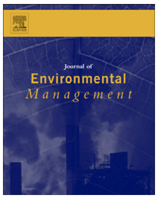
Journal of Environmental Management 188 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman



Research article

Removal of heavy metals from acid mine drainage using chicken eggshells in column mode

Ting Zhang [a], Zhihong Tu [a], Guining Lu [a, b, c, *], Xingchun Duan [d], Xiaoyun Yi [a, b], Chuling Guo [a, b], Zhi Dang [a, b]

[a] School of Environment and Energy, South China University of Technology, Guangzhou 510006, China
[b] The Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China
[c] Guangdong Provincial Engineering and Technology Research Center for Environmental Risk Prevention and Emergency Disposal, Guangzhou 510006, China
[d] Water Supply Management Center of Guangzhou Development District, Guangzhou 510663, China

ARTICLE INFO

Article history:
Received 22 May 2016
Received in revised form
4 October 2016
Accepted 28 November 2016
Available online 2 December 2016

Keywords:
Acid mine drainage
Eggshells
Fixed bed
Thomas model
Element mapping

ABSTRACT

Chicken eggshells (ES) as alkaline sorbent were immobilized in a fixed bed to remove typical heavy metals from acid mine drainage (AMD). The obtained breakthrough curves showed that the breakthrough time increased with increasing bed height, but decreased with increasing flow rate and increasing particle size. The Thomas model and bed depth service time model could accurately predict the bed dynamic behavior. At a bed height of 10 cm, a flow rate of 10 mL/min, and with ES particle sizes of 0.18–0.425 mm, for a multi-component heavy metal solution containing Cd^{2+}, Pb^{2+} and Cu^{2+}, the ES capacities were found to be 1.57, 146.44 and 387.51 mg/g, respectively. The acidity of AMD effluent clearly decreased. The ES fixed-bed showed the highest removal efficiency for Pb with a better adsorption potential. Because of the high concentration in AMD and high removal efficiency in ES fixed-bed of iron ions, iron floccules ($Fe_2(OH)_2CO_3$) formed and obstructed the bed to develop the overall effectiveness. The removal process was dominated by precipitation under the alkaline reaction of ES, and the co-precipitation of heavy metals with iron ions. The findings of this work will aid in guiding and optimizing pilot-scale application of ES to AMD treatment.

1. Introduction

Acid mine drainage (AMD), which is characterized by extreme acidity and a high level of dissolved heavy metals (Akcil and Koldas, 2006), is usually produced in the mining process. Because there are more than 17,481 mining companies in China, a large number of hazardous wastes are inevitably released annually from base-metal mining and smelting operations. Dabaoshan Mine, which is located in South China, is a typical site. Mud impoundment of this area mainly enters the Hengshi River, Wengjiang River, and several other tributaries. Local residents draw polluted water from these rivers to irrigate their crops, which resulted in a high mortality rate in the 1990s (Zhao et al., 2012; Zhuang et al., 2009). Heavy metals are toxic to aquatic organisms even at very low concentrations (Malkoc and Nuhoglu, 2006). However, the concentrations of Cd^{2+}, Pb^{2+} and Cu^{2+} exceed 0.4, 1.0 and 6.0 mg/L in the AMD from the Dabaoshan Mine area, which are 40, 5, and 12 times higher than the permitted limits of the Standards for Irrigation Water Quality of China (GB 5084-2005), respectively. The concentrations of iron ions are also high (37.0–347.7 mg/L Fe^{3+} and 8.0–159.9 mg/L Fe^{2+}) (Chen et al., 2015).

Zhao et al. (2012) found that Cd^{2+} is the major contributor to human health risk because of its easy absorption in crops in an acidic soil environment. Cd^{2+} and Pb^{2+} are considered potential carcinogens and are associated with the etiology of many diseases, especially cardiovascular, kidney, blood, nervous, and bone diseases (Järup, 2003). Cu^{2+} is an essential element, however, its high concentrations in food and feed plants are of great concern because of its toxicity to humans and animals (Kabata-Pendias and Mukherjee, 2007). Therefore, wastewaters containing heavy metals must be treated before being discharged into water bodies. Although several treatments are used for metal removal, such as precipitation, ion exchange and solvent extraction, biomaterial adsorption possesses

---

* Corresponding author. School of Environment and Energy, South China University of Technology, Guangzhou 510006, China.
E-mail address: GNLu@foxmail.com (G. Lu).

http://dx.doi.org/10.1016/j.jenvman.2016.11.076
0301-4797/

particular strengths because biomaterials are environmentally benign, abundant and cost effective (Kaduková and Virčíková, 2005; Ok et al., 2007).

According to the National Bureau of Statistics of China, domestic egg consumption reached 28,761 kilotons in 2014. Consequently, 3164 kilotons of eggshells (ES, ES account for 11% of the total weight of eggs) were generated, which is a problem because ES and the attached membrane attract vermin (Choi and Lee, 2015). Numerous studies have reported about metal ions adsorption on ES (Ahmad et al., 2012; Baláž et al., 2015; Ergüler, 2015; Flores-Cano et al., 2013; Guijarro-Aldaco et al., 2011; Yeddou and Bensmaili, 2007). However, application of ES to remove heavy metals from AMD in a fixed bed has not been reported. Direct addition of powdered adsorbents to remove heavy metals may be efficient, but adsorbent loss as wasted sludge can be rather severe (Chern and Chien, 2002). In process application, a fixed-bed column is effective for cyclic sorption because it allows more efficient use of the sorbent ability, results in better quality effluent (Volesky and Prasetyo, 1994), is easy to operate, has no particle loss problem, and bears continuous flow (Chern and Chien, 2002; Malkoc and Nuhoglu, 2006).

In this study, we investigated Cd^{2+}, Cu^{2+} and Pb^{2+} removal from AMD and also simultaneously considered removal of Fe. Chicken ES were chosen as a biosorbent for heavy metal removal from AMD. Granular ES were used in column mode. The aims of this work are as follows: (1) to measure the effects of different flow rates, bed depths and ES particle sizes on the breakthrough curves, (2) to analyze the concentration–time profile and fixed-bed performance, and (3) to obtain a model that is sufficiently sophisticated to describe the main system performance but also simple for analysis.

2. Materials and methods

2.1. Adsorbent and adsorbate preparation

Raw ES were provided by the canteen of the South China University of Technology, Guangzhou, China. The inner shell membranes were manually removed from the ES. The ES were washed three times with distilled water to remove impurities before being dried in a muffle furnace at 100 °C for 24 h. The materials were then ground and sieved through 80, 40, and 18 mesh stainless-steel screens to obtain 0.18–0.425 mm and 0.425–1 mm particles. The obtained sorbents were stored in a desiccator before the experiments.

AMD was sampled from the Dabaoshan Mine area, South China. Its initial concentrations of Cd^{2+}, Pb^{2+} and Cu^{2+} were 0.39 ± 0.04, 1.20 ± 0.10 and 6.30 ± 0.50 mg/L, respectively, and the pH was 2.4 ± 0.2. The concentration of Fe^{3+} ions was 195.20 ± 5.0 mg/L and the concentration of Fe^{2+} ions was only 5.1 ± 0.1 mg/L. The total Fe was considered in the following experiments. The other main constituents of AMD were SO_4^{2-} (2000–4500 mg/L), Zn (98–102 mg/L), Mn (49–62 mg/L), As (0.025–0.043 mg/L), Mg (128–140 mg/L), Cr (0.05–0.07 mg/L), Ni (0.4–0.5 mg/L) and Ca (110–270 mg/L), and the concentrations depended on the season and the year (Chen et al., 2015). The AMD solute was filtered using Whatman # 42 filter paper to remove suspended solids before running column system.

2.2. Adsorption studies

Continuous flow biosorption experiments were carried out in Perspex-tube column (2.1 cm internal diameter and 40 cm height) packed with a weighed amount of ES. The temperature of all experiments was maintained at 25 ± 2 °C. A 3 cm high layer of Ballotini balls (3 mm in diameter) was placed on top of the packed adsorbent for better flow distribution. Deionized water was used to wash the ES to remove air bubbles, avoid channeling, and remove potential impurities before running fixed-bed system. A rotameter was used to determine the actual flow rate. The pH change of the AMD was also monitored.

AMD solution was continuously pumped into the column in the up-flow direction by a peristaltic pump at 10, 20 or 30 mL/min until exhaustion. Experiments with three different bed depths, 10 cm (37 g of ES), 20 cm (74 g of ES) and 30 cm (110 g of ES), were operated at the same effluent flow rate (10 mL/min) with ES diameters of 0.425–1 mm. The influence of the ES grain size was investigated with ES diameters of 0.18–0.425 mm (40 g of ES) and 0.425–1 mm (37 g of ES) at the same effluent flow rate (10 mL/min) and bed depth (10 cm). In all tests, effluent samples were intermittently collected and analyzed with a double-beam atomic absorption spectrophotometer (SpectrAA-20, Varian).

The reversibility of metal adsorption and the sustainability were investigated by desorption experiments. Once the adsorption bed was exhausted, the ES were immersed in 0.1 M HNO_3 for 24 h and the amount of nitric acid used was such that the concentration of metal-laden ES was 37 g/L. The metal concentration after desorption was determined using the same method as that used for the effluent samples.

The total Fe and Fe^{2+} concentrations were determined by 1–10 phenanthroline spectrophotography with a spectrophotometer (UV-VIS Spectrum 2550, SHIMADZU) at 510 nm.

2.3. Adsorption model

The Thomas model equation for an adsorption column is as follows (Kapoor and Viraraghavan, 1998; Volesky and Prasetyo, 1994):

$$\frac{c_t}{c_0} = \frac{1}{1 + \exp(k_{Th} q_0 m / v - k_{Th} c_0 t)} \tag{1}$$

where c_t is the effluent metal concentration at time t, (mg/L), c_0 is the influent metal concentration (mg/L), k_{Th} is the Thomas rate constant (mL/min mg), q_0 is the maximum solid-phase concentration of solute (mg/g), m is the mass of ES in the column (g), and v is the flow rate (mL/min). The kinetic coefficient (k_{Th}) and adsorption capacity of the column (q_0) can be determined from a plot of c_t/c_0 against t at a given flow rate using the non-linear regression method.

The Adams–Bohart model is usually used to describe the initial part of the breakthrough curve. The equation is expressed as (Han et al., 2008):

$$\frac{c_t}{c_0} = \exp\left(k_{AB} c_0 t - k_{AB} N_0 \frac{Z}{F}\right) \tag{2}$$

where k_{AB} is the Adams–Bohart model kinetic constant (L/mg min), N_0 is the maximum adsorption capacity (mg/L), Z is the bed height of the column (cm), and F is the linear velocity calculated by dividing the flow rate by the column section area (cm/min). From this equation, values describing the operational parameters of the column can be determined from a plot of c_t/c_0 against t at a given bed height and flow rate using the non-linear regression method.

The bed depth service time (BDST) model expresses the service time (t) of the breakthrough curve. The equation is following (Ko et al., 2000; Othman et al., 2001):

$$t = \frac{N_0}{c_0 F} Z - \frac{1}{K_a c_0} \ln\left(\frac{c_0}{c_t} - 1\right) \tag{3}$$

where K_a is the rate constant of the BDST model (L/mg min). A plot