

Removal of Cr (VI) from Aqueous Solutions Using Peanut shell as Adsorbent

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Summary: The biosorption of Cr (VI) ions from aqueous solution by peanut shell (PNS) biosorbent was studied in a batch mode system. Factors affecting Cr (VI) biosorption such as pH (2-7), initial chromium ion concentrations (20-60 mg/l), contact time (6 h), adsorbent dosage (0.2-1.0 g) and temperature (293-313 K) were investigated. The adsorption equilibrium was established at 360 minutes. A comparison of the kinetic models has showed that pseudo-second order equation best described adsorption kinetics. Maximum adsorption was achieved at pH 2.0 and 3.0. The adsorption equilibrium data was fitted well to the Langmuir adsorption isotherm as compared to the Freundlich adsorption isotherm. The values of separation factor, R_L , was found between 0.0235 and 0.0633 ($0 < R_L < 1$) which pointed out favorable adsorption of Cr (VI) on PNS adsorbent. The adsorption capacity was measured in terms of monolayer adsorption and was found to be 4.32 mg/g at 313 K. The thermodynamic parameters (ΔG , ΔH and ΔS) values indicated the endothermic, non spontaneous and entropy driven system of the adsorption process.

Key Words: Peanut shell, pH, chromium, kinetic, isotherms, separation factor.

Introduction

Our environment is continuously contaminated through various pollutants. Heavy metals like Cu, Cd, Hg, Cr and Mn are among the most common pollutants in soil and water. In the present work we have focused on the removal of chromium (VI) from aqueous solution using the low-cost organic bio-waste of Peanut shells (PNS) as adsorbent. Chromium exists in various oxidation states such as Cr (III), Cr (IV), Cr (V) and Cr (VI). The two most stable states of chromium are Cr (III) and Cr (VI). Cr (III) is considered to be less toxic as compared to Cr (VI) due to its large size and less solubility in water. Cr (III) is considered as essential micronutrient [1]. Cr (VI) is most toxic due to its carcinogenic and teratogenic behavior on the human beings and other animals. Over exposure to Cr (VI) causes oedema, irritation to the eyes and skin, respiratory tract pulmonary congestion and liver damage [2]. Chromium has wide spread applications in various industries such as electroplating, leather industry, steel industry, photography, mining, aluminum conversion coating operations, paint and pigments, textile dyeing, wood preservations, nuclear power plants and chromate preparation industries [1-8]. The effluents of these industries have a major contribution to water pollution. The concentration of Cr (III) and Cr (VI) in the industrial effluents ranges from 0.5 to 270 mg/L [5]. According to the Environmental Protection Agency (EPA) of the United States of America (U.S.A) the tolerance limit of Cr (VI) for the released into inland surface water is 0.1 mg/L and the recommended limit for the drinking water is only 0.05 mg/L [9]. Several physical and chemical methods have been reported in literature for the removal of Cr (VI) from waste water. These

include ion exchange, membrane technology, electro dialysis, reverse osmosis, chemical precipitation, chemical oxidation or reduction and evaporation. However, these methods have considerable disadvantages such as chemical precipitation requires a massive amount of chemicals which produces large quantities of toxic sludge. This also results in high cost of supervision. Other available techniques such as electro dialysis, reverse osmosis, filtration and ion exchange etc have many drawbacks such as incomplete removal of heavy metals, high cost, tedious and complex operation, energy consumption and generation of toxic sludge. Thus valuable and eco-friendly methodologies are required to overcome this problem of heavy metals. In contrast to these methods adsorption is by far the most versatile and effective method for the removal of heavy metals and other toxic pollutants from contaminated water. This also solves the problems of poisonous sludge, incomplete removal and high cost as well as could be recovered for further use. Activated carbon (AC) is the most effective adsorbent for the removal of chromium and its adaptation to the pollutants loading due to its porous nature [8, 10]. Although activated carbon have efficient adsorption capacity for the uptake of heavy metals than other commercially available adsorbents. The main problem which is associated with the activated carbon (AC) is its high cost due to which it restricts the applicability of activated carbon for environmental protection. The adsorption technique will become inexpensive in the sense when the adsorbent is easily available, economical and have good adsorption capacity [8]. The natural materials that are produced from agricultural activities have

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good removal efficiency and can be used as low-cost adsorbents. Generally, the adsorbent prepared from low-cost materials may be either wastes or easily available in abundance. Biosorbent prepared from agricultural wastes have insoluble organic compounds and poly functional groups such as $-\text{NH}_2$, $-\text{COO}^-$, $-\text{C}=\text{O}$, OH^- and PO_4^{2-} [11]. These ions interact with Cr (VI) ions through the electrostatic forces of attraction due to which the biosorbents have effective potential for the removal of Cr (VI) and other pollutants from water. In the present study biosorbent of PNS was used without any chemical activation for the removal of Cr (VI) from aqueous solution.

Results and Discussion

The biosorbent prepared from the peanut shell was characterized by the following techniques.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM, JOEL, JSM-5910, Japan) was performed to investigate the surface morphology of the adsorbent before and after adsorption. The microstructure of unused PNS biosorbent as presented in Fig. 1 showed the porous morphology of the surface particles. Such surfaces are best suited for the adsorption of the adsorbates like Cr (VI). The adsorption capacity of PNS biosorbent for Cr (VI) ions was enhanced due to the presence of these pores. The Cr (VI) ions are driven into the fibrous cellulose structure of these pores which facilitate the adsorption process [12]. From the micrograph of used PNS a complete uniformity was observed in the surface indicating the accumulation of chromium ions into the pores of PNS surface as revealed in Fig. 2.

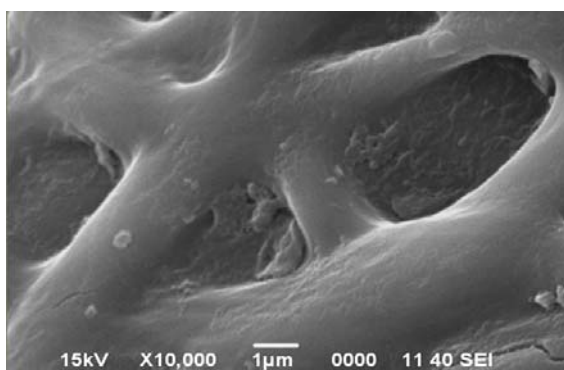


Fig. 1: SEM images of unused peanut shells.

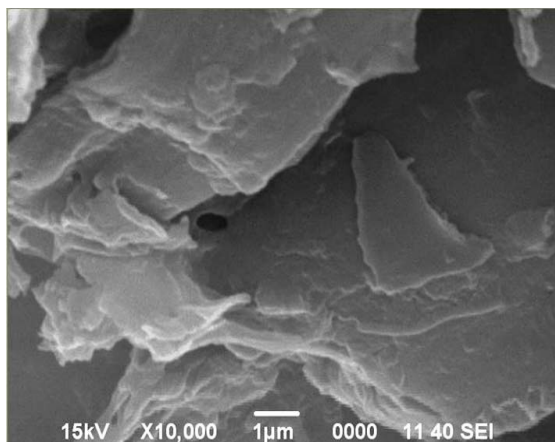


Fig. 2: SEM images of used peanut shell.

Fourier Transform Infrared Analysis (FT-IR)

Fourier transform infrared (Prestige IR-21) technique was used to investigate the surface functional groups which were responsible for the uptake of chromium ions from aqueous solutions. The spectra were measured in the range of $500\text{--}4000\text{ cm}^{-1}$. The peaks at around 1519 and 1041 cm^{-1} are associated with the stretching vibrations of secondary amines and $-\text{C}-\text{C}-$ groups [13]. The peaks about 2931 , 1095 and 887 cm^{-1} are attributed to the symmetric vibrations of $\text{C}-\text{H}$, $-\text{C}=\text{CH}_2$ and $\text{C}=\text{C}$ groups. The additional peaks less than 823 cm^{-1} are known as the finger print zone and are associated with the phosphate containing functional groups [2]. The broad peak at 2360 cm^{-1} is corresponding to the presence of $\text{O}=\text{C}=\text{O}$ molecule which might be due to the dissolution of carbon dioxide molecules in water. Alternatively the observed samples of used and unused biosorbent by FT-IR technique might contain the moisture i.e. water contents. The complete spectra of used and unused biosorbent (Fig. 3) did not show the clear difference of the functional groups however, a portion of the spectra from 640 to 1140 cm^{-1} determines and distinct those functional groups which are used up for the removal of chromium ions from aqueous solutions (Fig. 4). In Fig. 4 the peak at 848.67 cm^{-1} indicated the vibration modes of $\text{Cr}-\text{O}$ and $\text{Cr}=\text{O}$ bond which showed the uptake of chromium from aqueous solution onto the surface of PNS [14, 15]

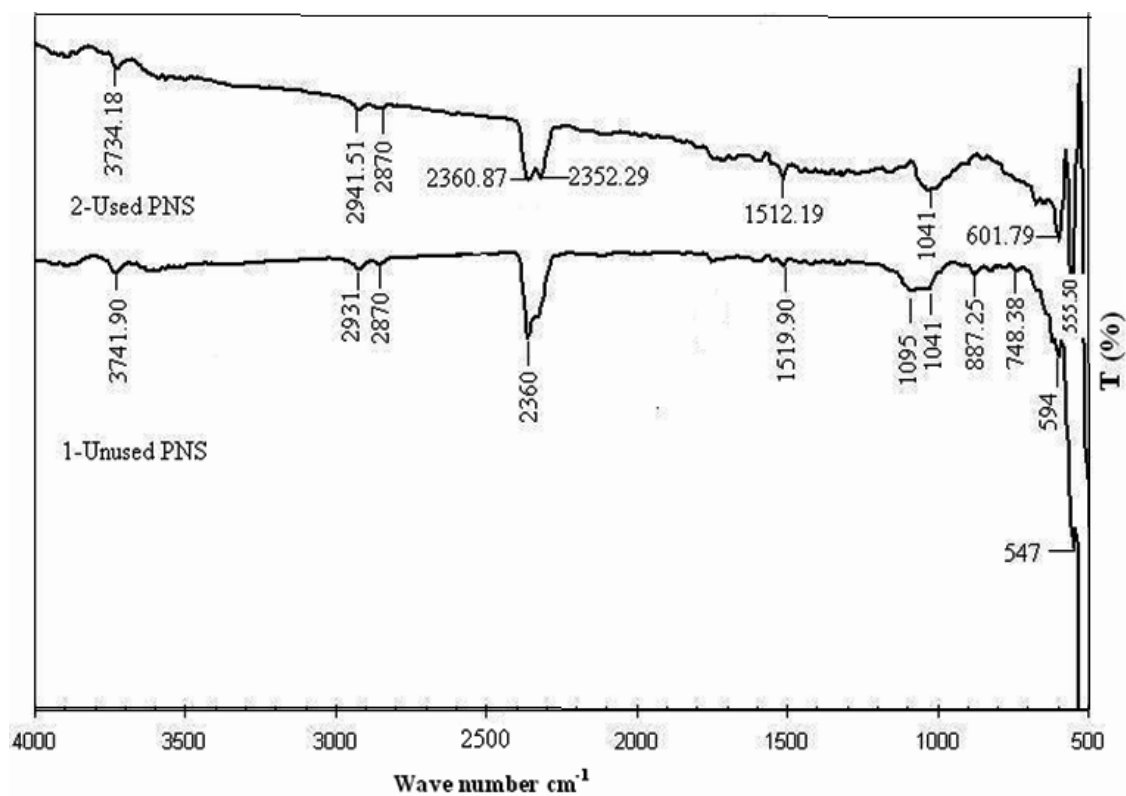


Fig. 3: Complete FT-IR analysis of peanut shell biosorbent.

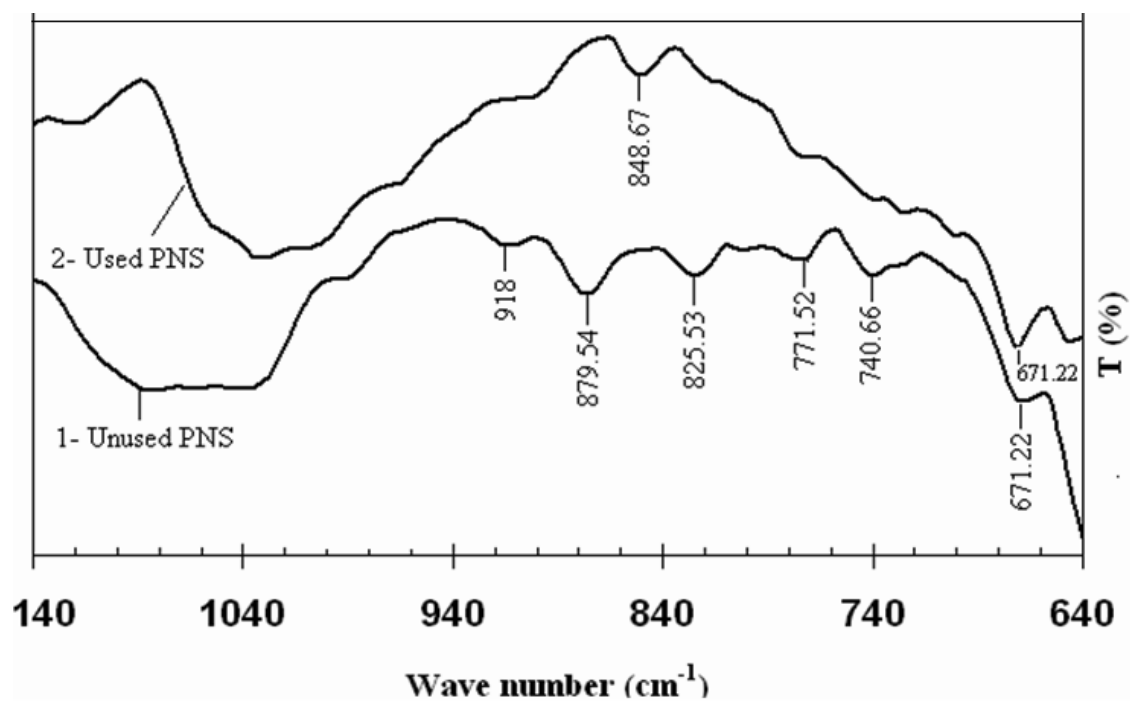


Fig. 4: Portion of the same FT-IR spectra from 640 to 1140 cm⁻¹ show changes before and after adsorption.

Surface Area Measurement

The BET surface area was determined from the nitrogen adsorption isotherm at 77 K using NOVA Quanta Chrome (NOVA 1200e). Before surface area determination each sample was degassed at 150 °C for 1 hour in nitrogen atmosphere. The surface area of PNS biosorbent was 1.78 m²/g.

Effect of pH on the adsorption of Cr (VI)

Solution pH for the metal ions uptake is one of the single most important parameter. The adsorption of Cr (VI) was studied in the pH range from 2 -7 keeping all the other parameters constant. It has been observed that as the pH increases the extent of adsorption of Cr (VI) decreases. Maximum Cr (VI) removal was observed at pH 2.0 and 3.0 as shown in Fig. 5. This could be explained that at low pH the dominant species is acid chromate ion species (HCrO₄⁻). The increase in initial pH of solution changes the HCrO₄⁻ to the other forms like CrO₄²⁻ and Cr₂O₇²⁻ [16].

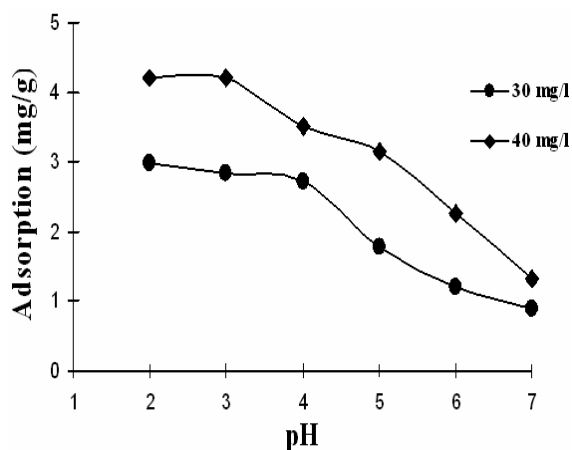
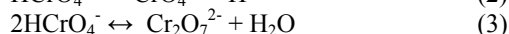
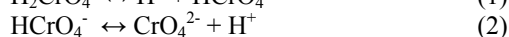
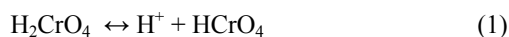
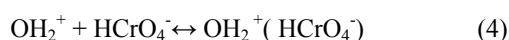


Fig. 5: Effect of pH on the adsorption of Cr (VI).

As in this scheme H⁺ is consumed, therefore, an increase in pH of the final solution is expected. On the other hand upon removal of HCrO₄⁻ a net production of hydroxide ions is produced in the solution as given in following equation [1].



At low pH the surface becomes positively charged which promotes the binding of the HCrO₄⁻ to

the positively charged surface [17, 18]. Secondly at high pH CrO₄²⁻ and Cr₂O₇²⁻ are the dominant species which are bulky in nature than HCrO₄⁻ and hence due to this, the repulsive forces among them are dominant than attractive forces of attraction between adsorbent and Cr (VI). This also leads to the less removal of Cr (VI) at high pH [18]. In addition the decrease in the adsorption of Cr (VI) at high pH might be due to the weakening of the electrostatic forces of attraction between the oppositely charged adsorbate and adsorbent [16]. The pH study showed that the optimum pH for Cr (VI) adsorption on PNS is from 2-4.

Effect of Contact Time on the Adsorption of Cr (VI)

Kinetic studies were performed to determine the contact time required to reach the equilibrium between the solid bound and free adsorbate in the solution. Other parameters such as pH (4), temperature (28±1 °C) and initial chromium concentration (40 mg/L) were kept constant. The adsorption in the first 20 minutes was slow but with the increase in contact time the rate of removal of chromium ions was increased until the equilibrium was established at 360 minutes. No significant adsorption has been observed after 360 minute as shown in Fig. 6. At the equilibrium position a maximum of ~88% adsorption was observed.

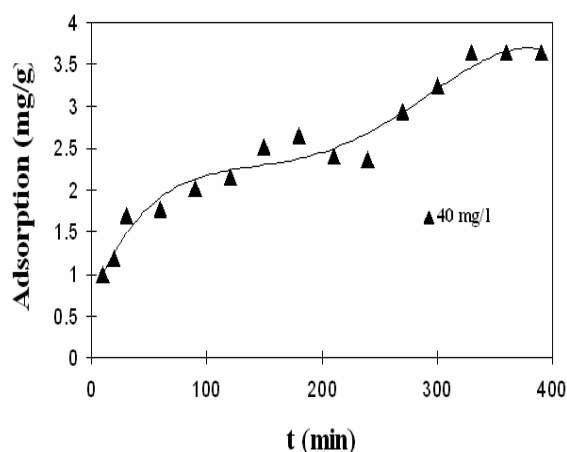


Fig. 6: Effect of contact time on the adsorption of Cr (VI).

Adsorption Kinetics

In order to find out mechanism that controls the adsorption process pseudo- first order and pseudo- second order rate equations were applied to the time study data. Pseudo-first order equation is used to determine the kinetic mechanism of the

adsorbate in the liquid solution and is commonly represented as

$$\ln(q_{e1} - q_t) = \ln q_{e1} - k_1 t \quad (1)$$

where k_1 is the rate constant min^{-1} of pseudo- first order equation, q_t is the amount of adsorbate adsorbed in time t and q_{e1} is the amount adsorbed at equilibrium for pseudo-first order equation. Both q_t and q_{e1} are in mg/g . The plot of $\ln(q_{e1}-q_t)$ vs t a straight line with a negative slope ($-k_1$) was obtained as shown in Fig. 7.

Same experimental data was applied to the pseudo-second order equation that is

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{1}{q_{e2}} t \quad (2)$$

where q_{e2} and q_t are the amount adsorbed at equilibrium and time t for pseudo-second order equation, k_2 (g min/mg) is the rate constant of the pseudo-second order equation.

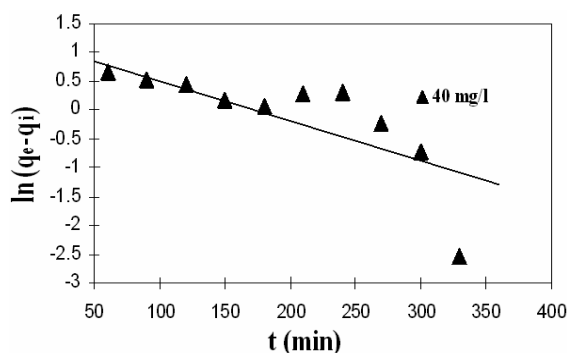


Fig. 7: Pseudo-first order equation determination

Plotting t/q_t vs t gives the straight line with slope ($1/q_{e2}$) and intercept ($1/k_2 q_{e2}^2$). The values of q_{e2} and rate constant k_2 were obtained from the slope and intercept of the straight line respectively (Fig. 8). The linearity of these graphs shows that pseudo-second order equation is best applicable to the adsorption data as compared to pseudo-first order equation due to its good regression coefficient value (R^2) as presented in Table-1.

Effect of Biomass Doses on the Adsorption of Cr (VI)

The extent of adsorption was studied with various biosorbent doses (0.2-1.0 g/40mL) as shown

in Fig. 9. Temperature (28 ± 1 °C), shaking speed (130 rpm), contact time (6 hours), pH (4) and initial Cr (VI) metal ions concentrations (30 and 40 mg/L), respectively were kept constant. The percent adsorption was increased from 66 to 100% and from 50 to 100% respectively due to the availability of more adsorption sites. However, the decrease in adsorption (mg/g) from 3.92 to 1.47 mg/g and from 4.22 to 1.68 mg/g was due to the fact that with the increase in adsorbent doses, chances of collision between the adsorbent particles enhances. This leads to the aggregation of the adsorbent molecules. This results in exposure of the actives sites of the adsorbent for the adsorption of Cr (VI) from aqueous solutions. On the other hand maximum amount of Cr (VI) adsorbed as the number of available active sites are exposed, resulting in the total increase in the removal efficiency.

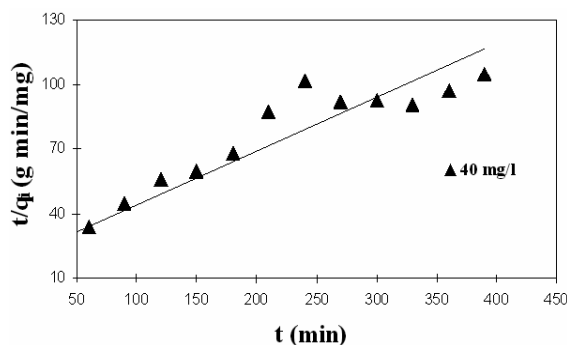


Fig. 8: Pseudo-second order equation determination

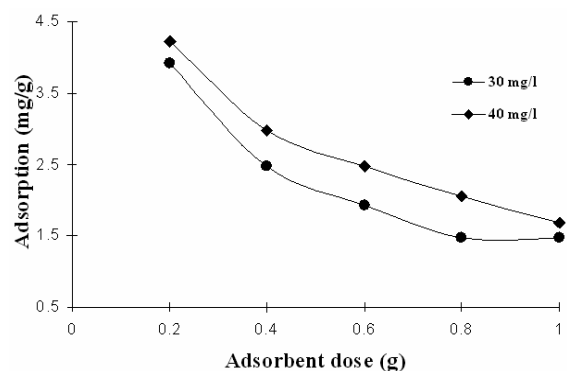


Fig. 9: Effect of adsorbent dosage on the removal of Cr (VI).

Table-1: Comparison of kinetic parameters of Cr (VI) biosorption onto Peanut shell biosorbent.

Concentration (mg/l)	Pseudo-first order equation model			Pseudo-second order equation model		
	$K_1(\text{min}^{-1})$	$q_{e1}(\text{mg/g})$	R^2	$K_2(\text{g.min. mg}^{-1})$	$q_{e2}(\text{mg/g})$	R^2
40	7.00×10^{-3}	3.29	0.6790	3.00×10^{-3}	4.01	0.9020

Effect of Temperature on the Adsorption of Cr (VI)

Effect of temperature on the adsorption of Cr (VI) was studied at three different temperatures (20, 30 and 40 °C). Shaking speed (130 rpm), contact time (6 hours), adsorbent dosage (0.4 g), pH (4) and initial concentrations of Cr (VI) metal ion were kept constant. When the initial Cr (VI) metal ion concentrations raised from 20 to 60 mg/L. It was found that the unit adsorption of Cr (VI) was increased at the biosorbent surface. The amount of Cr (VI) adsorption was increased with the rise in temperature (Fig. 10) due to the increase in the kinetic energy of the sorbent particles. Moreover, at high temperature due to the bond breaking of functional groups on the biosorbent surface there could be increase in the number of potential sites on the biosorbent surface, which may also increase the extent of adsorption with the rise in temperatures [13, 19]. As adsorbent is porous in nature and prospective of diffusion of the adsorbate could not be neglected. Therefore, the removal of Cr (VI) could be a diffusion controlled process and endothermic in nature. That could be the reason for the increase in uptake of Cr (VI) species with the rise of temperature [20]

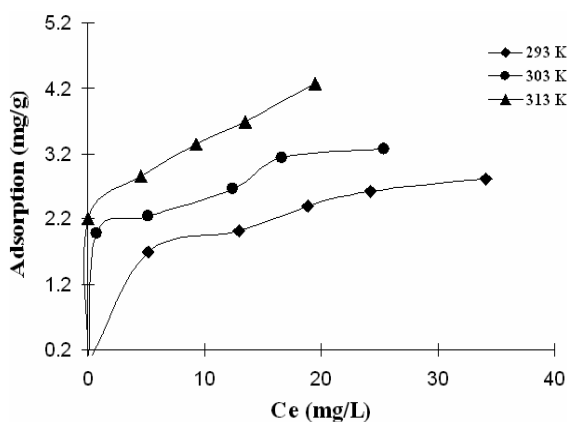


Fig. 10: Effect of temperature on the adsorption of Cr (VI).

Adsorption Isotherms

An adsorption isotherm is a graph of the amount adsorbed versus the pressure of the vapor phase or concentration in the case of adsorption from solution at constant temperature. Several models in literature have been reported to explain the experimental data. Among these adsorption isotherms Freundlich and Langmuir isotherms are most widely used to explain the biosorption equilibrium of the

heavy metal ions in the bulk solution and on the surface of biomass.

The Freundlich isotherm model suggests a monolayer adsorption with a heterogeneous distribution of the functional groups, accompanied interaction among the adsorbed molecules. The linear formula of Freundlich model is

$$\log X_a = \log K'_f + \frac{1}{n} \log C_e \quad (3)$$

The Langmuir model suggests that adsorbate uptake occurs on homogeneous surface by monolayer adsorption without the interaction of adsorbed ions/molecules. Additionally the model proposes identical energies of adsorption on the surface and no transmigration of the adsorbate (ions/molecules). The linear form of Langmuir equation is represented in the form of following equation given as

$$\frac{C_e}{X_e} = \frac{1}{K_l Q_{max}} + \frac{1}{Q_{max}} C_e \quad (4)$$

where X_e is the amount of the adsorbate adsorbed (mg/g) at equilibrium, C_e (mg/L) is the equilibrium concentration, K_l (L/mg) is the Langmuir equilibrium constant and Q_{max} (mg/g) is the total amount of the adsorbate required for complete monolayer coverage (mg/g).

Both the Freundlich and Langmuir isotherms were applied in the form of equations 3 and 4 as illustrated in Fig. 11 and 12. This indicates the linear relationship among the amount (mg) of Cr (VI) adsorbed per unit mass (g) of the biosorbent versus the concentration of Cr (VI) remained in solution (mg/L). The correlation coefficient ($R^2 = 0.9835$) value shows that Langmuir isotherm model is best applicable than the Freundlich isotherm model. Furthermore, study of the Langmuir isotherms was made on the basis of the dimensionless equilibrium constant (R_L), also recognized as separation factor which is described by equation 5.

$$R_L = \left(\frac{1}{1 + K_l C_o} \right) \quad (5)$$

where K_l is the Langmuir constant and C_o is the initial concentration of chromium (mg/L). The value of separation factor (R_L) is an indicator for the adsorption to be favorable or not. Adsorption is favorable when R_L value is between 0 and 1; as $R_L = 0$, adsorption is irreversible; $R_L = 1$, adsorption is linear and $R_L > 1$ interprets unfavorable adsorption. In

the present study the R_L values was found in between 0.0235 and 0.0633, showing the adsorption to be favorable [21].

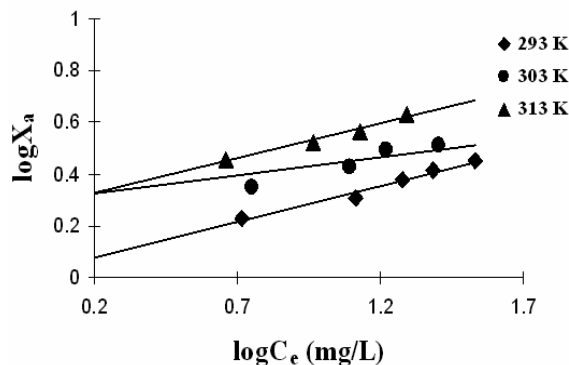


Fig. 11: Freundlich adsorption isotherms for the removal of Cr (VI) on the studied adsorbent.

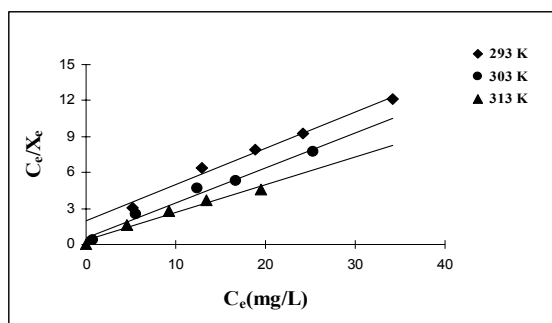


Fig. 12: Langmuir adsorption isotherms for the removal of Cr (VI) on the studied adsorbent.

q_{max} , K_L , K'_f , R^2 and n values of the Langmuir and Freundlich models were determined and are shown in Table-2.

Table-2: Langmuir and Freundlich isotherms constants.

Temperature (K)	Langmuir isotherms			Freundlich isotherms		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	n	K'_f (L/mg)	R^2
293	3.29	0.15	0.9867	3.58	1.05	0.9711
303	3.43	0.50	0.9835	3.83	1.43	0.9564
313	4.32	0.66	0.9717	3.70	1.87	0.9793

Thermodynamic Parameters

The thermodynamic parameters such as change in enthalpy (ΔH), change in free energy (ΔG) and change in entropy (ΔS) were determined by the following equations

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

$$\ln K_b = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

where as K_b is the Langmuir adsorption equilibrium constant, T is the adsorption temperature and R is the universal gas constant. From the plot of $\ln K_b$ vs $1/T$ as illustrated in Fig. 13 using equation 7 a straight was obtained from which ΔH and ΔS were calculated from the slope and intercept. From the positive value of ΔG it can be suggested that Cr (VI) adsorption onto PNS adsorbent is non-spontaneous in nature and requires small quantity of energy which is further supported by the positive value of ΔH [18, 22]. The decrease in the values of ΔG with the rise in temperature indicated that the system favors spontaneity at higher temperatures. The positive value of enthalpy (ΔH) indicates that the adsorption is endothermic in nature. The numerical value of ΔS implies randomness at solid surface of the sorbent in solution [23, 24]. The values of ΔH , ΔS and ΔG have presented in Table-3.

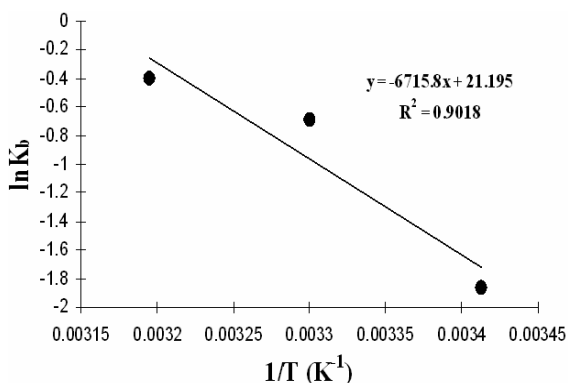


Fig. 13: Determination of thermodynamics parameters by Von t Hoff equation.

Table-3: Thermodynamic parameters of Cr (VI) adsorption on Peanut shell adsorbent.

Temperature (K)	ΔG (kJ. mol ⁻¹)	ΔS (J.mol ⁻¹ K ⁻¹)	ΔH (kJ. mol ⁻¹)
293	4.20		
303	2.44	176.22	55.83
313	0.67		

Comparison of the Present Study with other Studied Adsorbents

The adsorption capacity of the biosorbent used in the present study was compared to the adsorbents already studied. These results have been shown in Table-4.

Table-4: Adsorption capacities of various adsorbents reported in literature.

S.No	Adsorbents	Adsorption (q_{max})	Optimum pH	References
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1	AC (GA-3)	69.30	3.20	[25]
2	Eucalyptus bark	45.00	2.00	[26]
3	Wool	8.66	2.00	[1]
4	Distillery sludge	5.70	2.50	[27]
5	Coconut tree sawdust	3.46	3.00	[10]
6	Sawdust	3.30	6.00	[28]
7	Clinoptilolite	2.40	4.00-5.00	[29]
8	Red mud	1.60	5.20	[30]
9	Peanut shell	4.32	4.00	Present study

The results obtained from the present study are comparable to the other adsorbents in some cases. The adsorption capacities vary with the adsorbate concentrations, experimental conditions and surface modification. The low-cost biosorbent used in the present study is comparatively well suited to take care of Cr (VI) affected effluents.

Experimental

Materials and Method

All the chemicals used in the present work were of high percent purity and were used as such without further purification. $K_2Cr_2O_7$, H_2SO_4 , NaOH and $C_{13}H_{14}N_4O$ were purchased from Scharlue and Sigma Aldrich.

Preparation of Biosorbent

PNS biosorbent used in the present study were obtained from the local market of Qissa Khwani Bazar, Peshawar, Pakistan. The collected PNS were washed several times to make it free from dirt. These were dried and then grinded to achieve fine particles. Grinding of the biosorbent is a common practice because the fibrous nature of biosorbents do not allow the adsorbates to accumulate in the vicinity if not grinded finely. Subsequently the biosorbent was then sieved with 170 mesh ($\leq 88 \mu m$). The sieved particles were again washed several times with tap water to remove dust particles followed by washing with de-ionized water till all the apparent impurities such as dust, color etc were completely removed. Then it was dried at a temperature of $110^\circ C$ in an oven for 24 hours and was used as such when required.

Batch Biosorption Experiments

A series of experiments were performed in a batch mode technique for the biosorptive removal of Cr (VI) from aqueous solution on the PNS biosorbent for a particular period of time (360 minutes). Stock solution (1000 mg L^{-1}) of Cr (VI) was prepared by dissolving the required amount of $K_2Cr_2O_7$ in double distilled water. Test solutions of Cr (VI) were prepared from the stock solution by dilution method.

Known volume (40 mL) of each test solution was taken in conical flask and biosorbent doses were added to them. The pH of these solutions was adjusted by a pH rod with 0.1 M HCl and 0.1 M NaOH. After this, the batch biosorption experiments were performed at $28 \pm 1^\circ C$ with a shaking speed of 130 rpm for 360 minutes. Then the solutions were filtered after adsorption.

UV-Vis Spectra (UV-160A SHIMADZU Japan) determined the change in concentration of the filtrates. The reaction between Cr (VI) ions of filtrate and 1, 5-Diphenyl Carbazide ($C_{13}H_{14}N_4O$) developed a purple colored complex in the acidic medium of solution [31]. The absorbance and concentrations of reaction mixture (filtrate of test solution) were determined at a wavelength of 540 nm. The concentration of test solutions remained after adsorption was determined with the help of calibration curve. The amounts of Cr (VI) adsorbed in percent and in per gram (mg/g) were calculated by using equation 8 and 9.

$$R\% = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (8)$$

$$Q_{ad} = \left(\frac{C_i - C_e}{W} \right) \times V \quad (9)$$

where C_i (mg/L), C_e (mg/L), V (mL) and W (g) are the initial Cr (VI) concentration, equilibrium Cr (VI) concentration, known volume (mL) of Cr (VI) solutions and dry weight of the biosorbent respectively.

Conclusions

- Biosorption of Cr (VI) was strongly dependent on pH, adsorbent dosage and initial chromium concentration.
- The experimental data was best described by the Langmuir adsorption isotherms as compared to the Freundlich adsorption isotherms.
- The pseudo-second order kinetic model agrees well to the dynamic data for Cr (VI) biosorption onto PNS biosorbent surface.
- The numerical values of ΔH , ΔS and ΔG showed that the adsorption of Cr (VI) onto PNS is endothermic, entropy driven and non spontaneous in nature at the studied temperatures.
- The adsorption capacity of PNS for Cr (VI) adsorption in term of monolayer capacity (Q_{max}) was 4.32 mg/g .

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