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Removal of Cr (VI) from aqueous solutions by the nonliving biomass of Alligator weed: kinetics and equilibrium

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Abstract The removal of Cr (VI) from aqueous solutions using Alligator weed, a freshwater macrophyte, was investigated in batch studies. Various factors including solution pH, Cr (VI) concentrations, agitation time, and temperature were taken into account and promising results obtained. An initial solution pH of 1.0 was most favorable for Cr (VI) removal. The kinetic data were analyzed using several models, including the pseudo-second-order equation, external diffusion model, and intraparticle diffusion model. The comparison gave insight about the mechanism of adsorption and potential rate controlling step. The results suggested that the Cr (VI) adsorption at all temperatures was best represented by the pseudo-second-order equation. The external film diffusion played an important role in the adsorption mechanism. The Freundlich, Langmuir and Langmuir-Freundlich isotherms for the present system were analyzed. The best interpretation for the equilibrium data at different temperatures was given by the Langmuir-Freundlich isotherm. The Alligator weed could serve as low-cost adsorbent to remove Cr (VI) from aqueous solutions.

Keywords Batch adsorption · Cr (VI) · Alligator weed · Isotherm · Separation

1 Introduction

Environmental contamination by heavy metals is of growing concern because of health risks on humans and animals (Louhab et al. 2006). Cr (VI) is a cancer-causing agent and can pose health risks such as liver damage, dermatitis, and gastrointestinal ulcers (Dokken et al. 1999). The major source of Cr (VI) is the wastewater from electroplating and metal-finishing (Park et al. 2001). The conventional treatment method applied in these industries is based on the precipitation of the hydroxide form of Cr (III). In this method, Cr (VI) is removed by reduction to Cr (III) with reducing agents followed by precipitation with hydroxide compounds. However, this method has high costs associated with the chemical reduction (Dokken et al. 1999; Park et al. 2001). Contaminated waters containing low concentrations of Cr (VI) are typically treated with ion exchange resins. However, its application has also been found to be limited due to the high costs of synthetic resins (Dokken et al. 1999). As an alternative, a variety of inexpensive biomasses have been studied for their ability to remove Cr (VI) from aqueous solutions. Among these low cost adsorbents are microorganisms, seaweed, clay minerals, agricultural wastes, industrial wastes and various other low-cost materials (Bailay et al. 1999; Dokken et al. 1999; Park et al. 2001; Selvi et al. 2001; Rao et al. 2002; Babel and Kurniawan 2003; Lakatos et al. 2003; Yu et al. 2003; Kobya 2004; Bishnoi et al. 2004; Gupta and Ali 2004; Chun et al. 2004; Grag et al. 2004; Sheng et al. 2004; Kobya et al. 2005; Khezami and Capart 2005; Prasenjit and Sumathi 2005; Sen et al. 2005; Verma et al. 2006; Potgieter et al. 2006; Wang and Qin 2006).

Cost effectiveness is the main attraction of metal biosorption and accordingly biomass origin is a major factor to be taken into account (Vieira and Volesky 2000). In general, biomass can come from (1) industrial wastes; (2) organisms easily available in large amounts in nature; and (3) organisms of quick growth, especially cultivated or propagated for biosorption purposes (Vieira and Volesky).

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Alligator weed (a freshwater macrophyte) is an invasive plant that originates from South America and is currently invading many countries throughout the world. The plant invades agricultural areas and blocks drainage and irrigation channels causing problems on agricultural land. Other concerns of alligator weed include water pollution from plant decomposition and an increase in mosquito breeding areas. Alligator weed is currently listed as one of 20 weeds of national significance in Australia. In China, Alligator weed has high growth rate because of good climate conditions. Some nonliving biomass of freshwater macrophytes such as *Potamogeton lucens*, *Salvinia herzogii*, *Eichhornia crassipes* were excellent biosorbents for Cr (III), Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) (Schneider and Rubio 1999). The sorption mechanism by these biomaterials was found to proceed mainly by ion exchange reactions between the metal ions and the cationic weak exchange groups (e.g. carboxyl and phenolic hydroxyl) present on the plant surface (Schneider and Rubio 1999).

The objectives of this work were to characterize the potential of Alligator weed to remove Cr (VI) from single aqueous solutions. The effects of agitation time, solution pH, and solution temperature, Cr (VI) concentrations on its adsorption were investigated.

2 Materials and methods

Alligator weed was obtained from wild specimens growing in Lianyungang, China. The plant tissues were washed with tap water to remove the impurities and then soaked overnight in a 1:10 acetone solution. Afterwards, the material was rinsed with deionized water and dried at 60 °C and finally ground with a mill to pass through a 100-mesh sieve for subsequent biosorption experiments.

FT-IR analysis of the material used in this study was performed using a Fourier transform infrared spectrometer (WGH-30A, Tianjin, China). The biosorbent powders were blended with IR-grade KBr in an agate mortar and pressed into tablet. The spectra of the biosorbent were recorded.

The stock solution was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$)(AR grade) in de-ionized water. The stock solution was finally diluted to obtain standard solutions. Solutions of 0.1 mol/L NaOH and/or HCl were used for pH adjustment.

Kinetic studies were carried out at constant pH 1.0 with an initial concentration of 100 mg/L and adsorbent dose of 4 g/L at various temperatures (30, 40, 50 °C). In addition, to investigate the effects of initial concentration on kinetic performance, experiments were also carried out at constant pH 1.0 with two different initial concentrations (160 and 320 mg/L). After shaking, the solution samples were withdrawn at suitable time intervals. For the isotherm studies, 0.2 g of biosorbent was put into 50 mL solutions of various concentrations of Cr (VI). The flasks were shaken to reach equilibrium. A known volume of the solution was removed and centrifuged for Cr (VI) analysis. Effect of pH on the adsorption of Cr (VI) was studied by varying the pH from 1.0 to 6.0 at various initial concentrations (40, 80, 120 mg/L). The effect of temperature on adsorption equilibrium was studied by varying temperatures from 30 to 50 °C.

After these experiments mentioned above, the resulting solutions were centrifuged and the supernatant liquid analyzed. The concentrations of Cr (VI) were determined using diphenylcarbazide method. Diphenylcarbazide forms a red-violet complex selectively with Cr (VI), and the intensity of this complex was read at 542 nm using a UV-visible spectrophotometer.

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

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

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

$$remvoal(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

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.

3 Results and discussion

3.1 Infrared spectra analysis

In order to determine the functional groups responsible for Cr (VI) uptake, FT-IR technique was used. The infrared spectra are shown in Fig. 1. The absorption bands identified in the spectra and their assignment to the corresponding functional groups in the sorbent are listed in Table 1. Wave number of 3428.1 cm^{-1} indicates the possible presence of –OH, –NH groups on the sorbent surface. The bands that are observed at 2922.4 cm^{-1} and 618.2 cm^{-1} suggest the presence of C–H group. The strong peak at 1643.8 cm^{-1} band is caused by the C=O stretching band of the carboxyl group. The band appears at approximately 1056.0 cm^{-1} is due to C–O stretching vibrations of primary alcohol. These results indicate that the possible presence of several functional groups on the surface of the sorbent responsible for the Cr (VI) adsorption.

3.2 Effect of solution pH

Earlier studies on heavy metal biosorption have shown that solution pH is the single most important parameter affecting the biosorption process (Chen et al. 2002). To find the

Table 1 IR adsorption bands and corresponding possible functional groups

Wave numbers (cm^{-1})	Functional groups
3428.1	–OH, –NH
2922.4	–CH
1643.8	$–COO^-$, –C=O
1056.0	–C–O
618.2	–CH

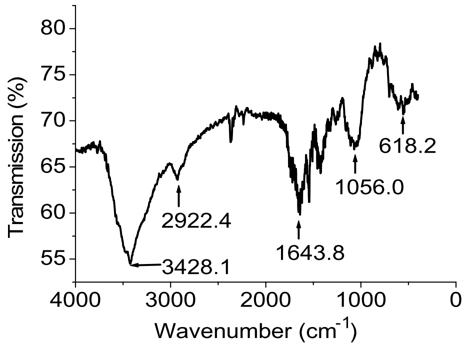

Fig. 1 Infrared spectra of the biosorbent used in this study

suitable solution pH for the effective biosorption of Cr (VI) ions by dried Alligator weed, experiments were performed at different initial solution pH values (1.0 to 6.0) for various initial Cr (VI) concentrations at 30 °C. Figure 2 shows that solution pH is an important parameter for the Cr (VI) biosorption process. The highest Cr (VI) biosorption capacities were found at solution pH 1.0 for various initial concentrations.

The pH dependence of metal uptake is largely related to the surface functional groups and metal solution chemistry (Chen et al. 2002). The dominant form of Cr (VI) at pH 1.0 is the acid chromate ion species ($HCrO_4^-$) and increasing pH shifts the concentration of $HCrO_4^-$ to other forms (e.g. CrO_4^{2-}). Figure 2 clearly indicates that it is $HCrO_4^-$ which was adsorbed preferentially onto the biomass. The Cr (VI) binding onto the biomass could be occurring either via positively charged ligands on the surface of biosorbent primarily electrostatically in nature or through the reduction of Cr (VI) to Cr (III) under strongly acidic conditions (Dokken et al. 1999; Park et al. 2001; Verma et al. 2006). This is in agreement with the findings obtained by (Verma et al. 2006) in the study of Cr (VI) sorption onto tamarind hull-based adsorbents.

3.3 Uptake kinetics

Kinetic experiments were performed using adsorbent dose, initial solution pH and initial Cr (VI) concentration of 4 g/L, 1.0 and 100 mg/L, respectively, for various temperatures.

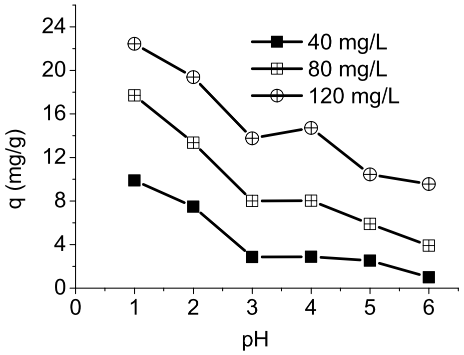

Fig. 2 Effect of solution pH on sorption capacities at various initial concentrations (adsorbent dose: 4 g/L; temperature 30 °C)

As shown in Fig. 3(a), Cr (VI) uptake seems to occur in two steps. The first step involved rapid metal uptake within the first 30 min of contact that was followed by the subsequent removal of the Cr (VI) which continued for a relatively longer period of time until sorption equilibrium was attained. Over 56, 68 and 75% of the total Cr (VI) removal occurred within the first 30 min at 30, 40, and 50 °C, respectively (Fig. 3(b)).

In order to analyze the adsorption kinetics of Cr (VI) onto the adsorbent, the pseudo-second-order equation (Ho and McKay 1999) was applied to the experimental data. This equation is expressed as

$$\frac{t}{q_t} = \frac{1}{q_{e,2}^2 k_2} + \frac{1}{q_{e,2}} t \tag{3}$$

where $q_{e,2}$ and q_t (mg/g) are the amounts of adsorbed Cr (VI) onto the adsorbent at equilibrium and at time t (min), respectively, k_2 (g/(mg min)) the rate constant of pseudo-second-order equation.

Using (3), t/q_t was plotted versus t for various temperatures and the parameters ($q_{e,2}$ and k_2) values were determined from the slope and intercept of the plots (Fig. 4(a)). The values of parameters k_2 and $q_{e,2}$ and of correlation coefficients are also presented in Table 2. The correlation coefficients had extremely high values and the calculated $q_{e,2}$ values agreed very well with the experimental values in the case of pseudo-second-order model. These results suggest the adsorption of Cr (VI) onto the adsorbent at various temperatures was best represented by the pseudo-second-order equation, which is based on the assumption that the rate-limiting step may be the chemisorption (Aksu 2001).

The effect of the adsorbent dose on the adsorption rate of the Cr (VI) ions from aqueous solutions was investigated with respect to changes in initial Cr (VI) concentrations at 30 °C and solution pH 1.0 for the entire time range investigated in this study. The experimental data conformed to the pseudo-second-order equation very well (Fig. 5). The data in Table 3 show that the Cr (VI) adsorption rate increased

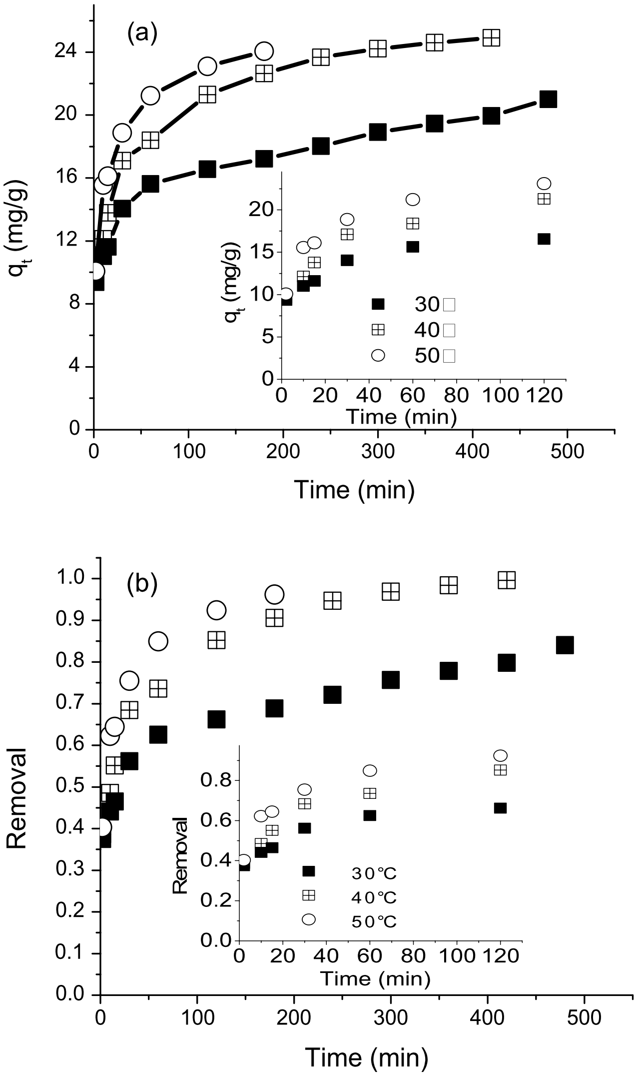

Fig. 3 Adsorption kinetics (**a**) and the removal rates (**b**) of Cr (VI) for Alligator weed at various temperatures. The *inset* shows a zoom for time ranges between 0 to 120 min (initial concentrations: 100 mg/L; adsorbent dose: 4 g/L)

Table 2 The fitting of using pseudo-second-order equation at various temperatures

Temp. (°C)	Exp. q_e (mg/g)	Pseudo-second-order $q_{e,2}$ (mg/g)	k_2 (g/(mg min))$\times 10^2$	R
30	21.0	20.7	0.266	0.9971
40	24.9	25.4	0.263	0.9991
50	24.0	24.7	0.578	0.9993

with the increased adsorbent dose. For the same adsorbent concentration, the Cr (VI) adsorption rate decreased with respect to the increase of initial Cr (VI) concentration.

Most sorption processes take place by a multi-step mechanism comprising (i) diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and (iii) physical and/or chemical adsorption at a binding site. Thus, it is essential to understand these mass transfer mechanisms in order to design a cost effective and efficient adsorption system.

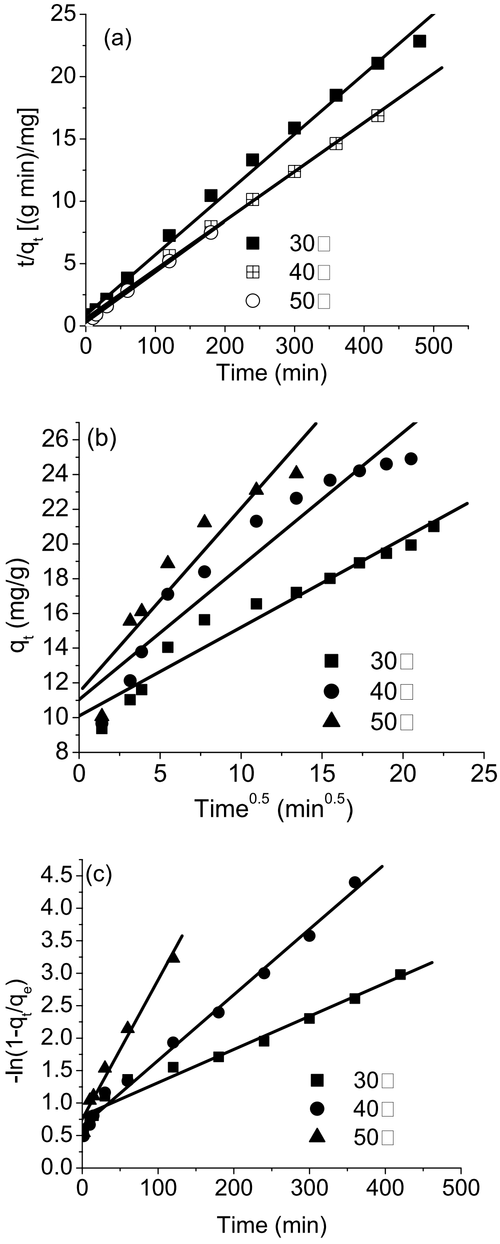

Fig. 4 Kinetic modeling for the Cr (VI) sorption onto Alligator weed for various temperatures ((**a**) pseudo-second order kinetic equation; (**b**) Weber-Morris diffusion equation; (**c**) Liquid film diffusion equation)

In this work, the intraparticle diffusion (Weber and Morris 1963) and external film diffusion (Bhattacharyya and Gupta 2007) models were used to investigate the rate-controlling steps of the adsorption process. These two equations are defined as follows, respectively,

$$q_t = k_i t^{0.5}, \tag{4}$$

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_{fd} t \tag{5}$$

where k_i (mg/g min$^{0.5}$) and k_{fd} (1/min) are the rate constants of intraparticle diffusion and liquid film diffusion models, respectively. Intraparticle diffusion plays a significant role in controlling the kinetics of the adsorption process, if the plot of q_t versus $t^{0.5}$ yields a straight line passing through the origin, with the slope giving the rate constant, k_i. Similarly, if external film diffusion equation is applicable, the plot of $\ln(1 - q_t/q_e)$ against t should give a straight line with zero intercept, from which k_{fd} can be determined from the slope of the plot.

Plots of Cr (VI) amounts adsorbed, q_t versus time$^{0.5}$, are presented for various temperatures in Fig. 4(b). Intraparticle diffusion rate constant k_i values and correlation coefficients are listed in Table 4. Significantly, the plots do not pass through the origin, indicating that the diffusion of Cr (VI) species into the pores of the adsorbent was not the dominating factor controlling the mechanisms of the adsorption process. The plots of $-\ln(1 - q_t/q_e)$ versus t are also linear (Fig. 4(c)) with low intercepts for various temperatures (Table 4). Although the intercepts are not zero, their small values suggest that external film diffusion played a significant role in adsorption process (Bhattacharyya and Gupta 2007). The film diffusion rate constants, k_{fd}, are also given for various temperatures in Table 4.

Table 3 Effect of adsorbent doses on the Cr (VI) adsorption rate for the entire time range studied at 30 °C and solution pH 1.0

Adsorbent doses	Initial concentration (mg/L)			
(g/L)	160		320	
	k_2 ((g min)/mg)	R	k_2 ((g min)/mg)	R
2	0.000737	0.9959	0.000948	0.9991
4	0.001266	0.9975	0.000540	0.9983
6	0.002681	0.9997	0.001063	0.9993
8	0.006714	0.9998	0.001813	0.9997
10	0.011516	0.9998	0.003258	0.9998

In view of the mentioned above, one may be tempted to argue that adsorption of Cr (VI) onto Alligator weed at various temperatures is more correctly described by more than one sorption equations.

3.4 Equilibrium modeling

The Freundlich isotherm is originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces of supporting sites of varied affinities. The Freundlich isotherm is defined generally by the following expression (Freundlich 1907):

$$q_e = K_f C_e^{1/n} \tag{6}$$

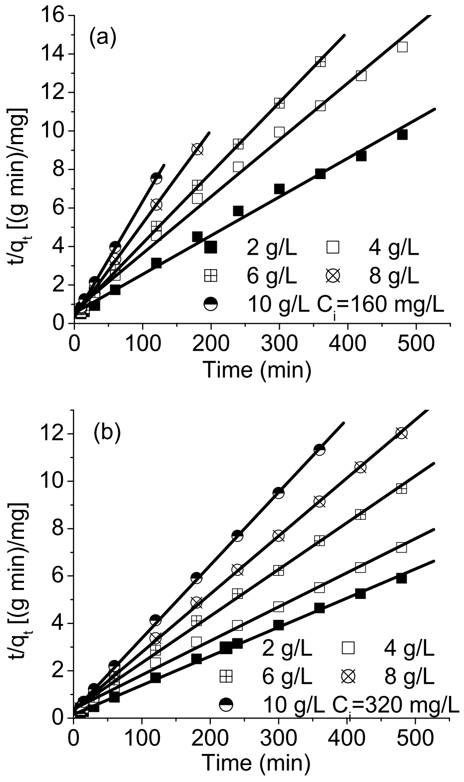

Fig. 5 Pseudo-second order kinetic plots for the adsorption of Cr (VI) onto Alligator weed at different initial concentrations ((**a**) 160 mg/L; (**b**) 320 mg/L) and adsorbent doses at 30 °C and solution pH 1.0

Table 4 The intraparticle and liquid film diffusion rate constants for the Cr (VI) adsorption at various temperatures

Temp.	Intraparticle diffusion			Liquid film diffusion		
(°C)	k_i (mg/(g min$^{0.5}$)) × 10	Intercept	R	k_{fd} (1/min)×10^2	Intercept	R
30	5.1	10.1	0.9745	0.51	0.80	0.9854
40	7.7	11.0	0.9598	1.01	0.64	0.9959
50	10.6	11.4	0.9399	2.14	0.75	0.9879

Table 5 The fitting of using nonlinear Freundlich and Langmuir isotherms at various temperatures

Temp.	Freundlich constants			Langmuir constants		
(°C)	K_f ((mg/g)/(mg/L)$^{1/n}$)	n	R	q_m (mg/g)	b (L/mg)	R
30	7.8088	2.367	0.9946	82.73	0.01988	0.9977
40	10.1883	2.528	0.9978	84.22	0.02813	0.9960
50	12.8600	2.657	0.9992	85.95	0.04395	0.9949

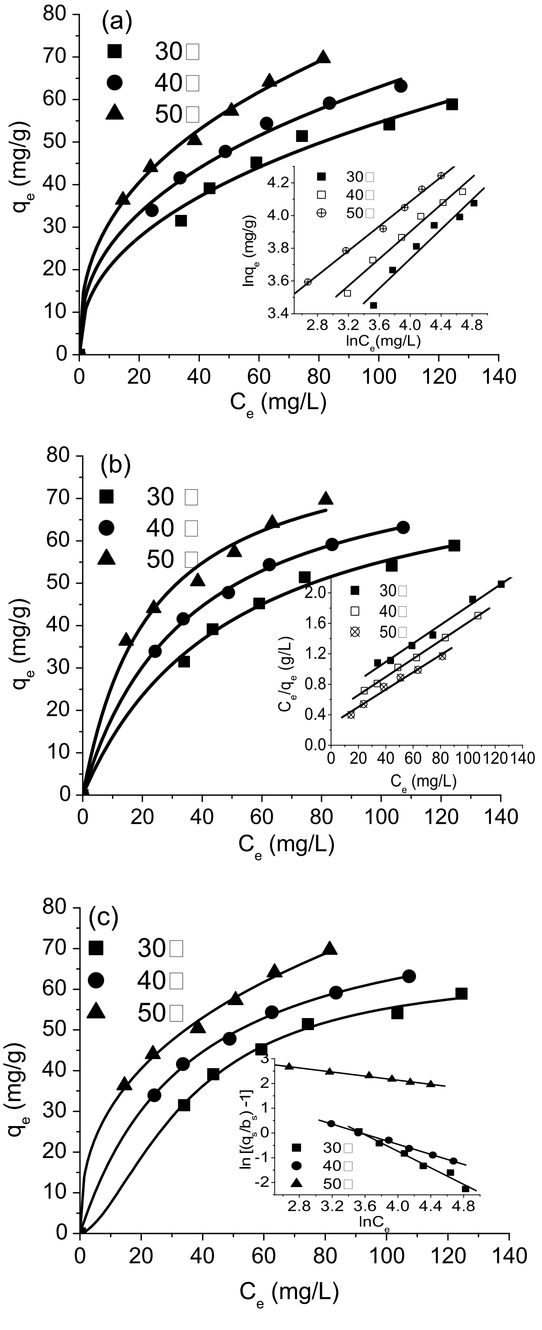

Fig. 6 Adsorption isotherms of Cr (VI) at various temperatures (Freundlich (**a**), Langmuir (**b**) and Sips (**c**) models)

Equation (6) can be easily linearized as:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{7}$$

where K_f ((mg/g)/(mg/L)$^{1/n}$) and n (dimensionless) are empirical constants, with K_f being related to the maximum binding capacity, and n related to the affinity or binding strength (Davis et al. 2003).

Freundlich plots for the Cr (VI) adsorption at various temperatures are given in Fig. 6(a). It illustrates that adsorption of Cr (VI) onto Alligator weed obeyed the Freundlich isotherms well. The corresponding Freundlich isotherm constants K_f and n together with the correlation coefficients (R) are listed in Table 5. K_f derived from the Freundlich equation is an indicator of adsorption capacity of a given adsorbent. The results obtained in the present study indicate the adsorption capacities (K_f) increased with increasing temperatures. The exponent n greater than unity at various temperatures in Table 5 indicates a favorable adsorption processes (Sun et al. 2005).

The Langmuir isotherm was originally developed to describe the gas-solid phase adsorption of activated carbon and later extended to empirically describe equilibrium relationships between a bulk liquid and a solid phase (Davis et al. 2003). The following form of the Langmuir equation is traditionally applied:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{8}$$

Equation (8) can be conveniently transformed to the following linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{9}$$

where q_m is the maximum uptake (mg/g), q_e the uptake capacity at equilibrium (mg/g), C_e the equilibrium solution concentration (mg/L), b the Langmuir constant (L/mg). Langmuir plots for the Cr (VI) adsorption at various temperatures are given in Fig. 6(b). Values of the Langmuir constants (q_m and b) in the Langmuir isotherms together with correlation coefficients (R) are also listed in Table 5. As can be seen in Table 5, the adsorption isotherm of Cr (VI) exhibited Langmuir behavior, which indicates a monolayer adsorption.

Due to the fact that the Freundlich and Langmuir isotherms fitted the equilibrium data at different temperatures almost equally well, the Langmuir-Freundlich equation was also applied to test the data sets.

The Langmuir-Freundlich model (Sips model) was analyzed by Sips who found that the energy distribution function corresponds to a symmetrical quasi-Gaussian function (Sips 1948). At low concentrations, the model reduces to the Freundlich model and in the case of a homogeneous surface, it reduces to the Langmuir model. The Langmuir-Freundlich equation is written as follows:

$$q_e = \frac{q_S b_S C_e^{1/n_S}}{1 + b_S C_e^{1/n_S}} \tag{10}$$

Equation (10) can be easily linearized as:

$$\ln\left[\frac{q_S}{q_e} - 1\right] = -\ln b_S - \frac{1}{n_S}\ln C_e \tag{11}$$

where q_s (mg/g), b_s (L/mg), n_s (dimensionless) are the constants in the Langmuir-Freundlich equation.

The Langmuir-Freundlich plots at various temperatures are shown in Fig. 6(c) and the calculated constants q_s, b_s and n are summarized in Table 6. Based on the obtained correlation coefficients at various temperatures (Table 5 and Table 6), the Langmuir-Freundlich equation was the model that furthered the best fit for the experimental equilibrium data.

Table 6 The fitting of using nonlinear Langmuir-Freundlich isotherm at various temperatures

Temp.	Langmuir-Freundlich constants			
(°C)	q_s (mg/g)	b_s (L/mg)	n	R
30	65.02	0.00295	0.6092	0.9988
40	83.39	0.02713	0.9844	0.9997
50	561.86	0.02194	2.36886	0.9991

3.5 Comparisons with other adsorbents

The maximum uptake capacities (q_m) for Cr (VI) of Alligator weed at temperature of 30 °C and other adsorbents reported in the literature are given in Table 7. The result indicates the maximum adsorption capacity at 30 °C obtained in this study is higher compared with those obtained from many other low-cost adsorbents.

The cost of this product arises mainly from harvesting (relatively cheap), drying, grinding, packing and transportation, which is a very low cost as compared with ion exchange resins, which cost between $5 and $28 (US)/kg (Schneider and Rubio 1999). Thus, it is believed that adsorption of Cr (VI) by dried Alligator weed appears to be a cheap and efficient alternative to be considered.

4 Conclusions

The Cr (VI) adsorption was found to be pH dependent and increased with the decrease in pH. The best interpretation for the equilibrium data at different temperatures was given by the Langmuir-Freundlich isotherm. From the kinetic studies at various temperatures, it is observed that adsorption of Cr (VI) obeyed the pseudo-second order equation very well. The external film diffusion played an important role in the adsorption mechanism. Compared to the results presented in the other published sources (cf. Table 7), the present biosorbent can be used for the removal of Cr (VI) from aqueous solutions.

Table 7 Comparison of adsorption capacity for Cr (VI) with various adsorbents (Langmuir model)

Adsorbent	q_m (mg/g)	pH	Temp. (°C)	X_{biomass} (g/L)	C_i (mg/L)	References
Zooglera ramigera	3	2	25	–	25–400	(Veglio and Beolcini 1997)
Chlorella vulgaris	24	2.5	20	1	25–250	(Veglio and Beolcini 1997)
Rhizopus arrhizus	62	2	25	1	25–400	(Prakasham et al. 1999)
Spirogyra	14.7	2	18	5	1–25	(Kratochvil and Volesky 1998)
Aeromonas caviae	69.95	2.5	20	2	5–350	(Loukidou et al. 2004)
Hazelnut shell	9.38	1.0	20	4	–	(Cimino et al. 2000)
	17.7	2.0	20	4	–	(Cimino et al. 2000)
S. obliquus	58.8	2	25	2	25–250	(Cetinkaya Dönmez et al. 1999)
C. vulgaris	79.3	2	25	2	25–250	(Cetinkaya Dönmez et al. 1999)
HSAC	60.38	2.0	30	5	50–300	(Kobya 2004)
Alligator weed	82.57	1.0	30	4	160–360	(This study)
Rhizopus nigrificans	123.45	2	25	1	50–500	(Sudha and Abraham 2002)

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