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Continuous-Flow Copper Adsorption in Regenerable Calcined Clay Columns

Marcelino L. Gimenes*[a] Ambrósio F. de Almeida Neto[b], Melissa G. A. Vieira[b], Meuris G. C. da Silva[b]

[a]Departament of Chemical Engineering, University of Maringá, UEM, 87020-900, Maringá-PR, Brazil
[b]School of Chemical Engineering, University of Campinas, UNICAMP, 13083-852, Campinas-SP, Brazil
marcelino.gimenes@gmail.com

Adsorption is currently recognized as an efficient and economical process for the treatment of toxic metals from wastewater. This process provides flexibility in the design and operation of treatment systems and in many cases generates a high-quality treated effluent. Furthermore, due to the reversibility of the adsorption adsorbents are sometimes regenerated by desorption suitable. Among the adsorbent materials, clays are characterized by their wide availability and low cost, which aggregates the potential they represent, especially when modified, resulting in scientific and industrial interest. Bentonite or smectite clays are widely used in industry, where applications are associated with their characteristic adsorbent and these properties can be improved by thermal and chemical treatments. Copper sorption behavior of calcined Bofe clay in consecutive adsorption–desorption cycles has been investigated in a packed-bed flow-through column during a continuous removal of copper from a 1.57 mmol/L aqueous solution at pH 5. The eluent used was HCl 0.1 mol/L. The adsorption and desorption were carried out for an average of 15 and 4 h, respectively, representing more than 2 days of continuous use of the adsorbent. The weight loss of mass after this time was 0.6 %. The Cu-sorption capacity of the calcined clay, based on the initial dry weight, was approximately 0.11 mmol/g. Sorption performance was indicated by shortening breakthrough time and a broadening mass-transfer zone. The column useful time, considered up to 1 mg Cu/L in the effluent, keeping aproximately in 100 min for all cycles. The mass-transfer zone, decreased almost linearly from 10 to 9 cm. Regeneration with HCl provided elution efficiencies up to 100%.

1. Introduction

Pollution is recurrently produced and accumulated in the environment (Kimura et al., 2011), and their recovery has become increasingly important as not only the treatment of wastewater is necessary, but the use of the byproducts is encouraged by cause economic and environmental benefits Thus, studies related to techniques for removal of metal ions, as well as the kinetics of the process are necessary for the viability of the recovery procedure.

Several studies have shown that the selectivity and efficiency of removal of pollutants, such as SO_2 adsorption in fluidzed bed (Vieira et al., 2011a), and toxic metals from effluent by adsorption process in fixed bed (Almeida Neto et al., 2012; Vieira et al., 2011b; Vieira et al., 2010a), are strongly dependent on the physical properties and chemical composition of the sorbent, but they have demonstrated the regeneration of beds or the changes caused by the elution.

Studies on metal removal using different adsorbents, as vermiculite (Nishikawa et al., 2013), rice husk ashes (Vieira et al., 2012), clays (Vieira et al., 2010b), and other materials have been reported in the literature. Various clays exhibit high selectivity and a high exchange capacity for various toxic metals and for this reason have been evaluated for removal thereof. However the clay minerals, due to the small size of its crystals coupled with variability of its forms and order-disorder structural require functioning as adsorbent identification, characterization and quantification.

Although the results involving removal of metals clays are significant and promising, there is still a need for a better understanding of these results with the regeneration of the adsorbent used by eluents that can

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produce concentrated solutions of metal ions. This study aims at evaluating hydrochloric acid for regeneration Bofe calcined clay, used as adsorbents for the removal of copper.

2. Experimental

2.1 Adsorbent

A sample of bentonite, from the Northeast region of Brazil, called Bofe; provided in raw form, was used as adsorbent. The Bofe clay was ground and the particles 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 hours. The characterization of this clay, involving various techniques and analyzes, was reported by Vieira et al. (2010a).

2.2 Dynamic experiments

Assays were performed in dynamic system in an acrylic column, jacketed, 1.4 cm inner diameter and 14.0 cm high. The bed height was used in tests of 14.0 cm. The feed solution containing copper metal species 1.57 mmol/L was fed by peristaltic pump at the bottom of column previously flooded with deionized water. The flow rate for copper removal onto Bofe calcined clay obtained by Almeida Neto et al. (2012) was 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, a correction was accomplished 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 (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 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.

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

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

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.

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

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.

2.3 Desorption evaluation

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 with respect to the amount of eluted metal. The amount of eluted metal (q_{el}) was calculated by integrating the 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 (Volesky et al., 2003) (Equation 4):

$$q_{el} = \frac{F}{m}\int C_c \cdot dt \tag{4}$$

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

2.4 Fitted model

With the aim of selecting an analytical solution that describes the behavior of the breakthrough curves of copper removal by Bofe calcined clay in fixed bed, a study of models based on those presented by Ruthven (1984) was accomplished. Among all the available models, the rate *quasichemical* solution (Equations 5 - 8) presented the best fit for most of the breakthrough curves. Statistica® version 5.0 was used as a computational tool to adjust the rate *quasichemical* solution to the experimental data of breakthrough curves.

$$\frac{\partial q}{\partial t} = kC(q_s - q) \tag{5}$$

$$\frac{C}{C_0} = \frac{e^{\tau}}{e^{\tau} + e^{\xi} - 1} \tag{6}$$

$$\tau = kC_0\left(t - \frac{z}{v}\right) \tag{7}$$

$$\xi = \frac{kq_0 z}{v}\left(\frac{1-\varepsilon}{\varepsilon}\right) \tag{8}$$

where, z is the height of the bed, v, the flow velocity, ε is the porosity of the bed, t is the process time and the parameters k and q_0, represent the constant removal rate and the quasichemical concentration of metal in the solid state at time zero of the elution.

3. Results and discussion

The breakthrough curves obtained in the tests with calcined Bofe clay, which operate in cycles of adsorption/desorption regenerated by HCl 0.1 mol/L are presented in Figure 1. It has been observed for the bed of calcined Bofe clay similar breakthrough curves behaviors, where three cycles were performed. The adsorption and desorption were carried out for an average of 15 and 4 h, respectively, representing more than 2 days of continuous use of the adsorbent. The weight loss of mass after this time was 0.6 %. The Cu-sorption capacity of the calcined clay, based on the initial dry weight, it was about 0.11 mmol/g. The column useful time, considered up to 1 mg Cu/L in the effluent, was kept approximately in 100 min for all cycles.

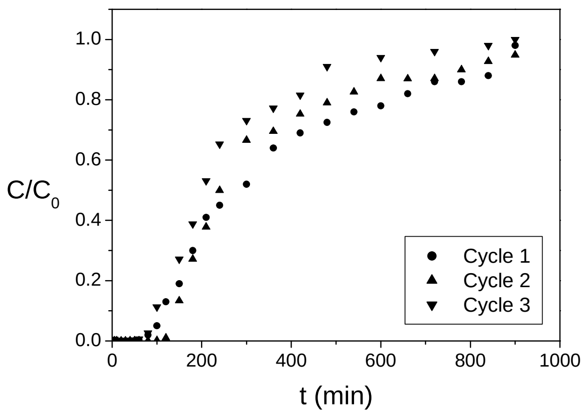

Figure 1: Breakthrough curves of cycles of removal of copper, C_0 = Cu^{2+} 1.57 mmol/L onto Bofe calcined clay and eluent HCl 0.1 mol/L

Table 1 shows the values of total (q) and useful amount removed (q_u), MTZ, and percentage of total removal (%RT) for the studied systems when the bed was regenerated by HCl. Thus, it can be noted a decrease in the total amount removed, probably due to the attack of HCl on the structure of the clay. The useful amount removed value showed a slight increase in breakthrough curve of the second copper adsorption, compared with the first cycle, but in the third cycle, the value fell following the trend of worsening the total amount and percentage of total removal. Sorption performance was indicated by a shortening a broadening MTZ. The MTZ decreased in the second breakthrough curve, but then increased in the third cycle, approaching the value displayed on the first breakthrough curve. The MTZ, decreased almost linearly from 10 to 9 cm.

Table 1: Parameters of breakthrough curves for removing Cu using HCl as eluent

Cycle	q (mmol/g)	q_u (mmol/g)	MTZ (cm)	%RT (%)
1	0.132	0.034	10.36	40.17
2	0.12	0.045	8.76	36.27
3	0.09	0.029	9.48	28.36

It was observed that adsorption and desorption occurred in acidic pH values: around 4.0 during removal and 3.0 during the elution. According to Almeida Neto et al. (2012) below pH 5 does not occur chemical precipitation of copper. Figure 2 presents kinetic results obtained during the regeneration of bed. The calcined Bofe clay supported two complete elutions, but after the third cycle during washing of the bed, the clay disrupted causing the impermeability of the bed. Regeneration with HCl provided elution efficiencies up to 100%, as shown in Table 2.

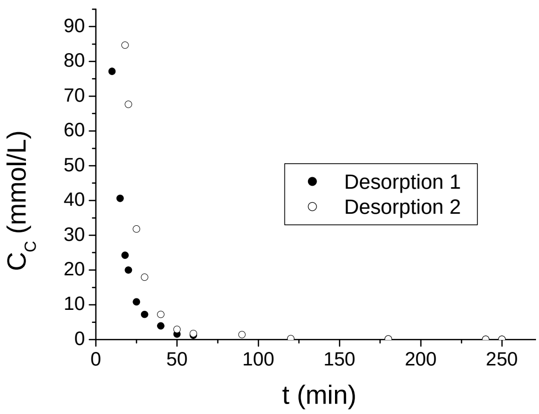

Figure 2: Desorption kinetic of Cu^{2+} adsorbed in calcined Bofe clay

Table 2: Parameters regeneration of the columns with HCl 0.1 mol/L

Elution	Elution time (min)	q_{el} (mmol/g)	%Elution	Error (%)
1	240	0.133	100.00	0.81
2	180	0.121	100.00	1.31

The clay's treatment with acid, replacing cations intercalated with H_3O^+. Comparing the data in Table 3, it is found that the exchangeable cations were not detected after treatment with HCl, showing the replacement of cations H^+ or Al^{3+} hydrated.

Table 3: Chemical analysis of Bofe clays calcined and treated with HCl obtained by X-ray Fluorescence

Bofe clay	Chemical Composition (%)											
	L.O.I.	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	Sum
Calcined	3.77	69.03	14.28	0.57	6.94	0.46	4.50	0.24	0.15	0.01	0.04	100.00
Calc. H^+	1.78	78.08	11.57	0.90	5.61	--	2.01	--	--	0.01	0.04	100.00

L.O.I. – Loss on Ignition

The experimental breakthrough curves were fitted by quasichemical model, as shown in Figure 3.

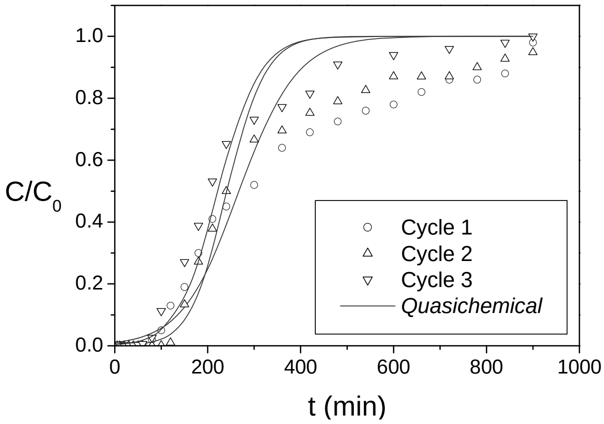

Figure 3: Quasichemical model fit the curves of Cu^{2+} by removing the calcined Bofe clay

The parameters of breakthrough curves obtained by the *quasichemical* model fit are presented in Table 4. The coefficients k and q_0 do not differ significantly for the three fitted curves as well as the behavior of the curves. Indeed, after elution, a similar kinetics is again established.

Table 4: Parameters of breakthrough curves for removing Cu using HCl as eluent

Cycle	k (L/mmol.min)	q_0 (mmol/g)
1	0.0112	0.0664
2	0.0185	0.0586
3	0.0165	0.0543

4. Conclusions

Elution with HCl 0.1 mol/L did not change the behavior of the breakthrough curves and could be used in three cycles. The adsorption and desorption were carried out for an average of 15 and 4 h, respectively, representing more than 2 days of continuous use of the adsorbent. The weight loss of mass after this time was 0.6 %. The Cu-sorption capacity of the calcined clay, based on the initial dry weight, was about 0.11 mmol/g. Sorption performance was indicated by a shortening breakthrough time and a broadening mass-transfer zone. The column useful time, considered up to 1 mg Cu/L in the effluent, was kept approximately in 100 min for all cycles. The mass-transfer zone, decreased almost linearly from 10 to 9 cm. Regeneration with HCl provided elution efficiencies up to 100%. The *quasichemical* model fit the data well in adsorption and desorption cycles. The methods used in this study were based on fundamentals of adsorption, without need for pH adjustment of the effluent, which simplifies steps and making the process more economical. Tests with synthetic wastewater samples showed that the fixed bed process is promising, but still needs to be investigated with other metals and undergoing expansion to allow scale up and to determine its technical and economic feasibility.

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References

Almeida Neto A. F. de, Vieira M. G. A., and Silva M. G. C. da, 2012, Cu(II) adsorption on modified bentonitic clays: different isotherm behaviors in static and dynamic systems, Materials Research, 15, 114-124, DOI: 10.1590/S1516-14392011005000089.

Geankoplis C. J., 1993, Transport Process and Unit Operatons. PTR Pretice Hall, New York, USA.

Kimura S. P. R., Almeida Neto A. F. de, and Silva M. G. C. da, 2011, Anthropogenic effects on the water quality at a pond in the Amazon region, Chemical Engineering Transactions, 24, 1255-1260, DOI: 10.3303/CET1124210.

Nishikawa E., Almeida Neto A. F. de, and Vieira M. G. A., 2012, Equilibrium and thermodynamic studies of zinc adsorption on expanded vermiculite, Adsorption Science and Technology, 30, 759-772, DOI: 10.1260/0263-6174.30.8-9.759.

Ruthven D. M., 1984, Principals of Adsorption and Adsorption Processes. John Wiley & Sons, New York, USA.

Vieira M. G. A., Almeida Neto A. F. de, Silva M. G. C. da, Carneiro C. N., and Filho A. A. de M., 2012, Characterization and use of in natura and calcined rice husks for biosorption of heavy metals ions from aqueous effluents, Brazilian Journal of Chemical Engineering, 29, 619-634, DOI: 10.1590/S0104-66322012000300019.

Vieira M. G. A., Almeida Neto A. F. de, Gimenes M. L., and Silva M. G. C. da, 2011a, Desulphuration of SO_2 by Adsorption in Fluidized Bed with Zeolite, Chemical Engineering Transactions, 24, 1219-1224, DOI: 10.3303/CET1124204.

Vieira M. G. A., Almeida Neto A. F. de, Silva M. G. C. da, Carneiro C. N., and Filho A. A. de M., 2011b, Influence of the system on adsorption of Pb(II) and Cu(II) by calcined rice husks: kinetic study, Chemical Engineering Transactions, 24, 1213-1218, DOI: 10.3303/CET1124203.

Vieira M. G. A., Almeida Neto A. F. de, Gimenes M. L., and Silva M. G. C. da, 2010a, Removal of nickel on Bofe bentonite calcined clay in porous bed, Journal of Hazardous Materials, 176, 109-118, DOI: 10.1016/j.jhazmat.2009.10.128.

Vieira M. G. A., Almeida Neto A. F. de, Gimenes M. L., and Silva M. G. C. da, 2010b, Sorption kinetics and equilibrium for the removal of nickel ions from aqueous phase on calcined Bofe bentonite clay, Journal of Hazardous Materials, 177, 362-371, DOI: 10.1016/j.jhazmat.2009.12.040.

Volesky B., Weber J., and Park J. M., 2003, Continuous-flow metal biosorption in a regenerable Sargassum column, Water Research, 37, 297–306, DOI: 10.1016/S0043-1354(02)00282-8.