Adsorption of Ions onto Treated Natural Zeolite

Cristiane da Rosa Oliveira, Jorge Rubio*

Programa de Pós Graduação em Engenharia de Materiais,
Laboratório de Tecnologia Mineral e Ambiental – LTM,
Departamento de Engenharia de Minas, Universidade Federal do Rio Grande do Sul – UFRGS,
Av. Bento Gonçalves, 9500/75, 91501-970 Porto Alegre - RS, Brazil

This work presents studies of modification of a natural zeolite by activation with Na^+ cations and functionalisation with Ba^{+2} and/or Cu^{2+} ions (FZ). The zeolite was characterized, modified and applied in adsorption studies of sulphate and isopropilxanthate ions as flocculated and powdered forms. The reuse of SO_4Ba-FZ was investigated by adsorption-removal of either Ba^{2+} or sulphate ions in stages. Equilibrium data showed that the FZ, flocculated or as powder, provide considerable removal of sulphate ions ($q_{mLangmuir}$: 1.15 and 1.35 meq.g^{-1}, respectively) and isopropilxanthate ($q_{mLangmuir}$: 0.35 and 0.93 meq.g^{-1}, respectively). The reuse of the SO_4-FZ, either powdered or flocculated also uptake significant amount of Ba^{2+} or sulphate ions ($q_{mLangmuir}$: 1.15 meq.g^{-1}), providing a new alternative for the exhausted adsorbent. Thus the activated and functionalised zeolites create new options on the materials engineering area with applications in environmental applied adsorption processes.

Keywords: *natural zeolites, modified materials, adsorption*

1. Introduction

Natural zeolites are hydrated aluminosilicates based on an infinite three-dimensional structure of tetrahedrons as TO_4 (T = Si, Al, B, Ge, Fe, P, Co) joined by oxygen atoms[4,14]. Zeolites have in its internal structure channels and cavities interconnected of molecular dimensions where compensation cations allowing the ion exchange[15,16] exist.

Zeolite materials allow an introduction of new functional groups through several processes of modification, improving substantially its activity and selectivity on the removal several substances[3,7,12,13,17]. Many authors show the use of modified natural zeolite on environmental applications, mainly anions uptake from effluents by adsorption processes[10,11,20,21].

The present work describes studies of characterization, modification (treatment) and application of a natural zeolite from Chile. The zeolites treatment (activation and functionalisation) was validated through of the application of the treated material as powdered, flocs and saturated forms in adsorption processes.

2. Materials and methods

2.1. Materials and reagents

A natural zeolite (NZ) from Minera Formas™ (Chile) was used as adsorbent. Reagents of analytical purity NaCl, $BaCl_2.2H_2O$, $Cu(NO_3)_2.3H_2O$, Na_2SO_4 and $((CH_3)_2CHOCS_2Na)$ were used on the activation, functionalisation and adsorption studies, respectively.

Studies of cationic exchange capacity of the zeolite used the reagent of analytical purity $(NH_4)_2SO_4$.) Aqueous solutions of methylene blue ($C_{16}H_{18}N_3SCI.3H_2O$) were used on the determination of the specific surface area of the zeolite, by adsorption.

The pH adjustment was done using HNO_3 and KOH solutions.

The polymers NALCO 8589 (cationic), MAFLOC 460 (cationic), MAFLOC 2880 (anionic) and QEMIFLOC AH1020 PWG (nonionic) were used on the flocculation studies.

2.2. Chemical analysis

Isopropilxanthate ions concentration was measured using the spectrophotometric method of analyse. This method consisted in direct measurement of the light absorbance, at 301 nm, of the aqueous solutions and results were compared with a calibration[22].

Sulphate ions and ammonia nitrogen concentrations were measured using the methods of analyze described in the Standard Methods for the Examination of Water and Wastewate[1].

The concentration of methylene blue was determined by spectrophotometry[19].

2.3. Chemical, physical and mineralogical characterization

The particle size distribution of powdered zeolite was determined using laser diffraction equipment (CILAS™1064).

The specific surface area of the zeolite was evaluated by methylene blue adsorption method. Thus, aqueous solutions (50 mL) of methylene blue (100 mg.L^{-1}) were mixed for 1hour at room temperature in the presence of different zeolite concentrations. The suspensions were stood up for 23 hours and resulting supernatants were centrifuged and analyzed (methylene blue residual concentration). The specific surface area, evaluated by the Langmuir using 1.08 nm^2 molecule^{-1} for the cross-sectional area[16,19] gave an experimental error of ±4.2 m^2.g^{-1}.

The cation-exchange capacity of the zeolites was determined by activation of material with an aqueous solution of NaCl. A know quantity of the natural zeolite (5 g) was mixed with 50 mL of a NaCl 1 M solution in a glass flask using a Wagner shaker (Marconi™) during 24 hours at room temperature. The resultant suspension was filtrated and washed three times with 300 mL deionised water. The wet activated material was dried at 100 °C for 24 hours and used in adsorption studies for ammonia uptake. Thus, a known quantity of activated zeolite (0.25 g) was mixed with 0.1 L of a solution (100 mg NH_3-N L^{-1}) in an agitated glass flasks for 2 hours. Data were calculated considering the number of equivalent-gram of ammonium cations (18 mg NH_3-N meq^{-1} NH_4^+) adsorbed[16] with an experimental error of ±0.02 meq NH_4^+ g^{-1}.

*e-mail: jrubio@ufrgs.br

The specific mass was measured by picnometry. Here, an amount of material was inserted in a picnometer with water at 4 °C until fulfilment of the volume of the recipient and measured the different masses. Thus, using the known masses of water, sample and recipient, results obtained allowed to determine the specific mass of the zeolite expressed in terms of g.cm^{-3} with an experimental error of ±0.007 g.cm^{-3}. The porosity was determined by the difference between the unit and the relation bulk specific mass and specific mass of the particle[5] with an experimental error of ±0.002.

Moisture of the zeolite was evaluated by gravimetric means. A sample (1 g) of the material was dried at 100 °C for 24 hours, cooled in a desiccator and its mass was monitored in an analytical balance (precision ±0.1 mg) by several times. The difference between the dried mass value and the equilibrium mass value was used to evaluate the moisture content (Experimental error: ±0.01 %).

Scanning electron microscopy (SEM-Philips™XL20) was used for photomicrographs as well as to analyze of zeolite composition (Energy Dispersion X ray, EDX). The sample was initially placed in a vacuum chamber for coating with a thin layer (few nanometres) of gold (Au).

Mineralogical structure of the zeolite was determined by Energy Dispersion X ray (EDX) using diffraction equipment (MPD-Philips™) indicating the main mineral phases of its crystalline structure.

Zeta potential measurements for the natural (NZ), activated (Na-Z) and functionalised zeolite (Ba-FZ or Cu-FZ), as a function of medium pH, were determined using a Zeta Plus™ equipment (Broohaven Instruments). Suspensions (0.01% v.v^{-1}) of the zeolite, previously sieved below 37 µm (400 Mesh Tyler™), in a 10^{-3} mol.L^{-1} solution of KNO$_3$ were used and the medium pH was controlled with the addition of HNO$_3$ (pH < 7) and KOH (pH > 7), separately.

2.4. Modification of zeolite

Modification was performed by stages of activation with sodium ions and functionalisation with barium and copper ions. Activation of the zeolite was carried out by contact of the powdered material with an aqueous solution of sodium chloride. A known quantity of the adsorbent (5 g) was mixed with 0.05 L of NaCl 1 M solution for 24 hours, at room temperature, and the suspension was agitated (at 50 rpm) in glass flasks using a Wagner shaker. Then, the suspension was filtered and the material washed with 0.3 L deionised water. The wet activated material was dried in a 100 °C for 24 hours and used in the functionalisation stage.

The functionalisation with barium and copper ions of the activated zeolite was performed contacting the powdered material samples with aqueous solutions of barium chloride and copper nitrate, respectively. Thus, 5 g were contacted with 0.05 L of the solutions (1.08 meq Ba.g^{-1} and 1.08 meq Cu.g^{-1}) for 24 hours at room temperature and the suspension agitated, at 50 rpm, in glass flasks in the same Wagner shaker. Then, the suspension was filtered, washed with 0.3 L deionised water, dried at 100 °C for 24 hours and used in the adsorption studies.

2.5. Flocculation studies

Flocculation studies of the modified zeolite were performed using Jar Test™ method. Thus, 1 g of the material was mixed with 0.5 L of deionised water. Thus, the suspensions were stirred for 15 minutes to achieve the adsorption equilibrium. Then, commercial synthetic polymers solutions were added to the suspensions under high shear with agitation (4 minutes at 120 rpm) followed by slow agitation (6 minutes at 50 rpm) for the flocs growth and finally, 5 minutes for the flocs settling. Then, the supernatant turbidity was measured. Best flocculant dosages were determined in duplicate tests. The experimental error was about 2.2 NTU and 0.8 NTU for the turbidity measurements using Ba-FZ and Cu-FZ, respectively.

2.6. Adsorption studies using functionalised zeolite

Adsorption studies of sulphate ions onto Ba-FZ were carried out in glass flasks containing 1 g of the adsorbent material and 0.1 L of synthetic solution with different concentrations of the solute. The studies of adsorption isopropilxanthate ions were performed using 0.1 L of aqueous solution of isopropilxanthate ions (60 mg.L^{-1}) and different concentrations of Cu-FZ in pH 8.0. The systems were agitated (50 rpm) in a Wagner shaker during 2 hours (value taken from adsorption kinetic studies which followed the same experimental procedure described above and varying the contact time). After adsorption completion, the suspensions were filtrated and analyzed (pH, temperature and ions concentration). Adsorption studies onto flocculated material used constant mass and a previous stage of flocculation.

The ions uptake (q), expressed as ions removal per unit mass of adsorbent material (mg.g^{-1}), was calculated from the experimental data (C_o, V, W and C_f) in each sample according to Equation 1.

$$q = \frac{V(C_o - C_f)}{m} \tag{1}$$

where, V is the volume of the solute aqueous solution, Co corresponds to the initial solute concentration, Cf, the final solute concentration and m is the mass of adsorbent material[2]

The equilibrium data (isotherm) were fitted by Langmuir and Freundlich models by non-linear regression using the Origin 4.1 software. Therefore, the experimental data fitted very well to Langmuir model (Freundlich model fitting was not showed here).

2.7. Reuse of the saturated zeolite

Reuse studies of saturated zeolite with sulphate ions (SO$_4$Ba-Z) were performed for the sequential uptakes of barium and sulphate ions. Powdered functionalised material (Ba-FZ) was saturated with sulphate ions in the adsorption studies using known concentration of an aqueous solution of sulphate ions (1800 mg.L^{-1}). The dried saturated material (SO$_4$Ba-Z) was reused through contact of 1 g of the adsorbent and a 0.05 L of barium chloride aqueous solution for 2 hours. The wet material was washed with 0.3 L deionised water, dried at 100 °C for 24 hours and used again on batch adsorption experiments of sulphate ions. In the case of the saturated flocculated materials reuse, the studies used the wet flocs from the washing process with deionised water. Figure 1 illustrates the different stages of the reuse of saturated flocculated materials. The sulphate ions uptake (q) was calculated as described in the adsorption studies.
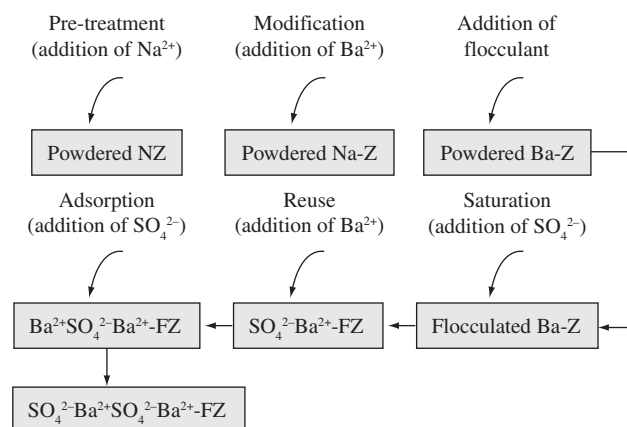
Figure 1. Staged reuse studies of saturated flocculated zeolites as "adsorbents". (NZ: natural zeolite; Na-Z: pre-treated zeolite; Ba-Z: modified zeolite with barium ions; and FZ: flocculated zeolite).

3. Results and Discussions

3.1. Chemical, physical and mineralogical characterization

The particle size distribution of the zeolite, obtained by laser diffraction method, is shown in Figure 2.

The size distribution analyze showed 100 % of the particles have minor size of 105 μm and the mean particle diameter (volumetric) obtained was about 25 μm (Experimental error: ±0.01 μm).

Additional results obtained on the characterization of the zeolite are shown in the Table 1.

Photomicrographs of the zeolite sample obtained by SEM, are shown in Figures 3 and 4.

The qualitative composition analysis (EDX) obtained for the zeolite shown in Figure 4 can be seen in Figure 5 and the mineralogical composition is represented in the Figure 6 and described in the Table 2.

The Figure 5 shows the peaks of the main chemical elements (O, Na, Al, Si, P, K and Fe) that are present in the structure of this natural zeolite, in agreement with the chemical composition (Table 2).

Zeta potential measurements obtained for the natural zeolite (NZ), activated zeolite (Na-Z) and functionalised zeolite (Ba-FZ and Cu-FZ), as a function of medium pH are shown in the Figures 7 and 8.

Figures 7 and 8 show that natural zeolite (NZ) surface groups are electronegative in all pH range studied. Yet, the samples of Cu-FZ and Ba-FZ kept the same charge density electronegative compared with the Na-Z indicating an adsorption mechanism during the stage of functionalised mainly by ionic exchange.

3.2. Flocculation studies

Results obtained on the flocculation studies of Ba-FZ and Cu-FZ, both in water, showed the cationic polymer Nalco 8589 was the best flocculant for these systems. Data of the investigations of optimal dosage as a function of the residual turbidity are show in the Table 3.

Table 3 shows that the concentrations of 1 mg.L^{-1} (0.5 mg.g^{-1}) and 3 mg.L^{-1} (1.5 mg.g^{-1}) for the systems (Ba-FZ + H$_2$O) and (Cu-FZ

+ H$_2$O), respectively, provided low turbidity of the supernatant and satisfactory formation of flocs.

3.3. Adsorption studies using functionalised zeolite

Kinetic adsorption studies showed rate constants values for sulphate and isopropilxanthate of 0.24 and 0.46 minutes^{-1} respectively. These values followed a first-order reaction kinetic model and reached the adsorption equilibrium in about 20 and 10 minutes (each case), indicating the existence of the adsorption equilibrium.

Figures 9 and 10 show equilibrium data (isotherms) for sulphate ions adsorption onto functionalised zeolite with barium ions as powdered and flocculated forms, respectively.
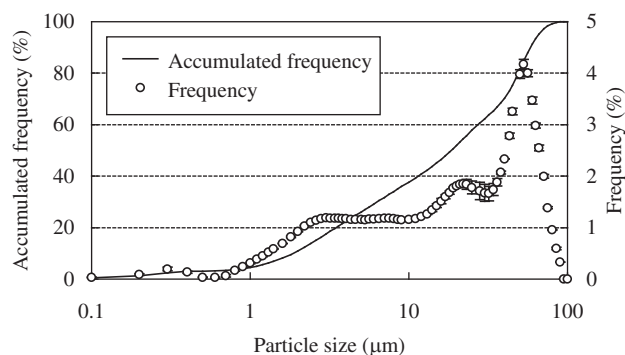
Figure 2. Particle size distribution of the zeolite. Erro exp.: ±0.012%.
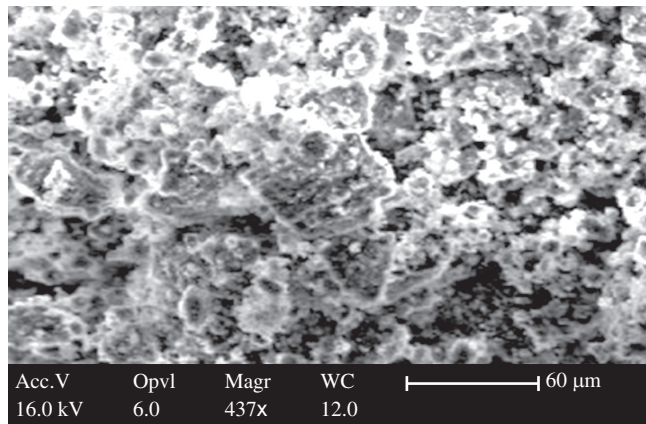
Figure 3. Image of zeolite particles obtained by scanning electron microscopy. Bar length is 50 μm. and the magnification 487x.
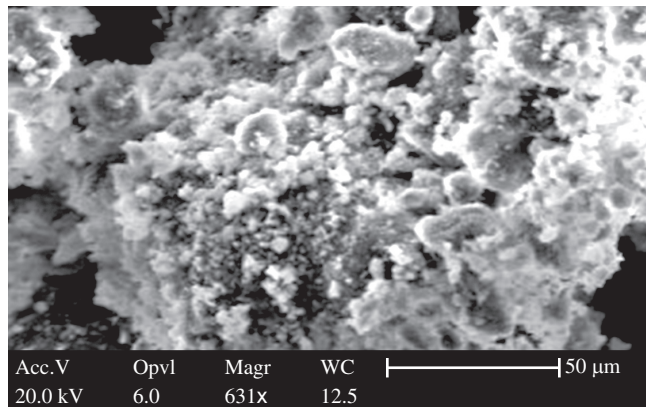
Figure 4. Image of zeolite particles obtained by scanning electron microscopy. Bar length is 50 μm. and the magnification 631x.
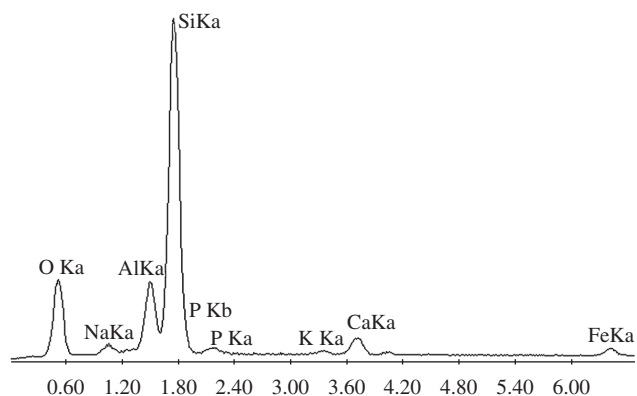
Table 1. Characterization data of natural zeolite.

Specific surface area	80 m^2.g^{-1}
Cation-exchange capacity	1.08 meq NH$_4^+$ g^{-1}
Specific mass	2.2 g.cm^{-3}
Porosity	0.89
Moisture	2.5%

Table 2. Mineralogical composition of the zeolite and respective peaks.

Phases	Peaks	Phases	Peaks
Clinoptilolite	2, 9, 10, 11, 15	Quartz	8, 13, 18, 21, 22, 23, 24, 25
Gismondine	17, 21	Mordenite	1, 12, 20, 9, 5, 19, 3, 4
Heulandite	7, 16	Offretite	6
Calcium Aluminosilicate	14		

Table 3. Influence of the Nalco 8589 as function of the residual turbidity of the supernatant for the systems (Ba-FZ + H$_2$O) and (Cu-FZ + H$_2$O).

[Nalco 8589], mg.L^{-1}	0.5	1.0	3.0	5.0	10.0
Turbidity (Ba-FZ + H$_2$O), NTU	15.5	16.5	36.5	59.7	83.2
Turbidity (Cu-FZ + H$_2$O), NTU	8.2	7.3	21.7	40.2	56.2

Temperature: 25 °C; Inicial turbidity: 352 NTU: [Ba-FZ]: 2 g.L^{-1}; [Cu-FZ]: 2 g.L^{-1}; Experimental error: (Ba-FZ): ± 2,2 NTU.; (Cu-FZ) ± 0,8 NTU.

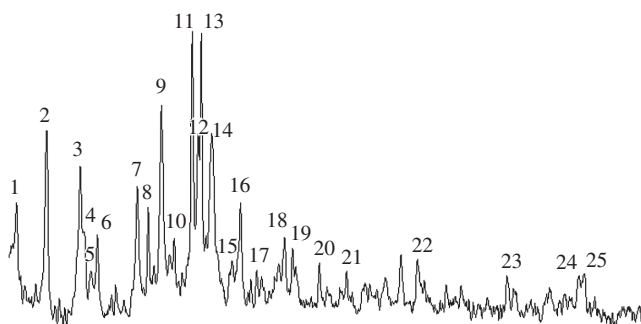**Figure 5.** Scanning electron spectral analyses of a zeolite.

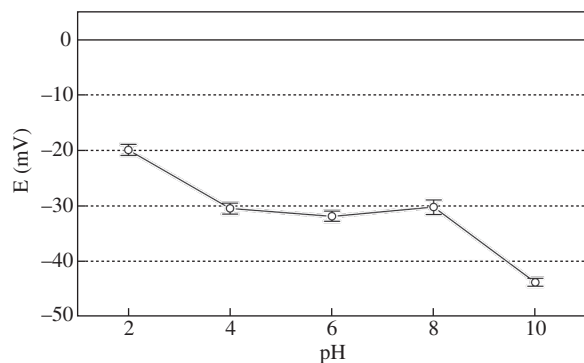**Figure 6.** Mineralogical composition of the zeolite obtained by EDX.

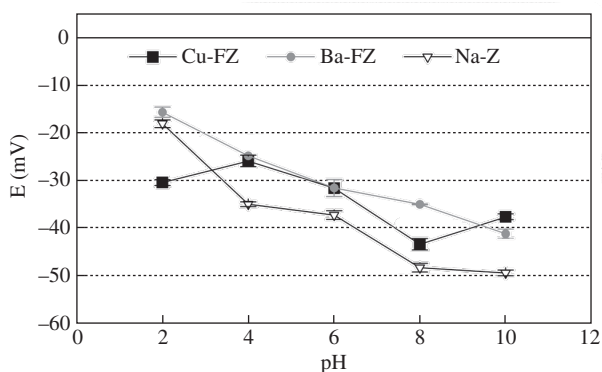**Figure 7.** Zeta potential of the natural zeolite. Experimental error: ±0.7 mV.

Figure 8. Zeta potential of the activated zeolite (Na-Z), functionalised zeolite (FZ) with barium ions (Ba-FZ) and cooper ions (Cu-FZ). Experimental error: Na-Z (±0.7 mV), Ba-FZ (±0.8 mV), Cu-FZ (±1.3 mV).

The data (Figures 9 and 10) shows value of the Langmuir parameter q_m of 1.35 meq.g^{-1} for the powdered material and 1.15 meq.g^{-1} for flocculated material. These results showed the fact of the adsorbent material is flocs form did not have influence on the adsorption capacity agreeing with others authors[6,8,9,18] that studied adsorption onto polymeric flocs.

Adsorption studies of isopropilxanthate ions onto Cu-FZ as flocculated and powdered forms, in value pH 8.0, show significant results with equilibrium data adjust in the Langmuir model (Figures 11 and 12).

Data of the Figure 11 show value of Langmuir parameter q_m of 0.35 meq.g^{-1} for powdered material and 0.93 meq.g^{-1} for flocs indicating a high influence of the flocculant polymer on the medium, probably, related with interactions between the polymeric chains of the flocculant and the carbonic chains of isopropilxanthate ions.

3.4. Reuse of saturated zeolite

Reuse studies showed high potential for sequential uptakes of barium and sulphate ions from aqueous solutions using saturated zeolite with sulphate ions (SO$_4$Ba-Z). Thus the SO$_4$Ba-Z uptake barium ions again and this material (BaSO$_4$-Ba-RZ) showed a high capacity of sulphate ions adsorption constituting a new adsorbent material possible of reuse.

Figures 13 and 14 show equilibrium data (isotherm) of sulphate ions adsorption onto reused zeolite with barium ions as powdered and flocculated forms.

Data of Figure 13 and 14 shows a q_m 1.15 meq.g^{-1} for powdered and flocculated materials. These results demonstrate the viability for reuse of the saturated materials, mainly by possibility of sequential
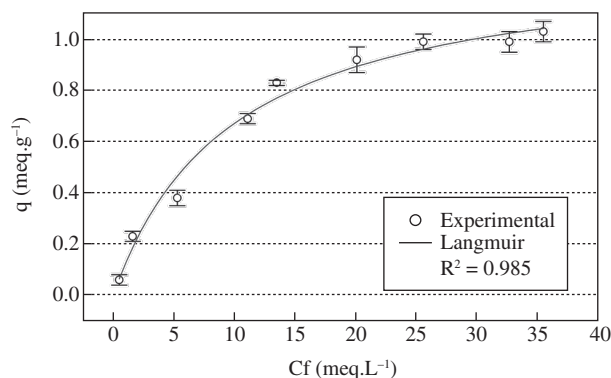
Figure 9. Equilibrium data (isotherm) of sulphate ions uptake, from aqueous solutions, by powdered modified zeolites. Contact time: 2 hours, Ba-Z: 10 g.L^{-1}, temperature: 25 °C, pH 6.0.
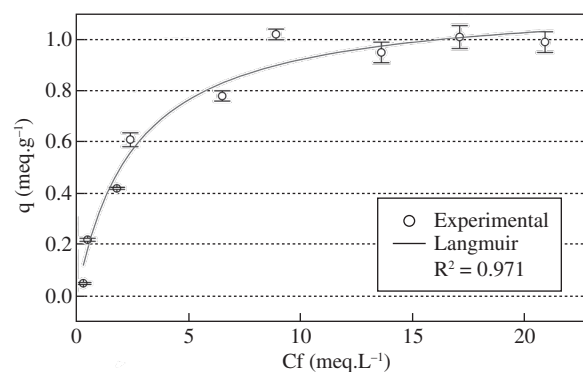
Figure 10. Equilibrium data (isotherm) of sulphate ions uptake, from aqueous solutions, by flocculated modified zeolites. Contact time: 2 hours, Ba-Z: 10 g.L^{-1}, temperature: 25 °C, pH: 6.0.
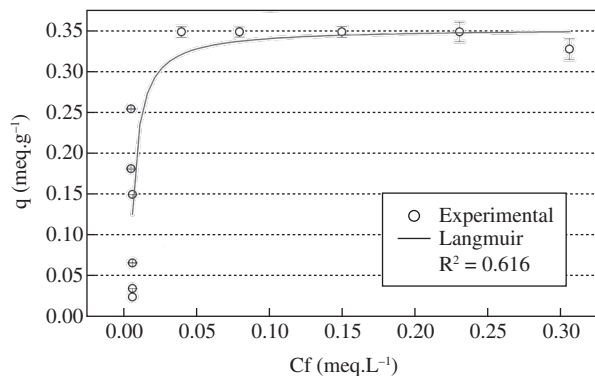
Figure 11. Equilibrium data (isotherm) of isopropilxanthate ions uptake, from aqueous solutions, by powdered modified zeolites. Contact time: 2 hours, CuZ: 10 g.L⁻¹, temperature: 25 °C, pH: 8.0. Experimental error: ±0,004 meq.g⁻¹.
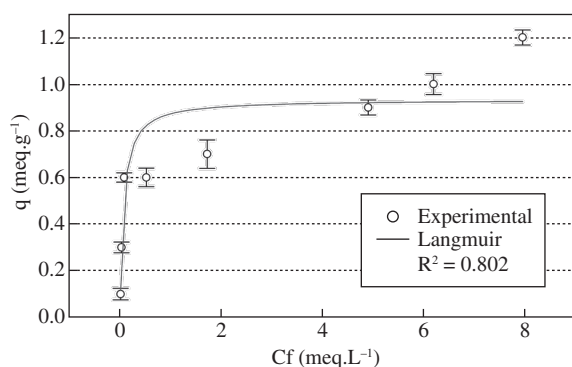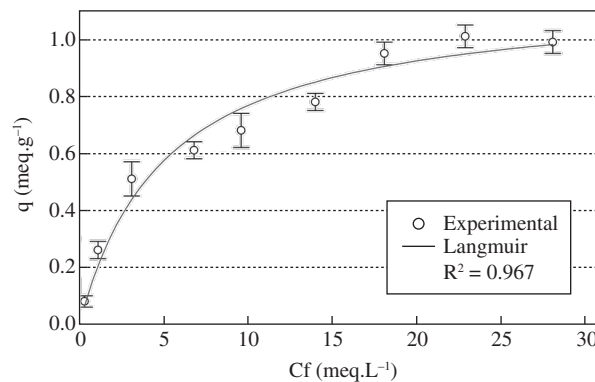

Figure 12. Equilibrium data (isotherm) of isopropilxanthate ions uptake, from aqueous solutions, by flocculated modified zeolites. Contact time: 2 hours, Cu-Z: 10 g.L⁻¹, temperature: 25 °C, pH: 8.0. Experimental error: ±0.05 meq.g⁻¹.
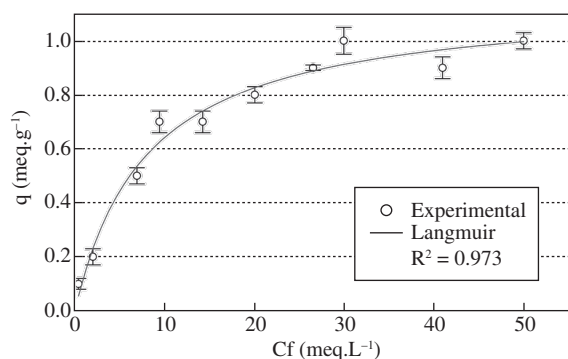
Figure 13. Reuse of powdered saturated zeolite. Equilibrium data (isotherm) for the sulphate ions uptake by $BaSO_4$-Ba-Z. Contact time: 2 hours, Ba-RZ: 10 g.L⁻¹, temperature, 25 °C, pH: 6.0.

adsorption of barium and sulphate ions with decrease of cost and absence of new waste production.

Furthermore, all residual solutions (resulted after adsorption) did not have significant either barium or copper ions concentration revealing the absence of desorption (ion exchange) from the surface of the zeolite. Other observation was the colour modification of the zeolite after adsorption of isopropylxanthate ions, confirming a reaction onto or into the particles, resembling the colour of the copper xanthate salt. Harris[12] reported that the name "xanthate" derived of the Greek word xanthos, which means "yellow" (adapted from the coloration of the insoluble salt of cuprous xanthate).

The Table 4 shows main results obtained in the present work.

Figure 14. Reuse of flocculated (and saturated) zeolites. Equilibrium data (isotherm) for the sulphate ions uptake from aqueous solutions. Contact time: 2 hours, Ba-RFZ-Ba: 10 g.L⁻¹, temperature: 25 °C, pH: 6.0.

Table 4. Summary of results – sulphate and isopropilxanthate removal studies.

Pollutant	Adsorbent material	q_m (meq.g⁻¹)
Sulphate ions	FZ-Ba	1.35
	RFR-Ba	1.15
	FFZ-Ba	1.15
	RFFZ-Ba	1.15
Isopropylxanthate ions	FZ-Cu	0.35
	FFZ-Cu	0.97

4. Conclusions

Natural zeolites from Chile have, in its crystalline structure mineralogical phase, clinoptilolite, gismondine, heulandite, offretite, quartz and calcium aluminosilicate. Zeolite samples show a mean particle diameter of 25.4 µm and the value for specific surface area, cation-exchange capacity, specific mass, porosity and moisture were of 80 m².g⁻¹, 1.08 meq NH₄⁺ g⁻¹, 2.2 g cm⁻³, 0.89 and 2.5%. Zeolite modification involved two stages of ion-exchange: an initial (activation) of the adsorbent material with sodium ions (Na-Z) and other of functionalisation with barium and copper ions (Ba-FZ and Cu-FZ). The latter promoted the application of the zeolite on adsorption processes through chemisorption mechanisms that apart from copper and barium ions uptakes, showed high adsorption of sulphate and isopropilxanthate ions for flocculated ($q_{sulphate}$: 1.15 meq.g⁻¹ and $q_{xanthate}$: 0.93 meq.g⁻¹) and as powdered form ($q_{sulphate}$: 1.35 meq.g⁻¹ and $q_{xanthate}$: 0.35 meq.g⁻¹). Yet, the reuse of the saturated zeolite, as flocculated and powdered forms, shows viability as a new adsorbent of sulphate ions (both, 1.15 meq.g⁻¹). Activated and functionalised zeolites, as powdered or flocculated forms, show new alternatives in the adsorption area and the exhausted zeolites can be reused as saturated adsorbents.

References

1. American Public Health Association. *Standard methods for the examination of water and wastewater*. 19 ed. Washington; 1995.