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## Removal of Chromium from Aqueous Solution using Vigna mungo Husk (Black Lentil): Kinetic & Thermodynamic Studies

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### ABSTRACT

The adsorption of chromium [Cr(VI)] ions from aqueous solution by Vigna mungo husk (VMH) was studied in batch adsorption system as a function of pH, contact time, adsorbent dosage, particle size and initial concentration. Maximum Cr(VI) removal was observed at pH 2. The experimental equilibrium adsorption data were compared with the various Langmuir, Freundlich, and Redlich-Peterson isotherms. Redlich-Peterson isotherm showed the best fit for the adsorption of chromium in VMH and Langmuir adsorption capacity was found to be 62.5 mg/g. Different kinetic models were applied to fit the experimental kinetic data and the best fit was obtained with the pseudo second-order model with a rate constant value of 0.0029 g/mg min. The temperature variation study of adsorption on VMH revealed that the adsorption process was endothermic, from the positive values of  $\Delta H^\circ$ . The results indicate that VMH can be employed as a low cost alternative to commercial adsorbent in the removal of Cr(VI) from water.

**Keywords:** Vigna Mungo; Adsorption; Chromium; Kinetics; Thermodynamics.

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## INTRODUCTION

Toxic metals are released into the environment in a number of ways. Coal combustion, sewage wastewater, automobile emission, battery industry, mining activities, heavy metals and the utilization of fossil fuels are just a few examples [1-5].

Chromium (VI) which has widespread use in leather tanning, paint and pigment manufacturing, chrome plating, wood preservation, fertilizers, textile dyeing, electroplating, cement, mining and photography industries [6], is a major metal pollutant of the environment. The permissible limit of chromium(VI) in drinking water is 0.05 mg/L [7].

Additionally, Cr(VI) is toxic to many plants, aquatic animals, and bacteria [8]. The United Nations Food and Agriculture Organization's recommended maximum level of chromium for irrigation water is 0.1 mg/l at the maximum [9]. Wastewater generated by these industries usually contain significant quantity of salt like sodium chloride, so the effect of this salt for the removal of chromium(VI) should be investigated [10,11].

The removal of toxic metal ions and recovery of valuable ions from mine wastewater, soil and water have become very important in economic and environmental problems [12-15]. Different conventional processes (precipitation, ion exchange, electrochemical process and/or membrane process) are usually applied to the treatment of industrial effluents, but the application of such processes are often limited because of technical or economic constraints [16].

The aim of this study is to investigate the chromium adsorption from aqueous solution, the effect of different parameters such as contact time, pH, adsorbent dose and initial chromium concentration on adsorption process and find the optimum adsorption isotherm as well as the rate of adsorption kinetics and Adsorption thermodynamics nature.

## MATERIALS AND METHODS

### Preparation of adsorbent

The VMH was collected from processing unit and was washed with clean water to remove colour and impurities. The husk was then naturally dried for 48 hours and the sieved husk (75 – 212  $\mu\text{m}$ ) was activated with 0.1N  $\text{H}_2\text{SO}_4$  for 24 hours. The activated adsorbent was then filtered out, washed with distilled water to remove free sulfuric acid (washed with distilled water until the pH is equal to distilled water) and naturally dried for 24 hours. These were subsequently used for the adsorption experiment.

### Preparation of hexavalent chromium solution

The stock hexavalent chromium [Cr(VI)] solution was prepared by dissolving 2.8289 g of analytical reagent (AR) of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) in 100 ml of double distilled water

and then different concentrations of 50, 100, 150, 200, 250 and 300 ppm, solutions were prepared by diluting the stock solution. These are the concentrations of hexavalent chromium solution which were prepared based upon which the whole experiment was conducted.

### **Batch adsorption study**

Batch equilibrium experiments were conducted by adding a 0.2 g of the activated adsorbent to 50 ml of the Heavy metal solution. The solution was shaken in rotating shaker at 130 rpm. The resultant solution with the adsorbent in the flask was filtered using Whatman No.42 filter paper. The filtrate was then analyzed for chromium using Photo electric colorimeter (AMIL Photo instrument).

### **pH**

0.2 g of VMH was added to 50 ml of the heavy metal solution at different pH (1 to 11) in an Erlenmeyer flask. The pH of the initial heavy metal solution was adjusted using 0.1 N HCl and 0.1 N NaOH accordingly. The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for chromium using Photo electric colorimeter.

### **Contact time**

The time required to attain equilibrium for 50, 100, 150, 200, 250 and 300 mg/l Cr(VI) concentrations was determined 0.2 g of the activated adsorbent material was added to 50 ml of the heavy metal solution in a flask, shaken and allowed to stand for 30, 60, 90, 120, 150 and 180 min. The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for chromium using Photo electric colorimeter.

### **Adsorbent dosage**

Adsorption of Cr(VI) was studied by increasing adsorbent dose from 0.1g to 0.8 g for 50 ml of Cr(VI) concentrations 50, 100, 150, 200, 250 and 300 mg/l. Keeping the pH of the heavy metal solution constant (pH of 2) following the results obtained earlier and allowed to stand for 150 min. The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for chromium using Photo electric colorimeter.

### **Particle size**

The batch adsorption experiments were carried out using various adsorbent sizes (0.21 to 0.85 mm) at pH 2, 29 °C, 150 rpm and various initial concentration of Chromium (50 to 300 mg/l). The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for chromium using Photo Electric Colorimeter.

### Initial chromium concentration

Thus experiment was carried out with various initial chromium concentration (50, 100, 150, 200, 250 and 300 mg/l) at constant temperature (29°C), pH (2), agitation speed (130 rpm), contact time (150 min) and 0.2 g of adsorbent dose and is allowed to attain equilibrium. After equilibration the filtrate was analyzed for chromium using Photo Electric Colorimeter.

## RESULTS AND DISCUSSION

### Effect of pH

pH is one of the most important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and/or inorganic ligands. Redox reactions, precipitation were strongly influenced by pH and on the other side, strongly influence the speciation and the biosorption availability of the heavy metals [17]. Metal sorption was critically linked with pH. It was observed from the Figure 1 that the uptake of Cr(VI) decreases with increase in pH. The highest sorption capacity of adsorbent for Cr(VI) was at pH 2 and the decrease in sorption capacity with increase in pH might be attributed to the changes in metal speciation and the dissociation of functional groups on the sorbent. Similar observation was recorded by Elliot and Weng for Cr(VI) onto fly ashes [18]. Optimum biosorptive removal of chromium(VI) at low pH 2 have been reported for *Rhizopus nigricans* [19], *Bacillus* sp. [20] and *Dunaliella* sp. [21]. Electrostatic interactions have also been demonstrated to be responsible for Cr biosorption by Fungi *Gonaderma lucidum* and *Aspergillus niger* [22,23].

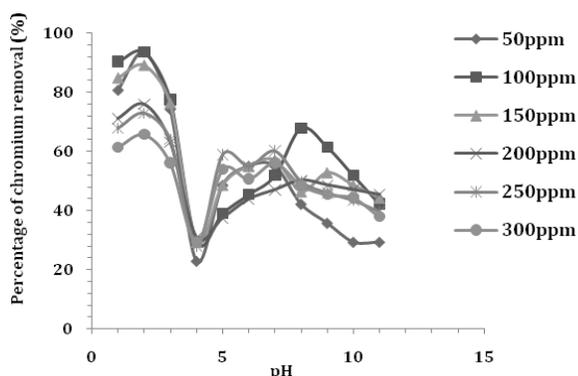


Figure 1 Effect of pH on chromium removal, (Agitation speed=130 rpm, temperature=29<sup>0</sup> C, adsorbent size=0.25 mm, contact time=150 min, adsorbent dose=0.2 g/50ml)

The decrease in the adsorption with increase of pH might be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal was high. The surface charge of adsorbent is positive at low pH, and this may promote the binding of the

negatively charged  $\text{HCrO}_4^-$  ions. The  $\text{HCrO}_4^-$  species were easily exchanged with  $\text{OH}^-$  ions at active surfaces of adsorbent under acidic conditions.

### Effect of Contact Time

The results of percentage Cr(VI) adsorption at pH 2, with increasing contact time were presented in Figure 2. It was found that the Cr(VI) adsorption percentage increased with increasing contact time. The initial rapid adsorption was due to the availability of the positively charged surface of the present adsorbent for adsorption of anionic Cr(VI) species present in the solution at pH 2.0. The later slow adsorption was probably due to the electrostatic hindrance between adsorbed negatively charged sorbate species onto the surface of adsorbent and the available anionic sorbate species in solution, and the slow pore diffusion of the solute ion into the bulk of the adsorbent. However, the contact time required for maximum Cr (VI) adsorption onto VMH was found to be nearly 150 minutes, which was independent of the sorbate concentration.

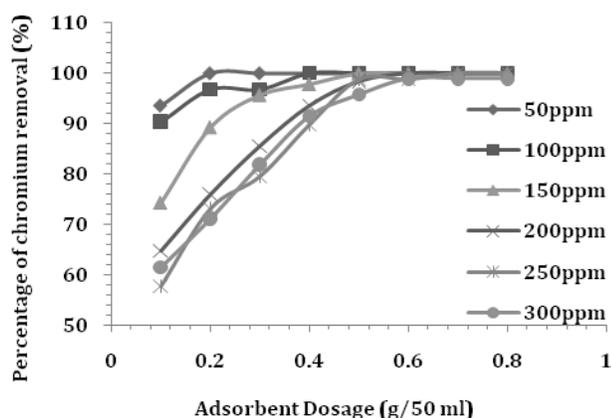


Figure 2 Effect of contact time on chromium adsorption, (Agitation speed=130 rpm, temperature=29<sup>o</sup> C, adsorbent size=0.25 mm, solution pH=2, adsorbent dose=0.2 g/50ml)

### Effect of adsorbent dose

The results indicated that the percentage of Cr(VI) adsorbed increased with an increase in adsorbent dosage for all Cr(VI) concentrations. The increase in percentage adsorption with the increase in adsorbent dosage is due to the increase in the number of adsorption sites (Figure 3). The amount of ions bound to the adsorbent and the amount of free ions remains almost constant even with further addition of a dose of adsorbent. It is evident from the result obtained that the removal capacity was high at high dose rate.

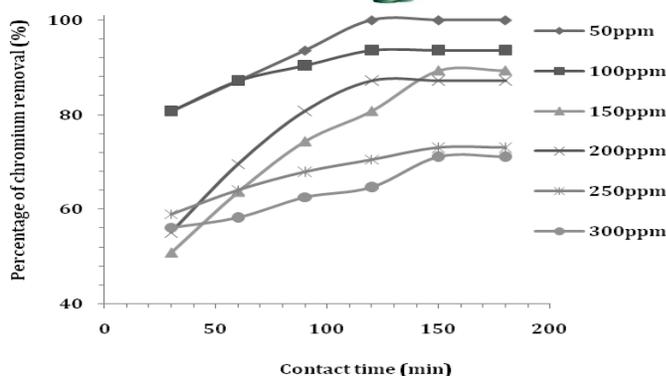


Figure 3 Effect of adsorbent dose on chromium adsorption, (Agitation speed=130 rpm, temperature=29<sup>0</sup> C, adsorbent size=0.25 mm, contact time=150min, solution pH=2, adsorbent dose=0.2 g/50ml)

### Effect of Particle Size

Effect of particle size on Cr(VI) sorption capacity of VMH is shown in Figure 4. It was evident that particle size of sorbents have a significant effect on Cr(VI) sorption. The larger sorbent size showed lesser Cr(VI) removal as compared to the smaller sorbent size. The reason might be that surface area available for adsorption decreases with the increase of particle size for the same dose of sorbent, providing less active surface sites for adsorption of sorbate. The results obtained were in accordance with adsorption processes, where smaller particles of sorbents enhance the rate of metal uptake. The removal of Cr(VI) ions at different particle sizes showed that the removal rate increased better with a decrease in particle diameter.

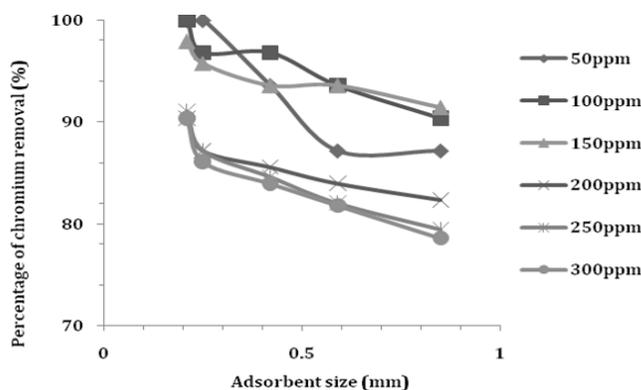
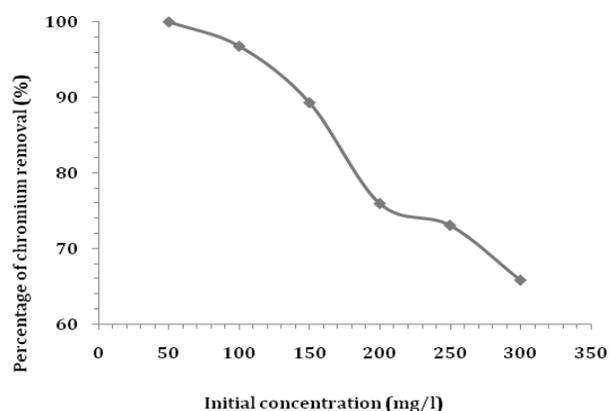


Figure 4 Effect of particle size on chromium adsorption, (Agitation speed=130 rpm, temperature=29<sup>0</sup> C, adsorbent size=0.25 mm, solution pH=2, adsorbent dose=0.2 g/50ml, adsorbent dose=0.2g/50ml, contact time=150min)

### Effect of Initial Concentrations

Effect of ionic strength, besides pH was also one of the important factors that influence the equilibrium uptake. Experimental results of the effect of initial chromium concentration on removal efficiency were presented in Figure 5. It was clear from the figure that chromium removal efficiency decreased with the increase in initial chromium concentration. In case of low chromium concentrations, the ratio of the initial number of moles of chromium ions to the available surface area of adsorbent was large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available site of adsorption becomes fewer, and hence the percentage removal of metal ions depends upon the initial concentration.



**Figure 5 Effect of initial concentration on chromium adsorption, (Agitation speed=130 rpm, temperature=29<sup>o</sup> C, adsorbent size=0.25 mm, solution pH=2, contact time=150 min, adsorbent dose=0.2 g/50ml)**

### Adsorption isotherm

To test the fit of data, the Langmuir, Freundlich and Redlich-Peterson models were applied to this study. The Langmuir [24] isotherm takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent; the linear equation is as follows:

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

Where  $K_L$  is Langmuir energy of adsorption constant (l/ mg),  $q_m$  is Langmuir monolayer sorption capacity (mg/g),  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  is the amount of Cr(VI) adsorbed per gram at equilibrium(mg/g).

The Freundlich [25] isotherm is an empirical equation employed to describe the heterogeneous system. The linear equation is as follows:

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

Where  $K_F$  is Freundlich constant (mg/g),  $n$  is Intensity of adsorption (l/g)

The Redlich-Peterson [26] isotherm combines both the Langmuir and Freundlich isotherm equations and the mechanism of adsorption is hybrid and does not follow ideal monolayer adsorption. The linear equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{\alpha} + \left(\frac{\beta}{\alpha}\right) C_e^\gamma$$

where  $\alpha$  (l/g),  $\beta$  (l/mg) and  $\gamma$  are the isotherm parameters

The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter ( $R_L$ ), which is defined by the following relationship

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

Where  $C_0$  is the initial Cr(VI) concentration (mg/l),  $R_L$  is a dimensionless separation factor,  $K_L$  is the Langmuir constant (l/mg). The  $R_L$  values for the present experimental data fall between 0 and 1, which is indicative of the favourable adsorption of Cr(VI) on VRH. The  $R_L$  values showed that the adsorption of Cr(VI) was more favourable for the higher concentration than the lower one, which is due to the effect of the pore diffusion sorption phenomenon.

**Table 1 Isotherm parameters value**

Isotherm	Parameter	Unit	Value
Langmuir	$q_m$	mg/g	62.5
	$K_L$	l/mg	0.075
	$R^2$	-----	0.979
Freundlich	$n$	l/g	2.545
	$K_F$	mg/g	9.705
	$R^2$	-----	0.867
Redlich-Peterson	$\alpha$	l/g	5.051
	$\beta$	l/mg	0.091
	$\gamma$	-----	0.9904
	$R^2$	-----	0.994

The obtained isotherm and correlation coefficients ( $R^2$ ) for the different models were shown in Table1. Our experimental data were found to fit well in the three-parameter model (Redlich-Peterson isotherm) in terms of  $R^2$  value. The Langmuir equation fitted the data nearly

as well as the three-parameter equation. Here the applicability of the two-parameter isotherm models for the present data approximately follows the order: Langmuir > Freundlich In the Langmuir equation,  $q_m$  (mg/g) was the measure of adsorption capacity under the experimental condition and the value was 62.5 mg/g.

### Adsorption Kinetics

Table 2 Linear form of adsorption kinetic models

Kinetic model	Linear equation	Plot
First-Order	$-\ln\left(\frac{C_t}{C_0}\right) = k_1 t$	t vs. $-\ln(C_t/C_0)$
Pseudo First-Order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$	t vs. $\log(q_e - q_t)$
Pseudo Second-Order	$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e} (t)$	t vs. $t/q_t$

Table 3 Adsorption kinetic models parameters and values

Kinetic model	Parameter	Concentration of Chromium (mg/g)					
		50	100	150	200	250	300
First- Order	$K_1$ (1/min)	0.0130	0.0170	0.0120	0.0110	0.0080	0.0060
	$R^2$	<b>0.7180</b>	<b>0.8860</b>	<b>0.9650</b>	<b>0.8750</b>	<b>0.8800</b>	<b>0.7950</b>
Pseudo First-Order	$k_1$ (l/min)	0.0094	0.0138	0.0207	0.0207	0.0207	0.0230
	$R^2$	<b>0.5000</b>	<b>0.7760</b>	<b>0.9740</b>	<b>0.9210</b>	<b>0.9190</b>	<b>0.9210</b>
Pseudo Second-Order	$k_2$ (g/mg min)	0.0029	0.0080	0.0014	0.0017	0.0014	0.0017
	$h$ (mg/g min)	4.1700	5.0000	1.9500	3.9400	4.3900	5.7500
	$R^2$	<b>0.9990</b>	<b>0.9970</b>	<b>0.9920</b>	<b>0.9870</b>	<b>0.9820</b>	<b>0.9910</b>

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption on the activated VMH was analyzed using first-order [27], pseudo first-order [28] and pseudo second-order [29]. The linear form of kinetic models presented in Table 2. The conformity between experimental data and the model predicted values were expressed by the correlation coefficients ( $R^2$ , values close or equal to 1). A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of Cr(VI) adsorption presented in Table 3. Here the applicability of the kinetic models for the present data approximately follows the order: pseudo second-order > pseudo first-order > first-order.

## Adsorption thermodynamic study

Table 4 Thermodynamic parameters for the adsorption of Chromium onto VMH

Cr con. mg/l	$\Delta H^\circ$ kJ/kmol	$\Delta S^\circ$ kJ/kmol*K	$\Delta G^\circ$ kJ/kmol				
			29°C	39°C	49°C	59°C	R <sup>2</sup>
50	16058.25	64.64	-1562.82	-1614.57	-2226.69	-2295.84	0.789
100	16832.25	65.23	-1158.77	-1614.57	-1923.62	-1983.36	0.871
150	17228.6	60.52	-509.82	-629.64	-987.33	-1273.88	0.958
200	17127.12	60.87	-584.33	-762.07	-1047.24	-1376.86	0.978
250	17138.61	60.06	-451.05	-713.85	-871.04	-1273.88	0.963
300	17475.6	60.01	-286.73	-526.70	-871.04	-1017.99	0.976

Gibbs free energy [30] change  $\Delta G^\circ$ , enthalpy  $\Delta H^\circ$ , and entropy ( $\Delta S^\circ$ ) were obtained from the experiments carried out at different temperatures 302K, 312K, 322K and 332K. Thermodynamic parameters such as change in free energy, enthalpy and entropy were determined using the following Van't Hoff equations

$$\Delta G^0 = -RT \ln K_0$$

$$\log K_0 = \frac{\Delta S^0}{2.303 R} - \frac{\Delta H^0}{2.303 RT}$$

Where  $K_0$  is the equilibrium constant,  $C_{solid}$  is the concentration of Cr (VI) at the solid phase (adsorbent) at equilibrium (mg/l),  $C_{liquid}$  is the liquid phase concentration of Cr (VI) at equilibrium (mg/l),  $T$  is the absolute temperature (K),  $R$  is the gas constant (kJ/kmol K). Van't Hoff equation was used to estimate the values of  $\Delta H^0$  and  $\Delta S^0$ . The values of  $\Delta H^0$  were within the range of 16058.25 to 17475.6 kJ/kmol indicating the chemisorption process. The positive values of  $\Delta H^0$  showed the endothermic nature of adsorption (Table 4). The negative values of  $\Delta G^0$  suggest that the adsorption is spontaneous. It was also observed that the negative values of  $\Delta G^0$  increases with increase in temperature, which indicate that the adsorption was preferable at high temperature, which was observed from the experimental data. The positive values of  $\Delta S^0$ , showed the increased disorder and randomness at the solid solution interface of chromium ion with adsorbent, while the adsorption there were some structural changes in the chromium ion and the adsorbent occur.

## Comparison with other adsorbents

**Table: 5 Comparison of adsorption capacity of Cr(VI) with other adsorbents.**

Adsorbent	Adsorption capacity (mg/g)	pH	Contact time (min)	Reference
Hydrous Stannic Oxide	03.48	2	090	31
Neem Leaf Powder	07.43	7	300	32
Tamarind Indica Pod shells	27.73	2	120	33
Cornelian Cherry	59.40	1	300	34
Wheat Brna	00.94	3	060	35
Solanum Elaeagnifolium	02.16	2	120	36
<i>Vigna mungo</i> Husk	62.50	2	150	Present Study

The comparison of adsorbent capacity of VMH with other materials reported in literature is given in Table 5. The sorption capacity of VMH was higher than adsorbents from various industrial and low-cost adsorbents.

## CONCLUSION

The study of adsorption of Cr(VI) on VMH as an efficient low cost adsorbent for the removal of toxic Cr(VI) from aqueous solution. Optimum pH for highest Cr(VI) sorption was 2. The contact time for the maximum adsorption required was nearly 120 min and equilibrium attained was nearly 150min. The adsorption kinetics for Cr(VI) at pH 2 has been well described by the pseudo 2<sup>nd</sup> order equations in the concentration range studied. The equilibrium sorption data was satisfactorily fitted in the order: Redlich-Peterson>Langmuir>Freundlich. In the Langmuir equation,  $q_m$  (mg/g) was the measure of adsorption capacity under the experimental condition and the value was 62.5 mg/g. The calculated values of the dimensionless separation factor from the Langmuir constant confirm favourable sorption of Cr(VI) onto VMH. The values of  $\Delta H^\circ$  were within the range of 16058.25 to 17475.6 kJ/mol indicating the chemisorption process. The positive values of  $\Delta H^\circ$  showed the endothermic nature of adsorption. The negative values of  $\Delta G^\circ$  showed that the adsorption is highly favorable and spontaneous.

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