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Biosorption of 2,4-dichlorophenol by immobilized white-rot fungus *Phanerochaete chrysosporium* from aqueous solutions

Juan Wu [a,b], Han-Qing Yu [a,*]

[a] *School of Chemistry, University of Science and Technology of China, Hefei, 230026 Anhui, China*
[b] *Institute of Life Sciences, Anhui University, Hefei, 230039 Anhui, China*

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Abstract

The fungus *Phanerochaete chrysosporium* was immobilized in several polymer matrices: Ca-alginate, Ca-alginate-polyvinyl alcohol (PVA) and pectin, and was then used as a biosorbent for removing 2,4-dichlorophenol (2,4-DCP) in wastewater. Immobilization of *P. chrysosporium* onto pectin was less efficient than that onto other matrices because of its poor mechanical strength and low adsorption efficiency. Ca-alginate immobilized fungal beads with biocompatibility exhibited good mechanical strength and adsorption efficiency over 60%. Among the different biomass dosages in Ca-alginate immobilized fungal beads, 1.25% (w/v) was the optimum. The adsorption data of 2,4-DCP on the blank Ca-alginate beads, free, and immobilized fungal biomass could be described by the Langmuir and Freundlich isotherms very well. Desorption operation was efficiently completed by using distilled water as eluant, and the desorption efficiency reached 82.16% at an optimum solid/liquid ratio of 14.3. The consecutive adsorption/desorption cycles studies employing the Ca-alginate immobilized fungal beads demonstrated that the immobilized fungal biomass could be reused in five cycles without significant loss of adsorption efficiency and adsorbent weight.

Keywords: Biosorption; Desorption; Fungal biomass; Immobilization; Isotherms

1. Introduction

Biosorption of heavy metals in aqueous solutions has received increasing attention in recent years (Kaçar et al., 2002; Bai and Abraham, 2003; Abu Al-Rub et al., 2004). As an efficient, cost-effective and environmentally friendly technique, biosorption for heavy metals and various organic pollutants has emerged as a potential alternative to the conventional techniques. *Phanerochaete chrysosporium* is a well-known white-rot fungus and it has a strong ability to degrade various xenobiotics (Benoit et al., 1998). A few studies have been carried out with *P. chrysosporium* for detoxifying chlorophenol-bearing effluents (Aksu and Yener, 1998; Benoit et al., 1998; García et al., 2000). Although it could be used to remove heavy metals from wastewater through adsorption of metal ions onto its mycelium (Kaçar et al., 2002), its biosorption potential for the removal of organic pollutants, e.g., chlorophenols, has not been fully investigated.

Most studies about biosorption have focused on the use of dead biomass in powdered form. This has practical problems, such as low mechanical strength, small particle size, difficulty in separating biomass from liquid stream after biosorption, and mass loss in post-separation. These problems can be solved through the immobilization of microbial cells on natural or synthetic polymers, which provides additional advantages over freely suspended cells. The immobilization of native biomass improves its mechanical strength, rigidity, size, porosity characteristics, and resistance to environmental restraints. Immobilized biomass also exhibits a greater potential in fixed/fluidized bed reactors because of minimal clogging under continuous flowing conditions, convenience for regeneration, reuse of

* Corresponding author. Tel.: +86 551 3607592; fax: +86 551 3601592.
E-mail address: hqyu@ustc.edu.cn (H.-Q. Yu).

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biomass and easy solid–liquid separation (Zulfadhyl et al., 2001).

The selection of immobilization matrix is crucial in the application of immobilized biomass. The polymer matrix determines the mechanical strength, rigidity, and porosity characteristics of the immobilized beads and their adsorption capacity. The physical entrapment of microorganisms inside a polymer matrix is one of the most widely used techniques for immobilization. Natural polymers, such as sodium alginate, chitin, chitosan, and cellulose derivatives, have been used as the matrices for immobilization (Prakasham et al., 1999; Bai and Abraham, 2003). Ting and Sun (2000) used polyvinyl alcohol (PVA) for the immobilization of yeast biomass and observed a high mechanical and chemical strength of the product. Chang et al. (1998) found that the adsorption capacity of Ca-alginate immobilized cells was greater than that of polyacrylamide-entrapped cells for adsorption of Pb^{2+}. Other matrices used for biomass immobilization include Na-alginate–PVA (Bai and Abraham, 2003), Mowital®B30H resin (Aksu et al., 2002), and polyacrylonitrile (Zouboulis et al., 2003).

Information is available about the use of immobilized white-rot fungi for the removal of heavy metals (Kaçar et al., 2002), but no study has been conducted on its use for the removal of chlorophenols from aqueous solutions. Therefore, the aim of this study was to evaluate the biosorption of 2,4-dichlorophenol (2,4-DCP) by *P. chrysosporium* biomass immobilized in various polymer matrices. 2,4-DCP is a typical chemical pollutant and is widely present in various industrial wastewaters. The effects of adsorption time and initial 2,4-DCP concentration on the adsorption capacity were studied in a batch system, and comparison of the adsorption capacity among blank beads, free, and immobilized fungal biomass were also performed. Biosorption equilibrium was modeled using the Langmuir and Freundlich isotherms. In addition, desorption efficiency of the biosorbent was evaluated with different solid/liquid (S/L) ratios, and the reusability of the immobilized fungal in adsorption/desorption cycles was also examined.

2. Methods

2.1. Preparation of biomass

A white-rot fungus, *P. chrysosporium*, obtained from the Institute of Microbiology, Chinese Academy of Sciences, Beijing, China, was used in this study. It was cultivated in the medium as previously described by Kirk et al. (1978). After 5-day incubation at 39 °C on an orbital shaker (150 rpm), the mycelial pellets were removed from the medium through filtration and inactivated through autoclaving (104 kPa, 121 °C) for 20 min. Then, the treated mycelial pellets were washed twice with distilled water. These treated mycelial pellets were immobilized in the subsequent step.

2.2. Immobilization methods of P. chrysosporium

2.2.1. Immobilization in Ca-alginate

Varying quantities of biomass (0.8–3%, w/v) were suspended in a 2% (w/v) Na-alginate solution and stirred. The mixture was then dropped into a 0.2 M $CaCl_2$ solution, and the drops of alginate–biomass mixture were later gelled into beads with a diameter of 4.0 ± 0.2 mm. The Ca-alginate immobilized *P. chrysosporium* beads were stored in 0.2 M $CaCl_2$ solution at 4 °C for 4 h to cure. The beads were rinsed twice with distilled water and stored at 4 °C prior to use. For blank Ca-alginate beads, similar procedures were used but without fungal biomass. Na-alginate solutions with different concentrations were also prepared to form the Ca-alginate immobilized fungal beads and blank Ca-alginate ones.

2.2.2. Immobilization in Ca-alginate–PVA

A Na-alginate–PVA mixture was prepared with different concentrations of PVA (1–6%, w/v) and a constant concentration of Na-alginate (2%). The biomass of 1.25% (w/v) was added in the mixture above and stirred. Ca-alginate–PVA immobilized fungal beads and blank beads were prepared using the same procedure for Ca-alginate immobilized fungal beads.

2.2.3. Immobilization in pectin

For biomass immobilization, 2%, 3%, and 4% (w/v) pectin solutions were prepared and the required dose of the biomass (1.25%, w/v) was mixed with the pectin solution. The mixture was then dropped into 0.2 M $CaCl_2$ solution for polymerization. The resultant beads were cured in 0.2 M $CaCl_2$ solution at 4 °C for 6 h. Blank beads were prepared with the same procedure for the immobilized biomass beads but without fungal biomass. All beads were rinsed thoroughly with distilled water and stored at 4 °C prior to use.

2.3. Biosorption studies

The biosorption of 2,4-DCP onto the blank beads, free, and immobilized fungal biomass was investigated in batch experiments. The stock solution of 2,4-DCP at 100 mg/l was prepared using distilled water, and all solutions used in tests were prepared by appropriately diluting the stock solution to a pre-determined concentration. For comparison, 0.5 g free biomass (dry weight), immobilized fungal beads containing 0.5 g biomass and blank beads were respectively mixed with 100 ml of 2,4-DCP solution with a known initial concentration at natural pH of 5.0 in a 250-ml glass Erlenmeyer flask. Flasks were agitated on a shaker at 180 rpm and 25 °C. Samples were taken from the solution at given time intervals and analyzed for 2,4-DCP concentration as described below.

For isotherm studies, the blank beads, free, and immobilized fungal biomass were respectively put into 2,4-DCP solutions with initial concentrations from 10.16 mg/l to 81.38 mg/l. All biosorption experiments were carried out at pH 5.0, which was found to be appropriate for biosorp-