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Adsorptive Removal of Pentachlorophenol by *Anthracophyllum discolor* in a Fixed-Bed Column Reactor

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Abstract This study investigates pentachlorophenol (PCP) adsorption by the white-rot fungus *Anthracophyllum discolor* in a fixed-bed column reactor. PCP adsorption at different concentrations (20, 30, and 50 mg L^{-1}) and pH values (5.0, 5.5, and 6.0) was determined and modeled using the Thomas model. Fourier transform infrared spectroscopy (FTIR) was used to identify functional groups of biomass that may participate in the interaction of PCP. The biosorption capacity of *A. discolor* was pH-dependent, and the PCP adsorbed increased with the decrease in the pH solution. Acid pH values of the influent gave an increase in saturation time in all PCP concentrations. By contrast, the increase in PCP concentration caused that the binding sites were filled quickly, resulting in a decrease in saturation time. The Thomas model was found suitable for describing the entire dynamic of the column with respect to the PCP concentration and pH of the solution. FTIR results showed that amines, carboxylates, alkanes, and C–O groups might participate in the PCP adsorption on the biomass surface. It was concluded that *A. discolor* biomass was a good adsorbent for PCP removal from influent with mainly acidic pH.

Keywords Biosorption · Pentachlorophenol · *Anthracophyllum discolor* · Fixed-bed column · Thomas model

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1 Introduction

Pentachlorophenol (PCP) is a pollutant which has a significant impact on the ecosystem and human health due to its high toxicity. Taylor et al. (2005) demonstrated that human cell exposure to 10 μM PCP for 1 h caused a progressive loss (greater than 80%) of lytic function within the six following days. Also, Neilson et al. (1990) determined a PCP concentration of 17 μg L^{-1} for embryo–larvae mortality. It is for this reason that it has been listed as a priority pollutant by the United States Environmental Protection Agency (US-EPA). The US-EPA has set 1 μg L^{-1} as the maximum legal limit of this compound for drinking water (USEPA 2003), while the minimum objective of environmental quality for various types of water is 2 μg L^{-1}, according to EU legislation (Estevinho et al. 2008).

In order to remove this compound from wastewater, conventional methods such as activated sludge processes are ineffective in removing PCP. Furthermore, physical or chemical methods including adsorption (Leyva-Ramos et al. 2009) and advanced oxidation treatments (Tanjore and Viraraghavan 1994) are expensive and rather inefficient (Robinson et al. 2001). Therefore, alternative low-cost biotreatment processes are currently being considered, most of which are based on lignin-degrading fungi. In this context, several studies (Cea et al. 2010; Rubilar et al. 2007; Tortella et al. 2008) have demonstrated that the white-rot fungus *Anthracophyllum discolor* is capable of degrading a high PCP concentration, attributed to its enzymatic system composed principally of manganese peroxidase. Nevertheless, the PCP adsorption on dead biomass of *A. discolor* has been not evaluated. In this respect, literature reviews show that fungal cells and their components are extremely efficient in the biosorption of chlorophenols such as 2,4-dichlorophenol (Wu and Yu 2006, 2008), *o*-chlorophenol, *p*-chlorophenol (Denizli et al. 2005), and PCP (Mathialagan and Viraraghavan 2009).

Studies developed by Mathialagan and Viraraghavan (2009) demonstrated that biomass of *Aspergillus niger* was an excellent adsorbent for the removal of PCP from aqueous solutions. Also, Wu and Yu (2008) determined that the white-rot fungus *Phanerochaete chrysosporium* was effectively used in the adsorption of 2,4-dichlorophenol.

The evaluation of pollutant adsorption in biomass is often developed with dead biomass to avoid the degradation process and determine only the retention of pollutant in the biomass (Li et al. 2009; Mathialagan and Viraraghavan 2009; Pang et al. 2011). In addition, the use of dead microbial cells is more beneficial than live cell because the toxic metabolites could not be formed and, in addition to this, the preparation of culture conditions for pollutant removal is not required (Mathialagan and Viraraghavan 2009). Furthermore, dead and dried biomass can be stored for long periods at room temperature with little risk of putrefaction, making it easier to use and transport. Therefore, dead biomass of white-rot fungi represents a good alternative for use as a sorbent.

In general, the studies of PCP adsorption with biomass of white-rot fungi have been carried out in batch and only a limited number of studies have focused on kinetic models and the effect of pH on PCP biosorption by fungal biomass. Therefore, the main objective of this study was to evaluate PCP adsorption by *A. discolor* biomass in a fixed-bed column reactor. The effect of different pH values and initial PCP concentrations on the adsorption were evaluated. The Thomas model was applied to experimental data in order to describe the entire dynamic of the column reactor with respect to the PCP concentration and pH of the solution. Additionally, Fourier transform infrared spectroscopy (FTIR) spectroscopy was applied to biomass of *A. discolor* to identify functional groups of biomass that participate in the adsorption of PCP.

2 Materials and Methods

2.1 Microorganism

A. discolor sp4 was obtained from the Environmental Biotechnology Laboratory, Universidad de La Frontera (Temuco, Chile). The fungus was transferred from slant culture tubes (maintained at 4°C and subcultured every 6 months) to malt extract agar (MEA) plates and incubated at 30°C for 5–7 days before being used for inoculum preparation.

2.2 Preparation of Biomass Pellets

One hundred milliliters of modified Kirk medium (Valentin et al. 2007) were placed in Fernbach flasks and inoculated with five plugs (diameter 6 mm) taken from a 5 to 7 day-old MEA fungal plate and incubated at 30°C in darkness. After 7 days, culture broth was homogenized with a blender for 1 min and used as inoculum. Two milliliters of inoculum (1.5 mg L^{-1} dry weight) were transferred into Erlenmeyer flasks (500 mL) containing 100 ml of modified Kirk medium. Cultures were incubated at 30°C on an orbital shaker at 150 rpm for 8 days in order to obtain pellets 2 mm in diameter. The formed pellets were washed with distilled water and killed by autoclaving (104 kpa, 121°C) for 20 min.

2.3 Microscopic Examination of Biomass Pellets

Microphotographs were taken of biomass pellets using a scanning electron microscope (SEM) to determine the size and surface structure of the fungal pellet (Fomina and Gadd 2002; Pasparakis and Bouropoulos

2006). The pellets were submerged in glutaraldehyde (2.5% *v*/*v*) for 15 min and washed with 0.1 M phosphate buffer (pH 7.0). The samples were post-fixed in osmium tetroxide for 2 h. Then, the samples were dehydrated by immersion in ethanol through a 50–100% ascending series of ethanol in distilled water, being left for 15 min at each stage. The samples were deposited onto the sample holder, coated with gold and examined with a JEOL JSM-6380LV 314 SEM electron microscope.

2.4 Potentiometric Titration of the Cell Wall

Surface charge of the cell wall was evaluated by acid–base titration in a N_2 atmosphere, using 0.1 N KOH and 0.1 N HCl. Briefly, 20 pellets of biomass (20 mg dry weight) were placed in a vessel containing 100 mL of deionized water. The titrations were carried out by adding titrant at 0.2 mL increments with at least a 20-min reaction time between each addition to allow the pH to stabilize.

2.5 Preparation of PCP Solutions

A stock solution of 500 mg L^{-1} of PCP was prepared in NaOH 0.1 N. To evaluate the effect of the initial concentration of PCP on the adsorption, three solutions of 20, 30, and 50 mg L^{-1} were prepared in distilled water by appropriately diluting the stock solutions. To evaluate the effect of pH on PCP adsorption, NaOH or H_2SO_4 (0.1 N) was used to set the pH value of each solution before being prepared. The pH values were: pH 5 (for the solution of 20 mg L^{-1} of PCP) pH 5.5 (for the solution of 20, 30, and 50 mg $L^{-1}$of PCP) and pH 6.0 (for the solution of 20, 30, and 50 mg $L^{-1}$of PCP).

2.6 Continuous Flow Adsorption Experiment in Fixed-Bed Column

Studies of biosorption were developed in two column reactors comprised of glass columns (1 cm internal diameter and 40 cm high) packed with 0.5 g dry weight of biomass in the form of pellets. Glass wool was placed both at the top and bottom of the column to prevent preferential flow and loss of mycelium, respectively. The PCP solution was held in a 4-L glass flask protected from light and kept at 25°C by circulating water through a thermoregulated bath. The solution was passed through the column in down-flow mode at a fixed flow rate of 1 mL min^{-1} by means of a peristaltic pump. Samples were collected from the effluent at pre-determined time intervals and the PCP residual concentration was analyzed until a constant effluent concentration of PCP was obtained. With the results obtained, breakthrough curves were determined for the PCP adsorption. The breakpoint was determined at C_e/C_i=0.30 and the saturation point at C_e/C_i=0.99, where C_e is the PCP concentration (in milligrams per liter) in the effluent and C_i is the PCP concentration (in milligrams per liter) in the influent.

2.7 PCP Extraction from Biomass Pellets

After sorption, PCP extraction from biomass was performed. For this, all the used biomass was placed in 100 mL Erlenmeyer flasks containing 20 mL of a hexane/acetone mixture (1:1 *v*/*v*) and shaken for 2 h at 200 rpm. Then, the solution was centrifuged (2,500 rpm for 10 min) and filtered using a 0.2-μm PTFS membrane (Millipore). An aliquot (1 mL) of the organic phase was taken for high performance liquid chromatography (HPLC) analysis. The average extraction efficiency was 95±5%. Every assay was conducted in duplicate and the mean value is represented by one data point in the figures. The deviation of the two points from the mean was found to be within ±5%.

2.8 Quantitative Determination of PCP

The concentration of PCP in the solution and from biomass extraction were determined with an HPLC equipped with a Merck-Hitachi L-7100 pump, a Rheodyne 7725 injector with a 20-μL loop, a Merck-Hitachi L-7455 diode array detector operating at 215 nm, and a Hitachi D-7000 data processor. A Lichrosphere 60 RP select B 250×4 mm column of 5 μm particle size with a LichroCART 4–4 guard column (Merck) was used. The mobile phase consisted of acetonitrile and phosphoric acid (1% aqueous solution) 1:1 (*v*/*v*) with a flow rate of 1 mL min^{-1} (PCP retention time was 12 min). Instrument calibrations and quantification were performed against the pure reference standard (0.05–5 mg L^{-1}). The procedure described was checked for recovery (which

ranged from 97% to 100%). The detection limit was 0.03 mg L^{-1}, considering the noise-to-signal ratio greater than 2.

2.9 Fourier Transforms Infrared Spectroscopy

The pellets of *A. discolor* were characterized before and after adsorption of PCP by FTIR spectroscopy studies. The biomass pellets were dried at 60°C for 24 h. Samples of 0.1 mg were mixed with 100 mg of KBr (FTIR grade, Aldrich Chemical Co., Milwaukee, WI, USA). The FTIR spectra were obtained using a Perkin Tensor 27.

2.10 Modeling of Column Adsorption

The Thomas model (Thomas 1944) was used to calculate the adsorption rate and the solid-phase concentration of PCP from continuous mode studies. The nonlinear form of the Thomas model can be expressed as follows:

$$\frac{C_e}{C_i} = \frac{1}{1 + \exp[\mathrm{Kt}(q_0 \times m - C_i \times V)/F]} \quad (1)$$

where C_e is the effluent PCP concentration (in milligrams per liter), C_i is the initial PCP concentration (in milligrams per liter) in the influent, K_t is the Thomas model rate constant (liters per minute per milligram), q_0 is the maximum PCP adsorption capacity (in milligrams per gram), m is the mass of adsorbent (in grams), V is the effluent volume (in liters), and F is the flow rate (in milliliters per minute). The constants K_t and q_0 were determined from the linear form of the Thomas model, which can be expressed as follows:

$$ln\left(\frac{C_i}{C_e} - 1\right) = \frac{Kt \times q_0 \times m}{F} - \frac{Kt \times C_i}{F} \times V \quad (2)$$

The experimental uptake ($q_{0,exp}$, in milligrams per gram) was measured from the following equation:

$$qo, \exp = \frac{qt}{X} \quad (3)$$

where X (in grams) is the weight of fungal biomass and q_t (in milligrams) is the total PCP adsorbed, determined at the end of the experiment by PCP extraction of biomass.

Breakthrough curves experimentally determined and predicted using the Thomas model were compared.

3 Results and Discussion

3.1 Morphology of the Pellets

The biosorption of PCP in the fixed-bed column reactor was evaluated with pellets of *A. discolor* of approximately 2 mm in size (Fig. 1). Figure 1a shows a general view of the pellet: a stable sphere of irregular surface composed of hyphal agglomeration formed by the effect of agitation during cultivation. Figure 1b is an image of the surface structure of the pellet under 400-fold magnification. The image shows the irregularly intertwined filamentous hyphae that form the pellet.

Fungal growth in pellets is the most favorable morphology for industrial processes because it reduces medium viscosity and allows the possibility of biomass reuse and thereby continuous operation of the process (Lin et al. 2008; Žnidaršic and Pavko 2001).

The biosorption studies were performed with dead biomass of *A. discolor* because it does not require a continuous supply of nutrients, the toxicity of PCP would not affect the fungal biomass and this could

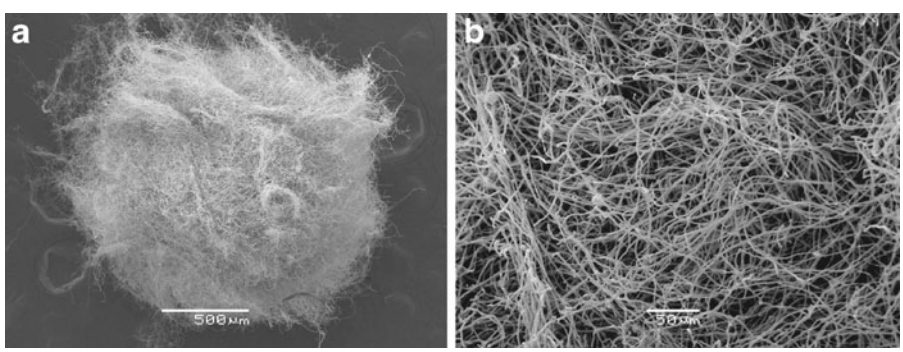

Fig. 1 SEM images of pellets of *A. discolor*: amplified 4 times (**a**) and amplified 400 times (**b**)

eventually be reused for new cycles of adsorption. In this sense, studies performed by Denizli et al. (2005) showed that dead *Pleurotus sajor caju* biomass could be used repeatedly (five adsorption/desorption cycles) for chlorophenol removal from aqueous solutions without noticeable loss of its adsorption capacity.

3.2 Effect of PCP Concentration and pH of Influent on PCP Biosorption in a Continuous Fixed-Bed Column Reactor

The effect of initial PCP concentration and pH of influent on the biosorption of PCP was investigated in a continuous fixed-bed column packed with *A. discolor* pellets. The adsorption breakthrough curves obtained with 20 mg L^{-1} of PCP at different pH values are shown in Fig. 2. The column with influent at pH 6.0 was rapidly saturated at 270 min (corresponding to 0.266 L), showing a lower adsorption capacity for the contaminant; by contrast, the column fed with influent at pH 5.5 and 5.0 were saturated after 510 (0.501 L) and 1,200 (1.187 L)min, respectively. In Fig. 2, it is clearly stated that the total area under the breakthrough curve of influent at pH 5.0 is much higher than those at pH 5.5 and 6.0, demonstrating a higher affinity of PCP for *A. discolor* biomass under these experimental condition.

The PCP adsorption was affected by the pH because it affects the ionization state of PCP and the net charge of the fungal cell wall (Radhika and Palanivelu 2006). In this sense, the net charge of the fungal wall was determined in order to evaluate its effect on PCP adsorption (Fig. 3). At pH 5.0, the net charge of the

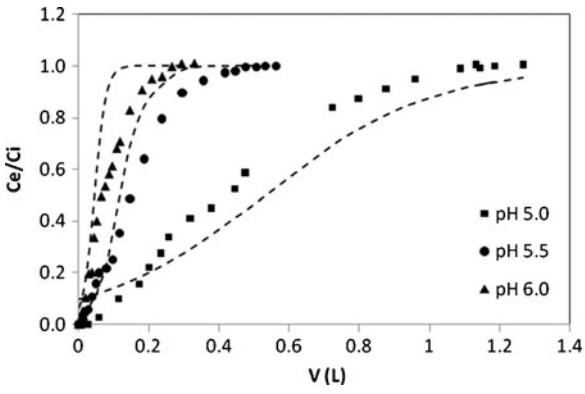

Fig. 2 Comparison of the experimental and predicted (Thomas model) breakthrough curves of PCP adsorption at pH 5.0, 5.5, and 6.0 (*Symbol*, experimental data; *discontinued line*, calculated from model; C_i—20 mg L^{-1}; F—1 mL min^{-1})

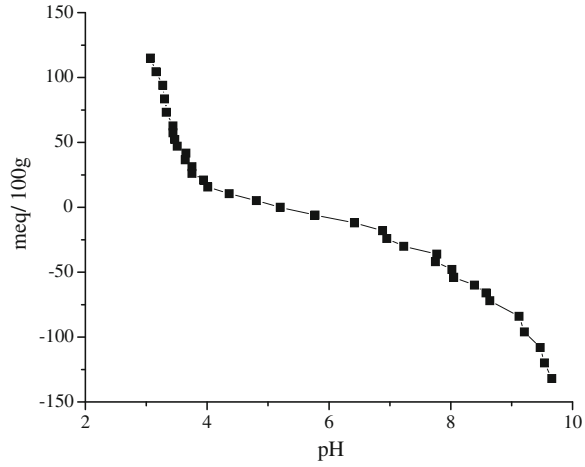

Fig. 3 Potentiometric titration of fungal cell wall in deionized water at 25±1°C

fungal wall was positive with 52 meq/100 g, whereas at pH 5.5 and 6.0, the net charge was negative with −57 and −112 meq/100 g of pellet. Mathialagan and Viraraghavan (2009) demonstrated that under neutral and basic pH conditions, the biomass of bacteria and fungi had a net negative charge and PCP was entirely in anionic form. Therefore, electrostatic repulsion between the biomass surface and anionic PCP may lead to a lower adsorption. By contrast, at low pH values, the biosorbent could be protonated (Aksu and Yener 2001; Mathialagan and Viraraghavan 2009) and the PCP molecule could be adsorbed by electrostatic interaction. Additionally, as the pH of the PCP solution is close to the pK_a of the pure compound, the adsorption increases due to the hydrophobicity of its neutral form (Cea et al. 2005).

The linearity of the Thomas equation of the curves with 30 and 50 mg L^{-1} of PCP was effective only for the relative concentration (C_e/C_i) >0.3 and <0.9 (not shown in Fig. 3) due to the nonlinearity of $\ln[(C_i/C_e)^{-1}]$ versus V for (C_e/C_i) >0.9. However, this model had a good prediction for adsorptive PCP in fixed-bed column reactor.

The effect of PCP initial concentration in the adsorption breakthrough curves was not evaluated a pH 5.0 due to the decreasing water solubility of PCP and at concentrations higher than 20 mg L^{-1} this compound can be found precipitated. Studies performed by Arcand et al. (1995) demonstrated that the solubility of PCP is further pH-dependent, being more soluble in alkaline pH.

In the breakthrough curves with 30 and 50 mg L^{-1} of PCP at pH 5.5 and 6.0, the highest amount of PCP

adsorbed was observed at pH 5.5 (Fig. 4). The column with influent of 30 mg L^{-1} of PCP at pH 5.5 was saturated at 380 min, corresponding to an influent volume of 0.389 L, whereas for the column fed at pH 6.0 saturation was at 200 min, the influent volume was 0.211 L (Fig. 4a). The results of the adsorption breakthrough curves obtained with 50 mg L^{-1} of PCP showed that for the column fed with influent at pH 5.5, the saturation was at 280 min (0.286 L), while at pH 6.0, it was at 200 min (0.190 L), respectively (Fig. 4b).

In comparing the two concentrations, it was observed that when the initial PCP concentration increased, the breakthrough became steeper and the breakthrough volume decreased. This indicates that binding sites become saturated more quickly at higher PCP concentrations, which is also confirmed by the earlier breakthrough time obtained.

3.3 Characterization of the Surface by FTIR

FTIR spectroscopy was used to obtain information on the nature of possible interactions between PCP and fungal biomass. The spectra were obtained at 32 scans/min^{-1} at a resolution of 2 cm^{-1} and expressed in transmittance in the 4,000–400 cm^{-1} range (Fig. 5). The IR bands of the spectrum for biomass before PCP adsorption were named as "A," "B," and so on. The IR bands after PCP adsorption were designated with the same letter but with a numerical subscript (A_1, B_2, etc.). As shown in Fig. 5, both spectra have a similar pattern with ten peaks observed. An intense peak at 3,425 cm^{-1} (named A and A1) is likely due to O–H and N–H stretching vibrations, indicating the presence of carboxylic groups and also representing stretching of the N–H amine groups. The peaks at 2,923 (named B and B1), 2,854 (C and C1), and 1,458 (F) cm^{-1} were due to C–H stretching vibrations of alkane groups ($–CH_2$) and deformation vibrations of methyl groups ($–CH_3$). The peaks at 1,645 (D), 1,641 (D_1), 1,550 (E), and 1,552 (E_1) cm^{-1} were due to the stretching vibrations C=O of carboxylate ($–COO^-$) and bending vibrations of –NH groups of chitin on the cell wall structure of the fungal biomass (Bayramoğlu and Arica 2008). Peaks at 1,320 cm^{-1} (H and H_1) corresponded to the C–O stretching vibrations of carboxylic acid derivatives. Bands at 1,244 (I and I_1), 1,039 (J), and 1,035 (J_1) cm^{-1} were due to the C–O stretching vibrations of ketones, aldehydes, lactones, or carboxyl groups.

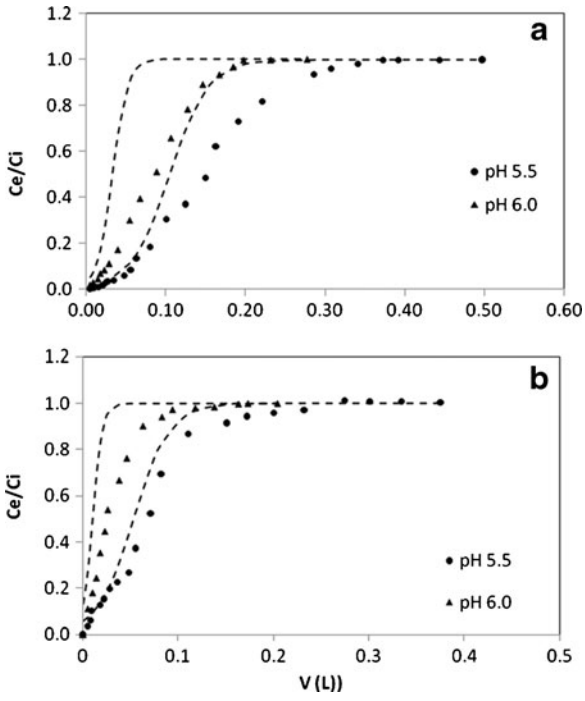

Fig. 4 Comparison of the experimental and predicted (Thomas model) breakthrough curves of PCP biosorption with 30 (**a**) and 50 (**b**) mg L^{-1} of PCP at pH 5.5 and 6.0 (*Symbol*, experimental data; *discontinued line*, calculated from model; *F*—1 mL min^{-1})

Some shifts in wave numbers from 1,641 (D_1) to 1,645 (D), 1,550 (E) to 1,552 (E_1) cm^{-1}, and 1,039 (J) to 1,035 (J_1) cm^{-1} as well as the omission of bands at 1,458 (F) cm^{-1} in the biomass after PCP adsorption were observed. This suggests that amines, carboxylates, alkanes, and C–O groups might participate in PCP adsorption on the surface of *A. discolor*, through different interactions such as charge transfer, hydrophobic partitioning of neutral species of PCP to cell wall, and hydrogen bonds with carboxylate or amine groups of the cell wall.

3.4 Application of the Thomas Model

The Thomas model was applied because it assumes plug flow behavior in the fixed-bed column. This model uses the Langmuir isotherm for equilibrium and second-order reversible reaction kinetics (Thomas 1944). Also, it is fitting for adsorption processes where the external and internal diffusion limitations are absent. Studies developed by Ahmad and Hameed (2010) and Wu and

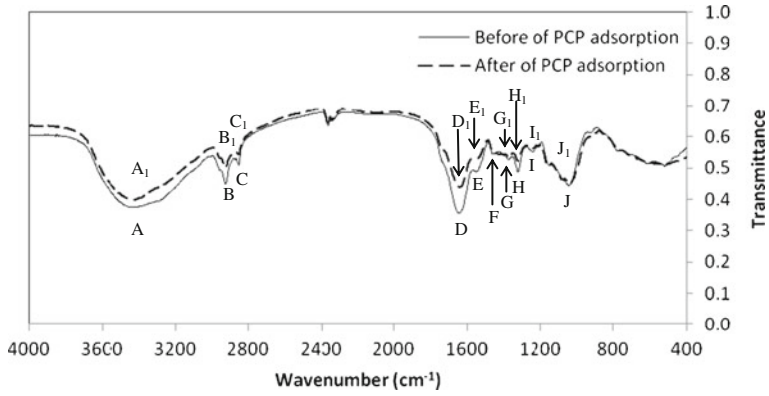

Fig. 5 Spectrum of FTIR analysis from biomass of *A. discolor*

Yu (2008) have demonstrated that the Thomas model is a suitable method for determining the adsorption process in columns where the external and internal diffusions will not be the limiting step.

The comparison of the experimentally and Thomas model-predicted breakthrough curves is shown in Figs. 2 and 4. The linearity of the Thomas equation at different initial pH and PCP concentrations was effectively

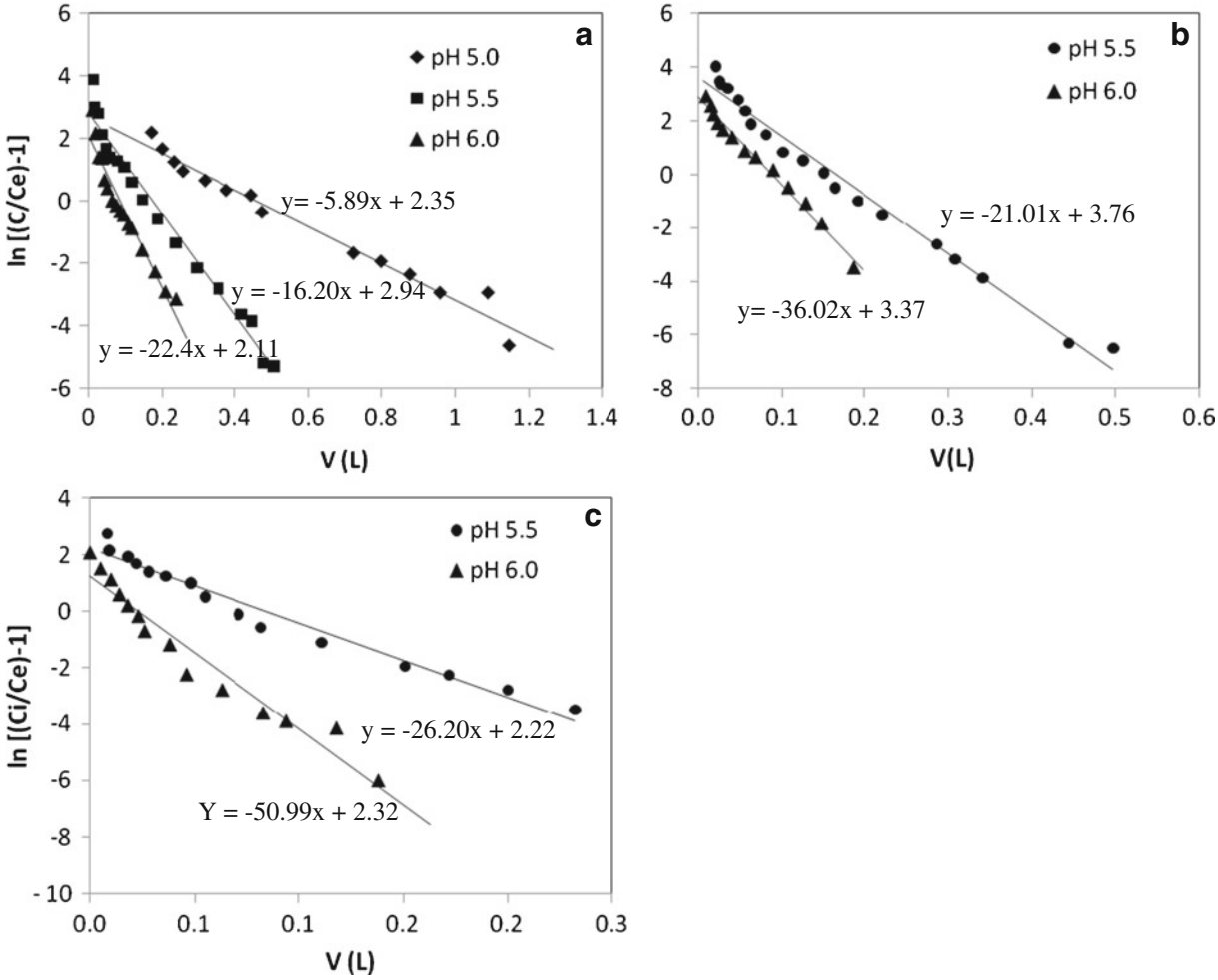

Fig. 6 Linearity of Thomas equation ($\ln[(C_i/C_e)-1]$ versus V) at 20 (**a**), 30 (**b**), and 50 (**c**) mg L^{-1} and different pH

Table 1 Thomas model parameter and the comparison between the measure ($q_{0,exp}$) and predicted ($q_{0,cal}$) maximum for PCP biosorption on *A. discolor* in continuous fixed-bed column reactor

Initial PCP concentration (mg L^{-1})	pH	q_{0exp} (mg g^{-1})	PCP adsorption (%)	$q_{0,cal}$ (mg g^{-1})	K_t (mL min^{-1} mg^{-1})	r^2
20	5.0	20.48±2.43	50.29±4.35	20.22±3.43	0.23±0.02	0.972
20	5.5	4.56±0.15	22.26±1.22	4.09±0.76	1.44±0.03	0.974
20	6.0	1.67±0.12	13.95±0.98	1.39±0.03	3.05±0.08	0.937
30	5.5	5.82±0.65	21.92±2.12	5.71±0.07	1.37±0.02	0.983
30	6.0	2.39±0.23	14.93±0.98	1.82±0.08	4.11±0.12	0.986
50	5.5	7.85±0.98	23.65±1.78	5.27±0.21	1.05±0.8	0.968
50	6.0	3.33±0.45	17.33±1.01	1.04±0.34	4.85±0.52	0.947

developed for the relative concentration (C_e/C_i) experimentally obtained (Fig. 6). In general, good fits were obtained in all cases with correlation coefficients ranging from 0.937 to 0.986 (Table 1). From Table 1, it can be seen that the value of the kinetic constant was influenced by PCP concentration and pH solution.

Table 1 shows the comparison of the Thomas equation coefficients and measurements of PCP adsorption on fungal biomass in a continuous fixed-bed column reactor. Adsorption data obtained from the Thomas model indicated that the equilibrium uptake q_0 of the adsorbent (milligrams per gram) increased and the rate constant K_t (milliliters per minute per milligrams) decreased when the pH of the influent decreased. As seen in Table 1, for the column fed with a PCP concentration of 20 mg L^{-1}, the measure maximums for PCP biosorptions on the fungal biomass ($q_{o,exp}$) were 20.48, 4.56, and 1.67 mg g^{-1}, which were recorded in columns with an initial pH solution of 5.0, 5.5, and 6.0, respectively, and these were similar to the predicted maximum for PCP biosorption on biomass ($q_{0,\ cal}$). The same behavior occurred at pH 5.5 and 6.0. As was explained previously, this effect may be due to the hydrophobicity of PCP at pH near pKa in its neutral form, increasing the PCP adsorption on fungal biomass.

In the same way, the measure and predicted maximum PCP adsorption capacity ($q_{o,exp}$, $q_{o,cal}$) corroborates that the higher initial PCP concentration increased the PCP adsorption. As shown in Table 1, for the column fed with influent at pH 5.5, the $q_{o,exp}$ was 4.56, 5.82, and 7.85 mg g^{-1} for initial PCP concentrations of 20, 30, and 50 mg L^{-1}, respectively. A similar effect occurred at 30 and 50 mg L^{-1} at pH 6.0.

A different effect demonstrated the rate constant (K_t), which decreases when the initial pH solution decreases. The same effect behavior was observed in the PCP concentration, with the K_t being higher at higher initial PCP concentrations.

Therefore, the results presented in Table 1 demonstrate that the best pH condition for the biosorption of PCP by *A. discolor* in a continuous fixed-bed column was pH 5.0, where the PCP adsorption was 50.29%.

4 Conclusions

Some general, promising conclusions may be derived from the results obtained here:

1. The PCP biosorption by *A. discolor* biomass in a fixed-bed column reactor was pH-dependent, and the PCP adsorption was higher and the time required longer for saturation at pH 5.0 than at pH 5.5 and 6.0.
2. The influent concentration in the column affected the breakthrough curve because the increase in initial PCP concentration led to a faster filling of the binding sites, resulting in a decrease in breakthrough and equilibrium time.
3. The results demonstrated that different functional groups, such as amines, carboxylates, alkanes, and C–O groups could participate in PCP adsorption on the *A. discolor* biomass.

Finally, *A. discolor* biomass may represent a good natural sorbent for PCP from aqueous solutions.

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References

Ahmad, A. A., & Hameed, B. H. (2010). Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *Journal of Hazardous Materials, 175*, 298–303. doi:10.1016/j.jhazmat.2009.10.003.

Aksu, Z., & Yener, J. (2001). A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents. *Waste Management, 21*, 695–702. doi:10.1016/S0956-053X(01)00006-X.

Arcand, Y., Hawari, J., & Guiot, S. (1995). Solubility of pentachlorophenol in aqueous solutions: The pH effect. *Water Research, 29*, 131–136. doi:10.1016/0043-1354(94)E0104-E.

Bayramoğlu, G., & Arica, M. Y. (2008). Removal of heavy mercury(II), cadmium(II) and zinc(II) metal ions by live and heat inactivated *Lentinus edodes* pellets. *Chemical Engineering Journal, 143*, 133–140. doi:10.1016/j.cej.2008.01.002.

Cea, M., Seaman, J. C., Jara, A., Mora, M. L., & Diez, M. C. (2005). Describing chlorophenol sorption on variable-charge soil using the triple-layer model. *Journal of Colloid and Interface Science, 292*, 171–178. doi:10.1016/j.jcis.2005.05.074.

Cea, M., Jorquera, M., Rubilar, O., Langer, H., Tortella, G., & Diez, M. C. (2010). Bioremediation of soil contaminated with pentachlorophenol by *Anthracophyllum discolor* and its effect on soil microbial community. *Journal of Hazardous Materials, 181*, 315–323. doi:10.1016/j.jhazmat.2010.05.013.

Denizli, A., Cihangir, N., Tüzmen, N., & Alsancak, G. (2005). Removal of chlorophenol from aquatic system using the dried and dead fungus *Pleurotus sajor caju*. *Bioresource Technology, 96*, 59–62. doi:10.1016/j.biortech.2003.11.029.

U.S. Environmental Protection Agency (2003). Environmental pollution and disease: links between exposure and health outcomes. Available on U.S. EPA web site at http://www.epa.gov/indicators/roe/pdf/tdHealth4-1.pdf

Estevinho, B. N., Ribeiro, E., Alves, A., & Santos, L. (2008). A preliminary feasibility study for pentachlorophenol column sorption by almond shell residues. *Chemical Engineering Journal, 136*, 188–194. doi:10.1016/j.cej.2007.03.081.

Fomina, G., & Gadd, G. (2002). Influence of clay minerals on the morphology of fungal pellets. *Mycological Research, 106*, 107–117. doi:10.1017/S0953756201004786.

Leyva-Ramos, R., Bernal-Jacome, L. A., Mendoza-Barron, J., & Hernandez-Orta, M. M. G. (2009). Kinetic modeling of pentachlorophenol adsorption onto granular activated carbon. *Taiwan Institute of Chemical Engineers, 40*, 622–629. doi:10.1016/j.jtice.2009.05.006.

Li, X., Xu, Q., Han, G., Zhu, W., Chen, Z., He, X., & Tian, X. (2009). Equilibrium and kinetics studies of cooper(II) removal by three species of dead fungal biomasses. *Journal of Hazardous Materials, 165*, 469–474. doi:10.1016/j.hazamat.2008.10.013.

Lin, Y., Liao, W., & Chen, S. (2008). Study of pellet formation of filamentous fungi *Rhizopus oryzae* using a multiple logistic regression model. *Biotechnology and Bioengineering, 99*, 117–128. doi:10.1002/bit.21531.

Mathialagan, T., & Viraraghavan, T. (2009). Biosorption of pentachlorophenol from aqueous solutions by a fungal biomass. *Bioresource Technology, 100*, 549–558. doi:10.1016/j.biortech.2008.06.054.

Neilson, A. H., Allard, S. A., Hynning, P. A., Remberger, M., & Viktor, T. (1990). The environmental fate of chlorophenolic constituents of bleachery effluents. *Tappi Journal, 73*, 239–247.

Pang, C., Liu, Y., Cao, X., Li, M., Huang, G., Hua, R., Wang, C., Liu, Y., & An, X. (2011). Biosorption of uranium(VI) from aqueous solution by dead fungal biomass of *Penicillium citrinum*. *Chemical Engineering Journal, 170*, 1–6. doi:10.1016/j.cej.2010.10.068.

Pasparakis, G., & Bouropoulos, N. (2006). Swelling studies and in vitro release of verapamil from calcium alginate and calcium alginate–chitosan beads. *International Journal of Pharmaceutics, 323*, 34–42. doi:10.1016/j.ijpharm.2006.05.054.

Radhika, M., & Palanivelu, K. (2006). Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent—Kinetics and isotherm analysis. *Journal Hazardous Material, B138*, 116–124. doi:10.1016/j.jhazmat.2006.05.045.

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology, 77*, 247–255. doi:10.1016/j.jhazmat.2006.05.045.

Rubilar, O., Feijoo, G., Diez, C., Lu-Chau, T., Moreira, M. T., & Lema, J. (2007). Biodegradation of pentachlorophenol in soil slurry cultures by *Bjerkandera adusta* and *Anthracophyllum discolor*. *Industrial and Engineering Chemistry Research, 46*, 6744–675. doi:10.1021/ie061678b.

Tanjore, S., & Viraraghavan, T. (1994). Pentachlorophenol-water pollution impacts and removal technologies. *International Journal of Environmental Studies, 45*, 155–164. doi:10.1007/s11270-007-9384-2.

Taylor, T. R., Tucker, T., & Whalen, M. M. (2005). Persistent inhibition of human natural killer cell function by ziram and pentachlorophenol. *Environmental Toxicology, 20*, 418–424. doi:10.1002/tox.20127.

Thomas, H. C. (1944). Heterogeneous ion exchange in a flowing system. *Journal of the American Chemical Society, 66*, 1664–1666. doi:10.1021/ja01238a017.

Tortella, G. R., Rubilar, O., Gianfreda, L., Valenzuela, E., & Diez, M. C. (2008). Enzymatic characterization of Chilean native wood-rotting fungi for potential use in the bioremediation of polluted environments with chlorophenols. *World Journal of Microbiology and Biotechnology, 24*, 2805–2818. doi:10.1007/s11274-008-9810-7.

Valentin, L., Lu-Chau, T. A., Lopez, C., Feijoo, G., Moreira, M. T., & Lema, J. M. (2007). Biodegradation of dibenzothiophene, fluoranthene, pyrene and chrysene in a soil slurry reactor by the white-rot fungus Bjerkandera sp. BOS55. *Process Biochemistry, 42*, 641–648. doi:10.1021/ja01238a017.

Wu, J., & Yu, H. (2006). Biosorption of 2,4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: Isotherms, kinetics and thermodynamics. *Journal Hazardous Material, B137*, 498–508. doi:10.1016/j.jhazmat.2006.02.026.

Wu, J., & Yu, H. (2008). Biosorption of 2,4-dichlorophenol from aqueous solution by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column. *Chemical Engineering Journal, 138*, 128–135. doi:10.1016/j.cej.2007.05.051.

Žnidaršic, P., & Pavko, A. (2001). The morphology of filamentous fungi in submerged cultivations as a bioprocess parameter. *Food Technology and Biotechnology, 39*, 237–252. doi:10.1016/j.cej.2007.05.051.