Removal of Chromium from Aqueous Solution Using Modified Pomegranate Peel: Mechanistic and Thermodynamic Studies

TARIQ S. NAJIM* and SUHAD A. YASSIN

Duhok University, College of Education,
Chemistry Department, Duhok, Iraq.

*AL-Mustansiriyah University, College of Science,
Chemistry Department, Baghdad, Iraq.

tariq_pru@yahoo.com

Received 14 March 2009; Accepted 10 May 2009

Abstract: Modified pomegranate peel (MPGP) and formaldehyde modified pomegranate peel (FMPGP) were prepared and used as adsorbent for removal of Cr(VI) ions from aqueous solution using batch process. The temperature variation study of adsorption on both adsorbents revealed that the adsorption process is endothermic, from the positive values of ΔH° . These values lie in the range of physisorption. The negative values of ΔG° show the adsorption is favorable and spontaneous. On the other hand, these negative values increases with increase in temperature on both adsorbents, which indicate that the adsorption is preferable at higher temperatures. ΔS° values showed that the process is accompanied by increase in disorder and randomness at the solid solution interface due to the reorientation of water molecules and Cr(VI) ions around the adsorbent surface. The endothermic nature of the adsorption was also confirmed from the positive values of activation energy, E_a , the low values of E_a confirm the physisorption mechanism of adsorption. The sticking probability, S^* , of Cr(VI) ion on surface of both adsorbents showed that the adsorption is preferable due to low values of S^* ($0 < S^* < 1$), but S^* values are lower for FMPGP indicating that the adsorption on FMPGP is more preferable.

Keywords: Mechanism, Modified pomegranate peel, Thermodynamic parameters, Activation energy, Sticking probability.

Introduction

One of the heavy metals that has been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties¹. Chromium has been considered as one of the top 16th toxic pollutants

and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern². In recent years, chromium concentration have been increasing in coastal water through the electroplating industry, metal finishing, leather tanning, chrome preparation and inorganic chemical productions³. There are various methods to remove Cr(VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis⁴. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost⁵. Utilizing the waste material from agriculture and industries can make treatment process economical and solve the solid waste disposal problem. The feasibility of several low cost, non-conventional adsorbents obtained from agricultural and industrial wastes was explored. The present work based on pomegranate peel which is an agricultural waste from pomegranate juice industry as an adsorbent for Cr(VI) removal from aqueous solution, this study will focus on the evaluation of thermodynamic parameters for adsorption of Cr(VI) onto modified pomegranate peel (MPGP) and formaldehyde modified pomegranate peel (FMPGP).

Experimental

Pomegranate peel was collected in the northern part of Iraq, dried in dark at atmospheric temperature, then milled and sieved to particle size of 500 μm . The milled pomegranate peel was divided into two parts. The first one was shaken with distilled water for overnight then filtered, this process was repeated for about ten times or until we get rid off all soluble colored materials or until we get constant weight. It was observed that more than 40% of pomegranate peel was soluble in water. The yield was dried in an air oven at 80 $^{\circ}\text{C}$ for overnight, then milled to 150 μm particle size, this part was named as modified pomegranate peel (MPGP). The second part was reacted with 8% formaldehyde solution in a ratio of pomegranate peel to formaldehyde 1:5 w/v at 60 $^{\circ}\text{C}$ for 4 hours⁶. The formaldehyde modified pomegranate peel (FMPGP) was filtered out, washed with deionized water to remove free formaldehyde and then activated at 80 $^{\circ}\text{C}$ for 24 hours in an air oven, the dried FMPGP was milled to 150 μm .

Preparation of Cr(VI) solution and analysis

A stock solution of Cr(VI) 500 mg/L was obtained by dissolving 1.4144 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 L of deionized water and the 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. The Cr(VI) content in the sorption solutions was determined by atomic absorption spectrophotometer type (AAnalyst 200 Perkin Elmer).

Adsorption thermodynamics

The batch experiments for determination of thermodynamic parameters were conducted using 0.1 g of MPGP or FMPGP adsorbents in 50 mL of Cr(VI) solution of different concentration at different temperatures, at the end of each experiment the sample were collected, filtered by Whatman filter paper No. 40, the filtrate was analyzed for residual Cr concentration.

Results and Discussion

Temperature effect on the adsorption of Cr(VI) onto MPGP

Thermodynamic parameters such as change in free energy ΔG° , enthalpy ΔH° and entropy ΔS° were determined using the following equations^{7,8}.

$$K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \quad (2)$$

$$\Delta G^0 = -RT \ln K_0 \quad (3)$$

$$\log K_0 = \frac{\Delta S^0}{2.303 R} - \frac{\Delta H^0}{2.303 RT} \quad (3)$$

Where, K_0 is the equilibrium constant, C_{solid} is the concentration of Cr(VI) at the solid phase (adsorbent) at equilibrium, C_{liquid} is the liquid phase concentration of Cr(VI) at equilibrium, T is the absolute temperature (K) and R is the gas constant. Vant Hoff equation was used to estimate the values of ΔH^0 and ΔS^0 . From the intercept and slope of the plot of $\log K_0$ vs. $1/T$ (Figure 1), the ΔS^0 and ΔH^0 can be determined. These values are presented in Table 1.

Figure 1. Plot of Van't Hoff equation for adsorption of Cr(VI) on to MPGP.

The values of ΔH are within the range of 3.65 to 14.24 kJmol⁻¹ indicates the physisorption process. From the results, we could make out that physisorption is much more favorable for the adsorption of Cr(VI) onto MPGP. The positive values of ΔH^0 show the endothermic nature of adsorption and it governs the possibility of physical adsorption^{9,10}. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of chromium ion adsorption increases, this rules out the possibility of chemisorption¹⁰. The values of ΔG^0 were obtained from the application of equation (2). The negative values of ΔG^0 (Table 1), show that the adsorption is highly favorable and spontaneous. It was also observed that the negative values of ΔG^0 increases with increase in temperature, which indicate that the adsorption is preferable at high temperature, which was observed from the experimental data. The positive values of ΔS^0 (Table 1), show the increased disorder and randomness at the solid solution interface of chromium ion with MPGP, while the adsorption there are some structural changes in the chromium ion and the adsorbent occur. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system⁸.

Table 1. Thermodynamic parameters for the adsorption of Cr(VI) on to MPPG.

Cr(VI) Con. mg/L	ΔH° kJ mol ⁻¹	ΔS° Jmol ⁻¹	ΔG° , kJ mol ⁻¹				R ²
			20 °C	30 °C	40 °C	50 °C	
10	3.651	17.686	-1.547	-1.708	-1.870	-2.061	0.9985
20	6.232	25.318	-1.214	-1.405	-1.739	-1.911	0.9734
30	13.244	47.355	-0.795	-0.973	-1.466	-2.143	0.9420
40	14.236	48.944	-0.058	-0.661	-1.249	-1.401	0.9308

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows¹¹:

$$\theta = \left[1 - \frac{C_e}{C_i} \right] \quad \text{or} \quad \frac{C_e}{C_i} = 1 - \theta \quad (4)$$

$$S^* = (1 - \theta) e^{\frac{-E_a}{RT}} \quad (5)$$

$$\ln S^* = \ln(1 - \theta) - \frac{E_a}{RT} \quad (6)$$

$$\ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \quad (7)$$

The sticking probability S^* , is a function of the adsorbate / adsorbent system under investigation, its value lies in the range $0 < S^* < 1$ for preferable process and is dependent on the temperature of the system¹¹. The ' θ ' is the surface coverage, which can be calculated from equation 4. The values of E_a and S^* can be calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$ respectively (Figure 2 & Table 2). The values of E_a were found to be 2.438, 4.034, 8.399 and 8.119 kJ mol⁻¹ for the adsorption of Cr(VI) onto MPPG. The positive values of E_a indicate the endothermic nature of the adsorption process which are in agreement with the positive values of ΔH° and lie in the range of physisorption. The sticking probability values were less than 1 (Table 2), which indicates that the probability of the Cr(VI) ions to stick on surface of MPPG is very high as $S^* \ll 1$, these values confirm that, the sorption process is physisorption.

Figure 2. Plot of $\ln(1-\theta)$ vs. reciprocal temperature for the adsorption of Cr(VI) onto MPPG.

Table 2. Sticking probability and activation energy for the adsorption of Cr(VI) onto MPGP.

Cr(VI) conc. mg/L	Ea kJ mol ⁻¹	S*	R ²
10	2.438	0.1279	0.9980
20	4.034	0.0727	0.9736
30	8.399	0.0139	0.9330
40	8.119	0.0175	0.9384

Effect of temperature on the adsorption of Cr(VI) onto FMPGP

The thermodynamic parameter ΔH° and ΔS° were determined from applying of Van't Hoff equation (equation 3). The plot of $\log K_o$ versus $1/T$ (Figure 3) can be used to estimate ΔS° and ΔH° where, the intercept is equal to $\Delta S/2.303R$ and the slope is equal to $-\Delta H/2.303R$. The Gibbs free energy ΔG° were determined from equation 2. The values of these parameters are tabulated in Table 3. The positive values of ΔH° show the endothermic nature of the adsorption process. The values of ΔH° are within the range of 1 to 93 kJ mol⁻¹ indicates the physisorption⁷. The values of ΔS° (Table 3) are positive and higher than that in the case of Cr(VI) adsorption on MPGP, which indicate an increase in disorder and randomness at the solid-solution interface during the adsorption of Cr(VI), this behavior can be attributed to the decreases of water molecule around the solute or surface during the adsorption process which lead to increase in degree of freedom of water molecule^{8,12}. The negative values of ΔG° (Table 3) show the adsorption is highly favorable and spontaneous. The same behavior was also observed, that the negative values of ΔG° increases with increase in temperature.

Figure 3. Plot of Van't Hoff equation for the adsorption of Cr(VI) onto FMPGP.

Table 3. Thermodynamic parameters for the adsorption of Cr(VI) onto FMPGP.

Cr(VI) Con. mg/L	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹	ΔG° , kJ mol ⁻¹				R ²
			20 °C	30 °C	40 °C	50 °C	
10	19.19	70.32	-1.525	-1.960	-3.013	-3.405	0.9541
20	23.10	80.83	-0.731	-1.320	-2.173	-3.010	0.9961
30	25.03	87.14	-0.599	-1.388	-2.202	-3.088	0.9999
40	18.06	62.03	-0.178	-0.809	-1.213	-2.009	0.9874

The activation energy (E_a) and sticking probability (S^*) were calculated from equation 7. From the plot $\ln(1-\theta)$ versus $1/T$ (Figure 4) E_a and S^* value can be calculated. The positive values of E_a indicate the endothermic nature of the adsorption, which are in agreement with positive values of ΔH° (Table 4). the sticking probability values were less than 1 and even less than values of Cr(VI) adsorption on MPGP, which indicate that the probability of Cr(VI) ions to stick on surface of FMPGP is very high as long $S^* \ll 1$ (Table 4). These values confirm that the sorption is physisorption.

Figure 4. Plot of $\ln(1-\theta)$ vs. reciprocal temperature for the adsorption of Cr(VI) onto FMPGP.

Table 4. Sticking probability and activation energy for the adsorption of Cr(VI) onto FMPGP.

Cr(VI) Conc., mg/L	E_a , kJ mol ⁻¹	S^*	R^2
10	13.81	0.0013	0.9539
20	15.32	0.0008	0.9904
40	16.72	0.0005	0.9979
60	10.85	0.0057	0.9825

References

- 1 Karthikeyan T, Rajgopal S and Miranda L R, *J Hazard Mater.*, 2005, **124**(1-3), 192-199.
- 2 Torresdey J L C, Tiemann K J and Armendariz V, *J Hazard Mater.*, 2000, **80**(1-3), 175-188.
- 3 Gao H, Liu Y, Zeng G, Xu W, Li T and Xia W, *J Hazard Mater.*, 2007, **150** (2), 446-452.
- 4 Verma A, Chakraborty S and Basu J K, *Separ Purif Tech.*, 2006, **50**(3), 336-341.
- 5 Li Q, Zhai J, Zhang W, Wang M and Zhou J, *J Hazard Mater.*, 2007, **144**(1), 163-167.
- 6 Saiful A A, Ghaniey Liew A, Suhardy D, Farizul H K, Irfan M D, *Am J Appl Sci.*, 2005, **2**(11), 1499-1503.
- 7 Arivoli S, Hema M, Karuppaiah M, and Saravanan S, *E Journal of Chemistry*, 2008, **5**(4), 820-831.
- 8 Arivoli S and Thenkuzhali M, *E Journal of Chemistry*, 2008, **5**(2), 187-200; Arivoli S and Hema M, *Int J Phys Sci.*, 2007, **2**, 10-17.
- 10 Arivoli S Kalpana K, Sudha R and Rajachandrasekar T, *E Journal of Chemistry*, 2007, **4**, 238-254.
- 11 Nevine K A, *J Hazardous Materials*, 2009, **165**(1-3), 52-62.
- 12 Sujatha M, Greetha A, Sivakumar P and Palanisamy P N, *E Journal of Chemistry*, 2008, **5**(4), 742-753.