

Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: Marine macroalgae and agricultural by-products

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Abstract

In this study, adsorption of Cr(VI) onto the four low-cost biosorbents (*Laminaria japonica*, *P. yezoensis* Ueda, rice bran and wheat bran) was investigated depending on solution pH, contact time, adsorbent concentration and adsorption isotherms by employing batch adsorption technique. The adsorption capacities were significantly influenced by solution pH, with lower pH favoring higher Cr(VI) removal for various biosorbents. The ionic strength of NaCl was also observed to have a significant impact on the Cr(VI) adsorption due to the competition of Cl⁻ in the aqueous solutions. The batch equilibrium data were correlated to Langmuir and Freundlich isotherms and the data fitted better to the Freundlich isotherm equation. The apparent thermodynamic parameters were calculated for each of the four biosorbents and the obtained numerical values showed that the Cr(VI) adsorption onto the various low-cost biosorbents is spontaneous, entropy-driven and endothermic processes. The batch kinetic data were correlated to the pseudo-first order and pseudo-second order models and the data fitted better to the pseudo-second order equation. An intraparticle diffusion model was applied to investigate the adsorption mechanisms. The adsorption capacities for various biosorbents studied in this work were inversely proportional to the adsorbent concentrations.

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1. Introduction

Cr(VI) is one of the most toxic heavy metals and on the list of priority pollutants due to its mutagenic and carcinogenic properties defined by the US EPA. Cr(VI) is mainly from electroplating, leather tanning, textile dyeing and metal finishing industries. The US EPA requires Cr(VI) in drinking water and inland surface waters is 0.05 and 0.1 mg/L, respectively [1].

Conventional treatment technologies utilized in electroplating and metal finishing plants suffer from disadvantages such as high disposal and chemical costs and incomplete reduction of Cr(VI). Contaminated waters containing low concentrations of Cr(VI) are typically treated with ion exchange resin; however, this method is also costly due to the high price of the resin [2]. Accordingly, cost effective treatment technologies are needed to meet these requirements. One of the promising

techniques for removal of toxic metals from aqueous solutions is the use of living or non-living organisms and their derivatives (i.e. biosorbents) [3]. Of the many types of biosorbents (i.e. algae, fungi, bacteria and yeasts) recently investigated for their ability to sequester heavy metals, marine algal biomass (seaweed) has been found to be an excellent biosorbent for metals due to its high uptake capacity and the abundance of the biomass in many parts of the world's oceans [3,4]. Biosorption in algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role [5]. Typical algal cell walls of Phaeophyta (brown algae) and Rhodophyta (red algae) are comprised of a fibrillar skeleton and an amorphous embedding matrix. The Phaeophyta algal embedding matrix consists predominately of alginic acid or alginate with a smaller amount of sulfated polysaccharide whereas the Rhodophyta contains a number of sulfated galactans [5]. The alginates have a high affinity for divalent cations while the uptake of trivalent cation has been ascribed mainly to the presence of sulfated polysaccharides in the cell wall of the brown algae [3]. These characteristics make them potentially

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excellent heavy metal biosorbents [3,5]. Some reviews that deal with biosorption by different types of brown algae include [5,6]. Blue-green algae *Spirulina Sp.* also have high uptake capacity for metals such as Cr^{3+} , Cd^{2+} and Cu^{2+} [7,8]. However, most of these studies mainly focused on the cationic metals such as copper, cadmium, lead and nickel. Tsui et al. [4] has reported that the brown seaweed (*Sargassum hemiphyllum*) has significantly lower capacities for As(V) and Cr(VI) at pH 5.0 compared to those of cationic metals such as lead, copper, silver, zinc, cobalt and nickel.

Another inexpensive source of biomass available in copious quantities is agricultural by-products. The mode of metal ion sorption by agricultural by-products is principally attributed to the intrinsic adsorption and coulombic interaction [9]. Recently, some raw agricultural by-products such as sawdust [10–12], wheat straw [13], hazelnut shell [1,14], rice husk [12], coir-pith [12], and apricot stone [15] have been tested for the decontamination of Cr(VI)-containing effluents. Rice bran, an undesirable agricultural residue, is a by-product of the rice milling industry. The estimated annual rice production of 500 million tonnes in developing countries, approximately 100 million tonnes of rice bran is available annually for utilization in these countries [16]. The compositions of rice bran are cellulose, hemi-cellulose, lignin, extractives, water and mineral ash [16,17]. Wheat bran is also an important agricultural residue in quantity and the lignocellulosic substrate is one of the main components [18]. Although abundant natural materials of cellulosic nature have been suggested as biosorbents, very less work has been actually done in this respect [19].

The main objective of this work was to evaluate the adsorption performance of locally derived marine macroalgae, namely *Laminaria japonica* (brown macroalga), *P. yezoensis* Ueda (red macroalga), and agricultural by products, namely rice bran and wheat bran for the removal of Cr(VI) from single aqueous solutions. The Cr(VI) adsorption equilibrium and kinetics were determined. Langmuir and Freundlich isotherm equations were employed to quantify the adsorption equilibrium. The effects of solution pH, adsorbent concentration, temperature and ionic strength on Cr(VI) adsorption were examined. An intraparticle diffusion model was used to investigate the adsorption mechanisms.

2. Materials and methods

The raw biomass of *L. japonica* and *P. yezoensis* Ueda were collected in Lianyungang, China. The biomass was washed with copious quantities of deionized water to remove extraneous materials and release common ions present in seawater and then sun-dried [3]. The sun-dried biomass was ground to particles of size fraction $<150\ \mu\text{m}$ for the following experiments. The raw rice bran and wheat bran was dried in an oven at $105\ ^\circ\text{C}$ for a period of 24 h, and then also ground and sieved to get size fraction $<150\ \mu\text{m}$ for adsorption experiments.

The stock solution was prepared by dissolving a known quantity of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) (AR grade) in de-

ionized water. The stock solution was finally diluted to obtain standard solutions.

Batch kinetic experiments were carried out at constant pH 1.0 with initial concentration (100 mg/L) and adsorbent dose of 4 g/L at temperature of $30\ ^\circ\text{C}$. After shaking, the solution samples were withdrawn at suitable time intervals. Batch equilibrium experiments were conducted using 125-mL polypropylene bottles at a total sample volume of 50 mL for each adsorption run. The samples were agitated in a reciprocating shaker to reach equilibrium. At the end of the reaction time, a known volume of the solution was removed and centrifuged for Cr(VI) analysis.

The effect of pH on adsorption of Cr(VI) onto the various biosorbents was investigated by varying the solution pH from 1.0 to 7.0. The effects of temperature and biosorbent concentrations on uptake of Cr(VI) were then examined. Finally, 8 and 16 g/L NaCl were employed as background electrolyte to investigate the effect of ion strength on uptake of Cr(VI). Temperature control was provided by the water bath shaker units. The solution pH was adjusted with strong acid (HCl) and/or strong base (NaOH) and recorded with a pH meter (PHS-3C).

The residual Cr(VI) concentrations were determined using diphenylcarbazide method [1]. Diphenylcarbazide forms a red-violet complex selectively with Cr(VI), and the intensity of this complex was read at 542 nm using a UV-vis spectrophotometer.

The amount of Cr(VI) sorbed by biosorbents (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{m} \quad (1)$$

where V is the solution volume (L), m is the amount of sorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium metal concentrations, respectively.

The Cr(VI) percent removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

3. Results and discussion

3.1. Effect of solution pH on Cr(VI) removal

Fig. 1 shows the effect of solution pH on Cr(VI) removal efficiency for the four biosorbents. The results indicate that the Cr(VI) removals are highly pH-dependent. At low solution pH, there exist a large number of H^+ ions, which neutralizes the negatively charged adsorbent surface thereby reducing the hindrance to diffusion of dichromate ions [20]. The pH dependence of metal adsorption is also related to metal solution chemistry. The Cr(VI) in the solution exists mainly in three oxidation states, i.e. $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and CrO_4^{2-} . The dominant form of Cr(VI) is HCrO_4^- over the range of $1.0 < \text{pH} < 3.0$ [1] while CrO_4^{2-} is dominant in the range of $\text{pH} > 6.0$. Fig. 1 clearly indicates that it

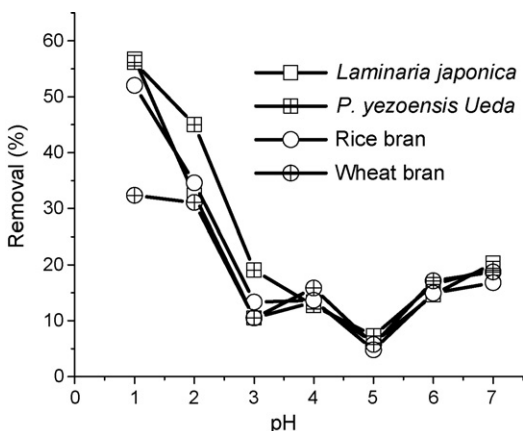


Fig. 1. Effect of pH on Cr(VI) removal (initial concentration 100 mg/L; adsorbent concentration 4 g/L; temperature 30 °C).

is HCrO_4^- which is adsorbed preferentially onto the biosorbents studied.

3.2. Determination of equilibrium time

Fig. 2 indicates the results of batch kinetic experiments conducted to determine the equilibrium time required for the uptake of Cr(VI) by the various biosorbents. In general, the equilibrium time needed for each of the four low-cost biosorbents was close to 9 h. Therefore, in subsequent equilibrium experiments, 12 h was deemed more than sufficient to achieve the adsorption equilibrium.

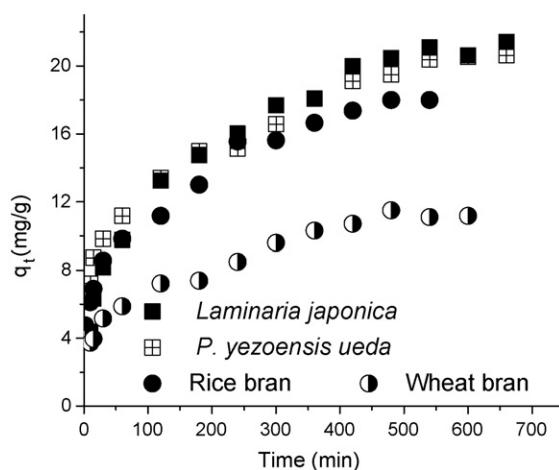


Fig. 2. Kinetic experimental studies of Cr(VI) adsorption (initial concentration 100 mg/L; solution pH 1.0; temperature 30 °C; adsorbent concentration 4 g/L).

3.3. Kinetic modeling

The kinetics of Cr(VI) sorption onto various biosorbents was investigated using the pseudo-first order and pseudo-second order kinetics models.

The pseudo-first order Lagergren model, traditionally used for describing sorption kinetics is generally expressed by the following Eq. [21]:

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{3}$$

where k (min^{-1}) is the Lagergren rate constant of the first sorption, evaluated from the slope of the plot of $\log(q_e - q_t)$ versus t

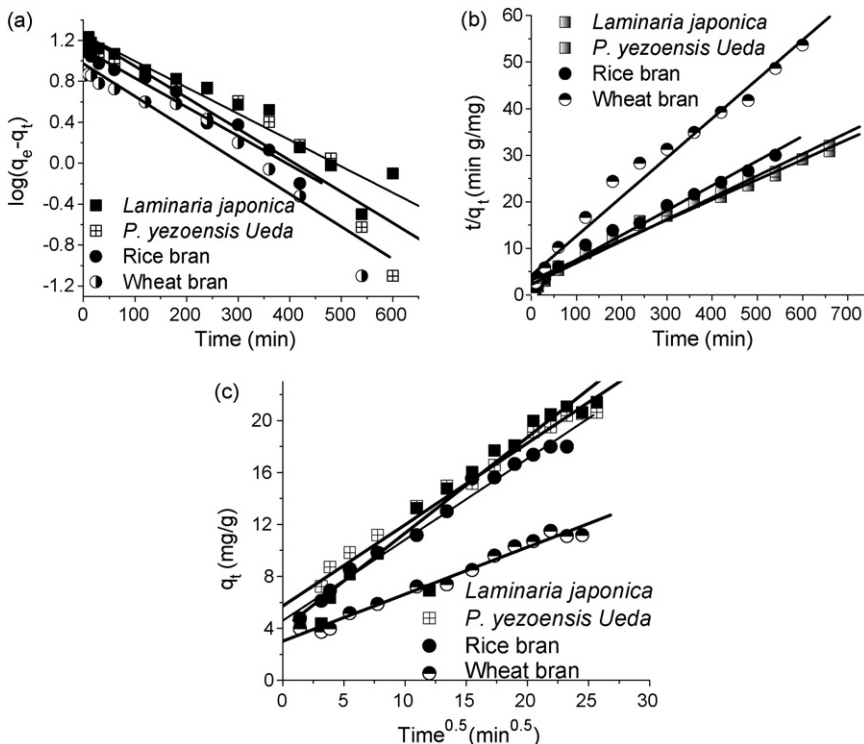


Fig. 3. Fitting of experimental data by three kinetic equations (a: pseudo-first order model; b: pseudo-second order model; c: intraparticle diffusion model) (initial concentration 100 mg/L; solution pH 1.0; temperature 30 °C; adsorbent concentration 4 g/L).

Table 1
Kinetic parameters for Cr(VI) adsorption onto the four biosorbents

	First order		Pseudo second order		Intraparticle diffusion	
	k_1 ($\times 10^3$) (min^{-1})	R	k_2 ($\times 10^3$) ($\text{g}/(\text{mg min})$)	R	k_d ($\text{mg}/(\text{g min}^{0.5})$)	R
<i>L. japonica</i>	2.57	0.9678	0.59	0.9949	0.7377	0.9856
<i>P. yezoensis</i> Ueda	3.06	0.9435	0.98	0.9929	0.6275	0.9874
Rice bran	2.83	0.9873	1.25	0.9927	0.6233	0.6623
Wheat bran	3.18	0.9629	1.68	0.9898	0.3621	0.9902

(Fig. 3(a)), q_t and q_e (mg/g) are the adsorption capacities at time t and equilibrium, respectively.

The pseudo-second order model [22] is generally written as in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_0^2} + \frac{t}{q_0} \quad (4)$$

where q_t is the amount of Cr(VI) adsorbed (mg/g) at time t (min), q_0 the amount adsorbed (mg/g) at equilibrium and k_2 the adsorption rate constant ($\text{g}/(\text{mg min})$). A straight line could be obtained and q_0 and k_2 can be calculated by plotting t/q_t versus t (Fig. 3(b)).

The kinetic parameters together with the corresponding correlation coefficients of Cr(VI) sorption onto various biosorbents are listed in Table 1. The results show the pseudo-second order model fitted the experimental data more appropriately.

In order to distinguish the film diffusion or intraparticle diffusion process, the Weber–Morris equation [23] was tested in the following form:

$$q_t = k_p t^{0.5} \quad (5)$$

where k_p is the diffusion rate constant. The plot of q_t versus $t^{0.5}$ is a straight line for four biosorbents as shown in Fig. 3(c), indi-

cating intraparticle diffusion process is predominant for these biosorbents used in this study. The values of k_p for various biosorbents are also given in Table 1.

3.4. Adsorption isotherm

The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents [5]. The Langmuir isotherm was originally developed to describe the gas–solid phase adsorption of activated carbon. In its formulation, binding to the surface was primarily by physical forces and implicit in its derivation was the assumption that all sites possess equal affinity for the adsorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase [5]. The following form of the Langmuir isotherm is traditionally applied:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (6)$$

where q_e (mg/g) is the sorption capacity at equilibrium, q_{\max} (mg/g) the maximum sorption capacity of the biosorbent, C_e (mg/L) the final equilibrium concentration of Cr(VI), b (L/g) the Langmuir adsorption constant.

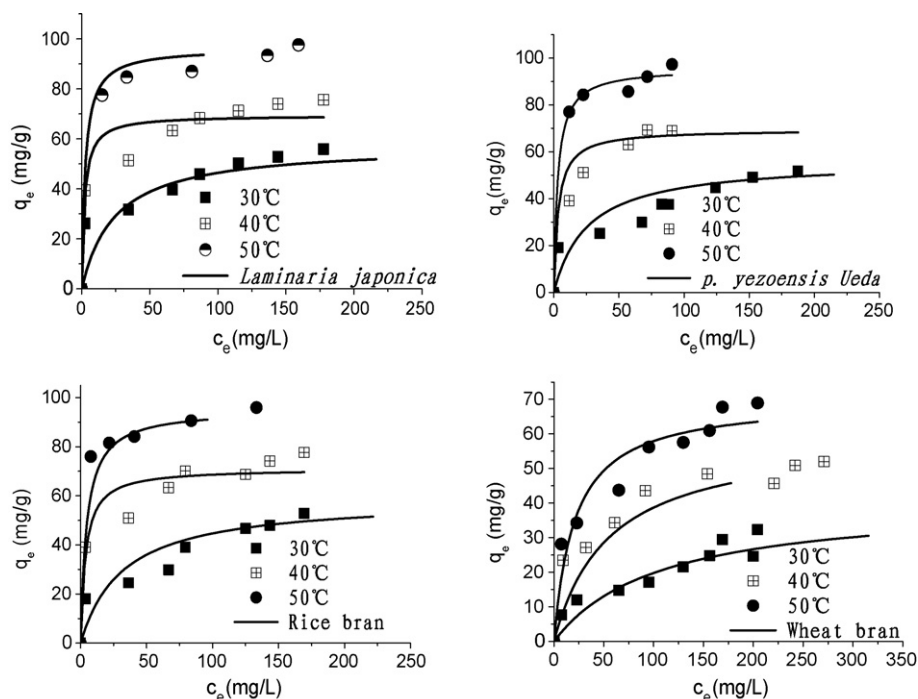


Fig. 4. Langmuir isotherms for Cr(VI) sorption onto four biosorbents at various temperatures (solution pH 1.0; contact time 12 h; adsorbent concentration 4 g/L).

Table 2
Parameters of Langmuir and Freundlich isotherms for Cr(VI) sorption onto four biosorbents at various temperatures

(°C)	Langmuir			Freundlich		
	q_{\max} (mg/g)	b (L/g)	R^2	K_f (mg ^(1-1/n) /g L ^{1/n})	n	R^2
<i>L. japonica</i>						
30	59.35	0.03769	0.9682	11.408	3.434	0.9965
40	69.44	0.4802	0.9682	31.569	5.994	0.9895
50	96.31	0.3859	0.9938	62.187	2.326	0.9968
<i>P. yezoensis Ueda</i>						
30	56.32	0.03863	0.8975	10.439	3.305	0.9828
40	69.47	0.2947	0.9504	30.468	5.865	0.9892
50	95.81	0.3297	0.9925	60.603	10.175	0.9950
Rice bran						
30	58.89	0.0314	0.9678	8.619	2.926	0.9976
40	69.44	0.4802	0.9682	31.569	5.994	0.9895
50	95.35	0.2194	0.9909	53.386	8.241	0.9954
Wheat bran						
30	40.80	0.00942	0.9482	2.577	2.325	0.9845
40	59.95	0.0181	0.9683	6.779	2.762	0.9818
50	70.03	0.0477	0.9365	13.601	3.301	0.9865

The Langmuir plots for Cr(VI) isothermal adsorption data for various biosorbents at different temperatures are shown in Fig. 4. The calculated constants q_{\max} and b together with correlation coefficients (R^2) are given in Table 2. The values of q_{\max} for all four biosorbents increased with the rise of temperatures, indicating the sorption processes are endothermic in nature. The constant, b , is related to the affinity between the adsorbent and adsorbate [24]. The values of b increased with increasing temperature only for *P. yezoensis Ueda* and wheat bran. In terms of implementation, biosorbents with the highest possible q_{\max} and a high value of b are the most desirable [5]. Of the four biosorbents, wheat bran showed the poorest

Cr(VI) adsorption performance compared to the other three biosorbents.

The Freundlich isotherm is originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surface supporting sites of varied affinities [5]. The Freundlich isotherm is defined by the following expression:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f and n are the Freundlich constants.

Freundlich plots for the Cr(VI) adsorption onto the four biosorbents at various temperatures are given in Fig. 5. It illus-

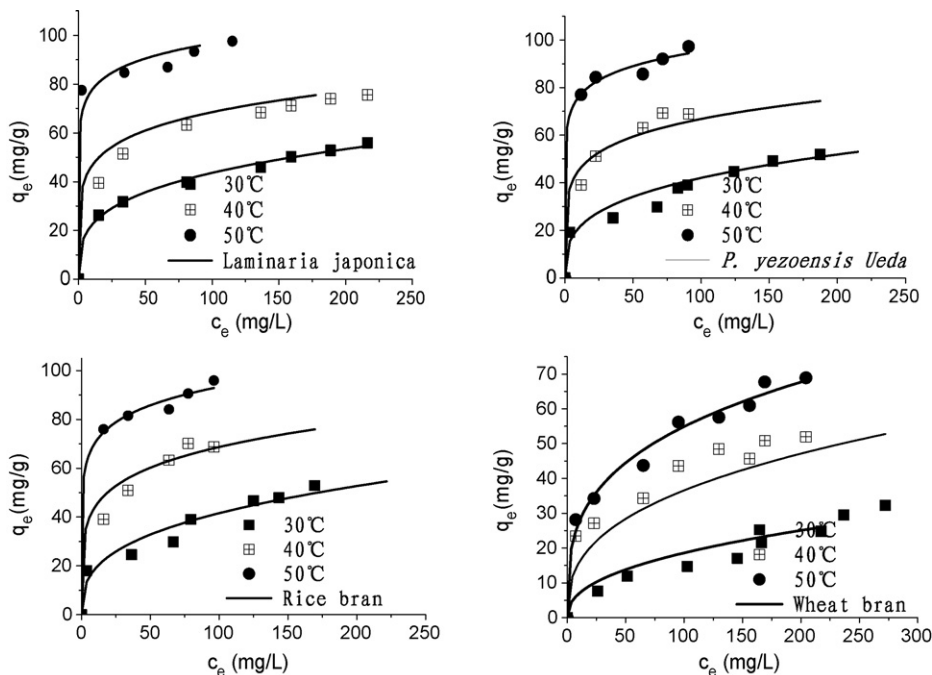


Fig. 5. Freundlich isotherms for Cr(VI) sorption onto four biosorbents at various temperatures (solution pH 1.0; contact time 12 h; adsorbent concentration 4 g/L).

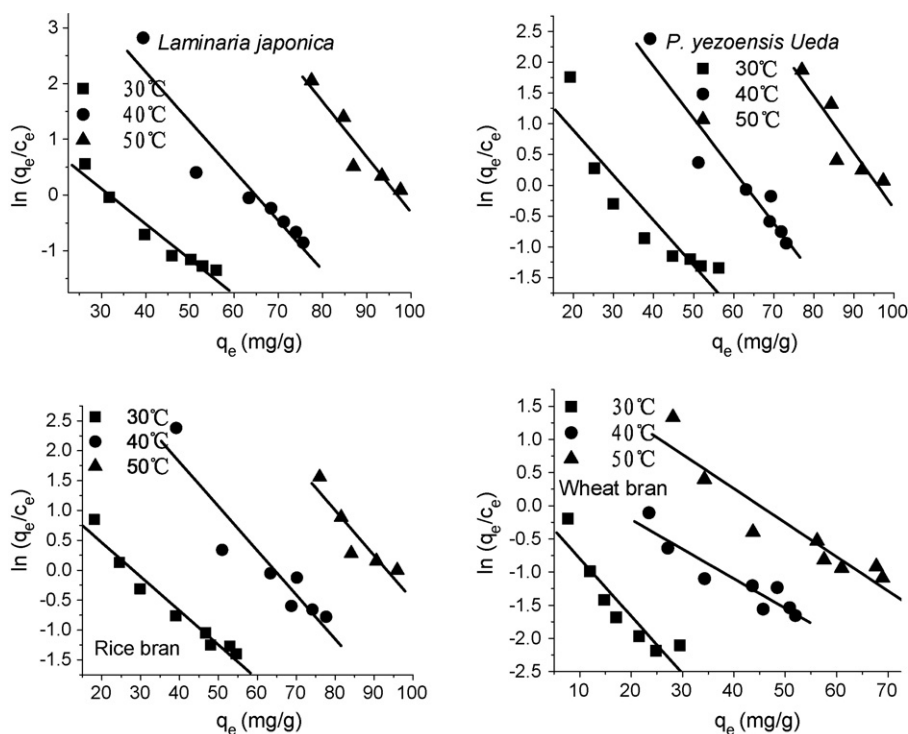


Fig. 6. Plots of $\ln(q_e/C_e)$ versus q_e for various biosorbents at various temperatures.

trates that adsorption of Cr(VI) onto the various biosorbents obeys the Freundlich isotherms very well. The corresponding Freundlich isotherm constants K_f and n together with the correlation coefficients (R^2) are also listed in Table 2. K_f derived from the Freundlich equation is an indicator of adsorption capacity of a given adsorbent [25]. The results obtained in the present study indicate the adsorption capacities (K_f) increased with increasing temperatures for the four biosorbents. The exponent n greater than unity at various temperatures for various biosorbents in Table 2 suggests a favorable adsorption processes [25].

The thermodynamic equilibrium constant, K_0 for the sorption reactions is determined by the method suggested by Khan and Singh [26] by plotting $\ln(q_e/C_e)$ versus q_e (Fig. 6) and extrapolating to zero. The endothermic nature of adsorption is indicated by an increase in the K_0 values with a rise in temperature [27]. Thermodynamic parameters (ΔG^0 , ΔH^0 , ΔS^0) for various biosorbents are calculated from the variation of the thermodynamic equilibrium constants K_0 at various temperatures according to the following Eqs. (8) and (9). Plots of $\ln K_0$ versus $1/T$ for various biosorbents are linear as indicated in Fig. 7. ΔH^0 and ΔS^0 are determined from the slopes and intercepts of the plots. The corresponding numerical values for ΔG^0 , ΔH^0 and ΔS^0 are given in Table 3.

$$\Delta G^0 = -RT \ln K_0 \quad (8)$$

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

The negative values of ΔG^0 except for Cr(VI) adsorption onto wheat bran at 30 and 40 °C indicate the feasibility of the process and also the spontaneity of adsorption reaction. The values of

ΔH^0 are positive for various biosorbents, showing these sorption processes are endothermic in nature. The positive values of ΔS^0 for four biosorbents suggest the increased randomness at the solid–solution interface during these adsorption processes [27].

3.5. Effect of adsorbent concentration on adsorption

Biomass concentration in solution affects the specific uptake and hence this effect needs to be taken into consideration in any application of biomass as biosorbents [19]. The effects of adsorbent concentrations on the adsorption of Cr(VI) onto the four biosorbents are shown in Fig. 8. Obviously, there is an increase in the specific uptake with the lower values of biomass concentrations. This may be attributed to the responsibility of

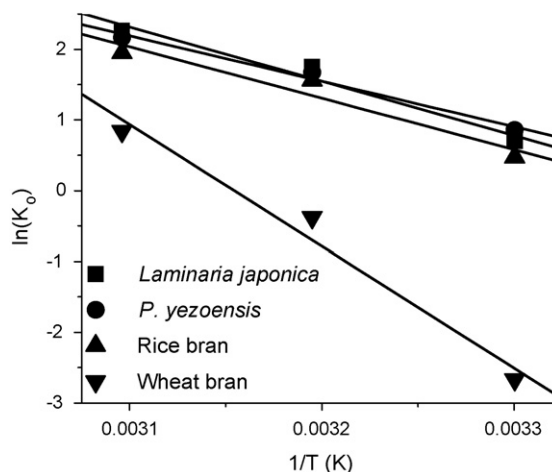


Fig. 7. Plots of $\ln(K_0)$ versus $1/T$.

Table 3
Thermodynamic parameters for Cr(VI) sorption onto various biosorbents at various temperatures

(°C)	K_o	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
<i>L. japonica</i>				
30	2.009	-1.757	63.868	217.254
40	5.771	-4.561		
50	9.605	-6.075		
<i>P. yezoensis Ueda</i>				
30	2.355	-2.158	53.469	183.966
40	5.334	-4.356		
50	8.740	-5.821		
Rice bran				
30	1.603	-1.189	60.460	204.343
40	4.771	-4.066		
50	7.037	-5.239		
Wheat bran				
30	0.069	+6.721	143.105	451.395
40	0.684	+0.988		
50	2.314	-2.253		

the specific uptake decrease to metal concentration shortage in solution. Fig. 8 also shows that removal efficiencies increased with the rise of the adsorbent concentrations. It should be noted that the lower removal efficiency could be observed for wheat bran when compared to those for other three biosorbents.

3.6. Effects of initial concentrations and ionic strength on adsorption

In this study, the distribution coefficient, K_D (mL/g), was used to indicate the adsorption affinity between adsorbate and

adsorbent. The K_D is defined as [28]:

$$K_D = \frac{(C_i - C_e) V}{C_e m}$$

where C_i and C_e (mg/L) are the initial and equilibrium concentrations in solutions, respectively. V/m (mL/g) is the ratio of the liquid volume over the mass of adsorbents.

The effects of Cr(VI) initial concentrations on the distribution coefficients at solution pH 1.0 are shown in Fig. 9. In general, the distribution coefficients for various biosorbents were

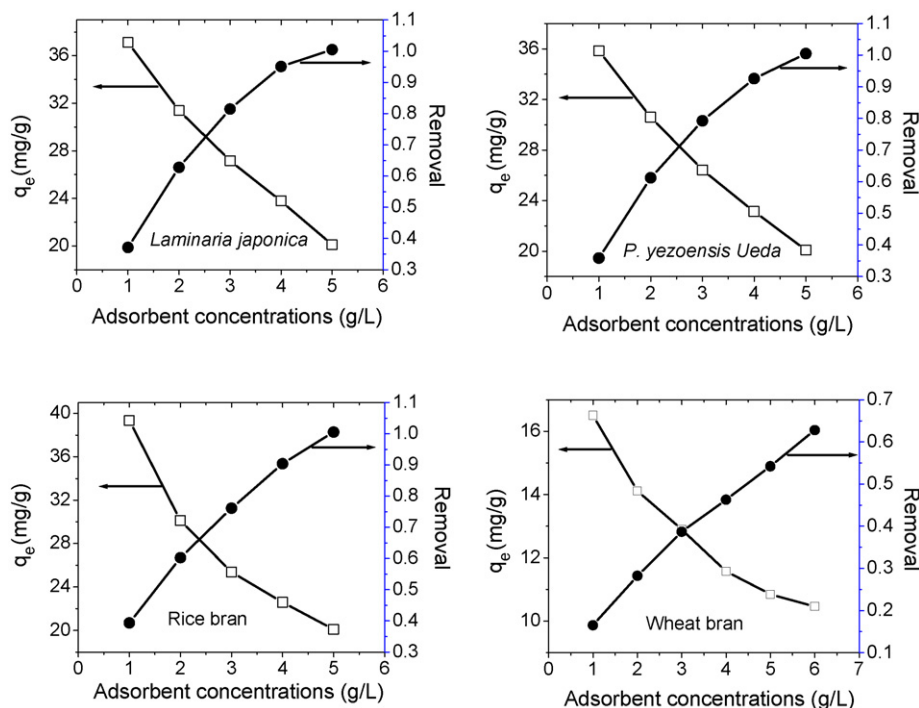


Fig. 8. Plots of effect of adsorbent concentrations on Cr(VI) adsorption for various biosorbents (initial concentration 100 mg/L; pH 1.0; temperature 30 °C; contact time 12 h).

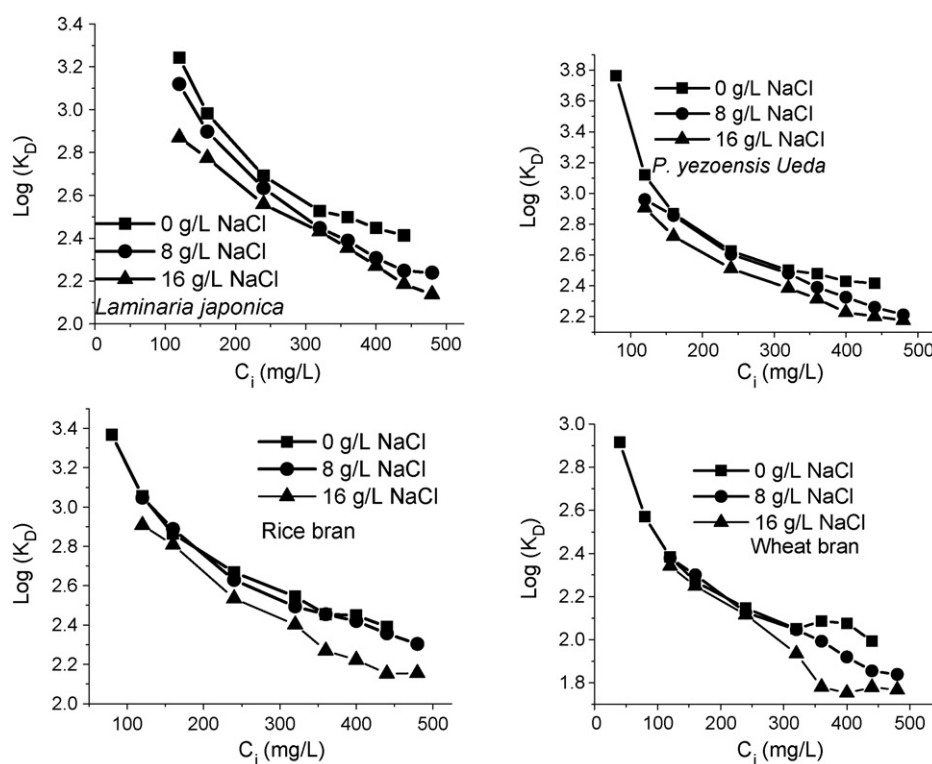


Fig. 9. Distribution coefficients (K_D) as a function of initial concentrations (C_i) in the absence and presence of NaCl electrolyte of different concentrations at solution pH 1.0 and 30 °C.

decreased to varying degrees with the increase of Cr(VI) initial concentrations.

Fig. 9 shows the influence of ionic strength on the adsorption of Cr(VI) onto the various biosorbents. Data were obtained for two concentrations (8 and 16 g/L) of background electrolyte (NaCl). The results indicate that Cr(VI) adsorption decreases for increasing ionic strength. That the extent of adsorption is sensitive to changes in concentration of supporting electrolyte indicates that electrostatic attraction may be a significant component of the overall adsorption in this system [29]. When the ionic strength is increased, the electrical double layer around the adsorbate chromium ion is compressed, which leads to a decrease in the electrostatic potential. The result is a reduction in the Cr(VI) adsorption.

Table 4
Comparison of adsorption capacity for Cr(VI) with various biosorbents

Biosorbents	Maximum uptake capacity (q_{max}) (mg/g)	References
Agricultural by-products		
Sugar cane bagasse	13.4	[1]
Maize cob	13.8	[1]
Sawdust	39.7	[1]
Wheat bran	40.8	This study
Rice bran	58.9	This study
Marine algae		
<i>Sargassum</i> (brown algae)	31.7	[29]
<i>Padina</i> (brown algae)	54.6	[29]
<i>P. yezoensis Ueda</i> (red algae)	56.3	This study
<i>L. japonica</i> (brown algae)	59.3	This study

3.7. Comparisons with other biosorbents

The maximum uptake capacities (q_{max}) for Cr(VI) of the four low-cost biosorbents and other biosorbents are given in Table 4. The result indicates the maximum adsorption capacities for wheat bran and rice bran at 30 °C obtained in this study are comparable to those obtained from other agricultural by-products. The maximum biosorption capacities at 30 °C for the *L. japonica* and *P. yezoensis Ueda* are comparable to those from the brown algae (*Padina* and *Sargassum*) reported by Sheng et al. [30].

4. Conclusions

Biosorption performances of the four low-cost biosorbents (i.e. *L. japonica* and *P. yezoensis Ueda*, rice bran and wheat bran) were investigated for the removal of Cr(VI) from single aqueous solutions. Results show that the sorption of Cr(VI) onto various low-cost biosorbents is a function of initial concentrations, solution pH, adsorbent concentrations, temperature and contact time. The equilibrium experimental data at various temperatures fitted well to the Freundlich and Langmuir isotherms. The apparent thermodynamic parameters suggest that an entropy-driven and endothermic sorption process for various biosorbents. The kinetic sorption data fitted well to the pseudo-second order kinetic model. The distribution coefficients (K_D) were inversely proportional to the initial concentrations of Cr(VI) and the background electrolyte.

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