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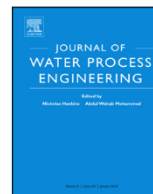
Adsorption and desorption processes for copper removal from water using different eluents and calcined clay as adsorbent

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ABSTRACT

In this work, the copper removal in fixed-bed of Bofe calcined clay was realized, in which the adsorption and desorption of copper ions, the time of equilibrium and kinetic curves were investigated. Different types of eluents were utilized for calcined clays bed regeneration. Desorption tests were performed using a NaCl solution at 1% and seawater both at pH 3. The results indicated that the regeneration of the bed with NaCl/HCl or saline water at pH 3 is very efficient and the elution was verified as 50%. Also, it was observed an increase in removal after exposure of the bed to the eluent. The highest adsorption capacities of copper were ≈0.3 mmol/g, on the Bofe calcined clay. The equilibrium time increased from 120 min to 400 min considering the first to the last cycle. During the regeneration process, the mass-transfer zone decreased almost linearly from 9.8 to 3.4 cm with the use of NaCl and from 9.9 to 6.7 cm with seawater. In addition, those eluents provide the ideal breakthrough behavior. The recovery efficiency of the water showed that the desorption of copper ions with NaCl or seawater is feasible and has great potential.

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1. Introduction

In Brazil, poor quality in rivers and reservoirs is a challenging issue due to the amount of waste disposed of directly into these bodies. This fact has negative impacts not only on the supply of drinking water, but also affects irrigation and the quality of fish harvested. Thus, studies related to techniques for adsorption of pollutants, as well as the kinetics of the process are necessary to evaluate the viability of the recovery procedure.

Some studies have shown that the selectivity and efficiency of pollutants adsorption, such as toxic metals by batch adsorption [1], adsorption in fixed bed from Cu^{2+} [2,3] and Ni^{2+} [4], and batch adsorption from dye [5] are strongly dependent on the physical properties and chemical composition of the adsorbent. However, these studies have not demonstrated the regeneration of adsorbent or the changes caused by desorption.

The use of different adsorbents for metal removal, as vermiculite [6], bentonites [1–4,7,8] and other low-cost adsorbents, and

bioadsorbents (such as rice husk ash [12]) has been investigated. The application of clays for adsorption or elimination of toxic metals present in wastewater has recently been the object of study because of numerous economic advantages [10–12]. The cost of clay is relatively low compared with other alternative adsorbent, including activated carbon, natural and synthetic zeolites and ion exchange resins. Another advantage in using clay as the adsorbent is related to the intrinsic properties such as specific surface area, excellent physical and chemical stability and other structural and surface properties [13].

Although the results involving the use of clays to metals removal are significant and promising, there is still a need for a better understanding of these results with the clay bed regeneration mainly for the study of solvents that can produce concentrated solutions of metal ions as reported studies by Ozdemir and Yapar [14]. This study aims to evaluate the copper adsorption and desorption using different eluents in the regeneration of Bofe calcined clay, as well as the modifications of the clay due desorption process and also the simulation of the adsorption process. The eluents used were NaCl 1% and seawater, both at pH 3. The seawater was chosen because of its natural concentration of chlorides and low cost, since there is no spent water or reagents for their preparation.

2. Experimental

2.1. Adsorbent and metal speciation

A sample of bentonite called Bofe, from the Northeast region of Brazil and provided in raw form, was used as adsorbent. The Bofe clay was grounded and the particles were separated by the sieving technique. Then thermal treatment was conducted for a particle size of 0.855 mm. The samples were subjected to calcination in muffle at 500 °C for a period of 24 h. The characterization of this clay, involving various techniques and analyze, was reported by Vieira et al. [4].

The adsorption experiments were conducted using an aqueous solution with $Cu(NO_3)_2 \cdot 3H_2O$ at a fixed concentration. Chemical diagrams of copper plotted against the pH were simulated using the programs Medusa and Hydra [15] in order to verify the several species in aqueous media. These diagrams have been made to remove the concentrations corresponding to the maximum concentration of ionic chemical species. Speciation was performed taking into account the stoichiometry of the salt.

2.2. Fixed-bed experiments

Assays were performed in dynamic system using an acrylic jacketed column with internal diameter of 1.4 cm and high of 14.0 cm. The bed height used in tests was 14.0 cm. The feed solution containing copper metal species at a concentration of 1.57 mmol/L was fed by a peristaltic pump at the bottom of column previously flooded with deionized water. The flow rate for copper removal onto Bofe calcined clay was obtained by de Almeida Neto et al. [3] was 4 mL/min. The feed solution was prepared from dissolution of the copper salt. The pH was controlled during the experiment and when its value was greater than 4.5 up, a correction was made by the addition of 1 mol/L nitric acid to obtain the desired value. The pH of the solutions was measured by a pH meter with automatic temperature compensation.

Samples of the solution eluted from the column were collected at pre-defined intervals by the fraction collector, and the copper concentration in each sample was determined by atomic absorption spectrophotometry.

Eqs. (1) and (2), respectively, are the quantities of metal retained in the bed until the breakthrough time (q_u) and until saturation (q), obtained by a mass balance in the column using the same saturation data, from breakthrough curves. The area under curve ($1 - C/C_0$) until the breakthrough time (t_b) is proportional to q_u, and until exhaustion of the bed is proportional to q.

$$q_u = \frac{C_0 F}{m} \int_0^{t_b} \left(1 - \frac{C|_{z=L}}{C_0}\right) dt \qquad (1)$$

$$q = \frac{C_0 F}{m} \int_0^{\infty} \left(1 - \frac{C|_{z=L}}{C_0}\right) dt \qquad (2)$$

where C_0 is the initial concentration in mmol/L, F is the flow rate in mL/min, m is the mass of adsorbent in g.

Eq. (3) represents the mass transfer zone (MTZ) of the total height (Ht) of the bed and can be calculated by substitution of Eqs. (1) and (2), according to Geankoplis [16].

$$MTZ = \left(1 - \frac{q_u}{q}\right) Ht \qquad (3)$$

The percentage of total removal (%RT) was determined by the fraction of metal in the solution which was retained in solid phase considering that all metal has been used in the process of bed's saturation.

2.3. Desorption evaluation

The saline solutions used in desorption were NaCl 1% and seawater collected on the coast of southeastern Brazil. NaCl and seawater were adjusted to pH 3 by the addition of HCl. The seawater used in this work had 21.26 g/L of chlorides, 12.96 g/L of sodium, 2.57 g/L of calcium, 2.44 g/L of potassium, 1.56 g/L of magnesium and 2.97 g/L of sulphates. By atomic absorption spectrophotometry, it was not detected the presence of copper ions in sea water used as eluent.

The elution curves obtained for the displacement of the metals of calcined clays were performed in dynamic system, using the same flow rate values held for the adsorption, and evaluated according to the amount of eluted metal. Eq. (4) presents the amount of eluted metal (q_{el}) calculated by the integration of elution curves. The area under the curve multiplied by the feed flow rate per gram of calcined clay leads to the amount of metal eluted [17]:

$$q_{el} = \frac{F}{m} \int C_c \cdot dt \qquad (4)$$

The elution percentage (%D) was measured considering 100% the total amount of removal (q) of the metal to be extracted from the clay.

2.4. Mathematical model of the adsorption

Bohart and Adams [18] model assumes that the adsorption rate is proportional to the residual capacity for adsorption and concentration of the adsorbed species, and it does not consider important the axial dispersion effect. In this case the intraparticle diffusion is negligible. The mass transfer rates satisfy the equations:

$$\frac{\partial C}{\partial t} + \frac{\rho_L}{\varepsilon} \frac{\partial q}{\partial t} + v \frac{\partial C}{\partial z} = 0 \qquad (5)$$

$$\frac{\partial q}{\partial t} = kC(q_s - q) \qquad (6)$$

where z is the height of the bed, v, the flow velocity, ε is the porosity of the bed, ρ_L is the density of the bed, t is the process time and the parameters k represents the constant removal rate.

The choice of this model is due to the fact that it considers that the removal capacity is constant and the isotherms obtained for the studied adsorbents showed irreversible behavior. Thus, for a better representation of this study we used sorption capacity of the adsorbent as the amount of metal removed when the system is in equilibrium. Eqs. (7) and (8) are the boundary conditions:

$$C(0, z) = 0 \Rightarrow q(0, z) = 0 \qquad (7)$$

$$C(t, 0) = \begin{cases} 0 \Leftrightarrow t = 0 \\ C_0 \Leftrightarrow t > 0 \end{cases} \qquad (8)$$

Eq. (9) is the analytical solution of the model of Adams and Bohart [18] given by Ruthven [19]:

$$\frac{C}{C_0} = \frac{e^{\tau}}{e^{\tau} + e^{\xi} - 1} \qquad (9)$$

where

$$\tau = kC_0 \left(t - \frac{z}{v}\right) \qquad (10)$$

$$\xi = \frac{kq_0 z}{v} \left(\frac{1 - \varepsilon}{\varepsilon}\right) \qquad (11)$$

q_0 represents the quasichemical concentration of metal in the solid state at time zero of the elution.

For each breakthrough curve, parameters k and q_0 were found. *Statisca 5.0* was used as a computational tool in fitting the *quasichemical* to the experimental data.

3. Results and discussion

3.1. Copper adsorption

The adsorption cycles were performed with copper concentration in the feed bed 1.57 mmol/L. Fig. 1 shows breakthrough curves obtained for calcined clay Bofe regenerated with NaCl and seawater. In Fig. 1A, the time t_b increases from 100 min to 400 min under the breakthrough #1. From the breakthrough #2 to the last performed breakthrough #5, the time t_b remains close to 400 min. Fig. 1B presented a similar behavior for breakthrough time when seawater was used in the copper desorption. After the first desorption, the breakthrough curves obtained had lower resistance to saturation.

Table 1 shows the total amount removed, the useful quantity removed, the *MTZ* and the percentage removal for each cycle Cu^{2+}/calcined Bofe clay. The copper removal obtained by saturating the bed in the first test cycle of the column was 0.297 mmol/g and it increased to 0.378 mmol/g when the second bed was regenerated by NaCl 1%.

The highest adsorption capacities of copper were ≈0.3 mmol/g, on the Bofe calcined clay. This value is higher than the one noted by Abollino et al. [20] with the use of a montmorillonite (sodium form), where removing the copper was of 0.048 mmol/g. As there is not a variation in the bed and the initial concentrations of copper in the solution (1.57 mmol/L), the increment of the amount of useful removal caused by the displacement of the breakthrough point after the first elution causes the decrease in the *MTZ* length. Comparing the first and the last *MTZ*, it has decreased by more than 1/3 of the first test maintaining the initial concentration. The *MTZ* decreased almost linearly from 9.8 to 3.4 cm with the regeneration using NaCl and from 9.9 to 6.7 cm using seawater. All response variables showed that the removal increased with the passage of the eluents. This fact can be mainly attributed to treatment with sodic eluent. Treatment of clays in order to transform them into sodic clays can be achieved by a chemical reaction.

Since it was observed a variation in the behavior of the breakthrough curves during the adsorption and desorption cycles, which initially showed resistance to saturation for the first curves and after elution they obtained a more ideal behavior. Probably, the other curves presented a process of adsorption coupled with ion exchange, providing the breakthrough curves close to the ideal behavior.

Table 1
Parameters for copper adsorption using NaCl and seawater as eluent.

Eluent	Breakthrough	q (mmol/g)	q_u (mmol/g)	MTZ (cm)	%RL
NaCl 1%	#1	0.297	0.088	9.85	39.47
	#2	0.378	0.309	2.54	56.79
	#3	0.359	0.265	3.64	53.92
	#4	0.341	0.265	3.14	51.32
	#5	0.38	0.264	4.27	57.21
Seawater	#1	0.328	0.095	9.94	41.1
	#2	0.445	0.221	7.05	55.82
	#3	0.473	0.264	6.18	59.29
	#4	0.43	0.22	6.83	53.85
	#5	0.436	0.22	6.92	54.6

3.2. pH effect

Fig. 2 presents copper speciation for two copper concentrations. According to these chemical diagrams the Cu^{2+} ions exist below of pH 5 with no precipitation.

Fig. 3 presents measured pH in the columns exit with breakthrough curves obtained at the fifth adsorption of copper by Bofe calcined clay regenerated by NaCl or seawater. The pH remained below 4.5 and followed a similar behavior in all adsorptions. According to Fig. 2 there is no copper precipitation during adsorption.

Fig. 4 shows the exponential decay of the fifth desorption kinetics of copper using NaCl and seawater. The measured pH values were also lower than 4.5. The pH of the solutions in the column outlet decreased during adsorption and increased during desorption.

Abollino et al. [21] obtained in a continuous system with the use of a Na-montmorillonite, which at low pH values (2.5–3.5), the hydrogen ion competes with heavy metals to surface sites. This effect is particularly avoided in this work because, as seen in Figs. 3 and 4, the lowest pH measured is above 3.5.

3.3. Desorption studies

Table 2 lists the parameters such as the amount of metal extracted from the bed and the percentage extraction for each desorption curve using the two eluents. Desorption process occurs predominantly in the first hour of contact, with both eluents. It was not possible to complete the regeneration of the bed in the fifth elution because clay suffered layers defoliation, dissolving the bed and making the column pressure insufficient to continue the experiment. Regeneration with NaCl or seawater at pH 3 provided
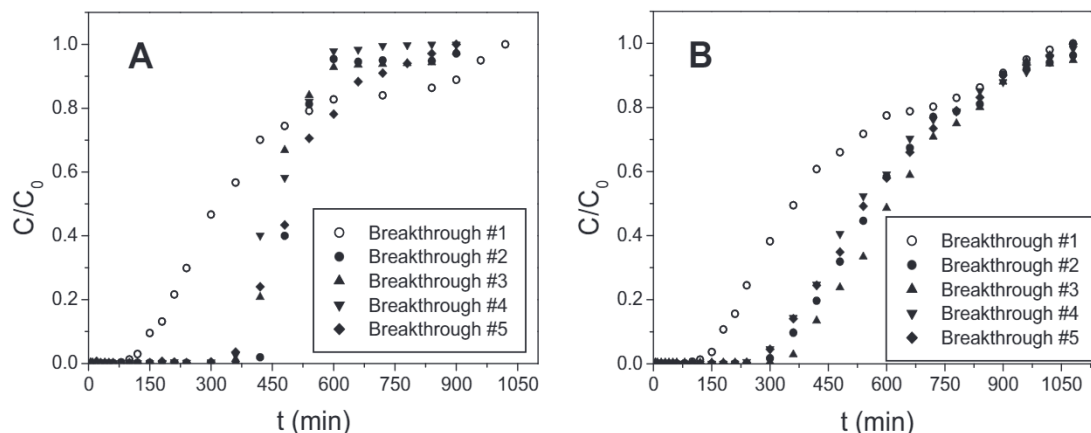

Fig. 1. Breakthrough curves of copper by calcined clay Bofe. Eluent: (A) NaCl 1% and (B) seawater.
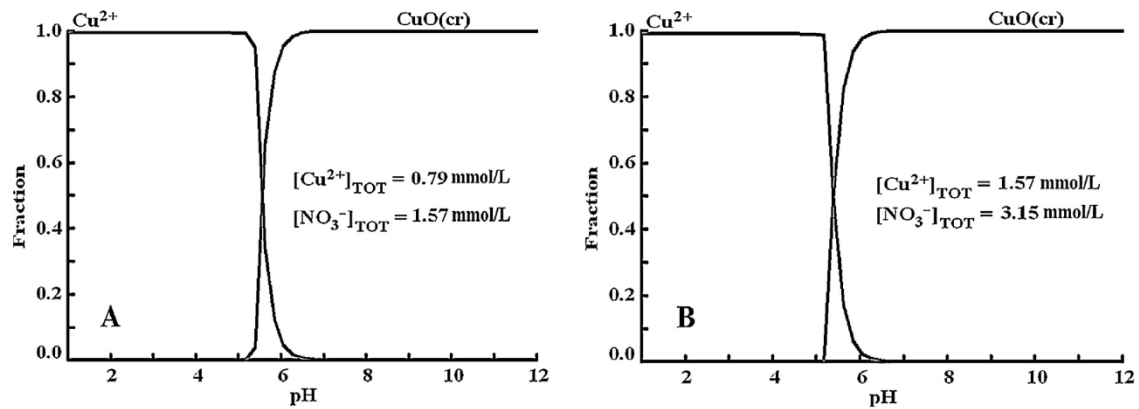
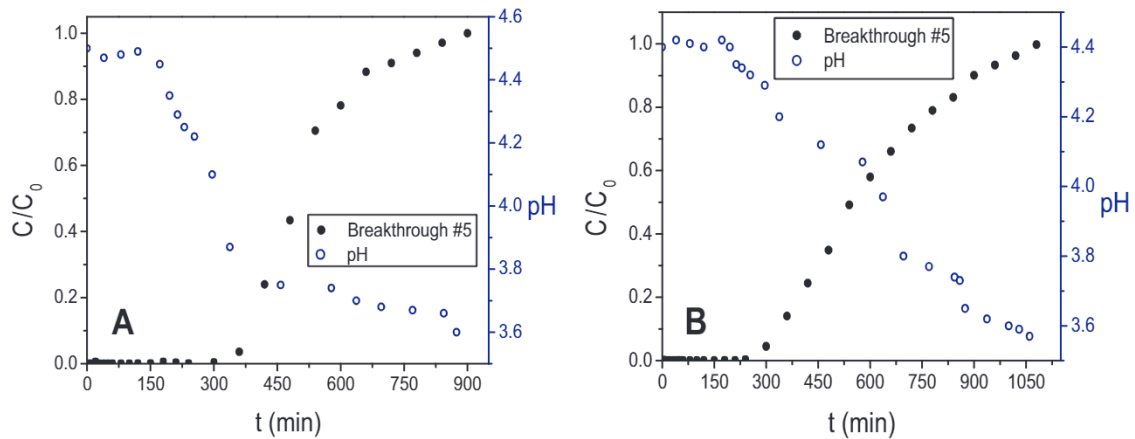**Fig. 2.** Cu speciation in the concentrations (A) 0.79 mmol/L and (B) 1.57 mmol/L.

Fig. 3. Breakthrough #5 using eluents (A) NaCl and (B) seawater.

3.4. Adjusted model and simulation

Table 3 presents parameter values for the *quasichemical* solution of the Bohart and Adams [18] model. It is observed that the parameter k varies with changes suffered by clays due to the passage of the eluents. This can be explained because a new breakthrough curve is established after elution. The parameter q_0, although it does not have any relation with k, also receives the influence of the changes observed. The increment of q_0 can be attributed to the increment in sodium-containing sites that are exchanged during the process.

Fig. 5 showed the function Bohart and Adams [18] obtained for each breakthrough curve, with breakthrough curves simulated for different heights of the bed not experimentally performed when NaCl was used as eluent.

Table 4 presents parameters for simulations of breakthrough curves. However, when the bed height increases there is an increased amount of useful adsorption. According to Table 4, the lower *MTZ* was simulated with a bed height of 14 cm, the same
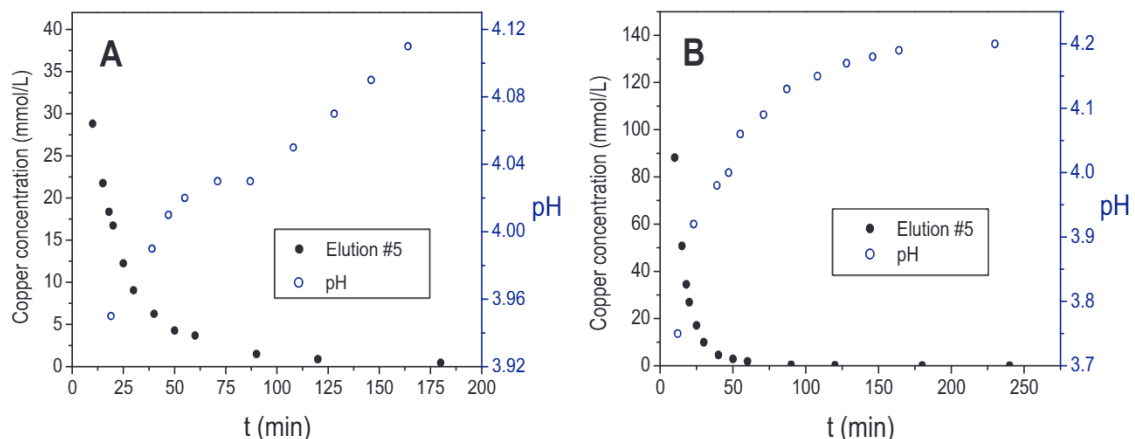
elution efficiencies around 50%. In addition, it provides the breakthrough ideal behavior.

Fig. 4. Desorption # 5 using (A) NaCl and (B) seawater, both with varying pH.

Table 2
Regeneration parameters of the columns.

Eluent	Desorption	Time (min)	q_{el} (mmol/g)	%D
NaCl 1%	#1	120	0.145	48.82
	#2	90	0.166	43.92
	#3	240	0.19	52.92
	#4	240	0.187	54.84
	#5	180	0.158	41.58
Seawater	#1	250	0.169	51.52
	#2	250	0.225	50.56
	#3	240	0.224	47.36
	#4	360	0.213	49.53
	#5	240	0.216	49.54

Table 3
Parameters of the solution *quasichemical*.

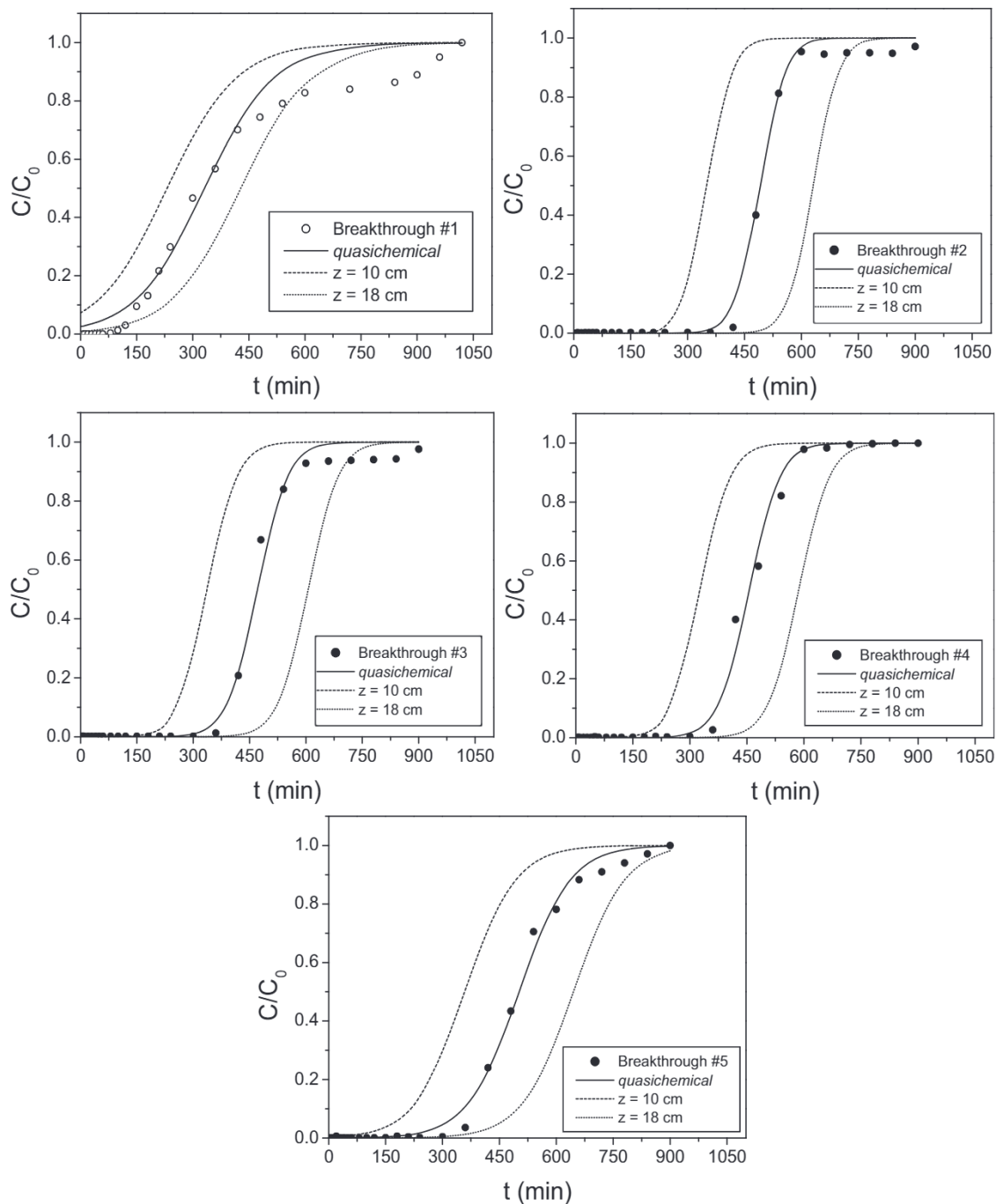| Eluent	Breakthrough	k (L/mmol min)	q_0 (mmol/L)
NaCl 1%	#1	0.007	215.0
	#2	0.025	318.0
	#3	0.019	305.0
	#4	0.019	295.0
	#5	0.01	325.0
Seawater	#1	0.007	300.0
	#2	0.0065	400.0
	#3	0.006	420.0
	#4	0.0055	380.0
	#5	0.0053	375.0

Fig. 5. Fit for breakthrough curves of copper in cycles of removal using NaCl as eluent.

value used experimentally. The relationship between the inner diameter and the height of the bed in the experiment was 1/10. The simulations showed that other ratios of internal diameter and bed height are not suitable for this system because *MTZ* calculated for the height bed simulated were higher than *MTZ* in the ratio diameter and height of the bed 1/10.

The values of the adsorbed amounts, q, q_u, as well as the removal percentage calculated in the simulations increased with bed height increase. It is known that the increment of the ratio between internal diameter of the continuous bed and adsorbent bed height as well as the increment of the amount of adsorbent mass cause the greater percentage of adsorbed amounts and removal.

The results of simulation for copper adsorption when seawater is the eluent were as good as those presented when NaCl is the eluent, as shown in Fig. 6.

Table 5 shows the simulation follow the same pattern shown above, when NaCl was used as eluent. However, the estimated values *MTZ* are larger, indicating that regeneration with seawater was not as good as with NaCl. This may be explained by the fact that the sea water is a mixture of dissolved salts.

3.5. Recovery efficiency of water

The recovery efficiency of water (REW) was evaluated by the volume of purified water (V_b) to the breakthrough time and the
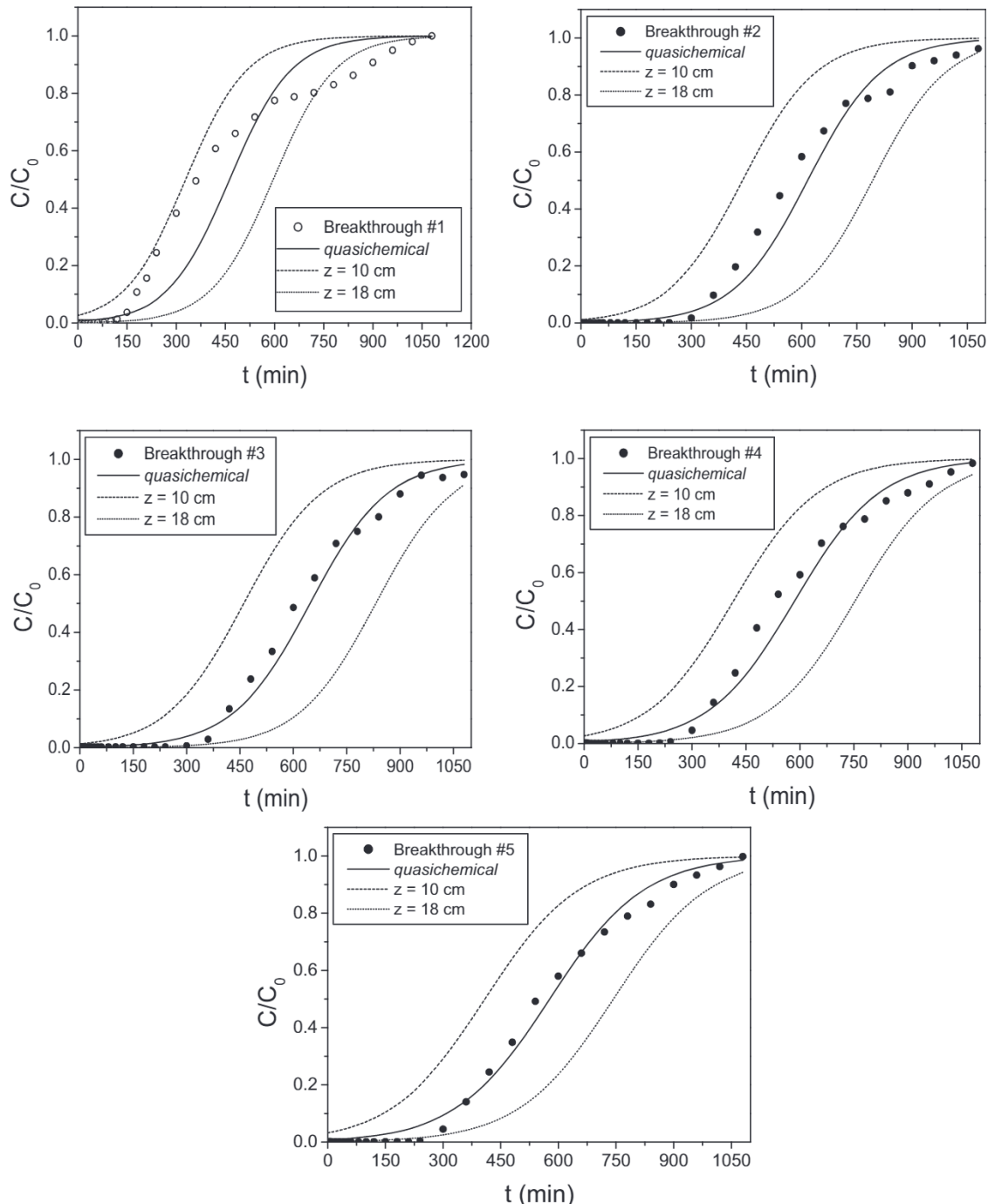

Fig. 6. Fit for breakthrough curves of copper in cycles of removal using seawater as eluent.

Table 4
Parameters of the simulated breakthrough curves for copper adsorption.

Breakthrough	z (cm)	q (mmol/g)	q_u (mmol/g)	ZTM (cm)	% RL
Eluent: NaCl 1% (pH 3)					
#1	10	0.177	0.0	10	23.43
	14	0.247	0.043	11.58	32.82
	18	0.318	0.108	11.87	42.19
#2	10	0.259	0.177	3.17	38.98
	14	0.363	0.309	2.09	54.57
	18	0.466	0.398	2.63	70.15
#3	10	0.249	0.176	2.93	37.44
	14	0.348	0.265	3.35	52.37
	18	0.448	0.354	3.77	67.32
#4	10	0.241	0.154	3.6	36.24
	14	0.337	0.264	3.01	50.65
	18	0.433	0.353	3.32	65.14
#5	10	0.265	0.13	5.08	39.87
	14	0.371	0.22	5.7	55.75
	18	0.476	0.309	6.31	71.55

volume of water spent in preparation of the eluent (V_E) used by the elution time. Considering that the volume V_E came from volume V_b, the REW was calculated by Eq. (12).

$$\text{REW} (\%) = \left(1 - \frac{V_E}{V_b} \right) \times 100 \qquad (12)$$

Table 6 brings the response variables for recovering water in the bed of the calcined clay. To regenerate the bed of calcined clay with seawater, water is unnecessary to prepare the eluent, being V_E values equal zero. Thus, REW values shown in Table 6 refer to the reclamation of water as 100% efficiency the highest value V_b obtained in the system. In this case, in the third cycle of adsorption and desorption, it was obtained an efficient water recovery of 100%. The seawater used as eluent in this work is a natural source of chloride ions, requiring only a small correction of pH for preventing the clay in the bed to become alkaline.

The performance of Bofe calcined clay compared to other reported in the literature is shown in Table 7. According to these data, the Bofe calcined clay presents excellent potential for copper removal and knowing its properties of adsorption and desorption reveals an alternative adsorbent with great competitiveness.

Table 5
Parameters of the simulated breakthrough curves for copper adsorption.

Breakthrough	z (cm)	q (mmol/g)	q_u (mmol/g)	ZTM (cm)	% RL
Eluent: seawater					
#1	10	0.245	0.043	8.26	30.7
	14	0.343	0.13	8.67	42.93
	18	0.44	0.219	9.04	55.15
#2	10	0.325	0.108	6.68	40.77
	14	0.455	0.219	7.26	56.98
	18	0.582	0.352	7.12	72.88
#3	10	0.341	0.108	6.84	42.78
	14	0.477	0.219	7.57	59.74
	18	0.607	0.352	7.57	76.08
#4	10	0.309	0.057	8.16	38.72
	14	0.432	0.174	8.37	54.11
	18	0.551	0.306	8.02	69.1
#5	10	0.305	0.042	8.61	38.21
	14	0.426	0.152	9.01	53.37
	18	0.544	0.263	9.31	68.16

Table 6
Recovery efficiency of water.

Cycle #	t_b (min)	V_b (mL)	V_E (mL)	REW (%)
Eluent NaCl				
1	130.8	523.2	480	8.8
2	425.2	1700.8	360	78.8
3	369.7	1478.8	960	35.1
4	365.3	1461.2	960	34.3
5	365.3	1461.2	720	–
Eluent seawater				
1	157.7	630.8	0	42.2
2	323.8	1295.2	0	86.7
3	373.3	1493.2	0	100
4	302.6	1210.4	0	81.1
5	300.0	1200.0	0	80.4

Table 7
Main results of copper removal.

Adsorbent	System	q (mmol/g)	Reference
Natural bentonite	Static	0.461	[1]
Fluidgel calcined clay	Dynamic	0.088	[2]
Bofe calcined clay	Static	0.08	[3]
RHA	Static	0.037	[9]
Pure clay	Static	0.529	[14]
Montmorillonite	Dynamic	0.048	[20]
Na-montmorillonite	Dynamic	0.048	[21]
Bofe calcined clay	Dynamic	≈0.3	This work

4. Conclusions

The results indicated that the regeneration of the bed with NaCl or seawater at pH 3 is very efficient and the elution was verified as 50%. Also, an increase in removal was observed after exposure of the bed to the eluent. The highest adsorption capacity of copper was ≈0.3 mmol/g, on the Bofe calcined clay. The elutions of copper with NaCl and seawater produced changes in calcined clays within the bed, turning them into sodic clays that were used up to five cycles of adsorption and desorption with different behaviors of breakthrough curves. The solution *quasichemical* for the Bohart and Adams model fits well to the data of breakthrough curves. The recovery efficiency of the water showed that the desorption of copper ions with NaCl or seawater is feasible and has great potential.

Acknowledgments

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