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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-

fied with 10.0 mol/l NaOH solution, and the blank was the same sample but acidified with 0.5 mol/l HCl solution. All data were obtained from triplicate assays. The amount of adsorbed 2,4-DCP was calculated as the difference between initial and final 2,4-DCP concentrations.

3. Results and discussion

3.1. Factors influencing biosorption of 2,4-DCP by mycelial pellets

3.1.1. Initial pH

The effect of initial pH on the equilibrium uptake capacity of 2,4-DCP by mycelial pellets of *P. chrysosporium* at pH 2.0–11.0 and 25 ± 1 °C is shown in Fig. 1. The biosorption of 2,4-DCP by fungi was significantly influenced by pH in a range of 2.0–11.0 ($p < 0.05$). Different initial concentrations of 2,4-DCP of 27.05 ± 1.05 and 50.13 ± 1.75 mg/l were chosen to compare the effect of initial 2,4-DCP concentration on uptake capacity. Similar trends were observed for the two different initial 2,4-DCP concentrations. In the natural state of pH 5.0 without pH adjustment, the adsorption of 2,4-DCP was of maximum level. The adsorption was slightly reduced in an alkaline medium, while it was minimum in an acidic medium. The effect of pH on the adsorption of 2,4-DCP was not significant at pH 5.0–8.0, and the uptake of 2,4-DCP at pH 5.0–8.0 was larger than that at other pH values.

Chlorophenols are weakly acidic, and pH has a significant effect on the degree of ionization of 2,4-DCP and the cell surface properties. The amount of adsorbed chlorophenol seemed to be related to the dissociation constant (pK_a), which is 7.89 for 2,4-DCP [2]. The ionic fraction of chlorophenolate ion increases with increasing pH, and chlorophenol could be expected to become negatively charged as pH increases. The surface charge on fungal biomass is predominantly negative at pH 3.0–10.0 [19,24]. At pH < 3.0, the overall surface charge on fungal cells becomes positive. Thus, 2,4-DCP was adsorbed to a lesser extent at pH ≥ pK_a, due to the repulsive forces prevailing at higher pH values. A lower pH value resulted in a higher undissociated fraction of 2,4-DCP and led to a decrease in 2,4-DCP uptake by the mycelial pellets. These results were in accord with those reported by Rao and Viraraghavan [19], in which the biosorption of phenol from an aqueous solution by *A. niger* was evaluated, and maximum removal of phenol was obtained at an initial pH of 5.1. An increase or decrease in pH from this optimum pH resulted in a reduction in the biosorption of phenol. They also reported that the electrostatic forces between the charged fungal surface and phenol played an important role in the biosorption of phenol. The subsequent experiments were conducted in a natural medium without pH adjustment.

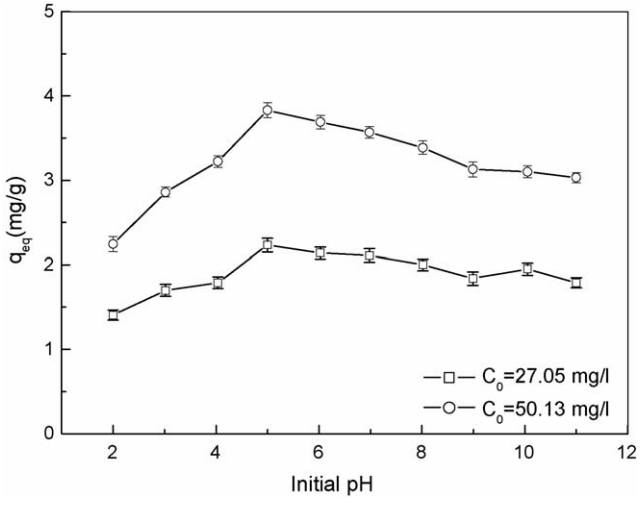


Fig. 1. Effect of initial pH on equilibrium sorption capacity of 2,4-DCP by mycelial pellets (particle size: 1.5–2.0 mm; biomass concentration: 5.0 ± 0.75 g/l; temperature: 25 ± 1 °C; agitation: 150 rpm).

3.1.2. Sorption time and initial concentration

It was observed from Fig. 2a that the uptake of 2,4-DCP by *P. chrysosporium* increased with increasing sorption time. No significant increase in the sorption was found after 90 min sorption, and the adsorption was rapid. The effect of initial 2,4-DCP concentrations on equilibrium time was not significant as well. The rapid adsorption feature was in agreement with the results of Kennedy et al. [3], Ning et al. [16] and Calace et al. [2], in which the time required for equilibrium was 3, 2 and 2 h, respectively.

The initial concentration provides an important driving force to overcome all mass transfer resistances of adsorbate between the aqueous solid phase and therefore increases the rate at which adsorbate molecules pass from the bulk solution to the adsorbent surface [9,13,25]. Accordingly, a high initial concentration of 2,4-DCP would enhance the adsorption process. As seen from Fig. 2a, the equilibrium sorption capacity increased with the increasing initial 2,4-DCP concentration from 6.85 ± 0.24 to 51.81 ± 1.82 mg/l, while the 2,4-DCP adsorption efficiency showed an opposite trend. The increase in sorption capacity of mycelial pellets with an increase in the initial 2,4-DCP concentration might be due to a higher probability of collision between the chlorophenol molecules and biosorbent.

3.1.3. Temperature

Four temperatures, i.e., 25, 30, 40 and 50 °C, were selected in this study. The effect of temperature on the biosorption of 2,4-DCP by *P. chrysosporium* at an initial concentration of 52.00 mg/l is shown in Fig. 2b. Adsorption increased with decreasing temperature. Thus, the optimum adsorption temperature, at which the sorption capacity of 2,4-DCP on mycelial pellets was the highest, was 25 °C in the studied temperature range. Similar results were reported for the sorption of 2,4-dimethyl phenol from aqueous solutions by coal fly ash [7], in which equilibrium adsorption capacity decreased with increasing temperature in a range of 304–324 K. These results indicate that the biosorption of 2,4-DCP by *P. chrysosporium* might be physical and exothermic in nature and the adsorption was favored at a low temperature [7,26].

3.1.4. Size of mycelial pellets

Fig. 2c shows a series of contact time curves at different mycelial pellet sizes (i.e., diameter), i.e., 1.0–1.5, 1.5–2.0 and

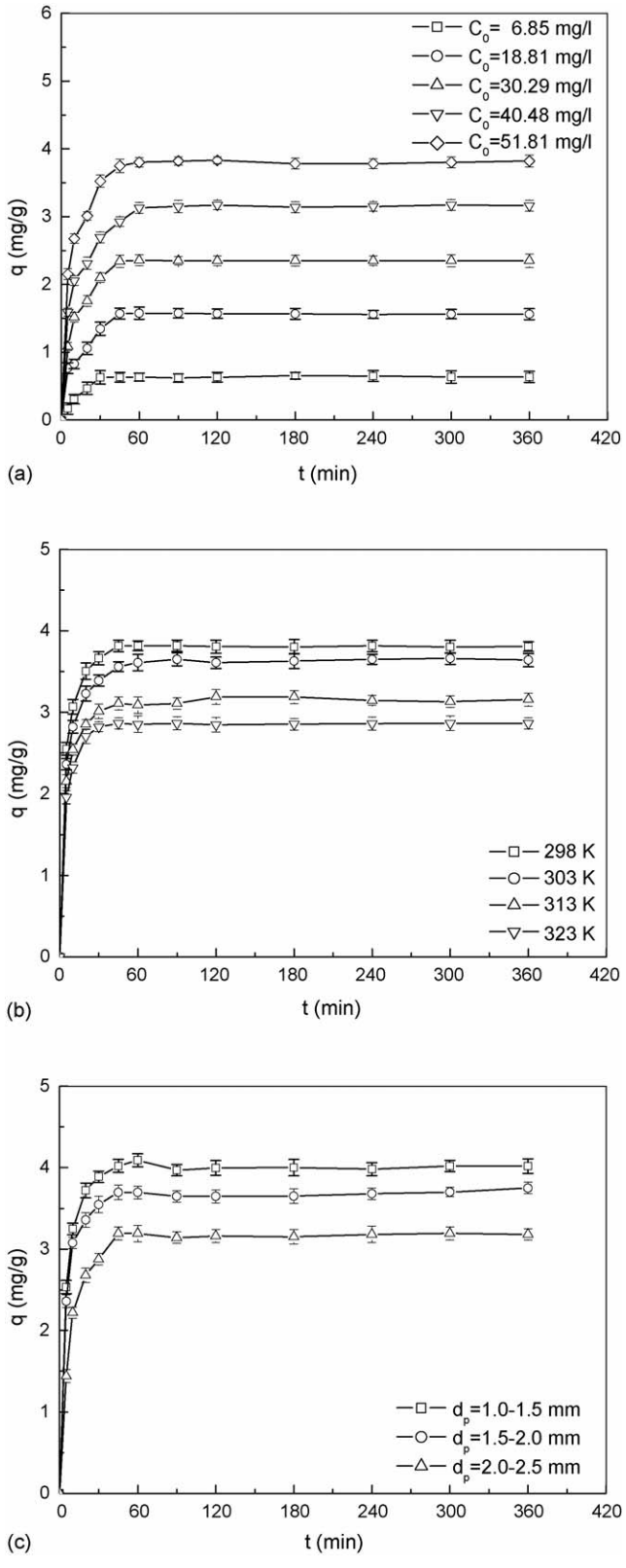


Fig. 2. Effects of (a) initial concentration (temperature: 25 ± 1 °C; particle size: 1.5–2.0 mm); (b) temperature (initial concentration: 52.00 ± 1.83 mg/l; particle size: 1.5–2.0 mm) and (c) size of mycelial pellet (initial concentration: 50.48 ± 1.76 mg/l; temperature: 25 ± 1 °C) on the sorption kinetics of 2,4-DCP by mycelial pellets (pH 5.0, biomass concentration: 5.0 ± 0.75 g/l and agitation: 150 rpm).

2.0–2.5 mm, at 25 ± 1 °C and an initial 2,4-DCP concentration of 50.48 ± 1.76 mg/l. The equilibrium sorption capacity of 2,4-DCP increased with an decrease in mycelial pellet size, suggesting that 2,4-DCP sorption might be associated with surface mechanisms. Similar result has been reported for the adsorption of cadmium by chitin [27]. A smaller size of pellet leads to a larger specific surface area, and results in a higher sorption capacity. Thus, surface of contact between adsorbent and the liquid phase plays an important role in the process of sorption [16,27]. Therefore, sorption kinetics of 2,4-DCP on mycelial pellets was affected by the pellet size.

3.2. Equilibrium modeling

Analysis of equilibrium data is important for developing a model that can be used for the design of adsorption systems. Several isotherm equations have been used for equilibrium modeling of biosorption systems [1,20,25]. Two classical adsorption models, i.e., Langmuir and Freundlich isotherms, are most frequently employed. In this work, the two models were used to describe the relationship between the amount of 2,4-DCP adsorbed and its equilibrium concentration in solutions at different temperatures.

3.2.1. Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is given as Eq. (1):

$$q_{eq} = \frac{Q^0 b C_{eq}}{1 + bC_{eq}} \quad (1)$$

where C_{eq} and q_{eq} are equilibrium concentration (mg/l) and the amount of adsorbed at equilibrium time (mg/g), respectively. Q^0 and b are Langmuir constants related to the capacity and energy of adsorption, respectively. The linearized form of the Langmuir equation is as follows:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^0 b} + \frac{C_{eq}}{Q^0} \quad (2)$$

Q^0 and b can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} [7,13,20].

The adsorption isotherms and linearized Langmuir adsorption isotherms of 2,4-DCP obtained at 25 ± 1, 30 ± 1, 40 ± 1 and 50 ± 1 °C are illustrated in Fig. 3a and b. The values of Q^0 and b calculated from the slope and intercept of the plots are also listed in Table 1. High regression correlation coefficients (>0.97) were found at all the temperatures studied, suggesting that the Langmuir model was applicable. The Langmuir constant Q^0 decreased with increasing temperature, while the variation of constant b was not significant, indicating that the adsorption capacity was higher at a lower temperature. Q^0 represents a practical limiting adsorption capacity when the surface is fully covered with adsorbed molecules and assists in the comparison of adsorption performance, particularly in cases where the adsorbent does not reach its full saturation. The decrease in Q^0 with increasing temperature was in good agreement with the experimental results on temperature effect described above.

Table 1
The Langmuir and Freundlich isotherm constants of 2,4-DCP adsorption on mycelia pellets at different temperatures and pH 5.0, particle size 1.5–2.0 mm

T (°C)	Langmuir constants				Freundlich constants			
	Q^0 (mg/g)	B (l/mg)	R^2	S.D.	K_F [(mg/g)(mg/l)^n]	n	R^2	S.D.
25	11.62	0.0147	0.986	0.190	0.232	1.256	0.998	0.016
30	11.72	0.0122	0.970	0.287	0.187	1.214	0.995	0.025
40	9.14	0.0141	0.995	0.162	0.179	1.263	0.997	0.019
50	8.05	0.0145	0.992	0.233	0.167	1.285	0.998	0.016

3.2.2. Freundlich isotherm

The Freundlich equation based on sorption on a heterogeneous surface is given below as Eq. (3):

$$q_{eq} = K_F C_{eq}^{1/n} \tag{3}$$

where K_F and n are the Freundlich constants, whereas K_F and n are indicators of adsorption capacity and adsorption intensity of the sorbents, respectively [1,4,16]. Eq. (3) can be linearized in logarithmic form as Eq. (4):

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \tag{4}$$

The values of K_F and n can be estimated respectively from the intercept and slope of a linear plot of experimental data of $\log q_{eq}$ versus $\log C_{eq}$. The Freundlich isotherm provides no information on the monolayer adsorption capacity in comparison with the Langmuir model [1,16,19].

The linearized Freundlich adsorption isotherms of 2,4-DCP obtained at different temperatures are shown in Fig. 3c. The values of K_F and n calculated from the plot are also given in Table 1 along with the regression correlation coefficients. The parameter K_F related to the sorption capacity increased with a decrease in temperature. Table 1 also shows that n was greater than unity, indicating that 2,4-DCP was adsorbed favorably by mycelial pellets at all the temperatures studied. The regression correlation coefficients of Freundlich model were close to 1.0, suggesting that the Freundlich model was also able to describe the adsorption equilibrium well. The Freundlich model exhibited a slightly better fit to the biosorption data of 2,4-DCP than the Langmuir model in the concentration and temperature ranges studied.

Both Langmuir and Freundlich isotherms could be used to describe adsorption equilibrium of heavy medals on different types of adsorbents well [10,13,27]. However, adsorption equilibriums of organic pollutants, such as phenol and chlorophenols, followed the Freundlich isotherm better than the Langmuir one [1,3,18].

3.3. Kinetic modeling

Fig. 2 shows that the adsorption of 2,4-DCP increased with the increasing sorption time. The adsorption rate was high in the first minute, but decreased until the equilibrium was reached. Similar trends were observed by other workers [2,9,18]. In order to find out the potential rate-controlling steps involved in the process of biosorption, kinetic models should be established. There are several kinetic models about adsorption of heavy metals [13,26], dyes [20,28] and chlorophenols [29]. To evaluate the biosorption kinetics of 2,4-DCP, two kinetic models were used to fit the experimental data at different initial concentrations, temperatures, and different sizes of mycelial pellets at pH 5.0.

3.3.1. Pseudo first-order Lagergren model

The pseudo first-order rate expression of Lagergren model [30] is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \tag{5}$$

where q_{eq} and q have their usual meanings, and $k_{1,ad}$ is the rate constant of first-order biosorption (min^{-1}). The integrated form of Eq. (5) is:

$$\log(q_{eq} - q) = \log q_{eq} - k_{1,ad}\frac{t}{2.303} \tag{6}$$

However, to fit Eq. (6) to experimental data, the value of q_{eq} (equilibrium sorption capacity) must be pre-estimated by extrapolating the experimental data to $t = \infty$. In addition, in most cases the first-order rate equation of Lagergren is usually applicable over the initial 30–50 min of the sorption process [7,20,26].

The plots of $\log(q_{eq} - q)$ as a function of sorption time are shown in Fig. 4. The linear relationships were observed only for the initial 45 min of sorption and the experimental data considerably deviated from the theoretical ones (not shown in the figure) after this short period. 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 first-order rate constants $k_{1,ad}$ decreased with increasing temperature up to 40 ± 1 °C, but then slightly increased with temperature up to 50 ± 1 °C. As for the effect of initial concentration on $k_{1,ad}$, the rate constant was higher at a lower initial concentration except for an initial 2,4-DCP concentration of 51.81 ± 1.82 mg/l. The $k_{1,ad}$ value decreased with increasing mycelial pellet size. This result is consistent with the observed results about the effect of pellet size on sorption of 2,4-DCP and is in accord with the work of Benguella and Benaissa [27], in which the cadmium sorption kinetics by chitin was largely determined by the particle size, and the rate constants decreased with increasing particle size.

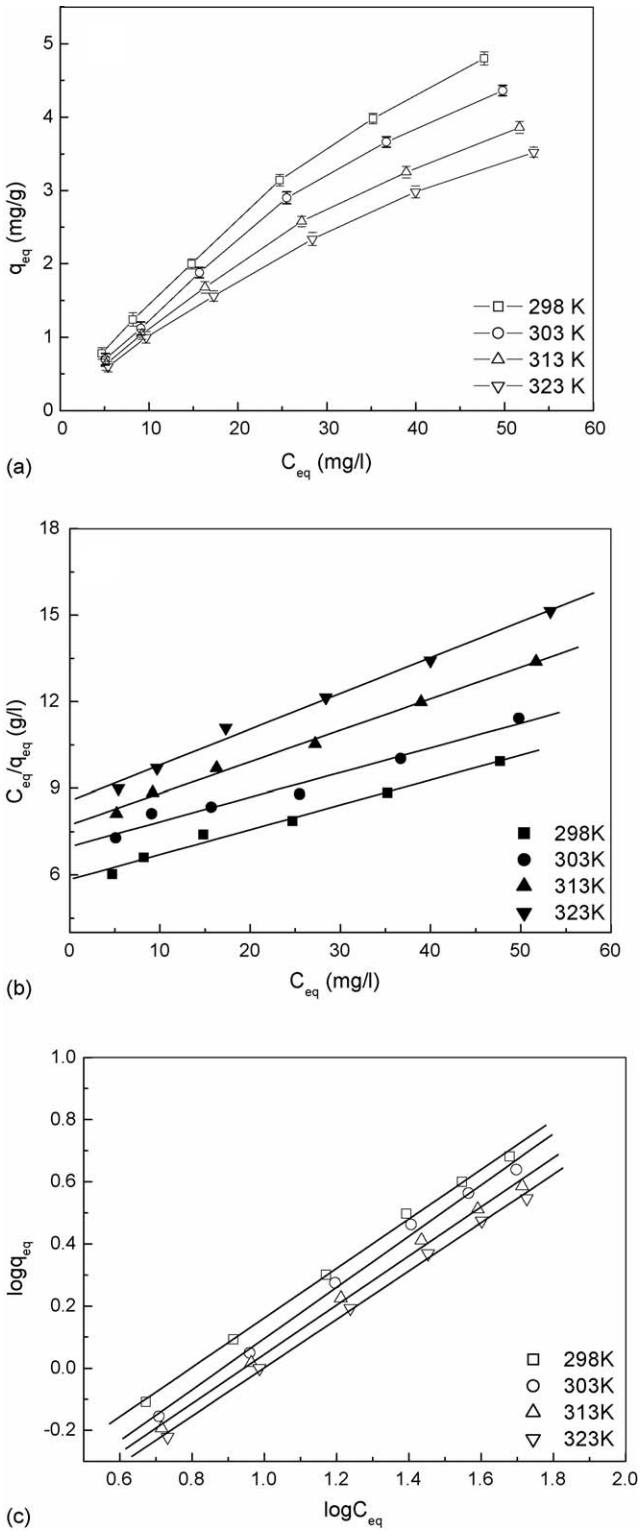


Fig. 3. (a) Adsorption isotherms and Linearized adsorption isotherms of (b) Langmuir and (c) Frundlich at different temperatures of 2,4-DCP by mycelial pellets (particle size: 1.5–2.0 mm; pH 5.0, biomass concentration: 5.0 ± 0.75 g/l and agitation: 150 rpm).

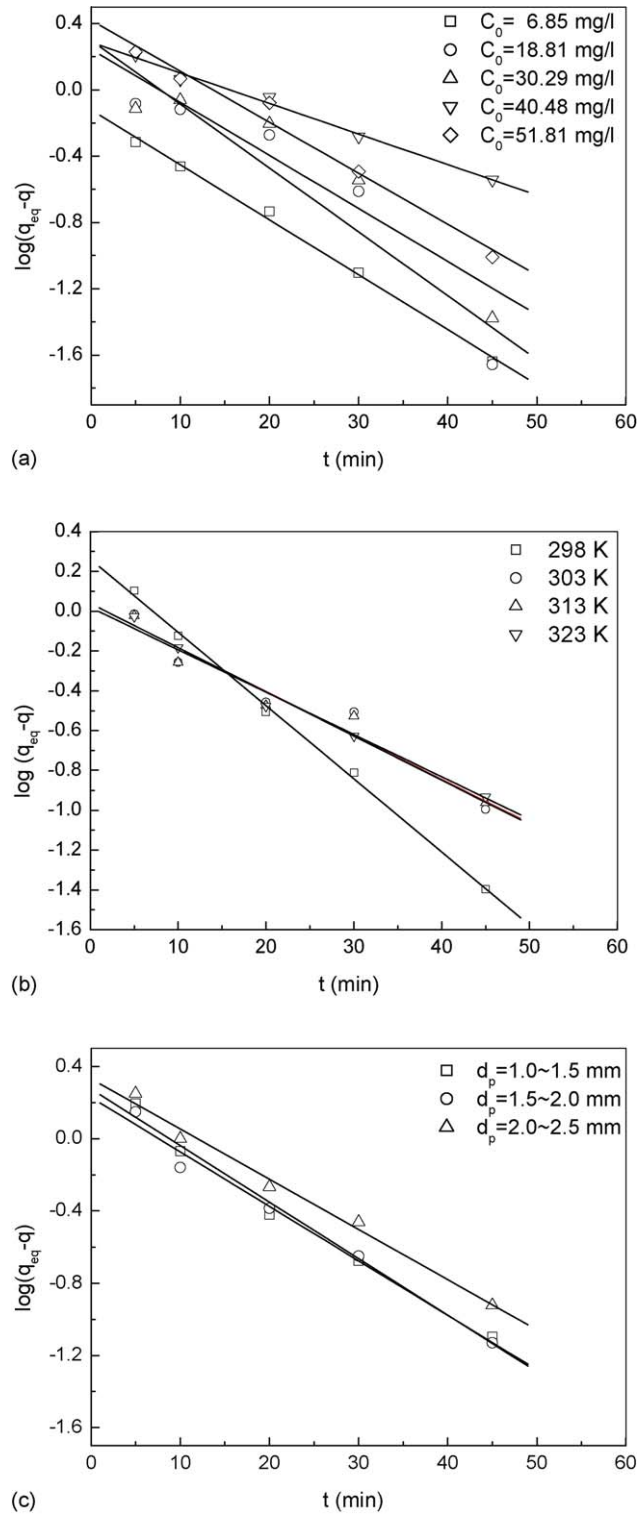


Fig. 4. Linearized pseudo first-order kinetic model for 2,4-DCP sorption by mycelial pellets at different (a) initial concentration (particle size: 1.5–2.0 mm; temperature: $25 \pm 1\,^{\circ}$C); (b) temperature (particle size: 1.5–2.0 mm; initial concentration: 52.00 ± 1.83 mg/l) and (c) size of mycelial pellet (initial concentration: 50.48 ± 1.76 mg/l, temperature: $25 \pm 1\,^{\circ}$C) (pH 5.0, biomass concentration: 5.0 ± 0.75 g/l and agitation: 150 rpm).

3.3.2. Pseudo second-order kinetic model

If the sorption rate is second-order, the pseudo second-order kinetic rate equation is expressed as [31]:

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \quad (7)$$

where $k_{2,ad}$ is the rate constant of second-order biosorption [g/(mg min)]. After integrating, the following equation is obtained:

$$\frac{t}{q} = \frac{1}{k_{2,ad}q_{eq}^2} + \frac{t}{q_{eq}} \quad (8)$$

It should be noticed that for the utilization of this model, the experimental value of q_{eq} is not necessary to be pre-estimated. By plotting t/q against t for the initial concentrations, temperatures, and mycelial pellet sizes studied, straight lines were obtained in all cases as shown in Fig. 5. 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. The results show that the second-order rate constant $k_{2,ad}$ decreased with an increase in initial 2,4-DCP concentration, temperature and size of mycelial pellets. The correlation coefficients for the second-order kinetic model were close to 1.0 for all cases, and the theoretical values of q_{eq} also agreed well with the experimental data. On the other hand, the correlation coefficients for the pseudo first-order kinetics were lower than those for the pseudo second-order one. In addition, the theoretical q_{eq} values obtained from the first-order kinetic model did not give reasonable values with significant deviations from the experimental ones. This suggests that the sorption of 2,4-DCP on mycelial pellets follow the second-order kinetics. The second-order kinetic parameters obtained could be used to determine the equilibrium sorption

Table 2
The first-order and second-order adsorption rate constants of 2,4-DCP at pH 5.0 (for different temperature: C_0, 52.00 ± 1.83 mg/l; particle size, 1.5–2.0 mm; for different initial concentrations: temperature, 25 ± 1 °C; particle size, 1.5–2.0 mm; for different sizes: C_0, 50.48 ± 1.76 mg/l; temperature, 25 °C and for all experiments: the biomass concentration: 5 g/l)

	$K_{1,ad}$ (min^{-1})	$q_{eq,cal}$ (mg/g)	R^2	$K_{2,ad}$ (g/(mg min))	$q_{eq,cal}$ (mg/g)	R^2	$q_{eq,exp}$ (mg/g)
T (°C)							
25	0.085	1.83	0.998	0.215	3.83	0.999	3.82
30	0.051	1.10	0.948	0.172	3.68	0.999	3.66
40	0.049	1.04	0.955	0.137	3.18	0.999	3.15
50	0.051	1.09	0.984	0.125	2.88	0.999	2.86
C_0 (mg/l)[a]							
6.85	0.076	0.76	0.996	0.264	0.65	0.999	0.65
18.81	0.089	1.99	0.892	0.142	1.59	0.999	1.58
30.29	0.074	1.76	0.884	0.117	2.38	1.000	2.35
40.48	0.042	1.94	0.990	0.070	3.21	1.000	3.17
51.81	0.071	2.63	0.981	0.094	3.85	1.000	3.83
d_p (mm)[a]							
1.0–1.5	0.072	1.89	0.987	0.178	4.03	1.000	4.09
1.5–2.0	0.069	1.69	0.986	0.120	3.73	1.000	3.75
2.0–2.5	0.064	2.15	0.988	0.099	3.22	1.000	3.19

[a] C_0: initial concentration of 2,4-DCP; d_p: size of mycelial pellets.

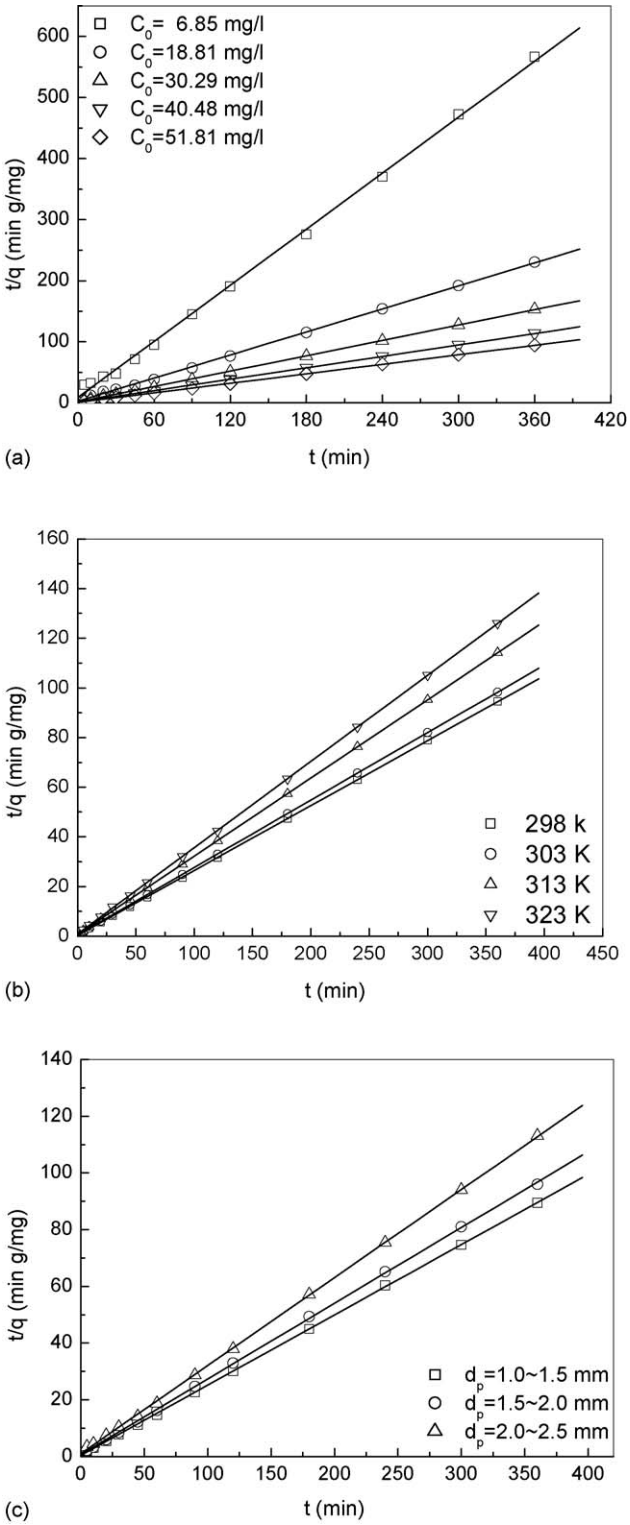


Fig. 5. Linearized pseudo second-order kinetic model for 2,4-DCP sorption by mycelial pellets at different (a) initial concentration (particle size: 1.5–2.0 mm; temperature: 25 ± 1 °C); (b) temperature (particle size: 1.5–2.0 mm; initial concentration: 52.00 ± 1.83 mg/l); (c) size of mycelial pellet (initial concentration: 50.48 ± 1.76 mg/l; temperature: 25 ± 1 °C) (pH 5.0, biomass concentration: 5.0 ± 0.75 g/l and agitation: 150 rpm).

Table 3
Rate constants of intraparticle diffusion of 2,4-DCP at pH 5.0 (for different temperature: C_0, 52.00 ± 1.83 mg/l; particle size, 1.5–2.0 mm; for different initial concentrations: temperature, 25 °C; particle size, 1.5–2.0 mm; for different sizes: C_0, 50.48 ± 1.76 mg/l; temperature, 25 °C and for all experiments: the biomass concentration: 5 g/l)

Temperature (°C)	k_{id} (mg/(g min$^{1/2}$))	C_0[a] (mg/l)	k_{id} (mg/(g min$^{1/2}$))	d_p[a] (mm)	k_{id} (mg/(g min$^{1/2}$))
25	0.138	6.85	0.138	1.0–1.5	0.106
30	0.157	18.81	0.229	1.5–2.0	0.151
40	0.203	30.29	0.262	2.0–2.5	0.195
50	0.292	40.48	0.329		
		51.81	0.366		

[a] C_0: initial concentration of 2,4-DCP; d_p: size of mycelial pellets.

capacity, percent of the removal of 2,4-DCP, rate constants and initial sorption rate for a bioreactor design.

3.4. Intraparticle diffusion

The kinetic results can be used to test the presence or absence of intraparticle diffusion and to determine whether intraparticle diffusion is the rate-limiting step for biosorption.

The linear plots (Fig. 6) demonstrat the presence of intraparticle diffusion in the sorption process of 2,4-DCP by mycelial pellets. All the curves had same features, i.e., an initial curve portion, followed by a linear portion and later a plateau. This indicates that more than one mode of sorption were involved in the sorption of 2,4-DCP. The initial curve portion was attributed to the boundary layer sorption, the linear portion to the intraparticle diffusion and the plateau to the equilibrium. If intraparticle diffusion is involved in the sorption process [2,7], a plot of adsorption uptake versus the square root of time will thus result in a linear relationship and the intraparticle diffusion should be the rate-controlling step if the line passes through the origin. Although in Fig. 6 there was a linear relationship over a period of time, they did not pass through the origin, suggesting that intraparticle diffusion was present, but not the only rate-controlling step, and that some other mechanisms might be involved in the biosorption of 2,4-DCP by *P. chrysosporium*. Scanning electron micrographs of *P. chrysosporium* mycelia and mycelial pellets are shown in Fig. 7a and b. Both pore diffusion and kinetic resistances are likely to affect the adsorption rate. The rate constants for the intraparticle diffusion k_{id} are listed in Table 3. The results show that k_{id} was higher at a higher temperature, initial 2,4-DCP concentration and larger size of mycelial pellets.

The entire adsorption process includes four steps: (1) migration of adsorbate molecules from bulk solution to the surface of the adsorbent; (2) diffusion through the boundary layer to the surface of the adsorbent; (3) adsorption at a site and (4) intraparticle diffusion into the interior of the adsorbent [32]. The results of intraparticle diffusion show an increase in the rate constant for intraparticle diffusion with increasing initial 2,4-DCP concentration, temperature and size of mycelial pellets. This is in consistent with the fact that diffusion needs some energy to overcome the mass transfer resistance. This observation is also supported by the results of other studies [28,32,33]. Hence, the

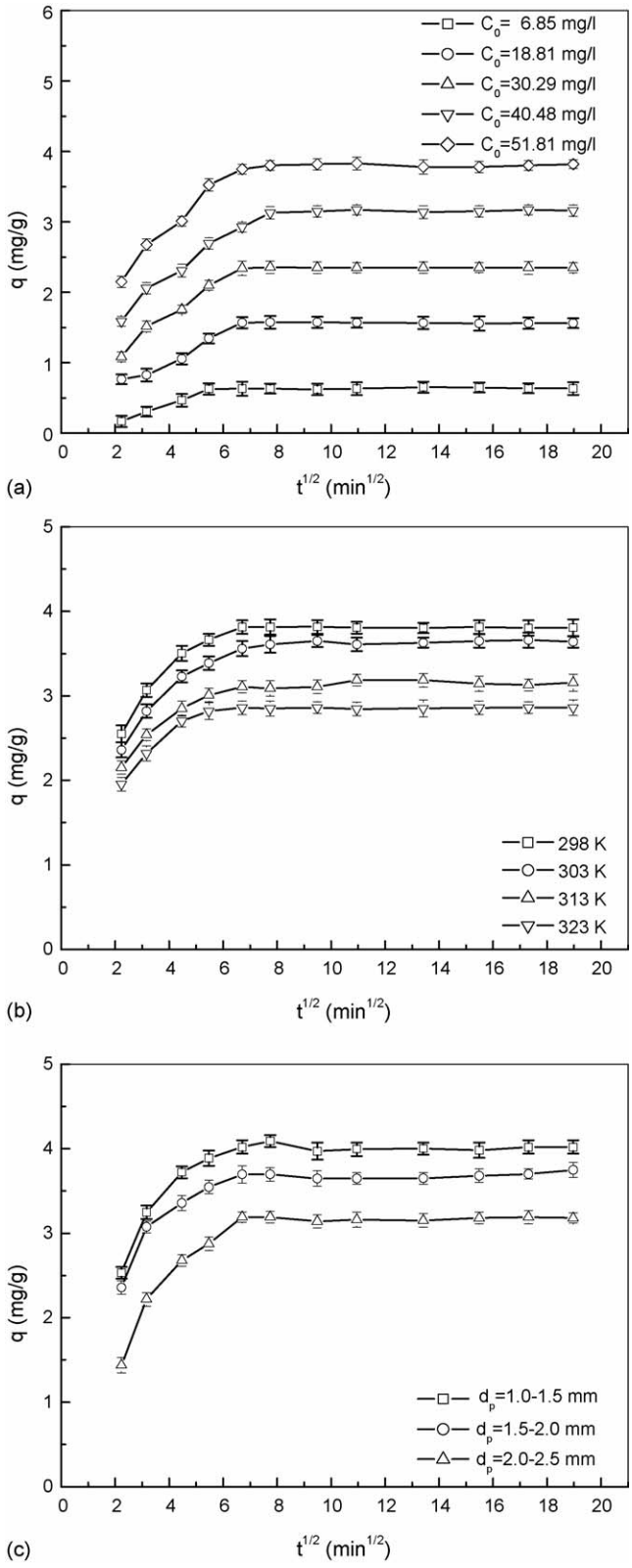
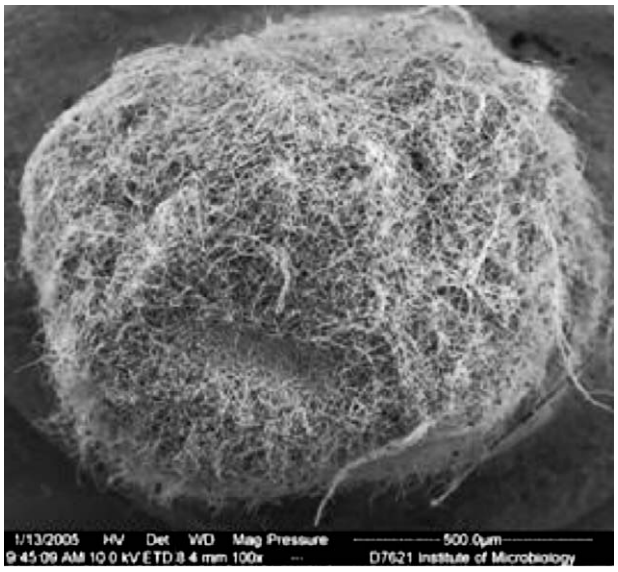
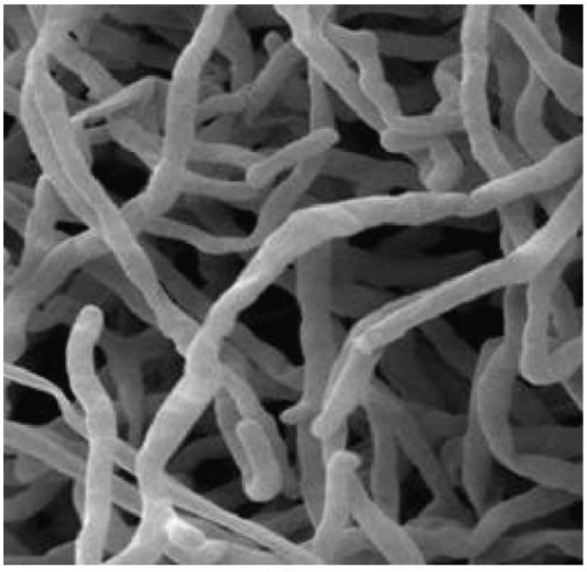


Fig. 6. Intraparticle diffusion plots for adsorption of 2,4-DCP by mycelial pellets at different (a) initial concentration (particle size: 1.5–2.0 mm; temperature: 25 ± 1 °C); (b) temperature (particle size: 1.5–2.0 mm; initial concentration: 52.00 ± 1.83 mg/l) and (c) size of mycelial pellet (initial concentration: 50.48 ± 1.76 mg/l; temperature: 25 ± 1 °C) (pH5.0, biomass concentration: 5.0 ± 0.75 g/l and agitation: 150 rpm).



(a)



(b)

Fig. 7. Images of *P. chrysosporium* (a) mycelia pellets and (b) mycelial.

presence of the intraparticle diffusion implied that both pore diffusion and kinetic resistances might affect the adsorption rate and that their relative effects varied with operating temperature.

3.5. Thermodynamic considerations

The second-order rate constant can be expressed as a function of temperature by the Arrhenius equation and the activation energy (E_a) can be determined as below:

$$k_{2,ad} = K_0 \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

$$\ln k_{2,ad} = \ln K_0 - \frac{E_a}{RT} \quad (10)$$

where K_0 is the temperature-independent factor (g/(mg min)), E_a the apparent activation energy of sorption (J/mol), R the gas constant [=8.314 J/(mol K)] and T is the adsorption temperature in Kelvin. Fig. 8 shows a linear plot of $\ln k_{2,ad}$ as a function of $10^3/T$ for 2,4-DCP adsorption at 25 ± 1 to 50 ± 1 °C. The apparent activation energy calculated from the slope of the plot was −16.95 kJ/mol. The activation energy was −8.0 kJ/mol for the cadmium(II) biosorption by *C. vulgaris* [13]. The apparent activation energy of −6.57 kJ/mol was estimated for the 2,4-dimethyl phenol adsorption with coal fly ash [7]. The negative activation energy indicates that the biosorption of 2,4-DCP by mycelial pellets was a physical adsorption.

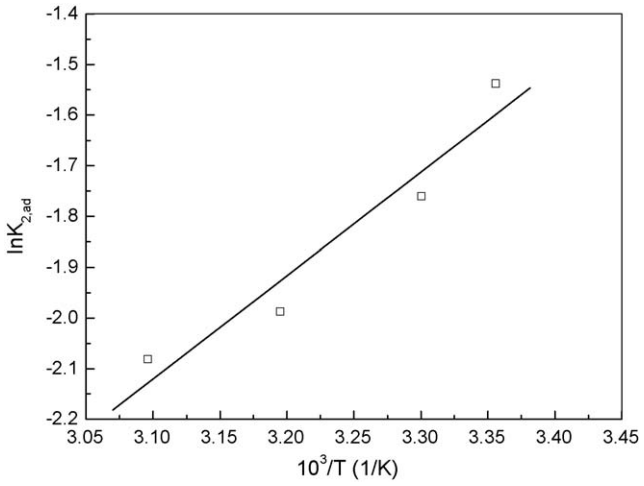


Fig. 8. Arrhenius plot for adsorption of 2,4-DCP by mycelial pellets.

Thermodynamic parameters for the adsorption such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy (ΔS°) were calculated using the Eq. (11) and van't Hoff (Eq. (12)):

$$\Delta G^\circ = -RT \ln K_p \quad (11)$$

$$\ln K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where K_p is the thermodynamic equilibrium constant, i.e., the ratio of the equilibrium concentration of 2,4-DCP on the adsorbent to that in the solution. This constant is determined using the method of Khan and Singh [34] by plotting $\ln(q_{eq}/C_{eq})$ versus q_{eq} and extrapolating to zero q_{eq} (Fig. 9). A plot of $\ln K_p$ as a function of $10^3/T$ yielded a straight line (Fig. 10). The values of ΔH° and ΔS° obtained from the slope and intercept of the plot are summarized in Table 4. The negative value of ΔH° (−10.88 kJ/mol) indicates the exothermic nature of adsorption. The negative value of ΔS° (−25.02 J/(mol K)) might be asso-

Table 4
Thermodynamic parameters for the biosorption of 2,4-DCP by *P. chrysosporium* at pH 5.0

Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol K))	E_a (kJ/mol)
25	−3.56	−10.88	−25.02	−16.95
30	−3.14			
40	−3.02			
50	−2.86			

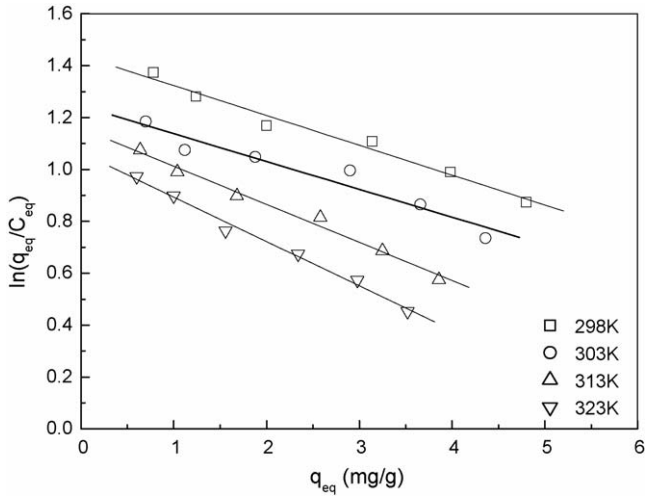


Fig. 9. Plots of $\ln(q_{eq}/C_{eq})$ as a function of q_{eq} for the adsorption of 2,4-DCP by mycelial pellets.

ciated with the adsorption of 2,4-DCP to the adsorbent, which resulted in a decrease in freedom degree of the systems during the adsorption. The negative value of ΔG° indicates the spontaneity of the adsorption process. The values of ΔG°, ΔH° and ΔS° were varied for different adsorption processes due to the different interactions between adsorbent and absorbate [26,35].

Fig. 2b shows that adsorption capacity decreased with an increasing temperature, and that the adsorption of 2,4-DCP by mycelial pellets seemed to be an exothermic process. It was confirmed by the thermodynamic analysis.

3.6. Significance of this work

Biosorption is a promising alternative to replace or supplement to the currently used treatment techniques for the removal of phenolics from wastewaters. The equilibrium and kinetic models in association with model parameters would be useful for the design of biosorption reactors and the establishment of wastewater treatment plants. However, more studies should be carried out to further explore the mechanisms of biosorption by biomass in depth and to provide more reliable information for the practical application.

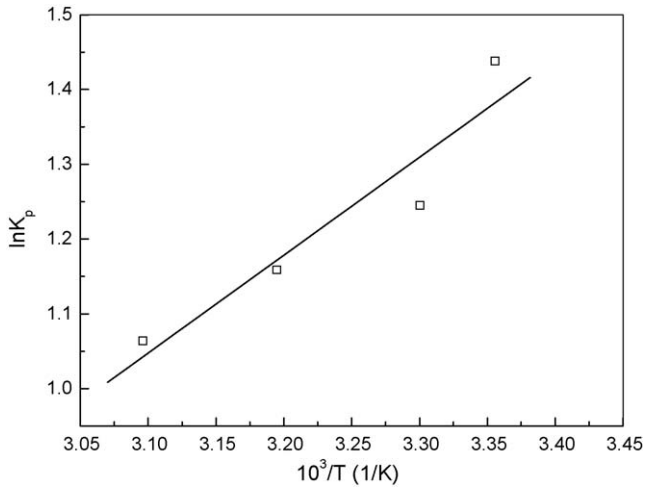


Fig. 10. van't Hoff plot for the adsorption of 2,4-DCP by mycelial pellets.

4. Conclusions

The high potential of mycelial pellets of *P. chrysosporium* to adsorb 2,4-DCP from aqueous solution was demonstrated in this study. The sorption capacity increased with an increase in initial 2,4-DCP concentration, but decreased with an increase in temperature and size of mycelial pellets. 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 by *P. chrysosporium* followed pseudo second-order adsorption kinetics. The second-order kinetic constants increased with increasing temperature and the apparent activation energy of biosorption was estimated as −16.95 kJ/mol. Thermodynamic analysis indicates that the biosorption process was exothermic. The relatively low apparent activation energy and ΔH° suggest that the adsorption of 2,4-DCP might be physical in nature and adsorption was favored at low temperatures. Both intraparticle diffusion and kinetic resistances might affect the adsorption rate and their relative effects varied with operating temperature in the biosorption of 2,4-DCP by mycelial pellets.

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