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Influence of rhamnolipids and Triton X-100 on adsorption of phenol by *Penicillium simplicissimum*

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ABSTRACT

The effects of rhamnolipids and Triton X-100 on phenol adsorption by *Penicillium simplicissimum* were studied. The optimum pH was 7 for phenol adsorption by all the test biomasses. The adsorption of phenol at pH 7 by biomass pre-treated with 0.05% Triton X-100, 0.2% Triton X-100, 0.05% rhamnolipids and 0.005% rhamnolipids was 3.4, 2.7, 2.4, and 1.8-fold, respectively, that of untreated biomass. The pseudo-second-order model and the Freundlich isotherms described the adsorption processes better than the pseudo-first-order model and the Langmuir isotherms, respectively. The pre-treatments by surfactants increased the zeta potential and hydrophobicity of *P. simplicissimum*. Analysis of the cell surface by Fourier transform infrared spectrometry, energy dispersive X-ray, and environmental scanning electron microscopy indicated that the pre-treatments by surfactants changed the cell surface functional groups, element concentrations and micrographs. The results indicated that surfactants can be potentially used to increase phenol adsorption.

1. Introduction

Phenolic pollutants are generated by numerous industrial activities and may be persistent in the environment (Liu et al., 2011a, 2010b; Parida and Pradhan, 2010). These compounds are a potential threat to human health due to their toxic nature (Park et al., 2010). Therefore, the removal of phenolic pollutants from effluents is necessary.

Adsorption processes have been widely used to control phenolic pollution because they are simple, cost-efficient, rapid, and reproducible (Parida and Pradhan, 2010; Park et al., 2010). Some microorganisms, such as *Funalia trogii* (Bayramoglu et al., 2009), *Phanerochaete chrysosporium* (Denizli et al., 2004; Wu and Yu, 2006), *Pleurotus sajor caju* (Denizli et al., 2005), and *Aspergillus niger* (Mathialagan and Viraraghavan, 2009; Rao and Viraraghavan, 2002), have been considered as adsorbents for phenol. Several pre-treatments, such as cetyltrimethylammonium bromide pre-treatment, heating, and immersing in solutions with sulfuric acid, have been used to improve adsorption efficiency by the microorganism biomass (Bayramoglu et al., 2009; Mathialagan and Viraraghavan, 2009; Rao and Viraraghavan, 2002).

Surfactants and biosurfactants are also known to alter cell surface properties (Yuan et al., 2007; Zhong et al., 2008), and since these compounds are effective at very low concentrations, their application is economically possible (Zhong et al., 2008). (Bio)surfactants change cell surface properties of microorganisms by adsorption onto the cell surface and altering cell surface hydrophobicity and/or potential (Ahimou et al., 2000; Ron and Rosenberg, 2002; Zhong et al., 2008). Surfactants can also cause the release of cell surface molecules such as proteins and lipopolysaccharides (Al-Tahhan et al., 2000; Hazen et al., 1990; Hua et al., 2003; Sotirova et al., 2008) and change membrane structure or disrupt protein conformation, altering important membrane functions such as transport and energy generation, which may increase membrane permeability leading metabolite leakage (Banat et al., 2010). The released metabolites may adhere to the cell surface and change cell surface properties. The saponin biosurfactants change the cell surface charge of *Penicillium simplicissimum* (Liu et al., 2011b), an organism used for removal of phenols (Zhou et al., 2011).

Since phenol has a benzene ring as hydrophobic moiety and a polar hydroxyl group, cell surface properties (such as hydrophobicity and charge) may play important roles in the adsorption of

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phenols. Therefore, the effects of anionic biosurfactant rhamnolipids (RL) and the non-ionic chemical surfactant Triton X-100 on cell surface properties of *P. simplicissimum* during growth and the adsorption of phenol by the biomasses were investigated. Fourier transform infrared spectrometry (FTIR), energy dispersive X-ray (EDX), and environmental scanning electron microscope (ESEM) analysis were performed to gain insight into possible mechanisms.

2. Methods

2.1. Microorganism and surfactants

The strain *P. simplicissimum* used in this study was isolated from soil samples from the Yuelu Mountain (Changsha, China) (Yu, 2007), maintained on potato dextrose agar and stored at 4 °C in the Environmental Lab at Hunan University. Biosurfactant RL was produced by *Pseudomonas aeruginosa* as described by Zhong et al. (2008). Triton X-100 (Scintillation Grade, purity >99%) was purchased from BDH Chemicals Ltd. (Poole, England).

2.2. Biomasses preparation and batch biosorption studies

The biosorbents were prepared according to the method described by Liu et al. (2011b). Briefly, *P. simplicissimum* was incubated at 30 °C, 150 rpm for 3 days in 500-mL Erlemneyer flask with 100 mL mineral salt medium (MSM) containing 20 g L^{-1} glucose as carbon source. RL was added into the culture medium to achieve initial concentrations of 0.005% and 0.05%, and Triton X-100 of 0.05% and 0.2%. After incubation, the fungal mycelium was collected, washed twice with MSM, freeze-dried, and ground to pass through a 180-mesh sieve. The cells from culture medium without surfactants were used as untreated biomass for phenol adsorption.

All experimental solutions were prepared in ultra-pure water with an initial resistivity of 18.2 MΩ cm^{-1} produced by Labconco Water Pro PS (Kansas, USA). The initial pH was adjusted with 1 M NaOH or HCl. The adsorption experiments were conducted in 50-mL Erlenmeyer flasks with 20 mL of solutions. The concentration of biomass in each flask was 0.5 g L^{-1}. After adsorption, the solutions were filtered using 0.45-μm Millipore Millex–HV membranes. Phenol concentration in the filtrate was measured at 270 nm using a UV–visible spectrophotometer (UV-2550, Shimadzu, Japan).

The amount of adsorbed phenol per gram biomass was obtained by using the general equation:

$$q_e = (C_0 - C_e)/W \quad (1)$$

where q_e (mg g^{-1}) is the amount of phenol adsorbed onto the unit amount of biosorbents, C_0 and C_e (mg L^{-1}) are the concentrations of phenol in the medium before and after adsorption, respectively, and W (g L^{-1}) is the concentration of the biosorbents.

For pH studies, experiments were conducted over a range of pH values by shaking phenol solutions with the untreated or surfactant pre-treated biomasses on a rotary shaker at 25 °C and 200 rpm for 6 h. Kinetic studies were conducted at pH 7, 25 °C, and 200 rpm. The samples were collected at various time intervals. For the pH and kinetic studies, the concentration of phenol was 200 mg L^{-1}. Isotherm studies were conducted at pH 7, 25 °C and 200 rpm with various concentrations of phenol (25, 50, 75, 100, 150, and 200 mg L^{-1}) for 6 h to ensure that equilibrium was reached.

All the adsorption experiments were performed in triplicate, and the standard deviation was lower than 5%. Controls were run to check the volatilization and adsorption of phenol to the glass walls of the flasks during the experimental course.

2.3. Adsorption kinetics and isotherms

The pseudo-first-order and the pseudo-second-order equations were employed to fit the adsorption dynamic data (Fierroa et al., 2008).

The pseudo-first-order equation is

$$\log(q_e/(q_e - q_t)) = K_f/2.303 \times t \quad (2)$$

The pseudo-second-order equation is

$$1/q_t = 1/(K_s \times q_e^2 \times t) + 1/q_e \quad (3)$$

where q_t (mg g^{-1}) is the adsorption capacity at contact time t, and K_f (min^{-1}) and K_s [g (mg min)$^{-1}$] are the constant of the pseudo-first-order model and the pseudo-second-order model, respectively.

Langmuir and Freundlich isotherms were adopted to describe the adsorption process. The Langmuir isotherm is

$$C_e/q_e = C_e/q_{max} + 1/(b \times q_{max}) \quad (4)$$

The Freundlich isotherm is

$$\ln q_e = \ln K_f + 1/n \times \ln C_e \quad (5)$$

where q_{max} (mg g^{-1}) is the maximum adsorption capacity, and b (L mg^{-1}), K_f [(mg g^{-1}) (L $mg^{-1})^{1/n}$] and n are the correlated characteristic constants (Xu et al., 2008).

2.4. Biosorption characterization

The chemical characteristics of the samples were analyzed by FTIR spectrometry (WQF-410) after the samples were prepared as KBr discs. All spectra were plotted using the same scale on the transmittance axis. The surface structure of biosorbents was analyzed by ESEM (Qutanta 200) coupled with EDX analysis (Qutanta 200). The acceleration voltage was constant as 20 kV, and the microprobe was focused at a magnification of 800. The samples were mounted on a stainless steel stab with double-stick tape. The biomasses were coated with a thin layer of gold under vacuum.

For zeta potential and hydrophobicity measurements, the biomass suspension at concentration of 0.5 g L^{-1} was shaken by vortex, allowed settling for 30 min, and the supernatant was separated carefully with liquid-transferring guns. Zeta potential was determined using a ZEN3600 Zetasizer Nano (Malvern Instruments, Malvern, UK) (Zhong et al., 2007). The relative hydrophobicity of biomasses was measured by assaying microbial adhesion to hydrocarbons (Zhong et al., 2007). The optical density of the biomass supernatant at 400 nm (OD_{400}) was adjusted to 0.6 ± 0.06 on the UV-2552 spectrophotometer (Shimadzu, Japan). Four milliliters suspension and 1.0 mL hexadecane were placed in a 7-mL centrifuge tube, mixed by vortex for 60 s, and the phases were allowed to separate over a period of 30 min at room temperature. The absorbance of the aqueous phase was measured at 400 nm. The difference between the optical densities of the aqueous phase before and after mixing with hexadecane was used to quantitate hydrophobicity:

$$\text{Hydrophobicity } (\%) = (1 - \text{OD}_{400} \text{ of aqueous phase after mixing} \times \text{with hexadecane}/\text{OD}_{400} \text{ of initial aqueous} \times \text{phase}) \times 100 \quad (6)$$

3. Results and discussion

3.1. Effect of pH

The effect of pH on the adsorption of phenol is shown in Fig. 1. For the five kinds of biomass, the adsorption capacities increased with pH from 2 to 7 and decreased when the pH increased from 7

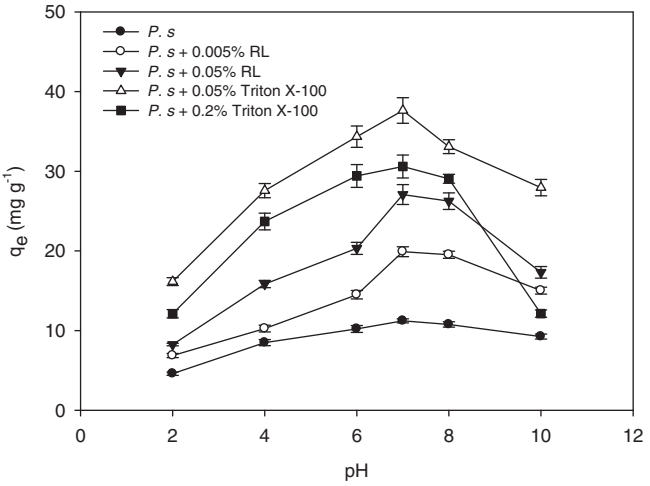

Fig. 1. Adsorption of phenol at various pH conditions by five kinds of biomass. Values are means of three replicates ± SD (standard deviation). *P.s*: *P. simplicissimum*.

to 10. In addition, pre-treatments with RL and Triton X-100 increased the adsorption capacity at all the pHs tested. Triton X-100 had stronger effects than RL (Fig. 1). For example, at pH 7, the adsorption capacity of *P. simplicissimum* pre-treated with 0.05% Triton X-100, 0.2% Triton X-100, 0.05% RL and 0.005% RL were 3.4, 2.7, 2.4, and 1.8-fold that of untreated biomass, respectively.

3.2. Adsorption kinetics

The adsorption kinetics of phenol by various biomasses is shown in Fig. 2. The time required for adsorption to reach equilibrium was about 120 min. Pre-treatments by surfactants enhanced adsorption of phenol. The fitting results of the kinetic models are shown in Table 1. The pseudo-second-order model fit the experimental data better with higher values of R^2 than those of the pseudo-first-order mode, which was in agreement with the previous investigations clarifying that the pseudo-second-order model is appropriate for the adsorption of low molecular weight adsorbates on small adsorbent particles (Liu et al., 2010a). The pseudo-second-order model has been applied to the adsorption of phenols by a variety of adsorbents (Liu et al., 2010a; Mathialagan and Viraraghavan, 2009; Xu et al., 2008).

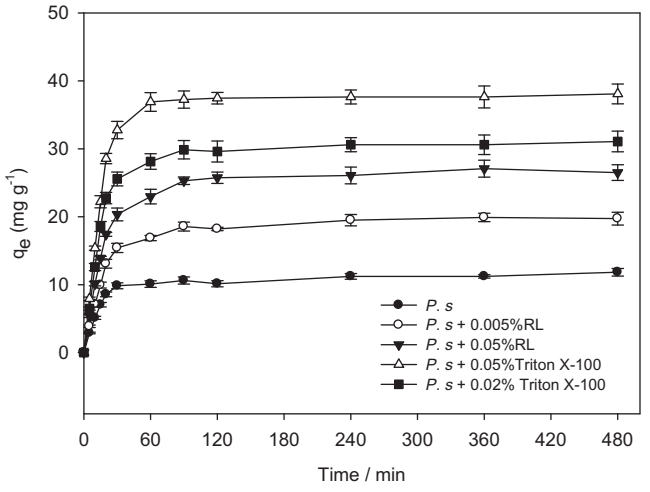

Fig. 2. Effect of contact time on phenol adsorption. Values are means of three replicates ± SD. *P.s*: *P. simplicissimum*.

3.3. Adsorption isotherm

The parameters of the Langmuir and Freundlich isotherms are shown in Table 2. Both the Langmuir and Freundlich isotherms described the adsorption process well, but the Freundlich isotherm was better since its R^2 was higher than that of the Langmuir isotherm. According to the q_{max} values of the Langmuir isotherm, the affinity order for phenol adsorption was as follows: *P.s* + 0.05% Triton X-100 > *P.s* + 0.2% Triton X-100 > *P.s* + 0.05% RL > *P.s* + 0.005% RL > *P.s*. The results also demonstrated that the pre-treatments by surfactants increased the adsorption capacity of phenol.

3.4. FTIR

The FTIR spectra of the biomasses before and after adsorption of phenol were shown in Fig. S1 in Supplementary data. The band at 3356 cm^{-1} likely resulted from the overlapping of O–H and N–H stretching (Liu et al., 2010b). The band at 2927 cm^{-1} is indicative of a C–H group (Mathialagan and Viraraghavan, 2009). The peaks at 1653 cm^{-1} can be designated as the C=O stretching in carboxyl or amine groups (Deng and Ting, 2005; Džambaski et al., 2011). The peak at 1545 cm^{-1} is indicative of the N–H bending (Mathialagan and Viraraghavan, 2009). The peak at 1232 cm^{-1} can be designated as the C=S stretching (Džambaski et al., 2011). The peak at 1035 cm^{-1} can be indicative of the C–N stretching vibrations (Liu et al., 2010b).

Pre-treatments with surfactants changed the FTIR spectra of *P. simplicissimum*. For example, the pre-treatment with 0.005% RL shifted the peaks at 3356, 1653, 1545, 1232 and 1035 cm^{-1} (Fig. S1A) to 3363, 1655, 1549, 1238, 1032 cm^{-1} (Fig. S1C), respectively. Meanwhile, the pre-treatment with 0.05% Triton X-100 also changed the peaks at 3356, 2927, 1232 and 1035 cm^{-1} (Fig. S1A) to 3296, 2931, 1244, and 1030 cm^{-1} (Fig. S1E), respectively. The results indicated that the pre-treatment of surfactants changed the functional groups on cell surface of *P. simplicissimum*.

The FTIR spectra also changed when phenol was adsorbed onto the untreated biomasses, indicating that the adsorption of phenol occurred exactly. For example, the FTIR spectrum peaks of the untreated biomass at 3356, 2927, 1545 and 1035 cm^{-1} (Fig. S1A) shifted to 3406, 2925, 1543 and 1038 cm^{-1} after phenol adsorption (Fig. S1B), respectively. Similar phenomena also occurred when phenol was adsorbed to the biomasses treated with RL and Trtion X-100.

The changed surface properties of *P. simplicissimum* by surfactants also influenced the adsorption of phenol. For example, the pre-treatment with RL shifted the peaks of FTIR spectra of the untreated biomass after phenol adsorption at 2925, 1653, 1543, and 1232 cm^{-1} (Fig. S1B) to 2927, 1655, 1547, and 1238 cm^{-1} (Fig. S1D), respectively. In addition, the pre-treatment with Triton X- 100 also shifted these corresponding peaks to 2927, 1655, 1550, and 1246 cm^{-1} (Fig. S1F), respectively.

3.5. EDX and ESEM

EDX analysis is one of the useful tools to evaluate the elemental characteristics of biomass. The element analysis of the untreated and surfactant pre-treated biomasses is shown in Table 3. In general, the treatments with RL and Triton X-100 decreased the concentrations of C, P, S, and K, but increased the concentrations of O and Cl. In comparison with Triton X-100, RL had stronger effects on concentrations of C, O, S, and Cl but weaker effects on those of P and K. ESEM microphotographs of various biomasses before and after phenol adsorption are shown in Fig. S2 in Supplementary data. The biomasses were mycelia before phenol adsorption (Fig. S2A, C, and E), and became aggregates after phenol adsorption

Table 1
Parameters of the pseudo-first-order and pseudo-second-order models.

Biomass[a]	q_e (exp.)[b]	The pseudo-first-order model			The pseudo-second-order model		
		q_e (cal.)	K_f	R^2	q_e (cal.)	K_s	R^2
P.s	11.22	7.17	0.0343	0.9245	12.21	0.0068	0.9953
P.s + 0.005% RL	19.90	14.03	0.0253	0.9670	22.42	0.0024	0.9934
P.s + 0.05% RL	27.08	20.24	0.0244	0.9766	30.96	0.0017	0.9958
P.s + 0.05% Triton X-100	38.08	23.59	0.0341	0.9373	43.10	0.0016	0.9893
P.s + 0.2% Triton X-100	30.74	23.97	0.0408	0.9766	34.97	0.0019	0.9923

[a] *P.s*: *P. simplicissimum*.
[b] Data were obtained from Fig. 2 at 360 min.

Table 2
Parameters of the Langmuir and Feundlich models.

Biomass [a]	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	n	R^2
P.s	14.43	0.0170	0.9885	1.2243	0.4249	0.9948
P.s + 0.005% RL	30.03	0.0104	0.9861	1.0404	0.5746	0.9860
P.s + 0.05% RL	50.51	0.0067	0.9331	0.6937	0.7273	0.9519
P.s + 0.05% Triton X-100	81.30	0.0053	0.9037	0.7774	0.7761	0.9657
P.s + 0.2% Triton X-100	72.46	0.0043	0.9040	0.5340	0.8010	0.9745

[a] *P.s*: *P. simplicissimum*.

(Fig. S2B, D, and F). There were some small holes on the surface of the untreated biomasses after phenol uptake (Fig. S2B); however, the number of small holes was reduced in biomass pre-treated with 0.005% RL after phenol uptake (Fig. S2D). Moreover, the surface of biomass treated with 0.05% Triton X-100 after phenol uptake was the smoothest. Several investigations also found that adsorption processes changed the structure of adsorbents (Liu et al., 2011b; Tunali et al., 2006).

3.6. Hydrophobicity and zeta potential

Cell surface hydrophobicity may be an important property affecting the adsorption of phenol by biomass. As shown in Fig. 3, the hydrophobicity of the untreated biomass was about 13.2%. The hydrophobicity of the biomasses pre-treated with 0.005% RL, 0.05% RL, 0.05% Triton X-100, and 0.2% Triton X-100 was 1.7, 2.0, 3.0, and 2.4-fold that of untreated biomass, respectively. Thus, pre-treatments with RL and Triton X-100 increased the hydrophobicity of *P. simplicissimum*. Triton X-100 had a stronger effect than RL.

Surface charge of biomasses can also play an important role in adsorption of phenol. The zeta potential of various biomasses is shown in Fig. 4. The untreated biomass was positively charged at pH 2 and negatively charged at pH above 3. In general, the pre-treatments by surfactants increased the zeta potential of *P. simplicissimum*. It was positively charged at pH 2 and pH 3, and negatively charged at pH above 4 after pre-treatment with 0.005% and 0.05% of RL. Moreover, the biomasses were positively charged at pH ranging from 2 to 5 and negatively charged at pH above 6 after pre-treatment with 0.05% and 0.2% of Triton X-100. It was interesting that the zeta potential of biomass pre-treated with Triton X-100 was generally higher than those of biomass pre-treated with RL when the pH was lower than 7.0.

Table 3
Element concentrations of the intact and surfactant pre-treated *P. simplicissimum*.

Element	Atom percents %		
	P.s [a]	*P.s* + 0.005% RL	*P.s* + 0.05% Triton X-100
C	83.48	69.57	71.59
O	14.40	28.37	26.81
P	0.82	0.46	0.37
S	0.20	0.16	0.17
Cl	0.49	1.09	0.73
K	0.61	0.35	0.34

[a] *P.s*: *P. simplicissimum*.

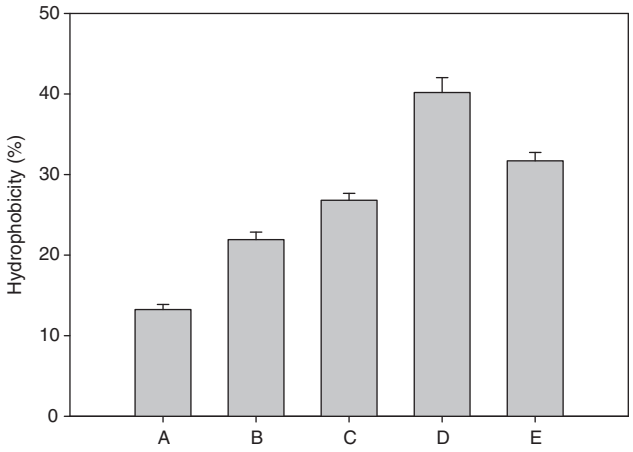

Fig. 3. Hydrophobicity. (A) Untreated biomass, (B) biomass pre-treated with 0.005% RL, (C) biomass pre-treated with 0.05% RL, (D) biomass pre-treated with 0.05% Triton X-100, and (E) biomass pre-treated with 0.2% Triton X-100. Values are means of three replicates ± SD.

Previous investigations have found that there are certain relationships between element component and cell surface properties (such as potential and hydrophobicity), which were dependent on the microorganism species (Mozes et al., 1988; Rouxhet et al., 1994). For some microorganisms, carboxylic, phosphate (or phosphodiester), thiol, and sulfonate groups are of the source of the negative potential on cell surface. In the present study, pre-treatments with RL or Triton X-100 increased cell surface zeta potential of *P. simplicissimum* (Fig. 3), which may be due to the decreased concentrations of C, P, and S on the cell surface (Table 3), since these elements are the main components of negatively charged groups. Hua et al. (2003) also found that the addition of biosurfactant BS–UC increased the positive charge of the cell surface of *Candida antarctica*. However, it was found that the addition of monorhamnolipid reduced the cell surface zeta potential of *C.*

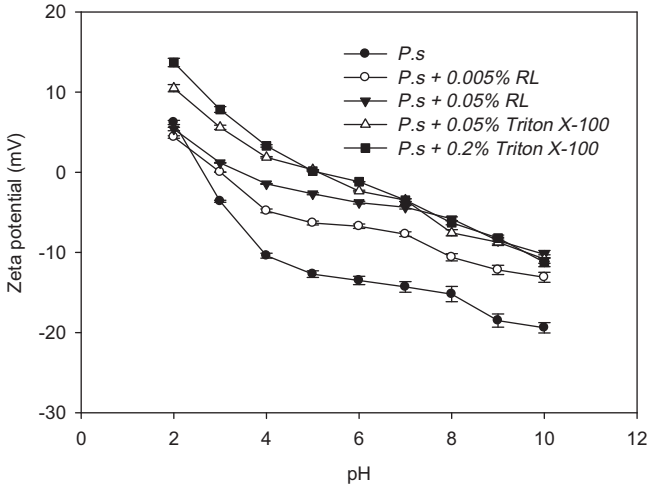

Fig. 4. Zeta potential of *P. simplicissimum* biomass under various pH conditions. Values are means of three replicates ± SD. *P.s*: *P. simplicissimum*.

tropicalis (Zeng et al., 2011). These results indicated that the effects of surfactants on cell surface properties are dependent on both surfactants and microorganisms.

In the current study, the optimum pH for phenol adsorption was 7 (Fig. 1). The effect of pH on the adsorption of phenol by *P. simplicissimum* was related to the characteristics of both phenol and biomasses. Generally, the fungus *P. simplicissimum* exhibited a net negative charge at neutral and basic pH conditions (Fig. 4). At the same time, phenol dissociates into the anionic form at pH over 7.0. Therefore, electrostatic repulsion between the negatively charged biomass surface and the anionic phenol may lead to a lower adsorption capacity. When the pH decreased, the negative charge on the biomasses also decreased (Fig. 4), and phenol tended to exist in the molecular form. Thus, a reduction in pH may remove electrostatic barriers between biomass and phenol and facilitate adsorption. When the pH decreased further, phenol became protonated and positively charged. This causes repulsion between the positively charged fungal surface and phenol molecules, leading to a decreased uptake of phenol (Aksu, 2005; Rao and Viraraghavan, 2002).

Pre-treatment with RL and Triton X-100 increased adsorption of phenol (Figs. 1 and 2 and Table 2) likely due to increased cell surface hydrophobicity (Fig. 3), which can increase hydrophobic interactions between biomass and phenol. Another reason may be the reduced negative charge of *P. simplicissimum* (Fig. 4), which can reduce electrostatic repulsion between biomass and phenol. In addition, the adsorption capacity of biomass pre-treated with Triton X-100 was higher than those of biomass pre-treated with RL (Figs. 1 and 2 and Table 2), which may be also due to the differences of hydrophobicity and zeta potential of *P. simplicissimum* (Figs. 3 and 4).

4. Conclusions

Pre-treatments with RL and Triton X-100 increased adsorption of phenol by *P. simplicissimum*. Triton X-100 had stronger effects than RL. The adsorption process followed the pseudo-second-order model better than the pseudo-first-order model, and followed the Freundlich isotherms better than the Langmuir isotherms. The enhancement in adsorption capacity may be due to the changed hydrophobicity and zeta potential, which may be caused by changed functional groups and element concentrations on the cell surface. The role of surfactants in changing cell surface properties is remarkable at low concentration of surfactants and thus surfactants are potentially cost-effective for remediation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.01.092.

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