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Biosorption of Cr(VI) from Aqueous Solution Using New Adsorbent: Equilibrium and Thermodynamic Study

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Abstract: Biosorption is one such emerging technology which utilized naturally occurring waste materials to sequester heavy metals from polluted water. In the present study cinnamon was utilized for Cr(VI) removal from aqueous solutions.It was found that a time of two hours was sufficient for sorption to attain equilibrium. The optimum pH was 2 for Cr(VI) removal. Temprature has little influence on the biosorption process. The Cr(VI) removal decreased with increase in temperature. The biosorption data was well fitted to Dubinin - Radushkevich (D-R), Freundlich and Tempkin adsorption isotherm models, although the correlation coefficient of Langmuir model was high but the calculated adsorption capacity did not agree with the experimental. The thermodynamic study reveals that the biosorption process is spontaneous and the spontaneity decreased with temperature increase and the process is exothermic accompanied by highly ordered adsorbate at the solid liquid interface. ΔH° values were negative and lie in the range of physical adsorption.

Keywords : Biosorption, Cinnamon, Isotherm models, Chromium(VI), Thermodynamic study .

Introduction

The application of biosorption in environmental treatment has become a significant research area in the past ten years.Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity[1]. Chromium(VI) is priority metal pollutant introduced into water bodies from many industrial processes such as tanning, metal processing, paint manufacturing, steel fabrication and agricultural runoff. Hexavalent chromium, which is primarily present in the form of chromate ($CrO_4^=$) and dichromate ($Cr_2O_7^=$), possesses significantly higher levels of toxicity than the other valency states[2]. Cr(VI) is suspected of being a carcinogen material and is quite soluble in the aqueous phase almost over the entire pH range in the natural environment. Accidental chromium ingestion causes stomach upsets, ulcers, kidney and liver damage and even death. Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials[3,4].

Removing metals from wastewater requires development of new sorbents. A wide range of commertial sorbents including chelating resins and activated carbons are available for metal sorption, but they are relatively expensive. In recent years, numerous low cost natural materials have been proposed as potential biosorbents. These include pomegranate peel[5,6], neem leaves[7], wheat bran[8], sargassum sp.seaweed[9], modified liginin[10]. Adsorption remains the most economical and widely used process for removal of toxic pollutants from wastewater. The other processes like precipitation, ion exchange, filtration, electrodeposition, membrane technology …*etc*., have many disadvantages including incomplete metal removal, use of expensive equipment, energy requirements and production of toxic sluge[11]. The objective of the present study is to evaluate the equilibrium and thermodynamic parameters of the new adsorbent derived from cinnamon bark to remove toxic chromium from aqueous solutions.

Experimental

Preparation of biosorbent

Cinnamon bark (cinnamonum zeylanicum) was collected from local market and dried then milled at mesh 80. The milled biosorbent was shaked with distilled water for overnight then filtered, this process was repeated for about five times or until we are certain that all soluble materials were removed. Finally the biosorbent was filtered and deried in an air oven at 80 ^{O}C for 3 h and stored in a sealed bottle in a dry place. FTIR spectrum of cinnamon was done by Shimadzu 8000 instrument .

Preparation of chromuim solution

A stock solution of Cr(VI) 500 mg / L was obtained by dissolving 1.4144 g of $K_2Cr_2O_7$ in 1 L of deionized water, this solution was used for further experimental solution preparation. The pH values were adjusted with 0.13 M HNO_3 or 0.1 M NaOH. Analytical grade reagents were used through out this study. Chromium content in the sorption solutions was determined by atomic absorption spectrophotometer type (AAnalyst 200 Perkin Elmer).

Adsorption isotherm and thermodynamic studies

Adsorption isotherm and thermodynamic studies experiments were carried out at different temperatures (20, 30, 40 and 50 ^{o}C) by shaking the biosorbent 0.1 g with 50 mL of Cr(VI) 10, 20, 30 and 40 mg / L solution for 120 minutes and pH 2.0 (it was found that 120 min. is the time to reach the equilibrium and maximum adsorption occurred at pH 2.0). The amount of chromium adsorbed on to biomass, q_e mg/g, was calculated using the following equation :

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

Where C_i and C_e are the initial and equilibrium liquid phase concentration mg / L of Cr(VI) respectively, V is the volume of the solution (L) and M is the weight of the adsorbent used (g) .

Results and Discussion

It was found that the maximum removal of chromium from aquous solution using cinnamon as adsorbent occurred at pH 2.0 and the required time for equilibrium was 120 minutes. So all batch biosorption experiments were done at these conditions. The FTIR spectrum of cinnamon Figure 1 revealed that the presence of phenolic or carboxylic group and ketonic or aldehyde groups which are reposibile for binding of metal ions.

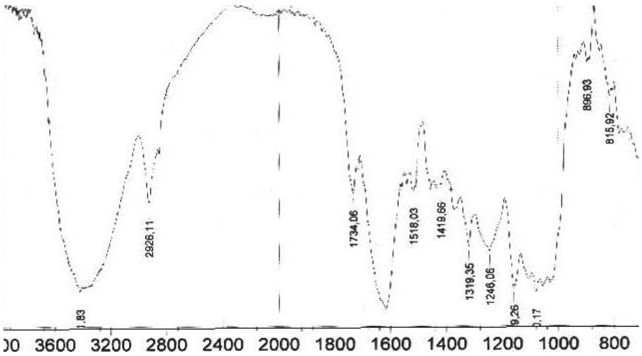

Figure 1. FTIR spectrum of cinnamon.

Adsorption isotherm

The distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir, Freundlich, Dubinin - Radushkevich (D-R) and Tempkin.

The Langmuir model assumes that the uptake of metal ions occurs on homogenous surface by monolyer adsorption without any interaction between adsorbed ions[12] . The linear equation of Langmuir is :

$$\frac{1}{q_e} = \left(\frac{1}{K_L Qm} \right) \frac{1}{Ce} + \frac{1}{Qm} \qquad (2).$$

Where Qm is the maximum monolyer capacity of the adsorbent (mg/g) and K_L is an equlibruim constant (L mg $^{-1}$). The plot of $1/q_e$ *versus* $1/C_e$ is presented in Figure 2.

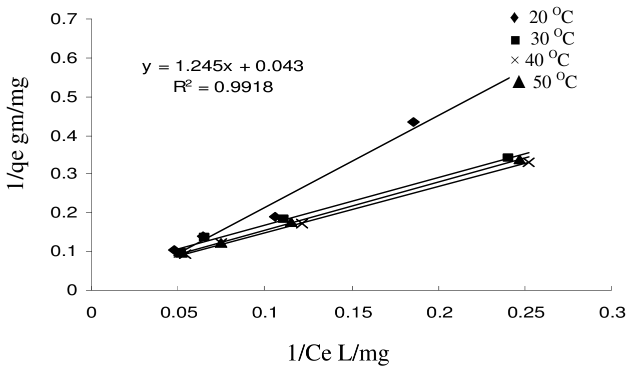

Figure 2. Langmuir plot for the adsorption of Cr(VI), 20, 30, 40 and 50 mg / L onto cinnamon 2g/L.

The calculated Qm values from Table 1, did not correlate with the experimental values, quite higher. So, although the R^2 is higher than 0.9693 but this isotherm is not applicable.

The Freundlich model assumes that the uptake of metal ions occurs on a heterogenous surface by monolyer adsorption[13]. The linear form of Freundlich model as follow:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

Where K_F and n are isotherm constants indicate the capacity and intensity of the adsorption, respectively. The linear plot of log q_e *versus* log C_e at each temperature Figure 3, indicates that the adsorption of Cr(VI) follow the Freundlich isotherm, Table 1, shows the Freundlich isotherm constants and R^2. The values of n were greater than one indicating that the adsorption onto cinnamon is favourable physical process except at 50 °C.

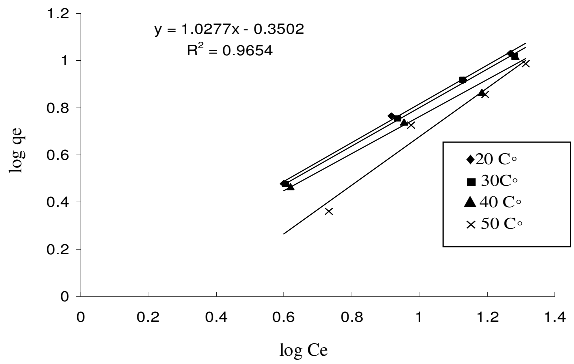

Figure 3. Freundlich plot for the adsorption of Cr(VI), 20, 30, 40 and 50 mg / L onto cinnamon 2 g/L.

Tempkin isotherm based on the assumption that the heat of adsorption of all models in the layer decreases linearity with coverage due to adsorbate- adsorbate repulsions[14]. It is commonly expreesed in the linear for as follows

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{4}$$

Where B_T= RT / b_T, T is the absolute temperature (K) and R universal gas constant 8.314 J. $mol^{-1}.K^{-1}$. The constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant. The adsorption data can be analysed according to equation 4 from a plot of q_e *vs.* ln C_e Figure 4, followed by determination of the isotherm constant A_T and B_T and R^2 Table 1, from values of R^2 the Tempkin isotherm is also applicable, although is less appliciple than Freundlich.

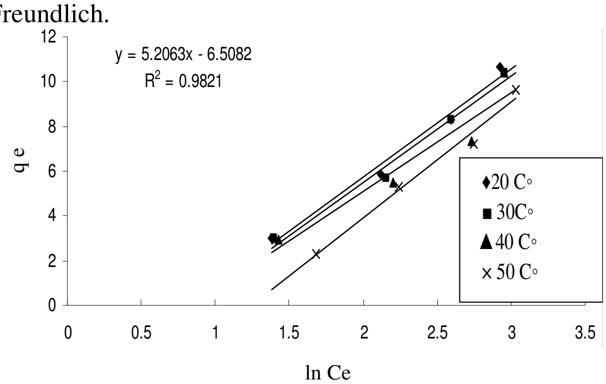

Figure 4. Tempkin plot for the adsorption of Cr(VI), 20, 30, 40 and 50 mg / L onto cinnamon 2 g/L.

Dubnin - RadushKevich (D-R) is another isotherm model. This model assumed that the characteristic of the sorption curves are related to the porosity of the adsorbent[15]. The final linear form is :

$$\ln q_e = \ln Q_m - K_{D\text{-}R}\,\varepsilon^2 \qquad (5)$$

$$\varepsilon = R\,T\,\ln\left(1+\frac{1}{C_e}\right)$$

Where $K_{(D\text{-}R)}$ is related to the adsorption energy and Q_m the maximum adsorption capacity, ε is the Polanyi potential. The mean energy of sorption (E) can expressed as follows :

$$E = \frac{1}{\sqrt{2K_{D-R}}}$$

From plot of ln q_e *versus* ε^2, Figure 5, the (D-R) constants and mean energy of adsorption can be calculated, Table 1.

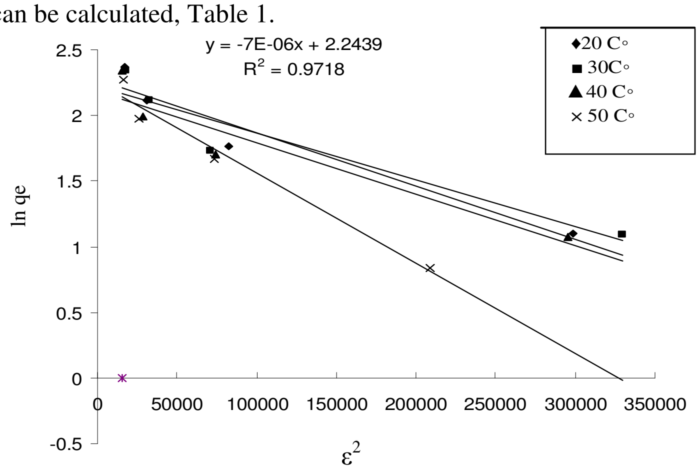

Figure 5. D-R plot for the adsorption of Cr (VI), 20, 30, 40 and 50 mg / L onto cinnamon 2g/L.

Table 1. Comparison of the collections isotherm parameters from Chromium 20, 30, 40 and 50 mg/L adsorption onto cinnamon.

Isotherm model	Isotherm parameters	Temperature, ◦C			
		20	30	40	50
Langmuir	Q_m, mg/g	34	31.9	23.26	40.98
	K_L, L mg^{-1}	0.025	0.025	0.035	0.01
	R^2	0.9996	0.9994	0.9918	0.9693
Freundilch	K_F	0.996	0.961	0.9585	0.466
	η	1.223	1.224	1.279	0.973
	R^2	0.9974	0.9977	0.9828	0.9654
Tempkin	B_T	4.86	4.03	4.42	5.21
	A_T	0.44	0.43	0.428	0.286
	R^2	0.9831	0.9798	0.9166	0.9821
D-R	Q_m, mg/g	11.66	12.49	10.94	10.25
	$K_{D\text{-}R}$ (mol^3 J^{-2})	9x10^{-6}	1x10^{-5}	1x10^{-5}	9x10^{-6}
	E, kJ mol	0.236	0.224	0.224	0.136
	R^2	0.9452	0.99	0.8796	0.8865

The mean energy of adsorption values were in the range of physical adsorption reactions. Although the correlation coefficients of (D-R) plots are lower than that of Langmuir plots, but Q_m values are consistent with the experimental values. On the other hand, Q_m values are slightly decreases with temperature increase, confirming the exothermic process[16]. On the light of the above discussion the (D-R) isotherm is more applicape.

Thermodynamic studies

In order to determine the thermodynamic feasibility and the thermal effects of the sorption, the Gibbs free energy (ΔG°), the entropy (ΔS°) and the enthalpy (ΔH°) of the adsorotion process were calculated. The ΔG° is the fundamental criterion to determine if a process occurs spontaneously. These parameters were determined using the following equations[17-19].

$$C_{liquid} \leftrightarrow C_{solid}$$

$$Ko = C_{solid} / C_{liquid} \quad (6)$$

$$\Delta G^o = - RTlnK_o \quad (7)$$

$$\log K_o = \Delta S°/2.303\ R - \Delta H° / 2.303RT \quad (8)$$

where K_o is the equilibrium constant, C_{soilid} is the concentration of Cr(VI) mg/L, at the solid phase (adsorbent) at equlibruim, C_{liqud} is the liqud phase concentration of Cr(VI) at equilibrium mg/L, T is the absolute temperature (K) and R is the gas constant, 8.314 J mol^{-1} K^{-1}. Vant Hoff equation (equation 8) was used to estimate the values of ΔH° and ΔS°. Plot of log K_o *vs.* 1/T gave a straight line Figure 6, from which ΔS° and ΔH° were determined Table 2.

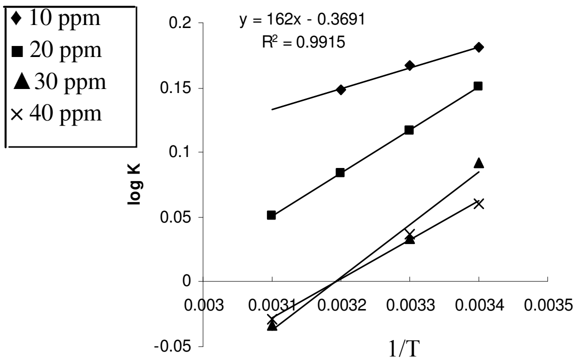

Figure 6. Plot of Van't Hoff equation for the adsorption of Cr(VI), 20, 30, 40 and 50 mg /L onto cinnamon 2 g/L.

The negative values of ΔH° indicate that the process is exothermic. On the other hand, the values of ΔH° are within the range of physiosorption process. The negative values of ΔG° Table 2 show the adsorption is favourable and spontaneous, on the other hand the positive and weak values of ΔG° indicates that the process is feasible but nonspontaneous especially at higher Cr(VI) concentration and temperature. The negative values of ΔS° indicate that the molecules of the adsorbent are highly ordered at the liquid solid interface Table 2.

Table 2. Thermodynamic parameters for the adsorption of Cr(VI) onto cinnamon.

Cr(VI) Conc.mg/L	ΔH° kJ mol^{-1}	ΔS° kJ mol^{-1}	ΔG° kJ mol^{-1} 20 °C	30 °C	40 °C	50 °C	R^2
10	-3.10	-7.07	-1.014	-0.870	-0.553	-0.370	0.9915
20	-6.37	-18.78	-0.938	-0.674	-0.201	-0.230	0.9997
30	-8.24	-26.41	-0.832	-0.487	+0.113	-0.205	0.946
40	-5.77	-18.41	-0.379	-0.295	+0.202	+0.180	0.99.28

Conclusion

The cinnamon has been identified as an effective biosorbent for removal of Cr(VI) at low concentrations. The adsorption process is pH dependent and the optimum pH was 2 and 2 h time was sufficient to attain equilibrium . The D-R, Freundlich and Tempkin isotherms were applicable and the Q_m was 12.49 mg/g. It was found that the biosorption process was spontaneous and exothermic.

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