



Research paper

Binary adsorption of zinc and copper on expanded vermiculite using a fixed bed column

Emanuelle Dantas de Freitas, Hewellyn Joacy de Almeida, Melissa Gurgel Adeodato Vieira*

Department of Processes and Products Design, School of Chemical Engineering, University of Campinas – UNICAMP, Albert Einstein Avenue, 500, 13083-852 Campinas, SP, Brazil

ARTICLE INFO

Keywords:

Copper
Zinc
Expanded vermiculite
Fixed bed

ABSTRACT

Increased wastewater production in the last several years has led to interest in new wastewater treatment technologies such as adsorption. This work evaluated the removal process of Zn^{2+}/Cu^{2+} binary solutions using expanded vermiculite as alternative adsorbent. Assays were performed in dynamic systems to evaluate the influence of operating flow rate, adsorbate initial concentration and molar fraction on the adsorption process. Expanded vermiculite presented higher selectivity for zinc in single solutions as well as in binary system.

1. Introduction

Industrial development in the last several years has led to an increase in wastewater production. Wastewater usually contains toxic elements that must not be discharged without appropriated treatment due to their high contamination potential and ability to affect the environment and living organisms (Abdel-Raouf et al., 2012). Therefore, it is important to develop waste and wastewater management policies in the sense of avoiding or minimizing water pollution (Perić et al., 2004).

Toxic metals are naturally present in the environment, but the large-scale use of these metals in industry is causing soil and water pollution, and may result in damages to living organisms and human health (Singh et al., 2011). Besides that, toxic metals are not biodegradable and may accumulate along the food chain, what demands new technologies development to remove these compounds from wastewater (Barakat, 2011).

Industrial wastewater is composed of a mixture of toxic metals, such as copper and zinc. These metals can be found together in paper production, oil refining and fertilizer industries, and therefore their joint removal is an important topic of study (Dean et al., 1972). Copper is an essential element for human health, but for fishes, it is the second most toxic element. Zinc is also beneficial to humans, but it is poisonous to animals and plants when in high concentrations, in addition to damaging soils due to its high mobility (Alloway, 1990). According to National Council for the Environment in Brazil (CONAMA) (Resolution 430/2011), the highest concentrations allowed in wastewater in Brazil are of 1 mg/L for copper and of 5 mg/L for zinc.

Many treatment techniques have been used in attempt to remove

these metals from wastewater, even when in low concentrations (Wang and Chen, 2009). Methods, such as precipitation, usually do not offer high efficiencies when treating large quantities of wastewater with low concentrations of pollutants (Lakherwal, 2014). In this sense, adsorption is a good alternative, considering that it is a simple and flexible operation, in addition to reducing treatment costs if appropriate adsorbent is chosen (Volesky et al., 2001).

Adsorption depends on the system properties, such as pH, temperature and stirring, and also on the adsorbent surface area and selectivity (El-Bayaa et al., 2009). Many materials have been studied as adsorbents to remove different contaminants such as rice husk (Vieira et al., 2014); clays (Almeida Neto et al., 2014; Cantuaria et al., 2016; Freitas et al., 2017; Lima et al., 2017); macrophyte (Pelosi et al., 2014); and sericin and alginate particles (Silva et al., 2016).

Vermiculite is a clay mineral that has presented good results as toxic metals removal adsorbent (Stylianou et al., 2007; Nishikawa et al., 2012b; Sis and Uysal, 2014). Vermiculite is composed of SiO_4 tetrahedral layers and $Mg(OH)_2$ and $Al(OH)_3$ octahedral layers. Some hydrated cations, such as magnesium and calcium, are located in the interlayer spaces and can be exchanged by cations in solution, leading to a high cation exchange capacity, in the range of 100 to 150 meq per 100 g of vermiculite (Maret and Sandstead, 2006). Along the crystal structure of vermiculite, there is from 5 to 20% of water that can be evaporated in elevated temperature in a process named exfoliation, generating the so called expanded vermiculite, which is lighter and chemically inert, once it has air particles between its layers (Marcos and Rodríguez, 2014).

The main objective of this work was to evaluate the binary adsorption of copper and zinc solutions in a fixed bed dynamic system.

* Corresponding author.

E-mail address: melissagav@feq.unicamp.br (M.G.A. Vieira).

<http://dx.doi.org/10.1016/j.clay.2017.07.004>

Received 30 November 2016; Received in revised form 3 July 2017; Accepted 5 July 2017
0169-1317/ © 2017 Elsevier B.V. All rights reserved.

Although static system studies are very usual (Chergui et al., 2007; Yang et al., 2015; Genç-Fuhrman et al., 2016), there is a lack of knowledge about the behaviour of adsorption in dynamic systems, endorsing the matter of this work. Firstly, a fluid dynamic study was conducted to determine the best operating flow rate based on the removal efficiency and mass transfer parameters. Then, the influence of the adsorbate initial concentration and the molar fraction on the competitive adsorption process was investigated.

2. Material and methods

2.1. Adsorbent

Brazilian expanded vermiculite used as alternative adsorbent and originated from Goiás state (Brazil) was provided by Brasil Minérios LTDA. It was grinded and sieved to obtain mean particle diameter of 0.855 mm. Vermiculite general formula was reported by Franco et al. (2011) as $[(Si_3Al)Mg_3(OH)_2O_{10} \cdot Mg_{0.5} \cdot nH_2O]$. The expanded vermiculite used in the present study was characterized by Nishikawa et al. (2012b), who obtained the chemical composition in agreement to the result presented by Franco et al. (2011), besides the presence of small amounts of chrome and titanium. The techniques of Helium pycnometry and Nitrogen physisorption were employed to determine the sample's real volume (0.8935 cm^3), which is the actual sample volume without considering porosity, and surface area ($23.2253 \text{ m}^2/\text{g}$), respectively. The apparent density of $2.3892 \text{ g}/\text{cm}^3$ was obtained by Mercury porosimetry and, combined with the real density also provided by Helium pycnometry ($2.4644 \text{ g}/\text{cm}^3$), allowed porosity to be calculated ($\epsilon_p = 1 - (\rho_{\text{apparent}}/\rho_{\text{real}})$) as 0.0305.

2.2. Vermiculite cation exchange capacity

The adsorbent cation exchange capacity (CEC) was determined based on the concentration of Na^+ ions exchanged by NH_4^+ (Lange, 1973). To accomplish this, expanded vermiculite was exchanged with Na^+ according to the methodology of Pereira et al. (2005). Vermiculite was added to water at concentration of 4% (w/w) under constant stirring. After 20 min, sodium carbonate was added at the proportion 100 meq/100 g of dried clay and maintained under stirring and heating, up to boiling point. At this point, the dispersion was cooled at room temperature under stirring for 20 min. Then, it was vacuum filtered, washed with ultrapure water (Reverse Osmosis, Gehaka, Brazil) and dried in an oven for 24 h at 105°C .

For the CEC assay, 2.5 g of dried sodic vermiculite was added to 100 mL of ammonium acetate 3 M under continuous stirring for 15 h. After this period, the supernatant was centrifuged and sodium amount was determined by atomic absorption spectrometry (AAnalyst 100, PerkinElmer). A similar procedure was followed by replacing ammonium acetate solution by water. The Na concentration after contact with water was subtracted from that released in the ammonium acetate solution to obtain C_{Na^+} . All determinations were carried out in triplicate and CEC was calculated by Eq. (1).

$$CEC = \frac{C_{\text{Na}^+} \cdot V_{\text{NH}_4^+}}{10 \cdot m \cdot f} \quad (1)$$

where, C_{Na^+} is sodium concentration obtained by atomic absorption spectrometry (mg/L), $V_{\text{NH}_4^+}$ is the volume of ammonium acetate solution (mL), m is the vermiculite mass (g) and f is sodium atomic weight, which is equal to 23.

2.3. Metal ions solutions

The adsorption experiments were conducted using aqueous solutions of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), both provided by Vetec. The solution concentrations

before and after the adsorption process were determined by atomic absorption spectrophotometer Shimadzu, model AA – 7000 and PerkinElmer, model AAnalyst 100.

2.4. Metal speciation

In order to assure the exclusive occurrence of the adsorption process, the pH of the metal solutions have to be maintained below the pH of precipitation for both metals. Therefore, copper and zinc speciation diagrams were obtained by simulation in Hydra and Medusa software (Puigdomenech, 2004), considering only aqueous solutions containing both nitrate salts. The chemical precipitation of copper and zinc in aqueous solution occurs in the pH range of 5.0–12.0. Hence, the pH of the solutions was controlled with a pH-meter Gehaka, model PG 1800, and adjusted at values lower than 4.5 by the addition of nitric acid.

2.5. Dynamic system assays

Dynamic experiments were performed in a glass column (15.0 cm in bed height and 1.5 cm inner diameter), packed with solid adsorbent. A peristaltic pump (Masterflex) promoted the upward flow of the metal solutions through the bed and outlet samples were collected periodically by an automatic sample collector (FC203 Fraction Collector). The concentrations of the inlet and outlet samples were measured by atomic absorption. Fig. 1 illustrates the experimental set up. Upward flow was chosen because it reduces the occurrence of preferential paths as well as improves fluid solid contact.

The breakthrough curves and the efficiency parameters to evaluate the fixed bed adsorption performance were obtained from the experimental data. Geankoplis (1993) describes a methodology to measure the mass transfer zone length (MTZ) and the useful (q_u) and total (q_t) amounts retained in the bed as a function of time. The breakthrough time (t_b) was considered as the time in which the outlet concentration reaches 5% of the feed solution concentration. Eq. (1) shows that the area under the curve $(1 - C/C_0)$ up to the breakpoint is proportional to q_u . According to Eq. (2), the area under the curve $(1 - C/C_0)$ until the bed saturation is proportional to q_t .

$$q_u = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{t_b} \left(1 - \frac{C}{C_0}\right) dt \quad (2)$$

$$q_t = \frac{C_0 \cdot Q}{1000 \cdot m} \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \quad (3)$$

In which C_0 is the concentration of both metals in column feed (mmol/L), Q is the feed solution flow rate (mL/min), m is the mass of adsorbent (g), C is the outlet concentration in a certain time t (mmol/L), t_b is the time to breakpoint (min) and H_L is the column height (cm).

The MTZ parameter is equivalent to the bed region in which the removal actually happens. Low values of MTZ indicate better efficiency in the removal until the ideal condition in which MTZ is zero and the

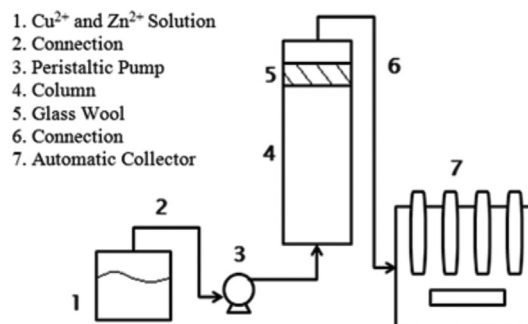


Fig. 1. – Schematic design of the fixed bed column adsorption system. Source: Adapted from Cantuaria et al. (2015).

Download English Version:

<https://daneshyari.com/en/article/5468880>

Download Persian Version:

<https://daneshyari.com/article/5468880>

[Daneshyari.com](https://daneshyari.com)