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Biosorption of 2,4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: Isotherms, kinetics and thermodynamics

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Abstract

The biosorption of 2,4-dichlorophenol (2,4-DCP) from aqueous solution on non-living mycelial pellets of *Phanerochaete chrysosporium* was studied with respect to pH, initial concentration of 2,4-DCP, temperature and pellet size. The fungal biomass exhibited the highest sorption capacity of 4.09 mg/g at an initial pH of 5.0, initial 2,4-DCP concentration of 50.48 mg/l, 25 °C and a pellet size of 1.0–1.5 mm in the investigated pH 2.0–11.0, initial concentrations of 5–50 mg/l, temperature 25–50 °C, and pellet size of 1.0–2.5 mm. The Freundlich model exhibited a slightly better fit to the biosorption data of 2,4-DCP than the Langmuir model. The biosorption of 2,4-DCP to biomass followed pseudo second-order adsorption kinetics. The second-order kinetic constants decreased with increasing temperature, and the apparent activation energy of biosorption was estimated to be −16.95 kJ/mol. The thermodynamic analysis indicates that the biosorption process was exothermic and that the adsorption of 2,4-DCP on *P. chrysosporium* might be physical in nature. Both intraparticle diffusion and kinetic resistances might affect the adsorption rate and that their relative effects varied with operation temperature in the biosorption of 2,4-DCP by mycelial pellets.

Keywords: Biosorption; 2,4-Dichlorophenol; Mycelial pellets; Equilibrium isotherm; Kinetics

1. Introduction

Chlorophenols are one type of hazardous wastes mainly produced during chemical processing, such as pesticide, paint, pulp and paper production and wood preservation operations [1]. As priority pollutants for their high toxicity at low concentrations [2], they have to be treated before being discharged into the receiving body of waters. Volatilization, adsorption and biodegradation are possible mechanisms for the removal of these chlorophenolic compounds from waste streams [3]. Among these methods, adsorption is a well-established and useful technique for treating chlorophenol-containing effluents [1,4,5].

Many adsorbents have been investigated for removing chlorophenols from wastewater. Activated carbon is one of the most effective ones, as it has a porous structure and provides a good capacity for the adsorption of organic compounds due to its high surface area [5,6]. However, activated carbon has a number of disadvantages, such as relatively high cost, expensive cost and considerable loss during chemical or thermal regeneration of spent carbon. This has led many researchers to search for more cost-effective and efficient adsorbents to remove organic contaminants from water and wastewater. Fly ash [7], peat [8], bentonite [9] and polymeric adsorbents [10,11] have been tested for the adsorption of organic pollutants.

Biosorption has been used for the treatment of wastewaters rich in heavy metals for several decades [12,13]. Currently, an increasing amount of studies has moved to the application of biosorption for organic pollutant removal [14,15]. For instance, activated sludge has been used for the treatment of some industrial effluents and domestic waste. Aksu and Yener [4] evaluated the biosorption of phenol and monochlorinated phenols on the dried activated sludge. Ning et al. [16] reported the equilibrium sorption isotherms and sorption kinetics of 2,4-dichlorophenol on live and chemically inactivated anaerobic biomass. They found that the anaerobic biosorption of 2,4-DCP was mainly a

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physicochemical process. In addition to activated sludge, some fungal mycelia and bacterial biomass have also been utilized for the adsorption of chlorophenols. Daughney and Fein [17] described the biosorption of 2,4,6-trichlorophenol by *Bacillus subtilis*. Benoit et al. [18] studied the biosorption characterization of 4-chlorophenol (4-CP) and 2,4-DCP on fungal mycelia (living and non-living) of *Emericella nidulans* and *Penicillium miczynskii*. The use of non-viable pretreated *Aspergillus niger* biomass to remove phenol from an aqueous solution was investigated by Rao and Viraraghavan [19]. These results evidenced two distinct phenomena: a faster sorption step due to physicochemical interactions between the organic chemicals and mycelium cell walls, followed by a slower uptake due to an absorption into the living mycelium and a partial biodegradation [4,18,20].

In this study, *Phanerochaete chrysosporium*, one white-rot fungus, was used for biosorption of 2,4-DCP from aqueous solution. It has been reported that there is no essential difference in pentachlorophenol uptake by granular and dispersed sludge [21]. The mycelial pellets composed of numerous mycelia have a large number of micropores and microchannels [22]. Thus, for an identical particle size, the actual surface area of these microbial pellets available for biosorption may be larger than that of compact spheres with no micropores. Furthermore, compared with other forms of adsorbents, such as dispersed and powdered adsorbents, mycelial pellets are easier to collect. Therefore, mycelial pellets of *P. chrysosporium* were used as a bio-adsorbent in this study.

So far, only a limited number of studies have been focused on the kinetic models and thermodynamic studies of chlorophenols biosorption in literature [2,5]. The objectives of this study were: (1) to evaluate the influences of different experimental parameters on biosorption, such as initial pH value (2.0–11.0), sorption time (0–360 min), initial concentration of 2,4-DCP (5–50 mg/l), temperature (25–50 °C) and pellet size (1.0–2.5 mm); (2) to establish a kinetic model that best described the biosorption of 2,4-DCP by mycelial pellets of *P. chrysosporium* and (3) to calculate the thermodynamic parameters such as ΔG°, ΔH°, ΔS° and the activation energy of the biosorption of 2,4-DCP by mycelial pellets.

2. Materials and methods

2.1. Microorganism and its growth conditions

P. chrysosporium, a white-rot fungus, obtained from the Institute of Microbiology, Chinese Academy of Sciences, Beijing, China, was used in this study. *P. chrysosporium* was grown in a liquid medium containing (g/l): glucose, 10.0; KH_2PO_4, 0.2; $MgSO_4{\cdot}7H_2O$, 0.5; $CaCl_2$, 0.1; NH_4Cl, 0.12; thiamine, 0.001 and 60 ml of trace element solution (containing g/l: nitrilotriacetate, 1.5; $MnSO_4{\cdot}H_2O$, 0.5; NaCl, 1.0; $FeSO_4{\cdot}7H_2O$, 0.1; $CoCl_2{\cdot}6H_2O$, 0.1; $ZnSO_4{\cdot}7H_2O$, 0.1; $CuSO_4{\cdot}5H_2O$, 0.01; $AlK(SO_4){\cdot}12H_2O$, 0.01; H_3BO_3, 0.01; $Na_2MoO_4{\cdot}2H_2O$, 0.01) [23]. The medium pH was adjusted to 4.5 with 1.0 mol/l HCl and 1.0 mol/l NaOH. The incubation was carried out at 39 °C in an orbital shaker incubator at 150 rpm for 5 days.

2.2. Preparation of the biosorbent

After 5 days of growth, the mycelial pellets were harvested through filtering. The biomass was then washed thoroughly with distilled water to remove the growth medium adhering on its surface. In order to exclude the possibility of biodegradation of 2,4-DCP by living mycelia, the mycelial pellets used in the all adsorption experiments were inactivated at 121 °C and 104 kPa for 20 min. The biosorbent used in this study was in the form of mycelial pellets without homogenization. Therefore, the particle size was the diameter of the mycelial pellet.

2.3. Chemicals

2,4-DCP (>99% purity) was purchased from Shanghai Chemical Co., China, and was used without further purification. All other inorganic chemicals were of analytical grade and were purchased from Shanghai First Reagent Co., China. Stock solutions were prepared by dissolving 0.1 g of 2,4-DCP in 1.01 of double-distilled water. The test solutions containing 2,4-DCP were prepared by diluting 100 ± 2.5 mg/l of stock solutions of 2,4-DCP to the desired concentrations. The 2,4-DCP concentrations of prepared solutions varied between 5 and 50 mg/l in the sorption experiments. The pH value of the solution in this study (2.0–11.0) was adjusted to the required value by using NaOH or HCl solutions. All solutions were stored in the dark at 4 °C prior to use.

2.4. Batch experiments

Sorption experiments were carried out in batch mode. The biomass concentration was 5.0 ± 0.75 g/l, i.e., 0.5 g (dry weight) of mycelial pellets was mixed with 100 ml of solution containing a pre-determined concentration of 2,4-DCP in a 250-ml glass Erlenmeyer flask, and the flask was covered to protect from light. All adsorption experiments were conducted in the dark to prevent photodegradation. Flasks were agitated on a shaker at 150 rpm and a constant temperature (25 ± 1 to 50 ± 1 °C). Samples were taken at given time intervals (5, 10, 20, 30, 45, 60, 90, 120, 180, 240, 300, 360 min), and were then centrifuged at 10000 rpm for 5 min. The supernatant was used for analysis of the residual 2,4-DCP.

Two control experiments, i.e., a flask containing 2,4-DCP but no biomass, and another containing biomass but no 2,4-DCP, were also run in parallel. It was observed that both adsorption of 2,4-DCP on the flask walls and release of 2,4-DCP from biomass could be negligible.

2.5. Analysis

The concentration of residual 2,4-DCP in the biosorption medium was determined by using a UV–vis spectrophotometer (UV752-GD, Shanghai Analytical Instrument Co.) at 306 nm. Previous experimental results show that the aqueous solution of 2,4-DCP in basic pH had a stronger absorbance at 306 nm than that in natural pH, and that the basification could eliminate the interference on analysis. Therefore, the sample was basi-