80% and 69%, respectively (Fig. 9).

3.4. Comparison between kaolinite types using adsorption isotherms

In order to compare the adsorption isotherms for white, pink and yellow kaolinite, assays were conducted using the optimised parameters. In Fig. 10, it is possible to observe that white (A) and pink (B) kaolinite adsorbed almost identical amounts of etheramine (33.05 and 34.32 mg g^{-1} , respectively), whereas yellow kaolinite (C) adsorbed much less (23.11 mg g^{-1}). This finding may be explained in terms of the chemical similarity of white and pink kaolinite, as well as by their analogous superficial areas

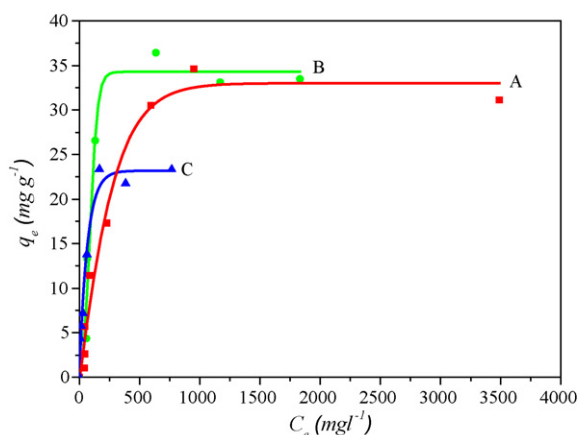


Fig. 10. Adsorption isotherms of etheramine on white (A), pink (B), and yellow (C) kaolinite.

Table 2

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

Isotherm	White kaolinite	Pink kaolinite	Yellow kaolinite
Langmuir			
q_m	34.67	35.96	25.78
K_L	0.005561	0.01370	0.02032
R^2	0.9710	0.9679	0.9663
χ^2	1.0424	1.4436	1.2600
Freundlich			
K_F	4.200	12.22	3.650
n_F	3.879	3.879	3.879
R^2	0.8553	0.8828	0.8857
χ^2	3.4947	6.2843	1.9767

(Table 1). The amounts of etheramine removed by the three kaolinite types were within the ranges reported for the adsorption of some dyes, including violet green (5.89 – 31.84 mg g^{-1}) and brilliant green (10.06 – 30.59 mg g^{-1}) [7], but above those of methylene blue (7.59 – 20.49 mg g^{-1}) [10] and blue aniline (16.66 – 20 mg g^{-1}) [8].

The results of applying Langmuir and Freundlich non-linear models to the adsorption of etheramine on white, pink and yellow kaolinite are presented in Table 2. The Langmuir isotherm has been employed for studies concerning the adsorption of metals and organic compounds on clays [8,14,15]. It is based on simple principles including the adsorption by a uniform monolayer containing a finite number of active sites, uniform adsorption energy and no transmigration of adsorbate over the surface plane. The Langmuir isotherm fails, however, in the sense that it presupposes the independence of the adsorbed molecules and the uniformity of the surface. The Freundlich isotherm attempts to overcome these deviations by assuming that adsorption occurs on heterogeneous surfaces and considers the interaction between the molecules of adsorbate. As is demonstrated by the data shown in Table 2, the Langmuir isotherm was the most appropriate for explaining the adsorption of etheramine on kaolinite. Similar findings have been reported for the adsorption by clays of polyvinylimidazole [11], cationic dyes [7,31], copper [15,32], lead [15] and zinc [32].

3.5. Comparison between kaolinite types using adsorption kinetics

Adsorption kinetic curves are often useful for explaining the mechanisms of adsorption. The values obtained by applying pseudo-first and pseudo-second-order kinetic models to the adsorption of etheramine by white, pink and yellow kaolinites are presented in Table 3. The χ^2 values are calculated using Eq. (11) and are given in Table 3. The removal of etheramine by kaolinite is better described by pseudo-second-order kinetics since the χ^2 values are less than those of pseudo-first-order model. A similar

Table 3

Comparison between adsorbents according to pseudo-first- and pseudo-second-order kinetic models.

Model	White kaolinite	Pink kaolinite	Yellow kaolinite
Experimental q_e (mg g^{-1})	15.42	16.01	14.74
Pseudo-first-order			
k_1 (min^{-1})	0.1737	0.2130	1.783
q_e (mg g^{-1})	15.44	16.02	14.48
R^2	0.9987	0.9995	0.9828
χ^2	0.017197	0.007428	0.217825
Second-order			
k_2 ($\text{mg g}^{-1} \text{ min}^{-1}$)	0.0385	0.0694	0.0266
q_e (mg g^{-1})	15.88	16.27	15.39
R^2	0.9999	0.9998	0.9953
χ^2	0.000982	0.002312	0.060825

situation has been reported for the adsorption by modified kaolinites of various dyes and metals including maxilon yellow 4GL and maxilon red GRL [33], blue aniline [8], lead [15], copper and zinc [32], and iron, cobalt and nickel [16].

4. Conclusions

The adsorption of etheramine on pink kaolinite attained equilibrium in 30 min and was favoured at pH 10.0 under conditions where the initial concentration of etheramine was 200 mg l^{-1} and the ratio of adsorbent to volume of etheramine solution was $1:100 \text{ g ml}^{-1}$. Adsorption was mainly influenced by pH, since this parameter modified the superficial charge of the adsorbent and the degree of dissociation of the adsorbate. At pH 10.0, the surface of kaolinite is predominantly negative, whilst etheramine is 50% ionised and 50% non-ionised, thus facilitating electrostatic interactions. Furthermore, at this pH, adsorption may be increased by the formation of ionic-molecular etheramine complexes on the surface of kaolinite.

The efficiencies of removal of etheramine by white, pink and yellow kaolinite were 77%, 80% and 69%, respectively. Analysis of the isotherms revealed that the q_m values were 33.03, 34.32 and 23.11 mg g^{-1} for white, pink and yellow kaolinite, respectively. Measured q_m values approximated towards those calculated using Langmuir and Freundlich adsorption models, although the former prevailed over the latter. Moreover, the adsorption of etheramine on kaolinite may best be explained in terms of a pseudo-second-order kinetic model. The results demonstrate that kaolinite is an adequate adsorbent for the remediation of etheramine-contaminated waters, since these plentiful and cheap materials present adequate physicochemical characteristics.

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