



Adsorption of Cr(VI) from aqueous solutions by low cost activated carbon

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ABSTRACT

The efficiency of activated carbon prepared from *Albizia lebbbeck* stem [ALSC] for the adsorption Cr(VI) ions from aqueous solution has been studied as a function of agitation time, adsorbent dosage, initial metal ion concentration, temperature and pH of adsorbate solution. The optimal conditions for the adsorption have been arrived and experiments were conducted to find out the Langmuir constants, Freundlich parameters and thermodynamic parameters such as ΔG° , ΔH° and ΔS° . Desorption studies were carried out for the recovery of both adsorbent and the metal ions.

(Key words: Activated carbon (ALSC), Chromium ion, Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters, Intraparticle diffusion, Regeneration pattern)

INTRODUCTION

In this paper, the adsorption behavior of Cr(VI) on *Albizia lebbbeck* Stem Carbon (ALSC) prepared from *Albizia lebbbeck* stem, as the adsorbent has been made. Batch mode experiments were carried out to study the effect of contact time on the removal of Cr(VI) ions with the variation of the dose of the adsorbent, variation of the initial concentration of the solution, variation of pH, variation of size of the adsorbent and variation of temperature. Langmuir[1] and Freundlich[2] models were tested and the results are interpreted.

RESULTS AND DISCUSSION

Effect of Dosage of ALSC

Experiments were conducted to find out the effect of the dose of the adsorbent on the removal of Cr(VI), namely, 2.0, 4.0, 6.0, 8.0 and 10.0 g/L respectively. Figure-1 represents the plot of Cr(VI) adsorbed in percentage for various doses of the adsorbent. The result indicates that the uptake of Cr(VI) ions per unit mass of the adsorbent increases with the increasing dose of adsorbent[3,4,5].

Effect of Contact Time

The effect of contact time on the removal of Cr(VI) by ALSC has been studied and the results are shown in figure-2. There is only a marginal increase in removal of Cr(VI) after the attainment of equilibrium[6,7]. The maximum amount of Cr(VI) adsorbed corresponding to the equilibration time is found to be 86.63 % for a weight of 2.0 g/L of the adsorbent.

TABLE-1 LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION OF Cr(VI) ONTO ALSC

S.No.	Temp., °C	Q _m (mg/g)	b (L/mg)	Correlation Coefficient (R ²)	K _F (mg/g)	n (L/mg)	Correlation Coefficient (R ²)
1	35	60.09	0.1197	0.9964	1.8199	1.6701	0.1197
2	40	59.77	0.1356	0.9963	1.8018	1.6983	0.1356
3	45	59.17	0.1639	0.9978	1.7533	1.7812	0.1639
4	50	55.24	0.2132	0.0046	1.6465	2.0052	0.2132

TABLE-2 VALUES OF R_L FOR Cr(VI) ADSORPTION ONTO ALSC

[Cr(VI)] _{ini.} , C ₀ (mg/L)	R _L values at different temperatures			
	35° C	40° C	45° C	50° C
50	0.456	0.425	0.380	0.359
100	0.294	0.270	0.234	0.190
150	0.217	0.198	0.169	0.135
200	0.172	0.156	0.132	0.105
250	0.142	0.129	0.109	0.085
300	0.121	0.109	0.092	0.073

TABLE-3 RATE CONSTANTS FOR THE ADSORPTION OF Cr(VI) (10³ k_{ad}, min⁻¹) AND THE CONSTANTS FOR FORWARD (10³ k₁, min⁻¹) AND REVERSE (10³ k₂, min⁻¹) PROCESS

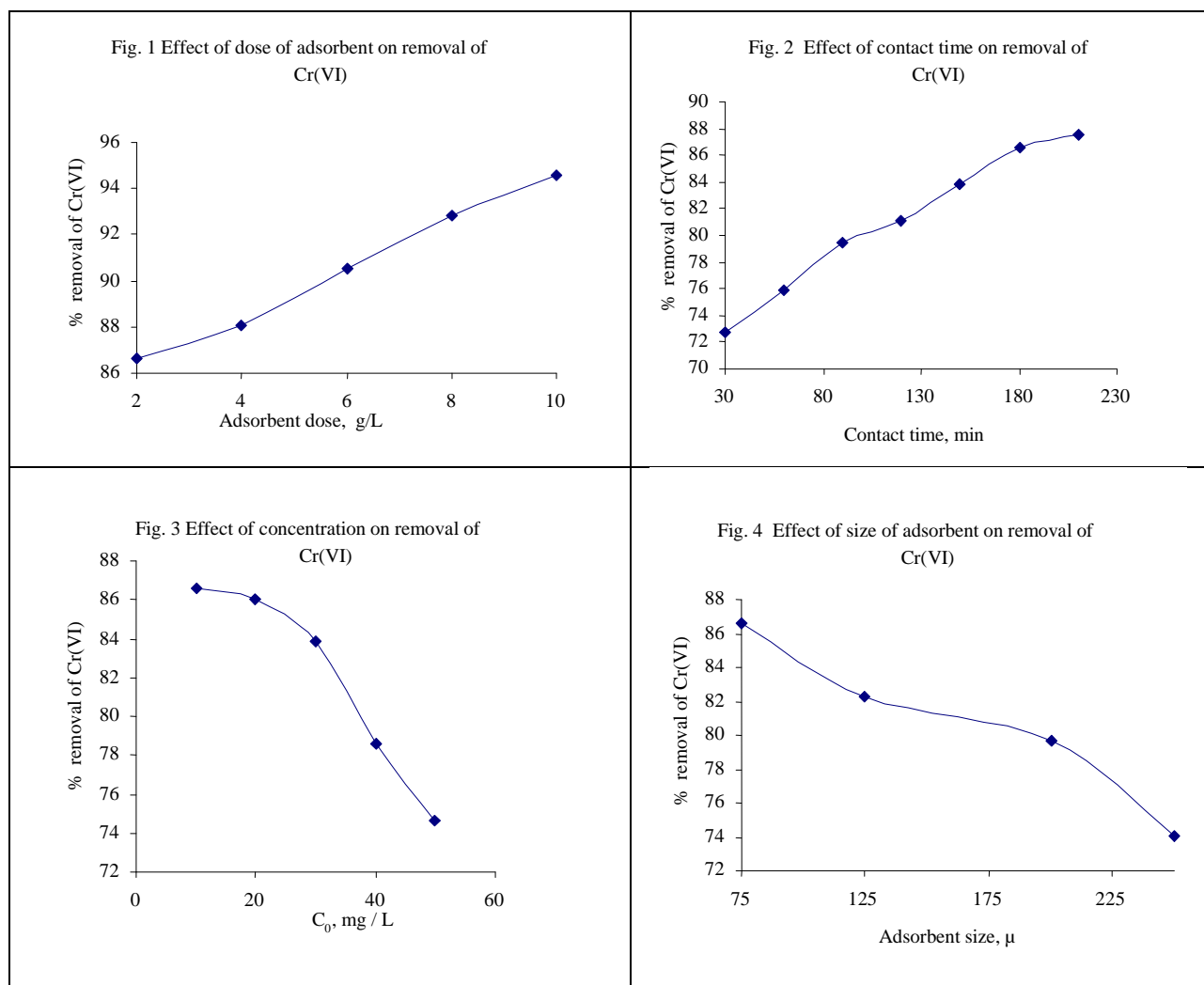
S.No.	[Cr(VI)] _{ini.} , C ₀ , mg/L	Temperature, °C											
		k _{ad}				35		40		45		50	
		35	40	45	50	k ₁	k ₂	k ₁	k ₂	k ₁	k ₂	k ₁	k ₂
1	10	13.54	15.89	18.51	20.74	11.73	1.81	13.96	1.93	16.69	1.82	19.41	1.33
2	20	9.10	11.46	13.57	15.92	7.83	1.27	10.04	1.42	12.07	1.50	14.35	1.57
3	30	7.81	8.66	9.69	11.43	6.55	1.26	7.40	1.26	8.43	1.26	10.16	1.27
4	40	5.62	6.21	6.93	7.57	4.41	1.21	4.99	1.22	5.69	1.24	6.36	1.21
5	50	4.54	4.90	5.42	5.85	3.39	1.15	3.74	1.16	4.21	1.21	4.57	1.28
6	60	3.92	4.79	5.25	5.56	2.78	1.14	3.48	1.31	3.90	1.35	4.21	1.36

TABLE-4 EQUILIBRIUM CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF Cr(VI) ONTO ALSC W_{adsorbent}, mg/L = 2.0; Adsorbent Size = 75-125 μ; pH = 1.5; Contact time = 180 min

S.No.	[Cr(VI)] _{ini.} , C ₀ , mg/L	Temperature, °C									
		K ₀				ΔG°				ΔH°	ΔS°
		35	40	45	50	35	40	45	50		
1	10	6.48	7.72	9.17	14.32	-4.78	-5.14	-5.84	-7.20	28.84	109.02
2	20	6.15	7.08	8.05	9.15	-4.65	-5.09	-5.52	-5.94	22.31	87.41
3	30	5.21	5.90	4.71	8.01	-4.22	-4.61	-5.02	-5.58	21.01	81.80
4	40	3.65	4.12	4.59	5.25	-3.31	-3.68	-4.02	-4.45	19.95	76.91
5	50	2.93	3.20	3.49	3.58	-2.75	-3.02	-3.30	-3.43	14.51	55.99
6	60	2.44	2.66	2.89	3.12	-2.28	-2.54	-2.80	-3.06	14.05	52.95

TABLE-5 EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF Cr(VI) ONTO ALSC

S.No.	[Cr(VI)] _{ini.} , C ₀ , mg/L	Temperature, °C											
		C _e (mg/L)				q _e (mg/g)				Cr(VI) removed (%)			
		35	40	45	50	35	40	45	50	35	40	45	50
1	10	1.3362	1.2081	0.9829	0.6402	8.6638	8.7919	9.0171	9.3598	86.63	87.91	90.17	93.59
2	20	2.7938	2.4738	2.2088	1.9947	17.206	17.526	17.791	18.005	86.03	87.63	88.95	90.02
3	30	4.8282	4.3473	3.8891	3.3305	25.171	25.657	26.110	26.669	83.90	85.50	87.03	88.89
4	40	8.5952	7.8112	7.1533	6.3998	31.440	32.188	32.846	39.099	78.60	80.47	82.11	84.00
5	50	12.699	11.901	11.115	10.900	37.300	38.098	38.884	39.099	74.60	76.19	77.76	58.48
6	60	17.411	16.351	15.401	14.529	42.589	43.648	44.598	45.470	70.98	72.74	74.33	75.78



Effect of Initial Metal ion Concentration

The results for the effect of concentration of adsorbate solution on removal of Cr(VI), viz., 10, 20, 30, 40 and 50 mg/L respectively showed that as the concentration of the solution increases, percentage removal of Cr(VI) decreases[8] (Fig.3).

Effect of Size of the Adsorbent

The experimental results of adsorption of Cr(VI) ions on to the activated carbon with various sizes (75-125, 125-200, 200-250, 250-300 μ) of the adsorbent are presented in figure-4. It is found that the adsorption is much favorable with the 75-125 μ size of the adsorbent[9].

Effect of pH

The effect of pH for the adsorption of Cr(VI) on to ALSC has been studied and the values are presented in figure-5. The optimum[10] pH is found to be 1.5 for the removal of Cr(VI).

Effect of Temperature

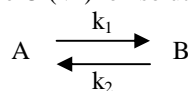
The effect of temperature on the adsorption of Cr(VI) has been studied and the values are presented in figure-6. The result indicates that the adsorption is maximum at higher temperature and found to be an endothermic process[11,12].

Adsorption Isotherms

The experimental data were analyzed by using linear form of the Langmuir[1] and Freundlich isotherms[2]. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (Fig.7). Values of Q_m and b were determined from slope and intercepts of the plots and are presented in table (Table-1). From the results, it is clear that the values of adsorption efficiency Q_m for ALSC decreases on increasing the temperature[13,14]. But the energy of adsorption shows an increasing trend. From the values, we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with high energy and no transmission of adsorbate in the plane of the adsorbent surface. The separation factor (R_L) was calculated and presented in table (Table-2). The values were found to lie between 0 and 1 and confirmed the adsorption process is favourable[15-17].

Linear plot of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Cr(VI) ion follows the Freundlich isotherm[13,14] (Fig.8). Values of K_F and n were found and given in the table (Table-1). However, the value of n is greater than one indicating the adsorption is much more favorable[16-18].

The homogeneous equilibrium between the Cr(VI) ion solution and the activated carbon has been expressed as:



Where k_1 is the forward rate constant and k_2 is the backward rate constant (Table-3). 'A' represents Cr(VI) ion remaining in the aqueous solution and 'B' represents Cr(VI) ion adsorbed on the surface of activated carbon. The results indicates that K_o values decreases with increase in the concentration of the Cr(VI) ion and increases with increase in temperature[19] (Table-4).

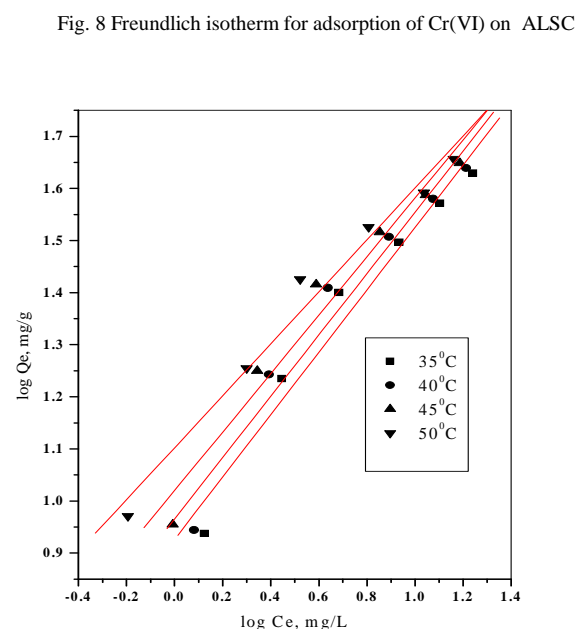
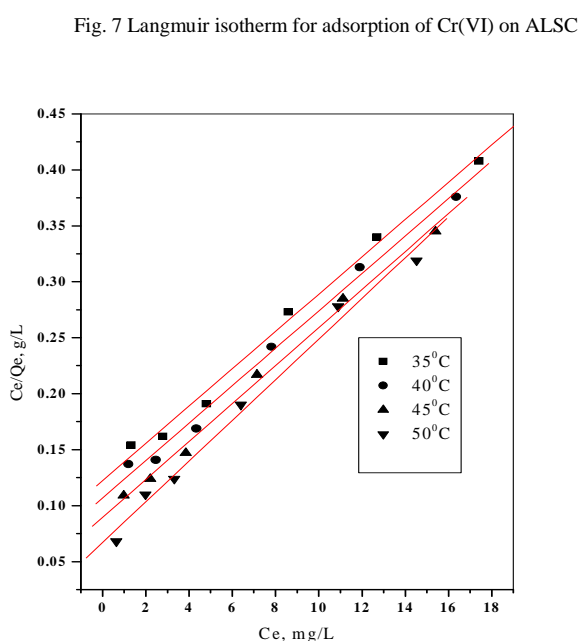
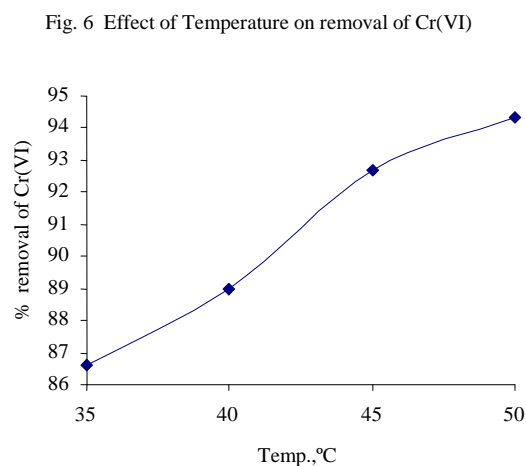
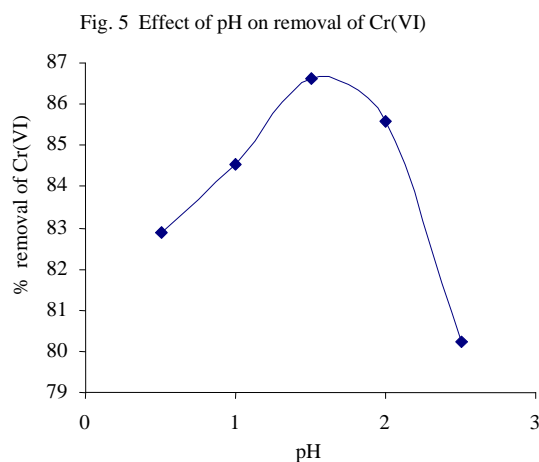
The K_p values obtained from the slope of the linear portions of the curve Q_t vs $t^{0.5}$ for various concentrations of the solution at 35 °C were 0.105, 0.176, 0.235, 0.294, 0.376 and 0.435 mg/g/min. The K_p values increased with increase in the Cr(VI) ion concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed Cr(VI) ion within the pores of the adsorbent.

The percentage of adsorption of ALSC increased with increase in the temperature of the system from 35-50 °C (Table-5). Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined and are presented in table (Table.4). The values are within the range of 1 to 93 kJ/mol indicating the favorability of physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of Cr(VI) ion. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. However, the low ΔH° value depicts that the metal ion is physisorbed onto the surface of the adsorbent[18,20].

The negative values of ΔG° (Table-4) shows that the adsorption is highly favorable for Cr(VI) ion. Further it confirms the spontaneous nature and feasibility process. In addition, the positive values of ΔS° show increasing randomness at the solid-liquid interface during the process. From the results, we could make out that the adsorption is purely physisorption rather than chemisorption. Enhancement of adsorption capacity of the activated carbon at higher temperatures is may be due to the enlargement of pore size and activation of the adsorbent surface[17-20].

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ion. If the adsorbed metal ion can be desorbed using neutral pH water or by very dilute acids, then the attachment of the metal ion of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the metal ion, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the metal ion, then the metal ion has held by the adsorbent through chemisorption[19]. The effect of various reagents used for desorption studies reveals that hydrochloric acid is a better reagent for desorption, because we could get more than 85 % removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ions by dilute mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through physisorption[20,21].



CONCLUSION

1. The equilibrium time, 180 min appears to be sufficient for the maximum adsorption of Cr(VI) species by ALSC, under the given set of experimental conditions and the maximum amount of Cr(VI) adsorbed is found to be 86.63 %, for a concentration of 10 mg/L with the dose of ALSC 2 g/L, at 35 °C with the optimum pH 1.5.
2. The percentage removal of Cr(VI) increases with the increase of the dose of the adsorbent and decreases with the increase of the concentration of adsorbate solution. Similarly, the minimum time required to achieve maximum adsorption also increases with the increase of the dose of the adsorbent.
3. The optimal pH to be fixed for further experimental work is 1.5.
4. The equilibrium data were found to be well represented by Langmuir and Freundlich isotherms and the results of thermodynamic studies have confirmed the adsorption is found to be an endothermic process.
5. The R_L values have confirmed the favorability of adsorption process.

6. All the above information reveals that the selected ALSC may be used as an adsorbent for the removal of Cr(VI) from waste waters.

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