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Kinetics, equilibrium and thermodynamic study on removal of Cr (VI) from aqueous solutions using low-cost adsorbent Alligator weed

Xue Song Wang*, Ye Ping Tang, Sheng Rong Tao

Department of Chemical Engineering, Huaihai Institute of Technology, Changwu Road, 59 Lianyungang, Jiangsu 222005, China

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ABSTRACT

The removal of Cr (VI) from aqueous solutions using Alligator weed, a freshwater macrophyte, was investigated as a function of initial pH, contact time, reaction temperature and adsorbent concentration in batch studies. An initial solution pH of 1.0 was most favorable for Cr (VI) removal. The kinetic experimental data fitted the pseudo-second-order equation, Elovich equation and Langmuir–Hinshelwood equation very well. The adsorption of Cr (VI) onto Alligator weed conformed to the linear forms of the Langmuir, Freundlich and Temkin equations. The removal efficiencies increased with the increased adsorbent dose from 1 to 8 g/L and were 86.6, 97.6 and 99.7% at the adsorbent dose of 8 g/L, solution pH 1.0 and temperatures of 30, 40 and 50 °C, respectively. Thermodynamic parameters (activation enthalpy change, activation entropy change and activation free energy change) revealed that the adsorption of Cr (VI) onto Alligator weed is endothermic, non-spontaneous, with a decreased randomness in nature.

1. Introduction

Environmental contamination by heavy metals is of growing concern because of health risks on humans and animals. Cr (VI) is a cancer-causing agent and can pose health risks such as liver damage, dermatitis, and gastrointestinal ulcers [1]. Several wastewaters, such as those produced during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, may contain undesirable amounts of chromium (VI) anions [2,3]. 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. Biosorption, a technically feasible and economical process, has gained increased creditability during recent years [3]. Although most current research of biosorption is oriented towards the removal of heavy metal cations, the uptake of toxic metal anionic forms by biomass has become a growing concern in this field [3]. The removal of Cr (VI) using various low-cost biosorbents including wool, olive cake, sawdust, pine needle, cactus leaves [4], waste tea [5], defatted rice bran, rice hulls, soybean hulls, cotton seed hulls and Bengal gram husk [6], *Ecklonia* sp. biomass [7], *Aeromonas caviae* biomass [3], brown marine algae *Laminaria japonica*, red marine algae *P. yezoensis Ueda*, agricultural by-products rice bran and wheat bran [8], has been previously studied with promising results.

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. In previous studies, the living biomass of Alligator weed showed a high potential for removing different metals including Co (II), Ni (II), Ag (I), Cd (II), Hg (II) and Pb (II) from the aquatic environment in laboratory experiences [9]. However, it has been demonstrated that the incorporation of heavy metals produces phytotoxic effects on plants resulting in inhibition of chlorophyll synthesis and biomass production that leads to death. Moreover, the use of phytotechnologies as secondary wastewater treatments implies the disposal of high volumes of contaminated plants [10]. The use of dead, dried aquatic plants, for metal removal as a simple biosorbent material has advantages in its high efficiency in detoxifying dilute effluents, minimization of the volume of chemical and/or biological sludge to be disposed of, no nutrient requirements, low cost, conservation, transport, handling. Also, the biomass loaded with heavy metals can be regenerated with acid and/or hydroxide solution that discharge small volumes of concentrated heavy metal [10]. In our laboratory, the non-living biomass of Alligator weed has been successfully used to remove Ni (II) and Zn (II) [11].

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* Corresponding author. Tel.: +86 518 85895408; fax: +86 518 85895409.
E-mail address: snowpine1969@yahoo.com.cn (X.S. Wang).

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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, adsorbent dose on its adsorption were investigated.

2. Materials and methods

Alligator weed was obtained from wild specimen 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 following biosorption experiments.

FT-IR analysis of the biosorbent used in this study was performed using a Fourier transform infrared spectrometer (FT/IR-5300). 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 surface area of the biomass was determined by the Brunauer–Emmett–Teller (BET). Nitrogen adsorption technique using a Quantasorb surface area analyzer (Model-05). The porosity and particle density were determined by mercury intrusion porosimeter (Micrometrics model-9310) and specific gravity bottle, respectively. The pore volume was obtained as the inverse relation of particle density. The moisture content of the biomass sample was obtained using thermal drying method. These results are listed in Table 1.

The stock solution (1000 mg/L) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in 1000 mL of deionized 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 using a PHS-3C pH meter using a combined glass electrode calibrated with buffers of pH 2, 4, and 7.

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, and 50 °C). In addition, to investigate the effects of adsorbent dose and 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) and adsorbent doses from 2 to 10 g/L at 30 °C, respectively. 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, and 120 mg/L). The effect of temperature on adsorption equilibrium was studied by varying temperatures from 30 to 50 °C. Temperature control was provided by the constant-temperature water bath shaker unit (THZ-82, China Jiangsu Jingtan Guosheng Instrumental Factory). Effects of various biosorbent doses on adsorption of Cr (VI) were investigated by varying the range of biosorbent dose with an initial Cr (VI) concentration 320 mg/L and agitation speed of 200 rpm at various temperatures.

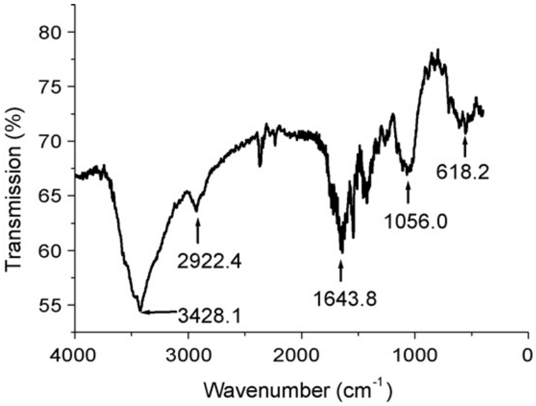

Fig. 1. Infrared spectra of the biomass.

The resulting solutions were centrifuged and the supernatant liquid analyzed. The concentrations of Cr (VI) were determined using diphenylcarbazide method. Diphenylcarbazide forms a purple-violet complex selectively with Cr (VI), and the intensity of this complex was read at 542 nm using a model 722 UV-visible spectrophotometer (China Shanghai Third Component factory). The detection limit of this method was 0.03 mg/L. Analyses were done triplicate samples. Controls comprised of adsorbent in deionized water blank and adsorbent-free Cr (VI) solutions.

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

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

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

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

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 adsorption bands identified in the spectra and their assignment to the corresponding functional groups in the sorbent are listed in Table 2. 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 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 primer alcohol. These results indicate that the possible presence of

Table 1
The properties of the biomass sample

Parameters	Values
Density (g/cm^3)	0.85
Specific surface area (m^2/g)	36.5
Porosity (%)	42.3
Pore volume (cm^3/g)	0.54
Moisture (%)	24.5

Table 2
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

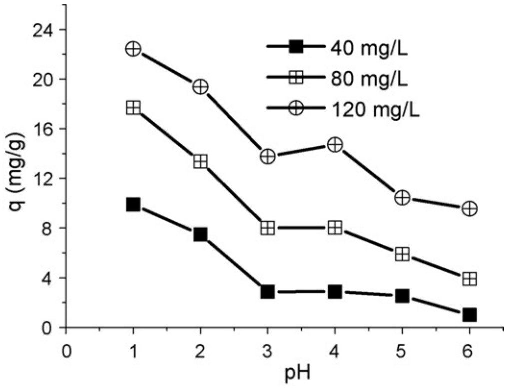

Fig. 2. Effect of solution pH on sorption capacities at various initial concentrations (adsorbent dose: 4 g/L; temperature 30 °C).

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 [12]. To find the suitable solution pH for the effective biosorption of Cr (VI) ions by dried Alligator weed, experiments were performed at different initial solution pH values (1.0–6.0) for various initial Cr (VI) concentrations at 30 °C. Fig. 2 shows that solution pH is an important parameter for the Cr (VI) biosorption process. The highest Cr (VI) biosorption 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 [12]. 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-}). Fig. 2 clearly indicates that it is $HCrO_4^-$ which is adsorbed preferentially onto the biomass.

3.3. Sorption 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. As shown in Fig. 3(a), Cr (VI) uptake seems to occur in two steps. The first step involves rapid metal uptake within the first 30 min of contact then followed by the subsequent removal of the Cr (VI) which continues for a relatively longer period of time until sorption equilibrium is attained. Over 56, 68 and 75% of the total Cr (VI) removal occurred within the first 30 min at various temperatures (Fig. 3(b)).

In order to evaluate the kinetic mechanism that controls the adsorption process, several equations (i.e. pseudo-first-order equation [13], Elovich equation [14], pseudo-second-order equation [15], and Langmuir–Hinshelwood equation [15]) were tested to interpret the experimental data.

The pseudo-first-order equation is the most widely used rate equation for the sorption of a solute from a liquid solution and is commonly represented by

$$\ln(q_{e,1} - q_t) = \ln q_{e,1} - k_{1,p}t \tag{3}$$

where $k_{1,p}$ (1/min) is the pseudo-first-order adsorption rate constant, q_t is the amount adsorbed at time t (min), and $q_{e,1}$ denotes the amount adsorbed at equilibrium, both in mg/g. The plot of $\ln(q_{e,1} - q_t)$ versus t gives the $k_{1,p}$ and $q_{e,1}$ values.

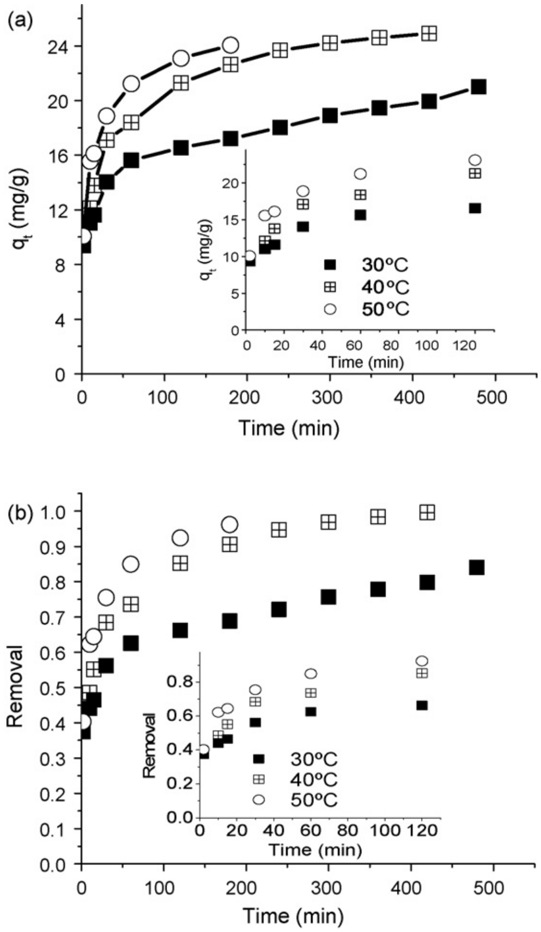

Fig. 3. Adsorption kinetics (a) and the removal rates (b) of Cr (VI) for Alligator weed at various temperatures. The inset shows a zoom for time ranges between 0 and 120 min (initial concentrations: 100 mg/L; adsorbent dose: 4 g/L).

The experimental data for various temperatures were fitted to the pseudo-first-order equation (Fig. 4) and the related parameters are summarized in Table 3.

The pseudo-second-order equation is applied in the following form

$$\frac{t}{q_t} = \frac{1}{k_{2,p}q_{e,2}^2} + \frac{1}{q_{e,2}}t \tag{4}$$

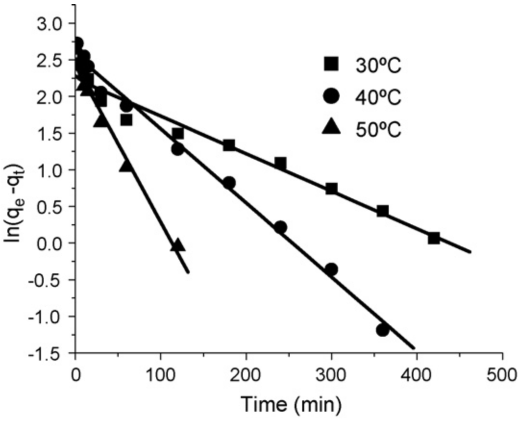

Fig. 4. The fitting of pseudo-first-order equation for various temperatures.

Table 3
The related parameters for various temperatures

Temperature (°C)	Experimental	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg/g)	$q_{e,1}$ (mg/g)	$k_{1,p}$ (1/min)	r	$q_{e,2}$ (mg/g)	$k_{2,p}$ ((g min)/mg)	r
30	21.01	9.42	0.00512	0.9854	20.71	0.002661	0.9971
40	24.91	13.06	0.01011	0.9959	24.69	0.002629	0.9991
50	24.05	11.30	0.02139	0.9879	25.44	0.005789	0.9993

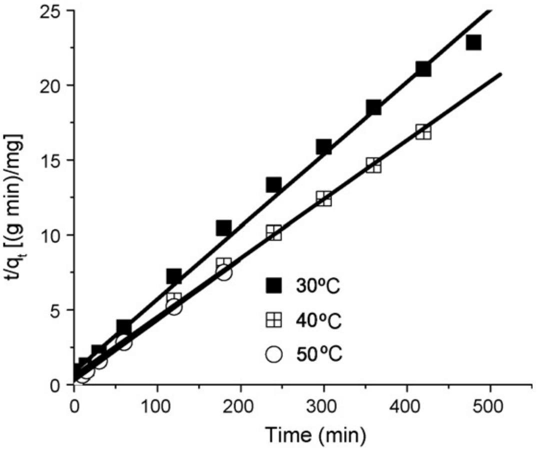

Fig. 5. The fitting of pseudo-second-order equation for various temperatures.

where $q_{e,2}$ is the maximum adsorption capacity (mg/g) and $k_{2,p}$ (g/(mg min)) the rate constant of the pseudo-second-order equation.

The fitting results are illustrated in Fig. 5 and the kinetic parameters for Cr (VI) adsorption by Alligator weed are also given in Table 3. Based on the obtained correlation coefficients (r), the experimental data conformed better to the pseudo-second-order equation, evidencing chemical sorption as rate-limiting step of adsorption mechanism [15]. The experimental q_e values are in agreement with the ones obtained form the fitting of pseudo-second-order equation, which do not happen with the pseudo-first-order kinetic equation.

The effect of the adsorbent doses on the adsorption rate of the Cr (VI) ions from aqueous solutions was further investigated with respect to changes in initial Cr (VI) concentrations at 30 °C and solution pH 1.0 for the entire time range investigated (Fig. 6). The data in Table 4 show that the Cr (VI) adsorption rate increased with the increased adsorbent dose.

The Elovich equation has previously been successfully used to describe the chemisorption of gas molecules onto the sorbent. The general explanation for this form of kinetic law involves a variation of the energy of chemisorption with the extent of surface coverage. Another plausible explanation could be that the active sites are heterogeneous in nature and therefore, exhibit different activation energies for chemisorption [16]. The Elovich rate equation can be written in the following form:

$$\frac{dq_t}{dt} = ae^{(-bq_t)} \tag{5}$$

On integration Eq. (5) with boundary conditions $q_t = q_t$ at $t = t$ and $q_t = 0$ at $t = 0$ becomes

$$q_t = \frac{1}{b}\ \ln(1 + abt) \tag{6}$$

where a and b are constants.

Fig. 7 shows that the theoretical Elovich equation fitted the experimental data very well for various temperatures. The effect of the adsorbent dose on the Elovich equation parameters with respect to changes in initial Cr (VI) concentrations at 30 °C and solution pH 1.0 for the entire time range investigated (Fig. 8). The constants a and b are given in Table 5. Teng and Hsien [17] proposed that the constant a is related with the rate of chemisorption and the constant b is related to the surface coverage. Therefore, increasing

Table 4
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 (g/L)	Initial concentration (mg/L)			
	160		320	
	$k_{2,p}$ ((g min)/mg)	r	$k_{2,p}$ ((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

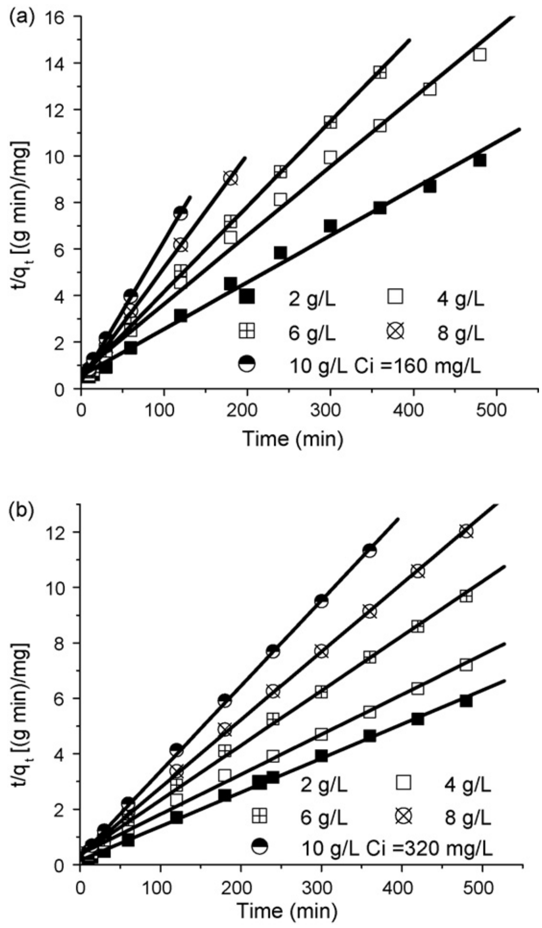

Fig. 6. Pseudo-second-order kinetic plots for the adsorption of Cr (VI) onto Alligator weed at different initial concentrations (a: 160 mg/L; b: 320 mg/L) and adsorbent doses at 30 °C and solution pH 1.0.

Table 5
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 (g/L)	Initial concentration (mg/L)					
	160			320		
	a (mg/g min)	*b* (g/mg)	*r*	*a* (mg/g min)	*b* (g/mg)	*r*
2	17.3910	0.1493	0.9850	825.8822	0.1347	0.9870
4	28.3498	0.2496	0.9945	18.7310	0.1016	0.9955
6	21.2597	0.2826	0.9951	36.3963	0.1578	0.9969
8	61.9776	0.4164	0.9932	96.1111	0.2269	0.9957
10	112.4986	0.5521	0.9854	257.0294	0.3183	0.9960

Table 6
The parameters of Langmuir–Hinshelwood equation

Temperature (°C)	$k_{0,\mathrm{LH}}$ (L/mg)	$k_{1,\mathrm{LH}}$ (1/min)	*r*
30	0.01332	0.00138	0.9800
40	0.01098	0.009	0.9761
50	0.01354	0.01112	0.9954

the concentration of solution and the mass of sorbent will increase the rate of chemisorption. If the constant *b* is related to the extent of surface coverage, then the increasing of the concentration of solution will decrease the available sorption surface for the sorbates. An increase in the mass of sorbent will increase the available surface for the sorbates. Fig. 9 show that the constants *a* and *b* were correlated to the initial concentration of solution and the mass of the sorbent.

In order to further elucidate the possible mechanism, the experimental data were also correlated to the Langmuir–Hinshelwood equation. The Langmuir–Hinshelwood equation is as follows:

$$-\frac{\mathrm{d}C_t}{\mathrm{d}t} = \frac{k_{1,\mathrm{LH}}C_t}{1 + k_{0,\mathrm{LH}}C_t} \tag{7}$$

Rearranging Eq. (7) gives:

$$\frac{\ln(C_0/C_t)}{C_0 - C_t} = \frac{k_{1,\mathrm{LH}}t}{C_0 - C_t} + k_{0,\mathrm{LH}} \tag{8}$$

where the $k_{1,\mathrm{LH}}$ (1/min) is the rate constant of the Langmuir–Hinshelwood equation and $k_{0,\mathrm{LH}}$ (L/mg) the constant.

Fig. 10 shows the Langmuir–Hinshelwood equation also fitted the experimental data well and the related parameters are listed in Table 6. The high correlation coefficients for various temperatures implied that the adsorption of Cr (VI) on the sorbent was closer to chemisorption.

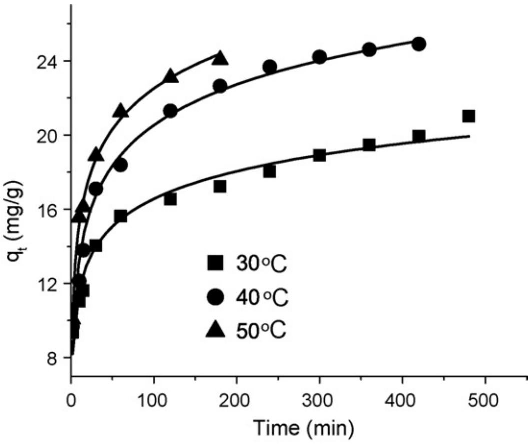

Fig. 7. The plots of the fitting experimental data of Cr (VI) adsorption on Alligator weed by Elovich equation.

3.4. Activation energy and thermodynamic parameters

The effect of temperature on Cr (VI) adsorption was examined in greater detail by applying the Arrhenius equation on the Langmuir–Hinshelwood rate constant data. The Arrhenius equation is

$$k_{1,\mathrm{LH}} = A_1 \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{9}$$

The linear form of Arrhenius equation can be obtained by rearranging Eq. (4):

$$\ln k_{1,\mathrm{LH}} = \ln A_1 - \frac{E_\mathrm{a}}{RT} \tag{10}$$

where A_1 is the pre-factor in the Arrhenius equation (mg/g min), *R* the gas constant (8.314 J/mol K), *T* the absolute temperature (K). A

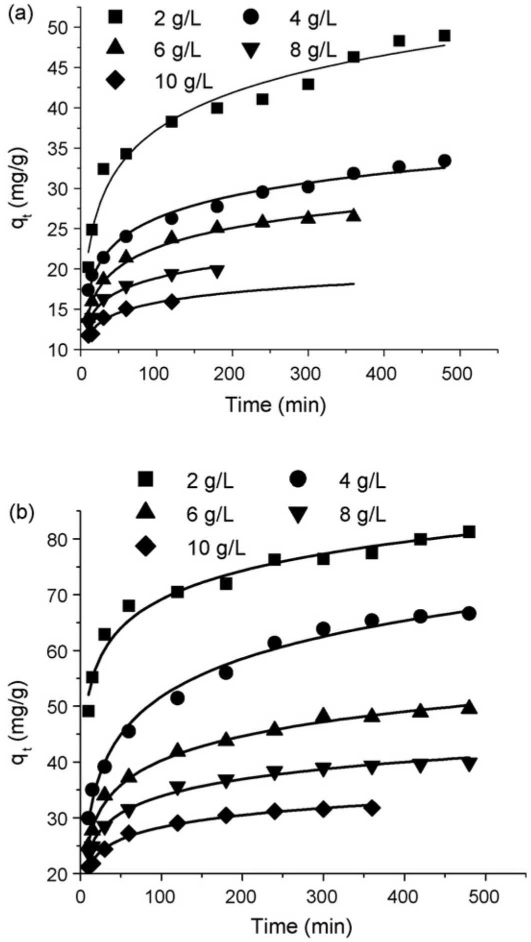

Fig. 8. Effect of adsorbent doses on the Cr (VI) adsorption rate for the entire time range studied at 30 °C and solution pH 1.0 by Elovich equation fitting.

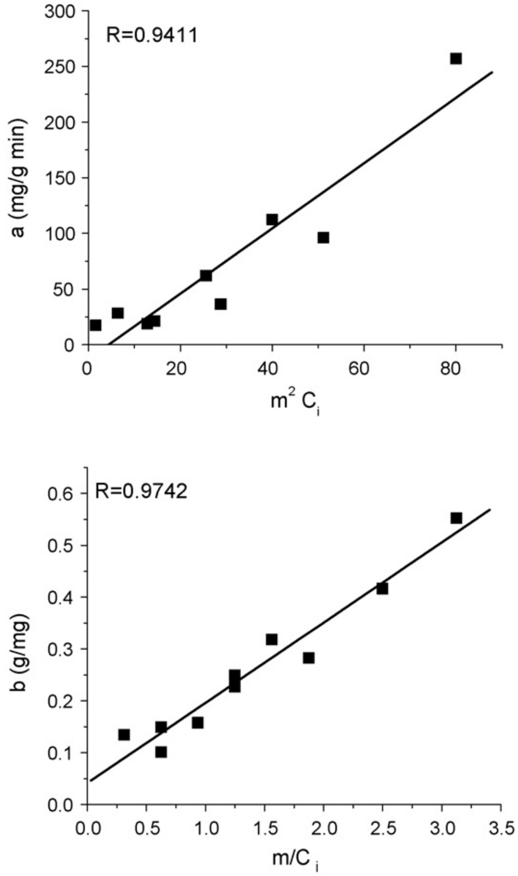

Fig. 9. The relations of the Elovich equation constants *a* and *b* with respective to the initial concentration (C_i) and the adsorbent mass (*m*).

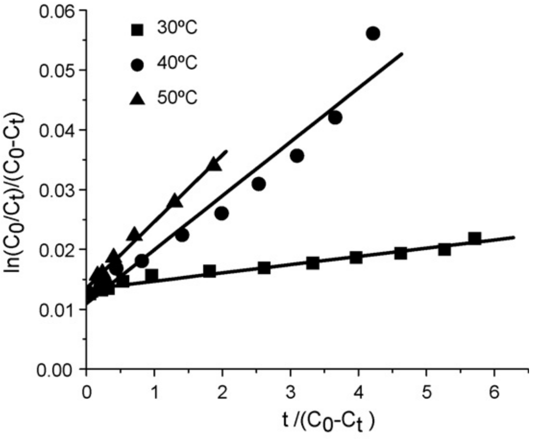

Fig. 10. The fitting of Langmuir–Hinshelwood equation for various temperatures.

plot of $\ln k_{1,\mathrm{LH}}$ versus $1/T$ yields a straight line, from which the E_a and A_1 can be obtained based on the slope and intercept, respectively.

The activation energy and the pre-factor were calculated according to Eq. (9) and are listed in Table 7. Generally, low E_a value (<42 kJ/mol) indicates diffusion-controlled process whereas higher E_a value (>42 kJ/mol) indicates chemically controlled process. A 85.58 kJ/mol E_a for the reaction of Cr (VI) adsorption onto sorbent used in this study indicates that the rate-limiting step in this case might be a chemically controlled process.

The thermodynamic parameters ($\Delta H^\circ_\#$, kJ/mol, $\Delta S^\circ_\#$, J/mol K and $\Delta G^\circ_\#$, kJ/mol for the adsorption process were also obtained using the following equations:

$$k_{1,\mathrm{LH}} = \frac{RT}{Nh} e^{(\Delta S^\circ_\#/R)} e^{(-\Delta H^\circ_\#/RT)} \tag{11}$$

$$\Delta G^\circ_\# = \Delta H^\circ_\# - T\Delta S^\circ_\# \tag{12}$$

where *R* is the gas constant (8.314 J/mol K), *T* the absolute temperature (K), *N* the Avogadro constant (6.022×10^{23} 1/mol) and *h* the Planck constant (6.626×10^{-34} J s).

Plotting the $\ln(k_{1,\mathrm{LH}}/T)$ against $1/T$ gives a reasonable straight line ($r = 0.9112$) (data not shown) and the values of $\Delta G^\circ_\#$, $\Delta H^\circ_\#$, and $\Delta S^\circ_\#$ were summarized in Table 7. The positive values of $\Delta H^\circ_\#$ as well as the negative value of $\Delta S^\circ_\#$ indicated that the adsorption process was endothermic, with a decreased randomness. The positive value $\Delta G^\circ_\#$ of suggested that Cr (VI) adsorption at various temperatures is non-spontaneous in nature.

3.5. *Adsorption isotherm*

In this study, three empirical adsorption models, namely Langmuir, Temkin and Freundlich equations were used to fit the experimental data at various temperatures:

$$\frac{C_e}{q_e} = \frac{1}{q_m b'} + \frac{C_e}{q_m} \tag{13}$$

$$q_e = B\ \ln A + B \ln C_e \tag{14}$$

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{15}$$

where b' (L/mg), *B*, *A* (L/mg), K_f ($(\mathrm{mg/g})/(\mathrm{mg/L})^{1/n}$) and *n* (dimensional) are constants, respectively. The constant b' of Eq. (13) is given by [18]:

$$b' = \frac{1}{55.5}\ \exp\left(\frac{Q_{\mathrm{diff}}}{RT}\right) \tag{16}$$

while the constant *A* is expressed as

$$A = \frac{1}{55.5}\ \exp\left(\frac{Q^0_{\mathrm{diff}}}{RT}\right) \tag{17}$$

where Q_{diff} (kJ/mol) is the differential adsorption heat at equilibrium and Q^0_{diff} (kJ/mol) the initial adsorption heat. The value of 55.5 is the concentration of water in solution expressed in mol/L.

Fig. 11 shows that the experimental equilibrium data at various temperatures conformed to the Langmuir isotherm very well. As a result, this leads to the suggestion that the adsorbed molecules do not interact with each other. In addition, straight lines were also obtained when q_e was plotted versus $\ln C_e$ at different temperatures

Table 7
Thermodynamic parameters for the sorption of Cr (VI)

Temperature (°C)	$\Delta H^\circ_\#$ (kJ/mol)	$\Delta S^\circ_\#$ (J/mol)	$\Delta G^\circ_\#$ (kJ/mol)	E_a (kJ/mol)	A_1 (1/s)
30	82.98	−57.86	100.5	85.58	1.0×10^{12}
40			101.1		
50			101.7		

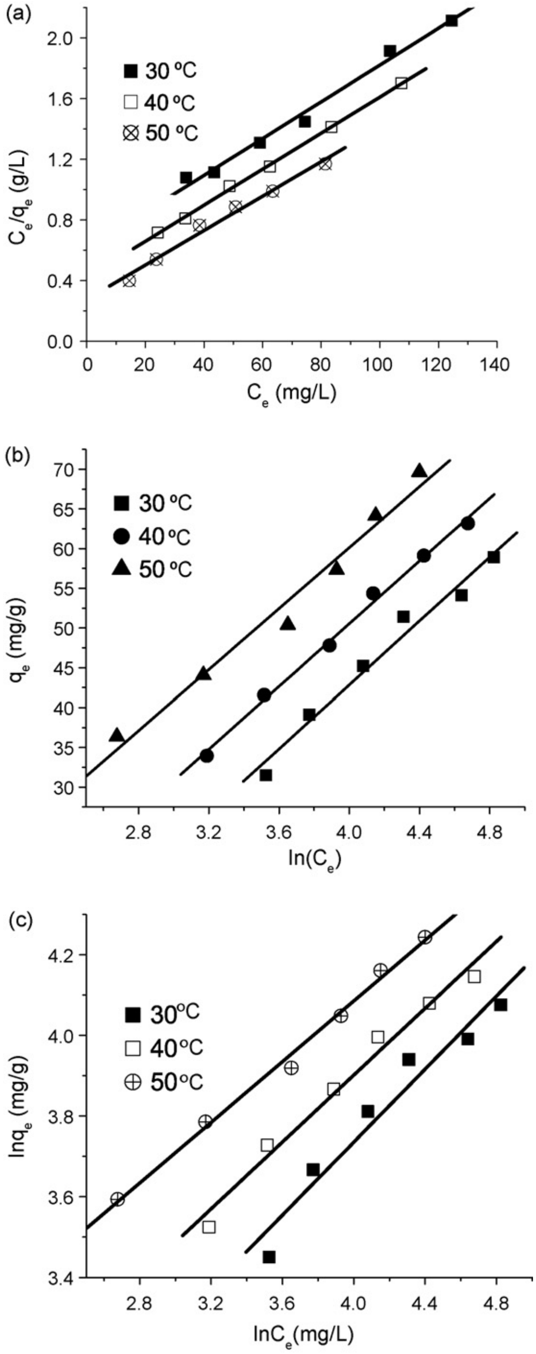

Fig. 11. Adsorption isotherms of Cr (VI) in linear forms of Langmuir (a), Temkin (b) and Freundlich (c) models.

Table 9
The fitting of using linear Freundlich isotherm at various temperatures

Temperature (°C)	Freundlich		
	K_f ((mg/g)/(mg/L)$^{1/n}$)	n	r
30	6.8531	2.209	0.9734
40	9.4189	2.411	0.9903
50	13.1967	2.657	0.9967

(Fig. 11), indicating that the adsorption of Cr (VI) on to the adsorbent followed the Temkin adsorption isotherm as well. The values of adsorption parameters of Langmuir and Temkin isotherms are summarized in Table 8.

The differential heat of adsorption is defined as the heat released or adsorbed upon adding a small increment of adsorbate to the surface of a solid. The value of differential heat of adsorption depends on the strength of the bond formed upon adsorption and the degree to which a surface is pre-covered with adsorbate. The differential heat of adsorption is equal to the initial heat of adsorption of adsorbate adsorbed to the surface directly minus the heat of dissolution of the adsorbed molecules. As expected, the values of differential adsorption heat (Q_{diff}) are smaller than those of initial differential adsorption heat (Q^0_{diff}) at various temperatures (Table 8). The relatively high values of the differential adsorption heat also show that adsorption of Cr (VI) on to the Alligator weed is chemical in nature.

Linear Freundlich plots for the Cr (VI) adsorption at various temperatures are given in Fig. 11(c). It illustrates that adsorption of Cr (VI) onto Alligator weed obeyed the Freundlich isotherms very well. The corresponding Freundlich isotherm constants K_f and n together with the correlation coefficients (r) are listed in Table 9. 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 indicates favorable adsorption processes.

3.6. *Effect of adsorbent dose*

To assess the influence of the adsorbent dose on the adsorption capacity and removal efficiency, Alligator weed dosages varying from 1 to 8 g/L were studied using Cr (VI) solution of 320 mg/L at various temperatures. As shown in Fig. 12, the adsorption capacities of the Alligator weed decreased as the adsorbent does increased from 1 to 8 g/L at various temperatures while the removal efficiencies increased since the equilibrium concentration of the Cr (VI) in solution was lower in the presence of high Alligator weed concentrations. More than 97 and 99% of Cr (VI) at temperatures of 40 and 50 °C respectively, could be removed from solution when the dose of Alligator weed was 8 g/L and the pH 1.0. However, at temperature of 30 °C, Cr (VI) removal efficiency was only 86% at the adsorbent dose of 8 g/L and solution pH 1.0. The difference in Cr (VI) adsorption capacities or removal efficiency at various temperatures indicates that the temperature change had apparent effect on the Cr (VI) removal efficiency.

Table 8
Adsorption parameters for the Cr (VI) adsorption onto Alligator weed at various temperatures

Temperature (°C)	Langmuir				Temkin			
	q_m (mg/g)	b' (L/mg)	r	Q^0_{diff} (kJ/mol)	B (mg/g)	A (L/mg)	r	Q^0_{diff} (kJ/mol)
30	82.57	0.01986	0.9919	27.60	20.10	0.1543	0.9874	32.76
40	84.17	0.02817	0.9903	29.42	19.73	0.2371	0.9976	34.96
50	88.11	0.04110	0.9919	31.37	19.19	0.4199	0.9879	37.62

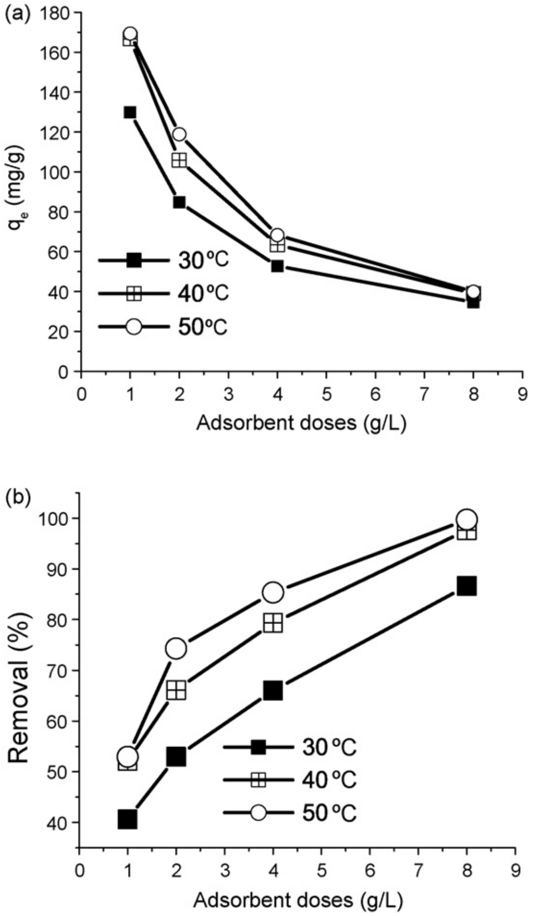

Fig. 12. Adsorption capacity (a) and removal efficiency (b) of Cr (VI) according to the adsorbent dose at various temperatures.

3.7. Desorption and regeneration

Desorption studies were performed using deionized water (pH 6.5) and alkali solution (0.2 mol/L NaOH) as desorbing agents to assess the feasibility for Cr (VI) recovery. The results showed that Cr (VI) recovery was not observed when deionized water was used to desorb Cr (VI) from previously loaded Alligator weed. There was also very little desorption with 0.2 mol/L NaOH. It was found that the percentages of Cr (VI) desorption was 2.6, 8.9 and 14.2% respectively at 1, 4 and 24 h of contact time. These findings implied that the Cr (VI) ions formed strong bonds with the biomass.

The Alligator weed is a low-cost material and can be used on use and throw basis. Moreover, regeneration of sorbent might not be economical as the cost regeneration chemical might be significant. From the environmental safety point of view, the Cr (VI)-laden biomass investigated should be collected and then burned. During burning process, Cr, loaded in the biomass, is concentrated into the ash due to its non-volatile nature. If the chromium concentration in the ashes is high enough, these ashes should be further refined to recover the Cr. In contrast, if the concentration of Cr is relatively low and the cost for the refinement of Cr is high, then burying should be taken into account (it should be noted that the volume is appreciably reduced when the biomass is burned into the ash).

3.8. Adsorption mechanism

In aqueous solution, the distribution of the Cr (VI) species mainly depends on solution pH and Cr (VI) concentration according to the following equilibrium equation:

$$\begin{tikzcd} H_2CrO_4 \arrow[r, leftrightarrow, "\log K = 0.382"] & HCrO_4^- \arrow[r, leftrightarrow, "\log K = -6.14"] \arrow[d, shift left, "\log K = 1.706"] & CrO_4^{2-} \\ & Cr_2O_7^{2-} \arrow[u, shift left] & \end{tikzcd} \qquad (18)$$

At pH values under 3.0, the acid chromate ion species ($HCrO_4^-$) were predominant in solution [19]. The possible mechanism of the adsorption process of Alligator weed towards Cr (VI) consists of two steps: (1) the binding of $HCrO_4^-$ to the positively charged groups present on the biomass surface and (2) the chemical bonding between $HCrO_4^-$ and adjacent functional groups of the biomass.

3.9. 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 10. 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 economic success of a biosorbent based on aquatic plant biomass depends a large extent on the growth rate of the plant. 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 (U.S.)/kg [27]. Thus, it is believed that adsorption of Cr (VI) by dried Alligator weed appears to be a cheap and efficient alternative to be considered.

Table 10
Comparison of adsorption capacity for Cr (VI) with various adsorbents (Langmuir model)

Adsorbent	q_m (mg/g)	pH	Temperature (°C)	C_i (mg/L)	References
Zooglera ramigera	3	2	25	25–400	[20]
Chlorella vulgaris	24	2.5	20	25–250	[20]
Rhizopus arrhizus	62	2	25	25–400	[21]
Spirogyra	14.7	2	18	1–25	[22]
Aeromonas caviae	69.95	2.5	20	5–350	[3]
Hazelnut shell	9.38	1.0	20	–	[19]
	17.7	2.0	20	–	[19]
S. obliquus	58.8	2	25	25–250	[23]
C. vulgaris	79.3	2	25	25–250	[23]
HSAC	60.38	2.0	30	50–300	[24]
Alligator weed	82.57	1.0	30	160–360	This study
Rhizopus nigrificans	123.45	2	25	50–500	[25]
Neem leaves	62.97	2	30	40–700	[26]

4. Conclusions

Adsorption capacity of Cr (VI) was pH dependent. The adsorption capacity increased with the decrease in pH. The removal efficiencies increased as the adsorbent dose increased at various temperatures. Adsorption isotherm data at various temperatures were in good agreement with the Linear Langmuir, Temkin and Freundlich equations. Thermodynamic parameters revealed that the adsorption process is endothermic, non-spontaneous, with a decreased randomness in nature. From the kinetic studies at various temperatures, it is observed that adsorption of Cr (VI) obeyed the pseudo-second-order equation, Elovich equation and Langmuir–Hinshelwood equation very well. Compared to the results obtained in the literatures, the present biosorbent can be used for the removal of Cr (VI) from aqueous solution.

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