

Removal of Cr(VI) From Waste Water By Peanut shell

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ABSTRACT

An Agricultural waste peanut shell has been used for the removal of Cr(VI) from aqueous solution. The effects of different parameters such as contact time, adsorbate concentration, pH of the medium and temperature were investigated and maximum uptake of Cr(VI) was 314.22 mg g⁻¹ at pH 2.0, initial Cr(VI) concentration of 200 mg L⁻¹, and temperature of 40°C. Effect of pH showed that peanut shell was not only removing Cr(VI) from aqueous solution but also reducing toxic Cr(VI) into less toxic Cr(III). The sorption kinetics was tested with first order reversible, pseudo-first order and pseudo second order reaction and it was found that Cr(VI) uptake process followed the pseudo-second order rate expression. Different thermodynamic parameters viz., changes in standard free energy, enthalpy and entropy have also been evaluated and it has been found that the reaction was feasible, spontaneous and endothermic in nature. The Langmuir and Freundlich equations for describing sorption equilibrium were applied and it was found that the process was well described by Langmuir isotherm. Desorption studies was also carried out and found that complete desorption of Cr(VI) took place at pH of 9.5.

1. Introduction

Due to rapid industrial development, direct and indirect discharges of heavy metals to the environment through wastewater have tremendously been increased. In industrial wastewater treatment chromium, copper, cadmium, lead, zinc and nickel are considered more toxic and receiving more attention of researchers^[1-3].

Chromium is a very harmful heavy metal and exists in various oxidative forms; however, the trivalent and hexavalent states are considered more essential in term of environmental pollution point of view^[4]. Cr(VI) is considered more harmful and toxic due to its high carcinogenic and resistant properties than Cr(III)^[5]. There are various Cr contamination sources such as electroplating, leather tanning, textile industries, metal finishing, nuclear power plants, and chromate preparation^[6]. According to Indian standards, the permissible limit of Cr(VI) for industrial effluents to be discharged to surface water is 0.1 mg L⁻¹. Over ingestion of Cr(VI) beyond the permissible limits can cause severe gastric damage, liver, kidney and lung cancer and other health related complications^[7]. So there is a dire need of significant management of wastewater contaminated by Cr(VI) before its release. Different conventional methods such as chemical precipitation, filtration, chemical oxidation and reduction, reverse osmosis, evaporation techniques, electrochemical and ion exchange methods are generally recommended for Cr (VI) removal from the environment^[8]. However, these methods are cost effective and generate a variety of secondary pollutants^[9]. Adsorption method is known to be the most promising technique and is considered as economically and operationally very effective for removing heavy metals from contaminated water, especially with the application of low-cost and high efficiency adsorbents^[10-15]. Therefore, it is necessary to search a low cost,

easily available and greater adsorption capacity adsorbent in order to reduce Cr(VI) ions from contaminated water. That's why in present investigation an agricultural waste peanut shell was used as adsorbent for the removal of Cr(VI) from aqueous solution.

2. Materials and method

2.1. Sorbent^[16]

Peanut shell is a byproduct of peanut milling plant. It was collected from M/s Shivangi peanut milling plant, Chunar, Mirzapur. It was washed twice with double distilled water to remove soluble lighter materials. Thereafter, it was dried in an oven at 70 °C for an hour. After that, it was crushed by mortar and pestle and sieved to less than 0.6 mm size. The surface area of Peanut shell was determined by a three point N₂ gas adsorption method using a Quantasorb Surface Area Analyser (model Q5-7, Quantachrome Corporation, USA). The bulk density was determined by densitometer. Porosity was determined by Porositometer (model: M7V, NGRI Hyderabad, India). X-Ray diffraction of the adsorbent was obtained using X-ray Diffractometer (model: ID-3000W, Rich Siefert and Company, Ahrensberg, Germany). Infrared spectra of the biosorbent were recorded using Infrared Spectrophotometer (model: FT/IR-5300, JASCO Corporation, Japan) in the range 4000 to 400 cm⁻¹. Percentage of volatile matter, ash and moisture were determined as given in the "Vogel's Text Book of Quantitative Chemical Analysis", 5th Edition, Bath Press Ltd, U.K.

Various physicochemical properties of Peanut shell thus obtained are given in **Table 1**.

2.2 Reagents

All the primary chemical used were of analytical

grade: potassium dichromate, hydrochloric acid, sodium hydroxide, 1,5-diphenylcarbazide, potassium permanganate etc. were purchased from E Merck, India, Ltd., Mumbai, India.

The stock solution containing 1000 ppm of Cr(VI) was prepared by dissolving 1.4143 g of $K_2Cr_2O_7$ in 500 mL of deionised, double distilled water. Required initial concentration of Cr(VI) standard was prepared by appropriate dilution of the above stock Cr(VI) standard solution.

2.3 Batch sorption experiment^[16]

Batch experiments were conducted by adding 1 g sorbent in 50 mL aqueous solution of potassium dichromate of desired concentration (100, 125 and 150 mg L⁻¹) at different temperatures (20, 30 and 40 °C) and pH (3.2, 4.0, 5.0, 5.5, 6.0, 6.6, 7.0, 8.0 and 9.0) in different glass bottles in a shaking thermostat set at 20, 30 and 40 °C at a constant speed of 125 rpm. The pH of the adsorbate solution was adjusted by adding 0.1M HCl or 0.1M NaOH. The progress of the adsorption process was observed at different time intervals till the attainment of saturation. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by centrifugation at 15000 rpm and the supernatant liquid was analyzed by AAS to determine the residual concentration of chromium ion. Blanks solutions were run under similar conditions of concentration, pH and temperature without the adsorbent in all the cases to correct for any adsorption on the internal surface of the bottles.

The amount of Cr(VI) adsorbed per unit mass of the biosorbent was evaluated by using the following equation:

$$q_{\max} = \frac{C_i - C_e}{W} \times V \quad (1)$$

The percentage removal of Cr(VI) was calculated as follows:

$$\text{percentage removal of Cr(VI)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

2.3.1 Effect of adsorbate concentration and contact time

It was studied using 50 mL Cr(VI) solution of concentration 200, 250 and 300 mgL⁻¹ and contact time 5-180 minute with an interval of 10 minute, respectively at pH 2.0, temperature 40 °C and 1 g of sorbent in 50 mL of aqueous solution.

2.3.2 Effect of Temperature

The effect of temperature on the sorption of Cr(VI) was investigated at different temperature 20, 30 and 40 °C at pH 2.0 and 1 g of sorbent into 250 mL of conical flask containing 50 mL of 200 mgL⁻¹ of Cr(VI) solution.

2.3.3 Effect of pH

Sorption experiment for the effect of pH were conducted by using 50 mL solution having 200 mgL⁻¹ Cr(VI) with 1g of sorbent at 40 °C and the pH of the solution was monitored from 1.4 to 8.5 by adding 0.1 M HCl and 0.1 M NaOH.

2.4 Desorption^[16]

Desorption experiments were carried out using double distilled water and aqueous solution of different known pH solutions such as 2.5, 3.5, 4.5, 6.5 and 9.5 as eluant. For all desorption experiments chromium loaded dead biomass of peanut shell was shaken with 50 mL of eluant solution. Desorption efficiency was calculated by using following equation:

$$\text{Desorption efficiency} = \frac{\text{amount of Cr(VI) desorbed}}{\text{amount of Cr(VI) adsorbed}} \times 100 \quad (3)$$

2.5 Chromium analysis^[16]

2.5.1 Chromium (VI) analysis

The pink coloured complex was formed when 1,5-diphenylcarbazide was added into Cr(VI) in acidic solution and concentration was determined spectrophotometrically at 540 nm by Spectronic 20 (Bausch and Lomb, USA)^[16].

2.5.2 Chromium (III) analysis

For the determination of Cr(III) concentration, Cr(III) (formed due to the reduction of Cr(VI) in to Cr(III) during the sorption process) was again converted to Cr(VI) by addition of excess $KMnO_4$ at high temperature (130-140 °C), thereafter 1,5-diphenylcarbazide was added. The pink coloured complex formed gives the concentration of Cr(VI) and Cr(III) which is total chromium. The Cr(III) concentration was calculated by the difference of the total chromium and Cr(VI) concentrations measured as above^[17].

3. Results and Discussion

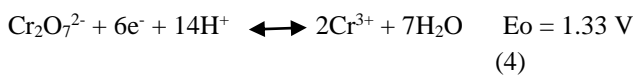
3.1 Effect of contact time and concentration^[16]

A series of experiments were performed at different adsorbate concentration viz., 200, 250 and 300 mg L⁻¹ and time interval of 10 minute at a temperature 40 °C and pH 2.0. The percentage removal of Cr(VI) was found to be 99.5, 94.30 and 88.15 % respectively (Figure 1). The extent of adsorption increased rapidly in the initial stages and became slower at later stages until the attainment of equilibrium. Equilibrium time for the adsorption of Cr(VI) on peanut shell at various adsorbate concentrations was found to be 110 minutes, which showed that equilibrium time was independent of the initial adsorbate concentration^[18].

3.2 Effect of pH^[16]

Experiments were performed by varying pH from 1.4 to 8.5 at temperature 40 °C and adsorbate concentration of 200 mgL⁻¹. Initially the uptake of Cr(VI) was increasing with increase of pH up to 2.0 and then decreased with the rise of pH from 2.0 to 8.5 (Figure 2). The optimum pH for maximum uptake of Cr(VI) was found at 2.0. This can be explained that since Cr(VI) exists in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} etc. in acidic medium and lowering of pH caused the surface of the biosorbent to become protonated to a

higher extent and as a result a strong attraction exists between these oxyanions of Cr(VI) and positively charged surface of the biosorbent. Hence, uptake increases with the decrease in the pH of the solution. Whereas at high pH biosorbent surface has been negatively charged and in addition to this there will be abundance of negatively charged hydroxyl ions in aqueous solution. Both of these factors can cause hindrance in the biosorption of negatively charged $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} etc. resulting in the decrease uptake of Cr(VI) at high pH value. Another change which was also observed at low pH (2.0) that the colour of the surface of biosorbent turned greenish during sorption. This was certainly due to the sorption of Cr(III) in a reduced form of chromium on the surface of the sorbent. Thus, during sorption of Cr(VI) on the surface of biosorbent, there was sorption of Cr(VI) as well as Cr(III). Reduction of Cr(VI) in to Cr(III) is also clear from the aqueous chemistry of Cr(VI) at low pH value. There, $\text{Cr}_2\text{O}_7^{2-}$ acts as an oxidant, to oxidize the surface of the biosorbent, while it is reduced to Cr(III) [19-21].



3.3 Effect of temperature^[16]

Experiments were performed at different temperatures 20, 30 and 40°C at concentration of 200 mg L⁻¹ and pH of 2.0. The percentage removal of Cr(VI) was increased from 92.10 to 99.50 with the rise in temperature from 20 to 40 °C (Figure 3). Equilibrium time for 20, 30 and 40 °C was found to be 110 minute indicating that the equilibrium time was independent of temperature. The above results showed the endothermic nature of the adsorption^[18]. The increased adsorption with temperature is also attributed to the increase in the number of adsorption site generated due to breaking of some internal bonds near the edge of active surface sites of adsorbent^[18,22].

3.4 Thermodynamic evaluation of the process^[16]

Thermodynamic parameters such as free energy (ΔG^0 , k cal mol⁻¹), enthalpy (ΔH^0 , k cal mol⁻¹) and entropy (ΔS^0 , cal mol⁻¹ k⁻¹) changes during the process were calculated using equations 5 to 7 on a temperature range of 20 - 40°C at 200 mgL⁻¹. The negative values of free energy change (ΔG^0) were an indication of the spontaneous nature of the adsorption process and more negative value with increase of temperature (-1.32, -1.84 and -2.76 kcal mol⁻¹ respectively) shows that an increase in temperature favours the sorption process. The positive value of ΔH^0 (22.34 kcal mol⁻¹) indicate that the sorption process was endothermic in nature and the negative values of ΔS^0 (79.78 cal mol⁻¹ k⁻¹) suggest the probability of a favourable adsorption^[23].

$$K_c = \frac{C_{Ae}}{C_e} \quad (5)$$

Where K_c is the equilibrium constant and C_{Ae} and C_e (both in mgL⁻¹) are the equilibrium concentrations for the solute on sorbent and in the solution respectively.

$$\Delta G^0 = -RT \ln K_c \quad (6)$$

$$q_{\max} = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of a plot of $\ln K_c$ versus $1/T$ (Figure 4).

3.5 Sorption isotherms^[16]

The isotherm constants were calculated from the slope and intercept of figure 5a (Langmuir isotherm) and figure 5b (Freundlich isotherm) and presented in Table 2. The value of r^2 was higher for Langmuir isotherm^[24] than for the Freundlich isotherm^[25], this means the Langmuir equation represented the adsorption process very well. This may be due to the homogeneous distribution of active sites on biosorbent surface. Values of Q^0 , which is defined as the maximum capacity of sorbent was calculated from the Langmuir plots in the range of 283.15-311.55 mg g⁻¹ at different temperatures. This indicate the good sorbing capacity of peanut shell^[16].

The equilibrium parameter R_L is defined as $R_L = 1/(1+bC_{A0})$. If R_L falls in the range $0 < R_L < 1$, it reflects the favourable adsorption process^[26]. In the present investigation, the equilibrium parameter was found to be in the range $0 < R_L < 1$ (Table 2). Hence the sorption process was very favourable and the peanut shell exhibited a good potential for the removal of Cr(VI) from aqueous solution^[26].

3.6 Sorption kinetics^[16]

In order to predict sorption kinetic models of Cr(VI), first order reversible^[27], pseudo-first order^[28] and pseudo-second order^[29] kinetic models were applied to the data. The effect of the initial Cr(VI) concentrations and temperatures was investigated to find the best kinetic model. The straight line plots of $-\ln(1-U_t)$ vs t (min.) were tested to obtain the first order rate constant at the different experimental conditions. Approximate linear fits were generally observed for all concentrations and temperatures, indicating that sorption reaction can be approximated to be of the first order reversible kinetics. The computed correlation coefficients 0.808 and 0.922 (Table 3) suggest a good agreement with first order reversible kinetic model. For the pseudo-first order sorption rate constant, the straight plots of $\log(q_e - q_t)$ against t (min.) were analysed. As linear fits were observed for all concentrations and temperatures, sorption reaction can be approximated to first order kinetics. The smallest correlation coefficient in this case was 0.862, which is still better than the first order reversible reaction model. The equilibrium rate constants of pseudo second order were determined by plotting t/q_t against t (min.). The kinetic constant and correlation coefficients of these models were calculated and are given in Table 3. Very Good correlation coefficients were obtained at all the concentration and temperatures for the pseudo second order kinetic model, indicating that the Cr(VI) uptake process followed the pseudo second order rate expression, so only the

pseudo second order plots are represented (figure 6a and 6b). Thus, the pseudo-second order kinetics was determined as a pathway to reach the equilibrium.

3.7 Intraparticle diffusion study^[16]

The rate constants for intraparticle diffusion (k_{id}) at different temperatures were determined using following equation^[30]:

$$q = k_{id} t^{1/2} \quad (8)$$

Where, q is the amount sorbed at time t and $t^{1/2}$ is the square root of the time. The values of k_{id} (9.358×10^{-3} , 1.465×10^{-2} and $1.585 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-1/2}$) at temperatures 20, 30 and 40°C respectively, were calculated from the slopes of respective plot q versus $t^{1/2}$ (Figure 7) at later stages. The dual nature of the curves was obtained due to the varying extent of sorption in the initial and final stages of the experiment. This can be attributed to the fact that in the initial stages, sorption was due to boundary layer diffusion effect whereas, in the later stages (linear portion of the curve) was due to the intraparticle diffusion effects. However, these plots indicated that the intraparticle diffusion was not the only rate controlling step because it didn't pass through the origin. This was further supported by calculating the intraparticle diffusion coefficient (\bar{D} , $\text{cm}^2 \text{ sec}^{-1}$) using the following equation^[31]:

$$\bar{D} = 0.03r^2 / t_{1/2} \quad (9)$$

where r (cm) is the average radius of the sorbent particle and $t_{1/2}$ (min.) is the time for half of the sorption. According to the Michelsen et al.^[30] a \bar{D} value of the order of $10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ is indicative of intraparticle diffusion as rate determining step. In this investigation, the values of \bar{D} (5.858×10^{-9} , 7.535×10^{-9} and $8.565 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ at 20, 30 and 40°C respectively) obtained was in order of $10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ which was more than two order of magnitude higher, indicated that the intraparticle diffusion was not the only rate controlling step. It was concluded that both boundary layer and intraparticle diffusion might be involved in this removal process^[16].

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4. Desorption Studies^[16]

Desorption results (Figure 8) indicated that 21.4, 44.4, 58.5, 74.5 and 100% of Cr(VI) were removed from the surface of the sorbent containing 9.95 mg g^{-1} of Cr(VI) at pH of 2.5, 3.5, 4.5, 6.5 and 9.5 respectively and temperature of 40 °C. The rate of sorption was thus highly pH dependent. The sorbate ions which were bonded weakly to the sorbent surface started to remove on increasing of pH, while they were completely desorbed when pH reached to 9.5.

4.1 Infrared studies

The characteristics IR band of dichromate ion at 750 and 860 cm^{-1} were shifted to 790 and 900 cm^{-1} after the sorption of Cr(VI) on the sorbent. It showed the binding of surface sites with the sorbate ions^[31]. The disappearance of above bands after desorption at pH 9.5 supported the desorption result for complete Cr(VI) detachment from the sorbent surface.

5. Conclusion

An agricultural waste peanut shell has been found to be a very economically viable and effective biosorbent for the removal of Cr(VI). The maximum removal of Cr(VI) was found to be 314.22 mg g^{-1} at pH 2.0, initial Cr(VI) concentration 200 mg L^{-1} and temperature of 40 °C. Adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages adsorption was due to intraparticle diffusion. Thermodynamic studies confirmed that the process was spontaneous and endothermic. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption. The best correlation coefficients were obtained using the pseudo second order kinetic model, indicated that the chromium removal process followed the pseudo second order rate expression. Desorption studies were also carried out and found that the complete desorption of Cr(VI) took place at pH of 9.5. The data thus obtained would be useful in designing and fabricating an efficient treatment plant for Cr(VI) rich effluents.

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Table 1 - Physical and Chemical properties of biosorbent Peanut shell

Surface area (m ² g ⁻¹)	425.00
Bulk density (g cm ⁻¹)	0.2438
Particle size (mm)	0.6 mm
Porosity	0.36
Proximate Analysis (%)	
Volatile matter	42.38
Moisture	7.75
Fixed carbon	31.52
Ash (Oxides of Al, Mn, Si, Fe and others)	18.43

Table 2 - Values of Langmuir and Freundlich sorption constants and R_L values of Cr(VI) sorption on Peanut shell at different temperatures

Temp. °C	Langmuir Constants			Freundlich constants			R_L
	Q^0 (mg g ⁻¹)	b (l mg ⁻¹)	r^2	n	k_F	r^2	
20	283.15	0.610	0.996	3.270	0.272	0.835	8.085×10^{-3}
30	297.85	0.178	0.994	4.510	0.335	0.885	2.990×10^{-3}
40	311.55	0.075	0.991	7.862	0.390	0.855	7.140×10^{-3}

Table 3 - A comparison of first-order reversible, pseudo-first order and pseudo-second order kinetic model rate constants obtained under different experimental conditions

Parameters	First order reversible					Pseudo-first order		Pseudo-second order		
	k_c	k'	$k_{1x} 10^3$	$K_{2x} 10^3$	r^2	$k_{sx} 10^{-2}$	r^2	h	q_e (cal)	r^2
C_0 (mg L⁻¹)										
200	15.25	0.075	66.25	4.35	0.585	6.635	0.998	0.470	12.775	0.942
250	34.75	0.065	60.20	1.75	0.655	5.945	0.997	0.515	15.625	0.658
300	157.35	0.050	48.95	0.35	0.499	4.910	0.998	0.545	18.215	0.836
Temperature (°C)										
20	34.75	0.065	61.85	1.80	0.655	5.896	0.998	0.355	13.285	0.864
30	15.25	0.075	66.25	4.35	0.585	6.635	0.998	0.470	12.775	0.942
40	7.85	0.085	74.50	9.55	0.835	7.625	0.999	0.539	12.655	0.836

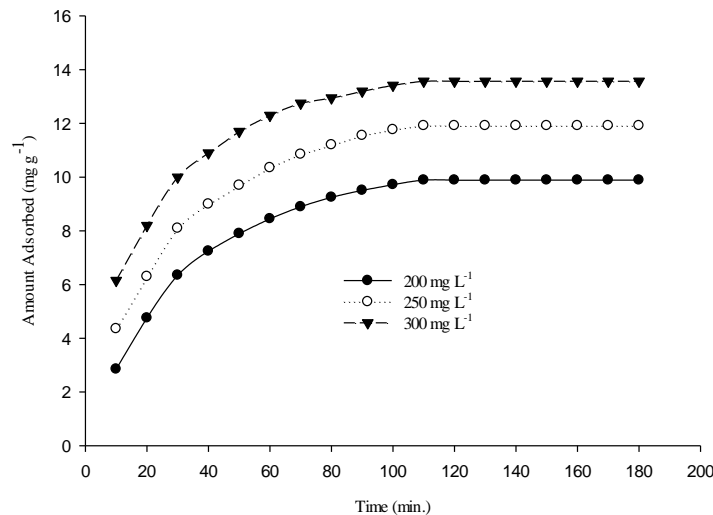


Fig. 1 Effect of contact time and initial adsorbate concentration on adsorption.

Conditions: pH 2.0, Temperature 40 °C, particle size < 0.6 mm, initial Cr(VI) concentration 200 mg L⁻¹, 250 mg L⁻¹, 300 mg L⁻¹

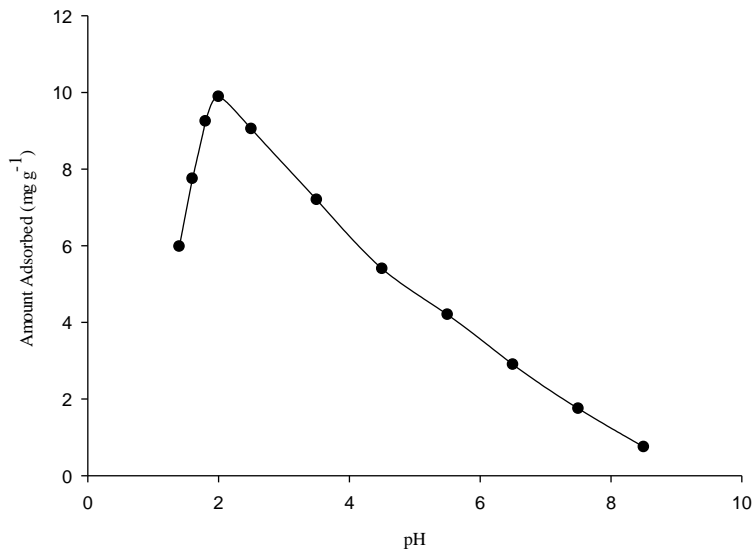


Fig. 2 Effect of pH on the adsorption by Peanut shell
 Conditions: initial Cr(VI) concentration 200 mg L⁻¹, pH 1.4-8.5, Temperature 40 °C, particle size < 0.6 mm.

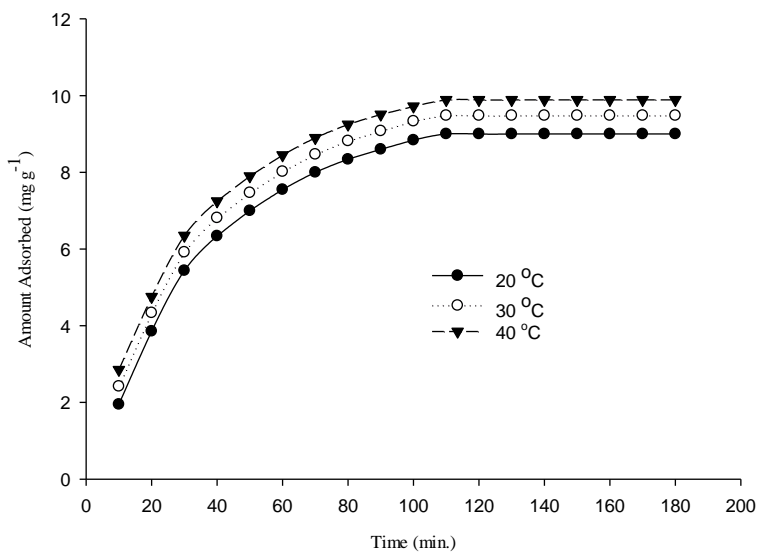


Fig. 3 Effect of temperature on the sorption by peanut shell
 Conditions: initial Cr(VI) concentration 200 mg L⁻¹, pH 2.0, particle size < 0.6 mm
 temperature 20 °C, 30 °C and 40 °C

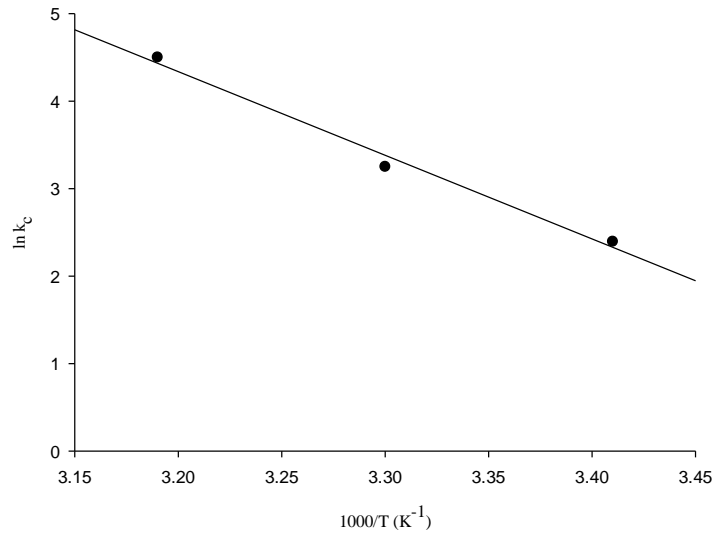


Fig. 4 A plot of ln kc against 1/T for Cr(VI) sorption by peanut shell
 Conditions: initial Cr(VI) concentration 200 mgL⁻¹, temperature 20, 30 and 40 °C

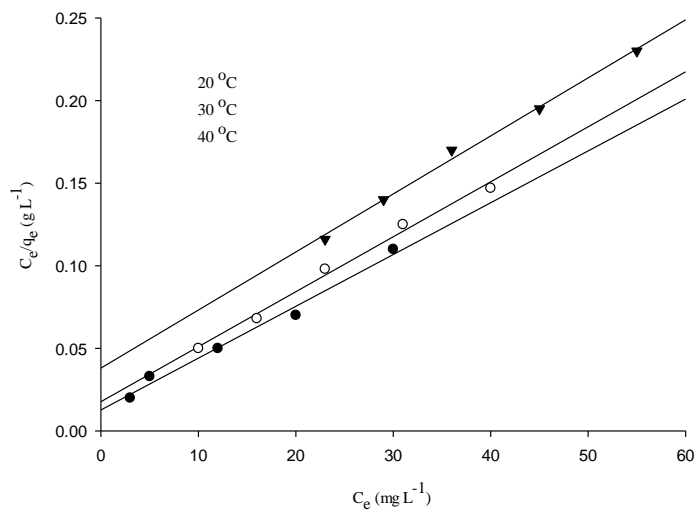


Fig. 5a Langmuir isotherm plot for Cr(VI) removal using peanut shell
 Conditions: pH 2.0, particle size < 0.6 mm, concentrations 200, 225, 250, 275 and 300 mg L⁻¹

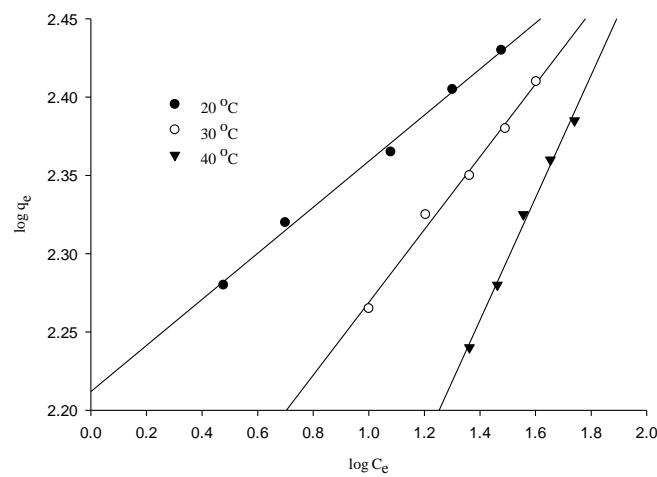


Fig. 5b Freundlich isotherm plot for Cr(VI) removal using peanut shell
 Conditions: pH 2.0, particle size < 0.6 mm, Concentrations 200, 225, 250, 275 and 300 mg L⁻¹

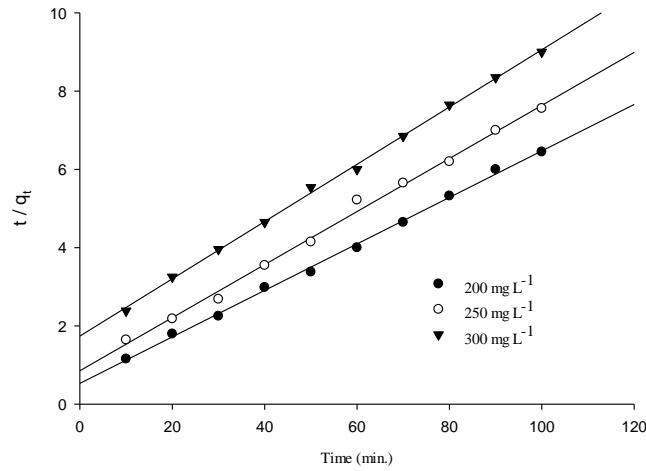


Fig. 6a Pseudo-second order plot for Cr(VI) removal using peanut shell at different concentration
Conditions: temperature 30 °C, particle size < 0.6 mm, pH 2.0

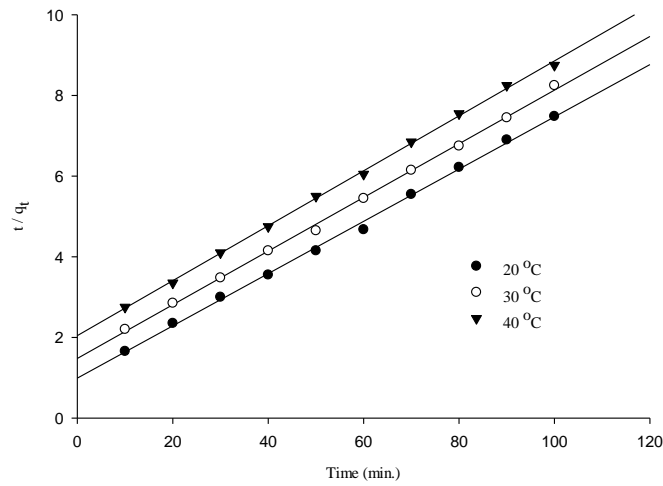


Fig. 6b Pseudo-second order plot for Cr(VI) removal using peanut shell at different temperatures
Conditions: concentration 200 mg L⁻¹, pH 2.0, particle size < 0.6mm.

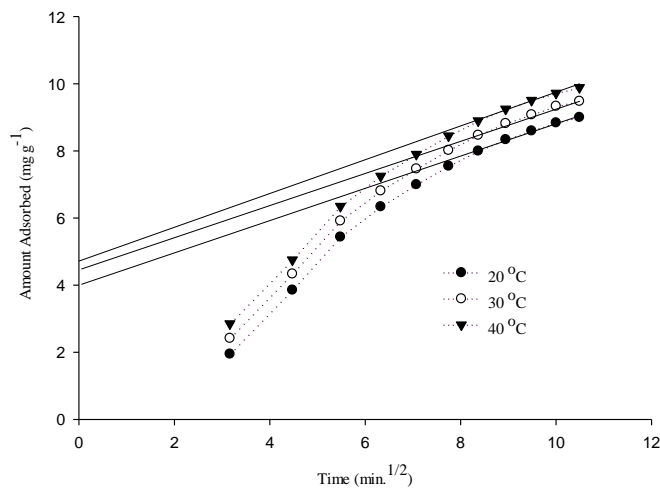


Fig. 7 Intraparticle diffusion plot for sorption of Cr(VI) on peanut shell at 20, 30 and 40 °C
Conditions: concentration 200 mg L⁻¹, pH 2.0, particle size < 0.6 mm.

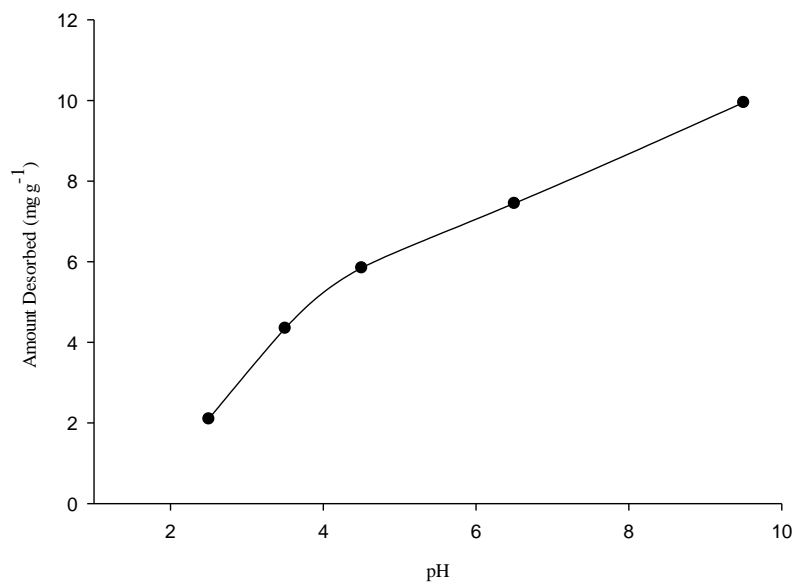


Fig. 8 Effect of pH on the desorption of Cr(VI) by peanut shell