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Study of pentachlorophenol biosorption by phanerochaete *Chrysosporium* Biomass: Kinetics and adsorption isotherms modeling

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ABSTRACT

Pentachlorophenol (PCP) is the organic compound that has been widely used in different industries. The Pollution of water by organic pollutants such as PCP is a worldwide environmental problem due to their persistence and toxicity. In this study, nonviable *Phanerochaete chrysosporium* fungus biomass was applied for PCP biosorption from aqueous solution. In order to adsorb PCP, the modified *Phanerochaete Chrysosporium* biomass with NaOH was used. The influence of various experimental parameters such as initial PCP concentration, solution pH and contact time on the biosorption efficiency was investigated. Kinetic studies were conducted at pH 5, 250 ml of different concentrations of PCP solution, 0.5 g of biomass and various contact time. The equilibrium time was found to be 2 h for fungus biomass to complete saturation. The correlation of pH and initial concentration in PCP biosorption was quite significant ($P_{value} < 0.01$). Kinetic studies represented the adsorption process followed by pseudo second-order kinetic model. The maximum monolayer adsorption capacity of *P. chrysosporium* fungus for PCP was found to be 12.13 mg/g according to Langmuir isotherm. Maximum adsorption was obtained at pH of 3. According to the obtained results, *P. chrysosporium* fungus appears to be an efficient biosorbent in PCP removal from aqueous solution in low pH conditions.

Keywords: Biosorption; Pentachlorophenol; *Phanerochaete Chrysosporium*; Biomass

INTRODUCTION

Pentachlorophenol (PCP) is a synthetic material, and does not occur naturally in the environment. Pentachlorophenol has been used in pesticides, herbicides, fungicide, molluscicide, algaecide and wood preservatives [1]. This widespread application could lead to PCP release into the environment especially water resources [2]. The liver, reproductive system, immune system, and the developing organism are the primary targets of PCP toxicity. In addition, exposure to PCP is also related to carcinogenic, renal, and neurological effects [3, 4]. The United States Environmental Protection Agency (US-EPA) set maximum contaminant levels for PCP in drinking water (1µg/L) [5]. Maximum discharge level of 1 mg/L is permitted for PCP-Na industries. However, at concentrations less than 0.1 mg/L, this compound will be toxic for plants, animals and human beings. Owing to its adverse effects, PCP must be removed from wastewaters before being released into the environment [6].

In recent years, several methods have been studied to remove PCP from industrial wastewaters. Nowadays, biosorption has been taken into huge consideration as an effective and ongoing process in water and wastewater purification due to its high efficiency in removing contaminants from water solution [7]. Fungal biomass can

eliminate considerable quantities of organic pollutants from aqueous solutions by adsorption [8, 9]. Earlier studies have reported that the dead fungal biomass has better removal efficiency than that of live biomass for biosorption of refractory compounds [10-12]. Until now, only a few studies have focused on kinetic and isotherms models and PCP biosorption studies. *Phanerochaete chrysosporium* (*P.chrysosporium*) is the model of white-rot fungus. In this study, modified *P.chrysosporium* fungus biomass, as a natural adsorbents was used in PCP biosorption from aqueous solution. The main objectives of the present study were: (1) to evaluate the effect of different experimental parameters on biosorption, such as pH, time and initial concentration of PCP; (2) to establish the isotherm and kinetic models that best described the biosorption of PCP by *P. chrysosporium* biomass.

MATERIALS AND METHODS

Biomass preparation

The strain *P. chrysosporium* (PTCC 5270) was purchased from the Persian Type Culture Collection of Iranian Research Organization for Science and Technology. *P. chrysosporium* was inoculated into a Sabouraud's broth medium in distilled deionized water. A volume of 100 ml of the medium was transferred to 250 ml conical flask. The flask were placed on a rotary shaker with a speed of 120 rpm. *P. chrysosporium* was thus cultured aerobically. *P. chrysosporium* grew as pellicles and its biomass was harvested after five days of growth by filtering through a 150 μm sieve and successive washing with tap water. In order to make the fungus nonviable, the biomass was autoclaved for 30 min at 121°C and 124 kPa (18 psi). The autoclaved biomass was washed again and dried in an oven (60°C) and then turned into a powder. The powdery biomass was boiled in 0.5 M NaOH solution for 15 min and after biomass chemical conditioning, the resulting mixture was filtered through a cotton filter cloth and washed [13]. The modified biomass was dried in an oven at 50–60 °C and was kept for further studies.

Adsorption experiments

The working solutions of PCP were prepared from stock solutions by appropriate dilutions. Sodium and potassium phosphates were used for PCP working solutions preparation. So, a constant pH could be maintained during biosorption experiments. If necessary, the 0.1 M NaOH and HNO₃ were used for pH adjustments. The PCP crystals (99% purity, Aldrich Chemicals) were used to prepare the stock solutions of 1000 mg/l PCP in NaOH (0.1 M). In order to determine the equilibrium time (21 ± 2 °C), 0.5 g of the biomass powder was added to 100 ml of the PCP solution in 250 ml conical flasks (concentration of 25 mg/l ,pH=5, time=6 h). All experiments were performed in duplicate and the mean values were used for data analysis. In this study, the effect of pH (3, 4, 5, 6, 7 and 8) and PCP concentration (10, 15, 20, 25, 30, 35 and 40 mg/L) on the biosorption efficiency were investigated. All experiments were conducted by shaking 100 ml PCP solution, separately, with 0.5 g NaOH conditioned *P. chrysosporium* biomass. After 2 h, the samples were filtered using cellulose acetate filters. Control samples were used to check the volatilization and adsorption of PCP to the glass walls of the conical flasks.

Isotherms and Kinetic studies

Kinetic studies were conducted at an optimum pH of 5 with 250 ml of 15, 25 and 35 mg/L PCP solution and 0.5 g biomass. The samples were collected at the following intervals: 5, 10, 15, 30, 45, 60, 90 and 120 min. Isotherm studies were conducted at pH of 5 with 100 ml of PCP solution of varying concentrations of 10, 15, 20, 25, 30, 35 and 40 mg/L, in the increments of 0.5 g conditioned biomass. In isotherm studies, traditionally, mass of the adsorbent is varied while keeping a constant solute concentration. But, when the adsorbent has a relatively high affinity for the solute, and the initial solute concentration is relatively low (as in this case), varying the concentration of the solute while keeping a constant adsorbent dose is accepted [14].

Analytical method

The PCP of samples was determined by reverse phase of HPLC (KNAUER, Company, Berlin Germany model Smartline Autosampler 3950 HPLC, A5005-1) with C18 column. The mobile phase was acetonitrile and distilled water (0.01 M, pH 6) in the ratio of 60:40 v/v and the detection was done with UV detector at 254 nm [15]. The utilization percentage of PCP was determined by measuring the peak area of pentachlorophenol (PCP) and its metabolite. PCP concentrations were measured by a calibration curve with a correlation coefficient of 0.998.

RESULTS

The effect of contact time

The pentachlorophenol uptake by *P. Chrysosporium* biomass at different contact times has been shown in Fig. 1. The amount of adsorbed PCP (mg/g) increased with increasing contact time and remained nearly constant after the equilibrium time.

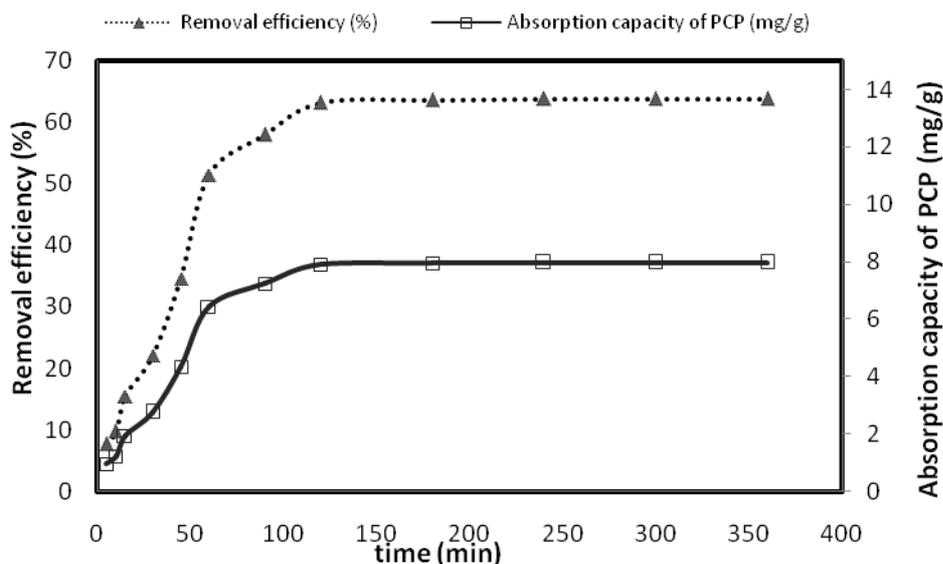


Fig 1. the variations of PCP concentration and Absorption capacity over time (pH=5 , amount of 0.5 g biomass in 250 ml, concentration of 25 mg / l PCP)

The effects of pH

The effect of pH on PCP biosorption is shown in Fig. 2. The biosorption of PCP by *P. Chrysosporium* biomass was significantly influenced by pH in the range 3.0–8.0 ($p < 0.001$). The results of the pH studies showed that the removal percent decreased with increasing pH (74.63% for pH=3 VS 49.81% for pH=8).

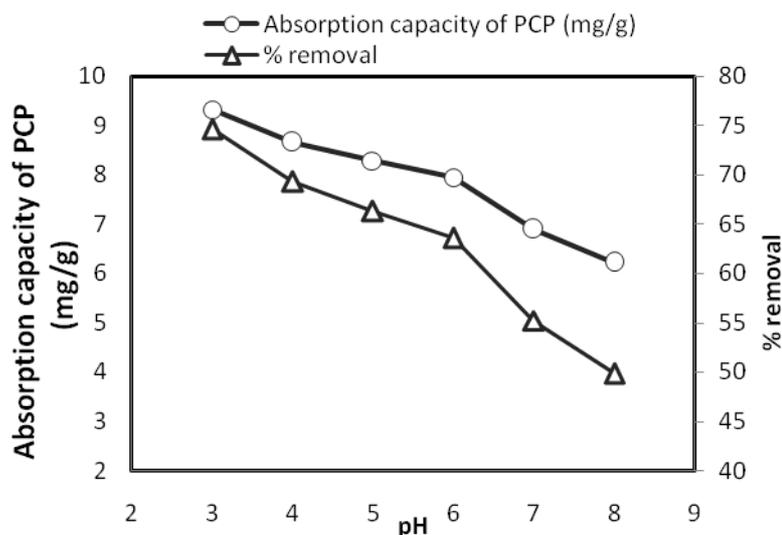


Fig 2. Removal percentage and the adsorption capacity of PCP at various pH rates by *Phanerochaete Chrysosporium* biomass. (Initial PCP Concentration=25 mg/l; Contact Time= 2 h.)

The effects of initial PCP concentration

As shown in Fig. 3, the adsorption capacity increased with the increasing initial PCP concentration from 3.71 to 9.47 mg/l, while the PCP adsorption efficiency showed an opposite trend.

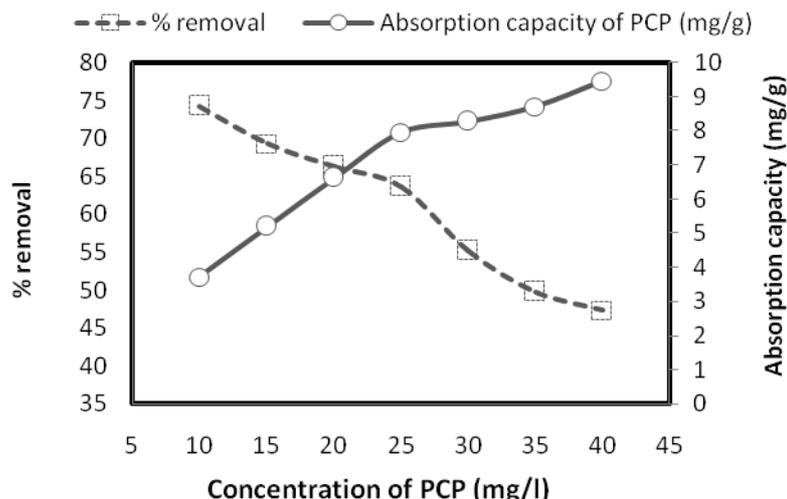


Fig 3. The removal percentage and absorption capacity at various initial PCP concentrations by *Phanerochaete Chrysosporium* biomass.(pH= 5; contact time = 2 h. amount of biomass 0.5 g in 250 ml)

Isotherm studies

Isotherm models equations used are presented in Table 1. The Langmuir isotherm model was selected for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the *P. Chrysosporium* biomass [16]. Where, q_e , introduces the amount of PCP adsorbed per unit mass of biomass (mg/g) and C_e , q_m , and b refer to the equilibrium concentration (mg/L), monolayer adsorption capacity (mg/g) and surface energy (L/g), respectively.

Table 1. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin constants for biosorption of PCP on *Phanerochaete Chrysosporium* biomass

Isotherm models	Model parameters	R ²
Langmuir $\frac{1}{q_e} = \frac{1}{q_m b} \left(\frac{1}{C_e} \right) + \frac{1}{q_m}$	$b=0.17$ $q_m(\text{mg/g})=12.13$	$R^2=0.992$
Freundlich $\log q_e = \log k + \frac{1}{n} \log C_e$	$k_f=9.8$ $n=2.32$	$R^2=0.943$

The Freundlich isotherm was studied to understand the possibility of multi-layer adsorption and non-linear energy distribution for the adsorption sites of the *P. Chrysosporium* biomass. The values of Freundlich constants are shown in the Table 1, where k_f and n are the values of adsorption capacity and intensity of adsorption. q_e is the amount of PCP adsorbed per unit mass of biomass [17].

Kinetic studies

To evaluate the biosorption kinetics of PCP, two kinetic models (the pseudo-first-order and pseudo-second-order models) were used to fit the experimental data at different initial concentrations. Fig. 4 and Table 2 show that PCP adsorption has increased with increasing sorption time. The results show that the second-order rate constant $k_{2,ad}$ decreased with the increase of initial PCP concentration.

The pseudo first-order rate expression of Lagergren model [19] is expressed as follows (1):

$$\log(q_{eq} - q) = \log q_{eq} - k_{1,ad} \frac{t}{2.303} \quad (1)$$

The plots of $\log (q_{eq}-q)$ as a function of sorption time are shown in Fig. 4. The rate constants $k_{1,ad}$ and theoretical values of q_{eq} calculated from the slope and intercept of the linear plots are summarized in Table 2 along with the corresponding correlation coefficients.

The pseudo second -order rate expression is expressed as follows (2):

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{t}{q_{eq}} \quad (2)$$

It should be noticed that for the utilization of this model, the experimental value of q_{eq} is not necessary to be pre-estimated. The second-order rate constants $k_{2,ad}$ and q_{eq} values presented in Table 2 were determined from the slopes and intercepts of the plots.

Table 2. Kinetic parameters of the pseudo-first-order and pseudo-second-order equations for PCP sorption on the *Phanerochaete Chrysosporium* biomass

C_0 (mg/l)	Lagergren-first order kinetic model			Pseudo-second order kinetic model			$q_{eq,exp}$ (mg/g)
	$K_{1,ad}$ (min ⁻¹)	$q_{eq,cal}$ (mg/g)	R^2	$K_{2,ad}$ (g/(mg min))	$q_{eq,cal}$ (mg/g)	R^2	
15	0.028	4.02	0.9255	0.02	5.67	0.9974	5.19
25	0.023	5.78	0.9306	0.016	8.51	0.9996	7.95
35	0.02	6.36	0.8858	0.014	9.34	0.9997	8.72

q_e : sorption amount at equilibrium, mg/g; $K_{1,ad}$: the rate constant of pseudo-first-order adsorption, min⁻¹; $K_{2,ad}$: the rate constant of pseudo-second-order adsorption, g/(mg min);

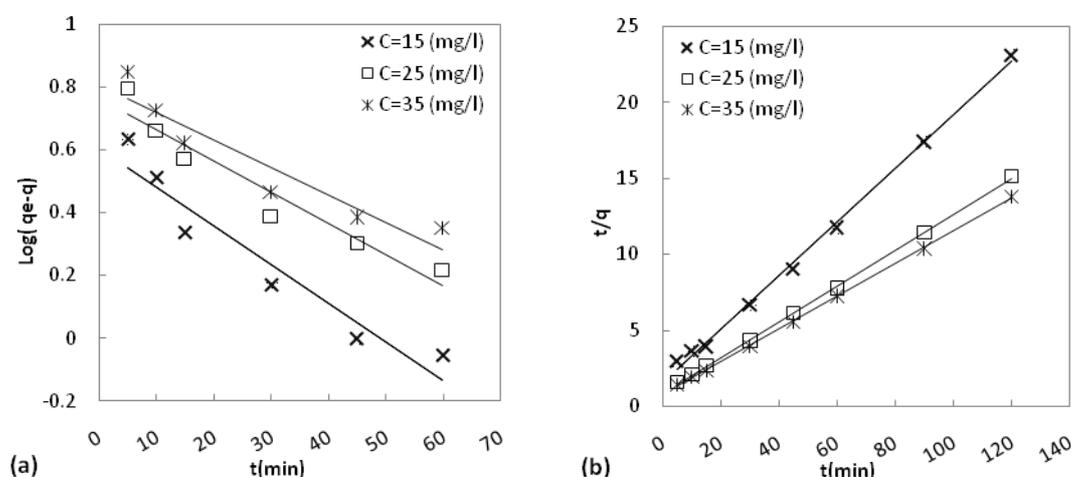


Fig 4. Linearized by pseudo-first order (a) and pseudo second-order (b) kinetic model for PCP sorption by *Phanerochaete Chrysosporium* biomass at different initial concentration .(pH of 5.0, biomass concentration: 0.5 g in 250 ml and agitation: 150 rpm)

DISCUSSION

The effect of adsorption parameters

The amount of PCP adsorbed (mg/g) increased with the increase of contact time and remained nearly constant after the equilibrium time. The uptake of PCP could be divided into two phases. The first phase was rapid corresponding to the uptake in the first 60 min after which the uptake increased slowly in the second phase and reached equilibrium after 120 min. Further increase in contact time did not enhance the biosorption, so the optimum contact time was selected as 2 h for further experiments. At this point, PCP removal reached the maximum value of 7.9 mg/g, while the removal efficiency was 63.2%. Similar results have been reported by other researchers. The rapid adsorption feature was in agreement with the results of Denizli et al.[20], and Viraraghavan et al [10], in which the time required for equilibrium was 3 and 2 h, respectively.

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. The results of the pH studies (Fig. 2.) showed that, the percent removal of PCP decreased with increase in pH (74.63% for pH=3 VS 49.81% for pH=8). These results were in accordance with those reported by Rao and Viraraghavan [13]. The pH not only influences the properties of a sorbent surface, but also affects adsorbate speciation in the solution. PCP, the strongest acid of the phenol family has a pKa value of 4.75. At acidic pH, PCP exists in the undissociated form, whereas at alkaline pH, over of PCP exists in the anionic form. Between these pH values, a combination of both forms is present [21]. The molecular and ionic species of chlorophenols are hydrophobic, but the negative form is less so, and as a result, sorption is generally observed to decrease where pH is more than pKa. Therefore, beyond the pH value of 5 (pKa of PCP = 4.75), PCP removal decreased drastically. The surface charge on fungal biomass is predominantly negative at pH of 3.0–10.0 [13]. Pentachlorophenol at neutral and alkaline pH range is generally in the form of electrostatic repulsion between the anions which are a negatively charged biomass surface and anionic PCP may lead to less absorption. Thus, a reduction in pH may remove electrostatic barriers between the biomass and PCP, and facilitate biosorption. Also at low pH, the biomass was surrounded by

hydronium ions which can increase the absorption pentachlorophenol [22]. Viraraghavan and et al [23] reported that the removal of PCP was dependent on the pH and decrease in PCP removal for an increase in pH solution. The pH of 5 was selected as an operating pH because at this pH, PCP was represented by the combination of both molecular and anionic species.

The initial concentration provides an important driving force to overcome all mass transfer resistances of adsorbate in the aqueous solid phase and therefore increases the rate at which adsorbate molecules pass from the bulk solution to the adsorbent surface [24]. As shown in Fig. 3, increase in the sorption capacity of *P. Chrysosporium* biomass with an increase in the initial PCP concentration might be due to the higher probability of collision between the PCP molecules and biosorbent.

The various adsorbents such as granular sludge, fly ash, activated carbon, pine bark, nylon fiber and fungal mycelia in earlier studies were used to remove PCP [9-11, 25, 26]. Generally, their sorption capacities for the adsorbate were less than 10 mg/g, however, Quintelas et al. reported up to 10 mg/g adsorption capacity for chlorophenol by a bacterial biofilm supported on granular activated carbon [27]. Also, Deng et al. (2011) reported that the sorption capacity had reached 270 mg/g for 2,4-dichlorophenoxyacetic acid by aminated biosorbent [28].

Isotherm studies

The Langmuir isotherm model was used for the estimation of maximum adsorption capacity on the *P. Chrysosporium* biomass. Maximum adsorption capacity (q_m) of 12.13 was obtained for fungal biomass that is corresponding to complete monolayer. The Langmuir biosorption constant related to the free energy of sorption was 0.17 (1/g). Experimental data were fitted well with the Langmuir model with a correlation coefficient of 0.99. The adsorption capacity of PCP by various adsorbent has been reported in other studies [25, 2]. A relatively low to moderate 'b'-value represents low surface energy and probable stronger bonding between PCP and biomass [18].

The Freundlich isotherm model was studied for describing the sorption of PCP based on multilayer adsorption and nonlinear energy distribution. The Freundlich constants K_f and n from Table 2 were found to be 9.8 and 2.32, respectively. The magnitudes of K_f and n show easy separation of PCP from the aqueous solution and indicate favourable adsorption. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model [17].

Kinetic studies

Predicting the sorption rate in the adsorption process is one of the important factors design as the sorption kinetics control the retention time and the reactor dimensions. The sorption rate constants are important physicochemical parameters for evaluating the quality of adsorbents [12,30,31]. To investigate the adsorption mechanism and rate-controlling steps, the kinetic data were described by the pseudo-first-order and pseudo-second-order models, respectively (Fig. 4 and Table 2). In the second-order kinetic model the correlation coefficients were about 1.0 for all cases, and the theoretical values of q_{eq} also agreed well with the experimental results. It was reported that the first-order model did not well fit to the kinetic data over the entire range of contact time in many cases [32]. The second-order model put forward by Ho and McKay [33], was used to describe chemisorption [34]. As shown in Fig.4, the pseudo second-order model described the experimental data well with the high correlation coefficients indicating the possible chemisorption occurred between the modified biomass and PCP. The results confirm that PCP adsorption on the sorbent followed the pseudo-first-order adsorption kinetics. Deng et al. reported that the removal of PCP and 2,4-dichlorophenoxyacetic acid by fungal biomass followed the pseudo-second order kinetics [12].

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