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ISOTHERM AND THERMODYNAMIC STUDIES ON THE ADSORPTION OF CHROMIUM (VI) ION ONTO ACTIVATED CARBON PREPARED FROM SILK COTTON FRUIT WALLS (*CEIBA PENTANDRA* L.)

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Abstract

The present work aimed to study the removal of chromium from aqueous solution by adsorption process using fruit walls of Silk Cotton (*Ceiba pentandra* L.) activated carbon. Batch adsorption experiments were carried out. Cr (VI) ion adsorption equilibrium was rapidly attained after 50 minutes of the contact time and it was described by the Langmuir, Freundlich, Temkin and Dubinin-Raduskevich adsorption isotherms over the entire concentration ranges from 12 to 24 mg/L. Thermodynamic parameters such as ΔH^o, ΔS^o and ΔG^o were calculated, which indicated that the adsorption was spontaneous and endothermic nature, which was evident by increasing the randomness of the Cr (VI) ion at the solid and liquid interface.

Keywords: Adsorption, Isotherms, Thermodynamics, Microwave, Zinc chloride, Activated carbon, *Ceiba pentandra* L., Cr (VI) ion.

1. Introduction

Chromium exhibits stability in Cr (III) and Cr (VI) oxidation states[1]. But hexavalent chromium is more toxic to living organisms than the trivalent chromium[2]. Therefore, removal of Cr (VI) ion from wastewater is essential before disposal. The use of activated carbons to remove organic and inorganic pollutants from waters is in practice worldwide, because of their high surface area, microporous character and the chemical nature of their surface[3]. Many investigators have studied the feasibility of less expensive material such as alginate beads[4], wheat straw[5], carbon developed from waste materials[6], biosorbents[7], activated sludge[8], fly ash[9], and agricultural waste [10] for the removal of chromium from waste water as evidenced from several previous reports. In this study, we have derived a low cost activated carbon from agricultural waste, namely fruit walls of Silk Cotton (*Ceiba pentandra* L.) for the removal of hexavalent chromium from aqueous solution.

2. Materials and Methods

2.1 Preparation of adsorbent through microwave method

50 g of the fruit wall powder was soaked with 60 % $ZnCl_2$ solution .The slurry was allowed to stand as such at ordinary conditions of temperature and pressure for a day to ensure the access of the $ZnCl_2$ in to the material. Then the slurry was subjected to microwave heating for 10 minutes with the power of 600 watts. The carbonized sample was washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reach 7. Then the carbon was filtered and dried at 378 K. Thus obtained carbon from the fruit walls of Silk cotton was designated as Microwave assisted Zinc chloride Activated Silk cotton Carbon (MWZASC). The carbon was ground well and the particle size ranging from 53 to 105 µm was taken for further study.

2.2 Preparation of stock Solution

1000 mg/L Cr (VI) ion stock solution was prepared by dissolving 2.828 g of Potassium dichromate (AR grade) in 1000 ml of double distilled water. The experimental solutions were prepared by proper dilution.

2.3 Adsorption experiments

The effect of parameters such as initial concentration of Cr (VI) ion, adsorbent dose and contact time was studied by batch mode technique because of its simplicity. Dose of the adsorbent was taken in 250 mL iodine flask and 50 mL and pre-determined concentration of the Cr (VI) ion solution was poured into the flask and the pH of the solution brought 2 by adding 0.1 N HCl solution. The content of the flask was agitated using rotary shaker with 130 rpm for pre-determined duration. Then the adsorbents were separated by centrifugation and concentration of the centrifugate was determined spectrophotometrically by diphenyl carbozide method. The percentage removal of the Cr (VI) ion from the solution and the quantity adsorbed by the adsorbent were calculated using concerned equations.

2.3.1 Diphenyl carbozide method

0.25% (W/V) solution of diphenyl carbozide was prepared in 50% (V/V) acetone. 1 mL of the sample solution was pipetted out into 25 mL standard flasks. To this 1 mL of 6 N H_2SO_4 was added followed by 1 mL of diphenyl carbozide and the total volume was made up to 25 mL using double distilled water. Concentration of Cr (VI) ion was estimated by the intensity of the reddish brown color developed due to complex formation using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm[11].

2.4 Data Processing Tools

Table 1 Data Processing Tools

S. No.	Parameters		Formulae
1.	**Mass balance relationships**	% of Removal	$(C_i - C_t)\times V/C_i$
		Quantity adsorbed at equilibrium, q_e	$(C_i - C_e) \times V/W$
		Quantity adsorbed at the time t, q_t	$(C_i - C_t) \times V/W$
3.	**Isotherms**	Langmuir Separation factor	$C_e/Q_e = 1/Q_0 b + C_e/Q_0$ $R_L = 1 / (1+ bCi)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\varepsilon^2$ $\varepsilon = RT \ln (1+1/C_e)$ $E = 1/ (2B)^{½}$
4.	**Thermodynamic Parameters**	Standard Free energy Change	$\Delta G° = -RT \ln K_c$
		Van't Hoff equation	$\ln K_c = \Delta S°/R - \Delta H°/R$

2.4.1 Nomenclature

C_i, C_t and C_e	Concentration at initial, at the time 't' and at equilibrium respectively
Q_e or q_e and q_t	Quantity adsorbed at the time 't' and at equilibrium respectively
V	Volume of the Chromium solution in liter (L)
W	Mass of the adsorbent in gram (g)
Q_0	Predicted adsorption efficiency
b	Adsorption energy (L/mg)
R_L	Separation factor
K_f and n	The adsorption capacity (mg/g) Intensity of adsorption
b_T	Tempkin constant related to heat of sorption (J/mg)
a_T	Equilibrium binding constant
q_D	Theoretical saturation capacity (mg/g)

B	Constant related to the mean free energy
ε	Polanyi potential
E	Mean free energy of adsorption
R	Gas Constant
T	Temperature (K)
K_d	Apparent equilibrium constant (Concentration in solid phase/concentration in liquid phase)
ΔG°	Standard free energy
ΔS°	Entropy of adsorption
ΔH°	Enthalpy of adsorption

3. Results and Discussion

3.1 Isotherm studies

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Temkin and Dubinin-Raduskevich adsorption isotherm models [12]. These isotherms are depicted in Figure 1.

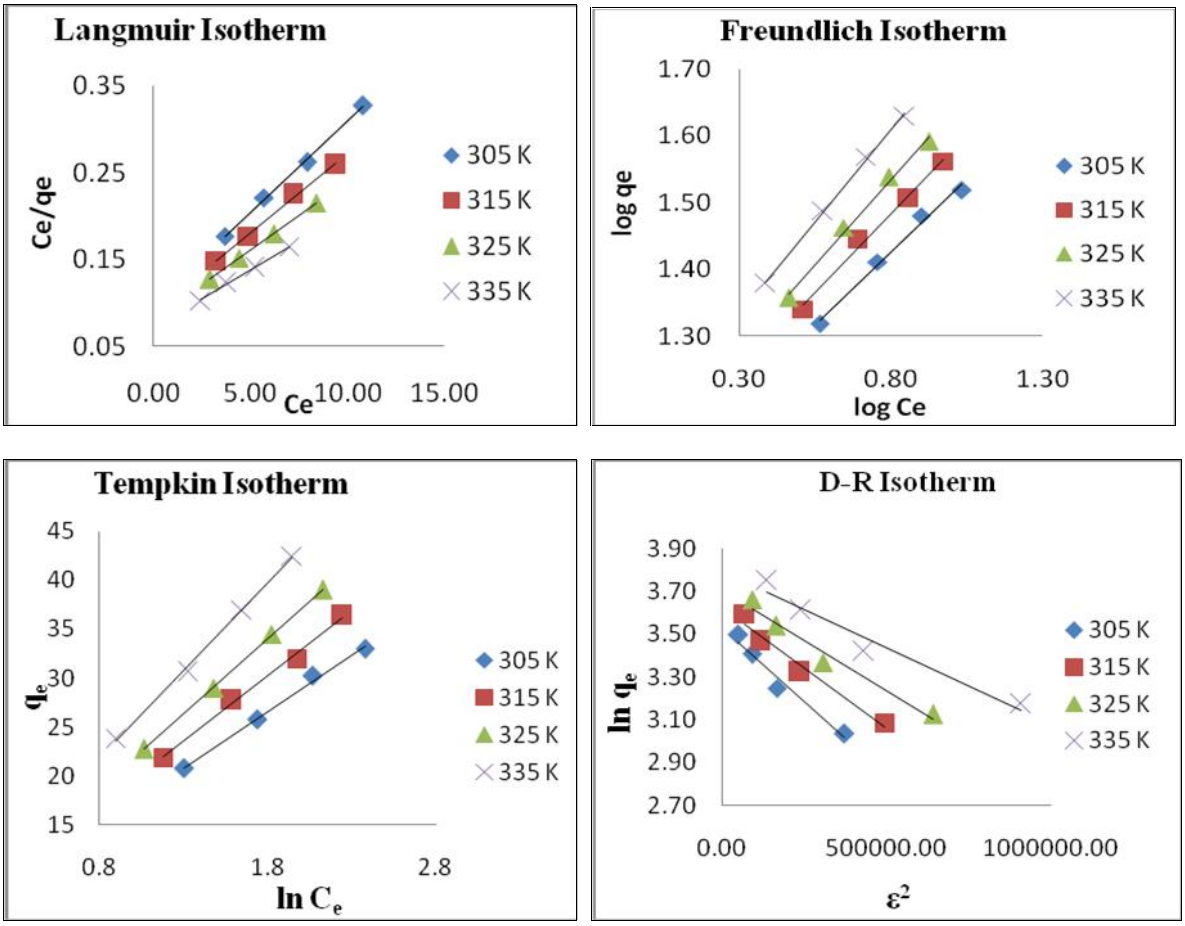

Figure 1 Isotherm Models

The regression coefficient values (R^2) of the studied isotherms are ranges from 0.98 to 1which interprets that the well-fitting of the data with the isotherm models studied and the values of constants derived are reliable.

The adsorption capacities (Q_0,$K_f$and q_D)obtained from the studied isotherm models were found to increase with the increase of temperature from 305 K to 335K. This kind of results was obtained in various similar studies[27] and describes the endothermic nature of the adsorption.The separation factor R_L values obtained from Langmuir adsorption are in between 0 to 1 indicate the favourable adsorption.R^2 values of isotherm plots revealed that Langmuir isotherm well describes in the present system that was the existence of identical adsorption site.

The values of n obtained from Freundlich isotherm are in between 1 and 10 which indicate cooperative adsorption [11].

b_T –The Temkin constant is related to the heat of adsorption. This b_T value ranged from from 156.02 to 219.53. The Temkin parameter a_T values give an idea about nature of adsorption, if a_T value is in between 0 and 8, then the adsorption is physical nature, otherwise it is chemical nature [11]. In our present study the a_T values ranged from 1.65 to 1.53 which indicate the adsorption is physical nature.

The mean free energy of adsorption E calculated from Dubinin-Raduskevich isotherm ranges from 0.70 to 0.03 which indicates the physisorption nature.

Table 2 Isotherm parameters for removal of Chromium (VI)ion by MWZASC

Langmuir Isotherm								Freundlich Isotherm		
Temperature (K)	Q_0 (mg/g)	b (L/mg)	R_L 12 ppm	R_L 16 ppm	R_L 20 ppm	R_L 24 ppm	R^2	n	k_f (mg/g)	R^2
305	47.84	0.209	0.29	0.23	0.19	0.17	0.99	2.29	11.92	0.99
315	54.94	0.203	0.29	0.24	0.20	0.17	0.99	2.13	12.80	0.99
325	62.89	0.196	0.30	0.24	0.20	0.18	0.99	1.96	13.41	0.99
335	74.07	0.191	0.30	0.25	0.21	0.18	0.99	1.80	14.62	1.00

DR Isotherm					Temkin Isotherm		
Temperature (K)	q_D (mg/g)	$B\times10^{-4}$ (mol^2/J^2)	E (kJ/mol)	R^2	b_T (g/mg)	a_T (L/g)	R^2
305	34.10	0.0002	0.07	0.98	219.53	1.65	0.99
315	37.31	0.0002	0.07	0.98	196.45	1.60	0.99
325	40.42	0.0018	0.02	0.99	176.04	1.51	1.00
335	44.67	0.0014	0.03	0.99	156.02	1.53	0.99

3.4 Thermodynamic Studies

Thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption are calculated, using Van't Hoff's plot, are given in Table 3. Negative standard free energy of adsorption indicates that the adsorption process is spontaneous in nature. The positive ΔH° values infer the endothermic nature of adsorption, which was confirmed by the experimental data i.e., adsorption capacity increased with the increase of temperature. Small ΔH° values infer that the bonding between Chromium (VI) ion and MWZASC surface should be very weak. Positive value of ΔS° suggests that the adsorption proceeds with increased randomness[13].

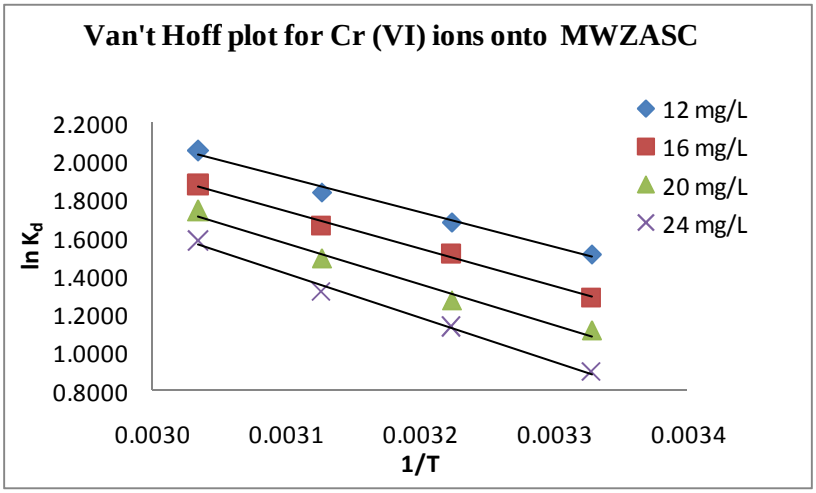

Figure 2 Van't Hoff plot

Table 3 Thermodynamic parameters for removal of Chromium (VI) ion by MWZASC

Thermodynamic Parameters and their results					
Concentration (mg/L)	Temperature (K)	k_d	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/mol
12	305	4.52	-2.07	-15.15	56.38
	315	5.38	-2.59		
	325	6.28	-3.09		
	335	7.80	-3.79		
16	305	3.61	-1.50	-16.29	56.37
	315	4.53	-2.14		
	325	5.27	-2.62		
	335	6.51	-3.29		
20	305	3.05	-1.07	-17.75	61.45
	315	3.56	-1.51		
	325	4.45	-2.16		
	335	5.69	-2.91		
24	305	2.44	-0.51	-19.03	63.77
	315	3.09	-1.14		
	325	3.71	-1.67		
	335	4.86	-2.47		

4. Conclusion

Microwave assisted zinc chloride activated carbon (MWZASC) was prepared from fruit walls of Silk Cotton (*Ceiba pentandra* L.) found to have good adsorption capacity. Experimental data indicated that MWZASC was effective in removing Chromium (VI) ion from aqueous solution. Equilibrium adsorption was achieved around 50 minutes for the dosage of 20 mg/50 mL of solution at room temperature of 305 K for the initial concentration of Chromium (VI) ion solutions ranging from 12 to 24 mg/L. The separation factor R_L values indicated that the adsorption was favourable. Thermodynamic study revealed that the adsorption system was spontaneous, endothermic with increased randomness.

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