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Adsorption and Regeneration Studies for the Removal of Chromium(VI) from the Wastewater of Electroplating Industry using Granular Activated Carbon

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Batch adsorption and desorption kinetics studies were carried out on electroplating wastewater using granular activated carbon with particle size 0.5–1.08 mm as an adsorbent. The effect of pH, Cr(VI) concentration, adsorbent dose and contact duration were studied in batch experiments. The desorption experiments were carried out by shaking granular activated carbon saturated with Cr(VI) in (i) distilled water (27 and 50°C) and (ii) 0.1 N NaOH. A reaction time of 1 h was maintained in the regeneration study. The removal of Cr(VI) was in general most effective at low pH values. The adsorption behaviour can be explained better on the basis of Freundlich and Langmuir adsorption isotherm model.

Key Words: Adsorption, Desorption, Granular activated carbon, Chromium(VI), Adsorption isotherms.

INTRODUCTION

Numerous industrial processes produce effluents that contain heavy metal contaminants. Since the majority of heavy metals do not degrade into harmless end products, their concentration must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose a threat to public health and/or affect the aesthetic quality of potable water. According to World Health Organization[1], the metals of most immediate concern are Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb. The maximum tolerance for total chromium for public water supply and bathing ghats has been fixed at 0.05 mg/L as per Indian Standard IS-2490-1974.

The removal of chromium by physicochemical techniques has been reviewed[2]. A variety of low cost materials like fly ash[3], wood charcoal[4], bituminous coal[5], lignite coal[6] and bagasse and coconut jute[7] have been tried by several investigators for Cr(VI) removal.

The composite sample was studied with the aspect of chromium(VI) removal by batch adsorption treatment using GAC as an adsorbent.

EXPERIMENTAL

Granular activated carbon with the specific surface area of 950–1050 m^2/g was used as an adsorbent for the treatment of electroplating wastewater. To carry out the investigation, a number of composite samples were collected from the electroplating industry and were analyzed according to standard procedure for various physicochemical characteristics.

(a) Batch Experiments

Batch equilibrium adsorption isotherm studies were conducted using electroplating wastewater having Cr(VI) in high concentration. The equilibrium isotherm measurements were carried out by keeping the solution volume (100 mL) and concentration constant while varying the amount of the added GAC (2–20 g/L) at an isothermal temperature of 27 ± 0.5°C. The system was kept under observation for 30 and 60 min of contact period. After the isothermal equilibrium, the GAC was separated by filtration with Whatmann No. 41 filter paper. The supernatant liquid was analyzed for Cr(VI). The amount of the metal adsorbed (mg) per unit weight of GAC (g), q_e, was obtained by mass balance.

The analysis of metal was accomplished with flame atomic absorption spectrophotometer in a nitrous oxide-acetylene flame and Cr(VI) was analyzed using a colorimetric method[8] by measurement of the intense red-violet complex formed by reaction of Cr(VI) with 1,5-diphenyl carbazide in an acidic medium. A UV-Visible (1201) spectrophotometer was used to obtain measurements of the chromophore complex at its absorbance of 540 nm.

(b) Regeneration Studies

In order to make the adsorption process more economical, it is necessary to regenerate the spent adsorbent (GAC). Desorption studies were carried out by shaking GAC saturated with Cr(VI) in (i) 100 mL distilled water (at 27°C and 50°C) and (ii) 100 mL of 0.1 M NaOH. A reaction time of 50 min was maintained in the regeneration study. The sorbent sample can be reused for further adsorption potential the regeneration cycle was repeated up to five times. After each cycle, the sorbent was washed with distilled water and dried.

RESULTS AND DISCUSSION

Tables 1 and 2 represent the data for the model of Freundlich and Langmuir adsorption isotherm for removal of chromium at 30 and 60 min of contact duration of GAC.

Batch adsorption studies were conducted to evaluate the effect of regeneration on the adsorptive mechanism and capacity of granular activated carbon. With increase in the regeneration cycle, corresponding removal of Cr^{6+} is decreased from 98.40 to 63.18% that means similar adsorption capacity of GAC is reduced in accordance.

TABLE-1
FREUNDLICH AND LANGMUIR DATA FOR REMOVAL OF Cr(VI) FROM WASTEWATER BY ADSORPTION ON TO GRANULAR ACTIVATED CARBON

Contact duration: 30 min Specific surface area: 950–1050 m^2/g

Treatment dose (g/L)	Data						
	C_{eq} (mg/L)	% removal	$x/m = q_e$ (mg/g)	log C_{eq}	log x/m	$1/q_e \times 10^2$	$1/C_{eq} \times 10^3$
Untreated	103.70	—	—	2.0158	—	—	9.6432
2.0	88.90	14.27	7.40	1.9489	0.8692	13.5135	11.2486
4.0	75.10	27.58	7.15	1.8756	0.8543	13.9860	13.3156
6.0	61.00	41.18	7.12	1.7853	0.8523	14.0515	16.3934
8.0	49.10	52.65	6.83	1.6911	0.8341	14.6520	20.3666
10.0	37.80	63.55	6.59	1.5775	0.8189	15.1745	26.4550
12.0	35.39	65.87	5.69	1.5489	0.7553	17.5670	28.2566
14.0	31.40	69.72	5.16	1.4969	0.7130	19.3638	31.8471
16.0	30.70	70.40	4.56	1.4871	0.6592	21.9178	32.5733
18.0	28.40	72.61	4.18	1.4533	0.6215	23.9044	35.2113
20.0	27.70	73.29	3.80	1.4425	0.5798	26.3158	36.1011

TABLE-2
FREUNDLICH AND LANGMUIR DATA FOR REMOVAL OF Cr(VI) FROM WASTEWATER BY ADSORPTION ON TO GRANULAR ACTIVATED CARBON

Contact duration: 60 min Specific surface area: 950–1050 m^2/g

Treatment dose (g/L)	Data						
	C_{eq} mg/L	% removal	$x/m = q_e$ (mg/g)	log C_{eq}	log x/m	$1/q_e \times 10^2$	$1/C_{eq} \times 10^3$
Untreated	103.70	—	—	2.0158	—	—	9.64
2.0	78.14	24.65	12.78	1.8929	1.1065	7.82	12.80
4.0	54.20	47.73	12.38	1.7340	1.0925	8.67	18.45
6.0	34.32	66.90	11.56	1.5355	1.0631	8.65	29.14
8.0	16.45	84.14	10.91	1.2162	1.0377	9.17	60.79
10.0	8.45	91.85	9.53	0.9269	0.9789	10.50	118.34
12.0	2.10	97.97	8.47	0.3222	0.9277	11.81	476.19
14.0	1.98	98.09	7.27	0.2967	0.8613	13.76	505.05
16.0	1.90	98.17	6.36	0.2788	0.8036	15.72	526.32
18.0	1.84	98.23	5.66	0.2648	0.7527	17.67	543.48
20.0	1.84	98.23	5.09	0.2648	0.7070	19.63	543.48

Eq. C_{eq} = Equilibrium concentration
x/m = removal (mg/L)/weight of adsorbent (gm/L): (1) For Freundlich plot, *i.e.*, x/m (2) For Langmuir plot, *i.e.*, q_e

Results of equilibrium adsorption of Cr(VI) on the GAC are shown in Fig. 1. The amount of the Cr(VI) adsorbed (mg) per unit mass of GAC, q_e, was obtained by using the equation

$$q_e = (C_i - C_e)V/M \quad \text{(i)}$$

where C_i and C_e are the initial and equilibrium concentrations of the metal ion in mg/L, M is the dry mass of GAC in grams and V is volume of solution in litres.

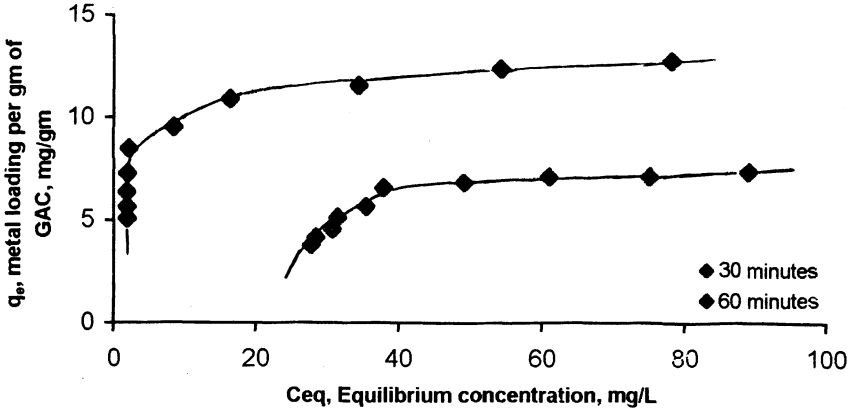

Fig. 1. Equilibrium adsorption of Cr(VI) on the GAC at 27°C

The equilibrium experimental data are correlated with Langmuir and Freundlich isotherm models. The Langmuir model assumes mono-layer adsorption while the Freundlich model is empirical in nature.

Freundlich model

$$x/m = KC_{eq}^{1/n} \quad \text{(ii)}$$

where x is the amount of metal ion adsorbed (mg/L), m is the weight of the adsorbent (g/L), C_{eq} is the metal-ion equilibrium concentration (mg/L) and K and 1/n are the constant characteristics of the system.

For linearization of data, the Freundlich equation is represented in logarithmic form as

$$\log x/m = \log K + 1/n \log C_{eq} \quad \text{(iii)}$$

Data presented in Tables 1 and 2 give the information about Freundlich and Langmuir adsorption isotherms along with per cent removal of Cr^{6+}. It can be seen that the removal of Cr^{6+} increases with increase in dosage of adsorbent as well as contact time. A decrease in adsorption per gram of adsorbent is observed on increasing the amount of adsorbent. The logarithmic value of equivalent concentration and removal per unit weight gives the linear plot for Cr^{6+} by GAC, which confirms the applicability of Freundlich adsorption isotherm.

The plot of log C_{eq} *vs.* log x/m gives a straight line with a slope of 1/n and log K is the intercept of log x/m at log $C_{eq} = 0$ indicating that the Freundlich adsorption isotherm model is applicable. The straight-line natures of the plots presented in Fig. 2 confirm the applicability of Freundlich isotherm model. The value of 1/n related to adsorption intensity is close to one, which indicates high adsorptive intensity at high equilibrium concentration. From the value of K, we can suggest that adsorptive capacity is increases with increase in contact time.

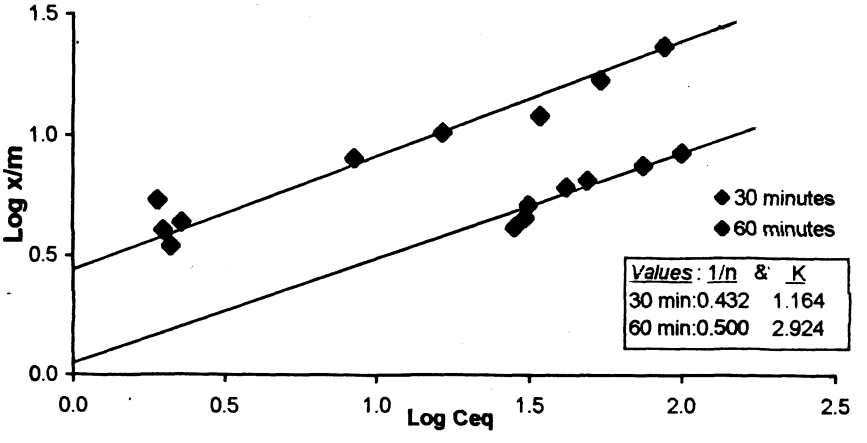

Fig. 2. Freundlich adsorption isotherm model for removal of Cr(VI) by GAC

Langmuir model

$$1/q_e = 1/\theta_0 b \cdot 1/C_{eq} + 1/\theta_0 \quad \text{(iv)}$$

where q_e = amount of metal ion adsorbed per unit weight of adsorbent (mg/g), θ_0 = Langmuir constant related to adsorption capacity (mg/g) and b = Langmuir constant related to adsorption energy (L/mg).

Fig. 3 shows Langmuir adsorption model for removal of Cr^{6+} using GAC. The observed linearity suggests the applicability of this isotherm and further confirms the mono-layer formation. The Langmuir constants related to adsorption capacity θ_0 (mg/g) have higher values indicating availability of more surface-active region on to adsorbent sites. The values of $b \times 10^3$ (L/mg) in terms of x/m related to adsorption energy.

The desorption and regeneration data are presented in Table-3, which suggests that with increase in the regeneration cycles of GAC, the adsorption capacity is found to decrease. The reduction in adsorption may lead to a decrease in the weight of adsorbent as consequence of alkali treatment. From desorption data for Cr^{6+} in the same table, it is obvious that the greater desorption takes place in 0.1 M NaOH. However, poor desorption occurs in distilled water at room temperature as well as at high temperature conditions. It means that a better performance of

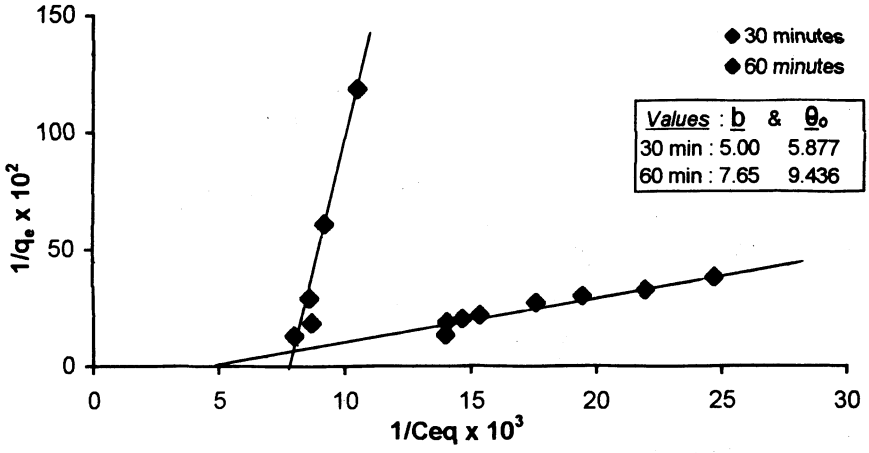

Fig. 3. Langmuir adsorption isotherm model for removal of Cr(VI) by GAC

per cent desorption of Cr(VI) in basic medium may be due to the presence of large OH^- ion concentration, which release Cr(VI) ions from the sorbent surface to the solution.

TABLE-3
DESORPTION AND REGENERATION DATA OF GAC ON REMOVAL OF Cr(VI)

Adsorbent: Granular activated carbon Initial concentration of Cr^{6+}: 103.70 ppm
Adsorbent dose: 20 gm/L Contact duration: 50 min

C_{eq} (ppm)	Adsorption		Desorption (mg g^{-1})			Recovery (%)			Recovery (%)
	mg g^{-1}	%	In D.W. at 27°C	In D.W. at 50°C	In 0.1 M NaOH	In D.W. at 27°C	In D.W. at 50°C	In 0.1 M NaOH	
1.65	102.1	98.40	2.13	0.65	97.12	2.05	0.62	95.16	—
2.14	101.6	97.93	1.42	0.20	95.78	1.36	0.19	94.30	99.52
10.78	92.92	89.60	1.12	—	86.40	1.08	—	92.98	91.05
24.00	79.70	76.85	0.78	—	70.20	0.75	—	88.08	78.10
38.18	65.52	63.18	0.49	—	55.00	0.47	—	83.94	64.20

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