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Biosorption of hexavalent chromium onto wood apple shell: equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The biosorption of Cr(VI) onto wood apple shell, batch adsorption experiments have been studied. Equilibrium adsorption isotherms, adsorption kinetics and thermodynamic parameters have been analyzed. The Langmuir monolayer adsorption capacity of wood apple shell for Cr(VI) was determined and was found to be 28.81, 29.58 and 31.45 $\mathrm{mg\,g^{-1}}$ at 299, 309 and 319 K, respectively. The analyzed kinetic data were following the pseudo-second order model. The thermodynamic parameters, such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated and interpreted. The negative value of Gibbs free energy change and positive value of enthalpy change indicate that biosorption is spontaneous and endothermic in nature, respectively. The standard zero free energy temperature (T°) of biosorption process is 274.6 K. Infrared spectroscopy study revealed the mechanism of Cr(VI) biosorption on powdered wood apple shell. Wood apple shell powder was shown to be a promising biosorbent for Cr(VI) removal from aqueous solutions.

Keywords: Wood apple shell; Biosorption: Chromium; Isotherms; Kinetics; Thermodynamics

1. Introduction

The use of heavy metals over the past few decades has been tremendously increased due to rapid industrialization in both developed and developing nations, which results an increased flux of metallic substances in the aquatic environment. The heavy metal enters in tissues through the food chain and accumulates in the body of all living organisms. If the heavy metals are ingested over the permitted concentration, they can cause severe health disorders. Therefore it is necessary to remove heavy metals from contaminated wastewater before discharging into the aquatic environment. Normally water treatment is not practiced by the industries and as a consequence, many times heavy metals are found in aquatic environment well above the permissible limit [1]. Hexavalent Chromium Cr (VI) is one of the major pollutant and most dangerous heavy metals in industrial effluent water, because it is a strong oxidizing agent which irritates animal and plant tissues. Cr(VI) is teratogenic, carcinogenic and mutagenic for mammals [2–4]. Cr(VI) is commonly used in the preparation of a large variety of industrial products, such as pigment for the manufacture of paints, inks, rubber, leather, ceramics, fungicides, electroplating, cement and photographic industries producing large quantities of effluents containing toxic metals [5,6]. Chromium is also found naturally in rocks, soil, plants, animals, and volcanic dust [7]. The recommended limit of Cr(VI) in potable water is only 0.05 $\mathrm{mg\,L^{-1}}$ [8]. But the industrial effluents contain much higher concentrations before discharging into the environment [9,10].

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To remove heavy metals from industrial waste water various conventional methods are available which includes ion exchange, chemical oxidation–reduction, precipitation, reverse osmosis, solvent extraction, electro-dialysis, ultra-filtration, etc. [11]. However, these methods have certain disadvantages, as these methods are expensive, requires sensitive operating conditions and produces huge quantity of secondary sludge [11].

The adsorption of heavy metals by activated charcoal is another powerful technology, but the high cost of activated charcoal has prevented its application in developing countries. Consequently, instead of activated charcoal, the low cost biomass, such as coconut shell, cotton seed hull, bagasse pitch, hazelnut shell, rice husk, wheat shell, walnut shell, etc. are being used recently for bioremediation of waste water [11–13]. Biosorption provides alternative path to the traditional physico-chemical methods to remove heavy metals utilizing low cost biomass [14]. Biomass seems to be a useable option to remove heavy metals due to its natural chemical composition, high abundance and economical, high efficiency of heavy metals removal from diluted solutions, regeneration of biosorbent and greater possibility of metal recovery [15].

In the present research work, the hexavalent chromium adsorption capacity of wood apple shell (*Limonia acidissima* L.) was studied. Wood apple is native and common fruit cultivated in Bangladesh, India, Pakistan, Sri Lanka and Southeast Asia East to Java. The fruit pulp of wood apple is used in several culinary preparations and has great medicinal values. Wood apple shell carries the polar functional groups, such as alcoholic, carboxylic, and ether groups which show that it is a lignocellulosic material [16].

The well-known adsorption kinetic, thermodynamic parameters and adsorption isotherm studies have been reported to interpret the adsorption behaviors at different temperature. In addition to the effect of temperatures, effects of pH and metal concentration on percentage of biosorption have also been investigated.

2. Materials and methods

2.1. Preparation and characterization of biosorbent

The wood apple fruits were collected from agricultural land of Pune district area and hard rind or shell was removed manually from fruit pulp, broken into small pieces. To remove dirt the shell was thoroughly washed with distilled water, dried in an oven at 333 K for 24 h, crushed and finally sieved through the 80–100 mesh size. The average particle size of powdered wood apple shell was measured by sieving method. Porosity and bulk density were measured by NaCl tracer and gravimetric studies [17]. The point of zero charge (pH_{pzc}) is the pH at which electric charge on sorbent surface is zero, which was determined by batch equilibrium technique [18]. Initial pH values (pH_i) of 25 mL of KNO_3 solutions (0.1 M) were adjusted in the pH range 2–8 using 0.01 M HCl or 0.01 M NaOH. Then to each sample 0.1 g of wood apple shell powder was added. Equilibrium was carried out by shaking sample flasks greater than equilibrium contact time (4 h) at 299 K. After equilibrium, the dispersions were filtered and the final pH of the solutions (pH_f) was measured. The point of zero charge was found from a plot of pH_f vs. pH_i. The surface area of powdered wood apple shell was measured by methylene blue adsorption method as this material is known to be adsorbed as a monolayer only on solid sorbents [19]. The biosorbent characterization results are summarized in Table 1.

2.2. Preparation of solutions

Stock solution of Cr(VI) was prepared (1,000 mg L^{-1}) by dissolving the appropriate quantity of $K_2Cr_2O_7$ (A.R. Grade) in distilled water. The experimental solutions were prepared by diluting the stock solution to the desired Cr(VI) concentrations. The chelating agent 1–5, diphenyl carbazide (CDH, New Delhi, India) were prepared by dissolving 250 mg in 50 ml A.R. Grade acetone.

2.3. Adsorption experiments

In pH studies 0.3 g wood apple shell and 50 mL Cr (VI) solutions (10 mg L^{-1}) with a range of pH values from 1.0 to 8.0 were transferred into a conical flask and shaken on a temperature-controlled orbital shaker at 60 rpm for 120 min the pH of solution was adjusted with 0.01 M HCl or 0.01 M NaOH solution using pH-meter. The chromium removal efficiency was determined as:

Table 1
Physico-chemical characterization of the powdered wood apple shell

Parameter	Value
Particle size (mm)	0.167
Bulk density (g L^{-1})	0.582
Porosity (%)	56.45
Moisture content (%)	3.34
Ash content (%)	1.365
pH_{zpc}	3.7
Surface area ($m^2 g^{-1}$)	13.34

$$\%\ \mathrm{Cr(VI)\ removal} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

where C_o (mg L^{-1}) and C_f (mg L^{-1}) are initial and final concentrations of Cr(VI) in the liquid-phase, respectively.

In the determination of adsorption isotherm at equilibrium, 0.3 g wood apple shell and 50 ml of different concentrations (25–200 mg L^{-1}) of Cr(VI) solutions were shaken up to equilibrium time at the initial pH 1.8 and different temperatures (299–319 K). The adsorption kinetic experiments were carried out by shaking 0.3 g wood apple shell powder with 50 ml different concentrations (25–100 mg L^{-1}) of Cr(VI) solution at initial pH 1.8 and at the temperature 293 K for different contact times (20–160 min). The amount of Cr(VI) adsorbed at equilibrium, q_e (mg L^{-1}) and at time t (min), q_t (mg L^{-1}), was calculated by general equation:

$$q = \frac{C_o - C_f}{M} \times V \quad (2)$$

where V (L) is the volume of Cr(VI) solution, M (g) is the mass of dry powdered wood apple shell. All the mixtures after adsorption were filtered using Whatman 41 filter paper, and the un-adsorbed Cr(VI) concentrations in the filtrate was estimated by diphenyl carbazide method spectrophotometrically [20], monitoring the absorbance at 540 nm on UV–visible spectrophotometer (systronic). All the batch experiments were carried out in triplicate and the mean values of three data-sets are presented to ensure accuracy, reproducibility, and reliability. The equilibrium data fitted to the isotherm models used in this study were solved by using the linear regressions. The linear regressions were employed to obtain the optimum adsorption isotherms, kinetic, and thermodynamic parameters by using Microsoft Excel applications.

2.4. Fourier transfer infrared spectroscopy (FTIR) analysis

Infrared spectra of powdered wood apple shell and Cr(VI)-adsorbed wood apple shell were obtained after drying the biosorbent mass at 343 K for 24 h. the spectra were recorded using a Fourier transform infrared spectroscope (SHIMADZU 8400S) by mixing finely powdered sample with potassium bromide (1:10).

3. Results and discussion

3.1. FTIR analysis

The functional groups before and after adsorptions of Cr(VI) were determined by FTIR spectrometer. The adsorption capacity of Cr(VI) is strongly influenced by type and number of functional groups on the surface of biosorbent [21]. The spectra were measured within the range 4,000–500 cm^{-1} and shown in Fig. 1. The Infrared spectrum of wood apple shell showed several intense bands around 3,340.62, 2,939.61, 2,897.18, 2,050.40, 1,734.06, 1,641.48, 1,506.46, 1,462.09, 1,427.37, 1,371.43, 1,323.21, 1,246.06, 1,161.19, 1,116.82, 1,053.17, 898.86, 829.42 and 669.32 cm^{-1}. The adsorption peaks in the region of 750–900 cm^{-1} can be assigned to aromatic –C–H stretching vibrations [21,22]. The –C–O, –C–C and –C–OH stretching vibrations can be attributed to adsorption peaks in the region of the 1300–1000 cm^{-1} [21,22]. The adsorption peaks in the region 1730–1,390 cm^{-1} can be assigned to –C=O stretching vibrations of aldehydes, carboxylates, and ketones [21]. The adsorption peaks at 2,939.61 and 2,897.18 cm^{-1} confirms the presence of –C–H stretching vibrations [21,23]. The peak at 3,340.62 cm^{-1} can be assigned to the –OH and –NH functional groups [21,24]. When wood apple shell was loaded with Cr (VI) ions, the shifts resulted in the characteristic peak locations from 3,340.62, 2,939.61, 2,897.18, 1,641.48, 1,161.19, 1,053.17, 829.42 to 3,319.60, 2,941.54, 2,889.46, 1,599.04, 1,165.04, 1,055.10, 831.35 cm^{-1}, respectively. So, –OH, –NH and –C=O seem to participate in the Cr (VI) binding. These shifts in the IR frequencies support that –COOH, –NH and –OH are responsible for the biosorption of Cr(VI) onto wood apple shell. Similar results were observed by other researchers as biosorption of Cu(II) onto chestnut shell [25] and biosorption of Cr(VI) from aqueous solution by the husk of Bengal gram [26].

3.2. Effect of pH

The pH of aqueous solution affects the adsorption of both cations and anions at the liquid–solid interface. The anion exchange capacity is strongly governed by the surface chemistry of the solid biosorbent and the pH of the solution. The pH effect on adsorption of Cr(VI) onto the wood apple shell is found that the adsorption capacity increased from 33.2% to greater than 90% with decrease in pH from neutral to acidic (7 to 2) as shown in Fig. 2. The result shows that the biosorption of Cr(VI) is strongly pH dependent. It totally depends upon the surface properties of the wood apple shell and chromium specification in solution [27]. In aqueous solution Cr(VI) species are represented in various forms, such as H_2CrO_4, $HCrO_4^-$, CrO_4^- and $Cr_2O_7^{2-}$ as a function of pH. The following equilibrium represents the effect of pH on Cr(VI) speciation [28].

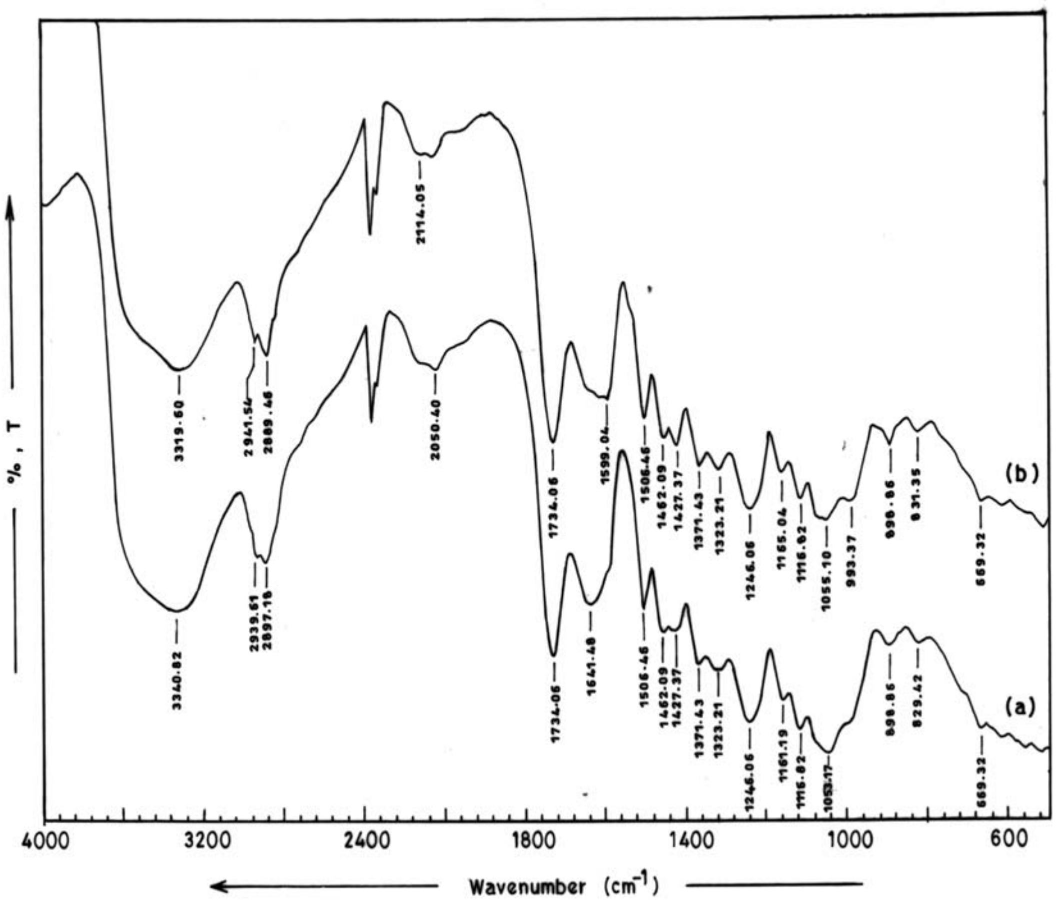

Fig. 1. FTIR spectrum of powdered wood apple shell (a) before adsorption and (b) after adsorption.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-, pK_a = 2.2 \quad (3)$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+, \; pK_a = 4.1 \quad (4)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+, \; pK_a = 5.9 \quad (5)$$

pH at the point of zero charge (pH_{pzc}) on surface of wood apple shell was found to be 4.3 (Fig. 3). This means that the net electric charge on sorbent surface was positive below the pHzpc and negative above the pH_{zpc}. The high biosorption of Cr(VI) below the pH at zero point charge can be explained by species of chromium and the biosorbent surface. There is strong electrostatic attraction between $HCrO_4^-$ species with protonated active site $[Ar–OH_2]^+$ of biosorbent surface in acidic condition as:

$$[Ar{-}OH_2]^+ + HCrO_4^- \rightarrow ArHCrO_4 + H_2O, \; pH<4.3 \quad (6)$$

where $[Ar{-}OH_2]^+$ is one of representative protonated active functional group on biosorbent surface. As the pH is increased above the zero point charge, there is reduction in electrostatic attraction between Cr(VI) species and biosorbent surface.

3.3. Adsorption isotherms

The equilibrium adsorption isotherm points to how the adsorbate molecule or ions are distributed between the solid phase and the liquid phase. To find out the suitable isotherm models, analysis of isotherm data by adapting to different isotherm models is an important step that can be used for design purpose. In the present research, the sorption equilibrium data of Cr(VI) on wood apple shell were analyzed in terms of Langmuir, Freundlich and Temkin isotherm model. Fig. 4 shows the typical equilibrium adsorption of Cr (VI) on powdered wood apple shell at 299, 309 and 319 K, the adsorption isotherm curves rises steeply at low concentrations and gradually approach to a plateau at higher concentrations.

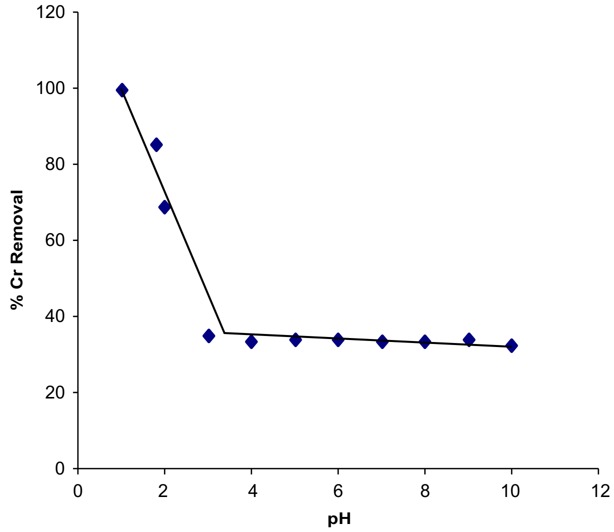

Fig. 2. Effect of pH on the biosorption of Cr(VI) ions ($10\,\mathrm{mg\,L^{-1}}$) onto powdered wood apple shell.

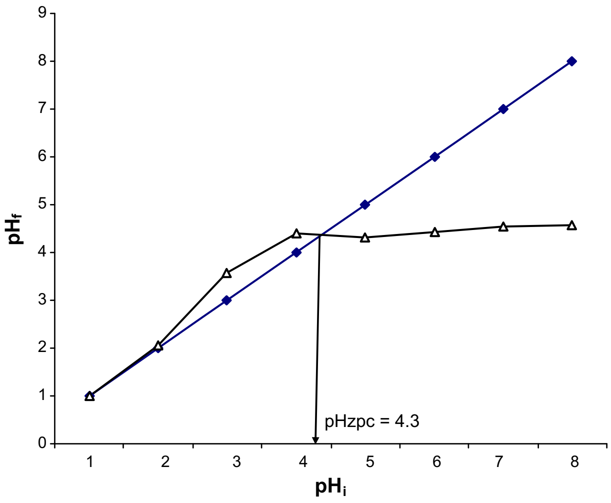

Fig. 3. Determination of pH at zero point charge on surface of biosorbent powdered wood apple shell.

The Langmuir isotherm model is based on ideal assumption of a total monolayer adsorption on adsorbent surface and expressed in linear form as follows [29]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{7}$$

where q_m ($\mathrm{mg\,g^{-1}}$) is the maximum monolayer adsorption capacity and K_L ($\mathrm{L\,mg^{-1}}$) is the Langmuir constant which is related to the heat of adsorption.

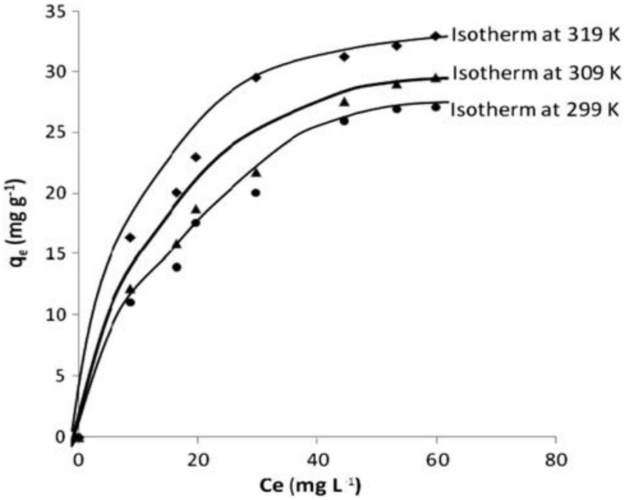

Fig. 4. Adsorption isotherm plot of Cr(VI) on powdered wood apple shell at pH 1.8.

The pH of Cr(VI) solution before and after adsorption was maintained 1.8 and estimated using digital pH-meter. The pH value remained constant during the adsorption process. The constants q_m and K_L are determined plotting the C_e/q_e vs. C_e which is tabulated in Table 2.

The essential dimensionless separation factor (R_L) of the Langmuir isotherm can be defined as [30]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

The value of R_L indicates adsorption isotherm to be either unfavorable ($R_L > 1$), favorable ($0 < R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). The calculated R_L values at different initial concentrations of Cr(VI) and temperature are in the range 0.04–0.2 in all experimental systems shown in Fig. 5, which confirms the favorable uptake process of chromium adsorption. Lower R_L values at higher initial concentration of Cr(VI) and higher temperature showed that the biosorption was more favorable at higher temperature and at higher concentration of adsorbate. Table 3 summarizes the comparison of Cr(VI) monolayer adsorption capacities (q_m) by various agricultural biomasses. The wood apple shell presents higher adsorption capacity than 6 from 12 different biosorbents, reflecting that utilization of wood apple shell in Cr(VI) removal from aqueous solutions shows promising future.

The Freundlich isotherm model is based on heterogeneous surface assumption [37] expressed by equation as:

Table 2
Isotherm parameters for Cr(VI) adsorption at different temperatures

Temp. (K)	Langmuir			Freundlich			Temkin			
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	$1/n$	R^2	K_t (L mg^{-1})	b	B (J mol^{-1})	R^2
299	28.81	0.0865	0.9763	7.045	0.2987	0.8808	0.3497	120.21	20.68	0.9454
309	29.58	0.215	0.9702	10.48	0.2561	0.9753	6.311	235.79	10.895	0.9305
319	31.45	0.40	0.9791	14.64	0.2079	0.961	19.14	251.39	10.55	0.9239

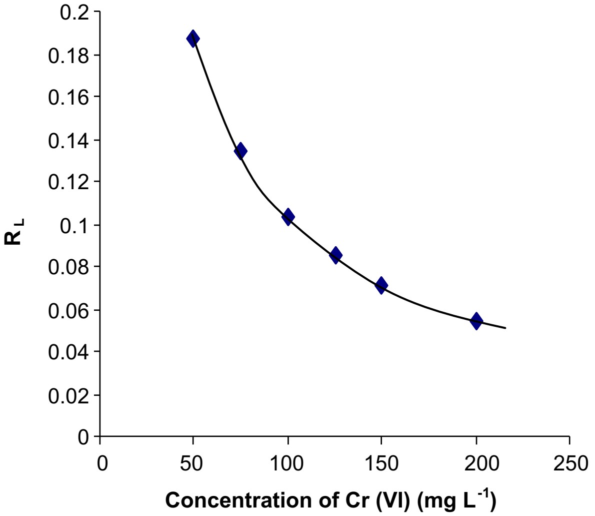

Fig. 5. Plot of separation factor (RL) with initial concentration of Cr(VI) ion at 299 K.

Table 3
A comparison of sorption of Cr(VI) ions with other biosorbent

Adsorbent	q_m (mg g^{-1})	References
Husk of Bengal gram	91.64	[26]
Iron(III) coordinated amino-functionalized poly(glycidyl methacrylate)-grafted cellulose	72.05	[31]
Cellulose modified with D-glucose	54.59	[32]
Wool	41.15	[33]
Olive cake	33.44	[33]
Pine needles	21.50	[33]
Saw dust	20.02	[34]
Beech saw dust	16.10	[35]
Palm pressed fibers	14.0	[36]
Almond	10.65	[33]
Sunflower stem	4.9	[27]
Wood apple shell	28.81	Present study

$$q_e = K_F C_e^{1/n} \qquad (9)$$

The linear form of the Freundlich adsorption equation is expressed by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (10)$$

where K_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$) and $1/n$ are the Freundlich constants. The plot of $\log q_e$ vs. $\log C_e$ enables the determination of isotherm constants K_F and $1/n$ (Table 2).

Temkin isotherm based on the heat of adsorption, which is due to the adsorbent and adsorbate interactions expressed in linear form as [38]:

$$q_e = B \log K_t + B \log C_e \qquad (11)$$

where $B = RT/b$ represent the heat of adsorption, T is the absolute temperature (K), R is the universal gas constant (J K^{-1} mol^{-1}), $1/b$ indicates the adsorption potential of the adsorbent and K_t (L mg^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. The plot of q_e vs. $\log C_e$ allows the determination of isotherm constants B (J mol^{-1}) and K_t (L mg^{-1}).

The experimental isotherm parameters along with regression coefficient are listed in Table 2. The adsorption isotherms based on parameters values are compared with experimental data at 299, 309 and 319 K. High R^2 values (>0.97) compared to the other models indicates that the biosorption of Cr(VI) onto wood apple shell follows the Langmuir isotherm model. The monolayer adsorption capacity (q_m) increased with increase in temperature, indicates that at higher temperature the adsorption capacity was higher and increase in Langmuir K_L with temperature confirms adsorption process was endothermic in nature.

Temkin isotherm constants at different temperatures from Table 2 show that there is a linear decrease in the standard enthalpy of adsorption

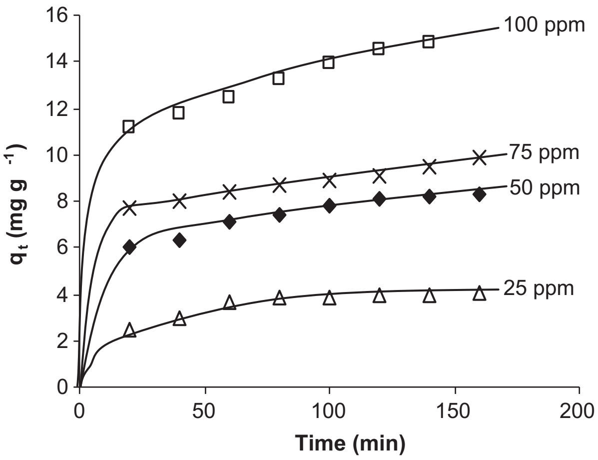

Fig. 6. Adsorption kinetics of Cr(VI) biosorption onto powdered wood apple shell at pH 1.8.

with surface coverage. Increase in Freundlich constant K_F with temperature shows the biosorption of Cr(VI) onto wood apple shell is more favored at higher temperatures [7].

3.4. Adsorption kinetics

Kinetic investigation was conducted further to reveal the adsorption mechanism of Cr(VI) onto wood apple shell. The pseudo-first-order and pseudo-second-order kinetic models have been tested for experimental data at different contact times. The effects of contact time on the uptake of Cr(VI) on the biosorbent are shown in Fig. 6. The figure shows that the adsorption process can be divided into two steps, the rapid 80% uptake of Cr(VI) was observed within first 20 min, and slow uptake of Cr(VI) observed until equilibrium was reached.

The pseudo-first order kinetic model was widely used for the adsorption liquid-solid system [39]. The general linear form of pseudo-first-order model is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{12}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of Cr(VI) adsorbed on wood apple shell at equilibrium and at time t (min), respectively, k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption process. The constants were determined experimentally by plotting the log (q_e–q_t) vs. t and listed in Table 4. The theoretical values (q_e, cal) differ from experimental (q_e, exp) indicates that the adsorption process does not follows the pseudo-first order kinetic.

The kinetic model based on the adsorption follows pseudo-second-order chemisorptions proposed by Ho and Mckay [40]. The linear form of pseudo-second-order equation is written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \tag{13}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant of adsorption. The constants q_e, k_2, and h_0 can be evaluated by plotting t/q_t vs. t. The initial rate of adsorption, h_0 (mg g^{-1} min^{-1}) is related as [41]:

$$h_0 = k_2 q_e^2 \tag{14}$$

The values of q_e, k_2, h_0, and R^2 are listed in Table 4. The plot of t/q_t vs. t gives an excellent straight line for all the experimental concentrations of Cr (VI) and all the R^2 are close to 1 (Table 4), confirming the applicability of pseudo-second-order model. In addition, there is only little difference between the q_e, exp and q_e, cal (Table 4), reinforcing the applicability of pseudo-second order. It can also be seen from Table 4 that with increase in initial Cr(VI) concentration, the initial adsorption rate (h_0) increases while the rate constant (k_2) of adsorption is fairly constant confirms pseudo-second order chemisorptions.

Table 4
Kinetic parameters for Cr(VI) adsorption onto wood apple fruit shell at different concentrations

C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order			
		$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h_0 (mg g^{-1} min^{-1})	R^2
25	4.05	2.505	0.02579	0.9760	4.47	0.01347	0.2692	0.9983
50	8.26	7.518	0.03316	0.8772	8.992	0.00764	0.6178	0.9975
75	9.90	2.755	0.01013	0.9934	10.23	0.00853	0.8929	0.9944
100	14.80	7.560	0.02303	0.9111	15.15	0.00887	2.036	0.9934

3.5. Adsorption thermodynamics

The important thermodynamic parameter, Gibbs free energy change for the adsorption process is related to equilibrium constant by the classic van Hoff equation as:

$$\Delta G^\circ = -RT \ln K \tag{15}$$

where ΔG° is the standard free energy change ($\mathrm{J\,mol^{-1}}$), T the absolute temperature (K) and R gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$), the equilibrium constant K for adsorption process is represented as follows [42]:

$$K = \frac{C_s}{C_e} \tag{16}$$

where C_s is the concentration of Cr(VI) on the adsorbent at the equilibrium and C_e is the equilibrium concentration of Cr(VI) in the liquid phase.

The Gibbs free energy change is also related to the heat of adsorption and entropy change at constant temperature by the well-known thermodynamic equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{17}$$

where ΔH° is enthalpy change ($\mathrm{J\,mol^{-1}}$), ΔS° is entropy change ($\mathrm{J\,mol^{-1}\,K^{-1}}$). The values of ΔH° and ΔS° can be calculated from the plot of ΔG° vs. T shown in Fig. 7. The calculated thermodynamic parameters for the biosorption of Cr(VI) onto wood apple shell are given in Table 5. The negative value of ΔG° indicates the feasibility of the process and the spontaneous nature of biosorption. The value of ΔG° is more negative with increase in temperature, suggests that higher temperature makes the biosorption easier. The positive value of ΔH° implies that the biosorption phenomenon is endothermic. The large positive value of ΔS° suggests more disorder at solid-liquid interface of biosorption process.

The standard equilibrium temperature (T°) is the temperature at which standard free energy is zero ($\Delta G^\circ = 0$) [43]. Value of T° for the present biosorption system is accurately and precisely obtained from plot of T vs. ΔG° shown in Fig. 8. The intercept on y-axis gives the value of standard equilibrium temperature (T°) equals to 274.6 K. This indicates the biosorption of Cr(VI) onto powdered wood apple shell at standard conditions was feasible at temperatures greater than 274.6 K and non feasible at temperatures less than 274.6 K up to absolute zero temperature [43].

Table 5
Thermodynamic parameters for the adsorption of Cr(VI) onto wood apple shell at different temperatures

T (K)	K	ΔG° ($\mathrm{kJmol^{-1}}$)	ΔH° ($\mathrm{kJmol^{-1}}$)	ΔS° ($\mathrm{Jmol^{-1}K^{-1}}$)	R^2
299	3.504	−3.117	33.792	123.2	0.989
309	4.747	−4.131			
319	7.695	−5.581			

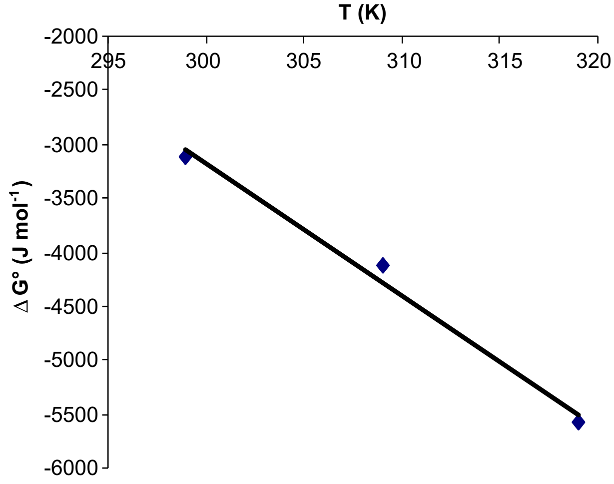

Fig. 7. Adsorption thermodynamic parameters of Cr(VI) onto powdered wood apple shell.

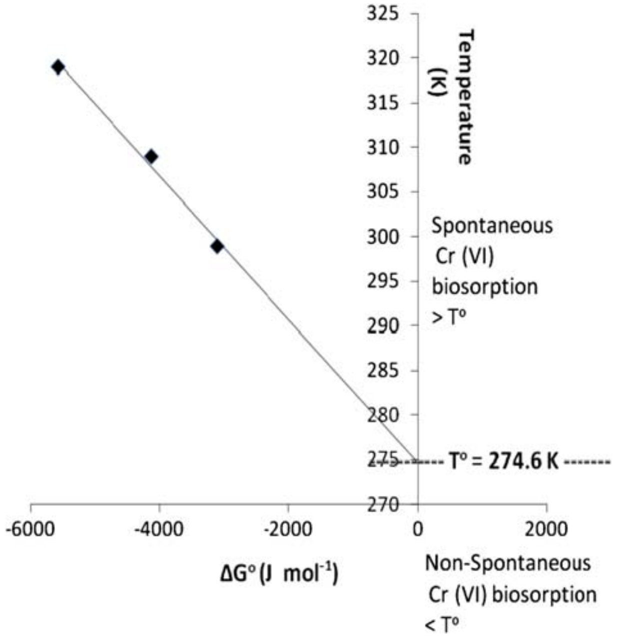

Fig. 8. Determination of standard equilibrium temperature (T°) for biosorption of Cr(VI) onto powdered wood apple shell.

4. Conclusions

This study investigated the removal of hexavalent chromium by wood apple shell powder from aqueous solution. The removal efficiency of Cr(VI) increased with decrease in pH and increased with increase in temperature. The pH at point of zero charge on surface of wood apple shell was found to be 4.3. The biosorption process followed the Langmuir isotherm model better than Freundlich and Temkin isotherm models. The Langmuir monolayer adsorption capacity of Cr(VI) on wood apple shell was 28.81, 29.58 and 31.45 $\mathrm{mg\,g^{-1}}$ at 299, 309 and 319 K, respectively. The adsorption dynamics analysis indicates that the pseudo–second-order equation fitted very well to the biosorption of Cr(VI) on wood apple shell ($R^2 > 0.99$). Thermodynamic analysis reveals that the removal of Cr(VI) from aqueous solution by wood apple shell was spontaneous, feasible and endothermic process at temperatures greater than standard equilibrium temperature ($T^\circ = 274.6\,\mathrm{K}$). The investigation shows that wood apple shell is a promising biosorbent for the removal of Cr(VI) from aqueous solutions.

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