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ORIGINAL PAPER

A comparative study on tetracycline sorption by *Pachydictyon coriaceum* and *Sargassum hemiphyllum*

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Abstract This study compared the biosorption of tetracycline, an antibiotic commonly used to treat bacterial infections, in aqueous solution under various conditions using two brown seaweeds commonly found in Hong Kong waters—*Pachydictyon coriaceum* and *Sargassum hemiphyllum*. Two environmental effects (temperature and shaking speed) and two chemical effects (pH and salinity) were investigated to determine the optimal conditions for sorption of tetracycline by biomass. It was found that the maximum biosorption capacity (q_{max}) of tetracycline by the two types of seaweed was generally higher at lower temperature (15 °C) and higher shaking speed (250 rpm). The sorption performances of *P. coriaceum* and *S. hemiphyllum* were better in slightly acidic solution (pH 3), with q_{max} around 9 mg/g for *P. coriaceum*. Higher salinity (100 mM NaCl) reduced the sorption ability of both brown seaweeds by reducing the solubility of the aqueous tetracycline. It was found that *S. hemiphyllum* could tolerate and had higher sorption in a slightly saline solution (50 mM NaCl), while *P. coriaceum* performed better without the presence of NaCl. This study provides crucial information for achieving optimal sorption of aqueous tetracycline using *P. coriaceum* over *S. hemiphyllum* as an effective biomass for removing antibiotics in wastewater.

Keywords Biosorption · *Sargassum hemiphyllum* · *Pachydictyon coriaceum* · Antibiotic

Introduction

Antibiotics are very widely used as therapeutic drugs for treating infectious diseases in both humans and animals (Kummerer 2009). However, many antibiotics cannot be totally absorbed or metabolized by human or animal bodies (Khetan and Collins 2007). Thus, large volumes of antibiotics are excreted and released into the natural environment unchanged or in the form of urine and faeces (McArdell et al. 2003). These waste antibiotics can cause negative ecological effects and may induce bacterial resistance by promoting antibiotic-resistance genes (Eguchi et al. 2004; Dantas et al. 2008). Because of their continuous introduction into the ecosystem, antibiotics are considered to be "pseudo-persistent" contaminants (Richardson et al. 2005; Hernando et al. 2006). Tetracycline is a typical antibiotic used to treat bacterial and protozoan infections in aquaculture that is commonly found in aquacultural ponds and effluent (Kim et al. 2004; Hoa et al. 2008). Tetracycline in the environment originates mainly from sewage treatment plants (STPs), agriculture (Zheng et al. 2012) and the disposal of unused medicines (Kummerer 2003). The uncontrolled release of tetracycline has the potential to cause severe harm to humans and the ecosystem, as soil microorganisms may develop resistance against antibiotics (Choi et al. 2008).

Positive relationships between the consumption of human pharmaceuticals and their concentrations detected in the influents of STPs have been noted (Stewart and Coasterton 2001; Göbel et al. 2005). Antibiotics including tetracycline, erythromycin, ciprofloxacin, trimethoprim and ampicillin are commonly found in STPs, and bacteria isolated from

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sewage reactors have shown resistance to these antibiotics (Adams et al. 2002; Costanzo et al. 2005; Westerhoff et al. 2005). A recent study found that a total of 11 antibiotics, including tetracycline, were discharged from the effluents of seven STPs into Hong Kong's Victoria Harbour, at a combined rate estimated at 14.4 kg/day (Minh et al. 2009).

Recently, various new technologies have been developed for removing contaminants in aqueous solution: the use of carbon nanotubes for the removal of methylene blue dye (Shahryari et al. 2010; Yao et al. 2010); removal of metal chromium in wastewaters using activated carbon from waste rubber tires (Gupta et al. 2013); adsorption of organic pollutants in water using C60 fullerene (Yang et al. 2006); and removal of toxic organic pollutants such as polyaromatic hydrocarbons (PAHs) from wastewater treatment systems using microbes and other advanced techniques (Gupta et al. 2012). Several conventional techniques such as coagulation, flocculation and sedimentation have been tested in removing antibiotics from environmental matrices in STPs (Homem and Santos 2011); however, some studies showed that the resulting removal efficiencies were low (with maximum removals of about 30 %) (Adams et al. 2002; Stackelberg et al. 2007; Vieno et al. 2007). Due to the low efficiencies of these methods, and the complexity of their use, new alternatives have been employed in many cases.

Biosorption is an emerging biotechnology aimed at reducing chemical concentrations in the aqueous compartment using dead, inactive or readily available biomass from various origins (Volesky 2003). A number of studies have investigated the use of brown seaweed to remove chemicals such as heavy metals or organics from sewage. For example, many studies have used *Sargassum* as biosorbent for the removal of metal ions such as nickel (Salman and Naser 2013), lead (Mohammad et al. 2011) and mercury (Esmaeili et al. 2012). Tsui et al. (2006) reported the removal of toxic metal ions (Ag, Cd, Co, Cd, Mn, Ni, Pb and Zn) by brown seaweed *Sargassum hemiphyllum*, while Chung et al. (2007) reported the removal of aqueous phenanthrene using the same type of brown seaweed. Ignacio et al. (2012) reported that the removal of tetracycline in algal ponds was mainly through biosorption and photodegradation. However, there is a lack of information concerning the removal of antibiotics using brown seaweed.

Sargassum hemiphyllum possesses some distinctive and attractive features for biosorption applications. It is relatively easy to collect, being abundant in coastal areas worldwide, it is more stable than bacteria produced through fermentation, and its cellulose structure minimises the required pretreatment, including in the immobilisation and granulation of microbes (Volesky 2003). Investigating the feasibility of using *S. hemiphyllum* to remove antibiotic contaminants in wastewater is thus worthwhile. *Pachydictyon coriaceum*, another brown seaweed, is a branched, bladed alga that grows from the lower intertidal to a depth of 13 m (Abbott and Hollenberg 1976). To the best of our knowledge, no studies exist focusing on using *P. coriaceum* to remove antibiotics in sewage.

The major aim of this study was to develop a simple, low-cost biosorption technique to remove antibiotics using the readily available brown seaweeds *S. hemiphyllum* and *P. coriaceum*. Tetracycline was chosen as a representative antibiotic for this study, as approximately 5,000 ng/L of tetracycline was found in the effluents from the Wan Chai East and Wan Chai West STPs in Hong Kong (Minh et al. 2009). It was hypothesised that dried biomass from the brown seaweeds *S. hemiphyllum* and *P. coriaceum* could be effective in removing tetracycline from the effluent of STPs. The objectives of the study were to (1) investigate the effectiveness of using dried *S. hemiphyllum* and *P. coriaceum* to remove tetracycline; (2) study the effects of factors including pH value, temperature, shaking rate and salinity on the uptake or removal of tetracycline; and (3) determine the optimal conditions for the removal of antibiotics in STPs using equilibrium isotherm models.

Materials and methods

Seaweed sampling and pretreatment

Sargassum hemiphyllum and *P. coriaceum* were collected as life stocks from relatively uncontaminated coastal sites on Lamma Island, Hong Kong. After being transported to the laboratory, the seaweeds were washed thoroughly with deionized water and then air-dried at 50 °C for 2–3 days. The dried seaweeds were then blended in a homogeniser to form finer particles. Seaweed particles sized between 0.2 and 1.0 mm were obtained by passing the processed seaweeds through standard stainless steel sieves. Once processed, the seaweed was stored in a desiccator before use.

Elemental contents of seaweed

The elemental proportions of *S. hemiphyllum* and *P. coriaceum* were obtained from previous studies. Takai et al. (2010) reported that *S. hemiphyllum* contained 37.7 % carbon and 2.1 % nitrogen, while *P. coriaceum* contained 38.9 % carbon and 2.5 % nitrogen. Another study (Yu et al. 2013) found that *S. hemiphyllum* contained 33.6 % carbon and 1.8 % nitrogen. These studies provided some useful basic data on the characteristics of the seaweed varieties used.

Standard preparation

To compare the equilibrium biosorption under different conditions, a standard sorption condition (temperature

25 °C, shaking speed 150 rpm, pH 6 and salinity of 0 mM NaCl) was established, and one factor was varied in each experiment, while the others were kept constant. Approximately 0.2 g of pretreated seaweed was added to 100 mL of deionized water in a 250-mL glass Erlenmeyer flask. 1,000 mg/L tetracycline stock solution was prepared by dissolving 0.1 g tetracycline (Sigma-Aldrich) in 1 M HCl solution until completely soluble. Tetracycline was added into each testing solution by adding 1,000 mg/L tetracycline stock using a glass syringe until the working concentration of 1–40 mg/L was obtained. The initial pH was adjusted using 0.1 M NaOH and 0.1 M HCl, and the actual concentration of tetracycline in the resulting testing solution was determined. The flasks were wrapped tightly in aluminium foil. To achieve equilibrium sorption between the seaweed and tetracycline, the flasks were shaken in a shaking incubator at 25 ± 1 °C for 24 h.

Sorption experiments

The influences of four factors, each with three levels of progressive variations, were investigated. These included two external factors, temperature (15–35 °C) and shaking speed (50–250 rpm). The other two factors were the pH (3–9) and salinity (0–100 mM NaCl). Sodium chloride was chosen to test the effect of salinity, as it is the major component of seawater. The standard method for preparing synthetic seawater with 31 % salinity using NaCl was used to produce the primary source, and other salinity levels were prepared by making appropriate dilutions (USEPA 2012). Other published studies have also used NaCl alone to study the influence of salinity (Cayllahua and Torem 2010; Albadarin et al. 2011). After achieving equilibrium sorption, the sample solution was filtered with a 50-μm glass fibre filter and drained directly into 2-mL vials. The vials were measured immediately and were triplicated for each level. A control sample (without *S. hemiphyllum* or *P. coriaceum* added) was used for each set of conditions and parameters investigated.

Quantification of tetracycline

The aqueous tetracycline was quantified using high-performance liquid chromatography (HPLC) equipped with a photodiode array detector (DAD; 1100 series, Agilent). Aliquots of 40 μL of sample was drawn and injected into the HPLC system by an autosampler. The separation was performed by the analytical reverse-phase C18 column, with 4.6 i.d. × 150 mm dimensions, 5 μm particle size and 80 Å pore size (Eclipse XDB-C18, Agilent), with the thermostat set at 30 °C. The eluting reagent consisted of 70 % oxalic acid, 20 % acetonitrile and 10 % methanol at a flow rate of 0.6 mL min^{-1}. The absorbance wavelength of DAD was set to 280 nm.

Table 1 Langmuir parameters for tetracycline biosorption on *S. hemiphyllum* and *P. coriaceum* under different investigated conditions

Factors	*S.hemiphyllum*			*P. coriaceum*		
	q_{max} (mg/g)	*b* (L/mg)	r^2	q_{max} (mg/g)	*b* (L/mg)	r^2
(A) Sorption temperature (°C)						
15	4.00	0.251	0.821	6.39	0.616	0.961
25	2.53	0.380	0.911	4.65	1.285	0.919
35	3.52	0.248	0.883	5.27	0.882	0.880
(B) Shaking speed (rpm)						
50	2.60	0.273	0.924	5.84	0.235	0.956
150	2.53	0.380	0.911	4.65	1.285	0.919
250	3.75	0.233	0.854	6.83	0.580	0.946
(C) Sorption pH						
3	3.80	0.109	0.884	9.03	0.120	0.930
6	2.53	0.380	0.911	4.65	1.285	0.919
9	3.37	0.445	0.899	4.91	1.465	0.877
(D) Salinity (mM of NaCl)						
0	2.53	0.380	0.911	4.65	1.285	0.919
50	2.92	0.408	0.924	4.79	0.454	0.949
100	2.78	0.230	0.751	4.79	0.286	0.917

q_{max} maximum biosorption capacity, b = Langmuir equilibrium constant

Determination of sorbed tetracycline by brown seaweed

The mass of tetracycline adsorbed per gram of *S. hemiphyllum* or *P. coriaceum* was determined after equilibrium had been achieved by the mass balance equation (Davis et al. 2000):

$$q_e = \frac{(C_i - C_e) \times V}{m} \times 1,000 \quad (1)$$

where q_e is the equilibrium tetracycline uptake by the adsorbents (mg/g); C_i is the initial tetracycline concentration (μg/mL); C_e is the equilibrium tetracycline concentration after the batch adsorption experiment (μg/mL); V is the volume of the tetracycline solution put in contact with the adsorbent (mL); m is the dry mass of seaweed (g); and the value of 1,000 is a conversion factor.

Biosorption isotherm modelling

The Langmuir (1918) and Freundlich equilibrium (1906) isotherms are commonly used adsorption models. The Langmuir model is based on several assumptions: (1) uniformly energetic adsorption sites, (2) monolayer coverage, and (3) no lateral interaction between adsorbed molecules, under the assumption that sorption takes place at specific homogeneous sites within the adsorbent (Langmuir 1918). The Langmuir model is expressed as:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

where q_{max} is the maximum biosorption capacity (mg/g), and b is the Langmuir equilibrium constant related to the energy of adsorption (L/mg); q_e is the equilibrium tetracycline uptake by the adsorbents (mg/g); and C_e is the equilibrium tetracycline concentration after the batch adsorption experiment (µg/mL).

The Freundlich model applies to multilayer adsorption and assumes that adsorption occurs at sites with different energy of adsorption (Freundlich 1906). The classical description of the Freundlich model is presented as:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

where K_f is the Freundlich capacity factor or the equilibrium adsorption constant (mg/g); n is the Freundlich intensity parameter, which is related to the biosorption intensity (Freundlich 1906); q_e is the equilibrium tetracycline uptake by the adsorbents (mg/g); and C_e is the equilibrium tetracycline concentration after the batch adsorption experiment (µg/mL). The value of n indicates the degree of nonlinearity between solution concentration and adsorption. If $n = 1$, the adsorption is linear; if $n < 1$, the adsorption is a chemical process; if $n > 1$, then the adsorption is a physical process (Awwad and Salem 2011). The value of n found in this study was between 1.23 and 2.20 for both seaweeds (Table 2), indicating physical biosorption of tetracycline onto the seaweeds.

The Langmuir and Freundlich isotherm models were derived from their linearised forms and expressed in Eqs (4) and (5), respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (4)$$

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_f \quad (5)$$

where q_{max} and b can be determined from a plot of C_e/q_e versus C_e, and K_f and n can be determined from a plot of ln q_e versus ln C_e.

Removal efficiency of tetracycline by brown seaweed

The percentage removal of tetracycline (%R) by the brown seaweed is expressed as:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (6)$$

where C_i is the initial concentration of tetracycline (µg/mL), and C_e is the equilibrium tetracycline concentration (µg/mL).

Results and discussion

Tetracycline sorption under different environmental and chemical conditions

Both the Langmuir (Table 1) and Freundlich (Table 2) models explained the sorption behaviour of the brown seaweed biomass. The tetracycline binding strength increased for larger values of K_f and b. The value of b, which depends on the adsorption/desorption rate ratio or apparent

Table 2 Freundlich parameters for tetracycline biosorption on *S. hemiphyllum* and *P. coriaceum* under different investigated conditions

Factors	*S.hemiphyllum*			*P. coriaceum*		
	K_f (mg/g)	n (g/L)	r^2	K_f (mg/g)	n (g/L)	r^2
(A) Sorption temperature (°C)						
15	1.16	1.70	0.978	2.28	1.56	0.998
25	0.73	1.94	0.982	2.40	2.10	0.991
35	0.74	1.69	0.989	1.90	1.90	0.987
(B) Shaking speed (rpm)						
50	0.62	1.89	0.990	1.11	1.45	0.998
150	0.73	1.94	0.982	2.40	2.10	0.991
250	0.75	1.64	0.987	2.36	1.52	0.998
(C) Sorption pH						
3	0.40	1.35	0.999	0.96	1.23	0.999
6	0.73	1.94	0.982	2.40	2.10	0.991
9	1.07	2.04	0.969	2.72	2.20	0.964
(D) Salinity (mM of NaCl)						
0	0.73	1.94	0.982	2.40	2.10	0.991
50	0.88	2.00	0.966	1.43	1.65	0.998
100	0.93	1.87	0.920	1.05	1.52	0.992

K_f Freundlich capacity factor, n Langmuir equilibrium constant

Table 3 Comparison of removal efficiency of some organic contaminants by different biosorbents at their maximum biosorption conditions

Biosorbent	Organic contaminant	Removal efficiency (%)	References
Sargassum hemiphyllum	Tetracycline	40	This study
Pachydictyon coriaceum	Tetracycline	70	This study
Ananas comosus	Basic Green 4	99	Chowdhury et al. (2011)
Sargassum hemiphyllum	Phenanthrene	98	Chung et al. (2007)
Acacia leucocephala bark	2,4,6-trichlorophenol	95	Kumar et al. (2012)
Pithophora sp.	Malachite green	90	Kumar et al. (2006)
Aspergillus fumigatus	Methylene blue	80	Abdallah and Taha (2012)
Thuja orientalis	Acid Blue 40	48.5	Akar et al. (2008)
Rhizopus arrhizus	Germazol Torquoise Blue-G	47.5	Aksu and Cagatay (2006)

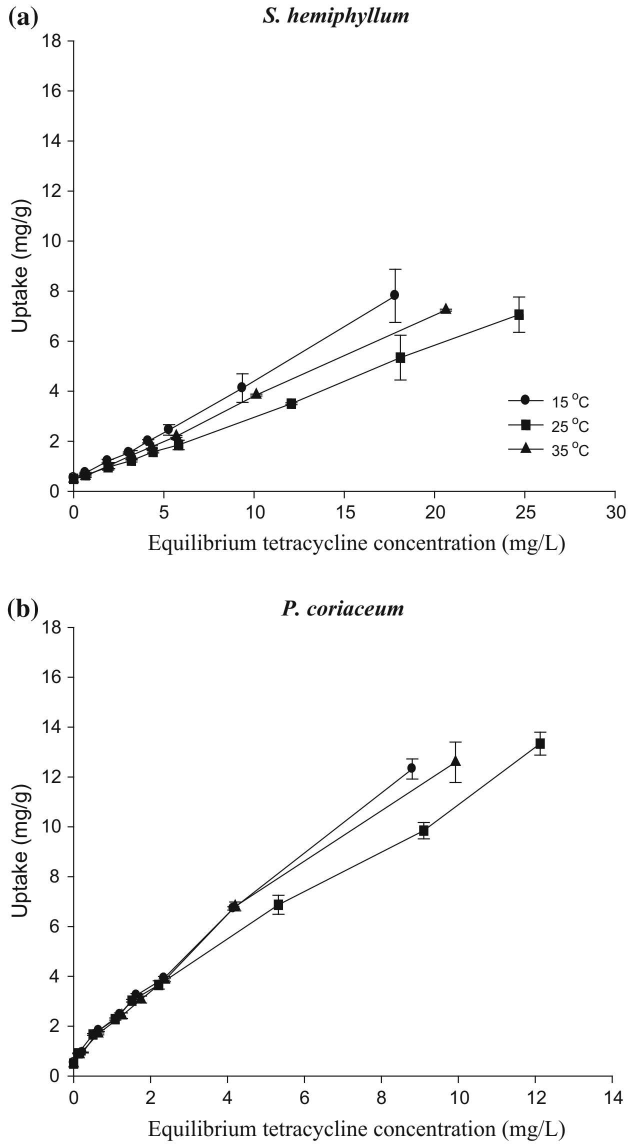

Fig. 1 Sorption isotherm of tetracycline by **a** *S. hemiphyllum* and **b** *P. coriaceum* at temperature of 15, 25 and 35 °C (shaking speed 150 rpm, pH 6 and salinity 0 mM)

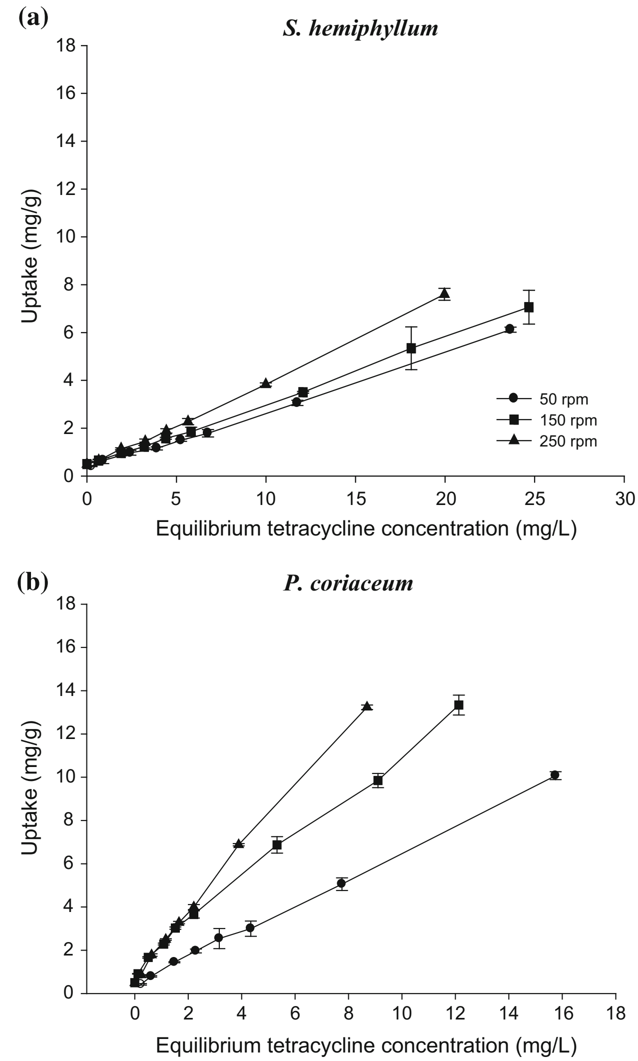

Fig. 2 Sorption isotherm of tetracycline by **a** *S. hemiphyllum* and **b** *P. coriaceum* at shaking speed of 50, 150 and 250 rpm (temperature 25 °C, pH 6 and salinity 0 mM)

energy of sorption, indicated the formation of strong bonds between tetracycline and brown seaweed (Hawari and Mulligan 2006; Solisio et al. 2008). The adsorption affinity was also reflected in the value of *n*, which was always greater than 1. This value implied a favourable physical adsorption process (Senthil et al. 2010). As clearly shown in Table 2, the adsorption of tetracycline by both *P. coriaceum* and *S. hemiphyllum* is favourable under all investigated conditions because all values of *n* are greater than 1.

Effect of temperature

Three levels of temperature were tested (15–35 °C) and maintained during the experiment, with other factors held at standard conditions (shaking speed 150 rpm, pH 6 and salinity of 0 mM NaCl). The tetracycline uptake and percentage removal by *S. hemiphyllum* and *P. coriaceum* are shown in Fig. 1. Sorption capacities and binding strengths were high at 15 °C, but decreased slightly at 35 °C for both brown seaweeds. According to the Langmuir model listed in Table 1A, the maximum tetracycline uptake ($q_{\max}$) by *S. hemiphyllum* was highest at 15 °C, where the uptake was 4.00 mg/g. The value of q_{max} for *P. coriaceum* was also highest at 15 °C, where the uptake was 6.39 mg/g. The sorption of tetracycline by *P. coriaceum* was better described by the Langmuir model than that of *S. hemiphyllum*, with $r^2 = 0.96$. However, for most of the conditions investigated, the Freundlich model was able to describe the tetracycline uptake and binding strength of the brown seaweed more accurately ($r^2 = 0.920$–0.999) than the Langmuir model ($r^2 = 0.751–0.961$). The values of K_f listed in Table 2A show that strong bonds and high binding affinities between tetracycline and both *S. hemiphyllum* and *P. coriaceum* were formed at 15 °C. The decrease in biosorption efficiency may be due to parameters such as the relative increase in the escaping tendency of tetracycline from the solid phase to the bulk phase, and the destruction of some active sites on the seaweed because of bond ruptures (Meena et al. 2005; Sarı et al. 2011). Moreover, 15 °C is a typical temperature in the coastal regions where brown seaweeds grow and metabolize. Generally, *P. coriaceum* possesses a greater tetracycline sorption capacity than *S. hemiphyllum* at the temperatures examined in this study.

Effect of shaking speed

Figure 2 shows the uptake of tetracycline by *S. hemiphyllum* and *P. coriaceum* under different shaking speeds over 24 h. Other factors were held at standard conditions (temperature 25 °C, pH 6 and salinity of 0 mM NaCl). Sorption capacities and binding strengths increased with shaking speed for the two seaweeds. Figure 2 shows a linear relationship between equilibrium tetracycline concentration and tetracycline uptake for both *P. coriaceum* and *S. hemiphyllum* at different shaking speeds. Both the Langmuir and Freundlich models (described in Tables 1B, 2B) show increased tetracycline sorption capacity with increased shaking speed for both brown seaweeds. At a shaking speed of 250 rpm, q_{max} was 6.83 mg/g for *P. coriaceum*, nearly double the value for *S. hemiphyllum*. The Langmuir model described the sorption of tetracycline at a shaking speed 250 rpm by *P. coriaceum* better than that by *S. hemiphyllum*, with *P. coriaceum* giving $r^2 = 0.95$. This finding is consistent with the basic theory of sorption, which predicts that increasing the contact rate between tetracycline and biomass will favour tetracycline mass transfer between the aqueous and solid phases (Chung et al. 2007). A shaking speed of 250 rpm allows good homogenisation and the establishment of equilibrium, improving biosorption capacity. Lower shaking speeds reduce the homogeneity of the solution, allowing the formation of a deposit of biosorbent grains and thus delaying the achievement of equilibrium (Mameri et al. 1999; Dilek et al. 2002). On the other hand, the results from the Freundlich model suggested that there was a stronger interaction between tetracycline and both brown seaweeds at higher shaking speeds. Using the Langmuir and Freundlich models, *P. coriaceum* performed better over *S. hemiphyllum* in the sorption of tetracycline at shaking speeds higher than 250 rpm. The higher biosorption capacity of tetracycline at 250 rpm is consistent with the report by Mameri et al. (1999), Selatnia et al. (2004) and Chergui et al. (2007) who found a decrease in biosorption capacity at shaking speeds away from 250 rpm.

Effect of pH

Figure 3 illustrates the uptake of tetracycline at different pH levels. Normal wastewater before discharging to STPs possesses a typical pH of 6.5–8.5, though some acidic wastewater can reach pH 3 (Macchi et al. 1993). Several studies have also noted reduced adsorption of organic pollutants onto biosorbents at pH lower than 4 or greater than 9 (Bulut and Aydm 2006; Chung et al. 2007). Therefore, three pH values spanning from acidic (pH 3) through neutral (pH 6) to alkaline (pH 9) conditions were used as representatives, while all other factors were kept at standard conditions (temperature 25 °C, shaking speed 150 rpm and salinity of 0 mM NaCl). Compared with the other studied factors, pH has a stronger effect on the biosorption of tetracycline. Observed sorption capacities were high at pH 3, but decreased at higher pH for both brown seaweeds. However, the trend was reversed for binding strength. Using the Langmuir model (Table 1C) for both *P. coriaceum* and *S. hemiphyllum*, the maximum biosorption capacity was high in very acidic solution (pH 3); moderate in alkaline solution (pH 9) and low in solutions close to neutral (pH 6). However, the values of b and K_f (Tables 1C, 2C) suggested that the binding and adsorption of tetracycline were very poor.

The results of this study may be best explained by the relationship between the binding mechanism of brown seaweed and the chemical structures of tetracycline and brown seaweeds which affects the surface charge of the biosorbent, the degree of ionisation of tetracycline in the solution and the dissociation of functional groups on the active sites of the biosorbent (Yeddou-Mezenner 2010). The pK_a values of the different functional groups of tetracycline are relevant here. Tricarbonylamide has a pK_a of 3.3; phenolic diketone of 7.68 and dimethylamine of 9.69 (Vu et al. 2010). Thus, at pH 3, tetracycline is protonated and carries a positive charge. However, at the same pH, the carboxylic, phosphate and amino groups on the cell surface become protonated, allowing the cell surface to be surrounded by hydronium ions, creating unfavourable conditions for the attachment of the positively charged tetracycline due to the increased repulsive force (Popa et al. 2003). This resulted in poorly adsorbed tetracycline at low pH for both brown seaweeds. This result is similar to the finding of Yeddou-Mezenner (2010) that the uptake of dye adsorption by *P. mutilus* at acidic pH is low due to the presence of excess hydrogen ions competing with dye cations for adsorption sites. However, in a slightly alkaline solution (pH 9), both *P. coriaceum* and *S. hemiphyllum* showed better binding and adsorption of tetracycline with relatively larger values of b and K_f. This may be due to the fact that at higher pH value (9), the cell surface consists mainly of carboxyl and phosphate groups, which carry

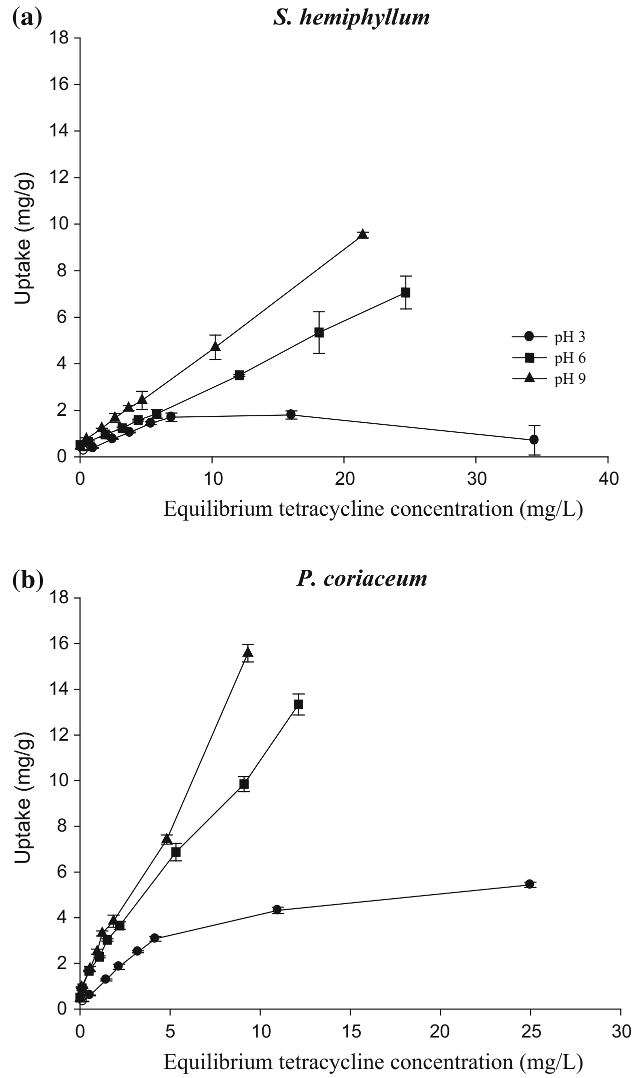

Fig. 3 Sorption isotherm of tetracycline by **a** *S. hemiphyllum* and **b** *P. coriaceum* at pH values of 3, 6 and 9 (shaking speed 150 rpm, temperature 25 °C and salinity 0 mM)

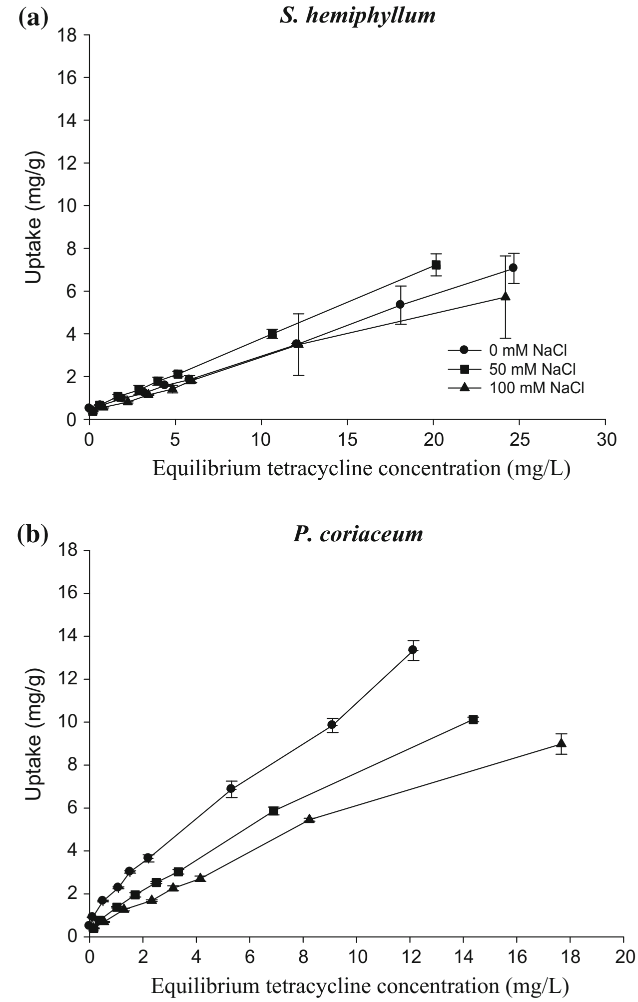

Fig. 4 Sorption isotherm of tetracycline by **a** *S. hemiphyllum* and **b** *P. coriaceum* at salinity of NaCl 0, 50 and 100 mM (shaking speed 150 rpm, temperature 25 °C pH 6)

negative charge (Szachowicz-Petelska et al. 2012), while tetracycline remains neutral at this pH. This produces a stronger intermolecular force between tetracycline and the brown seaweed cell surface. Thus, the binding affinity is higher, as reflected by the values of b and K_f. Another possible explanation is associated with the solubility of tetracycline in alkaline condition. The release of colloidal compounds from dead biomass increases the dissolved organic matter content in solution, which acts as a cosolvent-like colloid and thus increases the solubility of tetracycline (Chung et al. 2007). Generally, for both brown seaweeds, the biosorption capacity was larger at pH 3, even though the binding and adsorption with tetracycline were poor. Moreover, *P. coriaceum* showed higher sorption than *S. hemiphyllum* at the same pH.

Effect of salinity

Figure 4 shows the effect of salinity in the aqueous solution on the sorption performance of tetracycline. Again, other factors were kept at standard conditions (temperature 25 °C, shaking speed 150 rpm and pH 6). The sorption capacity and binding ability of *S. hemiphyllum* with tetracycline were better at 50 mM NaCl, while *P. coriaceu* performed better without NaCl. Tables 1D and 2D indicate the salinity-induced effects on the sorption performance of the aqueous tetracycline. The Langmuir and Freundlich models show that the sorption performance was poorer in more saline solutions (100 mM NaCl) for both brown seaweeds. This may have occurred because the additional electrolytes in the solution interact more strongly with the water molecules than the tetracycline does, thus reducing the solubility of the aqueous tetracycline and forcing it to

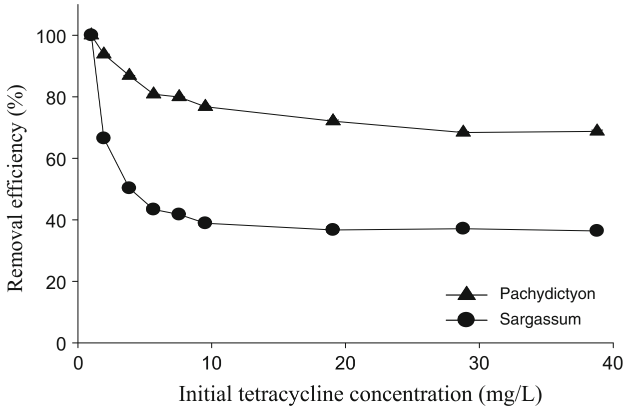

Fig. 5 Removal efficiency of tetracycline by *S. hemiphyllum* and *P. coriaceum* at standard condition (temperature 25 °C, shaking speed 150 rpm, pH 6 and NaCl ionic strength 0 mM)

adhere to surfaces such as the glass of the flask (Chung et al. 2007). The typical salinity of seawater is roughly equivalent to 600 mM NaCl. These results show weaker tetracycline sorption capacities for both *P. coriaceum* and *S. hemiphyllum* under higher salinity (100 mM NaCl). The sorption capacity of tetracycline by brown seaweed may even decrease in the coastal areas receiving urban discharges. The Langmuir and Freundlich models (Tables 1D, 2D) show that the sorption capacity and binding ability of *S. hemiphyllum* with tetracycline were higher at 50 mM NaCl, while *P. coriaceu* was better without NaCl. This is not surprising, since *S. hemiphyllum* has a higher tolerance for fluctuating salinity in its natural habit (Kaliaperuma et al. 2001).

At times, the biosorption isotherms may exhibit an irregular pattern because of the complex nature of both the sorbent material and its varied multiple sites, as well as the complex solution chemistry of some of the relevant metallic compounds (Volesky and Holan 1995). Compared with the findings obtained using biomass as a sorbent for removing heavy metal ions (Tsui et al. 2006) or organics (Kumar et al. 2012) with a typical $q_{\max}$ value above 10 mg/g, the values obtained in this study were relatively low. As the heterogeneous functional groups of brown seaweeds exist on the surface, studies have shown that the physical force between brown seaweeds and tetracycline is weaker (Cavas and Gokoglu 2011), which contributes to the poorer brown seaweed sorption capacity of tetracycline compared with metals. Despite the smaller tetracycline sorption capacity of the two investigated seaweeds, their binding and adsorption were not as poor as those for metals and organics. This indicated that brown seaweeds, particularly *P. coriaceum*, could serve as potential candidates for effectively removing antibiotics in STPs.

Removal efficiency of tetracycline and binding mechanism

The percentages of tetracycline removed from *S. hemiphyllum* and *P. coriaceum* were compared under standard conditions (temperature 25 °C, shaking speed 150 rpm, pH 6 and salinity of 0 mM NaCl; Fig. 5). Figure 5 shows the removal efficiency (RE) of tetracycline as a function of the initial tetracycline concentration C_i for *P. coriaceum* and *S. hemiphyllum*, instead of equilibrium tetracycline concentration C_e. The removal efficiency decreased with increasing initial tetracycline concentration and saturated at approximately 10 mg/L tetracycline. Standard conditions (temperature 25 °C, shaking speed 150 rpm, pH 6 and salinity of 0 mM NaCl) were used for comparison. Figure 5 shows that at the same initial tetracycline concentration, the removal efficiency of tetracycline by *P. coriaceum* is higher than that by *S. hemiphyllum*. *S. hemiphyllum* can remove about 40 % of aqueous tetracycline, while *P. coriaceum* can remove about 70 % under the investigated conditions. Table 3 compares the removal efficiency of tetracycline by different biosorbents with that of other organic contaminants in aqueous solution. The results differ from previous findings that *Sargassum* can remove more than 90 % of aqueous phenanthrene (e.g. Chung et al. 2007). However, the removal efficiency of tetracycline by *P. coriaceum* is higher than that for the removal of common dyes by *Thuja orientalis* or *Rhizopus arrhizus* (Aksu and Cagatay 2006; Akar et al. 2008). These differences may due to different sorption mechanisms between tetracycline and phenanthrene by brown seaweeds under different investigated conditions. Interaction between the functional groups of brown seaweeds and organic compounds is believed to be one of the factors contributing to the different binding behaviour (Kumar et al. 2012). Diffusion across the boundary layer of seaweeds is governed by the intraparticle diffusion model (Weber and Morris 1962). The diffusion process also depends on the boundary layer thickness and rate limiting step (Kumar et al. 2012). However, to the best of our knowledge, the exact binding mechanism between brown seaweeds and tetracycline remains unclear. This finding indicates that *P. coriaceum* may be a viable alternative biomass for removing tetracycline from the effluents of STPs.

Conclusion

It was found that the chemical factors pH and salinity played more important roles in determining the sorption of antibiotics than the environmental factors sorption temperature and shaking speed. The sorption capacities of *P.*

coriaceum and *S. hemiphyllum* were higher at a lower temperature (15 °C) and higher shaking speed (250 rpm). Both seaweeds had better sorption capacity in acidic solution (pH 3), but the adsorption and binding strengths were relatively poor. *S. hemiphyllum* had a higher sorption capacity in slightly saline solution (50 mM NaCl), while the sorption capacity of *P. coriaceum* was higher in the absence of NaCl. *P. coriaceum* had higher sorption capacity and binding strength than *S. hemiphyllum* in the sorption of antibiotics. The removal efficiency of *P. coriaceum* was 30 % before saturation, while *S. hemiphyllum* had an efficiency of about 60 %. To the best of our knowledge, this is the first scientific assessment of the biosorption of tetracycline by the dried biomass of *P. coriaceum* and *S. hemiphyllum*. In conclusion, *P. coriaceum* may be an alternative for the sorption of antibiotics in Hong Kong STPs. However, more attention should be given to understanding the binding and sorption mechanisms between antibiotics and these brown seaweeds.

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