Journal of Industrial and Engineering Chemistry 18 (2012) 198–204

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Eggshell and coral wastes as low cost sorbents for the removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solutions

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ARTICLE INFO

Article history:
Received 30 December 2010
Accepted 6 March 2011
Available online 4 November 2011

Keywords:
Eggshell
Coral
Heavy metal removal
Distribution coefficient
Langmuir isotherm
Biosorption

ABSTRACT

Rapid industrialization in Korea has led to the discharge of heavy metals to water, posing a threat to the environment. The use of natural materials as low cost sorbents for the removal of heavy metals from aqueous solutions has recently received increasing attention. The present study was conducted to evaluate the effectiveness of eggshell and coral wastes for the removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solutions. Batch equilibrium experiments were conducted using heavy metal solutions with waste eggshell and coral powders. Langmuir and Freundlich adsorption models were used for the mathematical description of sorption equilibrium. The maximum amounts of metals (Cu^{2+}, Pb^{2+} and Cd^{2+}) adsorbed were found to be 32.3, 22.9 and 4.47 mmol kg^{-1} for eggshell and 6.77, 5.52 and 1.03 mmol kg^{-1} for coral wastes, respectively. At low initial concentrations the adsorption of heavy metals onto both sorbents can be described as H-type (except for the Cd adsorption onto coral), indicating high-affinity isotherms and strong adsorbate–adsorptive interactions such as inner sphere complexes. However, the metal adsorption was described by L-type isotherm at high initial concentrations. Based on the distribution coefficient (K_d) values and the percentage of metal removed, the selectivity sequence in eggshells and coral wastes was found to be $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The K_d values and the percentage of metals removed were higher in eggshells than coral with its higher capacity to adsorb heavy metals. Based on the results of the present study, eggshell and coral wastes can be used for the removal of heavy metals from aqueous solutions.

1. Introduction

In Korea, rapid industrial development has occurred over a short period of time, resulting in contamination of the aquatic systems with a wide range of toxic contaminants [1]. The presence of inorganic pollutants such as heavy metals in aquatic systems is of considerable concern because of their non-biodegradability, mobility and toxicity. Heavy metals can accumulate in the human body over time, causing serious health effects [2–5]. Accordingly, the removal of heavy metals from wastewater has received a great deal of attention in recent years [6,7].

Several conventional physical and chemical wastewater treatment technologies including coagulation, filtration, evaporation recovery, precipitation, oxidation/reduction, electrochemical treatment, ion exchange and reverse osmosis have been used to remove heavy metals from aqueous systems. However, these methods are economically unfavorable or technically complicated, and are only used in special cases of wastewater treatment [3,8–11]. Moreover, most of these processes are only effective when there are high levels of metals in aqueous solution [8,12,13]. There has recently been increased interest in the development of new materials capable of removing toxic heavy metals from contaminated water [5].

The sorption process, which includes metal immobilization in contaminated water, has gained attention in the past few decades because it offers advantages such as high efficiency and low operating cost, and because it is eco-friendly when compared to conventional treatment methods [9,14–16]. Most sorbents used for the removal of heavy metals from wastewater are derived from waste materials that are abundant and low cost, such as seaweed, tea waste, fly ash, peat moss, orange peels, animal bones and coconut husks [17]. The use of micro-organisms such as bacteria, fungi, yeast and algae for the treatment of wastewaters containing toxic metal ions is also an attractive technique; however, it is not yet suitable for large scale applications [18,19].

In Korea, domestic egg consumption reached 806,402 tons in 2009, and this value has been increasing every year since 2003 [20]. Increased consumption has resulted in over 65,000 tons of

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doi:10.1016/j.jiec.2011.11.013

eggshell waste generated per year. Waste eggshells contain high contents of calcium carbonate (85–95%); therefore, their recycling or reuse has the potential to reduce environmental pollution while acting as a cost effective material for the immobilization of heavy metals in wastewater and soil [17,21]. In addition, coral powder consists of $>35\%$ $CaCO_3$ and is a natural resource that is abundant and inexpensive to obtain [22]. More recently, Ok et al. [21,23,24] reported that lime based waste materials such as eggshells and oyster shells can be used as an alternative to $CaCO_3$ for the immobilization of heavy metals in contaminated soils. However, little is known about the use of eggshells and coral to remove heavy metals from aqueous systems [25,26].

Therefore, this study was conducted to evaluate the effectiveness of waste eggshell and coral on the removal of heavy metals (Pb^{2+}, Cd^{2+} and Cu^{2+}) from aqueous solutions. The metal sorption was assessed based on the Langmuir and Freundlich adsorption isotherm models. The interactions of eggshell and coral wastes with metal ions were established by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy.

2. Materials and methods

2.1. Preparation of sorbents

Waste eggshells were collected from restaurants, in Chuncheon, Korea, while waste coral powder was obtained from a local fertilizer plant where coral is processed to fertilizer by extracting the calcium from the coral powder. The eggshells and coral powders were washed several times with distilled water to remove impurities, after which they were dried at 50 °C for five days in a forced air-drying oven. Both materials were then crushed mechanically and passed through a 1-mm sieve to obtain a homogeneous particle size. The prepared sorbents were then stored in a desiccator until further experimentation.

2.2. Sorption experiments

The sorption of Pb^{2+}, Cd^{2+} and Cu^{2+} onto eggshells and coral as a function of the initial concentrations was studied at 25 °C. Synthetic metal solutions were prepared individually by dissolving the appropriate amounts of lead nitrate [$Pb(NO_3)_2$], cadmium nitrate tetrahydrate [$Cd(NO_3)_2\cdot 4H_2O$] and copper nitrate pentahydrate [$Cu(NO_3)_2\cdot 5H_2O$] to obtain Pb^{2+}, Cd^{2+} and Cu^{2+} solutions, respectively. All reagents were AR-grade and were obtained from Sigma Aldrich Chemical Company. The initial metal concentrations were set at 10, 20, 40, 60, 100, and 150 mg L^{-1} for Pb, and 10, 20, 40 and 60 mg L^{-1} for Cd and Cu for each synthetic metal solution. For the sorption batch experiments, 1.0 g of each sorbent (eggshell and coral) was mixed with 40 mL of each initial metal solution in a 250 mL Erlenmeyer flask on a thermal shaker at 25 °C and 120 rpm. The pH of aqueous solution was maintained at 5.5 with 0.01 M HCl or 0.01 M NaOH throughout the reaction process. After 24 h, the suspensions were filtered using Whatman # 42 filter paper and the metals concentrations remaining in the supernatant were analyzed by ICP-AES (Perkin-Elmer, Optima 3100XL).

2.3. Sorption isotherm model

The Langmuir and Freundlich adsorption isotherm models were applied to the experimental data for the uptake of Pb^{2+}, Cd^{2+} and Cu^{2+} by the eggshell and coral wastes. The Langmuir equation is expressed as:

$$q = \frac{kC_e b}{(1 + kC_e)} \tag{1}$$

where C_e is the equilibrium solution phase concentration (mmol kg^{-1}), q the equilibrium solid phase concentration (mmol kg^{-1}), k is the enthalpy related constant, b is the Langmuir isotherm sorption capacity (mmol kg^{-1}). Eq. (1) can be rearranged to its linearized form as:

$$\frac{C_e}{q} = \frac{1}{kb} + \frac{C_e}{b} \tag{2}$$

Plotting C_e/q vs C_e gives Langmuir isotherm, where $1/b$ is the slope and $1/kb$ is the intercept.

The Freundlich equations in their non-linear and linear forms are expressed in Eqs. (3) and (4), respectively.

$$q = K_f {C_e}^{1/n} \tag{3}$$

$$\mathrm{Log}\, q = \mathrm{Log}\, K_f + \left(\frac{1}{n}\right) \mathrm{Log}\, C_e \tag{4}$$

where q and C_e were defined previously, K_f is the sorption capacity constant and n is the intensity constant.

Plotting Log q vs Log C_e gives Freundlich isotherm, where slope is the value of $1/n$ and intercept is equal to Log K_f.

2.4. Sorption affinity

To assess the sorption affinity, the percentage of metal sorption and the distribution coefficient were calculated using Eqs. (5) and (6), respectively:

$$\text{The percentage of metal adsorbed}(\%) = \left[\frac{(C_i - C_e)}{C_i}\right] \times 100 \tag{5}$$

$$K_d = \frac{q}{C_e} \tag{6}$$

where C_i is the initial added metal concentration (mg L^{-1}), C_e the equilibrium solution phase concentration (mg L^{-1}), K_d the distribution coefficient, and q_e is the equilibrium solid phase concentration (mg kg^{-1}).

2.5. Surface structure and functional group analyses of sorbents

The surface structure of eggshell and coral sorbents before and after sorption was analyzed by scanning electron microscopy (JEOl JSM-5410). Additionally, the functional groups of eggshell and coral wastes were determined by Fourier transform infrared spectroscopy (Bio Rad, FTS 3000MX).

2.6. Statistical analysis

All experiments were conducted in triplicate and the mean values of each experiment were used to calculate the sorption isotherm model parameters and sorption metal affinity. The Microsoft® Office Excel® computer program was used for data analysis.

3. Results and discussion

3.1. FT-IR characterization of sorbents

The FT-IR spectrum of eggshell and coral is shown in Fig. 1. The FT-IR spectra for eggshell and coral sorbents were evaluated in the range of 1000–4000 cm^{-1}. In both the eggshell and coral spectra, the bands appear to be centered between 1450 and 1500 cm^{-1}. These bands primarily correspond to the v3 (asymmetric stretching of carbonate) mode. Similar findings were reported by Kaczorowska et al. [27], who found that the main band in the FT-IR spectrum of red coral was at 1480 cm^{-1}, corresponding to the