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Biosorption of 2,4-dichlorophenol from aqueous solutions by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column

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Abstract

The continuous-flow adsorption of 2,4-dichlorophenol (2,4-DCP) from aqueous solution by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column was studied. The effects of flow rate, influent concentration of 2,4-DCP and bed depth on breakthrough curves and biosorption capacity were investigated. The experimental results showed that the breakthrough time decreased with increasing flow rate, increasing influent concentration and decreasing bed depth. The data also indicated that the equilibrium uptake of 2,4-DCP increased with decreasing flow rate and increasing influent concentration of 2,4-DCP. Two models were employed to predict the breakthrough curves and to determine the characteristic parameters of the column useful for column design. The Thomas model was able to predict the breakthrough curve in the range of relative concentration (C_e/C_i) higher than 0.3, whereas the validity of the Bohart-Admas model was limited to the initial part of breakthrough curve at all flow rates and influent concentrations of 2,4-DCP studied. The feasibility of reusing the immobilized fungal beads through five adsorption/desorption cycles in fixed-bed column was investigated.

Keywords: 2,4-DCP; Biosorption; Breakthrough curve; Fixed-bed column; Immobilization

1. Introduction

Chlorophenols are widely present in wastewaters discharged from industries and they are considered as priority pollutants because of their high toxicity at low concentrations. Thus, the adequate treatment must be taken before these wastewaters being discharged into receiving water body. The existing treatment methods, such as biodegradation [1], activated carbon adsorption [2] and solvent extraction [3] and so on, may be ineffective or extremely expensive, especially when the chlorophenols concentrations in the solutions are relatively high. Hence, efficient, cost-effective and safe methods are needed for the removal of chlorophenols from wastewater. Biosorption, as an efficient treatment means, is gaining increasing attention.

However, most of previous studies on biosorption were carried out with powdered biomass and batch systems [4–7]. Little is known about the biosorption behavior of toxic chlorophenolic compounds in continuous-flow fixed-bed column. The powdered biomass is difficult to use in applications due to its disadvantages, e.g., the small particle size and low mechanical strength, which may cause difficulty in the separation of biomass after biosorption and significant mass loss after regeneration. However, the immobilization of biomass improves biomass mechanical strength, rigidity, porosity and reusability. It also facilitates the separation of biomass from treated solutions. In addition, immobilization allows a higher biomass concentration and has resistance to unfavorable environments. Therefore, the immobilization of biomass has a greater potential than the powdered biomass in fixed-bed reactors.

Fixed-bed adsorption has been widely used in the treatment of metal-bearing effluents [8–12]. It is simple to operate, and it can be relatively easily scaled up from a laboratory-scale study. Comparing with batch procedure, a fixed-bed is more effective for the cycle operation of adsorption/desorption, and the reuse of adsorbents is also possible. Many of studies on the adsorption capacities of fungal biomass for heavy metals in fixed-bed have been reported [9,12–14]. However, only limited information is available on the biosorption of chlorophenols by immobilized fungal biomass in a fixed-bed column. The use of dried activated sludge immobilized with Mowital® B30H resin was examined in

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a continuous fixed-bed reactor for the removal of phenol from aqueous solution [15,16]. The biosorption of phenol by immobilized *Aspergillus niger* in polysulphone was investigated in a column study, and approximately 66% of phenol was removed in the column [17].

The performance of fixed-bed is usually described using the breakthrough curve. However, development of a model to accurately describe the dynamic behavior of adsorption in a fixed-bed column is usually difficult. The use of simple models without numerical solutions appears to be more suitable and has practical benefits. Several models have been applied to describe biosorption in fixed-bed column. The Thomas model [9,16,18], Yoon and Nelson model [16,19], Bohart-Adams model [12] and Clark model [10] usually have been applied to describe the biosorption process in a fixed-bed column. These semi-empirical models are easier to use and more efficient than the mechanistic models which need complicated mathematical solutions.

The white-rot fungus of *Phanerochaete chrysosporium* has been reported to be the potential biosorbent for phenol [4] and chlorophenols [5]. However, its application as a biosorbent in a fixed-bed column has not been investigated. The main objective of the present work was to examine the adsorption capacity of the immobilized *P. chrysosporium* biomass for 2,4-DCP in a fixed-bed column at different flow rates, influent concentrations, and bed depths. The Thomas and Bohart-Admas models were applied to experimental data to predict the breakthrough curves, the kinetic constants and the adsorption capacities of the fixed-bed. The reusability of biosorbent in five adsorption/desorption cycles was also investigated to evaluate the feasibility of applying this white-rot fungus in the removal process of chlorophenols.

2. Materials and methods

2.1. Preparation of biomass

The white-rot fungus used in the study was *P. chrysosporium* which was obtained from the Institute of Microbiology, Chinese Academy of Sciences, Beijing, China. It was cultivated in the medium as previously described by Kirk et al. [20]. After 5-day incubation at $39 \pm 1\,^{\circ}C$ on an orbital shaker (150 rpm), the mycelial pellets were collected by filtration and then killed by autoclaving (104 kPa, 121 °C) for 20 min. After that, these non-live mycelial pellets were directly immobilized.

2.2. Immobilization of fungal mycelial pellets

A 2% (w/v) of sodium alginate was prepared in hot distilled water ($60 \pm 1\,^{\circ}C$). After cooling, 0.5 g of mycelial pellets (dry weight) was mixed with 40 ml sodium alginate solution (1.25% of biomass concentration, w/v). The mixture was dropped into 0.2 M $CaCl_2$ solution with a burette and stirred to avoid aggregation of the beads. The resultant beads of 4 mm in diameter were cured in 0.2 M $CaCl_2$ solution at 4 °C for 4 h to complete gellation. For the preparation of blank Ca-alginate beads, similar procedures were used at the absence of fungal biomass.

2.3. Preparation of solutions

One hundred milligrams per liter of stock solution of 2,4-DCP was obtained by dissolving 0.1 g of 2,4-DCP in 1 l of distilled water. All solutions in this experiment were prepared by appropriately diluting the stock solution to the required concentrations. An analysis of the distilled water did not show the presence of 2,4-DCP. According to the previous studies [21], the pH value of each tested solution in this study was adjusted to 5.0 with 1.0 M of NaOH or HCl before adsorption.

2.4. Fixed-bed biosorption studies

Biosorption studies were carried out in a fixed-bed column (1.6 cm in internal diameter) with the column lengths of 20 cm, 30 cm, 35 cm, respectively. 1.6 ± 0.2 g, 2.1 ± 0.2 g and 2.6 ± 0.2 g (dry weight) of immobilized fungal beads was packed into the column with a bed depth of 15 cm, 22 cm and 26 cm, respectively. The 2,4-DCP-bearing solution at a known concentration was continuously pumped into the column upwards at a constant temperature of $25 \pm 1\,^{\circ}C$. The desired flow rate was regulated with a variable peristaltic pump. Samples were taken from the effluent at pre-determined time intervals and analyzed for the remaining concentration of 2,4-DCP in effluent. The experiments were continued until a constant effluent concentration of 2,4-DCP was obtained.

The desorption of adsorbed 2,4-DCP from the immobilized fungal beads in the column was carried out with distilled water at different flow rates. Samples were collected at given time intervals to study the elution kinetics. Later, the column was fed again with fresh 2,4-DCP solutions for the cycle operation of adsorption/desorption, in order to investigate the potential of reusing the beads for the removal of 2,4-DCP in the fixed-bed column. The blank experiments were also carried out using a fixed-bed column with Ca-alginate beads in the absence of fungal biomass.

The concentration of 2,4-DCP in the solution was determined using a UV–vis spectrophotometer (UV752-GD, Shanghai Instrument Co., China) at 306 nm [21].

All chemicals and reagents used in this study were of analytical grade. Data presented in this paper were the average values from two replicates, and the standard deviation was within 2%.

2.5. Calculations

The evaluation of the column performance was conducted by plotting 2,4-DCP relative concentration, defined as the ratio of 2,4-DCP concentration in effluent to 2,4-DCP concentration in influent (C_e/C_i), as a function of flow time (t, min).

The total adsorbed 2,4-DCP (q_t, mg) in the column for a given solute concentration and flow rate is calculated from the following equation:

$$q_t = \frac{Q}{1000} \int_{t=0}^{t=t_s} C_{ad}\, dt \quad (1)$$

where Q (ml/min) is the volumetric flow rate and C_{ad} (mg/l) is the adsorbed concentration.

The equilibrium uptake (q_{eq}, mg/g) based on the weight of fungal biomass can be calculated from the following equation:

$$q_{eq} = \frac{q_t - q_{t0}}{X} \quad (2)$$

where X (g) is the weight of fungal biomass in the immobilized fungal beads, q_t (mg) and q_{t0} (mg) are the total adsorbed 2,4-DCP based on the weight of the immobilized fungal beads and the weight of the blank Ca-alginate beads, respectively. All the values of q_{eq} in this study were calculated using Eq. (2).

3. Results and discussion

3.1. Effect of flow rate

The effect of flow rate on the biosorption of 2,4-DCP in the fixed-bed with bed depth of 22 cm was investigated. The flow rate was changed in the range of 1.0 ml/min, 1.5 ml/min, 2.0 ml/min, 2.5 ml/min and 3.0 ml/min, while the concentration of 2,4-DCP in influent was kept at 40.3 mg/l. The adsorption breakthrough curves obtained at different flow rates were shown in Fig. 1(A), and the breakthrough time (t_b, min), the equilibrium uptake (q_{eq}) and the total removal efficiency (R_t%) were given in Table 1. The results showed that the adsorption of 2,4-DCP on the immobilized fungal beads was strongly influenced by flow rate. All the breakthrough curves had a similar shape. The breakthrough curves shifted to the origin with increasing flow rate, and an earlier breakthrough time and saturation time were observed for a higher flow rate. Fig. 1(A) showed that 2,4-DCP concentration in the effluent increased rapidly after the breakthrough time; as the solution continued to flow, the fixed-bed became saturated with 2,4-DCP and 2,4-DCP concentration in the effluent approached the influent concentration. Both equilibrium uptake and total removal efficiency of 2,4-DCP decreased with the increasing flow rate, and their maximum values were obtained at the lowest flow rate of 1.0 ml/min (Table 1).

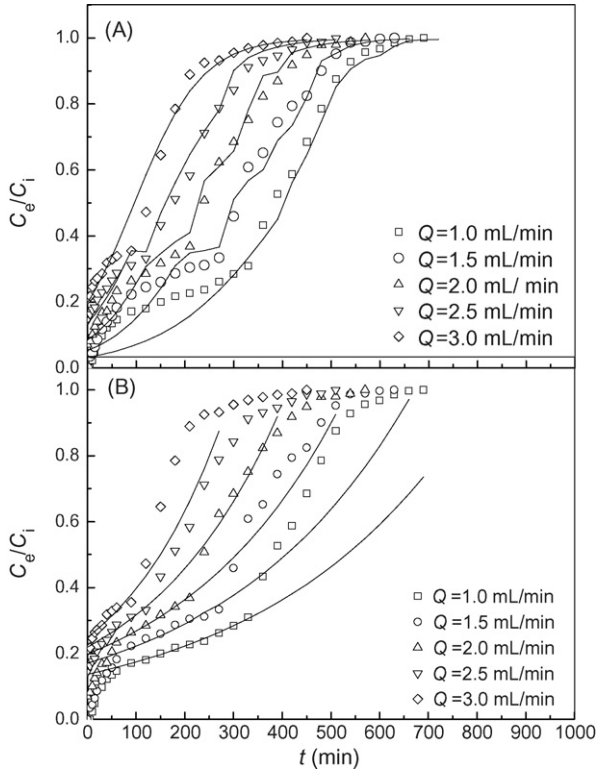

Fig. 1. Comparison between the measured and predicted breakthrough curves with the Thomas model (A) and the Bohart-Admas model (B) at various flow rates (symbols: experimental data; full lines: calculated from models; C_i = 40.3 mg/l, Z = 22 cm).

Table 1
The effects of flow rate (Q), influent concentration (C_i) and bed depth (Z) on the breakthrough time (t_b), equilibrium adsorption capacity (q_{eq}) and total removal efficiency of 2,4-DCP biosorption in the fixed-bed column

C_i (mg/l)	Q (ml/min)	Z (cm)	t_b (min)	q_{eq} (mg/g)	R (%)
20.9	1.0	22	420	5.2	72.6
40.3	1.0	22	330	9.0	66.4
40.3	1.5	22	270	7.9	42.9
40.3	2.0	22	210	7.5	34.1
40.3	2.5	22	120	6.9	27.6
40.3	3.0	22	90	5.8	22.3
59.6	1.0	22	210	11.3	59.5
80.4	1.0	22	90	12.2	52.1
40.4	1.0	15	240	9.0	66.4
40.2	1.0	26	390	9.0	66.3

The difference in the flow rates can result in important changes in the Reynolds numbers, and the Reynolds number increased with the increasing flow rate. At a higher Reynolds number, the residence time of the solute in the column was not long sufficient for the adsorption equilibrium to establish, the solution left the column before the equilibrium was achieved, resulting in an earlier breakthrough time. At a lower Reynolds number, the residence time in the column was longer, and the solute had sufficient time to interact with the surface of adsorbents. Similar results were obtained in the biosorption of phenol in continuous packed bed [16,17].

3.2. Effect of influent 2,4-DCP concentration

The breakthrough curves obtained at different influent concentrations (20–80 mg/l) and constant flow rate of 1.0 ml/min were shown in Fig. 2(A). As seen from Fig. 2(A), the breakthrough curves were dispersed, and the time required for the saturation of the immobilized beads was longer at a lower concentration of 2,4-DCP in influent. After breakpoint, the concentration of 2,4-DCP in effluent increased rapidly and finally approached the influent concentration. The equilibrium uptake of the immobilized fungal beads and the total removal efficiency related to the different influent concentration of 2,4-DCP were also compared in Table 1. The larger the influent concentration is, the smaller is the breakthrough time, and the larger is the equilibrium uptake. Although the equilibrium uptake of 2,4-DCP increased from 5.2 ± 0.5 mg/g to 12.2 ± 1.0 mg/g as the influent concentration was increased from 20.9 mg/l to 80.4 mg/l, the total removal efficiency showed an opposite trend.

The driving force for adsorption is the concentration difference between the solute on the adsorbent and the solute in the solution [22]. A higher concentration difference provides

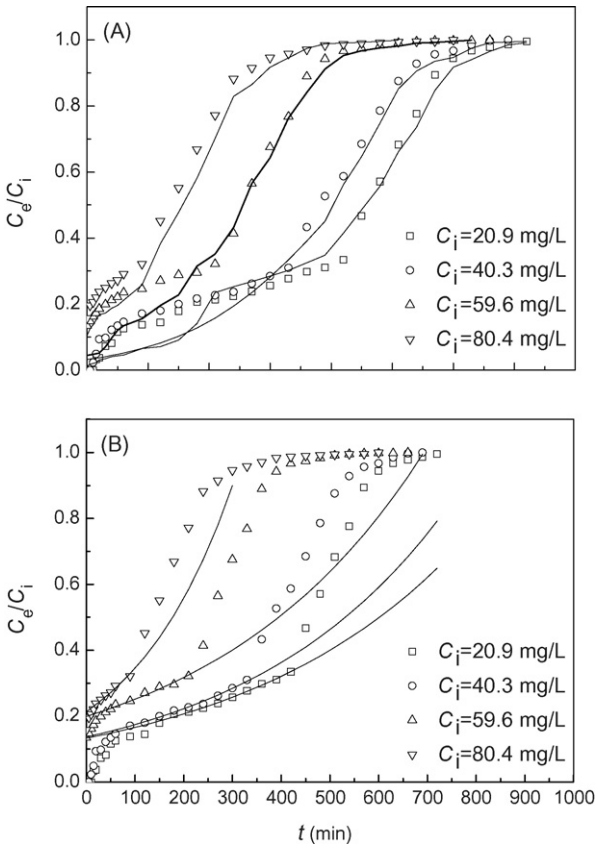

Fig. 2. Comparison between the measured and predicted breakthrough curves with the Thomas model (A) and the Bohart-Admas model (B) at various influent concentrations (symbols: experimental data; full lines: calculated from models; Q = 1.0 ml/min, Z = 22 cm).

a greater driving force for the adsorption process. That is to say, adsorption sites were quickly occupied by solute molecules at higher influent concentration, resulting in an earlier breakthrough. This may explain why a higher adsorption capacity was obtained in the column fed with a higher influent concentration of 2,4-DCP than that with a lower one.

The results from Fig. 2(A) and Table 1 indicated that the influent concentration of solute had obvious influence on the breakthrough time and adsorption capacity. The larger the influent concentration is, the shorter is the breakthrough time, and the larger is the equilibrium uptake.

3.3. Effect of bed depth

The adsorption capacities of fixed-bed column with bed depths of 15 cm, 22 cm and 26 cm were tested at a constant flow rate of 1.0 ml/min and influent concentration of 40 mg/l of 2,4-DCP. The breakthrough curves were illustrated in Fig. 3. The profiles tended to shift to the right as the bed depth increased. The breakthrough time was 240 min, 330 min and 390 min, respectively, at the bed depth of 15 cm, 22 cm and 26 cm (Table 1), suggesting that the breakthrough time increased with bed depth. This result could be explained by the fact that more adsorption sites were supplied for solute as the filled biomass increased. In addition, the equilibrium uptakes for 2,4-DCP at the three bed

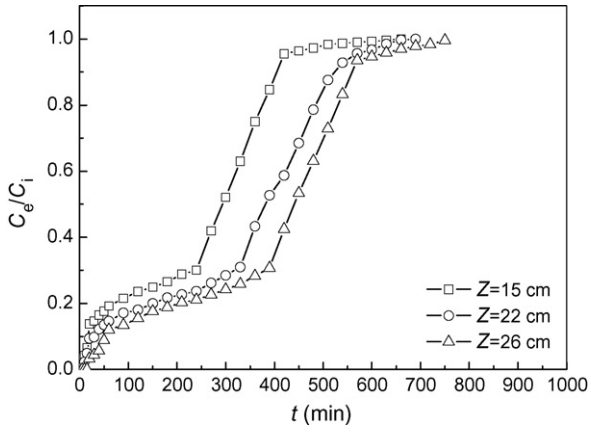

Fig. 3. Effect of bed depth on breakthrough curves of 2,4-DCP biosorption in the fixed-bed column (C_i = 40 mg/l, Q = 1.0 ml/min).

depths but with the identical flow rate and influent concentration were of a same level attributed to their same Reynolds numbers.

3.4. Modeling

Successful design of a column adsorption process requires prediction of the breakthrough curves and adsorption capacities under given operation conditions. The traditional mathematical models are based on the fundamental transport equation, the mass balance equation, the adsorption rate equation and the adsorption isotherm equation. All these equations usually require complex numerical methods to solve. Therefore, many simple empirical and semi-empirical mathematical models have been developed to model the breakthrough curves, such as the well-known Thomas model and Bohart-Admas model [9,12,16,17,19]. In general, these semi-empirical models are easier to use and more efficient compared with the use of full mechanistic models which are more complicated mathematically.

3.4.1. Application of the Thomas model

The Thomas model has the following form [23]:

$$\ln\left(\frac{C_i}{C_e}-1\right)=\frac{K_{Th}q_0X}{Q}-\frac{K_{Th}C_i}{Q}V_{eff} \quad (3)$$

where K_{Th} (ml/min mg) is the Thomas rate constant, q_0 (mg/g) is the maximum solid-phase concentration of solute, and V_{eff} is the volume of effluent. The values of K_{Th} and q_0 can be obtained from a plot of $\ln[(C_i/C_e)-1]$ against V_{eff} at a given flow rate and influent concentration.

The column data from the biosorption of 2,4-DCP by immobilized fungal beads were fitted to Eq. (3) to determine the Thomas rate constant (K_{Th}) and the maximum solid-phase concentration (q_0) from the slope and the intercept of the linearized Thomas equation plots [Fig. 4(A) and (B)]. The values of K_{Th}, q_0 and the correlation coefficients at all flow rates and influent concentrations studied were summarized in Table 2. As seen from Table 2, the values of K_{Th} and q_0 were influenced by both flow rate and influent concentration of 2,4-DCP. The maximum adsorption capacity (q_0) of the beads for 2,4-DCP was found

Table 2
Thomas model parameters and the comparison between the measured ($q_{0,exp}$) and predicted ($q_{0,cal}$) maximum adsorption capacity for 2,4-DCP biosorption on immobilized fungal beads in the fixed-bed column

C_i (mg/l)	Q (ml/min)	K_{Th} (ml/mg min)	$q_{0,cal}$ (mg/g)	$q_{0,exp}$ (mg/g)	R^2
20.9	1.0	0.456	4.5	5.2	0.987*
40.3	1.0	0.204	8.1	9.0	0.955*
40.3	1.5	0.287	7.3	7.9	0.948*
40.3	2.0	0.323	7.0	7.5	0.985*
40.3	2.5	0.347	6.5	6.9	0.988*
40.3	3.0	0.361	5.5	5.8	0.983*
59.6	1.0	0.127	11.6	11.3	0.996*
80.4	1.0	0.092	13.9	12.2	0.991*

* Model parameters estimated are statistically significant at 95% confidence level.

to decrease, but the Thomas rate constant (K_{Th}) increased with the increasing flow rate. As expected, the value of q_0 increased and the value of K_{Th} decreased with increasing influent concentration of 2,4-DCP. The experimental values in Table 2 also showed that at the flow rates and influent concentrations tested, the difference between the measured and predicted q_0 values was negligible. However, the linearity of Thomas equation was effective only for the relative concentration $(C_e/C_i) > 0.3$, and the linearity of Thomas equation did not exist for $(C_e/C_i) < 0.3$ (not shown in Fig. 4).

The breakthrough curves predicted with the Thomas model at different flow rates and different influent concentrations studied were shown in Figs. 1(A) and 2(A). Obviously, the breakthrough curves calculated from this model were in good agreement with experimental data for all flow rates and influent concentrations studied only in the range of $(C_e/C_i) > 0.3$, whereas a large discrepancy was found between the measured and predicted values for $(C_e/C_i) < 0.3$. Although the Thomas model was appropriate only for the column adsorption processes at $(C_e/C_i) > 0.3$, attributed to the nonlinearity of $\ln[(C_i/C_e) - 1]$ versus V_{eff} for $(C_e/C_i) < 0.3$, this model was able to give a good prediction of the maximum adsorption capacity for 2,4-DCP biosorption in the fixed-bed. The result that the Thomas model did not predict the initial part of the breakthrough curve well has also been reported by other researchers [24].

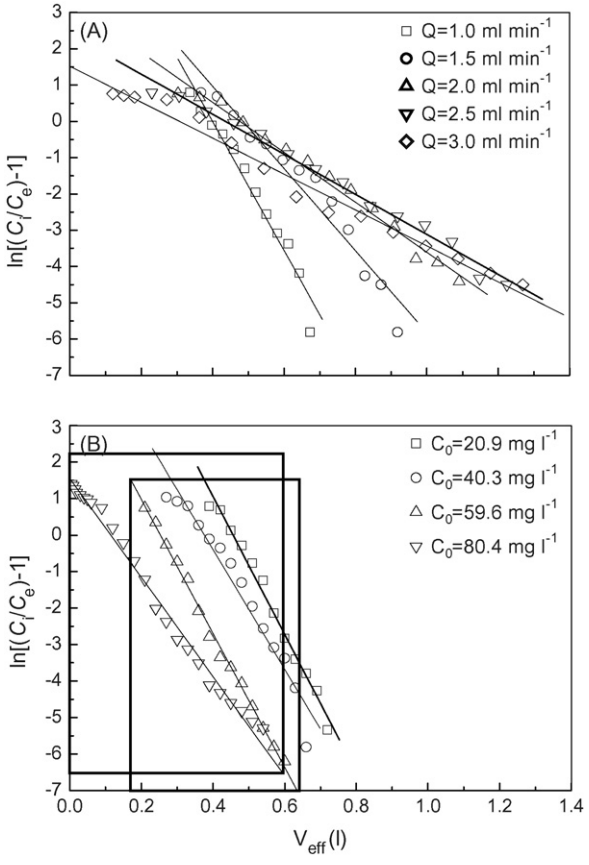

Fig. 4. Plots of $\ln[(C_i/C_e) - 1]$ vs. V_{eff} at various flow rates (A) and various influent concentrations (B).

In the Thomas model it is assumed that the external and internal diffusion is not the limiting step, and that Langmuir kinetics of adsorption–desorption is valid. In this case, no axial dispersion is derived with the adsorption. However, adsorption is usually controlled by interphase mass transfer and the effect of axial dispersion could not be neglected, especially at a low flow rate [16,17]. Such a discrepancy can result in errors when this model is used to predict column adsorption process, as seen in this study.

3.4.2. Application of the Bohart-Admas model

The Bohart-Admas model has the following form [25]:

$$\ln \frac{C_e}{C_i} = K_{AB} C_i t - K_{AB} N_0 \frac{Z}{U_0} \quad (4)$$

where K_{AB} is the kinetic constant (l/mg min), N_0 is the saturation concentration (mg/l), Z is bed depth (cm) and U_0 is the flow rate (cm/min). The characteristic parameters K_{AB} and N_0 can be determined from a plot of $\ln(C_e/C_i)$ against t at a given bed depth and flow rate.

The adsorption data of 2,4-DCP by immobilized fungal beads in the column were fitted to the Bohart-Admas model for different flow rate and influent concentration of 2,4-DCP studied [Fig. 5(A) and (B)]. The values of K_{AB} and N_0 calculated from the $\ln(C_e/C_i)$ versus t plots at all flow rates and influent concentrations studied were presented in Table 3 along with the correlation coefficients. As seen from Table 3, both the kinetic constant K_{AB} and maximum adsorption capacity N_0 were affected by flow rate and influent concentration of 2,4-DCP. The

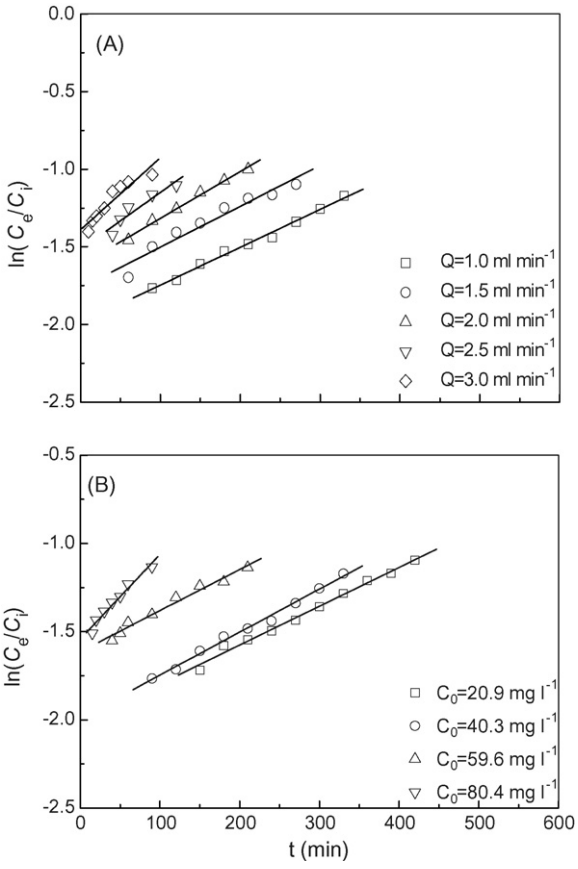

Fig. 5. Plots of $\ln(C_e/C_i)$ vs. t at various flow rates (A) and various influent concentrations (B).

values of K_{AB} increased with increasing flow rate and decreased with increasing influent concentration. As expected, the maximum adsorption capacity (N_0) decreased with increasing flow rate and increased with increasing influent concentration of 2,4-DCP. However, the linearity of Eq. (4) was effective only for the relative concentration $(C_e/C_i) < 0.3$, and the linearity of Eq. (4) did not exist for $(C_e/C_i) > 0.3$ (not shown in Fig. 5).

The breakthrough curves predicted from this model with respect to different flow rate and influent concentration tested were compared with the experimental breakthrough curves (Figs. 1(B) and 2(B)). It was clear that the Bohart-Admas model was valid only for the initial part of the breakthrough

Table 3
Bohart-Admas model parameters for 2,4-DCP biosorption on immobilized fungal beads in the fixed-bed column

C_i (mg/l)	Q (ml/min)	K_{AB} ($\times 10^5$ l/mg min)	N_0 (mg/l)	R^2
20.9	1.0	10.54	597.2	0.991*
40.3	1.0	6.06	985.2	0.992*
40.3	1.5	6.53	959.0	0.940*
40.3	2.0	7.50	935.1	0.992*
40.3	2.5	9.12	822.2	0.895*
40.3	3.0	11.55	757.5	0.883*
59.6	1.0	5.96	1143.5	0.975*
80.4	1.0	3.91	1329.1	0.968*

* Model parameters estimated are statistically significant at 95% confidence level.

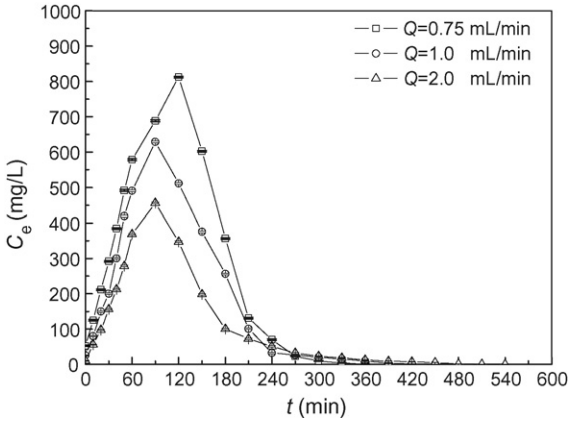

Fig. 6. Desorption curves for 2,4-DCP from the immobilized fungal beads using distilled water at various eluent flow rates ($C_i = 40.2$ mg/l, $Z = 22$ cm).

curves $(C_e/C_i) < 0.3$, whereas large discrepancies were found between the experimental and predicted curves for $(C_e/C_i) > 0.3$. This was attributed to the nonlinearity of $\ln(C_e/C_i)$ versus t for $(C_e/C_i) > 0.3$.

The Bohart-Admas model was originally established for the adsorption of the chlorine on charcoal [25]. In this model the adsorption rate is assumed to be proportional to both residual capacity of activated carbon and concentration of the adsorbing species. This model is often used for describing the initial part of the breakthrough curve [12,16]. Similarly, the application of this model in the prediction of 2,4-DCP biosorption process by immobilized fungal beads in column was also valid only for the initial part of the breakthrough curves with respect to flow rates and influent concentration of 2,4-DCP tested.

3.5. Adsorption/desorption cycles

Efficient elution of adsorbed solute from immobilized fungal beads in fixed-bed column is essential to ensure the reuse of beads for repeated adsorption/desorption cycles. Distilled water [26], $CaCl_2$ solution [27] and $NaNO_3$ solution [28] have been used to elute phenol and chlorophenols from biosorbents. In this study distilled water was chosen to desorb 2,4-DCP from the immobilized fungal beads as it did not cause any damages to the biosorbents.

Desorption curves, the plots of effluent concentration (C_e) versus elution time (t) for 2,4-DCP from the column at three flow rates, were given in Fig. 6. The adsorbed 2,4-DCP could be readily desorbed from the immobilized fungal beads in the column. All the curves showed a trend similar to other workers [8,10,18]. The majority of the adsorbed solute was desorbed in less than 300 min, 390 min and 480 min at flow rates of 0.75 ml/min, 1.0 ml/min and 2.0 ml/min, respectively. It was obvious that elution time increased with increasing flow rate of eluent, but similar desorption efficiencies ($D\%$) of $86.5 \pm 3.3\%$, $85.2 \pm 3.1\%$ and $84.3 \pm 3.4\%$ were obtained.

Then the column was fed with fresh solution of 2,4-DCP again to study the potential of reusing the immobilized fungal beads for the adsorption of 2,4-DCP. The reusability of immo-

Table 4
Results of adsorption/desorption cycle of 2,4-DCP in the fixed-bed column (Z = 22 cm; adsorption: C_i = 40.2 mg/l, Q = 1.0 ml/min; desorption: Q = 0.75 ml/min)

	Cycle number				
	1	2	3	4	5
Removal efficiency (%)	66.4	68.2	67.5	68.7	66.8
Desorption efficiency (%)	86.5	84.2	87.6	85.2	86.8

bilized fungal beads was studied in five adsorption/desorption cycles. The experimental results in Table 4 showed that the desorption operation of 2,4-DCP by distilled water from the immobilized fungal beads did not influence their adsorption capacity, and the immobilized beads could be used repeatedly in a continuous operation for 2,4-DCP removal from aqueous solutions.

3.6. Evaluation

Although the adsorption capacity of immobilized biomass of *P. chrysosporium* for 2,4-DCP is expected to be increased furthermore, this study demonstrates that the rapid adsorption, good mechanical stability of the immobilized fungal beads and simple desorption make the fungus a promising biosorbent as an alternative to other more costly materials. At the present time little is known about the biosorption behavior of chlorophenols from a synthetic medium or a real wastewater in a continuous-flow fixed-bed column. As a first step, the results of the present work might be able to provide useful information (e.g., kinetic parameters) for scaling up of utilization of immobilized *P. chrysosporium* for the biosorption of chlorophenols in real wastewaters. In addition, the modified models could be used for simulating the fixed-bed biosorption columns, and might be applicable to other multi-component systems which are employed to treat real wastewaters. However, it should be mentioned that further investigations are warranted to explore the utilization of immobilized biomass for the removal of chlorophenols from a real wastewater in a continuous-flow fixed-bed column and collect more information before this technique could be used at full-scale.

4. Conclusions

The biosorption of 2,4-DCP from aqueous solution by the immobilized *P. chrysosporium* biomass was investigated in a continuous-flow fixed-bed column. The experimental results showed that the flow rate, influent concentration of 2,4-DCP and bed depth were crucial parameters for the fixed-bed operation. The Thomas model were in good agreement with the experimental data only as the relative concentration (C_e/C_i) higher than 0.3. However, the Bohart-Admas model was limited to the initial part of the breakthrough curves with respect to all flow rates and influent concentrations of 2,4-DCP studied. The immobilized fungal beads could be reused in a continuous operation for the removal of 2,4-DCP from aqueous solutions using distilled water as eluent.

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