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Fluid Dynamic Study for Copper Removal onto Modified Clay in Fixed Bed

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Toxic metals cannot be biodegraded or destroyed, which leads to the need of their removal from industrial wastewaters. Therefore, so that you can design and optimize removal equipment (ion exchange/ adsorption column) is essential to characterize the adsorbent and to know the dynamics of adsorbate components in the experimental system. In this work, the bentonite clay called Fluidgel, from the northeast region of Brazil, calcined at 750 °C, was used as adsorbent for copper removal. The characterization methods used were Thermogravimetry (TG), X-ray Diffraction (XRD), N_2 adsorption (BET), and Scanning Electron Microscopy (SEM). The removal of copper from aqueous solution was carried out in a fixed bed, built in glass with 15 cm high and 1.5 cm in internal diameter. Several dynamic experiments were performed to evaluate the effect of flow in adsorption efficiency. The experiments were accomplished at room temperature, the adsorbent particle diameter was of 0.855 mm and the flow rate varied from 2 to 4 mL/min. The feed concentration of copper was about 1.57 mmol/L. The bentonite clay used presented a chemical composition according to the most clays of this group. The presence of water in the interlamellar spaces of the clay was confirmed by thermogravimetric analysis, where the TG curve indicated a weight loss of 11.5 %. The Fluidgel clay calcined at 750 °C showed a surface area of 11 m^2/g, whereas its commercial form presented 58 m^2/g. The breakthrough curves obtained at different flow rates showed different behaviors, indicating the effect of diffusional resistances. The flow rate of 2 mL/min was chosen as operating condition, since higher values of metal removal and lower mass transfer zone (MTZ) were obtained.

1. Introduction

Toxic metals are highly reactive and bioaccumulative, and therefore the body is unable to eliminate them. The most common are Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V, and Zn, been physiologically essential for many plants and animals, in particular copper which controls the enzyme activity that stimulates the formation of connective tissue and pigment that protects the skin, and thus contribute to human health. However, excessive levels of these elements can be extremely toxic.

Due to environmental problems generated by the considerable increase in discharges of industrial wastewater (Kimura et al., 2011) contaminated with toxic metals, combined with environmental laws increasingly strict, researches in this area have been necessary to seek alternative methods for low cost and more efficient in water treatment and evictions. In particular processes for purifying water using low cost materials, which involve the removal of toxic metals in very low concentrations at which conventional treatments have not been effective.

Among the various existing processes of toxic metal removal, the adsorption in fluidzed bed (Vieira et al., 2011a) and fixed bed has become very attractive in recent years, especially after the discovery of new adsorbents (Nishikawa et al., 2012; Vieira et al., 2012, 2011b) and, in the last fifty years, interest in the study of clays has grown, especially as regards their composition, structure and properties of its constituents (Almeida Neto et al., 2012; Bertagnolli et al., 2011; Vieira et al., 2010a,b). Various clays exhibit high selectivity and a high exchange capacity for various toxic metals and, for this reason, they have been evaluated for removal thereof. However, the clay minerals, due to the small size of its crystals

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coupled with a great variability of its forms and order-disorder structural require studies concerning adsorbent identification, characterization and quantification.
In this context, this study aimed to evaluate the potential of an alternative adsorbent such as sodium bentonite commercial clay, called as Fluidgel, for the removal of Cu^{2+} present in aqueous effluents in dynamic system. A study was conducted for the adsorption of copper into the porous bed, for the evaluation of the breakthrough curves behavior in fixed bed columns.

2. Experimental

2.1 Preparation and characterization

The commercial clay Fluidgel was ground and the particles separated by the sieving technique. The particles with a particle size suitable for the size of the bed (0.855 mm) were subjected to calcination at 750 °C in a muffle furnace for 24 hours. The calcination temperature was defined based on studies previously performed. The methods used to characterize these samples were: Thermogravimetry (TG), X-Ray Diffraction (XRD), N_2 physisorption (BET) and Scanning Electron Microscopy (SEM).

2.2 Operating conditions of fixed bed column

Assays were performed in dynamic system in an acrylic column, jacketed, 1.5 cm inner diameter and 15.0 cm high. The bed height used in tests was of 15.0 cm. The feed solution containing copper metal species was fed by peristaltic pump at the bottom of column previously flooded with deionized water. The flow rate varied at 2, 3, and 4 mL/min. The feed solution prepared from dissolution of the copper salt had their initial pH measured and when its value was greater than 4.5 up, correction has been effected by the addition of 1 M nitric acid to the desired value.
Samples of solutions eluted from the column were collected at intervals pre-defined by the fraction collector, and the concentration of metal species of copper in each sample was determined by atomic absorption spectrophotometry. The quantities of metal retained in the bed until the breakthrough time (t_b) and until saturation time (q_u and q, respectively) were obtained by mass balance in the column using the same saturation data, from breakthrough curves, demonstrating that the area under the curve ($1-C/C_0$) until the breakthrough time is proportional to q_u, and until exhaustion of the bed is proportional to q. The retained amounts q_u and q were calculated by Equations 1 and 2, respectively.

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

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

where C_0 is initial concentration in mmol/L, F is flow rate in mL/min, m is mass of adsorbent in grams.
Geankoplis (1993) presents a simplified method for calculating the length of the mass transfer zone (MTZ). The MTZ is a fraction of the total height (Ht) of the bed and can be calculated by substitution of Equations 1 and 2 results in Equation 3.

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

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

3. Results and discussion

3.1 Adsorbents characterization

TG and DTG curves obtained for the commercial clay are shown in Figure 1. The curves show one endothermic loss of moisture and water interlamellar ranging from room temperature to approximately 200 °C. The loss endotherm appearing in the range of 400 to 600 °C is related to loss of hydroxyl groups in the smectite. The loss endotherm at around 700 °C corresponds to decarbonation process of the clay.

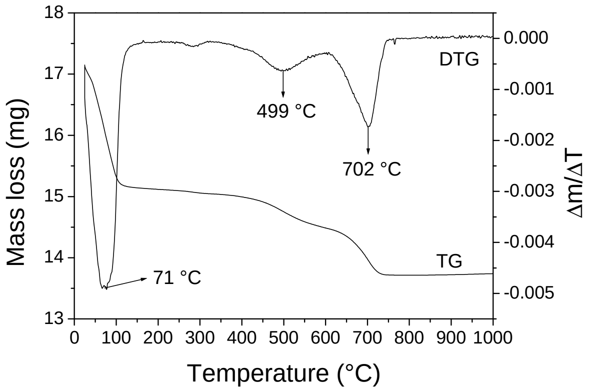

Figure 1: Thermogravimetric and DTG curves for the Fluidgel clay

Carbonates are present in this clay due to the sodium transformation process performed industrially. From this analysis we defined a temperature of 750 °C for the calcination of the adsorbent, because it checks the decarbonation of the commercial clay below this temperature. The decarbonation process is required for the removal of heavy metals, because the carbonates can cause precipitation of metals. The TG curve indicated a weight loss of 11.5 %.

Figure 2 shows the X-ray diffraction curves obtained by the powder method, for Fluidgel commercial clay, and its calcined form (Calc) at 750 °C. We observed that the commercial clay shows the highest intensity peaks characteristic of smectite-type clays and are within the range presented by the clay minerals of this group. The clay and its modified form have the different peaks corresponding to the interplanar distance $d_{(001)}$: 1.32 nm for commercial clay and 1.05 nm for the calcined clay, indicating that the thermal activation changes the layers of the Fluidgel clay.

The Fluidgel commercial clay showed two peaks in the region of 0.31 0.29 nm. These peaks attributed to sodium carbonate were not detected after calcinations. In all samples, we could observe the presence of other peaks in the ranges: 0.45 to 0.41 nm, corresponding to smectite, 0.25 nm corresponding to quartz, and 0.15 nm corresponding to the basal spacing $d_{(060)}$, indicating that the smectites are di-octahedral (Brindley and Brown, 1980).

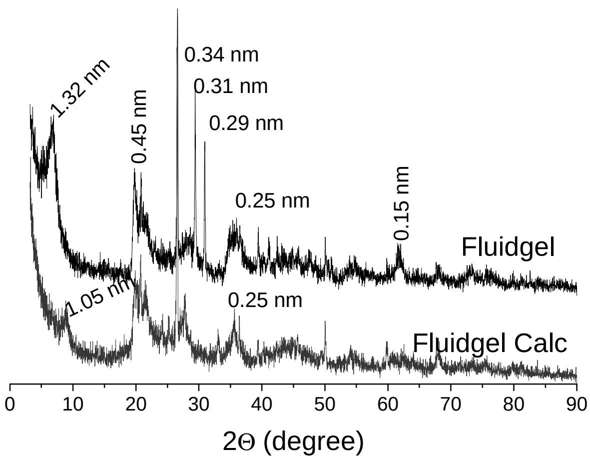

Figure 2: Diffractograms of commercial and calcined Fluidgel

The results of surface area of both commercial and calcined clays are shown in Table 1. We observed that with the thermal treatment, the surface area of the Fluidgel clay decreased, but not necessarily the removal of copper may be affected.

Table 1: The surface area of the samples obtained by the BET method

Fluidgel clay	Surface area (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)
commercial	58	14.995	13.177
calcined	11	2.313	5.237

The volumes of micropores (V_{mic}) shown in Table 1 are obtained using the adsorbed volumes (V_{ads}) at $P/P_0 = 0.10$ and the mesopore volume is calculated by Equation 4 (Gañán-Gómez et al., 2006):

$$V_{mes} = V_{ads\left(\frac{P}{P_0}=0.95\right)} - V_{ads\left(\frac{P}{P_0}=0.10\right)} \tag{4}$$

There is a significant reduction of micro and mesoporosity of Fluidgel clay after calcination evidenced by the sharp reduction in surface area.
The micrographs shown in Figures 3 and 4 correspond to commercial and calcined Fluidgel, respectively. Generally, from direct observation of micrographs, it can be seen that the commercial material has macropores that have not been evident in the calcined clay.

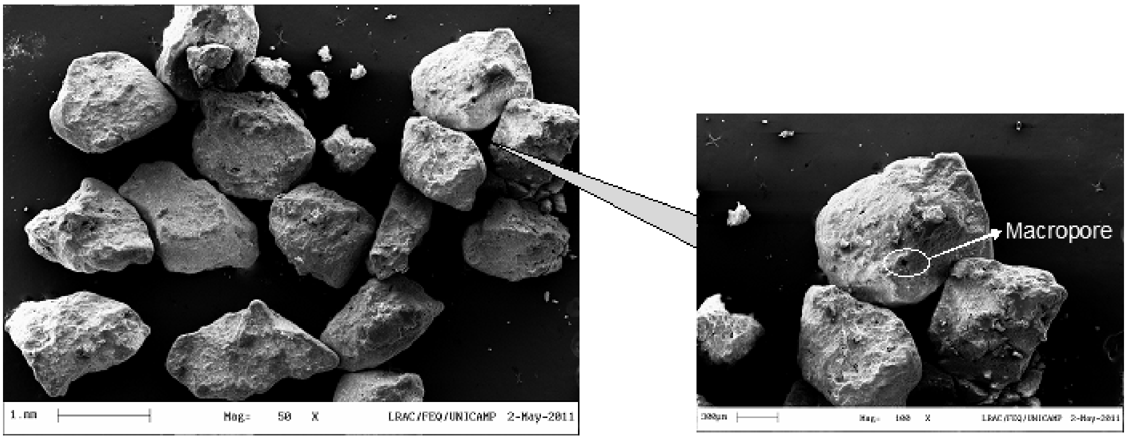

Figure 3: Microscopies of the commercial Fluidgel

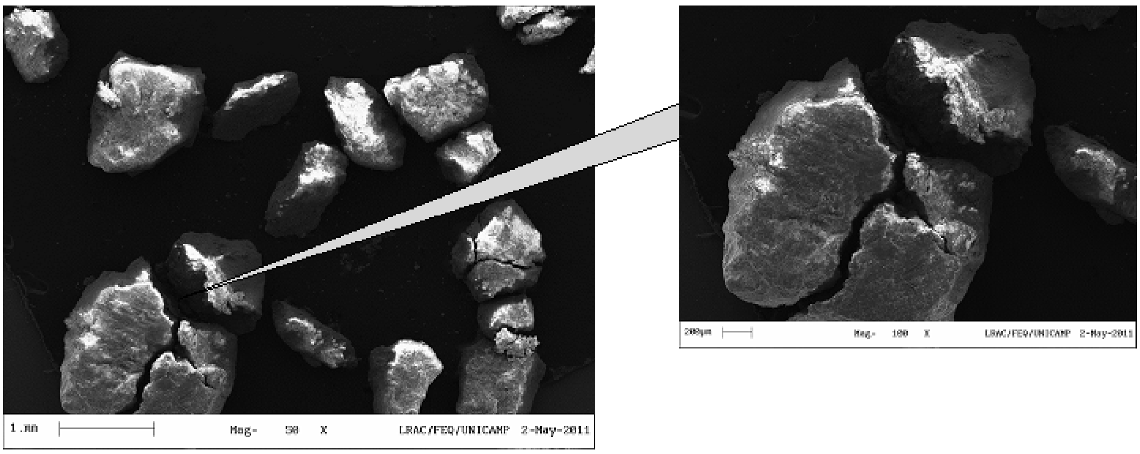

Figure 4: Microscopies of the calcined Fluidgel

3.2 Uptake flow
Figure 5 shows the experimental results of breakthrough curves at different operating flow rates for copper adsorption onto calcined clay. The initial metal concentration was about 1.57 mmol/L. The commercial form of Fluidgel clay could not be used in fixed bed due to its low mechanical resistance and also to the presence of carbonate in its composition, which leads to metals precipitation.

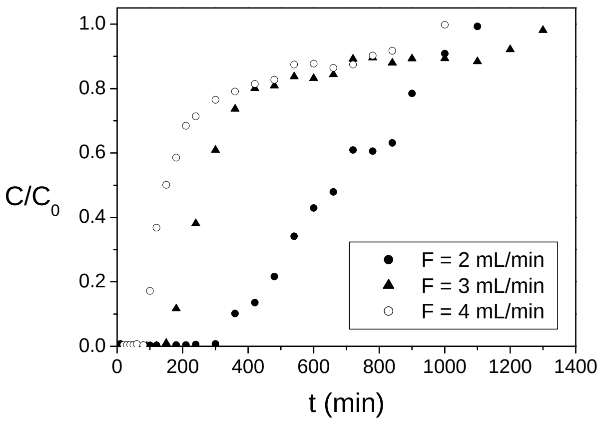

Figure 5: Experimental breakthrough curves for the system Cu^{2+}/calcined Fluidgel clay

From Figure 5 it was found that the breakthrough curves show different behaviors, which indicates a strong influence on the flow diffusional resistances. According to Geankoplis (1993), the mass transfer zone (MTZ) represented by the behavior of the breakthrough curve delineates an extension of the bed in which the concentration varies from the breakthrough time to the time of exhaustion. The shorter the length of MTZ, the closer to the ideal condition is the system is, indicating a low diffusional resistance and, therefore, a removal process more favorable. In the removal process in a fixed bed, increased flow results in a reduced resistance to mass transfer in the external liquid film of particles and, thus, also a reduction in MTZ, as observed by Vijayaranghavan et al. (2005). Table 2 presents the calculated values of MTZ, q_u, q (Geankoplis, 1993) and percentage of total removal (%RT). Table 2 shows that in the flow rate 2 mL/min was obtained shorter length of the MTZ (7.8 cm) and a low saturation resistance of the bed (Figure 5) for copper adsorption onto calcined Fluidgel clay.

Table 2: MTZ, q_u, q, and %RT for removal of copper on the calcined clay Fluidgel

Flow (mL/min)	q (mmol/g)	q_u (mmol/g)	MTZ (cm)	%RT (%)
2	**0.085**	**0.041**	**7.8**	**48**
3	0.088	0.033	9.4	29
4	0.057	0.014	11.3	25

4. Conclusions

The thermal analysis showed that 750 °C was the suitable temperature for calcination of the clay. The X-ray diffraction curves showed that calcination at 750 °C apparent caused damages to the structure of the mineral clay. Distortions caused by calcination modify the structure of the clay. The micrographs showed that the clays have size and shape characteristics of the montmorillonite group clays. The study of the mass transfer parameters as well as the breakthrough curves indicated that the most suitable operating flow, i.e. that which minimizes the diffusional resistances in the bed to remove copper by calcined Fluidgel clay was 2 mL/min. The breakthrough curves show that with increasing flow rate, the breakthrough and saturation times, the usable and the total capacities as well as the stoichiometric removal tend to lower values.

5. Acknowledgements

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