Chemical Engineering Journal 172 (2011) 783–791

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Biosorption behavior and mechanism of beryllium from aqueous solution by aerobic granule

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ARTICLE INFO

Article history:
Received 25 March 2011
Received in revised form 20 June 2011
Accepted 21 June 2011

Keywords:
Biosorption
Beryllium
Aerobic granule
Mechanism

ABSTRACT

The treatment of Be-contaminated wastewater has been paid little attention, although beryllium (Be) and its compounds are of high toxicity. In this research, aerobic granule was for the first time introduced to remove Be from aqueous solution. Influencing factors including reaction time, initial Be concentration, pH, biosorbent dosage, and coexistent metal ions (Cd, Cu, and Fe) were investigated in batch experiments. The aerobic granule, characterized by element analysis and CLSM, was abundant in carboxyl, phosphoryl, amine and hydroxyl groups. Potentiometric titration experiment demonstrated that the pH effect on biosorption depended on the surface charge of granule ($pH_{zpc} = 2.4$) and the species of Be (Be^{2+}, $Be(OH)^+$, and $Be(OH)_2$) in solution. The coexistent metal ions would either inhibit Be uptake through competitive biosorption or promote Be uptake via coprecipitation, depending on the K_{sp} of coexistent metals. Kinetic and isotherm modeling studies revealed that the experiment data could be well described by pseudo-second-order model and Langmuir isotherm, respectively. The maximum biosorption capacity obtained in this experiment was 14.0 mg/g. The sequential extraction test and XPS analysis suggested that precipitation and ion exchange were the dominant mechanisms under the experimental conditions, and FTIR analysis revealed that functional groups like carboxyl and hydroxyl played an important role in the biosorption of Be.

1. Introduction

Beryllium (Be) is an alkaline earth element of Group IIA. Aqueous Be has the highest surface charge density of any divalent ions, and is prone to combine with anions primarily through covalent bond [1]. As a unique metal material, Be owns favorable properties such as low density, high tensile strength and melting point, thus making it widely used in aerospace, ceramics, electronic and computer industries. Besides, the abilities to generate, reflect and capture neutrons broaden its application range to nuclear industry [2]. Be is mainly found in the form of beryl, phenacite, and helvine in the earth's crust. After mining, it is manufactured to metals or alloys, companied by its release and unavoidable contamination to the environment. Be and its compounds are of high toxicity. Exposure to Be can cause acute chemical pneumonitis, chronic beryllium disease, and even cancer [3,4]. International Agency for Research on Cancer (IARC) classified Be as a Group 1 carcinogen in 1993 [5].

Conventional treatment methods for Be-containing wastewater, such as lime-neutralization, ion-exchange and activated carbon adsorption, are found to be limited since their low removal efficiency or high cost [6,7]. To overcome these drawbacks, more attention has been paid to biosorption process. Biosorption has advantages of low cost, high efficiency, especially suitable in dealing with low heavy metal concentration wastewater, even at μg/L level [8]. Kinds of biosorbents, e.g. bacteria, algae and activated sludge, have been used for Be removal [9–11]. However, these studies mainly focused on the optimization of experimental conditions, and the mechanisms involved were not discussed in depth.

Aerobic granule, granulated from activated sludge, is increasingly drawing the interest of researchers engaging in the area of biotechnology. Compared with conventional suspended biosorbent, it has advantages of strong microbial structure, large surface area, high biomass retention, tolerance to toxicity, and good settleability [12]. Aerobic granule has been extensively investigated to remove nitrogen, phosphorus and organic compounds through biodegradation [13–15]. Moreover, as one of the promising biosorbents, aerobic granule was first applied to remove Zn from industry wastewater by Liu et al. [16], and a high sorption capacity of 270 mg/g was obtained. Since then, it has been extensively inves-

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doi:10.1016/j.cej.2011.06.062

tigated in removing heavy metals and nuclear waste [17–21]. To date, no information is available on the biosorption of Be by aerobic granule.

This study for the first time investigated the biosorption behavior of Be onto aerobic granule from aqueous solution. The sorption kinetics, isotherms, and influence of pH, biosorbent dosage and coexistent metal ions were discussed in detail. The mechanisms involved were deduced with the aid of potentiometric titration, sequential extraction test, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The information provided here could be helpful to further understand the mechanism of Be biosorption and facilitate the potential application of aerobic granulation technology in the treatment of Be-containing wastewater.

2. Methods

2.1. Materials and chemicals

The aerobic granules used in this study were cultivated from municipal wastewater sludge in a lab scale sequencing batch reactor, fed with synthetic wastewater [17]. Mature granules with a mean size of 1.0 mm were harvested, and washed three times with deionized water. According to Yan and Viraraghavan [22], heat treatment of the biomass could cause a loss of some functional groups on the cell surface, and decrease the uptake capacity. Here the aerobic granules were freeze-dried for experiment use.

Stock Be solution was prepared by diluting 1000 μg/mL of standard Be solution. The concentrations of Be, Cd, Cu, Fe were determined by inductively coupled plasma mass spectrometry (ICP-MS, ThermoElectron, XSeries II, USA).

2.2. Batch experiments

Batch experiments were conducted by mixing 50 mL of Be solutions with freeze-dried aerobic granules in 100 mL Erlenmeyer flasks. The flasks were then left to shake at 150 rpm and 25 ± 1 °C. The pH of each test solution was adjusted by either 0.1 M HNO_3 or 0.1 M NaOH. The influence of pH was studied by equilibrating the suspension in solution at pH range of 2.0–11.0. The concentrations of granules varied in the range of 0.5–4.0 g/L to study the effect of biosorbent dosage. The effect of possible coexistent metal ions (Cd, Cu, and Fe) was studied by varying their initial concentrations from 1 mg/L to 50 mg/L in binary systems. For the kinetic experiment, Be was added to granule samples at initial concentrations of 0.2 mg/L, 10 mg/L, and 50 mg/L, respectively. Samples were taken at specific time intervals. For the biosorption isotherm studies, the initial Be concentrations varied in the range of 0.2–60 mg/L.

All experiments were performed in duplicate, and the supernatants were filtered through 0.45 μm Millipore membranes before analysis. Metal-free and biosorbent-free blank samples indicated that the Be sorption onto flasks and the filtering membranes was negligible.

The biosorption amount, Q_e (mg/g), was calculated using the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{m}$$

where V is the volume of the metal solution (L), C_0 and C_e are the initial and equilibrium metal concentrations (mg/L), m is the dry weight of aerobic granules (g).

2.3. Analytical methods

2.3.1. Element analysis

A 1.0 mg of the prepared sample was used to determine the C, H, N, S and O contents by CHNS/O analyzer (Elementar, Vario EL, Germany). Meanwhile, 0.1 g of the sample was digested by nitric acid, and the inorganic element analysis was performed by ICP-MS [23].

2.3.2. CLSM

In the confocal laser scanning microscopy (CLSM) experiment, the hydrated samples were stained in the sequence of Syto 63 (total cells), FITC (proteins), Con A (α-polysaccharides), and Nile red (lipids) [24]. The stained granule was embedded for cryosectioning and frozen at −20 °C, and then every 60 μm sections were cut on a cryomicrotome and mounted onto the microscopic slides for observation. The internal structure of the granule was examined with CLSM (Leica, TCS SP2, Germany).

2.3.3. Potentiometric titration

The titration experiment was carried out using an automatic titrator (Mettler Toledo, T70, Switzerland), and under a nitrogen stream in order to remove CO_2. 0.3 g granule was added to 50 mL deionized water, with a background electrolyte concentration of 0.01 M NaCl. The suspension was first titrated to pH 2 by adding 0.1 M HCl, and then known amounts of 0.1 M NaOH were incrementally added until pH 11 was reached. The surface charge was calculated based on the electro-neutrality of the solution [25].

2.3.4. FTIR

The granule samples were mixed with spectroscopic quality KBr in the ratio of 1:100 for FTIR measurement. The IR spectras were collected by a Perkin-Elmer spectrometer (Bruck, Tensor 27, Germany) in the range of 400–4000 cm^{-1}. The background absorbance was measured using pure KBr pellets.

2.3.5. XPS

The XPS measurement was performed in the ultrahigh vacuum chamber of a Kratos Ultra XPS system (Kratos Analytical, Axis Ultra, England). The XPS spectra were recorded using the energy source of monochromatic Al K radiation (1486.71 eV) operated at 15 kV and 15 mA. For calibration, the binding energy of the spectra was standardized with the C 1s peak at 284.8 eV.

2.3.6. Sequential extraction

Be fraction test was carried out using 0.5 g pre-dried granule in a 50 mL centrifuge tube to extract each chemical species (ion-exchangable, acid soluble, Fe/Mn bound, organic bound and residual fraction). The detailed extraction procedure was described by Yao et al. [17].

3. Results and discussion

3.1. Characterization of biosorbent

Elemental composition of aerobic granule is shown in Table 1. The result showed that the main elements of biosorbent are C, H, N, O, and can be presented in a formula $CH_{1.9}O_{0.6}N_{0.2}$. Divalent metal ions, e.g. Mg and Ca existed, which are widely recognized to play an important role in the microbial aggregation [26,27]. The accumulated Ca in aerobic granule can enhance the structure strength, and act as adsorption sites for metal ions [28]. Other elements like Na and K are good ion exchangers for metal biosorption [29].

Multiple fluorescent staining and CLSM methods are frequently used to explore the detailed structure of aerobic granule. It can visualize the distribution of different components simultaneously