

Removal of Chromium from Aqueous Solution by Custard Apple (*Annona Squamosa*) Peel Powder as Adsorbent

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Abstract: Chromium has been widely used in various industries like textile, leather, chemical manufacture, metal finishing, paint industry and many other industries. Since hexavalent chromium is a priority toxic, mutagenic and carcinogenic chemical when present in excess, it is very much required to remove chromium from effluents before allowing it to enter any water system or on to land. In the present study, the removal of hexavalent chromium by adsorption on the Custard apple peel powder as adsorbent has been investigated in the batch experiments. The agitation time, the adsorbent size, adsorbent dosage, initial chromium concentration, temperature and the effect of solution pH are studied. The Freundlich model for Cr (VI) adsorption onto Custard apple peel powder is proved to be the best fit followed by Langmuir model and Tempkin model based on high regression coefficient R^2 value. The adsorption behavior is described by a pseudo second order kinetics. The maximum metal uptake is found to be 7.874 mg/g. The morphology on the surface of adsorbents and also the confirmation of chromium binding on adsorbent surface at different stages were obtained by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis. The results obtained in this study illustrate that Custard apple peel powder is expected to be an effective and economically viable adsorbent for hexavalent chromium removal from industrial waste water.

Keywords: Adsorption; batch technique; Isotherms; kinetics; custard apple peel powder.

1. Introduction

Water contamination with heavy metals is a very severe problem all over world [1, 2]. The world production of chromite ore is several millions of tons in a year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions. Chromium and its compounds are extensively used in metal finishing, leather tanning, electroplating, textile industries and chromate preparation [3]. In aqueous phase chromium mostly exists in two oxidation states, namely, trivalent chromium [Cr^{+3} and $\text{Cr}(\text{OH})^{2+}$] and hexavalent chromium (HCrO_4^- , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example it was reported that $\text{Cr}_2\text{O}_7^{2-}$ can cause lung cancer [4, 5].

Chromium (III) and Chromium (VI) have major environmental significance because of their

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stability in the natural environment. Hexavalent Chromium [Cr (VI)] is known to have 100 fold more toxicity than trivalent Chromium [Cr (III)] because of its high water solubility and mobility as well as easy reduction [6]. International agency for research on cancer has determined that Cr (VI) is carcinogenic to humans. The toxicological effect of Cr (VI) originates due to oxidizing nature as well as the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [8]. Therefore, the World Health Organization (WHO) recommends that the toxic limits of Cr (VI) in waste water at the level of 0.05 mg/L, while total Chromium containing Cr (III), Cr (VI) and other species of chromium is regulated to be discharged below 2 mg/L [7].

Several methods are used to remove chromium from the industrial wastewater. These include reduction followed by chemical precipitation [9], ion exchange [10], reduction [11], electrochemical precipitation [12], solvent extraction [13], membrane separation [14], evaporation [15] and foam separation [16]. Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as biosorbents and the binding of metals by biomass is referred to as biosorption. Since this noble approach is effective and cheap many researchers exploring appropriate biomaterials that effectively remove Cr (VI) from aqueous solutions [17, 18]. A variety of adsorbents like tamarind seeds [19], rice husk [20], *Azadirachta indica* [21], maize bran [22], red saw dust [23], wall nut hull [24], groundnut hull [25], carrot residues [26] were reported in literature for the removal of chromium from aqueous solutions or waste waters in a batch or column reactor system. Table 1 gives the brief findings and Cr (VI) metal uptake by different biosorbents.

In the present investigation, the use of Custard apple peel powder as an effective and inexpensive material for the removal of Cr (VI) from aqueous solution was described. The paper is organized as follows: Section 2 deals with the material and methods used for the estimation of chromium (VI) and the experimental description of the batch adsorption study. The results of the present study are given section 3 in which adsorption isotherms, kinetics, thermodynamics of the absorption of Cr (VI) on Custard apple peel powder are discussed and conclusions are given in section 4.

2. Materials and methods

2.1. The diphenyl carbazide method

A 0.25% (w/v) solution of diphenyl carbazide was prepared in 50% acetone. Each of the sample solutions (15 mL) containing various concentrations of Cr (VI) were pipette out into 25 mL standard flasks. To this 2 mL of 3 M H₂SO₄ was added followed by 1 mL of diphenyl carbazide and total volume was made up to 25 mL using deionised, double distilled water. Cr (VI) concentrations were estimated by the intensity of the red brownish color complex formed, was measured using UV-Visible spectrophotometer at 540 nm. The absorbance was measured indicating adherence to the Beer Lambert's law (0 to 30 mg/L).

Table 1. The brief findings and chromium (VI) metal uptake by various biosorbents

Material	Equilibrium Isotherms it follows	Kinetics it follows	Metal uptake (mg/g)	References
Sulfuric acid modified waste activated carbon	Langmuir, Freundlich	----	7.485	[27]
Nitric acid modified waste activated carbon	Langmuir, Freundlich	----	10.93	[27]
Iron (III) hydroxide	Langmuir, Freundlich	-----	0.47	[28]
Blast furnace slag	Langmuir, Freundlich	1 st order	7.5	[29]
Activated red mud	Langmuir, Freundlich	----	1.6	[30]
Ground nut hull	Langmuir, Freundlich	2 nd order	30.95	[25]
Neem leaf powder	Langmuir, Freundlich	2 nd order	7.43	[31]
Activated carbon from hazelnut	Langmuir	1 st order	170	[32]
Bentonite	Langmuir, Freundlich	----	0.51	[33]
Palygorskite clay	Langmuir, Freundlich	1 st order	58.5	[34]
Custard apple peel powder	Langmuir, Freundlich, Tempkin	2 nd order	7.87	Present work

2.2. Preparation of the adsorbent

The sorbents used were crushed Custard apple peel powder. The Custard apple peel was obtained from local market; materials were washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it is crushed in roll crusher and hammer mills. The material obtained through crushing and grinding is screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use. All the materials were used as such and no pretreatment was given to the materials. The average particle sizes were maintained in the range of 63 to 125 μm .

2.3. Preparation of chromium stock solution

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is used as the source for chromium stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. A 99% $\text{K}_2\text{Cr}_2\text{O}_7$ (2.835 g) is dissolved in distilled water of 1.0 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of Cr (VI) stock solution. Synthetic samples of different concentrations of Cr (VI) are prepared from this stock solution by appropriate dilutions.

$$\text{Cr equivalent to 1 gm} = \frac{\text{Molecular Wt. of } \text{K}_2\text{Cr}_2\text{O}_7 \times 100}{(\text{Atomic Wt of Cr} \times 2) \times \text{purity}} \quad (1)$$

2.4. Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate

the effect of different parameters such as adsorbate concentration (5-30 mg/L), adsorbent dosage (0.1-0.6 gm in 50 mL solution), agitation time (0 -120 min), pH (1-10), adsorbent size (63, 89 and 125 μm) and temperature (303-323 K). The solution containing adsorbate and adsorbent was taken in 250 mL capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1).

2.5. Metal analysis

Final residual metal concentration after adsorption was measured by UV-Spectrophotometer after sample was complexed with 1-5 Diphenyl carbazide. To estimate the percentage removal of chromium (VI) from aqueous solution, the following equation was used.

$$\text{Percentage removal of Cr (VI)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (2)$$

Where, C_{initial} and C_{final} are the concentrations of Cr (VI) at the beginning and at the end of the adsorption process. The metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \frac{(C_0 - C_e)V}{1000w} \quad (3)$$

Where q_e (mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, C_0 and C_e are the initial and equilibrium chromium ion concentration (mg/L), V is the volume of aqueous solution (mL), and w is the adsorbent weight (g).

3. Results and discussion

3.1. Effect of various parameters on the adsorption of chromium (VI) by custard apple peel powder

3.1.1. Characterization of custard apple peel powder

The scanning electron micrographs (SEM) of Custard apple peel powder before chromium (VI) adsorption and after chromium (VI) adsorption are shown in Figure 1 and 2. The surface morphology revealed that both materials were found to be irregular and porous and thus would facilitate the adsorption of metal ions on different parts of the materials. The SEM micrographs showed that pores with different sizes and different shapes existed on the external surface of Custard apple peel powder. The micrograph of Custard apple peel powder after chromium (VI) adsorption shows a reduction in the number of pores, pore space and surface area available (refer to Figure 2). Hence it is confirmed that there is metal adsorption on the surface of adsorbent. Furthermore, the EDS spectra of selected zones of Custard apple peel powder before adsorption and after adsorption were carried out to investigate the chemical constituents in the carbon matrix (Figure 3). It has been found from Figure 3(a) that Custard apple peel powder has carbon and oxygen on its surface before interaction with Cr (VI) ions, whereas in Figure 3(b) a new chromium peak was observed with the surface bearing groups of carbon and oxygen, which confirmed the Cr (VI) adsorption on Custard apple peel powder.

Removal of Chromium from Aqueous Solution by *Custard Apple (Annona Squamosa) Peel Powder* as Adsorbent

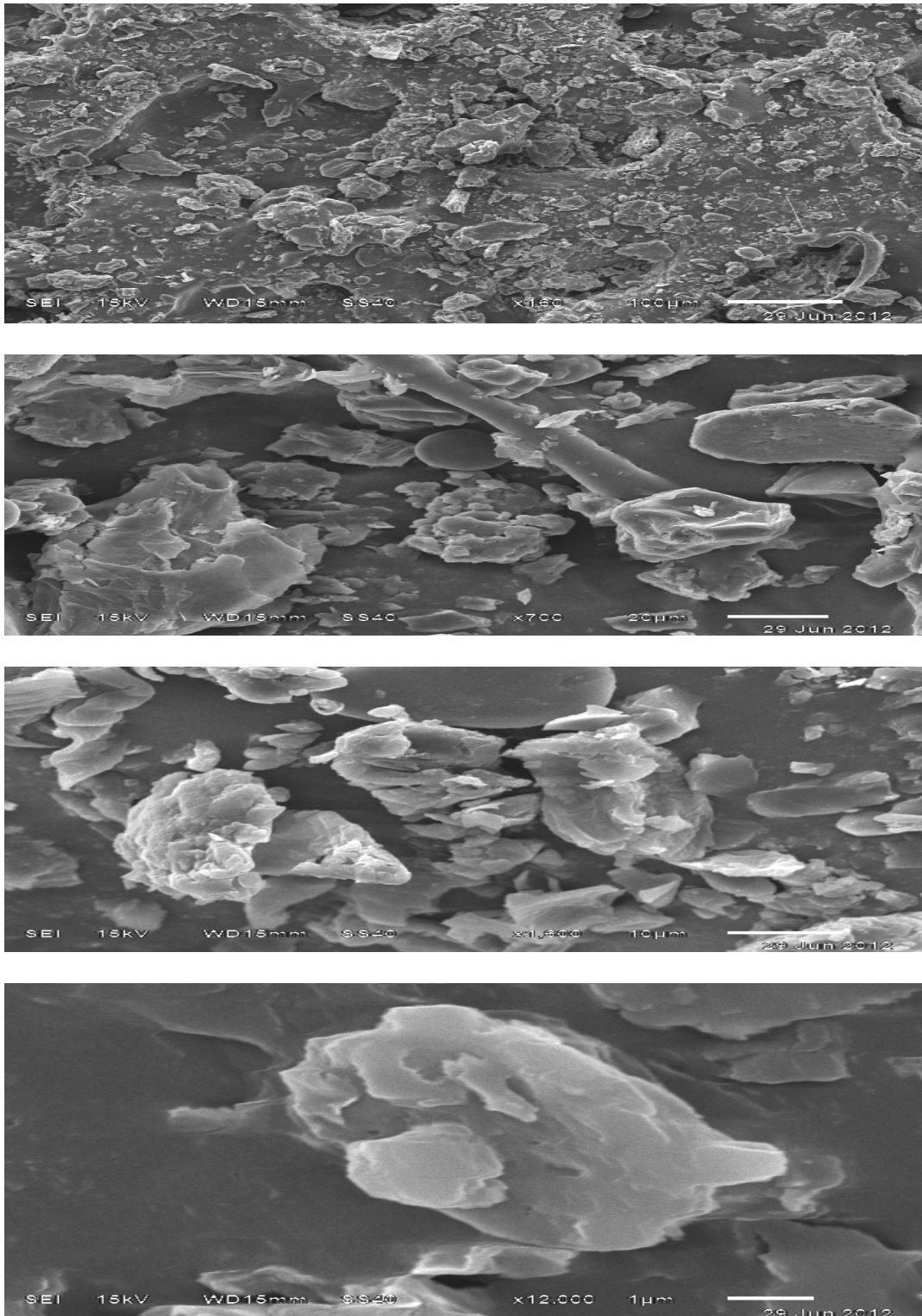


Figure 1. SEM images of custard apple peel powder before chromium (VI) adsorption

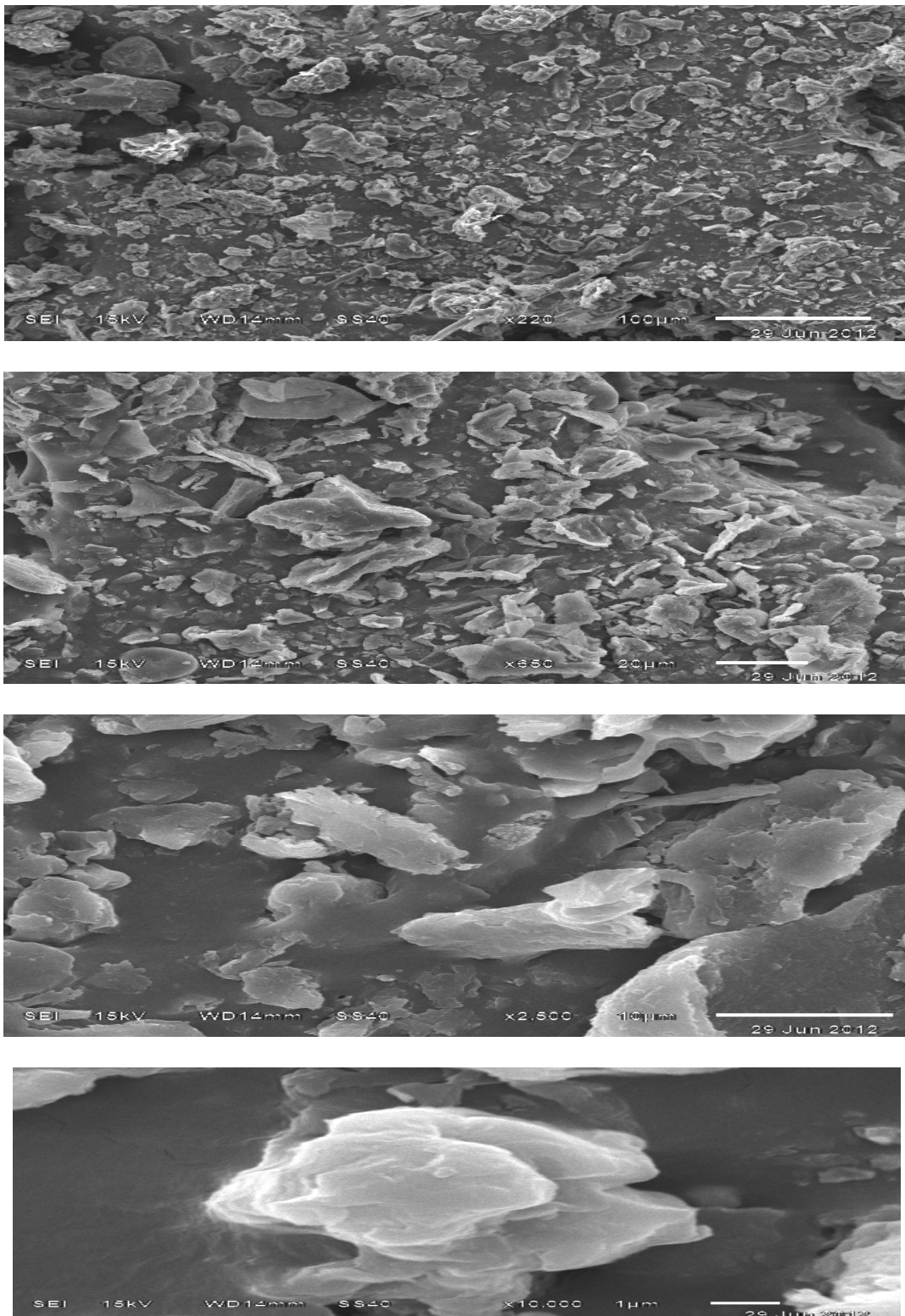


Figure 2. SEM images of custard apple peel powder after chromium (VI) adsorption

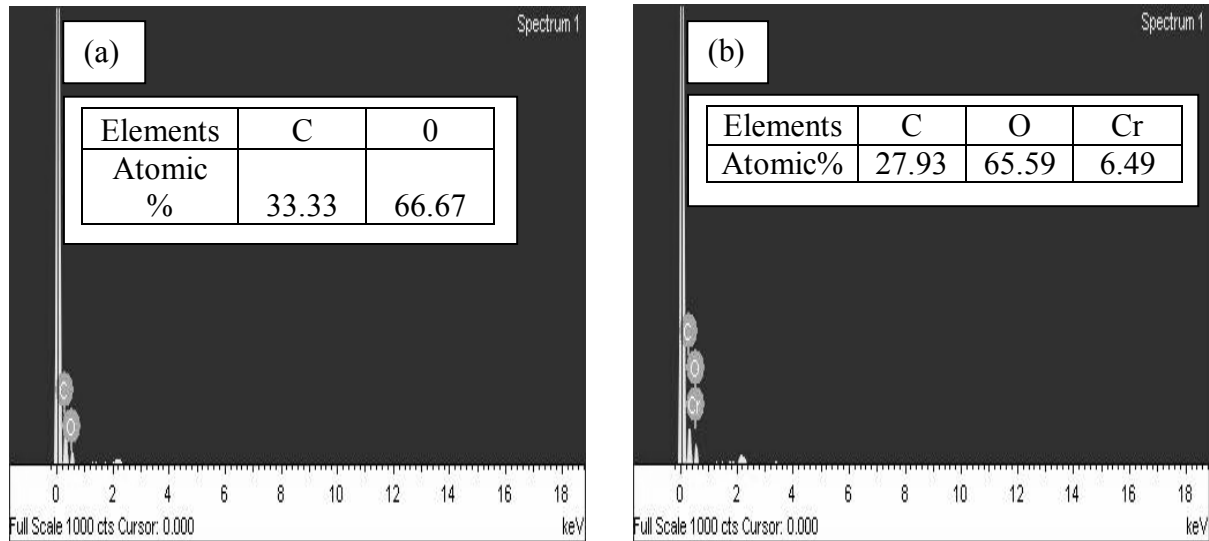


Figure 3. Energy - disperse spectra of custard apple peel powder (a) before chromium (VI) adsorption (b) after chromium (VI) adsorption

3.1.2. Effect of agitation time and Initial Cr (VI) concentrations

The equilibrium agitation time is determined by plotting the percentage removal of chromium (VI) against agitation time for different concentrations as shown in Figure 4. The percentage removal of chromium (VI) increases up to 50 min of the agitation time and thereafter no further increase is recorded by Custard apple peel powder as adsorbent. Adsorption equilibrium time is defined as the time required for heavy metal concentration in the solution to reach a constant value. It is observed that percentage removal of chromium decreases with increase in the initial concentration. Evidently such a behavior can be attributed to the maintenance of fixed number of binding sites in the fixed adsorbent dosage while increasing the concentration.

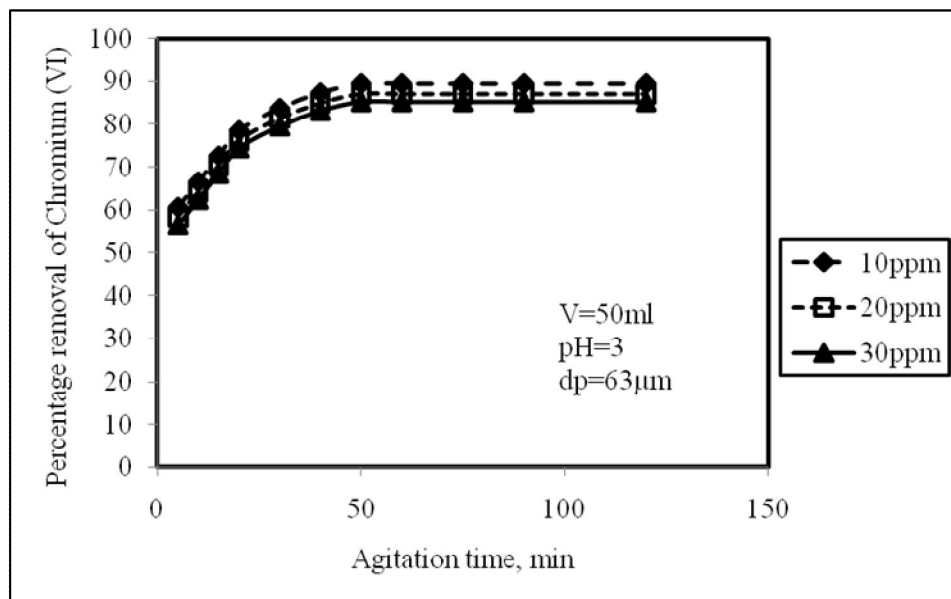


Figure 4. Variation of percentage removal of chromium (VI) with agitation time by custard apple peel powder at different initial concentration of Cr (VI) in solution

3.1.3. Effect of adsorbent dosage and size in aqueous solution

The variations in percentage removal of chromium (VI) and also metal uptake in aqueous solution with adsorbent dosage are shown in Figure 5. The percentage removal of chromium (VI) from aqueous solution increases from 58.25% to 90.07% and also metal uptake decreases from 5.825 to 1.501 mg/g with an increase in the adsorbent dosage from 0.1 to 0.6 g in 50 mL solution at 303 K for 63 μm size. The percentage removal of chromium (VI) from aqueous solution with adsorbent size is reported in Table 2. The percentage removal of chromium (VI) increases from 77.37 % (1.934 mg/g) to 87.21 % (2.180 mg/g) for 0.4 g of dosage in 50 mL (20 mg/L) of solution at 50 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 μm . This phenomenon is expected as the decrease in size of adsorbent results in the increase of the surface area and thereby the number of active sites is better exposed to the adsorbate.

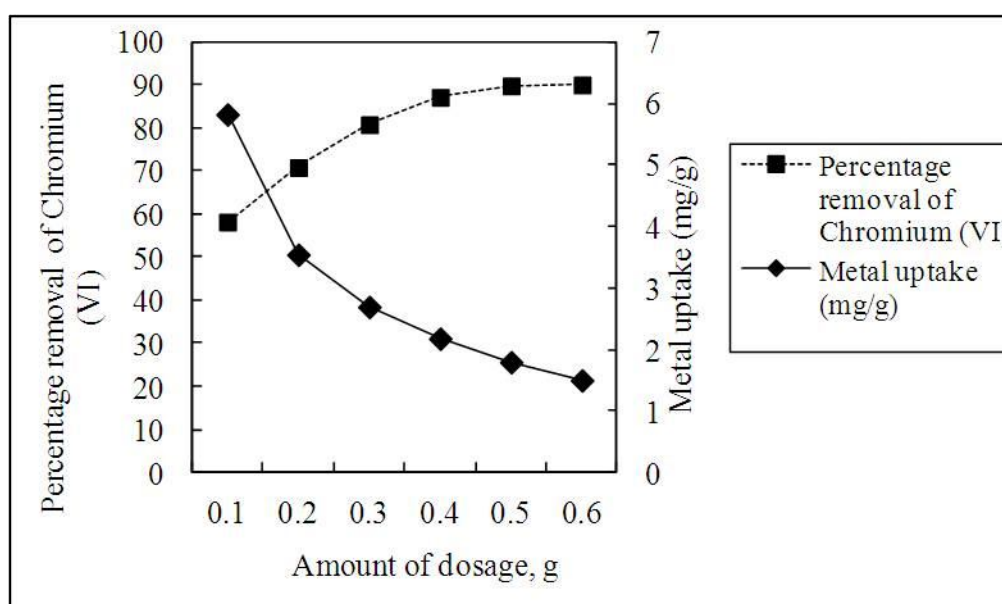


Figure 5. Variation of percentage removal of chromium (VI) and metal uptake with adsorbent dosage

Table 2. Effect of adsorbent particle size, $C_0=20$ mg/l; temp=303 K; $V=50$ mL; $t=50$ min; pH=3 and $w=0.4$ g

S.No.	Adsorbent average particle size, μm	Final concentration, mg/l	% Adsorption	Metal uptake (mg/g)
1	63	2.558	87.21	2.1803
2	89	3.31	83.45	2.0863
3	125	4.526	77.37	1.9343

3.1.4. Effect of pH of the aqueous solution

The pH value is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effect of pH on adsorption of chromium (VI) at different initial concentrations is shown in Figure 6. The maximum percentage removal of chromium (VI) (3.196 mg/g for 30 mg/L) for various initial concentrations is reported at pH value of 3. It is confirmed that adsorption of chromium

(VI) increases with increase in pH values from 1 to 3, after wards adsorption of chromium (VI) decreases with increase in pH values from 4 to 10. The principal driving force for metal ion adsorption is the electrostatic interaction, *i.e.* attraction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metal was found. In the present investigation, the maximum percentage removal of chromium (VI) is 90.47 % at pH = 3, 5 mg/L of initial concentration of chromium (VI) for 0.4 g of adsorbent (in 50 mL) and at a temperature of 303 K.

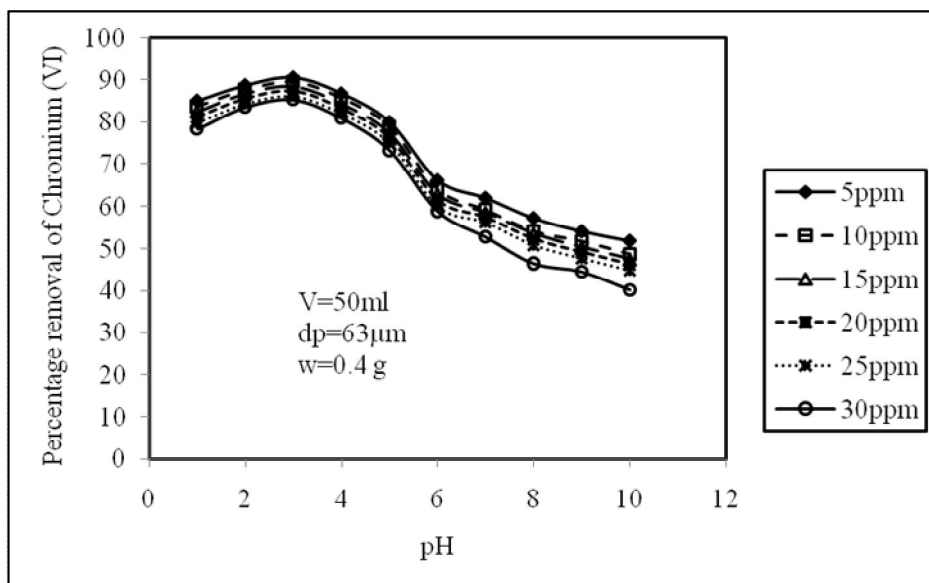


Figure 6. Effect of pH of aqueous solution on percentage removal of chromium (VI) at different initial concentrations

3.1.5. Effect of temperature

The effect of temperature on adsorption of chromium at different initial concentrations is shown in Figure 7. The maximum percentage removal of chromium is reported at temperature 323 K for various initial concentrations. It is confirmed that adsorption of chromium (VI) increases with increase in temperature values for all concentrations; *i.e.* the adsorption is endothermic in nature. Further, low initial concentrations of the solution showed improved percentage of adsorption in comparison with higher concentration solutions. The metal uptake is increased from 0.551 mg/g at 5 mg/L to 3.363 mg/g at 30 mg/L for a temperature range of 283-323 K. This increase in binding could be due to increase in surface activity and increased kinetic energy of the chromium (VI) metal ions.

3.2. Adsorption isotherms

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbent. This provides a relationship between the concentration of metal ions in the solution and the metal ions adsorbed on to the solid phase when the two phases are at equilibrium.

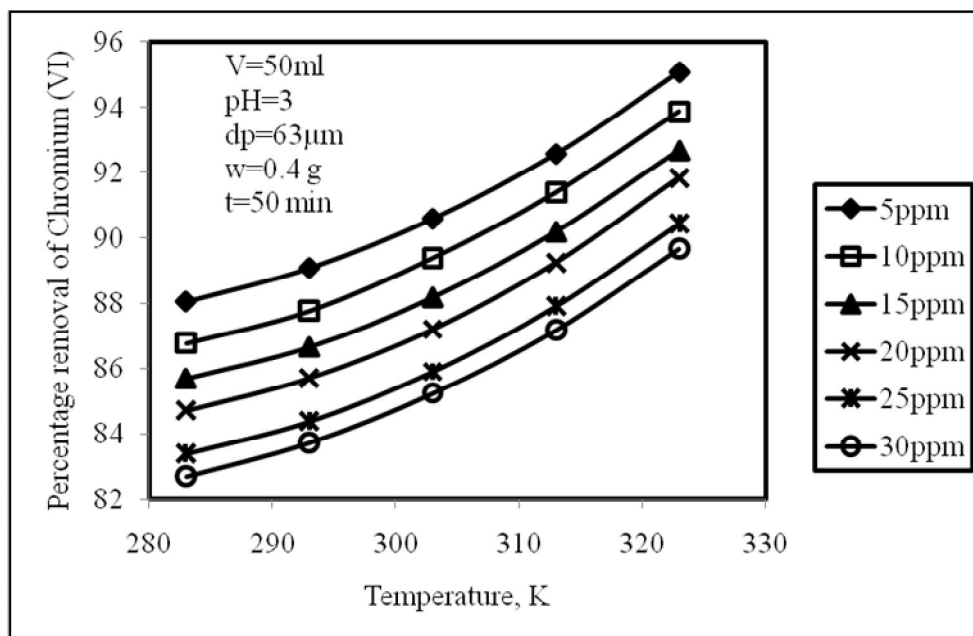


Figure 7. Variation of percentage removal of chromium (VI) with temperature by custard apple peel powder

3.2.1. Langmuir model

The Langmuir isotherm [35] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is of the form:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{4}$$

Here q_e is the metal concentration adsorbed in solid (biomass), C_e is the metal residual concentration in the solution. The q_{\max} is the maximum specific uptake corresponding to sites saturation, and b is the ratio of adsorption/desorption rates. The Langmuir isotherm in Eq (4) can be written as

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \tag{5}$$

The adsorption data for adsorption of Cr (VI) on Custard apple peel powder is plotted in Figure 8 (C_e/q_e vs C_e), shows good linearity for Langmuir isotherm. The equations with correlation coefficients are shown in Table 3. The q_{\max} is calculated from the slope and b is calculated from the intercept. It is observed that strong binding of Cr (VI) ions to the surface of Custard apple peel powder. The separation factor, R_L obtained (from Table 4) between 0.2144-0.6209 for various concentrations shows favorable adsorption ($0 < R_L < 1$).

- $R_L > 1$ Unfavorable adsorption
- $R_L = 1$ Linear
- $0 < R_L < 1$ favorable adsorption,
- $R_L = 0$ irreversible

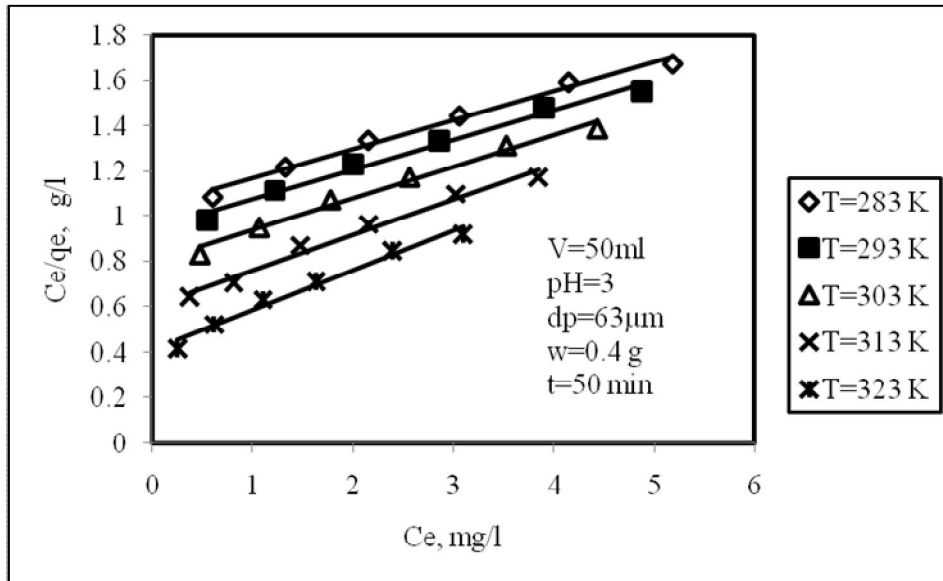


Figure 8. Langmuir isotherm for adsorption of chromium (VI) by custard apple peel powder

Table 3. Langmuir isotherms and its coefficients

S.No.	Parameters	Equation	q_{max}	b	RL	R^2
1	T=283K	$\frac{C_e}{q_e} = 0.127C_e + 1.040$	7.874	0.1221	<1	0.987
2	T=293K	$\frac{C_e}{q_e} = 0.131C_e + 0.943$	7.6336	0.1389	<1	0.984
3	T=303K	$\frac{C_e}{q_e} = 0.140C_e + 0.798$	7.1429	0.1754	<1	0.984
4	T=313K	$\frac{C_e}{q_e} = 0.157C_e + 0.602$	6.3694	0.2608	<1	0.981
5	T=323K	$\frac{C_e}{q_e} = 0.175C_e + 0.409$	5.7143	0.4278	<1	0.978

Table 4. $R_L = \frac{1}{1 + bc_i}$ values at pH=3; T=283K

C_i	R_L
5	0.6209
10	0.4502
15	0.3531
20	0.2905
25	0.2467
30	0.2144

3.2.2. Freundlich model

The Freundlich isotherm [36] is based on multilayer adsorption with interaction between adsorbed molecules. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. This relation can be reasonably applied to the low or intermediate concentration ranges. The Freundlich isotherm is represented by:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

Here K_f is the Freundlich constant and is also known as Freundlich capacity and n stands for adsorption intensity. The q_e is the amount of chromium (VI) adsorbed at equilibrium and C_e is the residual concentration of Cr (VI) in solution. The Freundlich equation is expressed linearly as.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

The values of K_f and n can be obtained from intercept and slope of a plot of $\log q_e$ versus $\log C_e$.

The adsorption data for the adsorption of Cr (VI) on Custard apple peel powder was plotted in Figure 9 shows good linearity for Freundlich Isotherm. The adsorption data is best represented by Freundlich isotherm. The equations with correlation coefficients (R^2) are shown in Table 5. Linearity of the relationship indicates strong binding of Cr (VI) to the adsorbent. The slope of isotherm (n) varies between 1.2547 and 1.4663 fulfilling the condition of $n > 1$ for favorable adsorption.

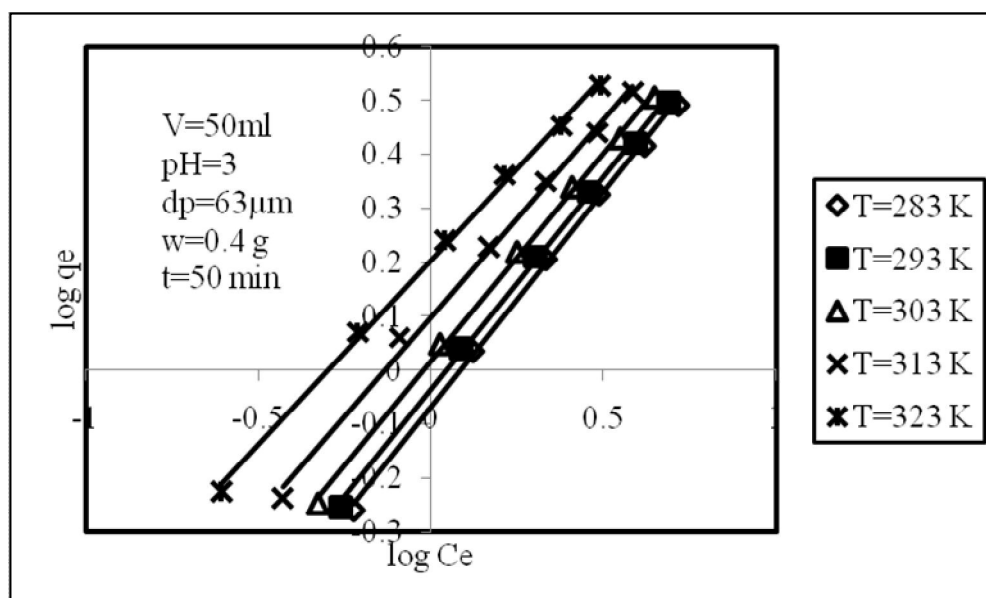


Figure 9. Freundlich isotherm for adsorption of chromium (VI) by custard apple peel powder

Table 5. Freundlich isotherms and its coefficients

S.No.	Parameters	Equations	K_f (mg/g)	n	R^2
1	T=283K	$\log q_e = 0.797 \log C_e - 0.069$	0.853	1.2547	0.998
2	T=293K	$\log q_e = 0.787 \log C_e - 0.036$	0.921	1.2706	0.998
3	T=303K	$\log q_e = 0.768 \log C_e + 0.016$	1.038	1.3021	0.998
4	T=313K	$\log q_e = 0.73 \log C_e + 0.098$	1.253	1.3699	0.995
5	T=323K	$\log q_e = 0.682 \log C_e + 0.202$	1.592	1.4663	0.997

3.2.3. Tempkin model

The Tempkin isotherm model [37] contains a factor that takes care of the adsorbent-adsorbate interactions. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage. The nonlinear form of Tempkin equation is given by Eq (8) and the linear form in Eq (9).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (8)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

Here $B_T = (RT/b_T)$. T is the absolute temperature and R is the universal gas constant. Constant b_T is related to the heat of adsorption. A_T is the equilibrium binding constant corresponding to the maximum binding energy. A plot of q_e versus $\ln C_e$ at a fixed temperature will give Tempkin isotherm constants, A_T and b_T .

The adsorption data for the adsorption of Cr (VI) on Custard apple peel powder was plotted in Figure 10 shows good linearity for Tempkin Isotherm. The equations with correlation coefficients are shown in Table 6. Linearity of the relationship indicates strong binding of Cr (VI) to the adsorbent.

3.2.4. Dubinin and radushkevich (D-R) isotherm

Dubinin and Radushkevich equation [38] is represented in a linear form by equation

$$\ln q_e = \ln Q_0 - K_{DR} \varepsilon^2 \quad (10)$$

Where K_{DR} ($\text{mol}^2 \text{kJ}^{-2}$) is a constant related to mean adsorption energy and ε is the Polanyi potential which can be calculated from the following equation

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (11)$$

The slope of plot of $\ln q_e$ versus ε^2 gives K_{DR} ($\text{mol}^2 \text{kJ}^{-2}$) and the intercept yields the sorption capacity Q_0 (mg/g). T is the absolute temperature in Kelvin and R is the universal gas constant ($8.314 \text{ Jmol}^{-1} \text{K}^{-1}$).

The sorption energy can also be worked out using the following relationship [39]

$$E = \frac{1}{(2 \times K_{DR})^{\frac{1}{2}}} \tag{12}$$

Where, E is the mean free energy of adsorption. If the value of E is between 1 and 16 kJ/mol, then physical adsorption prevails; and if the is more than 16 kJ/mol, then chemisorption prevails. The adsorption data for adsorption of Cr (VI) on Custard apple peel powder was plotted in Figure 11 shows non-linearity for D-R isotherm. The equations with correlation coefficients are shown in Table 7. From regression coefficient R^2 value, the adsorption data is not fit for D-R isotherm.

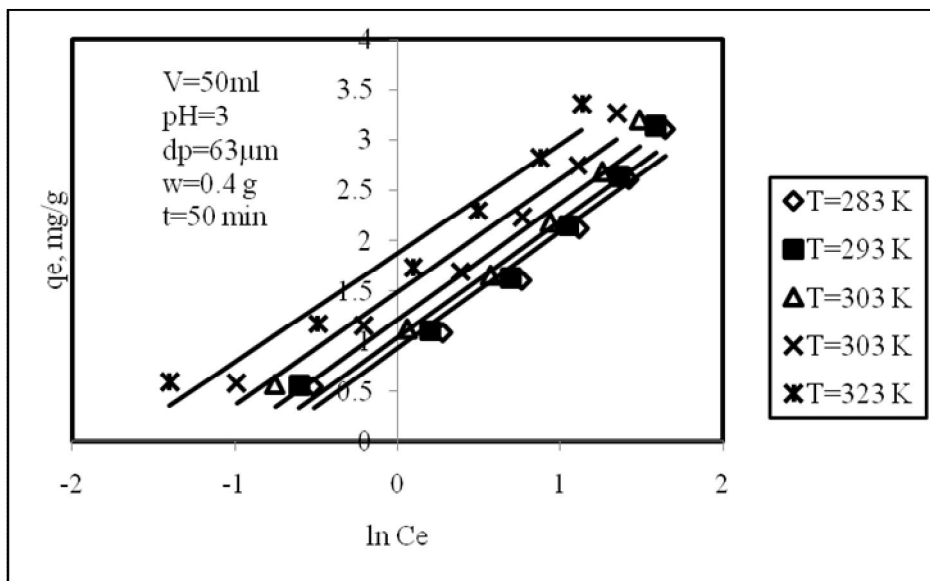


Figure 10. Tempkin isotherm for adsorption of chromium (VI) by custard apple peel powder

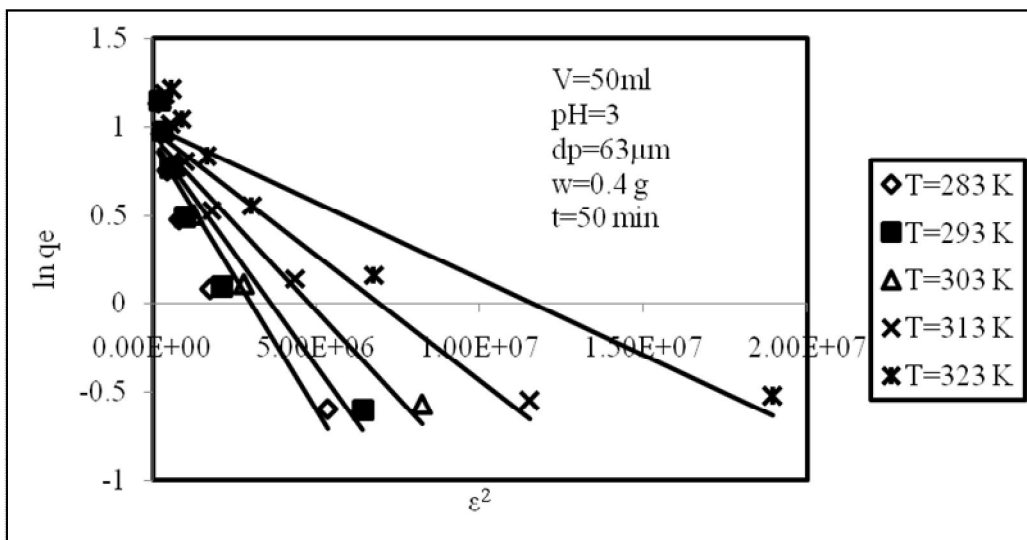


Figure 11. Dubinin and radushkevich (D-R) isotherm for adsorption of chromium (VI) by custard apple peel powder

Table 6. Tempkin isotherm and its coefficients

S.No.	Parameters	Equations	b_T	A_T (L/mg)	R^2
1	T=283K	$q_e = 1.163 \ln C_e + 0.930$	2023.09	2.225	0.955
2	T=293K	$q_e = 1.162 \ln C_e + 1.036$	2096.39	2.439	0.956
3	T=303K	$q_e = 1.155 \ln C_e + 1.213$	2181.08	2.858	0.956
4	T=313K	$q_e = 1.126 \ln C_e + 1.492$	2311.09	3.763	0.961
5	T=323K	$q_e = 1.078 \ln C_e + 1.872$	2491.12	5.678	0.958

Table 7. Dubinin and radushkevich (D-R) isotherms and its coefficients

S. No.	Parameters	Equations	K_{DR}	E (J/mole)	R^2
1	T=283K	$\ln q_e = -3 \times 10^{-07} \varepsilon^2 + 0.91$	3×10^{-7}	1290.99	0.887
2	T=293K	$\ln q_e = -3 \times 10^{-07} \varepsilon^2 + 0.925$	3×10^{-7}	1290.99	0.893
3	T=303K	$\ln q_e = -0.2 \times 10^{-06} \varepsilon^2 + 0.945$	0.2×10^{-6}	1581.14	0.894
4	T=313K	$\ln q_e = -1 \times 10^{-07} \varepsilon^2 + 0.983$	0.1×10^{-6}	2236.07	0.912
5	T=323K	$\ln q_e = -0.9 \times 10^{-07} \varepsilon^2 + 1.003$	0.9×10^{-7}	2357.02	0.904

3.3. Studies on kinetics of adsorption

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. The kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R^2 value). A relatively high R^2 value (close or equal to one) indicates that the model successfully describes the kinetics of Cr (VI) adsorption.

3.3.1. Pseudo - first order or lagergen kinetic model

It is the first equation for sorption of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (13)$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). The Eq (13) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (14)$$

The plot of $\log(q_e - q_t)$ vs t is linear from which k_1 can be determined from the slope. First order kinetics for adsorption of chromium (VI) by Custard apple peel powder is shown in Figure 12. Their equations with correlation coefficients are shown in Table 8. From the graph, the q_e is estimated for different process parameters and the estimated value is checked with the experimental value. From Table 8, it can be seen that q_{ecal} and q_{eexp} are not the same. Therefore, first order kinetics may not represent the adsorption kinetics, though the R^2 value is close to 1. The above model is not fit for hexavalent chromium removal on Custard apple peel powder adsorbent.

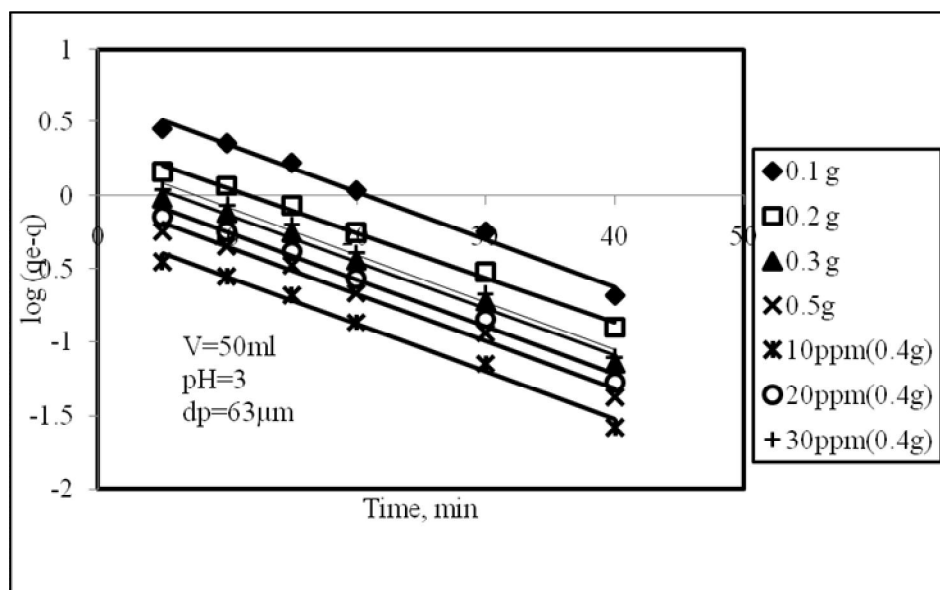


Figure 12. First order kinetics for adsorption of chromium (VI) by custard apple peel powder

Table 8. Lagergren pseudo first order coefficients

Kinetics	Parameters (adsorbent dosage and initial concentration of Cr(VI))	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, k_1, min^{-1}
1 st order	0.4 g and 10 ppm	$\log(q_e - q) = -0.032t - 0.227$	0.5929	1.1173	0.997	0.0737
	0.4 g and 20 ppm	$\log(q_e - q) = -0.032t + 0.071$	1.1776	2.1803	0.988	0.0737
	0.4 g and 30 ppm	$\log(q_e - q) = -0.032t + 0.250$	1.7783	3.1965	0.988	0.0737
	0.1 g and 20 ppm	$\log(q_e - q) = -0.032t + 0.675$	4.7315	5.825	0.987	0.0737
	0.2 g and 20 ppm	$\log(q_e - q) = -0.03t + 0.357$	2.2751	3.5445	0.992	0.0691
	0.3 g and 20 ppm	$\log(q_e - q) = -0.032t + 0.192$	1.5559	2.6277	0.989	0.0737
	0.5 g and 20 ppm	$\log(q_e - q) = -0.032t - 0.025$	0.9441	1.7974	0.988	0.0737

3.3.2. Pseudo-second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (15)$$

Where k_2 is the rate constant of pseudo second order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). Eq (15) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (16)$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (17)$$

k_2 is obtained from the intercept and q_e from the slope of the plot of t/q_t vs t . The second order kinetics for adsorption of chromium by Custard apple peel powder is shown in Figure 13. Their equation with correlation coefficients are shown in Table 9. From Table 9, it can be seen that q_{ecal} and q_{eexp} are almost same. Therefore, the second order kinetic model is fit for hexavalent chromium removal by Custard apple peel powder adsorbent.

3.3.3. Intra-particle diffusion model

The adsorption of hexavalent chromium on a porous adsorbent is the combination of four consecutive steps [40]; diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles [40]. According to Weber and Moris [41] if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time should be directly proportional to the square root of contact time t and shall pass through the origin which is defined mathematically in Eq (18)

$$q_t = K_{\text{diff}} t^{0.5} + C \quad (18)$$

where q_t is the amount of Cr (VI) adsorbed and t is the contact time. K_{diff} is the intra-particle diffusion coefficient. A plot of q_t against $t^{0.5}$ should give a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The value of K_{diff} can be calculated from slope. The higher values of K_{diff} illustrate an enhancement in the rate of adsorption.

The adsorption data for adsorption of Cr (VI) on custard apple peel powder was plotted in Figure 14 shows good linearity for Intra particle diffusion model. The equations with correlation coefficients are shown in Table 10. The R^2 values (refer to Table 10) are close to unity, conforming that the rate-limiting step is actually the intra-particle diffusion process. The values of K_{diff} calculated from slope provide information about thickness of the boundary layer, *i.e.* the resistance to the external mass transfer. The large the slope indicates the high external resistance.

3.4. Thermodynamics of adsorption

Adsorption is temperature dependent. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of adsorption (ΔH), change in

entropy of adsorption (ΔS) and change in Gibb's free energy (ΔG) [42].

The Van't Hoff equation is

$$K_D = \frac{C_{Ae}}{C_e} \tag{19}$$

$$\Delta G = -RT \ln K_D \tag{20}$$

where K_D is the equilibrium constant and C_{Ae} and C_e (both in mg/L) are the equilibrium concentrations for solute on the adsorbent and in the solution, respectively. The K_D values are used in Eq (19) and Eq (20) to determine the ΔG , ΔH and ΔS . Then K_D is expressed in terms of the ΔH (kJ/mol) and ΔS (kJ/mol K) as function of temperature.

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{21}$$

The slope and intercept of the plots are determined by plotting $\ln K_D$ as a function of $(1/T)$. The values of ΔH and ΔS are calculated for the slope and intercept respectively.

The adsorption data was plotted in Figure 15 shows good linearity for Van't Hoff equation. Their equations with correlation coefficients are shown in Table 11. From values of ΔH , the process is endothermic nature of adsorption as the values of ΔH are positive values. If the value of ΔS is less than zero, it indicates that the process is highly reversible. If the value of ΔS is more than or equal to zero, it indicates that the process is irreversibility of the process. The negative value for ΔG indicates that the spontaneity of adsorption whereas the positive values the non spontaneity of adsorption. The thermodynamic parameters such as free energy change, enthalpy change and entropy change for the adsorption of chromium (VI) on Custard apple peel powder show the feasibility, spontaneity, irreversibility and endothermic nature of adsorption.

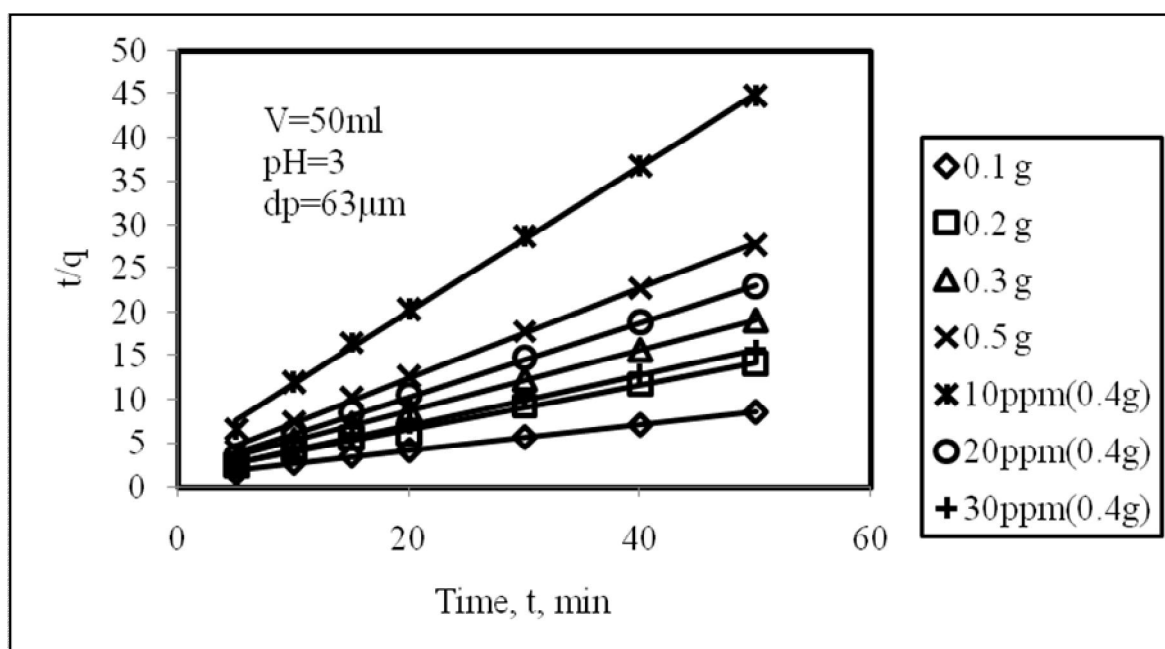


Figure 13. Second order kinetics for adsorption of chromium (VI) by custard apple peel powder

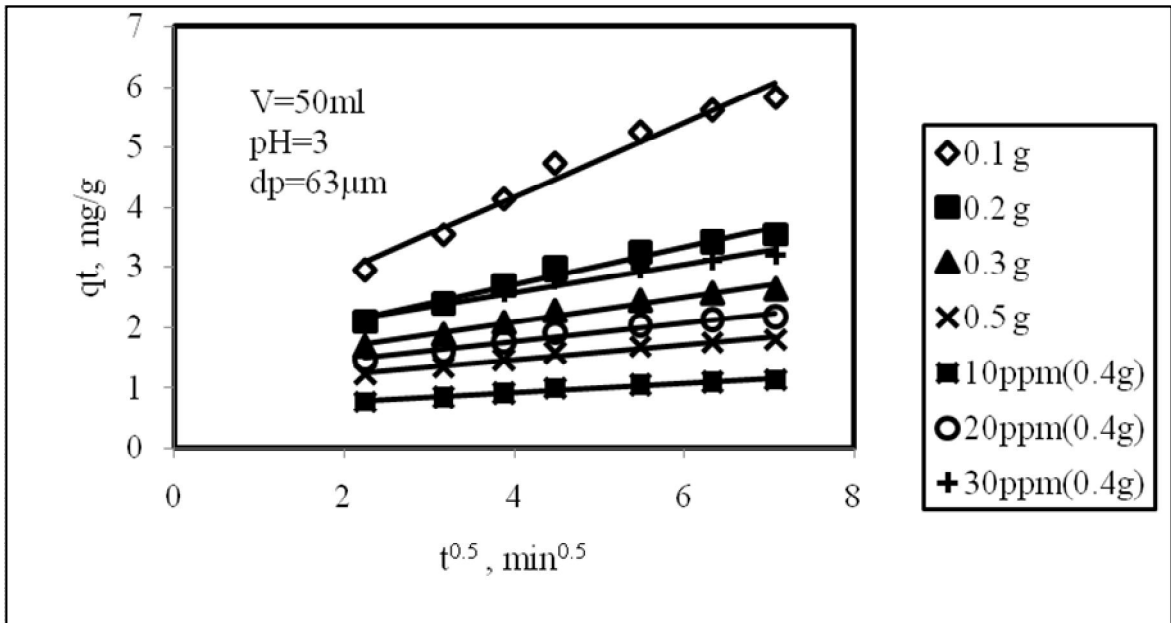


Figure 14. Intra particle diffusion model for adsorption of chromium (VI) by custard apple peel powder

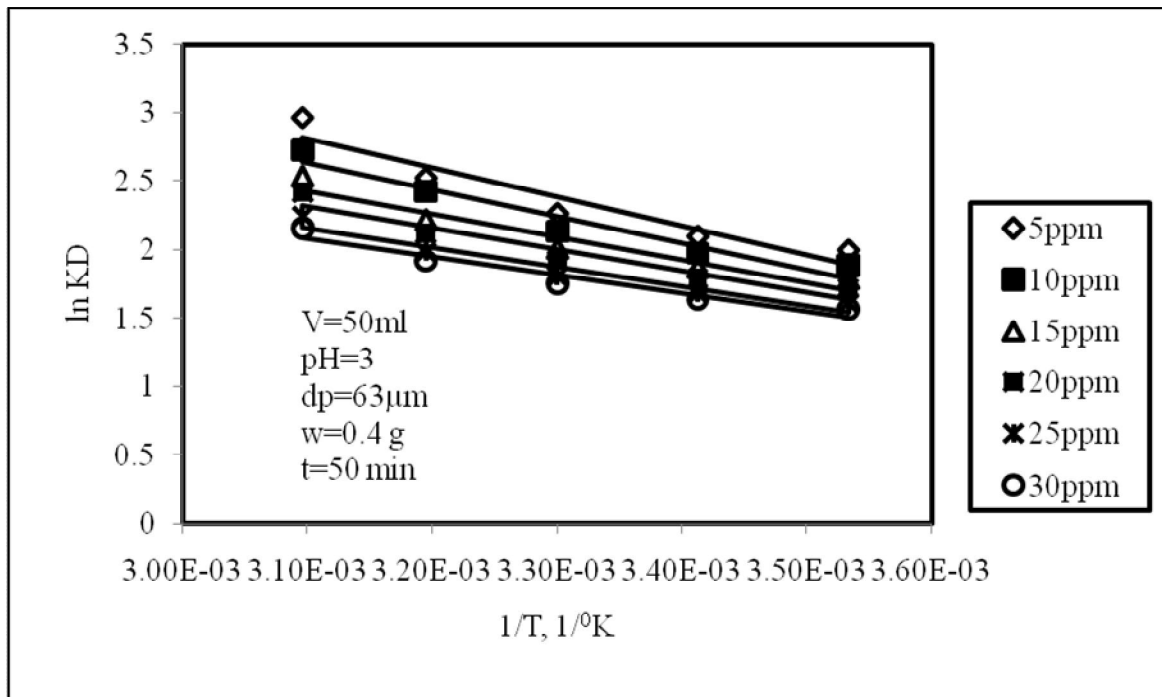


Figure 15. Van't hof equation

Table 9. Lagergren pseudo second order coefficients

Kinetics	Parameters (adsorbent dosage and initial concentration of Cr(VI))	Model equations	q_{ecal}	q_{eexp}	R^2	Rate constants, $k_2, \text{mg g}^{-1} \text{min}^{-1}$
2 nd order	0.4g and 10ppm	$\frac{t}{q} = 0.833t + 3.427$	1.2005	1.1173	0.998	0.2025
	0.4g and 20ppm	$\frac{t}{q} = 0.425t + 1.813$	2.3529	2.1803	0.998	0.0996
	0.4g and 30ppm	$\frac{t}{q} = 0.289t + 1.275$	3.4602	3.1965	0.997	0.0655
	0.1g and 20ppm	$\frac{t}{q} = 0.148t + 1.223$	6.7567	5.825	0.996	0.0179
	0.2g and 20ppm	$\frac{t}{q} = 0.254t + 1.513$	3.9370	3.5445	0.997	0.0426
	0.3g and 20ppm	$\frac{t}{q} = 0.349t + 0.1.714$	2.8653	2.6277	0.998	0.0711
	0.5g and 20ppm	$\frac{t}{q} = 0.518t + 2.111$	1.9305	1.7974	0.998	0.1271

Table 10. Intra particle diffusion model and constants

S. No.	Dosage, g and initial concentration of Cr (VI)	Model equation	R^2	K_{diff}	Constant, C
1.	0.1 g and 20 ppm	$q_t = 0.618t^{0.5} + 1.714$	0.972	0.618	1.714
2.	0.2 g and 20 ppm	$q_t = 0.308t^{0.5} + 1.471$	0.974	0.308	1.471
3.	0.3 g and 20 ppm	$q_t = 0.203t^{0.5} + 1.265$	0.972	0.203	1.265
4	0.5 g and 20 ppm	$q_t = 0.122t^{0.5} + 0.976$	0.972	0.122	0.976
5	0.4 g and 10 ppm	$q_t = 0.076t^{0.5} + 0.603$	0.972	0.076	0.603
6	0.4 g and 20 ppm	$q_t = 0.153t^{0.5} + 1.152$	0.973	0.153	1.152
7	0.4 g and 30 ppm	$q_t = 0.231t^{0.5} + 1.652$	0.971	0.231	1.652

Table 11. Thermodynamic parameters

Initial Conc, mg/L	Equation	ΔH , kJ/mole K	ΔS , kJ/mole K	ΔG , kJ/mole K				
				283	293	303	313	323
5	$\ln K_D = -2121\left(\frac{1}{T}\right) + 9.385$ $R^2=0.904$	17.634	0.082	-4.701	-5.113	-5.702	-6.56	-7.953
10	$\ln K_D = -1940\left(\frac{1}{T}\right) + 8.645$ $R^2=0.932$	16.129	0.072	-4.427	-4.801	-5.366	-6.3	-7.328
15	$\ln K_D = -1666\left(\frac{1}{T}\right) + 7.596$ $R^2=0.920$	13.851	0.063	-4.209	-4.558	-5.063	-5.77	-6.813
20	$\ln K_D = -1572\left(\frac{1}{T}\right) + 7.193$ $R^2=0.919$	13.069	0.059	-4.028	-4.364	-4.836	-5.51	-6.497
25	$\ln K_D = -1410\left(\frac{1}{T}\right) + 6.534$ $R^2=0.928$	11.723	0.054	-3.799	-4.111	-4.554	-5.17	-6.031
30	$\ln K_D = -1331\left(\frac{1}{T}\right) + 6.210$ $R^2=0.934$	11.066	0.052	-3.683	-3.993	-4.418	-4.99	-5.803

4. Conclusions

The Custard apple peel powder is capable of removing Cr (VI) from aqueous solution, up to 90.47% for an initial concentration of Cr (VI) 5 mg/L, adsorbent dosage of 0.4 g, adsorbent size of 63 μm , pH = 3 and at a temperature of 303 K. The Cr (VI) adsorption performance by Custard apple peel powder is strongly affected by parameters such as contact time, initial Cr (VI) concentration, pH, adsorbent dosage, adsorbent particle size and temperature.

The percentage adsorption of Cr (VI) is increased from 60.68 to 89.38 for 10 mg/L with increase in contact time from 5 to 120 mins. Adsorption process reached equilibrium stage at 50 mins of contact time.

With an increase in pH from 3 to 10, the adsorption of Cr (VI) is decreased from 89.38% to 48.81% for 10 mg/L solution. The optimum pH is taken at pH of 3.

With an increase in initial concentration of Cr (VI) from 10 to 30 mg/L for 0.4 g adsorbent dosage in 50 mL solution, the equilibrium adsorption of Cr (VI) is decreased from 89.38% to 85.24%.

With the increase in adsorbent dosage from 0.1 to 0.6 g (for 50 mL of solution) for initial concentration of Cr (VI) of 20 mg/L, the adsorption of Cr (VI) is increased from 58.25% to 90.07%.

The percentage removal of chromium (VI) increases from 77.37% (1.934 mg/g) to 87.21% (2.18 mg/g) for 0.4 g of dosage in 50 mL of solution for initial concentration of Cr (VI) of 20 mg/L at 50 min equilibrium agitation time with decrease in the adsorbent size from 125 to 63 μm

The percentage adsorption of Cr (VI) increased with increase in the temperature from 283 to 323 K for all initial concentrations of Cr (VI).

The Freundlich model for Cr (VI) adsorption onto Custard apple peel powder is proved to be the best fit followed by Langmuir model and Tempkin model for the experimental data. However, the data can not be described by Dubinin-Radushkevich-isotherm, since the correlation coefficient is very low.

The kinetics of the adsorption of Cr (VI) on Custard apple peel powder is best fit with pseudo second-order kinetics.

The thermodynamic parameters such as free energy change, enthalpy change and entropy change show the feasibility, irreversibility, spontaneity, endothermic nature and an increased randomness at the surface of the Custard apple peel powder.

The present batch study gives a platform for the designing of continuous flow systems with an industrial application at a commercial level also. Further, research is to be carried out to make the process economically viable at industrial scale with focus on Cr (VI) removal and regeneration of Custard apple peel powder.

References

- [1] Volesky, B. and Holan, Z. R. 1995. Biosorption of heavy metals. *Biotechnology Progress*, 11: 235-250.
- [2] Veglio, F. and Beolchini, F. 1997. Removal of metals by biosorption: a review. *Hydrometallurgy*, 44: 301-316.
- [3] Kowalshi, Z. 1994. Treatment of chromic tannery wastes. *Journal of Hazardous Materials*, 39: 137-144.
- [4] Sikaily, A. E., Nemr, A. E., Khaled, A., and Abdelwahab, O. 2007. Removal of toxic chromium from waste water using green alga *Ulva lactuca* and its activated carbon. *Journal of Hazardous Materials*, 148: 216-228.
- [5] Li, H., Li, Z., Liu, T., Xiao, X., Peng, Z., and Deng, L. 2008. A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads. *Bioresource Technology*, 99: 6271-6279.
- [6] Gomez, V. and Callo, M.P. 2006. Chromium determination and speciation since 2000. *Trends in Analytical Chemistry*, 25: 1006-1015.
- [7] World Health Organisation. 2004. "Guidelines for drinking water quality". 3rd ed., Geneva Vol. 1. 334.
- [8] Das, A. K. 2004. Micellar effect on the kinetics and mechanism of chromium (VI) oxidation of organic substrates. *Coordination Chemistry Reviews*, 248: 81-99.
- [9] Zhou, X., Korenaga, T., Takahashi, T., Moriwake, T., and Shinoda, S. 1993. A process monitoring/controlling system for the treatment of waste water containing (VI). *Water Research*, 27: 1049-1054.
- [10] Tiravanti, G., Petruzzelli, D., and Passino, R. 1997. Pretreatment of tannery wastewaters by an ion-exchange process for Cr (III) removal and recovery. *Water Science and Technology*, 36: 197-207.
- [11] Seaman, J. C., Bertsch, P. M., and Schwallie, L. 1999. In situ Cr (VI) reduction within coarse - textured oxide - coated soil and aquifer systems using Fe (II) solutions. *Environmental Science & Technology*, 33: 938-944.
- [12] Kongsricharoern, N. and Polprasert, C. 1996. Chromium removal by a bipolar electro - chemical precipitation process. *Water Science and Technology*, 34: 109-116.

- [13] Pagilla, K. R. and Canter, L. W. 1999. Laboratory studies on remediation of Chromium - contaminated soils. *Journal of Environmental Engineering*, 125: 243-248.
- [14] Chakravathi, A. K., Chowadary, S. B., Chakrabarty, S., Chakrabarty, T., and Mukherjee, D. C. 1995. Liquid membrane multiple emulsion process of chromium (VI) separation from waste waters. *Colloids and Surfaces A*, 103: 59-71.
- [15] Aksu, Z., Ozer, D., Ekiz, H. I., Kutsal, T., and Calar, A. 1996. Investigation of biosorption of chromium (VI) on *Cladophora crispata* in two-staged batch reactor. *Environmental Technology*, 17: 215-220.
- [16] Huang, S. D., Fann, C. F., and Hsieh, H. S. 1982. Foam separation of chromium (VI) from aqueous solution. *Journal of Colloid and Interface Science*, 89: 504-513.
- [17] Park, D., Yun, Y. S., and Park, J. M. 2010. The past, present and, and future trends of biosorption. *Biotechnology and Bioprocess Engineering*, 15: 86-102.
- [18] Mohan, D. and Pittman, Jr. C. U. 2006. Activated carbon and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials*, 137: 762-811.
- [19] Gupta, S. and Babu, B. V. 2009. Utilization of waste product (Tamarind seeds) for the removal of Cr (VI) from aqueous solutions: Equilibrium, kinetics and regeneration studies. *Journal of Environmental Management*, 90: 3013-3022.
- [20] Shafey, E. I. 2005. Behaviour of reduction-sorption of chromium (VI) from an aqueous solution on a modified sorbent from rice husk. *Water Air Soil Pollution*. 163: 81-102.
- [21] Sharma, A. and Bhattacharya, K. G. 2004. Adsorption of Pb (II) from aqueous solution by *Azardica indica* (Neem leaf powder). *Journal of Hazardous Materials*, 113: 97-109.
- [22] Hasan, S. H., Singh, K. K., Prakash, O. Talat, M., and Ho, Y. S. 2008. Removal of Cr (VI) from aqueous solutions using agricultural waste maize bran. *Journal of Hazardous Materials*, 152: 356-365.
- [23] Bryant, P. S., Petersen, J. N., Lee, J. M., and Brouns, T. M. 1992 Sorption of heavy metals by untreated red fir sawdust. *Applied Biochemistry and Biotechnology*, 34: 777-788.
- [24] Song, W. X., Zhong, L. H., and Rong, T. S. 2009. Removal of chromium (VI) from aqueous solution using walnut hull. *Journal of Environmental Management*, 90: 721-729.
- [25] Qaiser, S. 2009. Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study. *Electronic Journal of Biotechnology*, 12: 1-17.
- [26] Nasernejad, B., Zadeh, E., Bonakdar, T., Pour, B., Esmaail Bygi, M., and Zamani, A. 2005. Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewaters by carrot residues. *Process Biochemistry*, 40: 1319-1322.
- [27] Ghosh, P. 2009. Hexavalent chromium (VI) removal by acid modified waste activated carbons. *Journal of Hazardous Materials*, 171: 116-122.
- [28] Namasivayam, C. and Ranganathan, K. 1993. Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr (VI) from aqueous solution and chromium plating industry waste water. *Environmental Pollution*, 82: 255-261.
- [29] Srivastava, S. K., Gupta, V. K., and Mohan, D. 1997. Removal of lead and chromium by activated slag – blast - furnace waste. *Journal of Environmental Engineering*, 123: 461-468.
- [30] Pradan, J., Das, S. N., and Thakur, R. S. 1999. Adsorption of hexavalent Chromium from aqueous solution by using activated red mud. *Journal of Colloid and Interface Science*, 217: 137-141.
- [31] Venkateswarlu, P., Ratnam, M. V., Rao, D. S., and Rao, M. V. 2007. Removal of chromium from an aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent. *International Journal of Physical Sciences*, 2: 188-195.

- [32] Kobya, M. 2004. Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: Kinetic and equilibrium studies. *Bioresource Technology*, 91: 317-321.
- [33] Khan, S. A. and Riaz-ur-Rehman-Khan, M. A. 1995. Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Management*, 15: 271-282.
- [34] Potgieter, J. H., Potgieter, S. S., Vermaak, S. S., and Kalibantonga, P. D. 2006. Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, 19: 463-470.
- [35] Langmuir, I. 1918. Adsorption of gases on glass, mica, and platinum. *Journal of the American Chemical Society*, 40: 1361-1403.
- [36] Freundlich, H. 1906. Über die Adsorption in Lösungen (adsorption in solution). *Zeitschrift für Physikalische Chemie*, 57: 385-470.
- [37] Tempkin, M. J. and Pyzhev, V. 1940. Recent modifications to Langmuir isotherms. *Acta Physiochim URSS*, 12: 217-222.
- [38] Hall, K. E., Eagleton, L. C., Acrivos, A., and Vermeulen, T. 1996. Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. *Industrial and Engineering Chemistry Fundamentals*, 5: 212-223.
- [39] Mckay, G., Otterburn, M. S., and Sweny, A. G. 1981. Surface mass transfer processes during color removal from effluent using silica. *Water Research*, 15: 327-331.
- [40] Baral, S. S., Das, N., Roy Choudary, G., and Das, S. N. 2009. A preliminary study on the adsorptive removal of Chromium (VI) using seaweed, *Hydrilla verticillata*. *Journal of Hazardous Materials*, 171: 358-369.
- [41] Weber, W. J. and Morris, Jr. J. C. 1963. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division*, 89: 31-59.
- [42] Hamdaoui O. and Naffrechoux, E. 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two parameter models and equations allowing determination of thermodynamic parameters. *Journal of Hazardous Materials*, 147: 381-394.