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Thermodynamics of Chromium (VI) Removal From Aqueous Solution by Adsorption Technique Using Activated Carbon From Pods of Wood Apple and Commercially Available Carbon

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In this study activated carbon from pods of woodapple, an agro waste has been used as an adsorbent for removal of Cr(VI) from aqueous solutions. To analyze the efficiency of the activated carbon from woodapple (ACW) the experiments were also conducted with commercial activated carbon (ACC) and the results compared. The adsorption of Cr (VI) was carried out by varying the temperature and agitation time at two different pH . The negative value of free energy change (ΔG) and enthalpy (ΔH) show the spontaneous and exothermic nature of adsorption of Cr (VI) with respect to both the adsorbents used in this study .The positive value of entropy change (ΔS) indicate some structural changes in the adsorbate and the adsorbent and increased randomness during adsorption.

KEYWORD

Adsorption, Chromium, Adsorbent, Activated carbon, Thermodynamic parameters.

INTRODUCTION

Chromium can exist in a number of oxidation states. Industrial effluents are most likely to contain the trivalent, Cr(III), or the hexavalent, Cr(VI), forms. Of the two, the hexavalent form is generally thought of as being the more toxic (Coleman and Paran, 1991). Hence it is essential to remove it from wastewater. Activated carbon is the most widely used substance for the removal of heavy metals and other impurities from wastewater. Commercial activated carbon is effective for the removal of various pollutants. However, due to its high cost it is not affordable (Gupta *et al.*, 2003). So there is a need for low cost and readily available materials for the removal of toxic pollutants from water. Thermodyanamics has the remarkable ability to connect seemingly unrelated properties. Hence the present study is focused on use of activated carbon from the pod of wood apple (*Limonia Acidissia)* in the removal of Cr(VI) from aqueous solution from its thermodynamic standpoint. The thermodynamic parameters, such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the process of Cr (VI) adsorption has been presented in this paper.

MATERIAL AND METHOD

Collection of wood apple pod

Wood apple pod collected from a local juice manufacturing industry, Coimbatore, was cut into small pieces, dried in sunlight for 5 day and further dried in a hot air oven at 60°C for 24 hr. The completely dried material was chipped, powdered well and carbonized by chemical activation with concentrated sulphuric acid. Commercially activated carbon was obtained from Ree Chem Limited Reagents and Chemicals, Gaganphad, Hyderabad.

Equipment

Elico-110pH meter was used to measure pH. The pH meter was standardized using potassium hydrogen phosphate (pH 4). Digital Systronics colorimeter-112 was used for spectrophotometric work. Neolab electrical

[illegible]

Parameter	Adsorbents	
	ACC	ACW
Ash content, %	0.3871	0.0354
Moisture content, %	17.89	9.97
pH	6.87	2.41
Surface area, m^2/g	714.0	336.0
Bulk density, g/cc	0.2520	0.660
Specific gravity	0.9162	0.9019
Porosity, %	72.49	26.15

horizontal bench shaker (120 rpm - 200 rpm) with temperature control was used for agitation of solution containing adsorbent and adsorbate.

Batch experiment

All chemicals used were of analytical grade in order to assess the performance of the adsorbent and to avoid interference by other contaminants in wastewater, the experiments were conducted with aqueous solution of hexavalent chromium (adsorbate) prepared by dissolving 28 mg of potassium dichromate in 1L of double distilled water. 1 mL of stock solution = 100 μg of Cr (VI). Batch mode experiments were carried out to study the adsorption capacities of the adsorbents used in this study. Though industrial operations are not carried out batch- wise, these are simple and effective in evaluating the basic parameters affecting adsorption process.

Study of the effect of temperature on Cr (VI) removal

To study the effect of temperature, 100 mL of solutions containing 0.2 mg of Cr (VI) were shaken with 50 mg of activated carbon prepared from pods of wood apple (ACW) in a temperature controlled horizontal electrical bench shaker and agitated for various time intervals (10 to 180 min) at 300, 308 and 313 K, respectively at pH ~ 6.0 and at pH 2.5. After equilibration, the solutions were filtered and the residual Cr (VI) concentration was determined spectrophotometrically by diphenyl carbazide [illegible] (ACC).

RESULT AND DISCUSSION

Characterization of the adsorbents

Physical characteristics, namely ash content (%), moisture content(%), pH, surface area, bulk density, specific gravity, porosity (%) of the adsorbents used in this study were determined to identify the applicability of these adsorbents to remove Cr (VI) from aqueous solution by adsorption. The results of study are given in table 1.

Effect of temperature on Cr (VI) removal

Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate (Gupta *et al.*, 1990; Singh and Srivastava, 2001). Batch adsorption studies were carried out at pH 6.0 ± 0.02 and at pH 2.5 at various temperatures 300, 308 and 313K. With increase in temperature Cr (VI) removal was found to increase (Tables 2 and 3). This may be probably due to a decrease in the escaping tendency of the adsorbate species from the surface of the adsorbent. The enhanced adsorption of Cr (VI) may also be due to change in pore size and enhanced rate of intraparticle diffusion. This may also be attributed to the fact that boundary layer thickness decreases with an increase in temperature, causing increase in the boundary layer adsorption. This type of decrease in the thickness of the boundary layer and subsequent increase in the boundary layer adsorption with the increase in temperature may account for the exothermic nature of the adsorbate-adsorbent system. Thus as time interval was increased with increase in temperature a gradual increase in adsorption of Cr(VI) was noted. The percentage adsorption was found to be almost double in acidic pH than at pH 6.0 ± 0.02 in the case of both adsorbents used in this study.

Thermodyanmic parameter

The thermodynamic parameters, which characterize the equilibrium of a system, are the

Table 2. *Effect of agitation time and temperature for the adsorption of Cr (VI) onto ACW*

Conditions
Initial concentration of Cr (VI) solution = 0.20mg/L
Adsorbent dosage = 50mg

Time, min	Percentage of Cr (VI) removed					
	pH = 6.0 ± 0.02			pH = 2.5 ± 0.02		
	300k	308k	313k	300k	308k	313k
10	12.6	21.4	27.11	27.9	37.31	42.82
20	15.4	25.6	29.23	31.2	41.42	49.16
30	19.5	27.9	31.8	35.6	46.1	57.4
40	22.44	31.3	35.4	39.8	48.81	63.35
50	24.44	34.1	39.67	41.11	55.66	71.6
60	30.6	38.4	45.81	48.43	58.8	75.8
90	36.66	41.3	53.45	54.86	64.71	84.14
120	43.4	46.6	62.32	60.12	71.62	89.26
150	47.82	47.8	69.18	68.1	75.43	96.11
180	52.3	54.9	74.16	76.43	82.16	96.11

Table 3. *Effect agitation time and temperature for adsorption of Cr (VI) onto ACC*

Conditions
Initial concentration of Cr (VI) solution = 0.20mg/L
Adsorbent dosage = 50mg

Time, min	Percentage of Cr (VI) removed					
	pH = 6.0 ± 0.02			pH = 2.5 ± 0.02		
	300k	308k	313k	300k	308k	313k
10	26.08	28.14	36.72	28.2	71.4	74.4
20	29.34	34.89	40.81	33.5	73.6	75.9
30	31.52	36.21	45.52	36.4	78.8	76.7
40	34.78	46.3	49.41	40.6	79.1	78.4
50	38.04	58.6	54.42	43.7	81.2	79.2
60	40.21	59.2	59.56	49.9	83	81.9
90	44.56	64.3	65.77	55.6	87.4	89.4
120	47.82	66.4	70.6	61.4	87.6	89.4
150	51.82	68.7	76.7	69.7	88.0	89.4
180	51.8	80.2	82.3	75.4	88.0	89.4

Gibbs free energy change (ΔG), the enthalpy change (ΔH) and the entropy change (ΔS). These parameters were determined using the following relations (Stephan Inbaraj and Sulochana, 2002).

$$K_c = \frac{C_{Ae}}{C_e}$$

$$\Delta G = -RT l_n K_c$$

$$\text{Log } K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT_c}$$

where K_c is the equilibrium constant, C_{Ae} is solid phase concentration of Cr (VI) at equi-

[illegible]

Conditions: [illegible]
Initial concentration of Cr (VI) solution = [illegible]
Adsorbent dosage = 50mg

Adsorbent,	ACW						ACC					
pH	~6.0						~2.5					
T	K'sec^{1} (x10^{4})	ln Kc	ΔG, J/mole	K'sec^{1} (x10^{4})	ln Kc	-ΔG J/mole	K'sec^{1} (x10^{4})	ln Kc	-ΔGJ J/mole	K'sec (x10^{4})	ln Kc	-ΔGJ J/mole
300	2.5476	0.6816	1700.05	0.2287	0.6237	1555.63	1.967 x 10^{4}	0.6765	1687.33	1.266	0.2358	588.13
308	1.9771	0.9351	2394.52	1.8659	0.8275	2118.98	2.2767 x10^{4}	0.8227	2106.69	3.198	0.1625	2976.82
313	2.5738	0.9438	2456.033	2.3895	0.8711	2266.84	3.1386 x10^{4}	1.14377	2976.41	2.250	0.81093	2110.26
ΔS, J/mole	62.104			57.25			95.98			138.147		
ΔH, J/mole	-168.901			-1560.4			-272.24			-4876.09		

T-Temperature in Kelvin

librium, C_e is the residual concentration of Cr (VI) at equilibrium, R is the gas constant (J mole-1) and T is the temperature in Kelvin, ΔH and ΔS were obtained from the slope and intercepts van't Hoff plot (1/T vs ln Kc).

The values of ΔG, ΔS and ΔH for the adsorption of Cr (VI) using adsorbents ACC and ACW at pH 6.0 and 2.5 are given in table 4. The negative value of enthalpy (ΔH) for the adsorption of Cr (VI) process suggest the exothermic nature of adsorption of Cr (VI) with both the adsorbents ACC and ACW used in this study. The negative values of free energy change (ΔG) indicate the feasibility of the processes and the spontaneous nature of the adsorption of Cr (VI) species with respect to both the adsorbents used in the study. The positive value of ΔS indicates some structural changes in the adsorbate and adsorbent, and also reflects the affinity of the adsorbent for Cr (VI) species. The positive value of ΔS is also due to the increase randomness during the adsorption of Cr (VI) on the adsorbents ACC, and ACW. During the adsorption of Cr (VI), the adsorbed water molecules, which are displaced by the Cr (VI) species, gain more translation entropy than is lost by adsorbate species, thus following the prevalence of randomness in the system.

CONCLUSION

In this study an attempt has been made to prepare a low cost adsorbent from a solid waste, pod of wood apple and the adsorption process studied in terms of its thermodynamic standpoint. The negative value of free energy change (ΔG) and enthalpy (ΔH) show the spontaneous and exothermic nature of adsorption of Cr (VI) with respect to both the adsorbents used in this study .The positive value of entropy change (ΔS) indicate some structural changes in the adsorbate and the adsorbent and increased randomness during adsorption.

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