

Adsorption Process for Removal Chromium from Electroplating Wastewater by using Coconut Shell

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ABSTRACT

The electroplating wastewater industry is one of the major industries which generate a large portion of wastewater containing heavy metals. Electroplating units mostly scattered in urban areas. 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 electroplating wastewater. The extent of removal was found to be dependent on pH, contact time, adsorbent dose, and 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 indicates the feasibility of the process. Column studies have been carried out to compare these with batch capacities. The adsorption data obtained is found to fit well the Freundlich.

Keyword: adsorption, electroplating wastewater, Cr concentration, Cr(VI), coconut shell

1. INTRODUCTION

In recent years the use of adsorption technique for the removal of heavy metals has received global attention [1]. 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 [2]. 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 ([3,4].

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 as affected by the oxidation potential (E_h) and pH (Landrigan 1975). Under the pH (< 3), temperature (20-30°C) and reducing - oxidizing conditions commonly found in industrial wastewaters, the predominant species are bicarbonate, HCrO_4^- , dichromate $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{+3} . It is interesting to note that the divalent chromium ions, Cr^{+2} , may be found in extremely reducing environment. The concentration distribution between 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) (Stumm, 1970). The distribution of Cr (VI) species as function of pH for total Cr (VI) covering from 10^{-4} M to 6×10^{-3} M (or 5.2 to 312 ppm as Cr), an average concentration range which generally occurs in most industrial wastewaters. 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 [5].

2. 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 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 $\text{K}_2\text{Cr}_2\text{O}_7$ (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 75 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 150 °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.

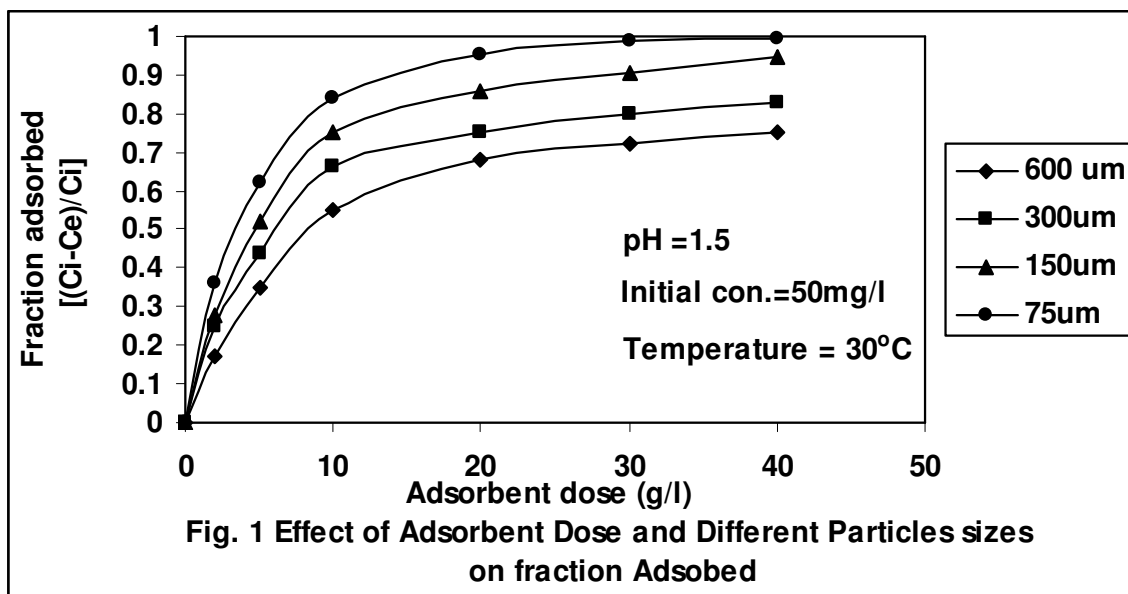
3. RESULTS AND DISCUSSION

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

4. 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).

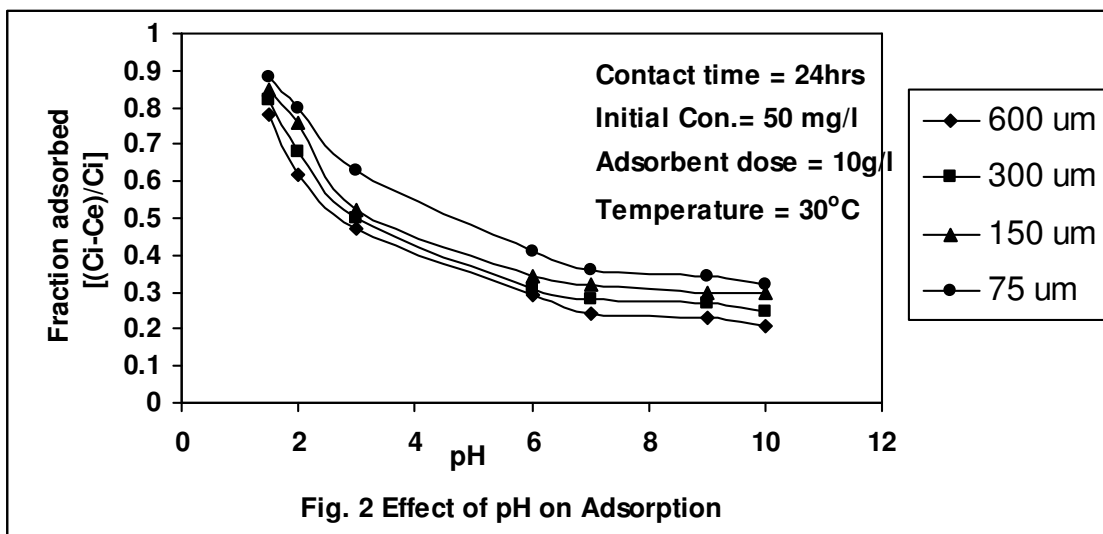


Influence of pH and particle size on Fraction Adsorbed

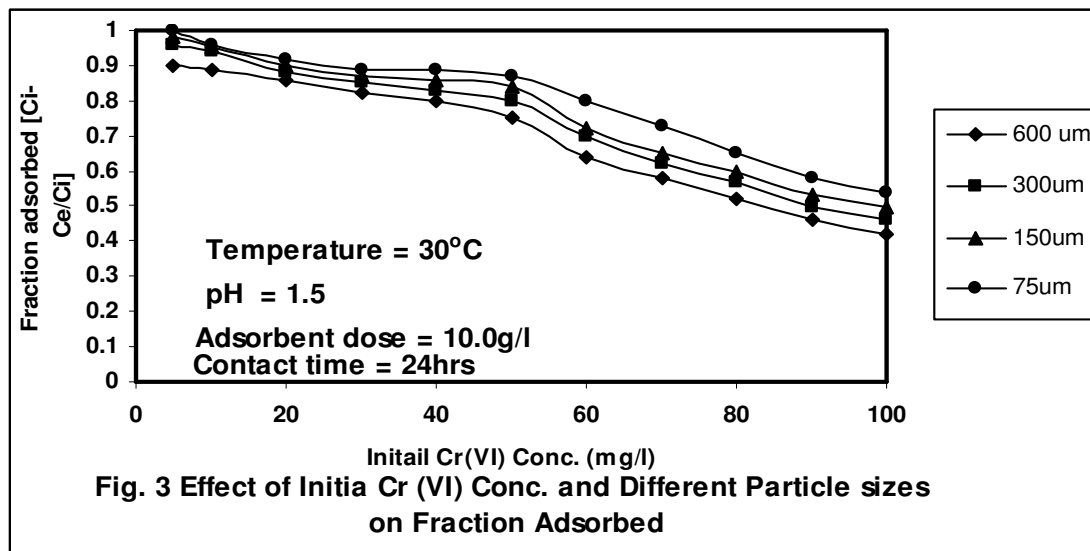
Influence of pH and particle size on fraction adsorbed is shown in Figure 2. The results show the maximum removal efficiency is observed at pH 1.5 for 75 um size particle. While on increasing the pH value it decreases. About 36 % removal efficiency is recorded at neutral pH 7. One of the reasons for 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 [6].

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 [7] 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.



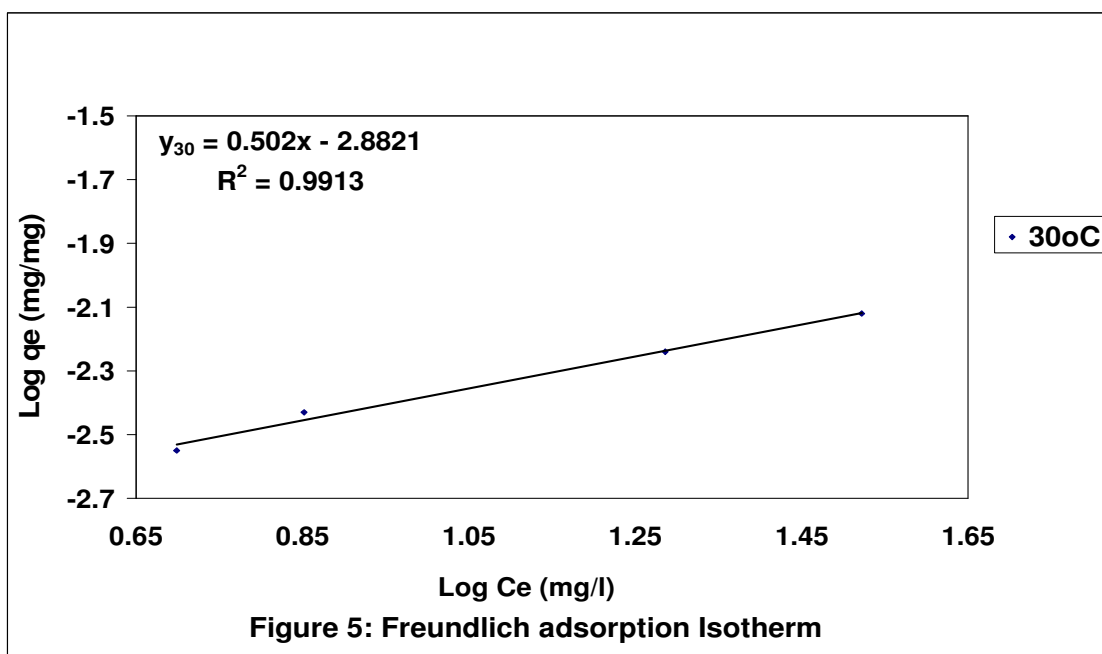
Effects of various Initial Cr (VI) Concentrations and particle size on Fraction Adsorbed.



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 absorbers. 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. Finer adsorption material offers a significantly lesser mass transfer diffusion resistance in microspores.

Adsorption Isotherms



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

$$q_e = \frac{x}{m} = K C_e^{1/n} \quad \text{IV}$$

The above equation is also referred as Van - Bemmelen equation. Fitting into the logarithmic form (Mahesh et al., 1999).

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \quad \text{V}$$

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

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.

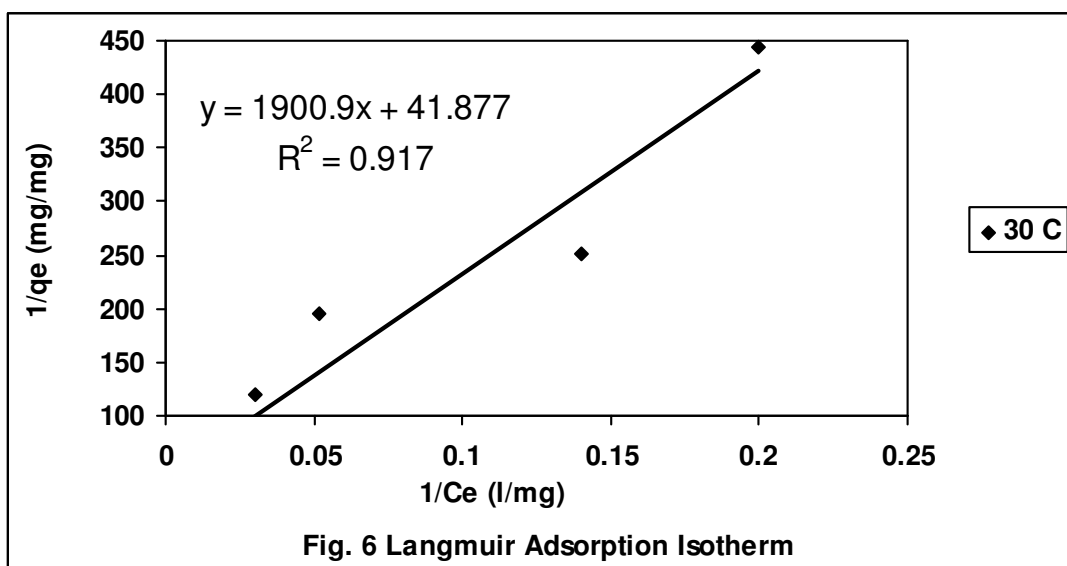


Table 1: Values of Langmuir and Freundlich Isotherms Constants

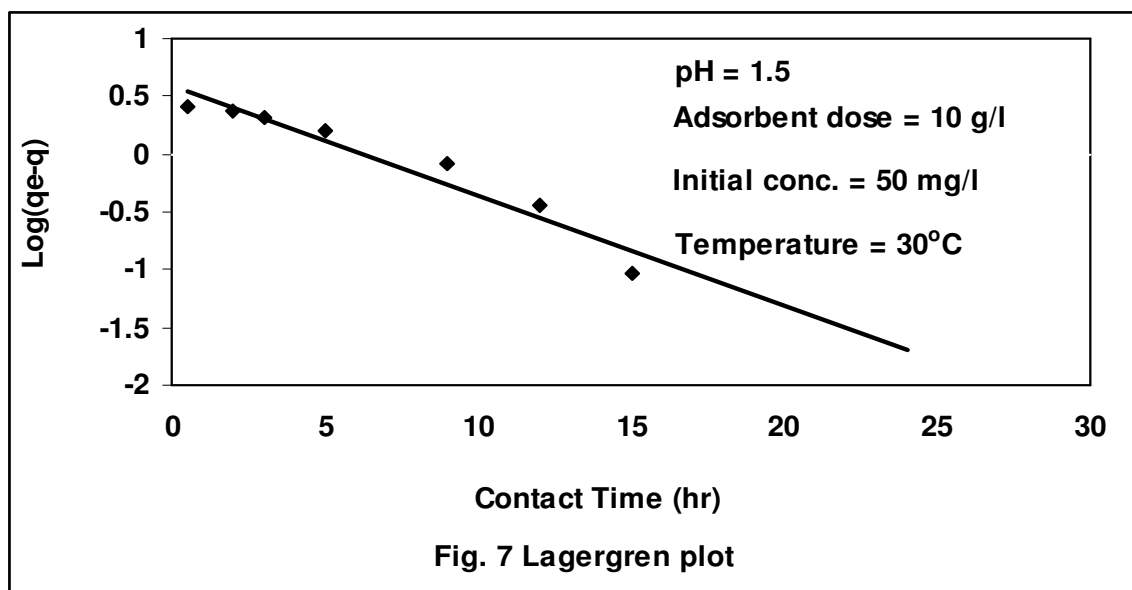
Temperature	Langmuir Constants				Freundlich Constants			Recommended Isotherms
	a	b	Cc	R _l	K	1/n	Cc	
30 ⁰ C	1900.9	0.0220	0.917	0.476	.0013	0.502	0.991	0.00131Ce ^{0.5} ₀₂

5. KINETICS OF ADSORPTION

$$\log(q_e - q) = \log q_e - \left(\frac{K_{ad}}{2.303} \right) t \quad \text{VII}$$

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

Which is nothing but a Lagergren equation. Where q and q_e are the amount adsorbed at equilibrium and any time t respectively. The straight line plots of $\log(q_e - q)$ 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 .



Thermodynamic Parameters

$$\ln b = \ln b_0 - \frac{\Delta H}{RT} \quad \text{VIII}$$

The apparent heat change (ΔH) related to Langmuir constant b , and should follow the Van't Hoff equation

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 ΔH 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 (ΔG) and (ΔS) are calculated using the following relationships.

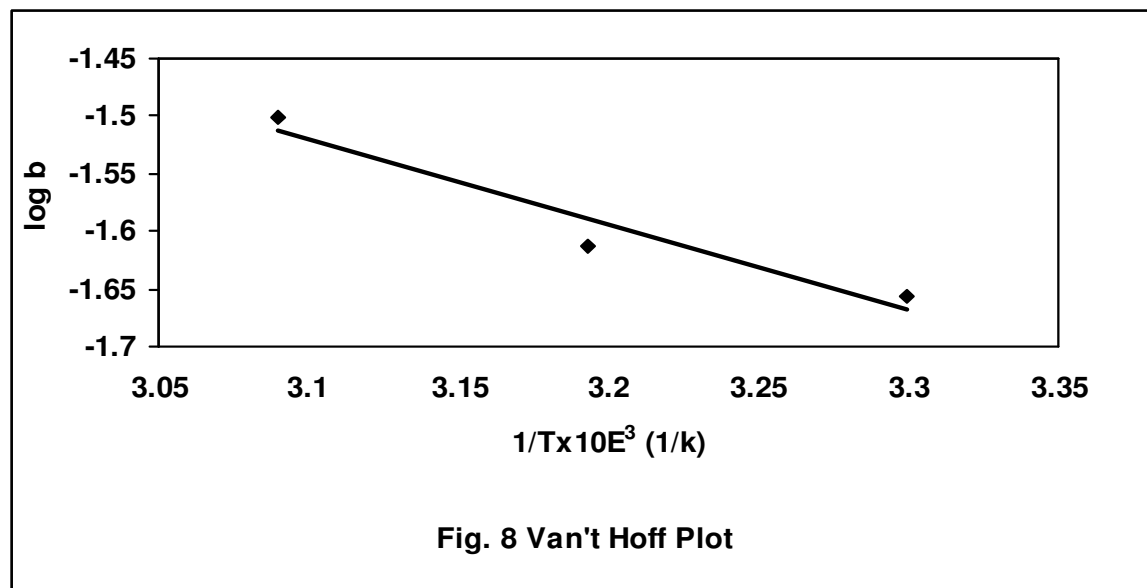
$$\Delta S = -RT \ln\left(\frac{1}{b}\right) \quad \text{IX}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \text{X}$$

The negative values of ΔG indicates the process to be feasible and spontaneous (Singh et al.1982) and positive values of entropy reflected the affinity of the adsorbent material. The values of ΔG and ΔS are listed in Table 2.

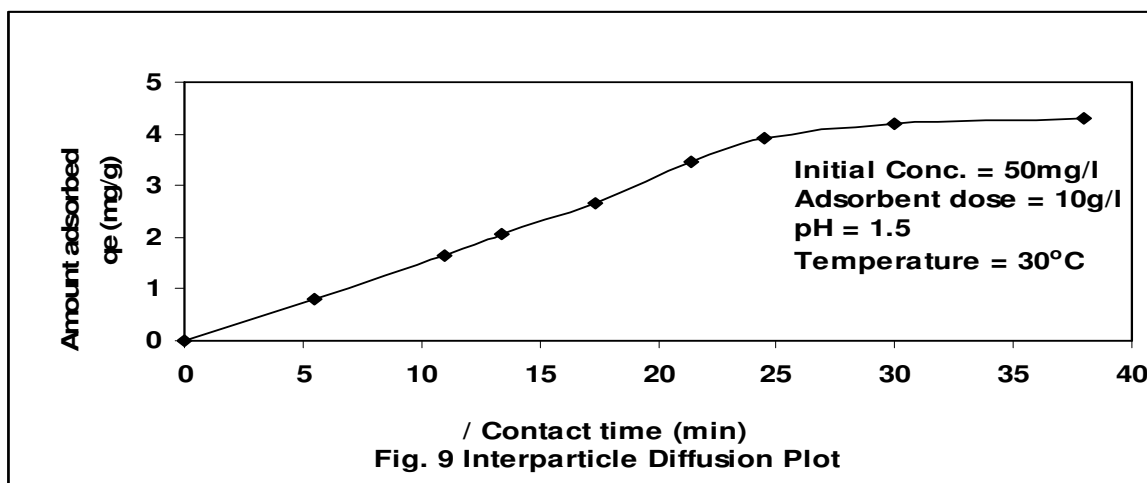
Table 2: Thermodynamic Parameters at Different Temperatures.

Temperature (°K)	- ΔG KJ/mole	ΔS j/mole
303	9.614	78.693

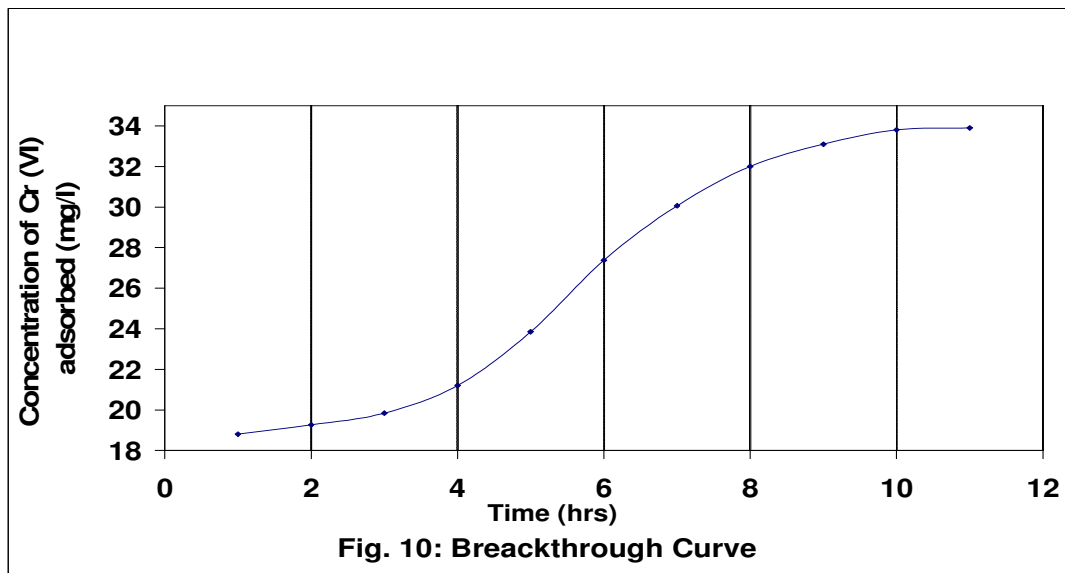


6. INTERPARTICLE DIFFUSION RATE

Plot of amount adsorbed per unit 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 microspores.



7. 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 .

8. 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.

9. CONCLUSIONS

In conclusion, it has been shown that the use of coconut shell, waste appears to be technically feasible, eco-friendly with high efficiency in the removal of cadmium from wastewaters. Besides it is composed entirely of agricultural waste and this help in the reduction of waste generation. They adsorbed comparatively like the expensive traditional activated carbon.

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