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Biosorption of phenol and 2-chlorophenol by *Funalia trogii* pellets

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ABSTRACT

The removal of phenol (Ph) and 2-chlorophenol (2-CPh) from aqueous solution by native and heat inactivated fungus *Funalia trogii* pellets were investigated. The effects of contact time, solid/liquid ratio, optimum pH and temperature on the phenols removal capacity by the pellets were established. The removal efficiency of phenols increased significantly with increasing biomass dose. The optimum pH was detected to be 8.0. The second-order equations are described and evaluated on the basis of a comparative estimation of the corresponding coefficients. The phenol removal equilibrium isotherm was modeled by the Langmuir equations. The enthalpy change values were obtained between −7.62 and −10.64 kJ/mol. This indicated that the uptake of phenols either on native or heat inactivated fungal pellets was based on a physical adsorption process.

1. Introduction

Phenols are widely distributed as environmental pollutants. Treatment of industrial wastewaters contaminated with phenolic compounds is a daunting problem. They exist in different concentrations in wastewaters disposed from many industrial processes, including petrochemical industry, coking, synthetic rubber, plastics, paper, oil refineries, as well as phenolic resin industries (Bayramoglu and Arica, 2008; Tepe and Dursun, 2008). Wastewater containing phenolic compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and long term ecological damage. Due to the high toxicity of phenols, they are strictly regulated, and their industrial use is increasingly avoided by substituting them with harmless compounds. The Environmental Protection Agency (EPA) calls for lowering phenol content in the wastewater to less than 1 mg/ml (Hallenbeck and Cunningham, 1986). Wastewaters containing phenols and other toxic compounds need careful treatment before discharge into the receiving large bodies of water reservoirs. Biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods are the most widely used methods for removing phenol and phenolic compounds from wastewaters (Ra et al., 2008). Problems such as high cost, low efficiency, and generation of toxic by-products are limiting factors for wide applications of some of these remediation strategies.

Among various physicochemical processes adsorption technology is extensively studied in recent years (Li et al., 2004). However, due to economic restraints, there is a growing interest in the preparation and use of low cost and unconventional adsorbents (Wu and Yu, 2007; Akar et al., 2008). The use of microorganisms such as algae, bacteria and fungi with the special surface properties for the biosorption of metallic and organic pollutants from contaminated solutions has long been studied on the laboratory scale and in field studies (Bayramoglu and Arica, 2009; Arica and Bayramoglu, 2005; Navarro et al., 2008). For example, phenol, 2-chlorophenol, and 4-chlorophenol have been effectively removed using a brown algae *Sargassum muticum*. 2,4-Dichlorophenol has been biosorbed from aqueous solutions by non-living fungal pellets of *Phanerochaete chrysosporium* (Aranda et al., 2006; Sampedro et al., 2007), and bacterial strains such as *Achromobacter* sp. and *Escherichia coli* (Quan et al., 2004).

The present study is designed to examine effective and low cost phenol and 2-chlorophenol removal by native or heat inactivated *Funalia trogii* pellets. The selected organism offers several advantages over already studied counterparts. While it forms a substantially high biomass for removal of toxic heavy chemicals from aqueous solutions, it also readily grows on cheap carbon sources (i.e., cellulose) and possesses several extra-cellular enzymes for bioremediation of various xenobiotics. In order to evaluate removal mechanism and kinetics, the effects of the removal parameters such as: (i) pH, (ii) temperature, (iii) equilibrium time and (iv) effect of phenolic compound concentrations on the removal efficiency were investigated.

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2. Methods

2.1. Microorganism and media

Pure culture of *F. trogii* (MAFF 430012) was obtained from MAFF GENE BANK Culture Collection (Kannondai, Tsukuba, Ibaraki, Japan), and was maintained by subculturing on malt dextrose agar slants. The growth medium and growth conditions for white rot fungi were previously described elsewhere (Arica et al., 2004). The cultivated fungus pellets of *F. trogii* were washed with sterile physiological saline solution several times to remove debris and undesirable particles. In some experiments pellets were heat inactivated (at 90 °C for 15 min) and used as such in phenol removal assays.

2.2. Phenolic solutions

Phenol and 2-chlorophenol were obtained from Sigma and used without further purification. A stock solution was prepared by dissolving 1.0 g of Ph and 2-CPh in 1.0 l of purified water. The concentrations of phenolic compounds for experiments were adjusted between 30 and 600 mg/l. The pH of several test solutions was set to range between 2.0 to 11.0 at the start of each experiment.

2.3. Degradation of phenol and 2-chlorophenol

F. trogii was grown in a medium containing (g/l) glucose, 10.0; KH_2PO_4, 2.0; $MgSO_4 \cdot 7H_2O$, 0.5; $CaCl_2$, 0.1; NH_4Cl, 0.12 and thiamine, 0.001 cultured on an orbital shaker at 100 rpm at pH 5.0 and at 30 °C for 6 days. After this period, the biomass was collected and rinsed and fungal mycelia (about 2 g on dry basis) were transferred into 250 ml flask containing fresh culture medium (100 ml) as described above that was supplemented with phenol and/or 2-chlorophenol (500 mg/l) instead of glucose. A 0.5 ml sample was removed and then 1.0 ml hexane was added to extract the remaining phenols in the culture medium. The phenolic compound concentration was determined by HPLC using these aliquots.

2.4. Analysis and biosorption studies

The biosorption of phenols onto the native and heat inactivated fungal pellet was investigated in a water jacketed batch reactor (inner volume: 150 ml). The reactor temperature was controlled with a thermo-circulator. Preliminary experiments demonstrated that when the biomass was incubated at 30 °C at 100 rpm for 24 h the adsorption had reached equilibrium.

The concentration of the phenolic compounds in the aqueous phase was measured by high performance liquid chromatography, HPLC (Dionex Co., Germering, Germany). The chromatographic determination of phenols was achieved on a Supelco C-8, HPLC column (150 mm × 4.6 mm i.d.; 5 μm) protected by a guard column (Supelco C-8; 20 mm × 4.0 mm i.d.). All sample solutions used in chromatographic studies were pre-filtered by a 0.2 μm membrane filter (Millipore). HPLC mobile phases A and B were prepared by adding acetic acid (0.1%) to methanol and acetic acid (0.1%) to Milli Q water, respectively. The mobile phases were filtered prior to use. The chromatographic determination was performed using a gradient at 1.5 ml/min flow-rate (in 0–20 min; phase A from 35% to 100% and phase B from 65% to 0% and return to phase A and B 35% and 65% in 5 min, respectively) and the sample injection volume of the auto sampler was 20 μl. The UV-visible detector was set at 270 and 274 nm for phenol and 2-chlorophenol and the temperature was maintained at 30 °C. Dionex CHROMELLEON® software was used and operated under Windows for data acquisition and integration.

Biosorption of phenols (i.e., phenol and 2-chlorophenol) from aqueous solutions onto native or heat inactivated fungal pellets were investigated in batch system and the amount of removed phenols was calculated as the difference between initial and final phenol concentrations.

To examine the effect of solid/liquid ratio (w/v) various amount of biosorbents on dry basis (between 0.25 and 2.0 g/l) was used in a 100 ml phenol containing solutions (concentration was adjusted to 200 mg/l phenol). The effects of pH and temperature on the removal performance of the fungal pellets were examined at pH value between 2.0 and 11.0 (by the addition of dilute HCl or NaOH solutions). Four different temperatures were selected for the study (15, 25, 35 and 45 °C). During adsorption assays, 6 h of incubation was found to be optimum. The effect of the initial phenol concentrations on biosorption was studied as noted above except that the concentration of phenols in the sorption medium varied between 30 and 600 mg/l.

The amount of biosorbed phenols per unit fungal biomass (mg phenols/g dry biomass) was obtained by using the following expression:

$$q = [(C_o - C) \cdot V]/m \quad (1)$$

where q is the amount of phenols biosorbed onto the unit amount of the biomass (mg/g); C_o and C are the concentrations of the phenols in the initial solution (mg/l) and after biosorption, respectively; V is the volume of the aqueous phase (l) and m is the amount of the biomass (g). The average of three repeat experiments is presented in the results.

2.5. Determination of desorption efficiency

In order to determine the desorption efficiency of the fungal preparation biomass, consecutive adsorption–desorption cycles were repeated three times by using the same biosorbent. Desorption was achieved by using methanol solution (25%; v/v). Phenol and 2-cholorophenol loaded *F. trogii* biomasses were placed in this desorption medium and stirred at 200 rpm for 2 h at room temperature. After eluting, the biomass was regenerated by washing with water. The final concentration in the aqueous phase was determined by using a HPLC as described before.

2.6. Evaluation of equilibrium biosorption isotherms

The Langmuir and Redlich–Peterson equations were used to define adsorption isotherms. The Langmuir equation is represented by the following expression:

$$q_e = q_m b C_e / 1 + b C_e \quad (2)$$

where C_e and show the residual phenols concentration (mg/l) and q_e the amount of phenolic compounds sorbed on the biosorbent at equilibrium (mg/g), b is the energy of sorption or sorption equilibrium constant (l/mg) of the system, and q_m is the maximum adsorption capacity. The equilibrium parameter, RL, is used to predict if an adsorption system is "favorable" or "unfavorable". It is obtained by the following relationship:

$$RL = 1/1 + bC_o \quad (3)$$

where C_o is the initial phenols concentration. The value of RL indicates the shape of isotherm to be either (i) unfavorable ($RL > 1$), (ii) linear ($RL = 1$), (iii) favorable ($0 < RL < 1$), and (iv) irreversible ($RL = 0$). The Freundlich equation is:

$$q_e = K_F (C_e)^{1/n} \quad (4)$$

where K_F and n are the Freundlich constants, and they are the indicators of the "adsorption capacity" and "adsorption intensity", respectively.