Pak. J. Chem. 2(3): 126-133, 2012
ISSN (Print): 2220-2625
ISSN (Online): 2222-307X

Full Paper
DOI: 10.15228/2012.v02.i03.p05

Accumulation of Heavy Metal Ions from Tanneries Wastes: An Approach For Chromium Removal Using Activated Charcoal

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ABSTRACT

The environment is under increasing pressure from solid and liquid wastes emanating from the leather industry. These are inevitable by-products of the leather manufacturing process and causes significant pollution unless treated in some way prior to discharge. The tanneries wastes samples were collected from Lahore Pakistan. The samples were digested by wet oxidation method and the concentrations of metals: Cr, Co, Cu, Cd, Mn, Zn, Ni and Pb were estimated in sediments and liquid waste samples by atomic absorption spectrophotometer.

The results show that the concentrations of these metals were higher than the values given by the national environmental quality standards. Selective separation of Cr ion from other metals was investigated in sediment sample TS2 by adsorption method using low cost natural adsorbent activated charcoal. The adsorption studies were carried out under the optimized conditions of adsorption like pH, shaking time and amount of adsorbent. The concentration of Cr after removal was determined by atomic absorption spectrophotometer. The adsorption equilibrium data were fitted in adsorption isotherm equations like: Freundlich, and Dubinin-Radushkevich equations at temperatures ranges from 303 to 318 K. Thermodynamic parameters ΔH, ΔS and ΔG were also calculated. The values of sorption free energy were estimated by employing D-R equation. The percent removal data show that about 99% removal was achieved by employing low cost adsorbent. This method can be employed on industrial scale for the treatment of solid and liquid waste before discharge into the main streams.

Key words: Tannery waste, sediments, liquid waste, adsorption, activated charcoal

1. INTRODUCTION

Environmental pollution is a growing hazard to human health. Tanneries are proliferating world-wide and their harmful effects on the environment are increasing yearly, because they are major consumers of chromium chemicals. The hazards to environment caused by the effluents from tanneries are currently an acute problem in Pakistan[1].The present free style way of disposal of the tanneries effluent is polluting air, soil, sub soil, surface water and underground water. Theses effluents contain not only Cr but also other pollutants such as toxic chemicals, metallic compounds, biologically oxidizable materials and large quantities of putrefying suspended matters. These pollutants load containing effluents, when discharged to water bodies ultimately affects the food chain as well as the ecosystem [2-4].

The potential toxicity of Cr (III) is well documented due to possible oxidation to Cr (VI) under environmental conditions [5]. Conventional methods for the removal of Cr from waste water by activated charcoal have been reported by many investigators [6]. In the past, charcoal or carbon columns has been used exclusively for the removal of trace quantities of organic compounds. However, several researchers have also demonstrated the ability of activated charcoal to remove heavy metals from aqueous waste stream[7]. The removal of Cr is of particular concern due to its widespread industrial use and its chemical complexity [8]. By employing low cost adsorbent it can be effectively removed to achieve the permissible level.

2. MATERIALS AND METHODS

2.1 *Sample Collection*

The sediments and liquid wastes samples were collected from selected tanneries of Lahore Pakistan as shown in Fig-1**.** They have been considered composite and representative of the total effluents emanating from the tanneries viz. mixed washing and chrome processing.

2.2 *Digestion of samples*

The sediment and liquid waste samples were digested with concentrated nitric acid (65%) at 140 °C using wet oxidation method.

2.3 *Analysis of samples*

The digested samples were analyzed by flame atomic absorption spectrophotometer by adopting standard calibration method [9]. A Shimadzu Atomic Absorption Spectrophotometer model (AA-670), using air acetylene flame, equipped with an automatic background corrector, standard cathode lamp and recorder was used, throughout this work. Triplicate sub-samples of sediments and liquid wastes were run to ascertain the precision of data.

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Received 22nd June 2012, Accepted 16th July 2012

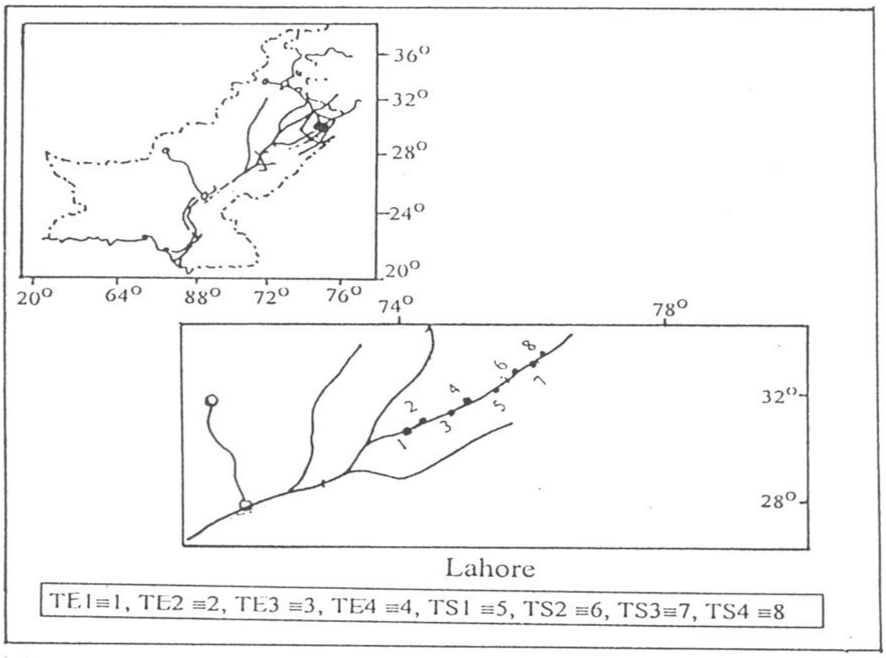

Fig-1: Study area showing sampliing site distribution for Tanning Industries of Pakistan

2.4 *Treatment of Tannery wastes*

The removal of chromium from TS2 sample was carried out by adsorption method using activated charcoal.

2.5 *Adsorption studies*

The adsorption measurements were carried out by batch method at temperatures ranges from 303 to 318K, by taking various initial concentrations of TS2 sample ranges from 8.0 to 54.0 mg/L.

2.6 *Optimization of pH*

The pH was varied from 2.0– 7.0 and adjusted with buffer solutions. The samples were run by keeping constant amount of adsorbent and shaking time. After specific time period the content were filter out and analyzed by atomic absoption spectrophotometer.

2.7 *Optimization of amount of adsorbent*

Activated charcoal of known amounts 0.01-0.5 gram was added in shaking flasks and placed in electric shaker for a desired time period. The contents of reagent bottles were filtered to separate the activated charcoal. Chromium was quantified in the filtrate by Atomic absorption spectrophotometer.

2.8 *Optimization of shaking time*

The shaking time also varied from 10 to 100 minutes by keeping the optimum amount of adsorbent and pH. After the intervals of 10 minutes each bottle was ejected and filters out the content. The filtrate was analyzed by Atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

The results of chemical analysis of liquid waste and sediment samples are shown in Fig-2 and 3 respectively. The present study revealed that in liquid samples, maximum concentration of Zn and Cr (176.0 and 170.0 mg/L) were found in TE2 sample. In sediment samples, the concentration of Cr is highest in TS2 (2200 mg/kg) and is also higher than maximum permitted level (100.0 mg/kg) [10]. The results showed that the level of Cr in sediment and liquid waste samples were higher than other metals because chromium sulphate is used as tanning agent in the tanneries and in being discharge as liquid waste without treatment. If the present mode of disposal of tannery effluent is continued, it is likely that the ground water of an extensive area would become highly saline and contaminated with toxic metals.

Table-1 summarizes relevant statistical parameters for various metals in tannery liquid wastes and sediments in terms of average concentration values, standard deviation (±SD), t- Test analysis for the comparison of averages and probability of t-values for relevant pairs of sediments and liquid wastes.

In liquid wastes samples, Zn and Cr showed the maximum average concentrations (44.55 mg L^{-1} and 44.50 mg L^{-1}), while in sediments Cr had the highest average concentration (822.9 mg kg^{-1}). The largest concentration dispersions were measured as a function of standard deviation (±SD) values. In liquid wastes it was observed for Zn and Cr (± 87.64 mg L^{-1} and ± 83.67 mg L^{-1}) and in sediments only for Cr (± 931.2 mg kg^{-1}).

The comparison of average concentrations of metals and probability of t-values for relevant pairs of sediments and liquid wastes showed that probabilities of t-values were significant for Co, Pb and Mn, while for Cr, Cd, Zn, Ni, Cu and Mg these were non- significant.

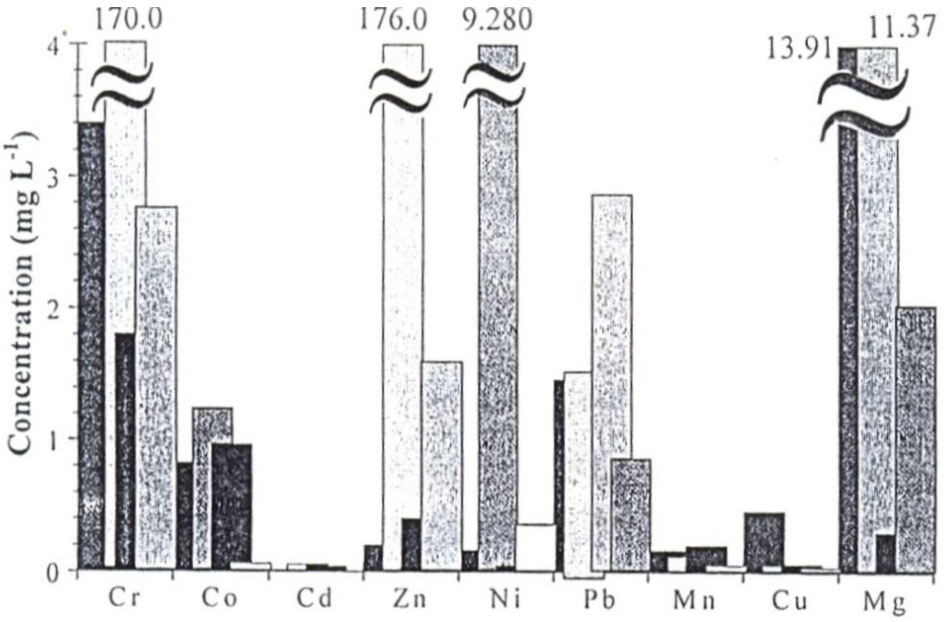

Fig-2: Levels of trace metals (mg L^{-1}) in liquid wastes of Tanneries samples from TE1 through TE4 (left to right)

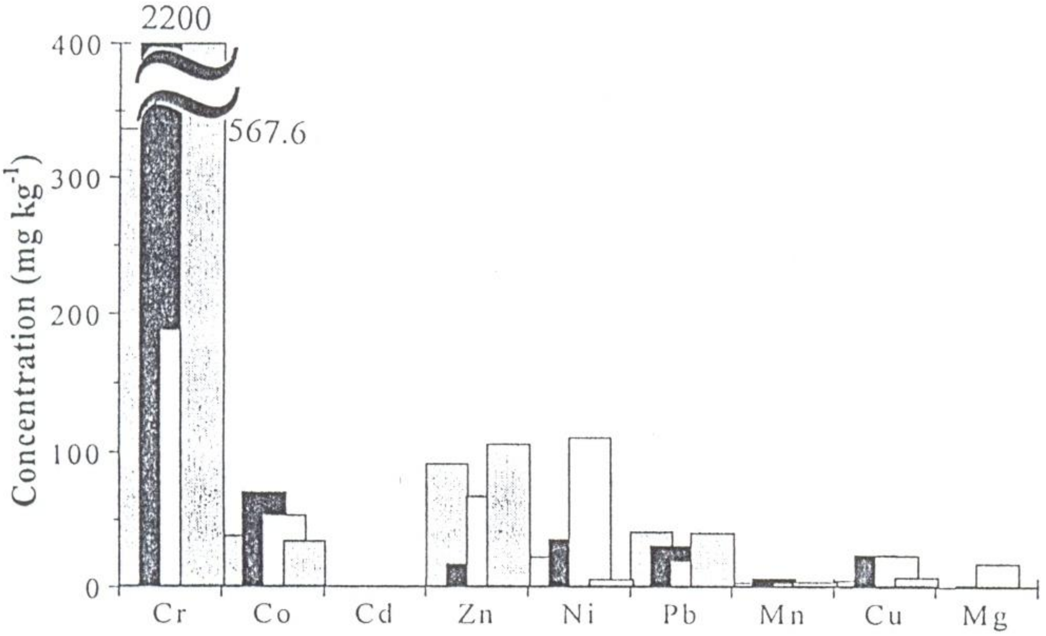

Fig-3: Levels of trace metals (mg kg^{-1}) in sediments of Tanneries samples from TS1 through TS4 (left to right)

Table-1: Statistical parameter of selected metals in liquid wastes and sediments (n= 4 and 4 respectively) from various Tanneries samples

Metal	**Liquid** wastes			**Sediments**			**t-value/Probability-t**	
	Range(mg/L)	**Standard deviation**	**± SD**	**Range(mg/L)**	**Standard deviation**	**± SD**		
Cr	1.800 - 170.0	44.50	83.67	188.0 - 2200	822.9	931.2	1.834	0.164
Co	0.060 - 1.240	0.770	0.505	34.60 - 71.00	49.45	16.53	6.043	0.009
Cd	0.005 - 0.053	0.027	0.023	0.048 - 0.340	0.162	0.125	2.118	0.156
Zn	0.200 - 176.0	44.55	87.64	17.34 - 106.4	70.94	39.08	0.425	0.699
Ni	0.040 - 9.280	2.460	4.549	6.000 - 111.0	43.80	46.41	1.749	0.179
Pb	0.860 - 2.870	1.694	0.845	19.96 - 41.96	33.51	10.29	5.748	0.011
Mn	0.050 - 0.200	0.132	0.064	3.200 - 6.790	4.457	1.598	5.335	0.013
Cu	0.036 - 0.460	0.150	0.206	5.380 - 24.08	15.20	10.19	2.916	0.062
Mg	0.291 - 13.91	6.900	6.746	0.039 - 18.00	5.178	8.573	0.251	0.818

Table-2 incorporates the correlation matrix for paired variables: sediments Vs. sediments and liquid wastes Vs. liquid wastes. The sediments Vs. sediments system showed strong positive correlation between Co-Cr, Mn-Cr, Mn-Co, Cu-Co and Mg-Ni with corresponding r values (0.782, 0.974, 0.733, 0.889 and 0.982 respectively). In liquid wastes Vs. liquid wastes system, strong positive correlations were found for Zn-Cr, Zn-Cd, Ni-Cr and Ni-Zn at r values (0.900, 0.745, 0.997 and 0.997 respectively).

To control the levels of metals in the effluent emitting from tanneries suitable measures were adopted to avert the steady degradation of the environment with particular regards to the quality of ground water [11].

The adsorption of chromium was carried out by using low cost adsorbent activated charcoal as a function of shaking time, pH and amount of activated charcoal.

Table-2: Statistical multiple correlations between paired sediments and liquid wastes from various Tanneries samples

Metal	Cr	Co	Cd	Zn	Ni	Mn	Cu	Mg	Pb
				Sediments Vs. Sediment					
Cr	-								
Co	0.782	-							
Cd	-0.630	-0.608	-						
Zn	-0.836	-0.992	0.564	-					
Ni	-0.262	0.388	-0.132	-0.284	-				
Mn	0.974	0.733	-0.590	-0.796	-0.337	-			
Cu	0.472	0.889	-0.668	-0.823	0.563	0.434	-		
Mg	-0.406	0.231	-0.101	-0.116	0.982	-0.477	0.613	-	
Pb	-0.027	-0.612	0.434	0.510	-0.945	0.053	-0.894	-0.902	
				Liquid wastes Vs. Liquid wastes					
Cr	-								
Co	0.619	-							
Cd	0.741	0.730	-						
Zn	0.900	0.616	0.745	-					
Ni	0.997	0.599	0.733	0.997	-				
Mn	-0.163	0.691	0.303	-0.137	0.159	-			
Cu	-0.321	0.102	-0.604	-0.331	0.332	-0.328	-		
Mg	0.448	0.456	-0.088	0.438	0.441	0.071	0.692	-	
Pb	-0.093	0.588	0.538	-0.091	-0.114	0.882	-0.142	-0.341	-

3.1 *Adsorption Studies*

3.2 *Effect of shaking time*

The optimum time for equilibrium was determined by shaking 50 mg/L stock solution of chromium nitrate, with fixed amount of activated charcoal by varying shaking time from 10 to 100 minutes. The sorption of chromium was found to be maximum at 60 minutes shaking time and afterward, it was remained constant. Therefore, 60 minutes shaking time was selected for all further studies [12].

3.3 *Effect of the amount of activated charcoal*

Another parameter which affects on the sorption phenomenon is the amount of activated charcoal. The sorption of chromium was increased as the amount of activated charcoal increased up to 0.1 g and with the further addition there was a decreasing trend in sorption. It may be due to the conglomeration of the charcoal particles especially at higher amounts. Therefore, 0.1g of activated charcoal and 50 mg/L stock solution of chromium nitrate were uses for all further studies [13]. The results are shown in Fig-4.

3.4 *Effect of pH*

The influence of pH on the adsorption of Cr on activated charcoal has been studied under the optimized conditions of shaking time and amount of adsorbent. The adsorption was increased with the increase in pH up to the value of 2 and afterwards it started to decreases. The results are shown in Fig-5. The influence of pH on chromium adsorption can be explained as: The hydrolysis of Cr takes place as the pH varies from 1 to 3, and the availability of free Cr ion is maximum at pH 2. Therefore, buffer with a pH of 2 was used for all further investigations [14]**.**

3.5 *Adsorption Isotherms*

Sorption isotherms were recorded by the variation of K_D and % removal values are shown in Fig-6 and 7 illustrating the temperature dependence of adsorption reaction in the range from 303 to 318K. The rates of adsorption and % removal were increased with the rise in temperature.

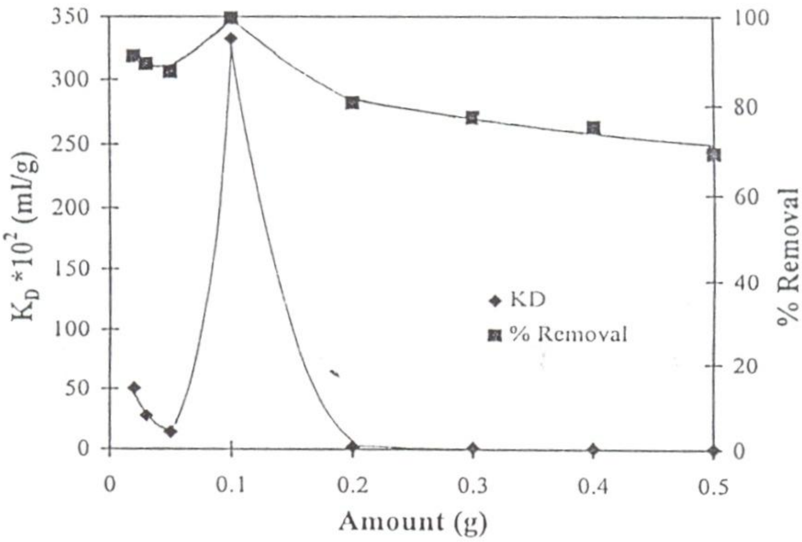

Fig-4: Influence of amount of Activated Charcoal on the adsorption of Cr [The Cr. Soln. conc. 50.00 mg L^{-1}]

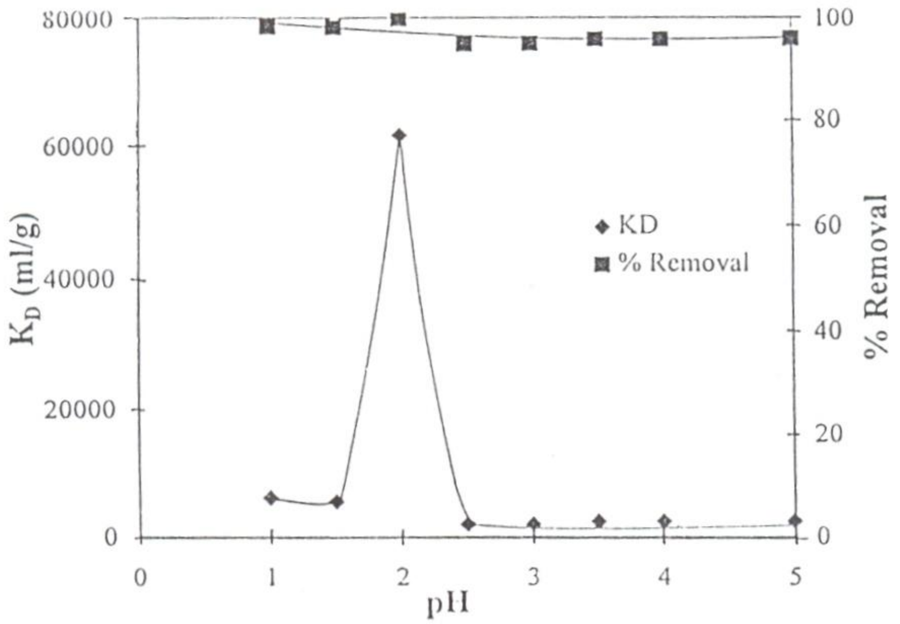

Fig-5: Influence of pH on Cr adsorption on Activated Charcoal [The Cr. Soln. conc. 50.00 mg L^{-1}]

This indicates that Cr adsorption is an endothermic process. These isotherms were L3 type by Gile's classification [15], indicating the strong tendency in the process of monolayer formation. The amount of Cr sorption per gram of charcoal was calculated using the following formula [16].

$$X_m = (C_o - Ce)\, V / m \qquad (1)$$

Where C_o is the initial solution concentration (mg/L) and C_e is the solution concentration at equilibrium (mg/L). V is the volume of solution in (L) and M is the amount of charcoal (g).

The distribution coefficients (K_D in ml/g) were computed in the following way [17].

$$K_D = (C_i - C_f / C_i) \times (V/M) \qquad (2)$$

Where C_f is the concentration of Cr remaining in the solution and C_i is the concentration of metal ions in original sample. V is the volume of the solution and M is the amount of adsorbent.

The % removal values were estimated by employing the following expression[18].

$$\%\ \text{Removal} = (C_i - C_f / C_i) \times 100 \qquad (3)$$

The data were fitted in Freundlich and Dubinin-Radushkevich (D-R) isotherms equations [19]. These results were subjected to Freundlich isotherm eq. in the form as:

$$X/m = KCe^{1/n} \qquad (4)$$

While K and 1/n are empirical constants, which are computed from the Freundlich isotherm are tabulated in Table 3. The value of n reveals the nature and strength of adsorptive forces involves. The higher fractional values of n signify the strong adsorption forces are operating on the surface of charcoal. However, the values of K were proportional to the heat of adsorption which increases with the temperature, also confirms the higher affinity of chromium adsorption on the surface of charcoal at higher temperatures. [20]

Table-3: Freundlich parameters for the Cr adsorption from TS2 sample

Adsorbent	Temperature(K)	n	K
Activated Charcoal	303	1.041	0.798
	308	1.026	1.013
	313	1.193	1.417
	318	1.363	1.921

As an alternative to Freundlich isotherm, the data were also fitted to Dubinin-Radushkevich (D-R) equation [21] **i**n the linearized from as follows:

$$\text{Ln } X/m = \text{Ln } Xm - K^{/}\varepsilon^{2} \qquad (5)$$

$$\varepsilon = RT\ln(1+1/Ce) \qquad (6)$$

Where Xm is the monolayer capacity of adsorbent, $K^{/}$ is a constant related to adsorption energy,.R is a gas constant, and T is Absolute temperature.The quantities X/m and Ce have their usual meanings. Values of X_m and $K^{/}$ were calculated from the intercept and slope of D-R plots are shown in Table-4.

Table-4: D-R Parameters for the Cr adsorption from TS2 sample

Adsorbent	Temperature (K)	Xm (mol/g)	-K (mol^2/KJ^2)	Ea (KJ/mol)
Activated Charcoal	303	5.135	1.145	0.661
	308	6.072	0.909	0.741
	313	6.240	0.807	0.787
	318	6.315	0.563	1.332

By making certain assumptions [22], the mean free energy of adsorption (Ea) was calculated from D-R parameter K as follows. [23]

$$Ea = (-2K)^{-1/2} \qquad (7)$$

It is evident from the data as shown in Table 2 , the values of sorption free energy (Ea) was increases with the rise in temperature, showing that there was an increase in adsorption with temperature.

The values of % Removal of chromium were increases with the temperature, showing that adsorption process is endothermic in nature. The results are tabulated in Table-5.

Table-5: Percent removal values of chromium at different temperatures from TS2 sample

Initial Conc. (mg/L)	% Removal			
	30°C	35°C	40°C	45°C
8.0	93.2	95.5	98.6	99.4
16.0	95.2	97.6	97.8	97.9
24.0	96.2	98.1	98.6	98.6
32.0	96.5	98.9	98.8	98.8
40.0	96.9	98.1	98.6	98.8
48.0	97.3	97.5	97.8	98.6
56.0	97.6	97.8	97.9	97.0
64.0	97.9	97.9	97.9	98.1

Thermodynamic parameters $\Delta \mathbf{G^o}$, $\Delta \mathbf{H^o}$ and $\Delta \mathbf{S^o}$ were also calculated as shown in Table-6.

The values of $\Delta \mathbf{H^o}$ and $\Delta \mathbf{S^o}$ were calculated from the slope and intercepts of the linear variation of ln K with the reciprocal of temperature, 1/T using the relation [24]

$$\text{Ln } K = \Delta \mathbf{S}/R - \Delta \mathbf{H}/(RT) \qquad (8)$$

Table-6: Thermodynamic Parameters for Chromium adsorption from TS2 sample

Adsorbent	**Temperature (K)**	**ΔH (kJ/mol)**	**$-\Delta G$ (kJ/mol)**	**ΔS ($kJ.Deg^{-1}$ mol^{-1})**
Activated Charcoal	303	22.695	0.340	7.600
	308	22.695	0.244	7.440
	313	22.695	0.557	7.420
	318	22.695	1.518	7.614

The Δ**G** values were calculated by employing Gibbs equation:

$$\Delta \mathbf{G}^{o} = - RT \text{ Ln } K \qquad (9)$$

WhileΔ **S** was calculated as:

$$\Delta \mathbf{S}^{o} = (\Delta \mathbf{H}^{o} - \Delta \mathbf{H}^{o}) / T \qquad (10)$$

The relatively large negative values of Δ $\mathbf{G}^{o}$, suggest the nature of Chromium uptake which is strong chemisorption and spontaneous process. Further the Δ $\mathbf{G}^{o}$ values were decreases with the rise in temperature showing that there is an increase in feasibility of adsorption at higher temperatures. The positive values of $\Delta\mathbf{H}^{o}$ indicate that the chromium-charcoal interactions were endothermic process. The values of $\Delta\mathbf{H}^{o}$ 22.7 (kJ/mol) during adsorption suggest the strong binding capacity of chromium with the active surface sites of charcoal. The positive values of $\Delta\mathbf{S}^{o}$ suggest that there is an increase in randomness at charcoal-solution interface during the adsorption of chromium on the surface of activated charcoal [25].

4. CONCLUSIONS

It is evident from the present studies that the suspended matter of tannery effluent contains considerable quantities of metals especially chromium which involves in the tanning process is settles down on the sediments of the pathway. Soil sediments tends to accumulate metals on a relatively long term basis since many metals in soil are not so mobile. Thus the distribution pattern of various metal species in sediments and liquid waste are not identical. This explains the overall higher contamination levels of metals in sediments than in liquid wastes. Effectiveness of the method as a means of removing chromium metal from the elevated amounts of other metals in dilute effluents to meet permissible discharge levels has also been studied. The results showed that the chromium, under optimized conditions, can be removed about (99.4 %) by using low cost adsorbent activated charcoal from dilute effluent solution. The simplicity of the method, allows economic removal of Chromium in a directly reusable form from dilute effluent streams.

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