Bioresource Technology 128 (2013) 30–35

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Ruthenium recovery from acetic acid waste water through sorption with bacterial biosorbent fibers

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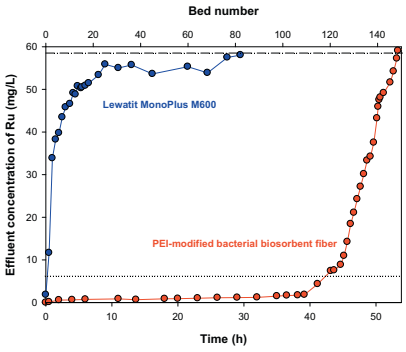
HIGHLIGHTS

- A fibrous type of bacterial biosorbent was evaluated on its Ru sorption capacity.
- The maximum Ru uptake of PBBF was 16.5 times higher than that of commercial resin.
- The PBBF showed a highly effective removal of Ru in a column system.
- The PBBF has potential as a biosorbent for Ru removal from acetic acid wastewaters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form 21 September 2012
Accepted 29 October 2012
Available online 9 November 2012

Keywords:
Bacterial biosorbent fiber
Chitosan
Ruthenium
Acetic acid waste solution
Continuous flow fixed-bed column

ABSTRACT

A fibrous bacterial biosorbent was developed to bind precious metal–organic complexes in batch and column processes. Polyethylenimine (PEI)-modified bacterial biosorbent fiber (PBBF) was prepared by spinning *Corynebacterium glutamicum* biomass-chitosan blends, coating them with PEI and cross-linking with glutaraldehyde. When an acetic acid waste solution containing 1822.9 mg/L Ru was used as a model waste solution, Ru uptake by the PBBF was 16.5 times higher than that of the commercial ion exchange resin, Lewatit MonoPlus M600. The maximum amounts of Ru uptake were 110.5, 16.0 and 6.7 mg/g for PBBF, raw biomass, and Lewatit MonoPlus M600, respectively. In a flow-through packed bed, PBBF exhibited the breakthrough time of 42.32 h. Therefore, PBBF can be considered as an alternative sorbent for recovery of anionic metal–organic complexes from waste solutions.

1. Introduction

Precious metals are used in various industries as catalysts. Increasing demand, limited availability and the generation of potentially toxic effluents (Wiseman and Zereini, 2009) make the recovery and removal of precious metals from wastewaters a worthwhile endeavor.

Conventional treatment methods for metals-bearing effluents include ion exchange, precipitation, membrane separation and solvent extraction. These methods have significant drawbacks such as incomplete metal removal, high capital costs, high chemical and/or energy requirements, and generation of toxic sludge or other waste products that require disposal. (Mack et al., 2007; Göksungur et al., 2005). Microbial biomasses have been studied as sorbents for

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http://dx.doi.org/10.1016/j.biortech.2012.10.146

metals (Dobson and Burgess, 2007; Vijayaraghavan and Yun, 2008) and have been shown to be cheaper than commercial sorbents (activated carbons and ion exchange resins), have a high sorption capacity even in low concentration solutions. These biomaterials are also abundant and environmental friendly (Mack et al., 2007; Vijayaraghavan and Yun, 2008). Therefore, when the microbial biomasses are made as a form of thin fibers, a rapid sorption along with high capacity can be achieved. This is motivation of the present study. *Corynebacterium glutamicum*, which was used in this present study, is widely employed for the biotechnological production of amino acids, and a large amount of biomass is produced as byproduct. Previous studies on *C. glutamicum* have shown adequate biosorption capacities for dyes (Won and Yun, 2008; Mao et al., 2009); however, the application of the powder form of the biomass on a commercial scale often suffers from solid–liquid separation problems after biosorption, poor mechanical strength, low rigidity, and a high pressure drop when used in a column (Vijayaraghavan and Yun, 2008). Immobilization of the biomass in a polymeric matrix allows control over particle size, easy separation of the biosorbent and wastewater, and a minimal pressure drop under continuous flow conditions (Vijayaraghavan and Yun, 2008; Mao et al., 2010).

In the present study, *C. glutamicum* was immobilized using chitosan as a binder. Chitosan can be readily modified into a variety of forms, such as beads, membranes and fibers or hollow fibers, for various fields of application (Guibal, 2004). Thin fiber biosorbent exhibits rapid kinetics as fiber diameters of less than 300 μm in diameter provide large surface areas and short path lengths for migration of metal ions to the binding sites. Since the fiber is sufficiently long, it can be used in a packed column without significant pressure drop and column clogging problems. Since chitosan undergoes partial dissolution and protonation of its amino groups in acidic environments, cross-linking with glutaraldehyde (GA) is advised (Boddu et al., 2008); however, cross-linking can also reduce the sorption capacity (Mao et al., 2011).

Chemical surface modification of the biomass can greatly improve its sorption capacity (Vijayaraghavan and Yun, 2008). One method for introducing binding sites onto the biosorbent surface is coating ionic polymer chains onto the surface of the biomass (Deng and Ting, 2005; Chassary et al., 2004).

Acetic acid is currently produced through the carbonylation of methanol in the presence of catalysts, such as precious metals (ruthenium, iridium and rhodium) (Sunley and Watson, 2000). These precious metals are complexed with organic materials in acetic acid waste solutions, causing difficulties in their sorption onto ion exchange resins. Therefore, in the present study the fibrous type of bacterial biosorbent was developed and its Ru sorption performance in batch and column processes was evaluated.

2. Methods

2.1. Chemicals and materials

Waste biomass of *C. glutamicum* was obtained from Daesang Corporation (Gunsan, Korea) in slurry form. The biomass was inactivated by contacting with HCl solution for 24 h, and had a moisture of 85% ± 0.5. Chitosan (degree of deacetylation: 84%; molecular weight: 300 kDa) was purchased from Texanmedtech (Seoul, Korea). Industrial grade polyethylenimine (PEI, molecular weight: 70 kDa) was purchased from Habjung Moolsan Co., Ltd. (Seoul, Korea). Acetic acid waste solution containing Ru was collected from the Samsung BP Chemicals Co., Ltd. (Ulsan, Korea) in pre-cleaned 20-L plastic containers. The strongly basic anion exchange resin, Lewatit MonoPlus M600 (Bayer, Germany), currently used for recovering Ru at Samsung BP Chemicals Co., Ltd., was used for comparison. All of the other chemicals were of analytical grade and purchased from Sigma–Aldrich Korea Ltd.

2.2. Preparation of PEI-modified bacterial biosorbent fiber

The fabrication process for PBBF was as follows. First, 5 g of chitosan (binder) was mixed with 100 mL of biomass slurry (containing about 15% (w/v) biomass), and 5 mL of 99.7% acetic acid was added. The mixture was stirred at 160 rpm with a mechanical stirrer for 24 h and extruded through a 25-hole stainless steel spinneret (0.1 mm in diameter) into an alkaline coagulation bath. The resulting fibers (chitosan-*C. glutamicum* blended fiber (CSBF)) were stirred, neutralized with sulfuric acid, and washed with distilled water. The washed CSBF was soaked in 1 L of a PEI solution (3% (w/v)) and stirred for 6 h at room temperature. The PEI-coated fiber was cross-linked with GA (0.6% (v/v)) for 2 h in order to fix PEI onto the fiber surface. The products were filtered using a 110-mm filter paper (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and washed with distilled water to remove PEI and GA residues from the fiber until the washed out water was neutral. Finally, the fibers were freeze-dried and sieved to obtain particle sizes below 300 μm. These fibers were subsequently used as the PBBF.

2.3. Analytical methods

Infrared spectra of raw biomass, chitosan, CSBF, and PBBF were obtained using a Fourier transform infrared spectrometer (FTIR, JASCO, FT/IR-4100, Japan). All samples were prepared as KBr discs and examined within a range of 600–4000 cm^{-1} in order to observe the change of some functional groups on the sorbents before and after PEI coating and GA cross-linking.

The surface-bonded states were analyzed using X-ray photoelectron spectroscopy (XPS). The analysis was conducted using an AXIS-NOVA spectrometer (Kratos Analytical, Ltd., UK) with monochromatic Al Kα as the X-ray source (1486.71 eV of photons) to determine the presence of C, N and O atoms on the surface of the samples. All of the binding energies were referenced to the neutral C_{1s} peak at 284.6 eV in order to compensate for surface charge effects. XPS spectra were recorded using an AXIS-NOVA spectrometer at the Korea Basic Science Institute (KBSI), Jeonju Center.

2.4. Determination of swelling ratio of the PBBF

The swelling ratio of the PBBF was determined by immersing the PBBF in the acetic acid waste solution at 25 °C for 10, 30, 60 and 120 min. Subsequently, the weight of the swollen fiber was measured and the swelling ratio was calculated using the following Eq. (1):

$$\text{Swelling ratio}(\%) = \frac{(W_t - W_0)}{W_0} \times 100 \quad (1)$$

In this equation, W_0 and W_t are the initial dried weight of the PBBF and the weight of the swollen PBBF at time t, respectively.

2.5. Batch studies

The sorption experiments were performed in a 50-mL polypropylene conical tube. The sorbent dosages, ranging from 0.5 to 10 g/L, were added to 30 mL of the acetic acid waste solution containing Ru. Each bottle was incubated on a rotary shaker at 160 rpm and 25 °C. After contact with the Ru solution for 24 h, the sorbents were separated through centrifugation at 4330*g* for 10 min. The Ru concentration in the supernatant was determined using inductively coupled plasma (Shimadzu, ICPS-7510, Japan) after appropriate dilution. The kinetic experiments were conducted in the same manner as the isotherm experiments except that the samples were collected at different time intervals.