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RESEARCH ARTICLE

Use of non-living lyophilized *Phanerochaete chrysosporium* cultivated in various media for phenol removal

Tímea Pernyeszi[1,2] · Viktor Farkas[1,2] · Attila Felinger[1,2] · Borbála Boros[1,2] · Imre Dékány[3,4]

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Abstract

The biosorption of phenol on non-living lyophilized mycelial pellets of *Phanerochaete chrysosporium* cultivated in liquid medium of various compositions was studied in batch biosorption system. The fungal cell surfaces were characterized by FTIR spectroscopy and specific surface charge determination. The sorption kinetics and equilibrium were evaluated using linear and non-linear regression. For adsorption equilibrium, a comparative evaluation is also presented using non-linear least-square estimation and linearization of the Langmuir and anti-Langmuir equations. The presence of mineral and vitamin materials in the liquid medium enhanced the adsorption capacity of fungal biomass for phenol. At optimum pH 5–6, the values of specific surface charge were 0.023 and 0.069 meq g^{-1} for various cultivations, and the maximum amounts of phenol can be adsorbed at these pH values. The maximum adsorbed phenol amounts by cells cultivated in simple and complex media were 4.53 and 13.48 mg g^{-1}, respectively, at an initial phenol concentration of 100 mg l^{-1}.

Keywords Phenol · *Phanerochaete chrysosporium* · Cultivation · Heat and pressure treatment · Lyophilization · Biosorption

Introduction

Phenols and derivatives are long half-life pollutants frequently found in industrial effluents and wastewaters (Antizar-Ladislao and Galil 2004; Thawornchaisit and Pakulanon 2007). For the removal of phenols from contaminated water biodegradation, thermal decomposition, adsorption, and liquid-liquid extraction are often used. Thermal decomposition and liquid-liquid extraction can be used to treat wastewater with concentrations of phenol above 3000 mg l^{-1} (Portela et al. 2001; Jiang et al. 2003). Nevertheless, a disadvantage of biodegradation is that microorganisms cannot survive in the

Highlights

?• Enhanced adsorption capacity of lyophilized *Phanerochaete chrysosporium* for phenol
- Relation between cell surface charge depending on pH and adsorption process
- Kinetics and equilibria is evaluated by non-linear least-square estimation
- Langmuir and anti-Langmuir models exhibit a good fit to the adsorption equilibria

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✉ Tímea Pernyeszi
ptimea@gamma.ttk.pte.hu

[1] Department of Analytical and Environmental Chemistry, Faculty of Sciences, University of Pécs, Ifjúság útja. 6., Pécs 7624, Hungary

[2] Environmental Analytical and Geoanalytical Research Group, Szentágothai Research Center, University of Pécs, Ifjúság útja 20., Pécs 7624, Hungary

[3] MTA-SZTE Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, University of Szeged, Aradi Vértanúk tere 1., Szeged 6720, Hungary

[4] Department of Medical Chemistry, Faculty of Medicine, University of Szeged, Aradi Vértanúk tere 1., Szeged 6720, Hungary

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presence of high amounts of phenol (Broholm and Erik 2000; Kibret et al. 2000). Traditionally, adsorption on activated carbon is the most widely used technique for the removal of phenols and their derivatives at lower concentration. The high cost of activated carbon has stimulated interest to use cheaper raw materials (Wang et al. 2007). Polymer-based adsorbents are widely employed for the removal of phenols, but the high cost of polymers has also stimulated interest in examining the feasibility of using cheaper and environmental-friendly adsorbents (Khan et al. 1997; Gupta et al. 2000; Alther 2002; Denizli et al. 2001, 2002).

Nowadays, biotechnological processes have attracted the attention for environmental decontamination. The study of biosorption has already given some positive results for removal of heavy metals using a variety of biomasses (Aksu 2001; Cruz et al. 2004; Wang and Chen 2006; Fagundes-Klen et al. 2007; Iqbal and Saeed 2007; Iqbal et al. 2007; Febrianto et al. 2009); however, information on the interaction of fungal biomass and phenol derivatives for technological applications is still limited (Hafez et al. 1998; Rao and Viraraghavan 2002; Denizli et al. 2002, 2004; Aksu 2005; Singhal et al. 2005; Wu and Yu 2006a, b, 2007, 2008; Navarro et al. 2008; Bayramoglu et al. 2009; Nadavala et al. 2009, Hailei et al. 2014). To our knowledge, application performance of white-rot fungi in bioremediation can be greatly improved by combination of nanotechnology (He et al. 2017).

Fungal biomass can take up considerable quantities of organic pollutants from aqueous solution by adsorption or a related process, even in the absence of physiological activity (Gadd and White 1989). In the concept of biosorption, several chemical processes may be involved such as adsorption, ion exchange (polysaccharides), complexation (proteins), and covalent binding. Based on the examination of the uptake by cell walls, it was concluded that the biosorption process involves uptake by both the cell walls and other cellular components of the microorganisms (Aksu 2005). The biosorptive sites on the microorganisms are carboxyl, hydroxyl, sulphuril, amino, and phosphate groups (Volesky and Holan 1995; Denizli et al. 2004). There is only little information about aminoacids and proteins, which play an important role in the biosorption process by biological sorbents. Chang and Hong showed that the mercury biosorption by inactivated cells of *Pseudomnas aeruginosa* PU21(Rip64) bacterial biomass is probably originated from the cysteine-rich transport proteins associated with the cell membrane (Chang and Hong 1994). A protein has been identified in *S. cerevisiae* strain 2200, which is able to bind incorporated cadmium (Mangir and Ehrlich 1989).oTh.

White-rot fungi are important environmental microorganisms, which have been applied in many fields. There are only a few studies on biosorption using *P. chrysosporium* biomass for the elimination of phenol and its derivatives (Aksu 2005; Aksu and Yener 1998; Antizar-Ladislao and Galil 2004; Bayramoglu et al. 2009; Benoit et al. 1998; Denizli et al. 2004; Farkas et al. 2013; Nadavala et al. 2009; Portela et al. 2001; Rao and Viraraghavan 2002; Thawornchaisit and Pakulanon 2007; Wu and Yu 2006a, b, 2007, 2008). The mycelial pellets composed of numerous mycelia have a large number of micropores and microchannels. 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 (Aksu 2005). Consecutive adsorption/desorption cycles using water studies employing fungal beads demonstrated that they could be reused in several cycles without significant loss of adsorption efficiency and adsorbent weight (Wu and Yu 2007). Comparing with other microbial masses, mycelial pellets are easier to collect; therefore, *P. chrysosporium* was selected for our study. Wu and Yu have used *P. chrysosporium* biomass as a sorbent material for removal of phenol and chlorophenols (Wu and Yu 2006a, b, 2007, 2008). They found that the adsorption capacity on mycelial pellets increased in the following order: phenol < 2-CP < 4-CP < 2,4-CP. The adsorption increased with decreasing water solubility and increasing octanol-water partitioning coefficients. The presence of 2-CP or 4-CP and the initial concentration of 2-CP and 4-CP had no significant effect on the adsorption of 2,4-DCP on fungal mycelial pellets. These findings suggest that partitioning was largely involved in biosorption mechanisms and that hydrophobicity might govern the biosorption of phenolic compounds by mycelial pellets (Denizli et al. 2004; Wu and Yu 2006b). So far, only a limited number of studies have been focused on the kinetic models and thermodynamic studies of phenol derivative biosorption in literature (Aksu and Yener 1998; Wu and Yu 2006a, 2008). Thermodynamic analysis indicates that the biosorption process is exothermic and that the adsorption of 2,4-dichlorophenol on *P. chrysosporium* might be physical in nature. Both intraparticle diffusion and kinetic resistances might affect the adsorption rate, and their relative effects vary with operational temperature in the biosorption of 2,4-DCP by mycelial pellets (Wu and Yu 2006b). The higher sorption of 2,4-DCP was explained with increase in the polarity, decrease in the pK_a of the phenol, and enhance in the hydrophobicity of the substituted benzene ring due to the increase in chlorosubstitution. The rapid adsorption on fungal cell wall surfaces was the main sorption phenomenon for the more hydrophobic molecules (Aksu 2005). However, an increased adsorption on activated carbon fibers (ACFs) occurred due to the textural properties of the ACFs in comparison of adsorption by fungal beads (Wang et al. 2007).

The novel objectives of our study were the followings:

- to present the role of cultivation medium composition for fungal beads, and its effect on adsorption process,

- to give a relation between specific cell surface charge and adsorption characteristics,
- to determine the adsorption isotherms and analyze the adsorption equilibrium using Langmuir and anti-Langmuir equations and
- to give a comparative study using linear presentations of kinetic and equilibrium equations and nonlinear least-square estimation for kinetic and equilibrium analysis.

Materials and methods

Microorganism and its growth conditions

Cultivation in simple liquid medium: *P. chrysosporium* (SZMC 1762 strain), a white-rot fungus—obtained from the Institute of Microbiology, University of Pécs—was maintained by subculturing on potato dextrose agar slants. Hyphal suspensions were prepared from 7-day-old cultures, grown on potato dextrose agar slants at 35 ± 2 °C (Iqbal and Saeed 2007). The liquid medium with simple composition contained (g l^{-1}) D-glucose, 10.0; KH_2PO_4, 2.0; $MgSO_4 \cdot 7H_2O$, 0.5; NH_4Cl, 0.1; $CaCl_2 \cdot H_2O$, 0.1; thiamine hydrochloride, 0.001 (Iqbal and Saeed 2007).

Cultivation in complex liquid medium: *P. chrysosporium* (SZMC 1762 strain)—obtained from the Institute of Microbiology, University of Pécs—was maintained by subculturing on substratum medium contained (g l^{-1}) D-glucose, 10; KH_2PO_4, 0.2; $MgSO_4 \cdot 7H_2O$, 0.05; $CaCl_2$, 0.01; ammoniumtartrate, 0.45; agar, 20; mineral solution, 1 ml and vitamin solution, 0.5 ml. Hyphal suspensions were prepared from 7-day-old cultures, grown on medium slants at 35 ± 2 °C. The liquid medium with complex composition contained (g l^{-1}) D-glucose, 10; KH_2PO_4, 0.2; $MgSO_4 \cdot 7H_2O$, 0.05; $CaCl_2$, 0.01; ammoniumtartrate, 0.45; mineral solution, 1 ml and vitamin solution, 0.5 ml. Minerals (g l^{-1}) were the following in stock solution: nitrilotriacetate, 1.5; $MgSO_4 \cdot 7H_2O$, 3.0; $MnSO_4 \cdot H_2O$, 0.5; NaCl, 1.0; $FeSO_4 \cdot 7H_2O$, 0.10; $CuSO_4 \cdot 5\ H_2O$, 0.01; $ALK(SO_4)_2 \cdot 12\ H_2O$, 0.01; H_3BO_3, 0.01; $NaMoO_4 \cdot 2\ H_2O$, 0.01; $CoCl_2 \cdot 6\ H_2O$, 0.1; $CaCl_2$, 0.082; $ZnSO_4 \cdot 7\ H_2O$, 0.10. In stock solution, the vitamins (g l^{-1}) consisted of biotin, 0.002; folic acid, 0.002; thiamine hydrochloride, 0.005; riboflavin, 0.005; pyridoxine hydrochloride, 0.01; cyanocobalamine, 0.0001; nicotinic acid, 0.005; D-calcium pantothenate, 0.005; *p*-aminobenzoic acid, 0.005; thioctic acid, 0.005 (Kirk et al. 1978).

The medium pH was adjusted to 4.5 with 0.1 mol l^{-1} HCl solution and 0.1 mol l^{-1} NaOH solution. The incubation was carried out at 35 ± 2 °C in an orbital shaker incubator at 150 rpm for 5 days.

Preparation of the biosorbent

After 5 days of cultivation in various liquid medium at 35 ± 2 °C, the resulted mycelial pellets were filtered, and then washed thoroughly with distilled water to remove the liquid medium adhering on its surface. The mycelial pellets used in all adsorption experiments were inactivated at 120 °C and 104 kPa for 20 min to avoid the biodegradation of phenol by living mycelia. The biosorbents were freeze-dried (HETO Dry Winner, Belgium) and used in the form of mycelium pellets without homogenization.

Chemicals

Phenol (> 99% purity) was purchased from Sigma-Aldrich Ltd. (Hungary) and was used without further purification. All other chemicals were of analytical grade. Stock solutions were prepared by dissolving 0.1 g of phenol in 1.0 l of distilled water. The test solutions containing phenol were prepared by diluting 100 mg l^{-1} of stock solution of phenol to the desired concentrations. The phenol concentrations of prepared solutions varied between 10 and 100 mg l^{-1} in the sorption experiments. The pH value of the solutions in this study (2.0–10.0) was adjusted to the required value by using 0.1 M NaOH and 0.1 M HCl solutions. All solutions were stored in the dark at 4 °C prior to use.

Batch experiments

Biosorption experiments were carried out in batch mode. The biomass concentration was 0.3 g l^{-1} (0.015 g of dry mycelial pellets mixed with 50 ml of solution containing 10–100 mg l^{-1} of phenol). Mycelial pellets and phenol solution were placed in a test tube, which was subsequently covered to prevent photodegradation. All adsorption experiments were conducted in the dark to avoid the formation of photodegradation products. Tubes were agitated on a shaker at 150 rpm and constant temperature (22.5 ± 2 °C). Samples were taken at given time intervals, and then centrifuged at 10,000 rpm for 10 min. The supernatants were used for analysis of the residual phenol. The amount of phenol adsorbed at equilibrium, q (mg g^{-1}), was obtained as follows:

$$q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where,

c_0 and c_e are the initial and equilibrium liquid phase concentrations (mg l^{-1}).
V is the volume of the solution (l) and
m is the mass of the dry biomass used (g).

The change of the solution's pH during the course of phenol adsorption was followed in each experiment, the pH value

slightly decreased. All experiments were performed in triplicate.

Analysis

Phenol concentration in supernatant was determined by HPLC. The HPLC system contains a liquid chromatograph (LC-10 AD_{VP}, Shimadzu), a micro vacuum degasser (DGU-14 A, Shimadzu), a system controller (SCL-10 A*VP*, Shimadzu), a diode array detector (SPD-M 10 A*VP*, Shimadzu), and an injector (7725i, Rheodyne). The LCMS solution software was applied on the HPLC system. The measurements were performed on the UV/VIS-photo diode array detector with detection at 270 nm. Chromatographic separations were performed on a Phenomenex Prodigy ODS3 C18 column (150 × 4.6 mm i.d., 5 μm, Phenomenex, USA). For separations, the mobile phase A, water and mobile phase B, methanol and a gradient program (0.03 min 42% B eluent, 8.00 min 60% B eluent, 8.10 min 42% B eluent, and 11.00 min 42% B eluent) were used. Operating conditions were as follows: flow rate 1.0 ml/min, column temperature ambient, and injection volumes 20 μl of the standard and samples. Calibration curve of the standard was made by diluting stock solution of standard in water to yield 10–100 mg l^{-1}.

Determination of cell surface charge

The surface charge properties were determined by measuring the flow potential of various fungal biomass in aqueous suspension of 1.0 g l^{-1} concentration. The flow potential values of fungal cells in aqueous suspension at different pH values were determined using the Particle Charge Detector (Mütek Typ PCD 02, Germany). The biomass of 0.01 g was suspended in 10 ml of deionized water and pH was adjusted to between 3.0 and 10.0 using 0.1 M NaOH and 0.1 M HCl solutions. After pH adjustment, mixtures were equilibrated in a magnetic stirrer for 24 h and the flow potential values were measured. The specific surface charge of fungal cells at various pH in aqueous suspension of 1 g l^{-1} was determined by titration using aqueous solution of cationic surfactant like cetylammonium bromide (CTAB). The concentration of cationic surfactant was 0.1 g l^{-1} and the volume of the oppositely charged fungal suspension was 10 ml. The 10 ml of fungal suspension was measured into the detector cell and then defined volumes of surfactant solution were added. Between every titration point, a waiting of 15 min was needed under dynamic condition to reach the charge compensation equilibrium.

FT-IR spectroscopy

The FTIR spectra of fungal biomass of *P. chrysosporium* was obtained by using FTIR spectrophotometer (Thermo Science, England). For FTIR spectra, approximately fungal biomass (2 mg) was mixed with KBr (200 mg) and pressed into a tablet form by pressing the ground mixed material with the aid of a bench press. The FTIR spectrum was then recorded.

Results and discussion

Surface characteristics of fungal cells

To confirm the existence of functional groups (amino, carboxyl, and phosphate) on the fungal biomass, the FTIR spectra and surface charge properties of fungal biomass preparations cultivated in various liquid medium were determined (Figs. 1a, b, 2 and 3a, b). In Fig. 1a, the FTIR spectra of fungal biomass cultivated in a liquid medium with simple composition and in Fig. 1b the FTIR spectra of fungal biomass cultivated in a liquid medium with vitamins and minerals are presented. From this comparison of FTIR spectra, we can conclude that there is no difference between spectra of various fungal preparations. The FTIR spectra of both fungal preparations have intense peaks at a frequency level of 3500–3200 and 1540 cm^{-1} representing amino group stretching vibrations. The amino group stretching vibration bands of fungal preparations are superimposed on the side of the hydroxyl group band at 3500–3300 cm^{-1}. The strong peaks at around 1650, 1400, and 1240 cm^{-1} are caused by the C=O stretching band of carbonyl groups. The phosphate groups show some characteristic absorption peaks around 1150 and 1078 cm^{-1} representing P=O and P=OH stretching, respectively. The band between 610 and 535 cm^{-1} for the fungal cells represents C–N–C scissoring and it is only found in protein structure (Bayramoglu et al. 2006). Bayramoglu have found the same surface characteristics by FTIR spectra of *P. chrysosporium* biomass (Bayramoglu et al. 2006). Also, the rough and porous surface of fungal biomass exemplified by SEM can be a factor providing an increase in the total surface area (Bayramoglu et al. 2006).

In Fig. 2, the flow potential values of fungal biomass cultivated in liquid medium with simple and complex composition can be seen at different pH values in aqueous suspension. The specific surface charge of the fungal cells was estimated by measuring of the flow potential in fungal suspension. The surface charge of cells was measured as negative value in the pH range of 4.3–9.8 for both fungal preparations (Fig. 2). Other researchers also reported that the overall surface of various fungal biomasses was negatively charged at the pH values between 3.0 and 11.0 (Rao and Viraraghavan 2002; Aksu 2005; Wu and Yu 2006b). At various pH values between 4.0 and 8.0, the amount of specific surface charge of fungal cells was also determined by charge density titration using aqueous solution of CTAB. In Fig. 3a, b, the titration curves in aqueous suspension of fungal biomasses with simple and complex

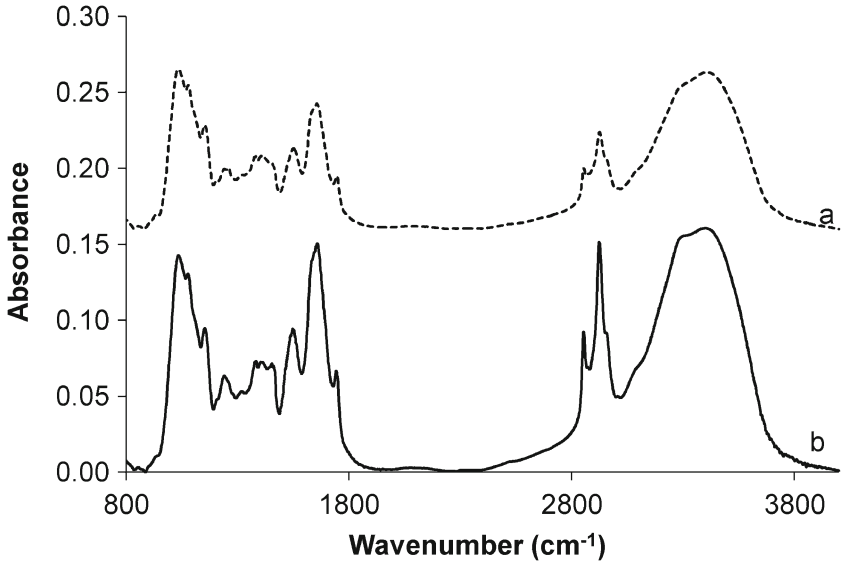

Fig. 1 The FTIR spectra of non-living *P. chrysosporium* biomass cultivated **a** in a liquid medium with simple composition, **b** in a liquid medium with complex composition containing minerals and vitamins

composition are presented at various pH. The calculated values of specific surface charge of both *P. chrysosporium* preparations at different pH values are summarized in Table 1 and presented in Fig. 4a. Lower surface charge value was obtained for fungal biomass cultivated in simple medium than for fungal biomass grown in complex medium at pH values between 3.9 and 8.2. The values of specific surface charge of fugal biomass samples are collected in Table 1. In Fig. 4b, the adsorbed amounts of phenol are presented against the specific surface charge values of various fungal cells in aqueous suspension.

Effect of initial pH on phenol biosorption in aqueous suspension

Studies on phenol biosorption showed that the pH value of the solution was an important factor for both solution chemistry and surface characteristics of biosorbents (Denizli et al. 2004; Wu and Yu 2006a, b). The effect of initial pH on the equilibrium uptake capacity of phenol by mycelial pellets of *P. chrysosporium* grown in simple and in complex medium at pH 2.0–9.0 and 22.5 ± 1 °C is shown in Fig. 5. The initial concentration of phenol was 25.0 mg l^{-1} and the biomass concentration was 0.3 g l^{-1}. The adsorption of phenol was not significant at pH 2.0–4.0 and 7.0–9.0 in aqueous suspension, and in the range of pH 5.0–6.0, the adsorption of phenol was at maximum level (Fig. 4a, b).

Phenols are weakly acidic, and pH has a significant effect on the degree of ionization and the cell surface properties. The amount of adsorbed phenol seemed to be related to the dissociation constant (pK_a), which is 9.9 for phenol (Aksu 2005; Silva and Faria 2009). The ionic fraction of phenolate ion increases with increasing pH, and phenol could be expected

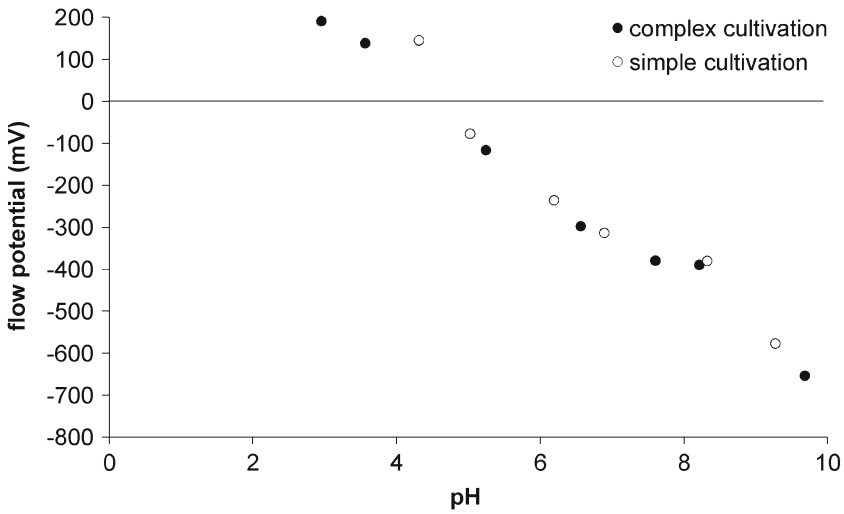

Fig. 2 The values of flow potential of non-living *P. chrysosporium* biomass in aqueous suspension are presented against various pH of aqueous suspension. **a** Fungal biomass cultivated in a liquid medium with simple composition. **b** Fungal biomass cultivated in a liquid medium with complex composition containing minerals and vitamins. The biomass concentration was 0.3 g l^{-1}, the temperature was 22.5 °C. Error bar represents SD; $n = 3$

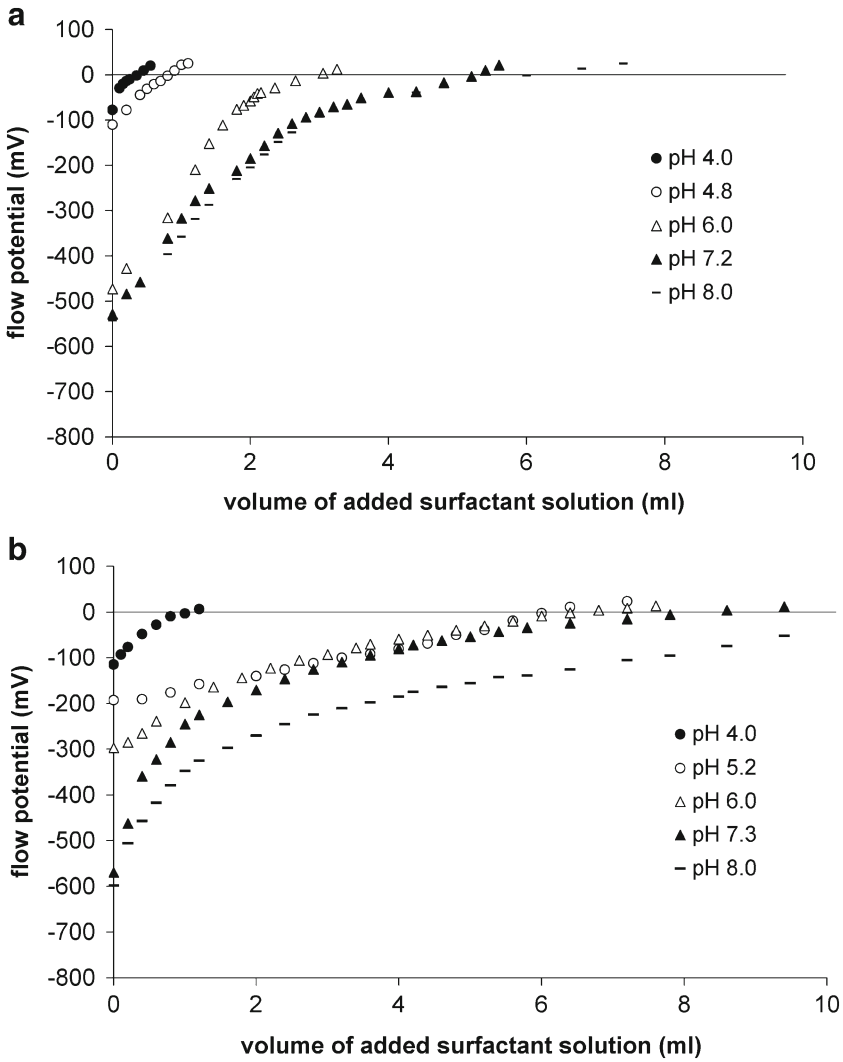

Fig. 3 Titration curves of *P. chrysosporium* biomasses by CTAB in the aqueous suspension at various pH values. **a** Fungal biomass cultivated in liquid medium with simple composition. **b** Fungal biomass cultivated in liquid medium with complex composition containing minerals and vitamins. The cationic surfactant concentration was 0.1 g l^{-1}, the biomass concentration was 0.3 g l^{-1}, the temperature was 22.5 °C

to become negatively charged as pH increases. Unionized phenol molecules would be attracted, possibly by physical forces (Aksu 2005). The surface charge of fungal biomass is predominately negative at pH 4.0–10.0 (Figs. 2 and 3) (Rao and Viraraghavan 2002; Wu and Yu 2006a, b). Phenol 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 phenols and led to a decrease

Table 1 The specific surface charges of *P. chrysosporium* determined using titration by CTAB at various pH in aqueous suspension. (a) Fungal biomass cultivated in a liquid medium with simple composition, (b) fungal biomass cultivated in a liquid medium with complex composition containing minerals and vitamins

Phanerochaete chrysosporium	pH	Volume of added surfactant solution (ml)	Specific surface charge (meq g^{-1})
Simple cultivation	4.2	0.4	0.011
	4.8	0.8	0.023
	6.0	2.5	0.069
	7.2	5.3	0.145
	8.0	6.4	0.176
Complex cultivation	3.9	1.1	0.03
	5.2	6.0	0.165
	6.2	6.5	0.178
	7.4	8.0	0.220
	8.2	11.2	0.307

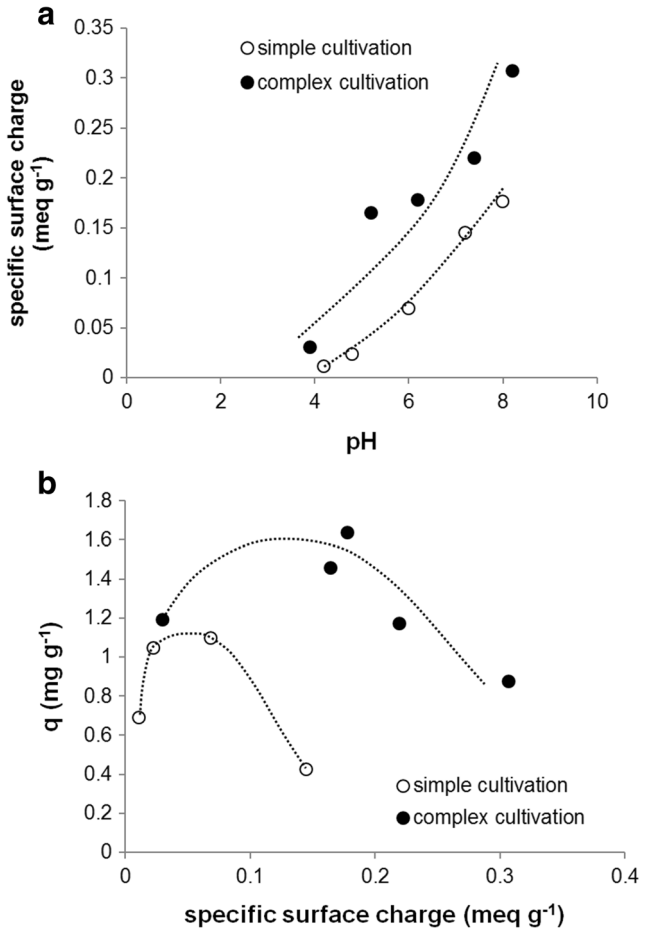

Fig. 4 **a** The values of specific surface charge are presented against pH of aqueous suspension containing various fungal cells. **b** The adsorbed amounts of phenol are presented against specific surface charge of various fungal cells in aqueous suspension

in phenol uptake by mycelial pellets. Wu and Yu evaluated the 2,4-dichlorophenol biosorption by *P. chrysosporium* in aqueous solution, and the maximal removal of 2,4-dichlorophenol was obtained at an initial pH of 5.0–6.0 (Wu and Yu 2006a, b). The highest adsorption for phenol, *o*-chlorophenol, *p*-chlorophenol, and 2,4,6-trichlorophenol was measured at pH 6.0 (Wu and Yu 2006a). They also reported that the electrostatic forces between the charged fungal surface and 2,4-dichlorophenol played an important role in the biosorption of phenol. These results were accorded with those reported by Denizli et al., in which the removal of chlorophenols from synthetic solutions using *P. chrysosporium* was also studied (Denizli et al. 2004). Aksu explained the change in biosorption due to pH with the ionization of phenols and chlorinated phenols, alterations in the sorbent surface, and the interaction of phenols and chlorinated phenols with the cells with primarily electrostatic forces or complex formation or electron share in nature or membrane transport (Aksu 2005).

The subsequent experiments were conducted in a natural medium without pH adjustment, at around pH value of 5.5.

Adsorption kinetics of phenol on *P. chrysosporium* biomass cultivated in various liquid medium in aqueous suspension

The adsorption kinetics of phenol was investigated by *P. chrysosporium* biomass grown in liquid medium having various compositions at a suspension concentration of 0.3 g l^{-1}. The adsorption was slightly reduced in an alkaline medium, while it was at minimum in an acidic medium (Wu and Yu 2006a, b; Iqbal and Saeed 2007; Iqbal et al. 2007). The biosorption experiments were carried out at the natural state of pH 5.5 in the biomass suspension. The initial phenol concentration was 50 mg l^{-1}. In Fig. 6a, the adsorbed amounts of phenol are presented against the adsorption time in the case of fungal biomass cultivated in simple and complex liquid medium. Using fungal biomass cultivated in simple and complex liquid medium in the equilibrium at initial phenol

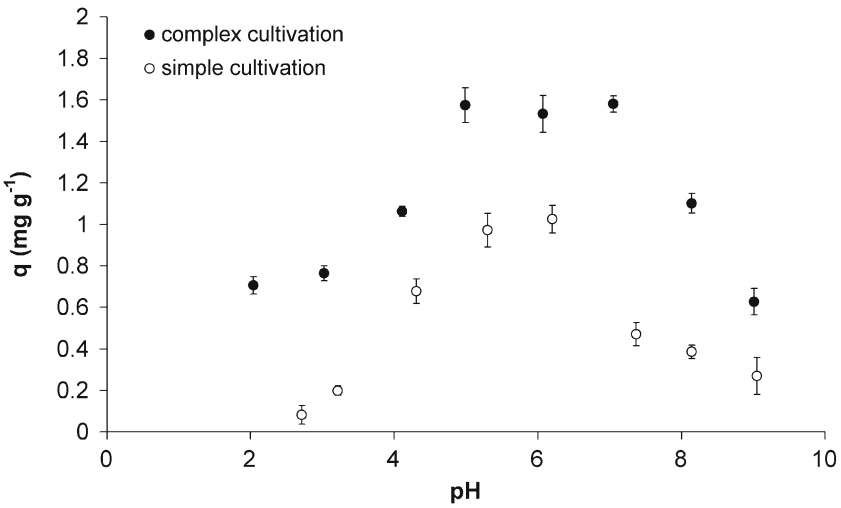

Fig. 5 The effect of pH on biosorption of phenol by *P. chrysosporium* in aqueous suspension. Initial phenol concentration was 25.0 mg l^{-1}. (•) Fungal biomass cultivated in liquid medium with simple composition, (o) fungal biomass cultivated in liquid medium with complex. The biomass concentration was 0.3 g l^{-1}, the temperature was 22.5 °C. Error bar represents SD; $n = 3$

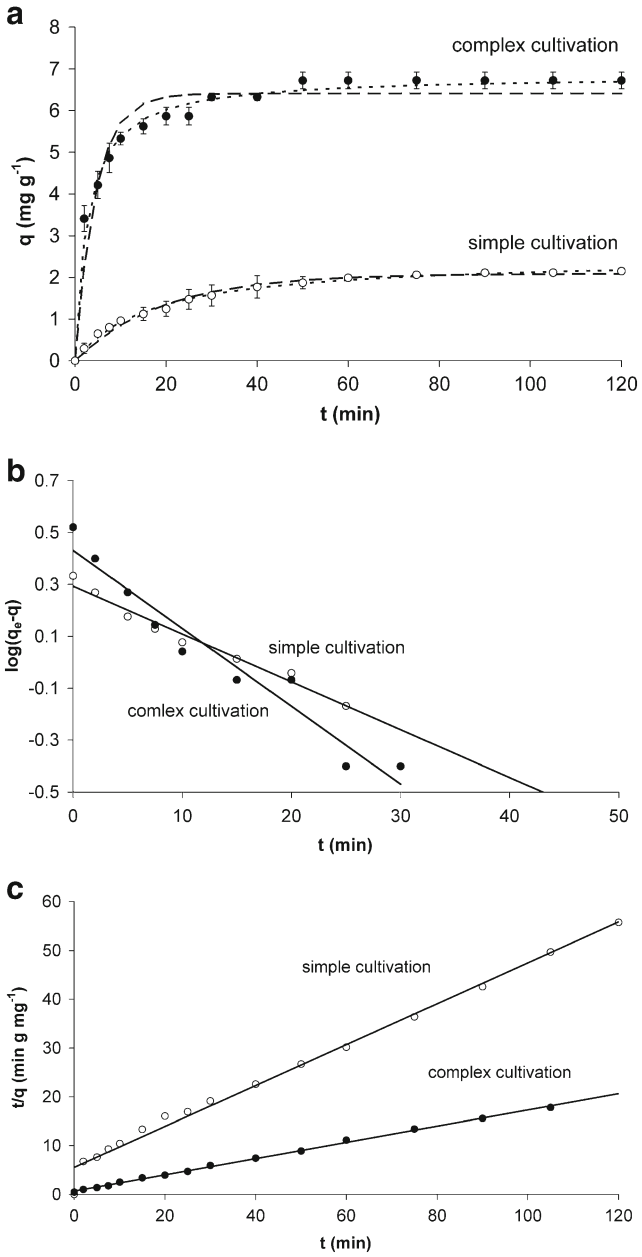

Fig. 6 **a** Time-course profile with calculated data from (——) pseudo-first-order model and (···) second-order model using non-linear regression. **b** Linearized pseudo-first-order kinetic model. **c** Linearized pseudo-second-order kinetic model of phenol bioadsorption by mycelial pellets of *P. chrysosporium* grown (o) in a liquid medium with simple composition, (•) in a liquid medium with a complex composition containing minerals and vitamins from aqueous solution at the biomass concentrations of 0.3 g l^{-1} at pH 5.5. Initial concentration was 50.0 mg l^{-1}, the temperature was 22.5 °C, and the biomass concentration was 0.3 g l^{-1}. Error bar represents SD; $n = 3$

concentration of 50.0 mg l^{-1}, the maximum adsorbed phenol amounts were $q_{eq,\ exp} \approx 2.15$ and 6.73 mg g^{-1}, respectively (Table 2, Fig. 6a). The results show that adsorption equilibrium was reached during 60 min in both cases. The adsorption rate was higher in the first 30 min, but decreased until the equilibrium was reached. Similar trends were found by other workers (Benoit et al. 1998; Calace et al. 2002; Wu and Yu 2006a, b). It should be noticed that the adsorption of phenol increased with an increase of sorption time and initial phenol concentration.

To evaluate the biosorption kinetics of phenol, two kinetic models were used to fit the experimental data at pH 5.5 (Wu and Yu 2006a, b; Febrianto et al. 2009). The kinetic constants calculated from linearized form of kinetic equations and non-linear regression have been compared (Table 2). Only limited information exists on the comparison of kinetic evaluation of phenol derivative biosorption by *P. chrysosporium* (Wu and Yu 2006a, b; Febrianto et al. 2009).

Pseudo first-order kinetic model

The pseudo first-order equation of Lagergren is generally expressed as follows (Febrianto et al. 2009):

$$\frac{dq}{dt} = k_1\left(q_{eq} - q\right) \tag{2}$$

where k_1 is the rate constant of pseudo first-order sorption (min^{-1}). Integrating this equation for boundary conditions: $t = 0$ to t and $q = 0$ to q_{eq} gives

$$\log\left(q_{eq} - q\right) = \log\left(q_{eq}\right) - \frac{k_{1,ad}}{2.303}t \tag{3}$$

A plot of $\log(q_{eq} - q)$ against of t should give a linear realtionship with the slope of $k_{1,\ ad}/2.303$ and intercept of $\log q_{eq}$. By plotting $\log(q_{eq} - q)$against t for the initial concentration in the case of both biomass, straight lines were obtained as shown in Fig. 6b. The values of first-order rate constant $k_{1,\ ad}$ and $q_{eq}$with correlation coefficients in Table 2 were determined from the slopes and intercepts of the linear plots and from non-linear regression. The value of first-order rate constant $k_{1,\ ad}$ was calculated as $4.24 \cdot 10^{-2}$ g mg^{-1} min^{-1} for simple fungal biomass, while for fungal biomass cultivated in complex liquid medium, the value of $k_{1,\ ad}$ was $6.91 \cdot 10^{-2}$ g mg^{-1} min^{-1} at initial phenol concentration of 50.0 mg l^{-1}. From non-linear regression, the value of first-order rate constant $k_{1,\ ad}$ was calculated as $5.20 \cdot 10^{-2}$ g mg^{-1} min^{-1} for simple fungal biomass, while for complex fungal biomass, the value of $k_{1,\ ad}$ was $2.20 \cdot 10^{-1}$ g mg^{-1} min^{-1} (Fig. 6a). The theoretical q_{eq} values found from this model using linearized form did not give reasonable value for complex cultivation, only for simple cultivation. From non-linear regression, the theoretical q_{eq} values were 2.09 mg g^{-1} for simple and 6.41 mg g^{-1} for complex cultivation (Fig. 6a). On the basis of results, the pseudo first-order model using non-linear regression can be described the adsorption results of phenol onto fungal biomass.

Table 2 The pseudo-first-order and second-order rate constants of phenol at different initial phenol concentrations using *Phanerochaete chrysosporium* biomasses cultivated in liquid medium having various composition at pH 5.5. The temperature was 22.5 °C, the biomass concentration was 0.3 g l^{-1}, the initial phenol concentration was 50 mg l^{-1}

Linear regression							
pseudo-first-order constants				pseudo-second-order constants			
	$k_{1,ad}$ (min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2	$k_{2,ad}$ (g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2	$q_{eq,exp}$ (mg g^{-1})
Simple cultivation	$4.24 \cdot 10^{-2}$	1.96	0.973	$2.56 \cdot 10^{-2}$	2.46	0.998	2.15
Complex cultivation	$6.91 \cdot 10^{-2}$	2.69	0.946	$7.17 \cdot 10^{-2}$	6.85	0.999	6.73
Non-linear regression							
Simple cultivation	$5.20 \cdot 10^{-2}$	2.09	0.985	$2.42 \cdot 10^{-2}$	2.47	0.995	2.15
Complex cultivation	$2.20 \cdot 10^{-1}$	6.41	0.930	$5.30 \cdot 10^{-2}$	6.85	0.987	6.73

Pseudo second-order kinetic model

If the adsorption rate is of second-order, the pseudo second-order kinetic rate equation is expressed as follows (Aksu and Tezer 2000; Wu and Yu 2006a, b; Febrianto et al. 2009):

$$\frac{dq}{dt} = k_{2,ad}\left(q_{eq} - q\right)^2 \tag{4}$$

where $k_{2,ad}$ is the rate constant of second-order biosorption (g mg^{-1} min^{-1}). After integration, the following equation is obtained:

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{t}{q_{eq}} \tag{5}$$

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 concentration in the case of both biomass, straight lines were obtained as shown in Fig. 6c. The second-order rate constants $k_{2,\,ad}$ and q_{eq} values with the correlation coefficients presented in Table 2 were determined from the slopes and intercepts of the plots and non-linear regression. From linearized presentation, the value of second-order rate constant $k_{2,\,ad}$ was calculated as $2.56 \cdot 10^{-2}$ g mg^{-1} min^{-1} for simple fungal biomass, while for fungal biomass cultivated in complex liquid medium, the value of $k_{2,\,ad}$ was $7.17 \cdot 10^{-2}$ g mg^{-1} min^{-1} at initial phenol concentration of 50.0 mg l^{-1} (Fig. 6c, Table 2). Using non-linear regression, the value of second-order rate constant $k_{2,\,ad}$ was calculated as $2.42 \cdot 10^{-2}$ g mg^{-1} min^{-1} for simple fungal biomass, while for fungal biomass cultivated in complex liquid medium, the value of $k_{2,\,ad}$ was $5.30 \cdot 10^{-2}$ g mg^{-1} min^{-1}. Theoretical q_{eq} values were 2.47 mg g_{-1} for simple cultivation and 6.85 mg g^{-1} for complex cultivation. The values of correlation coefficients were higher and the theoretical q_{eq}values were close to the experimental q_{eq} values with pseudo-second-order model (Fig. 6a, Table 2). Regarding the effect of cultivation composition and comparison of the applied mathematical methods on phenol biosorption kinetics, there is no available information in the literature. The biosorption of 2,4-dichlorophenol from aqueous solution on non-living pellets of *P. chrysosporium* grown in the same complex medium was also studied by Wu and Yu (Kirk et al. 1978; Wu and Yu 2006a, b). Based on their experiments, they found that the 2,4-dichlorophenol biosorption process followed pseudo-second-order kinetics using linearized presentation of kinetic equations. The pseudo-second-order kinetic constants decreased with an increase in initial concentration, temperature, and mycelial pellets for 2,4-dichlorophenol biosorption by *P. chrysosporium* (Wu and Yu 2006a, b).

The correlation coefficients for the first- and the second-order kinetic models using non-linear regression were close to 1.0, and the theoretical values of q_{eq} also agreed well with the experimental data for both biosorbents. By comparison of two kinetic models with linear and non-linear regression, we can conclude that phenol sorption kinetics on mycelial pellets of *P. chrysosporium* can be described by both kinetic models using non-linear regression. However, using linear presentation, only the pseudo-second-order kinetic model gives reasonable result. The kinetic parameters can be used to determine the equilibrium sorption capacity, percent of the removal of phenol, rate constants, and initial sorption rate for a bioreactor design.

Adsorption isotherms of phenol by *P. chrysosporium* biomass cultivated in various liquid medium in aqueous suspension

The biosorption isotherms of phenol by mycelium pellets cultivated in the liquid medium with various composition were evaluated in the initial concentration range of 10 −100 mg l^{-1} at biomass concentration of 0.3 g l^{-1}. The adsorbed amounts of phenol are presented against the equilibrated phenol concentration in the suspension (Fig. 7a). It can be seen in Fig. 7a that the uptake of

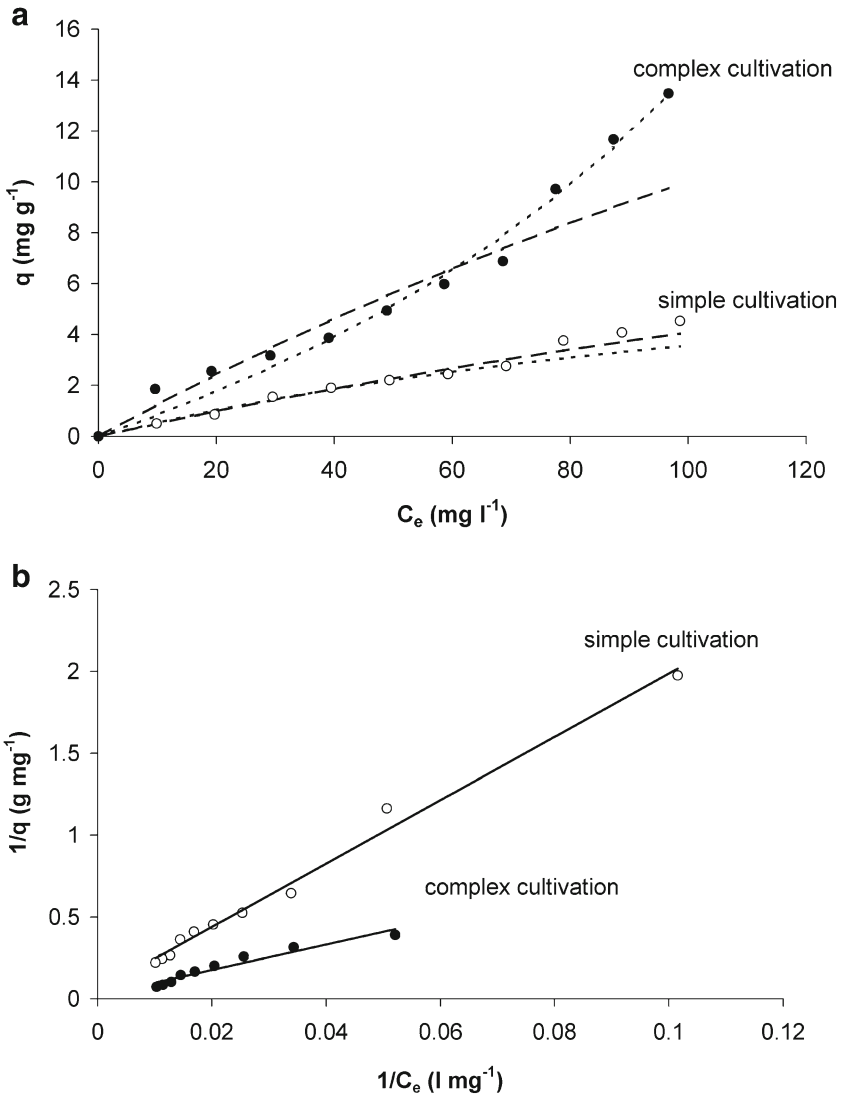

Fig. 7 **a** Phenol adsorption isotherms by mycelial pellets of *P. chrysosporium* cultivated () in a liquid medium with simple composition, (●) in a liquid medium with a complex composition containing minerals and vitamins from aqueous solution at the biomass concentration of 0.3 g l^{-1} in the initial phenol concentration range of 10–100 mg l^{-1}, at pH 5.5. Figure also shows the (···) line calculated from the non-linear estimation and (——) line recalculated with constants from linearized isotherm equation. **b** Linearized presentation of bioadsorption isotherms of *P. chrysosporium* cultivated (○) in liquid medium with simple composition, (●) in a liquid medium with complex composition. Error bar represents SD; $n = 3$

phenol by biomass increases with increasing of the initial phenol concentration in solution. At initial phenol concentration of 100 mg l^{-1}, the maximum adsorbed amount by fungal biomass cultivated in a complex culture was about $q_{max,\ exp} \approx 13.48$ mg g^{-1}. On the other hand, it was about $q_{max,\ exp} \approx 4.53$ mg g^{-1} using biomass cultivated in a simple liquid medium (Fig. 7a). From the experimental results, we can conclude that the culture medium containing mineral and vitamin materials enhance the adsorption capacity of the biomass of *P. chrysosporium* for phenol. These findings are shown in Fig. 7a, where the comparison of adsorption isotherms determined using fungal biomasses cultivated in various liquid medium can be seen at the same biomass dosage in suspension.

The analysis of equilibrium is important for developing a model that can be used for the design of biosorption systems. Two classical adsorption models, Langmuir and Freundlich isotherms, are most frequently employed (Aksu and Tezer 2000; Denizli et al. 2001; Wang and Chen 2006; Wu and Yu 2006a, b, 2007, Wang et al. 2007; Febrianto et al. 2009). With our biosorption experimental results, the Langmuir and anti-Langmuir isotherm equations could be applied for analyzing the adsorption equilibria (Fig. 7a, Table 3).

Langmuir and anti-Langmuir isotherms

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

$$q_{eq} = \frac{Q^0 b C_{eq}}{1 + b C_{eq}} \tag{6}$$

where, C_{eq} and q_{eq} are the equilibrium concentrations (mg l^{-1}) in the solution and in the adsorbent at equilibrium (mg g^{-1}), respectively. Q_0 and b are the Langmuir constants related to

Table 3 The Langmuir isotherm constants of phenol on micelial pellets cultivated in liquid media with simple and complex compositions in the initial concentration range of 10−100 mg l^{-1} at pH 5.5. The temperature was 22.5 °C, the biomass concentration was 0.3 g l^{-1}

Phenol biosorption	From nonlinear least-square estimation				From linearized presentation		
	Langmuir model						
P. chrysosporium	$q_{max,exp}$ (mg g^{-1})	b (l mg^{-1})	Q^0 (mg g^{-1})	R^2	B (l mg^{-1})	Q^0 (mg g^{-1})	R^2
Simple cultivation	4.53	$6.12 \cdot 10^{-3}$	9.41	0.984	$2.64 \cdot 10^{-3}$	19.53	0.990
	Anti-Langmuir and Langmuir model						
Complex cultivation	13.48	$4.35 \cdot 10^{-3}$	–	0.981	$2.86 \cdot 10^{-3}$	45.04	0.938

the capacity and energy of adsorption, respectively. The linearized form of the Langmuir equation is as follows:

$$\frac{1}{q_e} = \left(\frac{1}{bQ^0}\right)\frac{1}{C_{eq}} + \frac{1}{Q^0} \tag{7}$$

The values of Q^0 and b can be determined from the linear plot of $1/q_e$versus $1/C_e$(Benoit et al. 1998; Aksu 2001; Febrianto et al. 2009).

The so-called anti-Langmuir model describes a concave upward isotherm (Cavazzini et al. 2002). Its equation is as follows:

$$q = \frac{Q^0 C_e}{1 - bC_e} b > 0. \tag{8}$$

Harrison and Katti have recommended a direct non-linear least-square estimation for the determination of the Langmuir constants due to the hazards of linearization of the Langmuir model (Harrison and Katti 1990). In this study, we give a comparison for Langmuir constants calculated from linearized presentation of isotherm and from non-linear least-square estimation (Fig. 7a, b, Table 3).

The non-linearly estimated adsorption isotherms of phenol obtained using biomass cultivated in liquid medium with various composition are shown in Fig. 7a with experimental data. The values of $Q_0$and $b$calculated from the linearized presentation of Langmuir equation and non-linear least-square estimation using Solver add-on are also given in Table 3. The Langmuir constant b is an indicator of the stability of the combination between adsorbate and adsorbent surface, and a constant related to the free energy or net enthalpy of adsorption (Borókvo 2002; Dékány and Berger 2002).

Using linearized presentation, the calculated values are $Q_0 = 19.53$ mg g^{-1} and $b = 2.64 \cdot 10^{-3}$ l mg^{-1} for biosorption by simple cultivated biomass, while Q_0 is 45.05 mg g^{-1} and $b$is $2.86 \cdot 10^{-3}$ l mg^{-1} for complex cultivated biomass. For Langmuir constant b, about the same values are calculated.

Using non-linear fitting, the estimated values of the Langmuir constants are $Q^0 = 9.41$ mg g^{-1} and $b = 6.12 \cdot 10^{-3}$ l mg^{-1} for biosorption by simple cultivated biomass. For biomass grown in complex medium, the estimated value of b is $4.35 \cdot 10^{-3}$ l mg^{-1} using anti-Langmuir model, which refers to anti-Langmuir adsorption behavior due to the enhanced adsorption capacity by complex medium containing mineral and vitamin compounds (Table 3) (Borókvo 2002; Dékány and Berger 2002).

The theoretical maximum adsorption capacity, Q^0, calculated from linearized presentation is higher than it is obtained using non-linear estimation for simple cultivated biomass. On the surfaces of both fungal biomass, in the equilibrated phenol concentration range of 10−100 mg l^{-1} at temperature of 22.5 °C, the monolayer is not saturated. It can be found in the literature that the biosorption equilibrium of organic pollutants—such as phenol and chlorophenols—follows the Langmuir isotherm (Wu and Yu 2006a, b, 2008; Iqbal and Saeed 2007).

In Fig. 7a, the experimentally determined isotherm data, as well as the results of non-linear least-square estimation and the calculated isotherms using adsorption constants from linearized Langmuir isotherm equation are presented. The isotherms in the case bioadsorbent with complex composition have rather different shape than in the case of bioadsorbent with simple composition.

The anti-Langmuir model is concave upward and is the plot of the experimental data of phenol adsorption by biomass with complex composition (Borókvo 2002; Dékány and Berger 2002; Farkas et al. 2013). Still, the linearized data fitting procedure suggests a Langmuir-type behavior. Due to the hazards of equation linearization, the non-linear least-square estimation can be strongly recommended for modeling bioadsorption-equilibrium (Harrison and Katti 1990). Figure 7a demonstrates that the results of the fitting of the linearized data may not represent the experimental ones.

Conclusions

The potential of non-living lyophilized mycelial pellets of *P. chrysosporium* cultivated in liquid medium with simple

and complex composition to adsorb phenol molecules from aqueous solution was demonstrated in this study. The biosorption capacity of *P. chrysosporium* biomass was affected by cultivation parameters of liquid medium. Adding mineral and vitamin materials to the liquid medium increased the adsorption capacity of fungal biomass. The kinetics of phenol biosorption to the biomass of *P. chrysosporium* can be described by pseudo-first- and second-order kinetic models according to the non-linear regression. In the concentration range of 10–100 mg l^{-1}, the monolayer coverage was not reached in the suspension of both *P. chrysosporium* preparations. At optimum pH 5–6, the values of specific surface charge were 0.023 and 0.069 meq g^{-1} for various cultivation, and the maximum amounts of phenol can be adsorbed at these pH values. The experimental maximum adsorbed phenol amounts by cells cultivated in simple and complex medium were 4.53 and 13.48 mg g^{-1}, respectively. The Langmuir and anti-Langmuir models exhibited a good fit to the adsorption data of phenol using non-linear least-square estimation. In dilute suspension of fungal preparation in liquid medium with complex composition, the negative value of Langmuir constant *b* calculated from non-linear least-square estimation refers to anti-Langmuir adsorption behavior. Varying the composition of culture medium, the fungal surface properties and thus adsorption capacity can be optimized for removal of various organic pollutants in contaminated waters.

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