ELSEVIER

Chemical Engineering Journal 136 (2008) 156–163

Chemical Engineering Journal

www.elsevier.com/locate/cej

Biosorption of copper by immobilized marine algal biomass

Ping Xin Sheng, Kin Ho Wee, Yen Peng Ting *, J. Paul Chen

Department of Chemical & Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

Received 9 August 2006; received in revised form 16 February 2007; accepted 21 March 2007

Abstract

The characteristics of poly(vinyl alcohol) (PVA) cryogel as an immobilization matrix were examined for the uptake of copper by a brown marine algal biomass, and compared with freely suspended biomass. Biomass-embedded PVA cryogel beads were robust and showed stability under a wide range of pH (1–13). SEM analysis revealed the rugged surface of the beads and changes in its surface compositions before and after metal binding. The surface area and pore size of the beads were highly dependent on the concentration of the biomass immobilized within the PVA beads. The immobilized beads showed lower copper uptake capacity than the freely suspended *Sargassum*. A positive correlation was also found between copper uptake capacity and the concentration of the immobilized biomass (5–30 g/L). The metal uptake capacity of the beads was also dependent on the solution pH. It was shown that immobilization matrix exerted mass transfer resistance for copper uptake by the PVA-*Sargassum* beads. The metal sorption rates were enhanced at higher biomass loading within the beads, or with an increase in the initial copper concentration, or with hydration of the beads before use. The kinetics of copper biosorption by the immobilized PVA cryogel bead could be well modeled by a pseudo first-order equation.

Keywords: Biosorption; Poly(vinyl alcohol) cryogel; *Sargassum*; Copper

1. Introduction

Biosorption is essentially the passive and physicochemical binding of metal ions to chemical sites naturally present in a biomass. The non-viable form of the biomass has been proposed as a potential biosorbent over living biomass since the former is a dead material which requires no nutrients, and problems associated with metal toxicity in living biomass and the need to provide suitable growth condition also do not arise [1]. Biosorption could be employed most effectively in aqueous solutions with pollutants present at trace concentrations (typically below 100 mg/L) and where conventional physical and chemical treatment methods are either ineffective or costly [2,3].

Various biomass of microbial, fungal, algal or crustacean origin have been investigated as biosorbent materials. In particular, many studies have focused on marine algae due to its easy availability and high uptake capacity [2,3]. Indeed, a few brown algae showed much higher uptake capacity than that of activated carbon, natural zeolites and synthetic ion exchange resins [4].

Unfortunately, free algal cells are not suitable for use as a column packing since the cells tend to clump together and excessive hydrostatic pressure are required in order to generate suitable flow rates. Furthermore, since the algal cells are inherently fragile, high pressure may cause disintegration of the free biomass. The fragility problem has been alleviated by the immobilization of the algae within a suitable porous matrix. Amongst the various immobilization methods, entrapment (whereby the biomass is enclosed within a polymeric matrix) is one of the most commonly used methods. Poly(acrylamide) gel, calcium alginate gel and poly(vinyl alcohol) (PVA) cryogel are among the porous matrices that have been used to immobilize non-viable algae and to permit their use in packed columns for metal ion recovery.

Poly(acrylamide) gel was the first polymer used for cell entrapment, but the free radicals generated in the course of polymerization were found to be toxic to both microorganisms and humans [5]. The gels prepared from natural polysaccharides such as alginates, κ-carrageenan and agarose are commonly used in cell immobilization [6]. These natural hydrogels unfortunately abrade easily [7] or dissolve in the presence of competitive ions [8], thus limiting their application under actual process effluent conditions. The use of poly(vinyl alcohol) gel as a matrix for cell immobilization has been extensively studied in various biological systems. PVA cryogel offers various advantages over

* Corresponding author. Fax: +65 6779 1936.
E-mail address: chetyp@nus.edu.sg (Y.P. Ting).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.03.033

the conventional alginate hydrogels including low cost, high durability and chemical stability, and non-toxicity to viable cells [9].

This work examines the use of PVA gel as an immobilization matrix for the uptake of copper by *Sargassum* sp. The beads were first characterized using SEM and BET analysis. The robustness and stability of the PVA cryogel beads were also investigated. A series of experiments was then carried out to study the effect of physicochemical conditions on the biosorption of copper by the immobilized PVA cryogel beads.

2. Materials and methods

2.1. Chemicals and biomass

Copper nitrate was obtained from Merck (Germany). Poly(vinyl alcohol) (average molecular weight 72,000 Da) was purchased from FLUKA. All chemicals are of analytical reagent grade. A 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were prepared for pH adjustment.

The raw biomass of *Sargassum* sp. was harvested from the coasts in Singapore. The biomass were washed with deionized water to remove extraneous materials and dried overnight at 60 °C. The dried biomass was then ground to various particle sizes and stored before use.

2.2. Immobilization

Blank PVA cryogel beads were fabricated using the iterative freeze–thaw–freeze method [10,13,14]. Firstly, 10 g of PVA was dissolved in 100 mL deionized water and stirred with a magnetic stirrer at 80 °C. During the dissolution, the solution volume was maintained at 100 mL by adding deionized water. After all the PVA had been dissolved, the polymer solution was cooled to room temperature and continuously stirred for 12–16 h to ensure a uniform solution. The resulting 10% PVA solution was transferred to an extrusion contraption by a peristaltic pump at very low flow rate (<5 mL/min) and introduced dropwise into liquid nitrogen, with a longitudinal coaxial air flow to control the bead size. The needle size used was 19 G (1.1 mm). The frozen beads were then placed in a freezer with temperature held at approximately −20 °C for 1–2 h. Next, all the beads were transferred to a refrigerator to be thawed at 4 °C. When all the beads have regained their characteristic elastic behavior, they were contacted with liquid nitrogen again. This freeze–thaw–freeze cycle was repeated twice (i.e., a total of three cycles). The beads were finally left in a dessicator for several days and periodically taken out for weight measurement. The beads were ready for experimental use only when consecutive measurements indicated no change in weight.

Biomass in the size range 65–212 μm was immobilized within PVA cryogel beads in the same manner as that for the blank PVA cryogel beads, except that the biomass was thoroughly mixed with the PVA solution before extrusion. Few batches of biomass-loaded beads of different biomass concentration (5 g dry biomass/L PVA solution, 10, 20, 30 g/L) were fabricated. The resulting *Sargassum*-immobilized PVA cryogel beads were referred to 5, 10, 20 and 30 g/L PVA-*Sargassum* beads, respectively. In this study, the PVA-biomass solution in excess of 30 g/L biomass concentration was too viscous for the experimental apparatus used; the concentrated solution often clogged the hollow needle used for extrusion.

2.3. Metal biosorption experiments

The pH of the metal solutions in the conical flasks was first adjusted to the desired values by using 0.1 mol/L HNO_3 or NaOH; the sorbent was then added into the solutions while stirred at 200 rpm at room temperature (22 ± 1 °C). The pH was measured at 20–30 min interval and adjusted accordingly. The supernatant samples for kinetics experiments were taken at periodic time intervals. For pH effect and isotherm experiments, the flasks were agitated until the pH was stable for more than 3 h. The supernatant taken during experiments was acidified and filtered (0.45 μm), and the metal concentrations were measured by an inductively couple plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima 3000). The metal uptake was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{W} \quad (1)$$

where q is the metal uptake, V the solution volume, W the amount of biomass, and C_i and C_f are the initial and the final (or equilibrium) metal concentrations, respectively.

All experiments in this work were conducted in duplicate and the average results were presented.

2.4. Abrasion test

A 2 g of blank or biomass-loaded PVA cryogel beads were stirred in 1.0 L deionized water at 400–500 rpm. Fifty beads were randomly taken before and after stirring, and their diameters and weights were measured with a digital micrometer caliper (Mitutoyo 323) and a digital balance (Mettler Toledo B204-S), and the results were analyzed to establish the robustness of the beads.

2.5. Chemical stability

Using 0.1 M hydrochloric acid and sodium hydroxide, solutions of pH from 1 to 13 were prepared. The beads were soaked and stirred at 150 rpm for 72 h after which 50 beads were removed, thoroughly rinsed with deionized water and dried, before the weight was measured.

2.6. Scanning electron microscopy

The beads were visualized using a scanning electronic microscope (JEOL, JSM-5600 V, Japan) in order to directly observe the surface microstructures of the bead at different forms. SEM requires an ion coating with platinum by a sputter coater (JEOL, JFC-1300, Japan) for 40 s in a vacuum at a current intensity of 40 mA after preparing the sample on metallic studs with double-sided conductive tape.