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Plate column biosorption of Cu(II) on membrane-type biosorbent (MBS) of *Penicillium* biomass: Optimization using statistical design methods

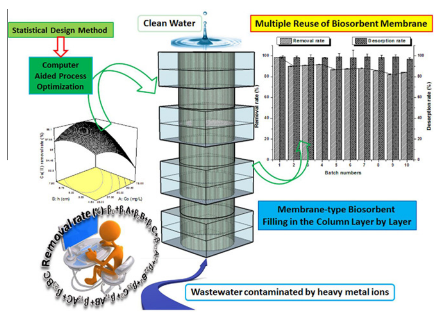
Gang Xiao, Xin Zhang, Haijia Su *, Tianwei Tan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, PR China

HIGHLIGHTS

- A low cost membrane-type biosorbent (MBS) of *Penicillium* biomass was prepared.
- MBS was piled into a plate column reactor layer and layer for Cu(II) biosorption.
- A set of statistical design methods were employed for Cu(II) removal optimization.
- A quadratic regression model was established with the error less than 1.22%.
- MBS could be reused for 10 cycles without obvious loss of its adsorption ability.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on the coupling of biosorption and membrane separation, a low cost membrane-type biosorbent (MBS) of *Penicillium* biomass was prepared. The surface morphology, pore properties and functional groups were studied via the characterization of MBS. Batch biosorption experiments indicated the maximum biosorption capacity of Cu(II) on MBS was 126.58 mg/g and about 90% of that on chitosan membrane. A plate column reactor filled with multi-layer of MBS was built for treatment of wastewater contaminated by Cu(II). The biosorption process factors were screened using Plackett–Burman design and three significant variables were selected for further optimization via response surface methodology (RSM) based on Box–Behnken model. A statistically second-order polynomial model was constructed with the error below 1.22%, on the basis of which the three-dimensional response surfaces were plotted. The prepared membrane-type biosorbent could be used successfully for 10 biosorption–desorption–regeneration cycles without decreasing its biosorption ability obviously.

1. Introduction

Industrial activities unfortunately generate polluted waste streams, with special focus on heavy metals which can cause lasting threaten to the ecosystem and human health because of their non-degradability and bioaccumulation properties. Among these heavy metals, copper(II), mainly from smelting and electroplating industries, is one of the most widespread contaminants (Dönmez and Aksu, 1999) and has been a major issue because of its systemic effects such as hemolysis, liver and kidney damage, and fever with influenza syndrome (Chowdhury and Saha, 2011). The discharge of Cu(II) wastewater is strictly regulated (Özer et al., 2009). Conventional treatment technologies apply chemical precipitation, electrolysis, ion-exchange, activated carbon adsorption and membrane separation (Kurniawan et al., 2006). Most of these methods have some limitations for industrial applications, such

* Corresponding author. Address: College of Life Science and Technology, PO Box 53, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China. Tel.: +86 10 64452756; fax: +86 10 64414268.

E-mail address: suhj@mail.buct.edu.cn (H. Su).

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as high capital and operating costs, incomplete metal ion removal and secondary pollution as hydroxide or concentrated effluents (Çabuk et al., 2007), especially in treating high volumes of wastewater with dilute metal concentration (Karthikeyan et al., 2007).

Biosorption is an alternative method to remove heavy metals from dilute aqueous solutions and offers significant advantages over the conventional technologies such as low cost, mild operating conditions, no secondary pollution and abundant biomaterial resources containing bacteria (e.g. *Micrococcus luteus* (Puyen et al., 2012)), fungi (e.g. *Trichoderma asperellum* (Tan and Ting, 2012)), seaweed (e.g. *Sargassum* sp. (Yang et al., 2011)), industrial biomass wastes (e.g., *Penicillium chysogenum* waste biomass from antibiotics fermentation industry (Tan and Chen, 2000)), agricultural wastes (e.g. soybean meal waste (Witek-Krowiak and Reddy, 2013)), etc. Over the past decades, the fermentation industry for beverages, food additives and antibiotics has rapidly developed in China, and over 80 million tons of waste mycelia (inactive biomass) enter the eco-environment every year. Furthermore, it has been reported that these waste biomass such as *Streptoverticillium cinnamoneum* (Puranik and Paknikar, 1997) and *P. chysogenum* (Tan and Chen, 2000) show a high performance for dilute wastewater treatment contaminated by heavy metals, thus removing heavy metals and reducing the problem of solid residue disposal.

The waste biomass in its free form is however generally of small particle size, poor mechanical strength and low rigidity, causing the difficulty of the liquid–solid separation after biosorption and high pressure drop in a fixed-bed module (Wang and Chen, 2009). In recent years, various efforts have been focused on the immobilization of biomass, which is a potential way to overcome these problems. Alginate (Tan and Ting, 2012), polyurethanes (Li et al., 2008), polyacrylamide, polysulfone, polyvinyl alcohol (Bai and Abraham, 2003) as well as some natural polymers such as chitosan (Yang et al., 2011), sawdust (Li et al., 2008) and orange peel cellulose (Lai et al., 2008) have been employed for biosorbents immobilization. Among these supporting matrices, chitosan, as a natural hydrophilic biopolymer with abundant $-NH_2$ and –OH groups which can chelate metals to form complexes (Hasan et al., 2006), has been considered as a good carrier for biomass immobilization (Yang et al., 2011). Su et al. (2003) selected chitosan as shell to coat *P. chysogenum* mycelium and the surface molecular imprinting adsorbent has been prepared showing a higher mechanical strength and better stability compared with the original mycelium. However, when applied in the column system, which is a promising method for industrial wastewater treatment, the surface molecular imprinting adsorbent was cumbersome for operation and easy to lose after soaked and scoured by wastewater (Zhang et al., 2011). So, a low-cost and easy immobilization method for preparing anti-corrosion biosorbent with higher stability and a convenient column filling and operation pattern should be developed for industrial application of heavy metals biosorption.

Moreover, the treatment efficiency of the column reactor was affected by many factors, such as initial concentration of the target pollutant (copper ions in the present study), pH value, biosorbent dosage, reaction time and velocity of flow. In order to obtain the optimum processing efficiency, it's essential to identify the optimal combination of factors as well as interactions among factors, which, if possible, is time-consuming and of high-cost using univariate method (Bingöl et al., 2012). So, in recent years, statistical based multivariate design methods have been used to reach the summit rapidly and cheaply in wastewater treatment systems as well as many other processes (Özer et al., 2009; Hasan et al., 2010; Ranjan et al., 2011), such as factorial design, mixture design, combined design and response surface design.

In this present paper, with coupling of biosorption and membrane-separation technologies, the membrane-type biosorbent (MBS) of *Penicillium* biomass was prepared and the surface morphology, pore properties and functional groups were studied by the characterization of the biosorbent. Biosorption performance of MBS for Cu(II) was evaluated by batch experiments with chitosan membrane as the control group. MBS was further used for the removal of Cu(II) in a plate column reactor. The effects of operating parameters such as the initial Cu(II) concentration, bed height, reaction time, pH value and flow rate on the Cu(II) removal were assessed using statistical design methods. The Plackett–Burman design was used to screen the most significant variables from the five factors and the response surface methodology (RSM) was used to optimize the biosorption process based on Box–Behnken design. A second-order polynomial model was used to obtain the optimum operating conditions with respect to the highest Cu(II) removal rate. Moreover, MBS could be used successfully for 10 biosorption–desorption–regeneration cycles without obvious loss of its adsorption ability which was valuable for actual industrial applications.

2. Methods

2.1. Biomass and chemical

Mycelium obtained from waste biomass of *Penicillium* was provided by Shandong Dongchen Biological Engineering Co., Ltd. Chitosan with 85% degree of deacetylation was extracted from shrimp shells by Jinan Haidebei Marine Bioengineering Co., Ltd. All chemicals obtained from Beijing Chemical Plant, including HNO_3, $Cu(NO_3)_2\cdot 3H_2O$, NaOH, HCl, epichlorohydrin and acetic acid were of analytical grade, and used without further purification. HNO_3 was diluted to 0.1 mol/L for adjusting the pH value of Cu(II) solution. 2000 mg/L Cu(II) solution was prepared and further diluted to the required concentrations for biosorption experiments.

2.2. Preparation of MBS

Penicillium biomass was dried at 60 °C in an air-supplied oven for 20 h, then crushed in a disintegrator and sieved to powder with particle size $\leqslant$180 μm. 0.2 g chitosan was dissolved in 10 mL acetic acid (2.5% v/v), then 2.0 g of mycelium powder was added dispersing with 100 W ultra-sound for 10 min. 1 mL Epichlorohydrin, a crosslinking agent, was added, then the mixture emulsion was magnetic stirred for 1 h at ambient temperature. The mixed slurry was spread on a 0.3 × 0.3 m glass plate and the membrane-type biosorbent with thickness of 0.7–0.9 mm was obtained. The prepared biosorbent was then soaked into 0.25 mol/L NaOH (as solidifying solution) for 2 h. Finally, the membrane was washed with distilled water and dried at 60 °C for 5 h. The chitosan membrane was prepared using the same method without mycelium addition.

2.3. Characterization of MBS

The surface morphology of the prepared membrane-type biosorbent was assessed by a field emission scanning electron microscope (FE-SEM) (Hitachi S4700, Tokyo, Japan) and the sample was coated with a thin layer of gold under vacuum condition.

The pore characteristic of MBS was evaluated by a mercury intrusion instrument (AutoPore IV 9500 V1.09, Micromeritics Instrument Corporation, Atlanta, USA) under pressure of 0.0007–413.6854 MPa and the sample weight was 0.5940 g.

FTIR analyses were performed on KBr discs with a 2% finely ground sample, analyzed in a Varian 3100 FTIR spectrometer and the infrared spectra of chitosan, mycelium and the prepared biosorbent (before and after adsorption of Cu(II) ions) were recorded in the wavenumber region of 4000–400 cm^{-1} at 2 cm^{-1} spectral resolution.