



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.

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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 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 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 .

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

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

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].

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

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]:

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

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:

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

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

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:

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

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

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

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

where

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

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

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

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