



# Adsorption Process for Wastewater Treatment by using Coconut Shell

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## Abstract

Adsorption of heavy metal on the solid surfaces is an important technique to remove them from the industrial wastewaters. The purpose of the present study is to evaluate the ability of agro-waste material coconut shell to remove Cr (VI) from wastewater. The extent of removal was found to be dependent on pH, contact time, adsorbent dose, concentration of metal and particle size. The adsorption follows a first order kinetics. The adsorption process is endothermic with a maximum adsorption of 83 percent at 30° C for an initial concentration of 50 mg/l at pH 1.5. Thermodynamics parameters indicate the feasibility of the process. Column studies have been carried out to compare these with batch capacities.

**Keywords:** Adsorption, Cr (VI), industrial wastewater, coconut shell.

## Introduction

In recent years the use of adsorption technique for the removal of heavy metals has received global attention<sup>1</sup>. Several researchers have been working on the heavy metals removal. However, most of them have used commercially available activated carbon in their studies. The high cost of activated carbon and its loss during the regeneration restricts its application. Thus there is need to undertake studies to substitute the costlier commercial activated carbon with the unconventional, low cost and locally available agricultural waste adsorbents<sup>2,3</sup>. India is an agricultural country and generates considerable amount of agricultural wastes such as sugar cane bagassess, coconut jute, nut shell, rice straw, rice husk, waste tea leaves, ground nut husk, crop wastes, peanut hulls, fertilizer wastes etc. Successful studies on these materials could be beneficial to the developing countries and could be easily incorporated in development of appropriate technologies. The successful utilization of agricultural waste in the treatment of wastewater would be quite economical due to its high adsorption capacity<sup>4-8</sup>.

The widespread use of chromium has caused large amounts of chromium waste to be disposed of into the environment and, unlike metals such as cadmium and lead, the different toxicity of trivalent and hexavalent chromium makes the assessment of potential health risks a challenging undertaking. Hexavalent chromium compounds tend to be more mobile and toxic than trivalent chromium compounds<sup>10</sup>. There is an abundance of literature documenting the carcinogenicity of several hexavalent chromium compounds. Furthermore, exposure to hexavalent compounds has been found to cause ulceration of the skin, perforation of nasal septum, inflammation of the larynx and damage to the kidneys and lungs. On the other hand, trivalent chromium has been found to be an essential trace element in the

human diet and deficiency in trivalent chromium has been linked with poor sugar metabolism<sup>11</sup>.

The stability of the various chromium species is dependent upon the various reduction, oxidation and pH conditions. The stable domains for various chromium species in aqueous system are affected by the oxidation potential ( $E_h$ ) and pH<sup>12</sup>. Under the pH (<3), temperature (20-30°C) and reducing - oxidizing conditions commonly found in industrial wastewaters, the predominant species are bicarbonate,  $\text{HCrO}_4^-$ , dichromate  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Cr}^{+3}$ . It is interesting to note that the divalent chromium ions,  $\text{Cr}^{+2}$ , may be found in extremely reducing environment. The concentration distribution between  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  is largely governed by the total Cr (VI) present. The fraction of  $\text{Cr}_2\text{O}_7^{2-}$  only becomes significant at high concentration of total Cr (VI)<sup>13</sup>. The distribution of Cr (VI) species as function of pH for total Cr (VI) covering from  $10^{-4}$  M to  $6 \times 10^{-3}$  M (or 5.2 to 312 ppm as Cr), an average concentration range which generally occurs in most industrial wastewaters<sup>14</sup>.

It is obvious that treatment of electroplating wastewaters prior to municipal discharge is necessary to alleviate this problem. However, the current methods of treatment are both expensive and inconsistent in operation due to poor selectivity. Ion exchange is unpredictable and inefficient due to many interfering agents present in the system. Recently a few researchers have explored the possibility of using agricultural waste adsorbent for the Cr (VI) removal<sup>15-18</sup>.

## Material and Methods

**Collection of Samples:** Aligarh is a medium sized semi industrialized town located in northern India 135 Km South – East of New Delhi. The city is famous for the manufacturing of locks and other building materials for the indigenous as well as

exports markets. A number of water samples from various parts of the town were analyzed to identify the contaminated ground and surface waters. The samples of electroplating effluents were also collected from the discharge points of the factory / surroundings and ground water samples in its nearby and stored as per standard methods before analyzing the physico-chemical parameters. All the samples were tested for detection of pH, chloride, alkalinity, suspended solids, fluoride, total dissolved solids and heavy metal (chromium) contamination. The study reveals that most of the places the ground water is safe for drinking purpose, except a few places where the ground water was observed to be hard and contained chromium (VI) contamination. However the chromium contamination in the surface water was found above the prescribed safe limit. In order to have waste of uniform characteristics and to avoid interference with other impurities the laboratory wastewater was prepared by dissolving a known amount of potassium dichromate in a known volume of distilled water. For 1000 mg/l-hexavalent-chromium concentration 2.282 g  $K_2Cr_2O_7$  (AR Grade) is dissolved in 1.0 L of distilled water.

**Adsorbent:** The coconut shell was first dried at a temperature of 150 °C for 5 hours. After grinding it was sieved to obtain particle size of 600 micron, 300 micron, 150 micron and 150 micron (Indian Standard Sieve). It was then washed several times with distilled water to remove dust and other impurities. Finally it was dry again in an oven at 50 °C for 6 hours. The adsorbent was then stored in desiccator for the final studies.

**Batch Studies:** In order to understand the adsorption behavior a number of batch studies have been conducted to investigate the effect of adsorbent dose and contact time, pH, concentration of metal, and particle sizes. For these studies, wastewater of various concentrations of Cr (VI) was prepared from the stock solution and kept separately in glass stoppered conical flasks. Then suitable doses of adsorbent were added to the wastewater. The system is equilibrated by shaking the contents of the flasks at room temperature so that adequate time of contact between adsorbent and the metal ion is maintained. The suspension is filtered through Whatman No. 1 filter paper and the filtrate is analyzed to evaluate the concentration of Cr (VI) metal in the treated wastewater by using atomic absorption spectrophotometer. All the analyses have been carried out according to the Standard Methods.

**Column Studies:** Column studies were conducted using a glass column (Internal diameter =1.0 cm). Adsorbent was suspended in distilled water for 15 minutes by shaking in a beaker at the speed of 150 rpm, and then transferred in to the glass column. The glass wool was kept at the bottom and top ends in order to avoid its loss with the liquid flow or floating. The flow rate was

maintained at 1.0 l / d.

## Results and Discussion

The results obtained from the above studies have been discussed with plausible explanations as follows:

**Effects of Adsorbent dose and Particle size on Fraction Adsorbed:** The response of adsorbent dose and contact time on the removal of Cr (VI) is presented through Figure 1. The observation reveal that an increase in the fraction adsorbed of Cr (VI) occurs with corresponding increase in the dose of coconut shell up to certain level, beyond which the fraction adsorbed remains constant. It is evident that a dose of 10g/l is sufficient to remove 53.3 - 84.1% Cr (VI) for 75 um particle size. The increase in the removal efficiency with simultaneous increase in adsorbent dose and particle size is due to the increase surface area and hence more active sites are available for the adsorption of Cr (VI)

**Influence of pH and particle size on Fraction Adsorbed:** Influence of pH and particle size on fraction adsorbed is shown in Figure 2. The results show the maximum removal efficiency is observed at pH 1.5 for 75 um size particle. While on increasing the pH value it decreases. About 36 % removal efficiency is recorded at neutral pH 7. One of the reasons for the better adsorption capacity observed at low pH values may be attributed to the large number of  $H^+$  ions present at these pH values, which in turn neutralize the negatively charged hydroxyl group (-OH) on adsorbed surface thereby reducing hindrance to the diffusion of dichromate ions. At higher pH, the reduction in adsorption may be possible due to abundance of  $OH^-$  ions causing increased hindrance to diffusion of positively charged dichromate ions. It is the common observation that the surface adsorbs anions favorably in low pH range due to the presence of  $H^+$  ions<sup>19</sup>. whereas, the surface is active for the adsorption of cations at higher pH values due to the accumulation of  $OH^-$  ions<sup>20</sup>

**Effects of various initial Cr (VI) concentrations and particle size on fraction adsorbed:** The effects of initial Cr (VI) concentrations on fraction adsorbed (figure-3) were studied over the wide range of chromium concentration (5-100 mg/l). It may be observed that the chromium uptake is rapid during the initial period of adsorption and the maximum removal (86- 100%) is achieved at 5-20 mg/l concentration for 75 um size particle. The removal efficiency of chromium decreases when chromium concentration is increased. However the removal efficiency is recorded as 87.3 % at a concentration of 50 mg/l. In a similar study<sup>7</sup> obtained 90% removal efficiency at a Cr (VI) concentration of 10 mg/l in a dose of 1.0 g/100 ml at a contact time of 1.5 hr when the pH of the solution was 2.0.

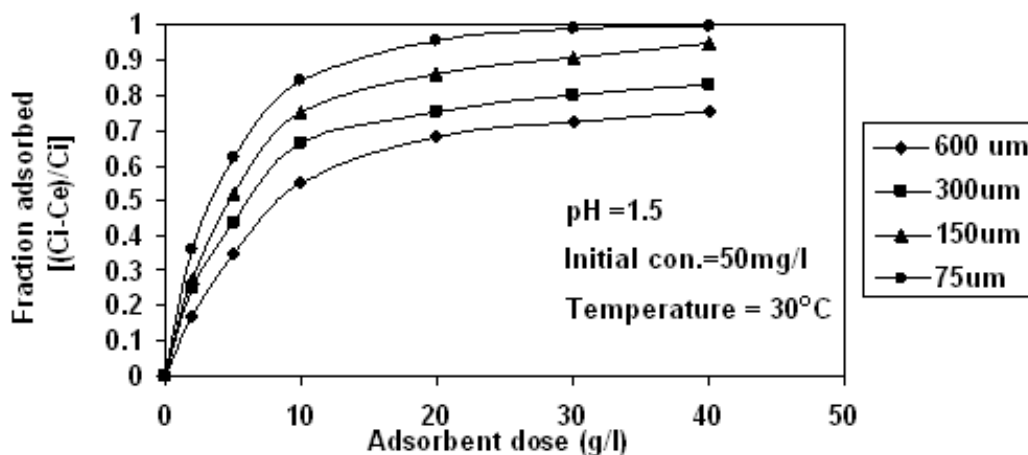


Figure-1  
 Effect of adsorbent dose and different particles sizes on fraction adsorbed

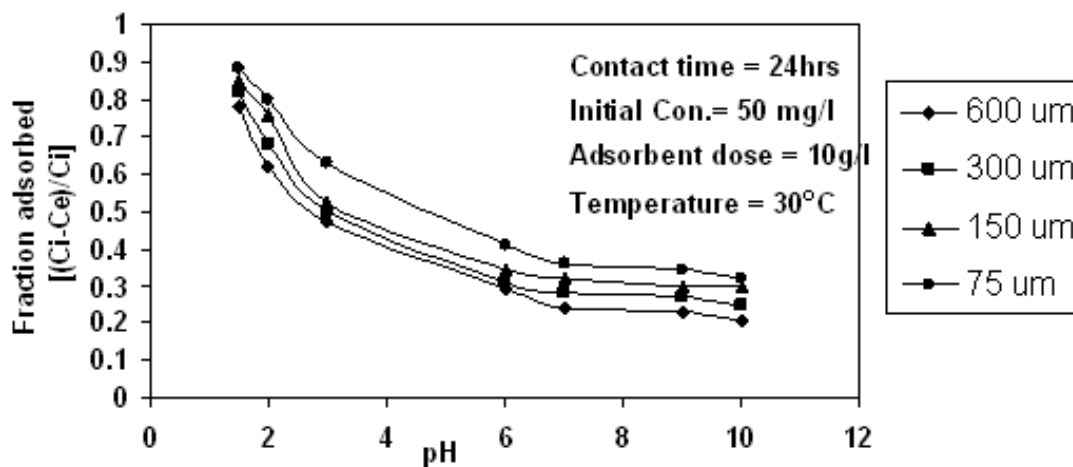


Figure-2  
 Effect of pH on adsorption

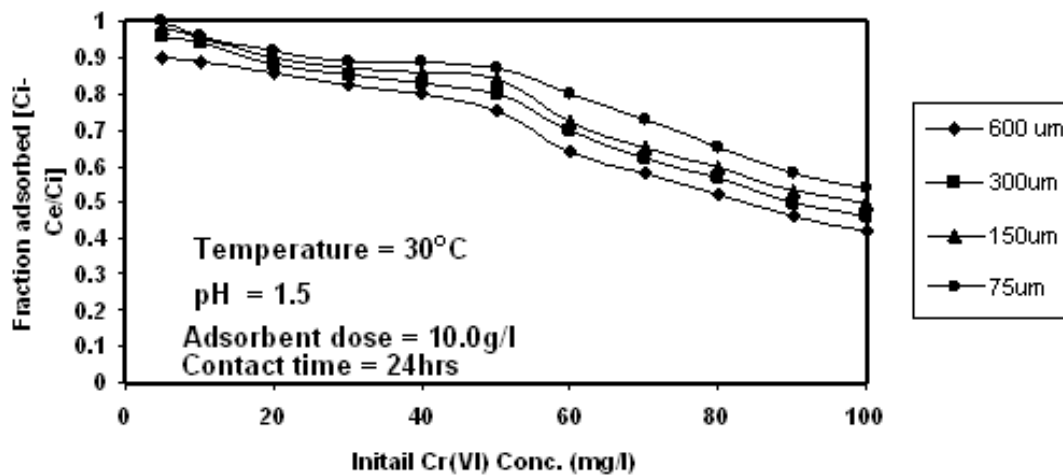


Figure-3  
 Effect of initial Cr(VI) concentration and different particle sizes on fraction adsorbed

**Effect of variation of contact time and different particles sizes on fraction adsorbed:** The adsorbent particle size has significant influence on the adsorption time and kinetics of adsorption. The influence of particle size furnishes important information for achieving optimum utilization of adsorbent and on the nature of breakthrough curves for designing packed bed adsorbers. Three particle sizes 75 micron, 150 micron, 300 micron and 600 micron sieve (Indian standard Sieves) under optimal conditions of adsorbent dose, pH and contact time with an initial adsorbate concentration of 50mg/l were studied. A plot fraction adsorbed against contact time shown in figure-4 indicates that, with an increase in adsorbent particle size, fraction decreases. This may be explained on the basis of the active surface area available for the adsorption, which is greater for small particle sizes<sup>21</sup>. Finer adsorption material offers a significantly lesser mass transfer diffusion resistance in micropores.

**Adsorption Isotherms:** Experimental evaluation of isotherm constants is a standard practice for judging the feasibility of an adsorbing system. Batch experiments were performed to obtain data and were analyzed using the Freundlich and Langmuir models<sup>22</sup>

Langmuir can be represented by the following mathematical relationship.

$$\frac{1}{\frac{x}{m}} = \frac{a + bC}{1 + aC} \quad (1)$$

$$\frac{1}{\frac{x}{m}} = \frac{1}{b} + \frac{1}{a + bC} \quad (2)$$

Where x = amount of material adsorbed (mg), m = weight of the adsorbent (mg), C = concentration of material remaining in solution after adsorption is complete (mg/l), a and b = empirical constants, a linear plot should result when the quantity 1/ (x/m)

is plotted against 1/C. The constants a and b can be determined from the slope and intercept of the plot (figure-5). The essential features of the Langmuir isotherm can be expressed in terms of dimensionless separation factor  $R_L$ .

$$R_L = \frac{1}{(1 + b C_i)} \quad (3)$$

Where  $C_i$  is the initial concentration and b is the Langmuir constant, separation factor  $R_L$  indicates the isotherm shape. The values are given in table-1. If  $R_L > 1$  the nature of adsorption is unfavorable,  $R_L = 1$  the nature of adsorption is linear,  $0 < R_L < 1$  the nature of adsorption is favorable,  $R_L = 0$  the nature of adsorption is irreversible

$$q_e = \frac{x}{m} = K C_e^{1/n} \quad (4)$$

Freundlich adsorption isotherm model applied to equilibrium data is expressed as,

The above equation is also referred as Van - Bemmelen equation. Fitting into the logarithmic form

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \quad (5)$$

$$\log \left[ \frac{(C_i - C_e)}{C_i} \right] = \log K + \frac{1}{n} \log C_e \quad (6)$$

Where, x/m is the amount of Cr (VI) adsorbed per unit mass of adsorbent (mg/mg) and  $C_e$  is the equilibrium concentration of aqueous solution. K is a constant, which is measure of adsorption capacity, and 1/n is a measure of adsorption intensity (figure-6). Langmuir and Freundlich adsorption isotherm constants are shown in table-1.

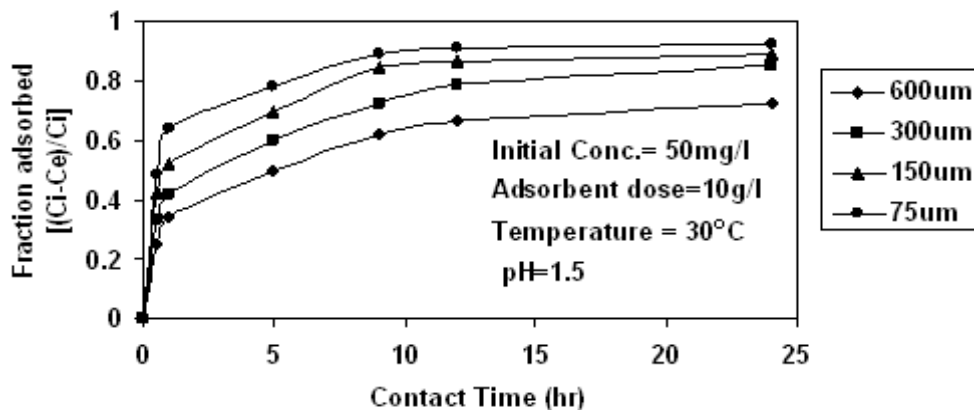


Figure-4  
 Effect of contact time and particle size on fraction adsorbed

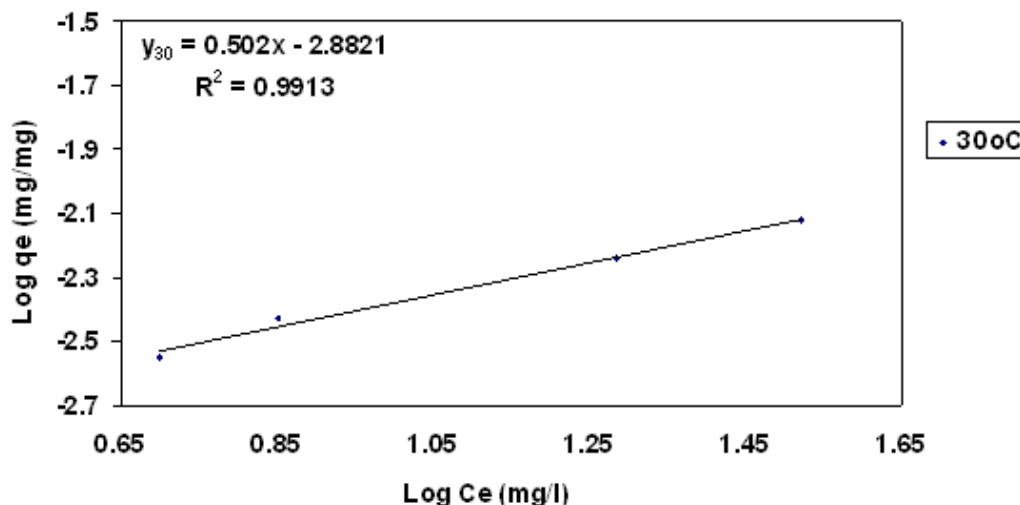


Figure-5  
 Freundlich adsorption isotherm

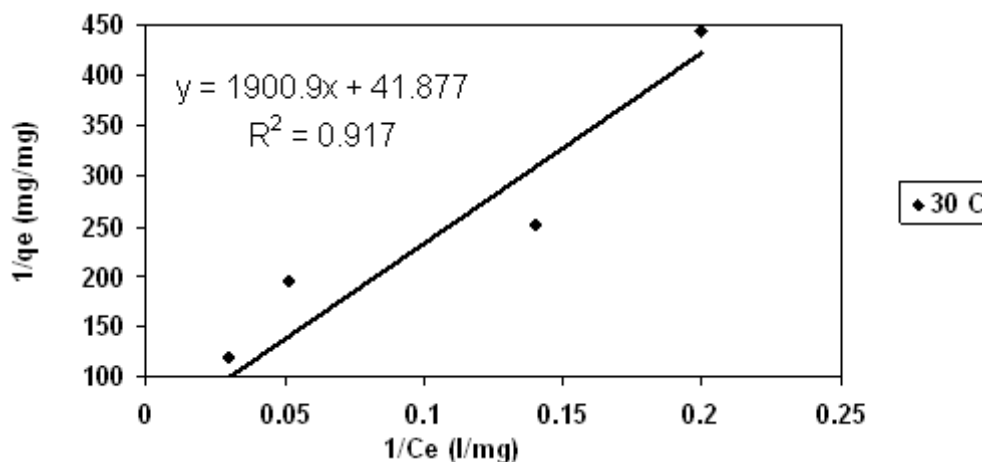


Figure-6  
 Langmuir adsorption isotherm

Table-1  
 Values of Langmuir and Freundlich Isotherms Constants

Temperature	Langmuir Constants				Freundlich Constants			Recommended Isotherms
	a	b	Cc	R <sub>l</sub>	K	1/n	Cc	
30 <sup>0</sup> C	1900.9	0.0220	0.917	0.476	.0013	0.502	0.991	$0.00131Ce^{0.502}$

**Kinetics of Adsorption:** The kinetic modeling for the removal of chromium (VI) by coconut shell has been carried out using the following first order rate expression

$$\log(qe-q) = \log qe - \left( \frac{K_{ad}}{2.303} \right) t \quad (7)$$

Which is nothing but a Lagergren equation. Where q and qe are the amount adsorbed at equilibrium and any time t respectively. The straight line plots of  $\log(qe-q)$  Vs t for the adsorption show the validity of Lagergren equation and suggest the first order kinetics (Figure 7). The rate constant  $K_{ad}$  is  $0.2194^{23}$ .

**Thermodynamic Parameters:** The apparent heat change ( $\Delta H$ ) related to Langmuir constant b, and should follow the Van't Hoff equation

$$\ln b = \ln b_0 - \frac{\Delta H}{R T} \quad (8)$$

The enthalpy changes of sorption as calculated from the slope of  $\ln b$  Vs  $1/T$  (figure-8) is found 14.23 KJ/mole. The positive  $\Delta H$  values confirm the endothermic nature of the sorption process and suggest the possibility of strong binding between sorbate and sorbent.

The change in free energy ( $\Delta G$ ) and ( $\Delta S$ ) are calculated using the following relationships.

$$\Delta S = -RT \ln \left( \frac{1}{b} \right) \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (10)$$

The negative values of  $\Delta G$  indicates the process to be feasible and spontaneous<sup>24</sup> (Singh et al.1982) and positive values of entropy reflected the affinity of the adsorbent material. The values of  $\Delta G$  and  $\Delta S$  are listed in table 2.

mass of adsorbent versus square root of time is shown in figure 9. It is seen from this plot that there are two distinct linear sections, the initial steep linear portion and the final relatively flat linear part. The initial linear part indicates that the interparticle diffusion, the latter, less steeper linear, part suggested that adsorption is being controlled by the micropores.

Table-2

Thermodynamic Parameters at Different Temperatures

Temperature (°K)	- $\Delta G$ Kj/mole	$\Delta S$ j/mole
303	9.614	78.693

**Interparticle Diffusion Rate:** Plot of amount adsorbed per unit

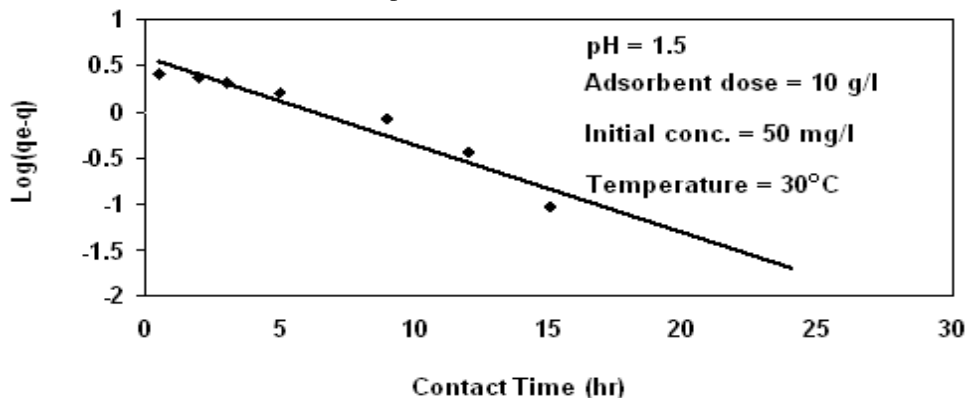


Figure-7  
 Lagergren plot

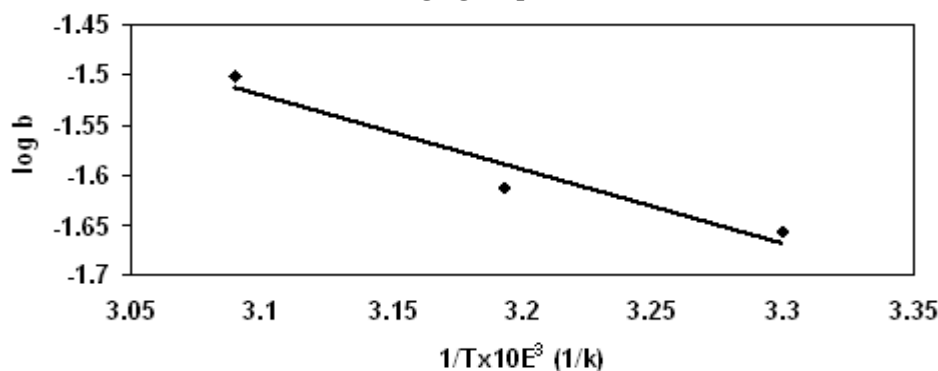


Figure-8  
 Vant Hoff plot

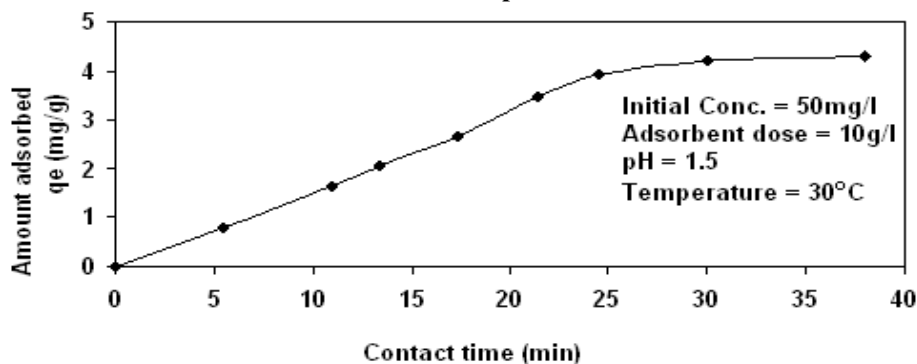


Figure-9  
 Interparticle diffusion plot

**Column Study:** The breakthrough curve plotted in Figure 10. The column was run till the coconut shell in the adsorption column gets exhausted and the treated effluent was analyzed at different time intervals. Column capacities were found greater than the batch capacities due to continuously large concentration at the interface of the sorption zone as the sorbate solution passes through the column while the concentration gradient decreases with time in a batch process<sup>25</sup>.

**Desorption Test:** Desorption test was conducted for coconut shell after their use in the equilibrium adsorption studies. About 10 g of saturated adsorbent was placed in an 300 ml capacity stoppered BOD bottle with double distilled water and was shaken at room temperature for over two hours. After this the adsorbent was filtered and the suspension was analyzed for the chromium content. No chromium was detected in the water. Thus it indicate that adsorbed chromium was not being desorbed.

## Conclusion

The following conclusions can be drawn from the present study: The percentage removal of the chromium is found to increase with decrease in chromium concentration, increase in adsorbent dose and decrease in particle size. The removal is found rapid in initial stages followed by slow adsorption up to saturation limit. An adsorbent dose of 10 g/l is sufficient to remove 83 % Cr (VI) from the wastewater having an initial concentration of 50 mg/l. The chromium uptake capacity of coconut shell investigated is found to be high in the lower pH (1.5). Chromium adsorption follows first order rate equation. The negative values of free energy changes indicate the spontaneous nature of the process. Positive values of enthalpy change indicate towards the endothermic nature of the adsorption. The adsorption data obtained is found to fit well the Freundlich isotherm, Plot of amount adsorbed versus square root of the time show that

Interparticle diffusion is the rate controlling step. The data obtained during the present study is quite useful in developing an appropriate technology for the designing a wastewater treatment plant for the removal of chromium (VI). Coconut shell exhibits a high degree of Cr (VI) removal and it can be utilized for the treatment of industrial wastes containing chromium (VI) concentrations between 10-100 mg/l. Regeneration studies are not necessary with the view that the cost of the adsorbent is very low and it can be disposed off safely.

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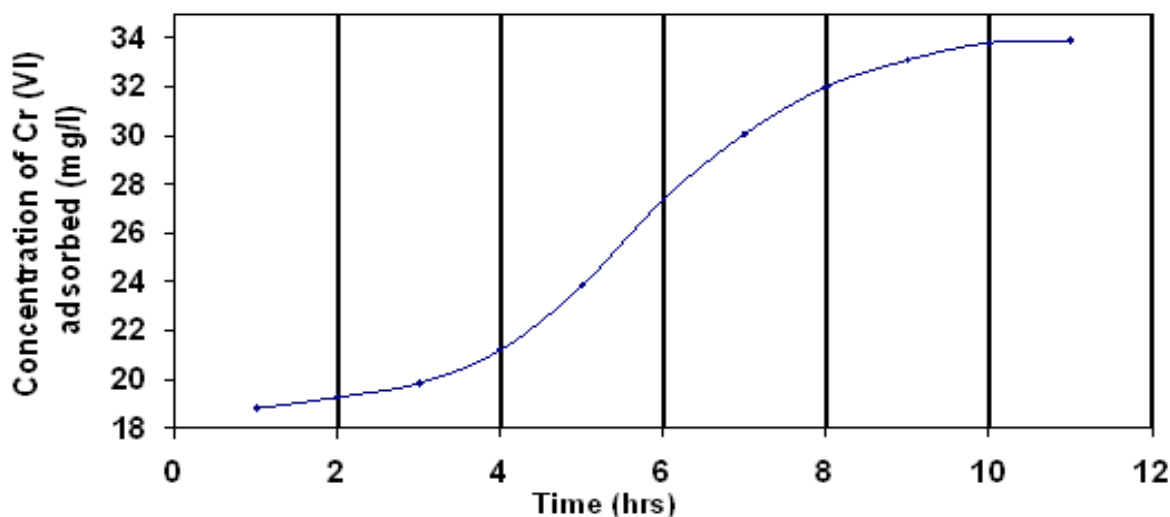


Figure-10  
Breakthrough curve

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