



Adsorption Studies on the Removal of Chromium (VI) from Wastewater Using Activated Carbon Derived from Water Hyacinth

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ABSTRACT

In this study, Cr(VI) is removed from Wastewater using activated carbon derived from water hyacinth as an unconventional adsorbent. The aquatic plants commonly referred as aquatic weeds found in rivers, lakes and water logged areas pose a number of problems in water resource utilization. This work deals with one such weed "water hyacinth" which was selected to prepare activated carbon. The physical and chemical characteristics of the activated carbon prepared were determined. The study determines the parameters that influence adsorption process such as pH, initial metal ion concentration, contact time and adsorbent dosage. The suitability of Freundlich and Langmuir models was investigated for each chromium sorbent system. The Lagergren's constants were calculated for different initial concentrations of metal ions.

INTRODUCTION

Conventional treatment process currently applied for the removal of Cr(VI) from the liquid phase is generally based on chemical precipitation and coagulation. However, these processes generate large amounts of sludge and are considered to be ineffective, especially for the treatment of large quantities of dilute aqueous streams such as wastewater discharges and the solution generated during pump-and-treat process at contaminated sites (Talokar 2011).

In industrial wastewater mostly the chromium is found in two forms, one is hexavalent and other is trivalent, whereas the hexavalent form is more common and hazardous to biological activities. Cr(III) is comparatively insoluble and required by microorganisms in low quantities as a predominant trace metal nutrient, while Cr(VI) is of great concern because of its toxicity. Cr(VI) has been reported to be a primary pollutant to all living beings (Gupta et al. 2010). Cr(VI) is used in various industries and hence large quantities of chromium are released into the environment. Sources of chromium waste leading to aquatic pollution include electroplating, steel fabrication, paints and pigments, mining, leather tanning, textile dyeing and treatment units (Kanawade & Gaikwad 2011).

The commercial activated carbon has the limitation of being relatively high in cost; it becomes necessary to divert the attention alternatively towards the cheap raw materials which could be effectively converted to carbonaceous form so that it possesses the properties comparable to that of

commercial activated carbon. In this connection (water hyacinth) has been carbonized by acid method and after assessing its characteristics it was decided to use this material for the removal of toxic Cr(VI) from the aqueous system (Kannan & Thambidurai 2008).

This paper envisages the study of an environmental friendly natural adsorbent involving less cost compared to widely used activated carbon. Based on these results we can conclude that it is possible to use this activated carbon for removing Cr(VI) from wastewater.

MATERIALS AND METHODS

Hexavalent chromium: Hexavalent chromium supplied by S.D Fine Chemicals Limited, Mumbai, India was used as an adsorbate and was not purified prior to use. Double distilled water was used for preparing all the solutions and reagents.

Water hyacinth: The water hyacinth was procured from local ponds in and around Coimbatore. Its roots were separated and cleaned with water thoroughly for many times in order to eliminate the earthy matter and all the soil particles. After that, it was dehydrated in a muffle furnace at a temperature of 95°C for about 21 hrs. The dried roots were then burnt for about 2 hours. The remaining residue was then creased, sieved and stored in bottle for further use. The dried material was used for the preparation of activated carbon using physical and chemical methods.

Preparation of activated carbon: The powdered water hyacinth was treated with concentrated sulphuric acid in the

ratio (1:2). The contents were kept in air at 160°C for about 24 hours. Then it was washed well to remove any free acid. After washing, the washed materials were dried in an air oven at 110±5°C. The dried materials were thermally activated in a muffle furnace at about 800°C for 15 minutes. The activated carbon was then produced and sieved to particle size 0.100-0.200 mm. The characterization of WHC and CAC is summarized in Table 1.

Preparation of aqueous solution: Potassium dichromate (AR grade) was used as a source of hexavalent chromium. Stock solution of chromium was prepared by dissolving 0.2828 g of potassium dichromate in 1000mL double distilled water (APHA 1992). Hydrochloric acid (1N, 0.05N), sulphuric acid (1:1), potassium permanganate (0.1N) and sodium azide (0.5%) were prepared using double distilled water. Complexing reagent was prepared by dissolving 20mL of diphenyl carbazide and 300mg of phthalic anhydride in 100mL of methanol (Namasivayam & Kadirvelu 1994). The characterization of chromium plating wastewater is summarized in Table 6.

Laboratory work/batch experiments: Batch adsorption studies were conducted to access performance of each adsorbent for the removal of chromium. To study the adsorption capacities of the each adsorbent, batch experiments were conducted in 300mL BOD bottles provided with lid. The BOD bottles were washed well with chromic acid before and after use. 100mL of solution containing 10mg/L of Cr(VI) ions under investigation were taken in the bottles. After the addition of carbon, the bottles were equilibrated for specific periods of time in a rotary mechanical shaker. At the end of the equilibration period, the solutions were filtered using a G₃ crucible if essential and the concentration was measured by using a spectrophotometer (Meena et al. 2005). The percentage of Cr(VI) adsorption from aqueous solution was computed by the following equation.

$$\text{Adsorption (\%)} = \frac{C_1 - C_f}{C_1} \times 100$$

Where, C₁ - C_f are the initial and final Cr(VI) concentrations.

Analytical procedure: A suitable aliquot of the sample solution containing not more than 20µm of chromium in a final volume of 40mL was transferred into a 50mL volumetric flask. 2.5mL of diphenyl carbazide reagent was added and mixed well. The solution was diluted upto the mark with distilled water. The absorbance was measured against a reagent blank at 540 nm using 1.0 cm cell. Measurements were completed within 15 minutes after mixing of the reagents and after allowing a standing time of 5minutes. A calibration curve was prepared by following the above procedure

and the concentration of Cr(VI) in the sample aliquot was recognized with inference to the calibration curve (Ahemad & Quereshi 1999).

Instruments: The Cr(VI) concentration measurements were carried out using Systronics 21D atomic absorption spectrophotometer. The solution pH was measured with Elico digital pH meter by using a combined glass electrode. The shaking was carried out in rotary mechanical shaker for equilibration studies.

RESULTS AND DISCUSSION

The application of carbon in water and wastewater treatment process is primarily due to its enormous capacity for the removal of contaminants by the adsorption process. Though the commercial activated carbon has been widely employed for the removal of organics and noxious gases, it may be pointed out that only very little alteration has been remunerated for the removal of inorganics from water and wastewater (Mazumder et al. 2011).

Examination of water hyacinth carbon in connection with the removal of Cr(VI), indicated that within 5 hours of equilibration time, the maximum removal of 98% could be achieved for an initial Cr(VI) concentration of 10mg/L. The optimum pH range at which complete removal of Cr(VI) was observed over the range 0.5-1.0. However, the recovery of Cr(VI) was found to be poor in this pH range (25%) only. It may be due to the high reduction process which occurs under high acidic conditions (Kannan & Thambidurai 2008).

The recovery of Cr(VI) was found to be 82% at a pH of 2.0. Hence, this pH was maintained for subsequent investigations. The optimum carbon doses for maximum removal of Cr(VI) was found to be 200mg/L at pH which worked out a Cr(VI) to carbon ratio of 0.015 when an initial Cr(VI) concentration of 30mg/L was considered.

Effect of pH: The extent of Cr(VI) adsorption as a function of pH for initial concentration of 30 mg/L is shown in Fig. 1. It is clear that water hyacinth is effective for Cr(VI) removal over the pH range 0.5 to 2.0. In acidic pH, the adsorbent surface may be protonated and hence the positively charged adsorbent removes higher amount of Cr(VI) in the anionic form HCrO⁴⁻. With increase in pH of the system the degree of protonation of the surface reduced gradually and hence decreased adsorption was noticed.

Effect of agitation time and initial Cr(VI) concentrations: The percentage adsorption of Cr(VI) on the adsorbent increased with increase in agitation time and attained equilibrium after 300 minutes as shown in Fig. 2. The percent removal was found to be 98.2, 95.0 and 91.0% at the initial concentration of 10, 20 and 30 mg/L of Cr(VI) respectively.

Table 1: Comparison of characteristics of water hyacinth carbon (WHC) and commercial activated carbon (CAC).

Sl.NO	Control test	CAC	WHC
1.	Bulk density (g/L)	1.12	0.67
2.	Moisture %	1.03	0.45
3.	Ash %	9.85	5.93
4.	Fixed carbon content	97.09	94.07
5.	Solubility in Water %	1.0	1.83
6.	Solubility in acid %	5.0	3.46
7.	pH	9.85	5.2
8.	Decolorizing power (mg/g)	6.2	30.0
9.	Phenol number	5.15	20.00
10.	Ion exchange capacity (meq/g)	Nil	0.004
11.	Surface area (m ² /g)	303	277
12.	Iron content	0.2	0.0699

Table 2: Effect of Cr(VI) concentration on sorption.

Initial concentration of Cr(VI) ions (mg/L)	Time (mins)	Residual Chromium	Amount of adsorbed	% adsorbed
10 mg/L	30	4.25	5.75	57.5
	60	2.10	7.9	79.0
	120	1.02	8.98	89.8
	180	0.42	9.588	95.8
	240	0.19	9.78	98.11
20 mg/L	300	0.18	9.82	98.2
	30	8.51	11.49	57.45
	60	5.0	15.0	75.00
	120	3.1	16.9	84.50
	180	2.2	17.8	89.00
30 mg/L	240	1.1	18.9	94.50
	300	1.0	19.0	95.00
	30	13.8	16.20	54.0
	60	10.52	19.48	64.93
	120	7.12	22.88	76.27
300	180	4.2	25.8	86.0
	240	3.18	26.82	89.4
	300	2.7	27.3	91.0

The data are given in Table 2. The equilibrium concentration was found to be independent of Cr(VI) concentration. The time curves in Fig. 2 are single, smooth and continuous leading to saturation, suggesting the possibility of formation of monolayer coverage of Cr(VI) on the surface of the adsorbent.

Effect of agitation time and particle size: Cr(VI) solutions of 30 mg/L concentration was agitated with 1g of adsorbent at particle size 0.100-0.200 mm for different agitation times. Maximum removal was found to be at 300min and the percent removal was 89.73%.

Effect of adsorbent dosage: Dosage of adsorbent was verified from 0.5 to 3 g for 100mg/L concentration of Cr(VI) is shown in Fig. 3. The data for dosage of 1g, 1.5g and 2g of

Table 3: Adsorption rate constant at different dosage (Lagergren studies).

Adsorption dosage (g)	Time (mins)	Residual Chromium (mg/L)	Amount of adsorbed	% of adsorbed	$(C_{max} - C_t) / \log$	$(C_{max} - C_t)$
1 g	30	14.12	15.88	52.93	11.04	1.0429
	60	11.24	18.76	62.53	8.16	0.9117
	120	8.67	21.33	71.10	5.59	0.74747
	180	5.67	24.33	81.10	2.59	0.4133
	240	3.47	26.53	88.43	0.39	0.4089
1.5 g	300	3.08	26.92	89.73	-	-
	30	12.26	17.74	59.14	9.94	0.9974
	60	8.42	21.58	71.93	6.10	0.7856
	120	5.21	24.79	82.64	2.89	0.4609
	180	3.02	26.92	89.73	0.76	-0.1192
2 g	240	2.58	27.42	91.40	0.26	-0.5850
	300	2.32	27.68	92.26	-	-
	30	6.72	23.28	77.60	6.46	0.8102
	60	3.53	26.42	88.06	3.32	0.5211
	120	1.12	28.88	96.26	0.86	-0.0655
300	180	0.66	29.34	97.80	0.40	-0.3979
	240	0.42	29.58	98.93	0.16	-0.7959
	300	0.26	29.74	99.13	-	-

adsorbent for 30mg/L Cr(VI) concentration are given in Table 3. The results show that quantitative removal of Cr(VI) is possible with 2g of adsorbent at the equilibrium time of 300 min. The increase in percent adsorption with increase in adsorbent dosage is due to the availability of more surface area of the adsorbent for adsorption.

Desorption studies: Desorption studies help to elucidate the nature of adsorption, recovery of metals from wastewater and recycling of adsorbent. Desorption was tried at different pH values ranging between 6.0 and 12.0. Increasing the pH of the desorbing medium increased the desorption of Cr(VI) and maximum desorption of 82% was found at pH 12. Increasing the pH would deprotonate the surface and hence the adsorbent surface would suspend the negatively charged HCrO⁴⁻ species (Selvaraj et al. 1998). The incomplete desorption may be due to the presence of impurities which may also act as an adsorbent for chromium.

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100$$

Adsorption isotherms: The adsorption studies were conducted at fixed initial concentration of Cr(VI) by varying the adsorbent dosage. Then the equilibrium data obtained were analysed in the light of Langmuir and Freundlich isotherms

The Freundlich equation is given by-

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

Table 4: Freundlich and Langmuir isotherm parameter for Cr(VI) sorption and separation factor (at 30°C and 0.100mm - 0.200mm).

Freundlich isotherm				Langmuir isotherm			
C_{eq}	Q_e	$\log C_{eq}$	$\log Q_e$	C_e	Q_o	C_e / Q_o	R_L
10	9.8	1	0.9921	10	9.80	1.024	0.9009
20	18.4	1.3010	1.2648	20	18.40	1.0869	0.8196
30	27.2	1.4771	1.4345	30	27.20	1.029	0.7518
40	34.12	1.6020	1.5330	40	34.12	1.1723	0.6944
50	40.05	1.6989	1.6026	50	40.05	1.2484	0.6452
60	44.50	1.7781	1.6484	60	44.50	1.3483	0.6024
70	46.62	1.8451	1.6685	70	46.62	1.5015	0.5650
80	50.12	1.9031	1.7002	80	50.12	1.5955	0.5319
90	52.24	1.9542	1.7182	90	52.24	1.7228	0.5025
100	54.36	2.0000	1.7353	100	54.36	1.8395	0.4762

Table 5: Characteristics of Langmuir adsorption isotherm.

Sl.No	Separation factor R_L	Types of isotherm
1	$R_L > 1$	Unfavourable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favourable
4	$R_L > 0$	Irreversible

Table 6: Characteristics of chromium plating Wastewater.

Sl No	Parameters	Concentration (mg/L)
1	pH	8.84
2	Turbidity, NTU	232
3	Total solids	4380.0
4	Suspended solids	435.0
5	Conductivity, mS/cm	13.64
6	COD	1714
7	Chlorides	668
8	Chromium(VI)	38.12
9	Total chromium	43.54
10	Sodium	631.0

Where, C_{eq} is the equilibrium concentration (mg/L), x/m is the amount of adsorbed per unit mass of WHC (mg/g), n is the indication of favorability and K is the capacity of adsorbent. The plot of $\log(x/m)$ Vs $\log C_e$ is linear which shows that the adsorption follows Freundlich isotherm for Cr(VI) as shown in Fig. 4. The calculated n and K values are 1.36 and 2.046 respectively. The data obtained are given in Table 4.

The Langmuir equation is given by-

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

Where C_e is equilibrium concentration of Cr(VI) (mg/L), q_e is the amount of Cr(VI) adsorbed per unit weight of adsorbent (mg/g), Q_o is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption. The linear plots of C_e/q_e Vs C_e show that the adsorption obeys Langmuir model in Fig. 5. Data are given in the Table 4. Values of Q_o and b are 106.06 and 0.011

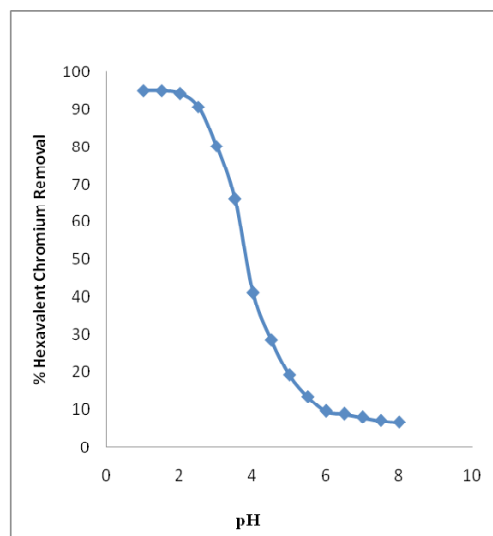


Fig. 1: Effect of pH.

respectively.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which can be defined as,

$$R_L = 1 / (1 + bC_e)$$

Where b is the Langmuir constant and C_e is the initial metal ion concentration (mg/L). The parameter indicates the isotherm shapes as given in Table 5.

Adsorption kinetics: The rate constant study for adsorption for different amounts of adsorbents was studied in light of the Lagergran's equation.

$$\log(C_{max} - C_t) = \log C_{max} - (K_{ad}/2.303)t$$

The data regarding the rate constant study for adsorbant dosage of 1g, 1.5g and 2g for initial Cr(VI) concentration at 30mg/L are given in Table 3. A plot of $\log(C_{max} - C_t)$ Vs t is represented in Fig. 6. Linear plots $\log(C_{max} - C_t)$ Vs t indicate the applicability of the above equation. The K_{ad} values calculated from the slopes of plots at 30mg/L of Cr(VI) at different dosages are 0.0141, 0.0170 and 0.0182.

CONCLUSION

The present study shows that the activated carbon prepared from water hyacinth is an effective adsorbent for the removal of Cr(VI) from wastewater. The adsorption of Cr(VI) by activated water hyacinth carbon has been well fitted for both Freundlich and Langmuir models. The data would be utilized for designing and fabricating the wastewater treatment plants. It can be concluded that in addition to the above ad-

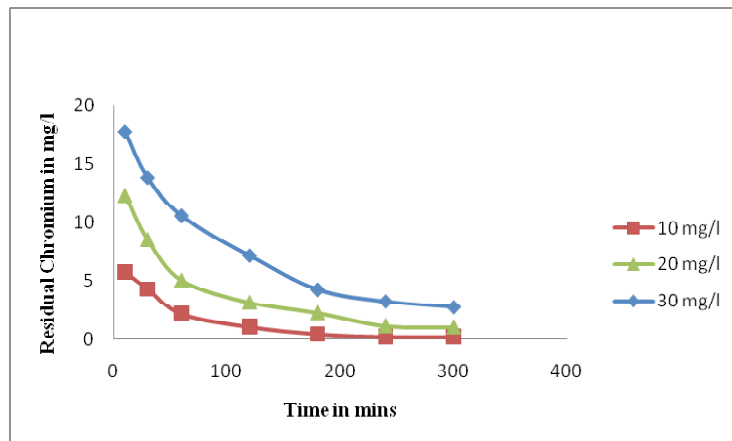


Fig. 2: Effect of initial concentrations of Cr(VI) on sorption.

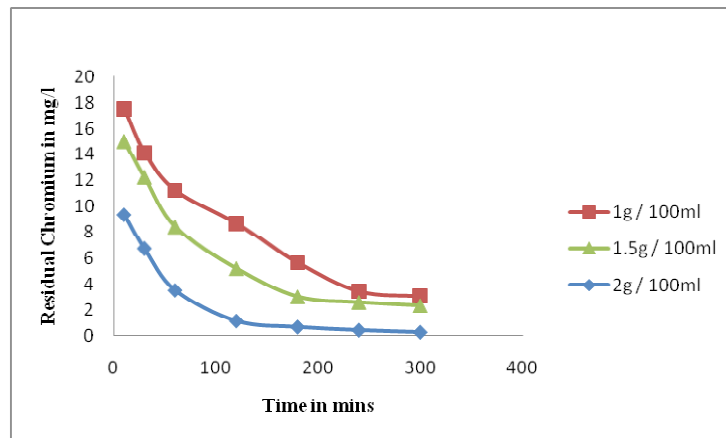


Fig. 3: Effect of adsorbent dosage of Cr(VI) on sorption.

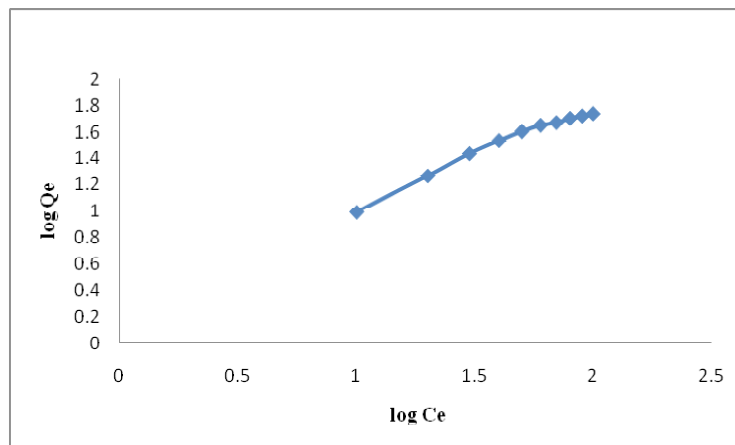


Fig. 4: Langmuir Isotherm.

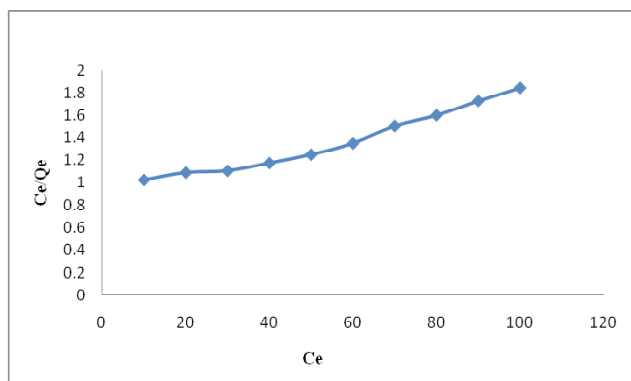


Fig. 5: Freundlich Isotherm.

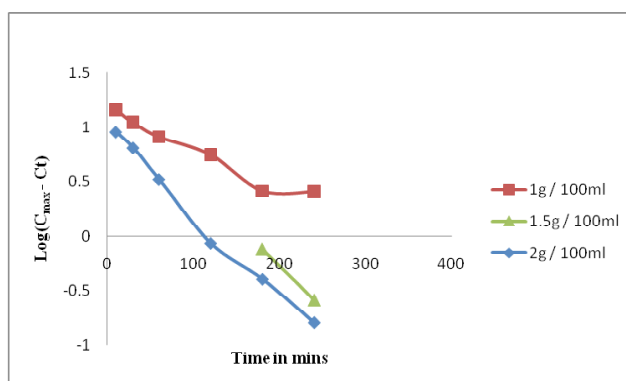


Fig. 6: Lagergren plot for the adsorption rate.

vantages the activated water hyacinth carbon could also be considered for commercial applications.

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