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Study on the removal of hexavalent chromium using a new biosorbent

Tariq Suhail Najim*, Safana A. Farhan, Rasha M. Dadoosh

Polymer Research Unit, College of Science, Mustansiriya University, Baghdad, Iraq
Tel. +964 1 7703608825; email: tariq_pru@yahoo.com

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ABSTRACT

Peppermint leaves (PML) have been explored as an effective and cheap adsorbent for removal of toxic Cr(VI) ions from aqueous solutions using batch system. Adsorption of Cr (VI) ions onto PML was found to be pH dependent and maximum removal of Cr(VI) ions was obtained at pH 2. It was also found that after 180 min of PML contact with chromium solution at the concentration of 0.3846 mmol/L, more than 95% of Cr(VI) ions can be removed. The equilibrium data were fitted with the Langmuir and Freundlich models. The adsorption kinetic data were best fitted with the pseudo-second-order. The activation energy E_a of the adsorption process was determined as 23 kJ mol^{-1}, which may indicate a physisorption process. The Gibbs free energy, enthalpy, and entropy of the process were also determined, and their values revealed that the process is spontaneous and endothermic accompanied with randomness at the solid/solution interface.

Keywords: Peppermint leaves; Adsorption; Thermodynamic; Activation energy; Cr(VI) ions

1. Introduction

Chromium has long been used in electroplating, leather tanning, metal finishing, and chromate manufacturing industries. Effluents from these industries contain both trivalent chromium Cr(III) and hexavalent chromium Cr(VI), with concentrations ranging from tens to hundreds of mg/l [1]. Cr(VI) occurs as highly soluble and toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$), which are suspected to be carcinogens and mutagens [2]. In contrast Cr(III), having lower toxicity, is generally regarded as much less dangerous pollutant [3].

The chemistry of Cr(VI) is greatly dependent on pH of the solution. In acidic media Cr(VI) exists mostly in the form of chromate $HCrO_4^-$ [4] ions. At pH between 4 and 6, $Cr_2O_7^{2-}$ and $HCrO_{4-1}$ ions exist in equilibrium and under alkaline conditions pH > 8, it exists predominantly as chromate anion CrO_4^{2-} [5]. Cr (VI) is most commonly encountered in the chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$ anions. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate). The various treatment techniques available for the removal of Cr(VI) from aqueous effluents are chemical reduction [6], nanofiltration [7], bioaccumulation [8], ion exchange [9], and adsorption, which are the most widely used techniques for removing metal and dyes from industrial effluents.

Adsorption is a well known equilibrium separation process, in which the adsorbent may be mineral,

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*Corresponding author.

organic, or biological origin. Activated carbon [10–12], resins and polymers [13–16], agricultural wastes [17–19], and natural polymers were effectively used for the removal of toxic metal ions from aqueous solutions [20,21]. The presence of reactive chemical groups in polymer chains made these polymers an interesting and attractive adsorbents for water decontamination. Most leaves of plants and herbs are composed of biopolymers which include carbohydrates, fibers, protein, and tannin [22,23]. The peppermint plants are available in most part of Iraq as wild plants. In this work, the PML are employed for the removal of Cr(VI) ions from aqueous solutions under equilibrium conditions using batch technique.

2. Experimental

2.1. Materials

Potassium dichromate $K_2Cr_2O_7$ was supplied by Aldrich with purity 99.5%: hydrochloric acid and sodium hydroxide were of analytical grade reagents. Peppermint leaves (PML) were collected from Baghdad area, dried at room temperature away from sunlight, ground and then sieved to a particle size of 300–500 μm.

2.2. Instrumentation

FTIR spectrophotometer type (Jasco-4200) was used for determination of functional groups vibrations using KBr disc method. Temperature controlled shaking water bath type (Jeio Tech. BS-11) Korea, four-digit balance type Kern ABS Germany, UV–Visible spectrophotometer type Varian 100 Conc, and pH meter type Trans BP 300 were used throughout this work.

2.3. Adsorption study

A stock solution of Cr(VI) ions was prepared by dissolving 1.4144 g of $K_2Cr_2O_7$ in 1 L of deionized water to prepare 500 mg/L of Cr(VI), proper concentration of the adsorbate was prepared from the stock solution through dilution with deionized water. The pH of the adsorbate solution was adjusted during the dilution steps using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide. The batch adsorption experiments were performed on a temperature controlled shaking water bath with a shaking rate of 140 rpm. At the end of a predetermined time interval, the Cr (VI) loaded adsorbent was removed by filtration and the remaining Cr(VI) in the filtrate was estimated by UV–visible spectrophotometer using calibration curve. The calibration curve obtained from standard solution of potassium dichromate absorbance vs. Cr (VI) concentration at $pH \geqslant 12$ using NaOH solution ($\lambda_{max} = 375\,nm$, $\varepsilon = 4{,}900\,cm^{-1}\,M^{-1}$), [5,13]. Determination of Cr(VI) as chromate ion (yellow color) which is dominate at higher pH, is more sensitive than its determination as dichromate form (orange) in aqueous solution. The effect of initial pH from 1 to 6, adsorbent dosage from 1 to 14 g/L, contact time from 5 to 180 min, and Cr(VI) ions initial concentration of 20–120 mg/L on the adsorption process was performed. The equilibrium capacity q_e was calculated according to Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

The removal efficiency $R\%$ of Cr(VI) was determined using Eq. (2)

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration, C_e is the concentration of unremoved Cr(VI) after certain contact time, V is the volume of sample (L) and W is the weight of PML powder (g).

3. Results and discussion

3.1. FTIR spectroscopy

FT-IR spectra for both fresh and Cr(VI) loaded PML were obtained by KBr pellets method using FT-IR spectrophotometer type (Jasco 4200) to explore the functional groups present in the biomass and to look into possible Cr(VI) binding sites as shown in Fig. 1. The fresh biomass displays a number of absorption peaks, reflecting the complex nature of PML. The FTIR spectroscopic analysis shows broad peak at 3,500–3,200 cm^{-1}, representing O–H and N–H stretching (the surface hydroxyl and amine groups). A change in peak position in the spectrum of the chromium-loaded PML indicates the binding of the metal with amino and hydroxyl groups. The band observed at 2,940 and 2,904 cm^{-1} are assigned to the stretching aliphatic C–H groups. The band present at about 1,732 cm^{-1} is assigned to C=O (band from carboxylic or ester groups). The peak around 1,650 cm^{-1} corresponds to C=O (amide band primarily a stretching band). The shifting of this peak to 1,639 cm^{-1} indicates the involvement of

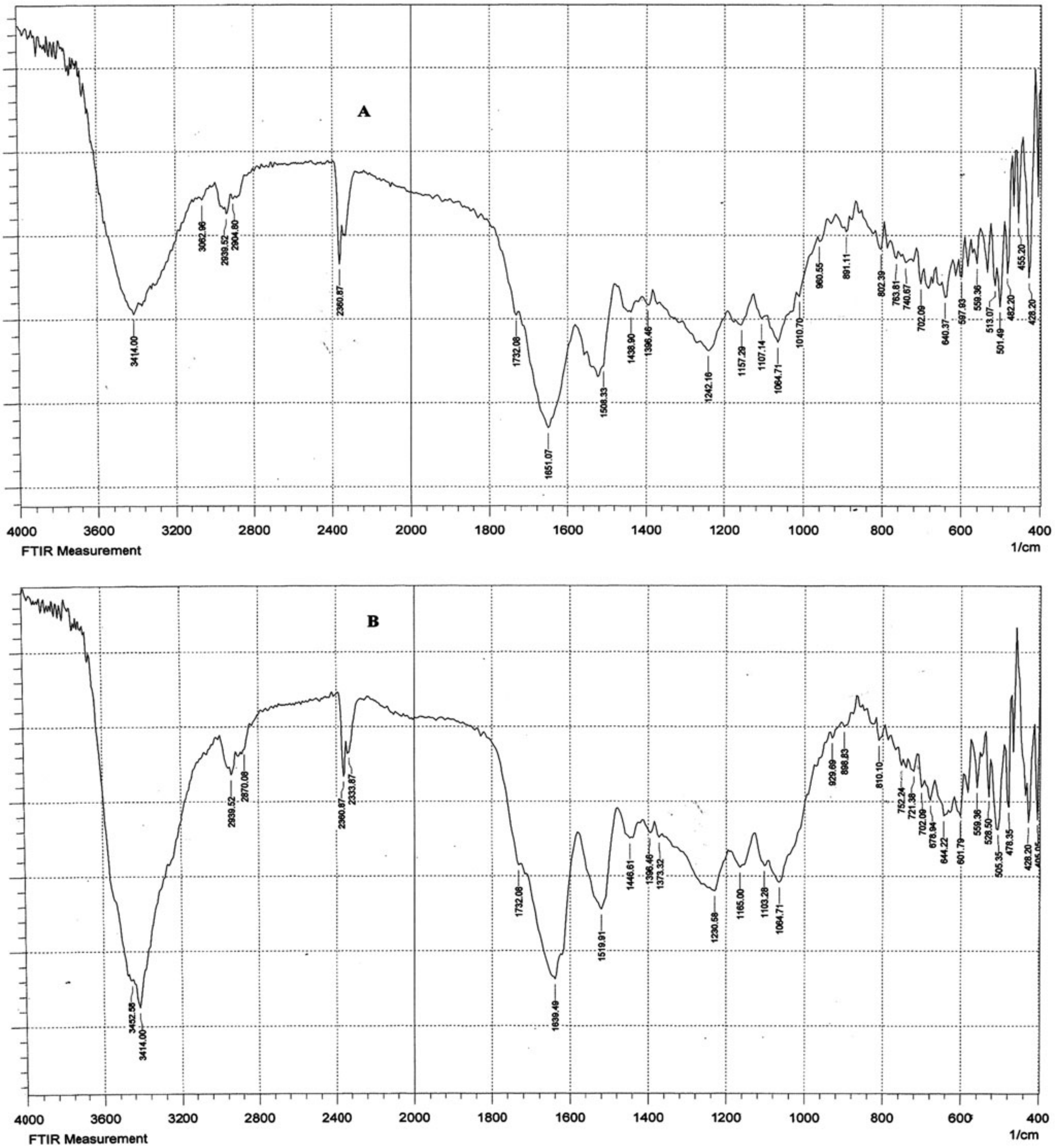

Fig. 1. FTIR spectrum of (A) PML (B) Chromium loaded PML.

C=O of amides in the adsorption process. The peak around 1,396 cm^{-1} may indicate the stretching vibration of NO_2. The peaks observed around 1,242 and 1,064 cm^{-1} could be assigned to SO_3 stretching vibration, C–O stretching of polysaccharides, respectively. Several researchers [25,26] affirm that the hydroxyl, carboxyl, sulfonate, amine, amide, imidazole, and phosphate groups are the main functional groups responsible for the biosorption process. Some of these groups are present on the PML and may interact with the chromium ion during the adsorption process.

3.2. Effect of pH

Initial pH is one of the most important factors that affect the adsorption process. It affects both the surface charge of the adsorbent and the ionization degree of the adsorbate. To investigate the role of pH in Cr(VI) removal efficiency, the initial pH of Cr(VI) solution varied in the range of 1–5. The variation of pH vs. the percent removal of Cr(VI) which is shown in Fig. 2. It can be seen that the percent removal of Cr(VI) was 95% at pH 2 and 2 g/L of PML, at pH higher than 2 the percent removal of Cr(VI) decreased to 11%, at pH 5.

As previously explained, the dominant form of Cr (VI) ions at pH 2 is $HCrO_4^-$. So, this anion can be attracted to the positive charge on the adsorbent which is generated in the acidic medium (due to protonation of the carbonyl, amine, amide, and hydroxyl groups). Based on this result, removal mechanism might be due to the attraction between the negatively charged Cr(VI) ions and the positively charged adsorbent groups. Amino, carboxyl, sulfonate, and hydroxyl groups of biomaterials are suspected to bind anionic Cr(VI) ions with the aid of protons in aqueous phase [5,27–30] as follows:

$$\text{B–NH}_2\ (s) + \text{HCrO}_4^- + \text{H}^+\ (aq) \rightarrow \text{B–NH3}^+ \ldots \text{HCrO}_4^-\ (s)$$

$$\text{B–COOH}\ (s) + \text{HCrO}_4^- + \text{H}^+\ (aq) \rightarrow \text{B–COOH}_2^+ \ldots \text{HCrO}_4^-\ (s)$$

$$\text{B–SO}_3\text{H}\ (s) + \text{HCrO}_4^- + \text{H}^+\ (aq) \rightarrow \text{B–SO}_3\text{H}_2^+ \ldots \text{HCrO}_4^-\ (s)$$

$$\text{B–OH}\ (s) + \text{HCrO}_4^- + \text{H}^+\ (aq) \rightarrow \text{B–OH}_2^+ \ldots \text{HCrO}_4^-\ (s)$$

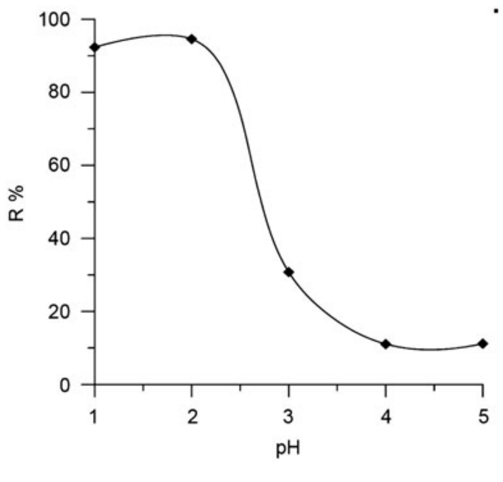

Fig. 2. Effect of pH on Cr(VI) adsorption onto PML.

As the pH of the aqueous phase is lowered, the large number of protons can easily coordinate with these functional groups present on the biomaterial surface. Thus, low pH makes the biomaterial surface more positive, which enhance the binding of anionic Cr(VI) ion species with the positively charged groups on the adsorbent. The low pH also accelerates the redox reaction in aqueous and solid phase, since the protons participate in these reactions [31,32]. Thiol, phenolic, lignin, and tannin groups have been reported as electron-donor groups of biomaterials [33–36]. The possibility of Cr(VI) reduction to Cr(III) by PML powder is not excluded but not investigated in this study.

3.3. Effect of initial concentration of Cr(VI)

The concentration of Cr(VI) in solution determines the toxicity of the solution. Therefore, the effect of initial concentration of Cr(VI) on the removal efficiency of Cr(VI) by PML powder was investigated. For this purpose 0.1 g of adsorbent was contacted for 180 min with 50 ml of Cr(VI) solutions with different initial concentrations (20–120 ppm). It was found that the removal efficiency is decreased and the adsorption capacity increased with increase of the initial concentration of Cr(VI), this trend was also found by other investigators [37,38]. The decrease in removal efficiency can be explained by the fact that all adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

3.4. Effect of contact time and determination of adsorption kinetic

In order to evaluate the optimal time required for nearly complete removal of Cr(VI) from aqueous solution, 0.1 g of PML powder was exposed to 50 ml of chromate solution with concentration of 20 ppm. The Cr(VI) concentration was measured after different contact times by the measurement of the UV–vis absorption peaks spectrophotometrically. The reduction of the absorption peak intensity during contact time indicates the reduction of Cr(VI) concentration in solution in contact to the adsorbent. The Cr(VI) removal efficiency after different contact times were calculated using Eq. (2); results showed that after 130 min of contact at 35˚C, over 96% of chromate ions in the solution has been removed by PML powder. The data obtained from the effect of time on the

Table 1
The kinetic parameters of the adsorption of Cr(VI) onto PML powder.

Temp (°C)	Q_e exp (mg /g)	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
		Q_e cal (mg/g)	k_1 (min^{-1})	Δq_e (%)	R^2	Q_e cal (mg/g)	k_2 (g mg^{-1} min^{-1})	Δq_e (%)	R^2
25	9.53	6.06	0.026	36.5	0.997	10.06	0.46	5.5	0.997
35	9.67	5.15	0.033	46.7	0.981	10.02	0.80	3.6	0.999

adsorption of Cr(VI) onto PML powder were then regressed against the pseudo-first-order Eq. (3) [39], and second-order Eq. (4) [40], kinetic models.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{3}$$

$$t/q_t = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{4}$$

where k_1 and k_2 are the rate constants of the pseudo-first and second-order kinetics, respectively. From the slope and intercept of plot of log $(q_e - q_t)$ vs. time, k_1 and q_e were determined, the results are shown in Table 1. The second-order rate constant k_2 and q_e were determined from intercept and slope of Fig. 3, and presented in Table 1. However, the pseudo-second-order kinetic model provided a near-perfect match between the calculated and experimental q_e values. Furthermore, the correlation coefficient of the pseudo-second-order plot Fig. 5 is 1.00.

As a result, the sorption system appears to follow pseudo-second-order reaction kinetic. On the other hand, the second-order-rate constant increases with increasing temperature from 25 to 35°C, which indicates that the adsorption is enhanced with increasing temperature, as shown in Table 1.

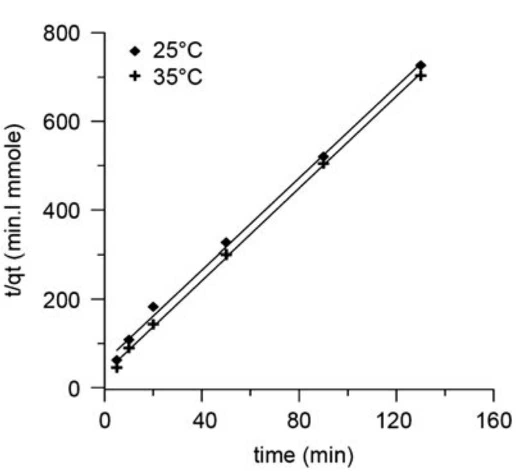

Fig. 3. Pseudo-second-order plot at 25 and 35°C.

3.5. Adsorption isotherms

The relation between Cr(VI) initial concentration and its extent of removal from aqueous solutions was studied at various Cr(VI) concentrations at fixed PML dose and temperature. Adsorption data for a wide range of adsorbate concentrations are the most commonly described by adsorption isotherms, such as Langmuir and Freundlich, which relate adsorption capacity, q_e (adsorbate uptake per unit weight of the adsorbent) to equilibrium adsorbate concentration in the bulk liquid phase C_e.

The Langmuir isotherm [41] is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the suface. The langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{\max} \times b}\right) + \left(\frac{1}{Q_{\max}}\right)C_e \tag{5}$$

where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the amount of metal adsorbed at equilibrium (mg/g), and $Q_{\max}$ (mg/g) is the maximum quantity of metal per unit weight of adsorbent, whereas b (L/mg) is a constants related to the affinity

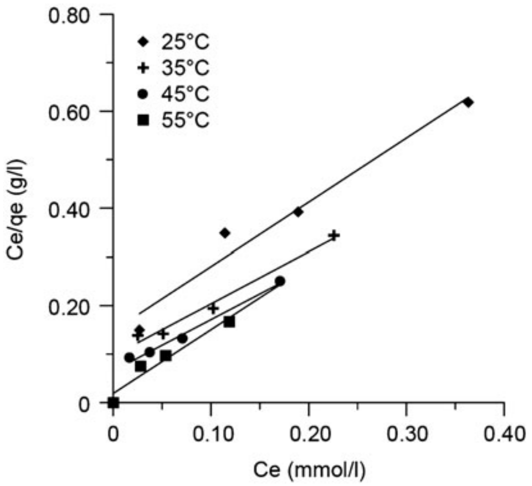

Fig. 4. Langmuir adsorption isotherm of Cr(VI) onto PML.

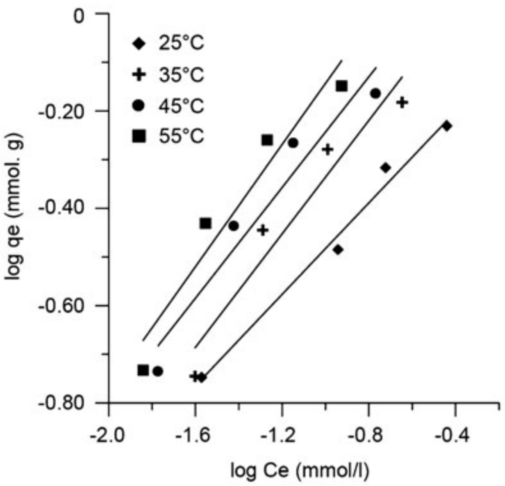

Fig. 5. Freundlich adsorption isotherm of Cr(VI) onto PML powder.

of binding sites with the metal ions [42]. Plotting of C_e/q_e vs. C_e, at 25, 35, 45 and 55°C, gives straight lines, Fig. 4, with correlation coefficients (R^2) of 0.966, 0.982, 0.989, and 0.997, respectively as given in Table 2. The values of b is increased with increasing temperature, which implies increasing affinity between the adsorbent and metal ions with increasing temperature. The essential characteristics of Langmuir can be expressed in terms of a dimensionless equilibrium parameter, R_L, which describes the type of isotherm [11,43], and is defined by: $R_L = \frac{1}{1+b\times c_o}$ where b (L/mg) is the Langmuir constant and C_o is the initial concentration of Cr(VI) solution. The R_L value indicates the type of the isotherm as follows:

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L for different Cr(VI) initial concentrations at 55°C are listed in the following table:

Cr(VI) concentration (mg/l)	R_L value
20	0.102
40	0.054
60	0.036
80	0.027

It is clear that all the values of R_L range between 0 and 1, indicating favorable adsorption of Cr(VI) onto PML powder, furthermore, the values of R_L decreases with increasing temperature (Table 2), it decreases from 0.225 at 25°C to 0.102 at 55°C, which indicates that the reaction is more favorable at higher temperature.

Furthermore, the Freundlich adsorption isotherm [44], can be applied to the adsorption data using the linear form of the Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F and n are the Freundlich constants, related to the capacity of adsorbent and favorability of the adsorption, respectively. Plotting of log q_e against log C_e at different temperatures, (Fig. 5), straight lines were obtained. The Freundlich constants and correlation coefficients are presented in Table 2. As shown by the results, the values of n range from 2.13 at 25°C to 1.59 at 55°C (i.e. $n > 1$) showing that the adsorption of Cr(VI) onto PML powder is favorable and physical in nature [38].

3.6. Effect of temperature and determination of thermodynamic parameters

The temperature dependence of the adsorption was calculated by the linearized Arrehenius equation [45] at two temperatures 25 and 35°C:

$$\ln K = \ln A - \frac{Ea}{RT} \tag{7}$$

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8}$$

where E_a is the activation energy of the adsorption (kJ mol^{-1}), k_1 and k_2 are the pseudo-second-order rate constants at 25 and 35°C, respectively, R is the gas constant (8.314 J mol^{-1}K^{-1}), and T is the solution temperature (K). The activation energy value gives information on whether the adsorption is mainly physical or chemical. Physisorption process normally had activation energy of 5–50 kJ mol^{-1}, while chemisorption had higher activation energy 40–800 kJ mol^{-1} [46]. From Eq. (8) the activation energy was calculated and found to be 23 kJ mol^{-1}, and given in Table 3. It was concluded from these results that the adsorption process involved physisorption. The thermodynamic parameters, like Gibbs free energy, enthalpy, and entropy of adsorption were calculated from the values of Langmuir constant (b) at different temperatures:

$$\Delta G = -RT\ln b \tag{9}$$

Table 2
The Langmuir and Freundlich constants and correlation coefficients of isotherm models at different temperatures.

Temperature (K)	Langmuir isotherm				Freundlich isotherm		
	$Q_{\max}$ (mg/g)	b	R^2	R_L	$1/n$	K_f	R^2
298	39.3	0.17	0.966	0.225	0.469	0.97	0.985
308	48.7	0.21	0.982	0.191	0.582	1.76	0.932
318	49.2	0.31	0.989	0.139	0.568	2.11	0.988
328	50.8	0.44	0.997	0.102	0.627	3.05	0.934

Note: Cr(VI) concentration, 20–80 mg/L, adsorbent concentration, $2\,\mathrm{g\,L^{-1}}$,agitation speed, 140 rpm, contact time,180 min at pH 2.

Table 3
Thermodynamic parameters of Cr(VI) adsorption by PML powder.

T (K)	ln b (L/mg)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1}K^{-1})	ΔH (kJ mol^{-1})	E_a (kJ mol^{-1})
298	−1.76	−4.36	–	–	–
308	−1.55	−3.97	–	–	–
318	−1.17	−3.10	72.80	26.22	23
328	−0.82	−2.24	–	–	–

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

The plot of ln b vs. $1/T$ is given in Fig. 6, ΔS and ΔH were calculated from the intercept and slope of the plot and tabulated with other thermodynamics parameter in Table 3. The negative values of ΔG suggest that the adsorption process is spontaneous. The positive value of ΔH indicates the endothermic process, while the positive value of ΔS shows the increased randomness at the sorbent/solution interface during the adsorption of chromate ions onto PML powder.

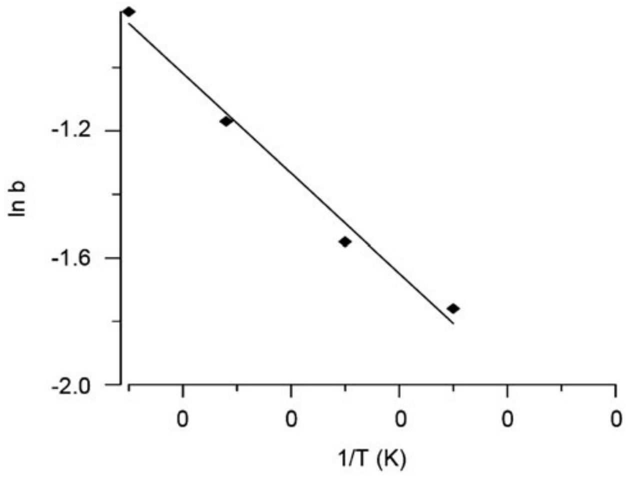

Fig. 6. Plot of the Langmuir constant ln b vs. $1/T$.

4. Conclusions

The PML as solid phase extractor have the following advantages:(i) Stable, inexpensive, environment friendly, and rich in functional groups that have the ability to bind metal ions. (ii) It has the pronounced capability for the uptake of Cr(VI) ions in aqueous solution at strongly acidic medium pH 1–2 with no need to chemical modification. (iii) It was applicable for the removal of Cr(VI) ions with percentage recovery >95% using batch technique. (iv) Its sorption data were fitted well with Langmuir and Freundlich models with correlation factor $r^2 = 0.997$ and 0.934 at 55°C, respectively, and obeying pseudo-second-order model $r^2 = 0.999$. Furthermore, the process was spontaneous and endothermic with randomly distributed metal ions at solid/liquid interface.

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