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Polyvinyl alcohol-immobilized *Phanerochaete chrysosporium* and its application in the bioremediation of composite-polluted wastewater

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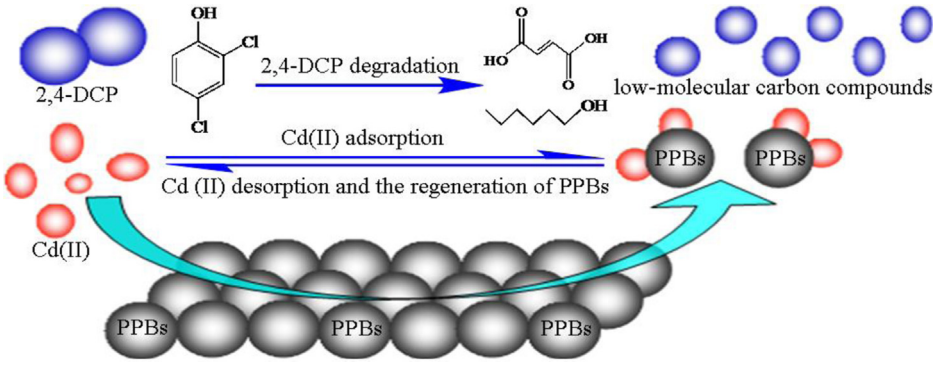
HIGHLIGHTS

- PVA-immobilized *P. chrysosporium* beads (PPBs) were fit for wastewater treatment.
- Removal rates of Cd(II) and 2,4-DCP at optimum conditions were up to 78% and 95.4%.
- 2,4-DCP removal rates were beyond 90% with varying initial 2,4-DCP concentrations.
- PVA was vital to Cd(II) removal besides the function groups in *P. chrysosporium*.
- Maximum recovery of the Cd(II)-laden PPBs after reuse three times was 98.9%.

GRAPHICAL ABSTRACT

Schematic diagram of polyvinyl alcohol-immobilized *Phanerochaete chrysosporium* beads (PPBs) for Cd(II) removal and 2,4-DCP degradation.



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ABSTRACT

A novel biosorbent, polyvinyl alcohol (PVA)-immobilized *Phanerochaete chrysosporium*, was applied to the bioremediation of composite-polluted wastewater, containing both cadmium and 2,4-dichlorophenol (2,4-DCP). The optimum removal efficiency achieved was 78% for Cd(II) and 95.4% for 2,4-DCP at initial concentrations of 20 mg/L Cd(II) and 40 mg/L 2,4-DCP. PPBs had significantly enhanced the resistance of *P. chrysosporium* to 2,4-DCP, leading to the degradation rates of 2,4-DCP beyond 90% with varying initial 2,4-DCP concentrations. This research demonstrated that 2,4-DCP and secreted proteins might be used as carbon and nitrogen sources by PVA-immobilized *P. chrysosporium* beads (PPBs) for Cd(II) removal. Fourier transform infrared spectroscopy analysis showed that hydroxyl and carboxyl groups on the surface of PPBs were dominant in Cd(II) binding. The mechanism underlying the degradation of 2,4-DCP into fumaric acid and 1-hexanol was investigated. The adsorption–desorption studies indicated that PPBs kept up to 98.9% of desorption efficiency over three cycles.

1. Introduction

Population growth, rapid industrialization, and urbanization have contributed to contamination of water with metal and organic pollutants. Contamination of water with a combination of heavy

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metal and organic pollutants has received increasing attention with rapid industrial development in recent years. Contamination by cadmium (Cd) is a major public concern due to its high toxicity to aquatic organisms and humans [1,2]. Trace amounts of Cd(II) in the environment could cause severe damage to the biological organization, from the molecular level to the community level [3]. According to U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO), the permissible limit of cadmium in drinking water is 0.005 mg/L. 2,4-Dichlorophenol (2,4-DCP), widely used as a fungicide, pesticide, and wood preservative, can provoke disturbances in the structure of cellular bilayer phospholipids, causing strongly carcinogenic and mutagenic effects on organisms [4]. Listed as a priority pollutant by EPA, the limit for 2,4-DCP content has been set at 0.093 mg/L by the Grade I–III National Surface Water Environmental Quality Standard.

Biosorption is an efficient, cost-effective, flexible, and environmentally friendly technique [5] that has attracted more attention owing to its application in the treatment of wastewater containing composite pollutants of heavy metal and organic compounds. *Phanerochaete chrysosporium* (*P. chrysosporium*), the model strain of white rot fungi, is well known for its unique xenobiotics degradation and heavy metal removal with admirable biosorption capacity [6–10]. However, the application of *P. chrysosporium* is limited in wastewater treatment processes owing to its poor mechanical strength, low resistance, and long degradation time [11].

Some of the advantages of immobilized whole cells over freely suspended cells include increased mechanical strength, efficient biosorbent regeneration, easier solid–liquid separation, and higher bacterial cell density [5,8,12]. The immobilized biomass can also be shielded from unfavorable environmental conditions, including high pollutant concentrations and predators [13]. PVA is preferred over other polymers for cell immobilization owing to its lower cost, higher mechanical strength, durability, non-toxicity, good biocompatibility, and biodegradable properties [14–16]. Moreover, PVA beads demonstrate high stability within a pH range of 1.0–13.0 [17]. PVA-immobilized cells have been proven to be efficient in the biodegradation of hazardous contaminants, including aromatic compounds [15,18], phenolic compounds [19–21], and crystal violet [22], as well as in the uptake of heavy metals by immobilized fungal biomass [23,24].

The objective of this study was to immobilize *P. chrysosporium* using PVA as the support material. Sodium alginate, zeolite powder, silicon dioxide, activated carbon, and Tween 80 were also used as additives to improve the mechanical properties of the crosslinking immobilized carrier. Using NaH_2PO_4 solution as a crosslinking agent, Cd(II) removal and 2,4-DCP degradation by PVA-immobilized *P. chrysosporium* beads (PPBs) were studied. The effects of biomass dosage, and initial concentrations on adsorption and degradation capacities in a batch system were investigated. The pH of solutions and the content of extracellular proteins of *P. chrysosporium* were also analyzed. The removal pathways and mechanisms of PPBs were explored by using scanning electron microscopy (SEM) equipped with the energy dispersive X-ray analysis (EDAX), Fourier transform infrared spectroscopy (FTIR), and gas chromatography–mass spectrometry (GC–MS). The current study demonstrated that PPBs had great removal efficiency and practical applicability in wastewater treatment with co-pollutants (Cd(II) and 2,4-DCP).

2. Materials and methods

2.1. Materials

P. chrysosporium (BKMF-1767) was maintained by subculturing on potato dextrose agar (PDA) slants at 4 °C, and then introduced into PDA plates for 7 days at 37 °C. Spore suspensions were obtained by dissolving the spores into sterile distilled water, and then adjusted to a concentration of 2.0×10^6 CFU/mL using a turbidimeter (WGZ-200, Shanghai, China).

2,4-DCP was procured from Tianjin Guangfu Fine Chemical Research Institute. All other reagents used were of analytical grade and were purchased from Shanghai First Reagent Co., China. 1.0 g/L Cd(II) was prepared as the experimental stock solution by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ in ultrapure water (18.25 MΩ/cm). 500 mg/L of 2,4-DCP stock solution was prepared and stored at 4 °C. Different concentrations of Cd(II) and 2,4-DCP were prepared by diluting the stock solutions.

2.2. Preparation of the gel solution and the crosslinking agent

The gel solution was prepared by dissolving PVA (10%, w/v), Na–alginate (1%, w/v), silicon dioxide (2%, w/v) and zeolite powder (1%, w/v) into 0.9% NaCl solution in a reactor, which was immersed in a 80 °C water bath with slowly stirring. 1.0 M NaH_2PO_4 solution, as the crosslinking agent, was obtained by dissolving NaH_2PO_4 into saturated boric acid solution. The gel solution and the crosslinking agent were sterilized by autoclave at 111 °C for 30 min and then cooled to approximately 45 °C before using.

2.3. Preparation of PPBs

P. chrysosporium spore suspension of 20% (w/v) firstly mixed evenly with activated carbon (3%, w/v). Then, the spore suspension and sterile Tween 80 (1%) were added to the gel solution and mixed well. The mixture was trickled into a gently stirred 1.0 M NaH_2PO_4 solution using 5 mL syringe and cured for 2 h to form stable microspheres. After that, the prepared microspheres were rinsed and immersed in 0.9% NaCl solution for 12–24 h under sterile condition, and then transferred into the culture medium and incubated in an incubator (ZHWY, Shanghai, China) at 37 °C and 150 rpm. After 3 days of incubation, all samples (PPBs) were harvested for the succeeding experiments.

The pH of solutions was adjusted to 6.5 according to previous study with 0.1 M HNO_3 or NaOH at the beginning of experiments. All experiments were carried out in 500 mL conical flasks containing 200 mL aqueous solution at 37 °C with 150 rpm.

2.4. Effect of biomass dosage

The various dosages of PPBs (0.9, 2.5, 4.1, 8.0, 11.9, and 15.8 g/L) and 4.1 g/L of PVA beads without *P. chrysosporium* were added to the solutions with 20 mg/L Cd(II) and 40 mg/L 2,4-DCP to determine their influence on the adsorption and degradation performance.

2.5. Effect of initial Cd(II) concentration

In order to determine the effect of initial Cd(II) concentration on Cd(II) removal and 2,4-DCP degradation, a series of Cd(II) solutions (0, 5, 10, 20, 40, 80, 120, 160, and 200 mg/L) were prepared and the initial 2,4-DCP concentration in each of the flask was maintained at 40 mg/L.

2.6. Effect of initial 2,4-DCP concentration

Various concentrations of 2,4-DCP and an initial Cd(II) concentration of 20 mg/L were prepared. The initial 2,4-DCP concentration was adjusted to 0, 5, 10, 20, 80, 100, 120, and 160 mg/L to investigate the optimum initial 2,4-DCP concentration and the effect of initial 2,4-DCP concentration on the removal of Cd(II) and 2,4-DCP.