



Research paper

Binary adsorption of silver and copper on Verde-lodo bentonite: Kinetic and equilibrium study



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ABSTRACT

Removal and recovery of toxic metals from wastewater by adsorption is an efficient alternative, especially when using uncommon adsorbents. In the present work, silver and copper binary adsorption onto Verde-lodo bentonite was evaluated in static systems. Kinetic studies under different initial metal concentrations and molar fractions were performed. Kinetic models were adjusted to experimental data, and the External mass transfer resistance model (EMTR) presented the best fitting. The binary kinetic assays revealed that copper presents higher adsorption capacity than silver. Higher total concentrations presented an influence on the adsorption process due to increasing competition for active sites. Equilibrium studies were carried out and the results confirmed the preferential copper adsorption in binary solution with silver. Copper ions were better adsorbed at higher temperatures and silver ions at lower temperatures. The maximum adsorption capacities were 0.110 mmol/g for copper at 60 °C and 0.090 mmol/g for silver at 20 °C. Binary equilibrium models were fitted and the Langmuir-Freundlich model best represented the experimental data. The comparison between Verde-lodo clay characterization, prior and post adsorption, indicated that the process caused no significant changes in the morphology, crystal structure, functional groups and thermal stability of the material.

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1. Introduction

In the past years, pollution control has become one of the main society concerns. Many of natural resources have been employed in an unrestricted way, resulting in their depletion. Among these resources, water deserves further attention since it is finite and vital to the vast majority of live organisms.

Toxic metals are naturally present in aqueous environments; however, an increasing concentration of these pollutants has been noticed as a result of industrial activities, mining and household waste generation (Yu et al., 2014). Toxic metals are highly soluble in water and easily absorbed by living organisms. Once in the food chain, they may reach humans and, therefore, should be removed when detected in elevated concentrations (Barakat, 2011).

Industries involving electroplating processes, i.e. surface treatments by chemical or electrolytic process, produce effluents rich in a wide variety of toxic metals, such as copper, zinc, silver, gold and cadmium (Chiu et al., 1987). Copper is an essential element for living organisms, being present in many enzymes and proteins (Alloway, 2010), and does not present a significant risk towards humans. However, aqueous plants, invertebrate beings and fishes may be affected by this copper presence (Eisler, 1998). Silver presents high toxicity even in low

concentrations and its malleability, ductility, electrical, and thermal conductivity make it an ideal subject for recovery and reutilization (Alloway, 2010).

The region of Limeira-SP (Brazil) is known by the jewelry industries that generate large quantities of wastewater (Moreira and Fazza, 2008). The presence of toxic metals, such as silver and copper, in the wastewater leads to the need for removal and recovery technologies. Different methods have already been employed for this purpose such as chemical precipitation, ion exchange, and electrochemical removal. However, they present limitations and a complete removal is not always possible. Furthermore, these techniques require high operation energy and produces toxic waste (Volesky, 2001). In this context, adsorption has been applied as an efficient method to improve wastewater treatment quality (Stofela et al., 2015; Silva et al., 2015; Vieira et al., 2014; Lima et al., 2014).

As an alternative to activated carbon, different materials may be used as adsorbent, reducing costs and improving efficiency. Bentonites have shown high removal potential (Đukić et al., 2015; Chinoune et al., 2016; Vhangweleb and Mugerua, 2015) and present high cation exchange capacity and structural characteristics, allowing the interspersing of many organic and inorganic compounds (Pusch, 2015). Verde-lodo bentonite is easily found in Brazil, commonly in São Paulo, Paraná, Paraíba and Bahia states (DNPM, 2014). It was evaluated as adsorbent of silver ions (Cantuaria et al., 2016) and copper ions (Almeida Neto et al., 2012) from single component solutions, exhibiting high

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removal efficiencies. Besides that, since Verde-lodo is an abundant, low cost material, the adsorption process becomes even more attractive (Padilla-Ortega et al., 2013).

Based on the above considerations, the main objective of this work was to evaluate silver and copper binary adsorption onto Verde-lodo bentonite through kinetic and equilibrium studies, as well as to check the adsorption influence on the clay structure by its characterization after the process. Binary adsorption studies may be highly complex but they best reflect the reality, once the presence of only one metal is a rare condition in nature or wastewaters. Silver and copper single ions adsorption on bentonite or montmorillonite has been extensively studied (Praus et al., 2008; Almeida Neto et al., 2012; Koyuncu and Kul, 2014; Cantuaria et al., 2016). Although different adsorbents have been evaluated for the binary adsorption of copper and silver (Hanzlík et al., 2004; Wang et al., 2011; Kampalananwat and Supaphol, 2014), the employment of Verde-lodo bentonite for that purpose has not been investigated yet, which endorses the relevance of the present paper.

2. Materials and methods

2.1. Adsorbent

Verde-lodo bentonite originally from Boa Vista-PB (Brazil) was provided, in its raw form, by Dolomil Ltd. The adsorbent material was grounded and sieved to obtain a particle diameter in the range 0.71–1.00 mm, and later calcined at 500 °C for 24 h in muffle furnace. The calcination was performed to provide the adsorbent material a higher mechanical stability (Almeida Neto et al., 2012).

2.2. Chemical speciation analysis

Speciation diagrams for silver and copper ions were obtained by Hydra and Medusa software, considering the different concentrations and molar fractions applied in the kinetic studies (Puigdomenech, 2004). This step was performed to evaluate the pH range that should be used in order to avoid metal precipitation. Silver ions are stable up to pH 9.0, and copper ions are stable up to pH 5.2. In light of those values, it was determined that the adsorption tests should be conducted below 5.0 pH, avoiding chemical precipitation.

2.3. Kinetic assays

The adsorption kinetics of silver and copper onto Verde-lodo clay was evaluated. Different solutions with varying concentrations and molar fractions were prepared by dissolving silver nitrate (AgNO_3), provided by Merck, and copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), provided by Vetec, in deionized water. Each solution specification is described in Table 1.

Kinetic assays were conducted using 10 g of adsorbent per 1.0 L of metal solution under constant stirring for 16 h. At specific time intervals, aliquots were removed and centrifuged. The silver and copper concentrations were analyzed with an atomic absorption spectrophotometer. Kinetic models of pseudo first order (Lagergren, 1898), pseudo second order (Ho and McKay, 1998), intra-particle diffusion (Weber and Morris, 1963; Chen et al., 2003), Boyd et al. (1947), and external mass

transfer resistance model (EMTR) (Ponnusami et al., 2010; Puranik et al., 1999) were adjusted to the experimental data. The equations of each model are given in Eqs. (1)–(6).

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (2)$$

$$q = k_i \cdot t^{1/2} + c \quad (3)$$

$$F = 1 - \left(\frac{6}{\pi^2}\right) \cdot \exp(-B_t) \quad (4)$$

$$\frac{dC}{dt} = -K_{TM} \cdot a \cdot [C(t) - C_p(t)]^2 \quad (5)$$

$$\frac{dC_p}{dt} = \frac{K_{TM} \cdot V}{m \cdot q_{max} \cdot K_L} [1 + K_L \cdot C_p(t)]^2 \cdot [C(t) - C_p(t)] \quad (6)$$

where q is the adsorbed amount in an arbitrary time t (mmol/g), q_e is the adsorbed amount in equilibrium (mmol/g), obtained through the experimental data adjustment, k_1 is the pseudo first order adsorption rate constant (min^{-1}), k_2 is the pseudo second order adsorption rate constant ($\text{g}/\text{mmol} \cdot \text{min}^{-1}$), k_i is the intra-particle diffusion model parameter ($\text{mmol}/\text{g} \cdot \text{min}^{0.5}$), c is a parameter related to the boundary layer thickness, F is the ratio q/q_e , B_t is a parameter of the function F , C_p is the solute concentration in liquid-solid interface (mmol/L), K_{TM} is the mass transfer coefficient (min^{-1}), V is the solution volume (L), m is the adsorbent mass (g), q_{max} is the maximum adsorbed amount in equilibrium (mmol/g), K_L is the Langmuir equilibrium model constant (L/mmol) and C is the liquid phase concentration in an arbitrary time t (mmol/L).

2.4. Equilibrium assays

To obtain the equilibrium isotherms, 50 mL of binary solutions with different silver and copper initial concentrations and molar fractions were mixed with 0.5 g of adsorbent under 200 rpm stirring rate for 6 h. The assays were performed at 10, 20, 40, and 60 °C. Initial and final solutions concentrations were measured by an atomic absorption spectrophotometer. Silver and copper removal by bentonite or montmorillonite has been usually understood as an adsorption process (Praus et al., 2008; Koyuncu and Kul, 2014). Thus, equilibrium experimental data were adjusted by the following binary isotherm models: competitive Langmuir, non-competitive Langmuir and Langmuir-Freundlich, according to Eqs. (6)–(8), respectively. The models parameters were obtained from binary adsorption experimental data (Luna et al., 2010).

$$q_{e,i} = \frac{Q_0 \cdot K_{L,i} \cdot C_{e,i}}{1 + K_{L,i} \cdot C_{e,i} + K_{L,j} \cdot C_{e,j}} \quad (7)$$

$$q_{e,i} = Q_0 \cdot \left(\frac{K_{L,i} \cdot C_{e,i} + K_{L,j} \cdot C_{e,i} \cdot C_{e,j}}{1 + K_{L,i} \cdot C_{e,i} + K_{L,j} \cdot C_{e,j} + K_{L,j} \cdot C_{e,i} \cdot C_{e,j}} \right) \quad (8)$$

$$q_{e,i} = \frac{Q_0 \cdot K_{LF,i} \cdot (C_{e,i})^{1/n_i}}{1 + K_{LF,i} \cdot (C_{e,i})^{1/n_i} + K_{LF,j} \cdot (C_{e,j})^{1/n_j}} \quad (9)$$

The coefficients i and j are the metals present, q_e is the adsorbed amount in equilibrium (mmol/g), Q_0 is the maximum adsorbed amount of metal ion per adsorbent mass unit (mmol/g), C_e is the solution concentration in equilibrium (mmol/L), K_L , K_{LF} , and n are parameters of the isotherm models. The Modified Competitive Langmuir equilibrium model, Eq. (10), was also applied and the parameter Q_0 is different for

Table 1
Solutions employed in the kinetic studies.

Solution	Silver concentration (mmol/L)	Copper concentration (mmol/L)
A	0.5	0.5
B	1.0	1.0
C	2.0	2.0
D	1.5	0.5
E	0.5	1.5

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