

ADSORPTION THERMODYNAMIC AND KINETIC STUDIES OF Cr(VI) BY CHITOSAN FLAKE MODIFIED WITH CITRIC ACID VIA CROSSLINKING WITH GLUTARALDEHYDE

Ho Thi Yeu Ly^{1*}, Nguyen Xuan Tong², Le Van Tan²

¹*Ho Chi Minh City University of Technical Education*

²*Industrial University of Ho Chi Minh City*

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Abstract

In this study, the sorption of Cr(VI) from aqueous solution onto the cross-linked chitosan grafting with citric acid (C-Gch) was investigated in a bath system. The optimum conditions for the adsorption were found to be pH 1 and 720 min of contact time. The maximum adsorption capacity of Cr(VI) at pH 1 was found to be 32 mg Cr(VI) /g C-Gch after 720 min of contact time. Adsorption kinetic data were tested using pseudo-first order and pseudo-second order. The obtained results confirmed that the adsorption process of Cr(VI) followed the pseudo-second kinetic model. It was shown that the adsorption process is presumably a chemisorption. Thermodynamic parameters including changes in the standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also calculated.

Keywords. Cr(VI), modified chitosan, citric acid, adsorption thermodynamic.

1. INTRODUCTION

Toxic metal ions in trace quantities are difficult to remove from aqueous solution. Adsorption is a promising alternative for such situations. Recently, the search for new and innovative technology to remove toxic heavy metal ions from diluted wastewater has focused on the removal of heavy metal by various low-cost materials [1, 3, 8, 12]. Among the many low cost absorbents identified, chitosan is known as a bio-absorbent which is derived from chitin, a polysaccharide foundation in the exoskeletons of shellfish like shrimps and crabs has been identified as a potential absorbent material [5, 9, 10]. The presence of large number of functional groups such as amino group (NH_2) and hydroxyl group (OH) that acts as active sites on the surface of chitosan allow having a high adsorption capacity for metal ions [4, 5]. The disadvantage of raw chitosan is its poor acidic resistance and low mechanical strength [5, 8]. Therefore, it is necessary to improve the chemical resistance of chitosan to apply in practice. Several studies have reported that the applicability of chitosan including raw chitosan flakes and casting chitosan could be improved by its crosslinking with a chemical agent such as epichlorohydrin (EPI) or glutaraldehyde [8, 9]. The crosslinked chitosan was found to be stable in acidic

solution. However, the adsorption capacities of those crosslinked chitosan were reduced, primarily because the active functional groups on chitosan surface became inaccessible in the crosslinked polymer network. The possible solution for this problem is to graft on the crosslinked chitosan with new active functional groups, which can be tailored so that the grafted materials become compatible with the optimal pH range for metal sorption, as well as the interactions between those functional groups are controllable. Recently, low ionic carboxylic acids such as citric acid, and their salts were used to graft onto chitosan for site-specific delivery of a non-polar drug [6]. The presence of functional groups of citric acid, when grafted on the crosslinked chitosan, may potentially become active site for heavy metal ions absorption.

Industrial and mining wastewaters are important sources of pollution of heavy metal [2, 13]. Pollution by chromium is of considerable concern as the metal has found widespread use in electroplating, metal finishing, leather tanning, nuclear power plant and textile industries. Chromium is found in either +3 or +6 oxidation states, as all other oxidation states are not stable in aerated aqueous media. The +6 is known toxic even at low concentration, with a potential carcinogenic effect, where as the +3 is an

essential micronutrient for organisms and plants and become toxic in higher levels [1, 3, 11].

This paper presents the results of an adsorption study of Cr(VI) ions using crosslinked chitosan flakes grafted with citric acid. The grafting process was conducted by pre-reaction of chitosan flakes with glutaraldehyde followed by reaction with citric acid. Batch experiments were performed to evaluate effective parameters such as pH, contact time and temperature on the adsorption of Cr(VI) ions. The behavior of the adsorption of Cr(VI) ions by grafted chitosan flake was investigated using kinetic and isotherm models.

2. MATERIALS AND METHODS

The chitosan in flake forms with deacetylation degree of 87 % and molecular weight of 10^5 - 10^6 (Da) was supplied from Research and Development Center for Radiation Technology (VINAGAMMA Center). Flakes were ground and sieved. The fraction with a particle size of 0.25 to 0.4 was selected for adsorption study. Glutaraldehyde, Cr(VI) and the other reagents were supplied from Merck Company. All solutions were prepared with doubly distilled water. Cross-linked chitosan was prepared by adding 50 g of chitosan flakes to a beaker containing 750 ml of 2.5%(v/v) glutaraldehyde solution. The mixture was agitated for 12 hours at 250 rpm and then rinsed several times with distilled water [6]. An obtained orange solid was Cross-linked chitosan (Gch) which dried at room temperature. Acid citric grafting process was conducted by immersing 60 g of Gch in 240 ml of aqueous 2.0 % (w/v) citric acid solution at pH 5, temperature of 40 °C for 24 hrs. The citric acid grafted chitosan flakes (C-Gch) was repeatedly washed with deionizer water, thoroughly dried in air and under vacuum at 60 °C [6]. Batch adsorption experiments were conducted to determine the effect of pH, contact time and temperature on the adsorption of Cr(VI) ions by C-Gch. For investigation of effect of pH, 0.1 g C-Gch was added into flasks containing 50 ml of 20 and 50 mg/l Cr(VI) solution. pH of the solution was adjusted from 1 to 6 by adding either 0.5 M sulfuric acid or 0.5 M sodium hydroxide solution. The mixtures were shaken for 720 min at room temperature (29 ± 1 °C). The effect of the contact time was studied by variation of shaking time while maintained concentration of Cr(VI), pH, adsorbent dose constant. Effects of temperature were determined in the same manner as experiments mentioned above by varying the temperature while kept other parameters constant. Adsorption isotherm was

investigated by varying the concentration of Cr(VI) in the range of 20 to 100 mg/l of Cr(VI).

The solutions after adsorption were filtered and the filtrates were analyzed for Cr(VI) by UV-Vis. The removal efficiency (%) and adsorption capacity of Cr(VI) was determined by relationship [5, 8]:

$$P(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where P is adsorption percentage (%), q_e is adsorption capacity (mg/g), C_0 is the initial Cr(VI) concentration (mg/L), C_e is the final or equilibrated Cr(VI) concentration (ppm), V is the volume of the Cr(VI) solution (L) and m is the weight of the adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Effect of contact time on the adsorption of Cr(VI) by C-Gch

The effect of contact time on the adsorption of Cr(VI) was studied under conditions: 0.1 g of adsorbent; pH 1.0; room temperature ($29 \text{ }^\circ\text{C} \pm 1$); 20 and 50 mg/L Cr(VI). The adsorption experiments were carried out for contact times ranging from 15 to 840 min. The results obtained are shown in Fig. 1.

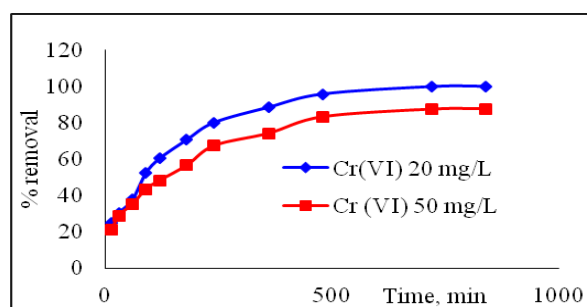


Fig. 1: Effect of contact time on the adsorption of Cr(VI) at different concentrations.

It was found that the adsorption percentage of Cr(VI) increased with the contact time and reached equilibrium after 720 min. This time was suggested to apply for next experiments.

3.2. Effect of pH on the adsorption of Cr(VI) by C-Gch

pH is an important factor for the adsorption process. Because, pH of solution controlled the charge of the adsorbent surface and existence of Cr(VI) ions in the solution. The effect of pH on the

adsorption of Cr(VI) from aqueous solutions was studied by determining the adsorption capacity at different pH values. The concentration of Cr(VI) in the solution was maintained at 20 and 50 ppm in all the runs. The contact time (t) was kept as 720 min. The initial pH of the solutions was varied from 1 to 6. The relation of adsorption percentage and pH was given in Fig. 2. The results showed that the Cr(VI) adsorption percentage (%) by C-GCh was strongly depended on the pH of the solution from 1 to 4.0. At a pH higher than 4.0, the adsorption capacity remarkably decreased. Chromium (VI) forms stable complexes, such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^{2-} , CrO_4^{2-} and HCr_2O_7^- , depending on the pH of the solution. The fraction of any particular species depends on the chromium concentration and pH of the solution [1]. The extent of adsorption of Cr(VI) increased with a decreasing pH of the solution. At the lower pH values, the amine group of chitosan undergoes protonation, leading to the increased electrostatic attraction between NH_3^+ and sorbate anion [1, 9]. As the pH increases, deprotonation of amino group occurs, resulting in a decrease of adsorption.

3.5. Adsorption isotherm

The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state [5, 10]. The experimental

adsorption data were fitted the Langmuir, Freundlich Temkin and Redlich-Peterson isotherm equations (Fig. 3).

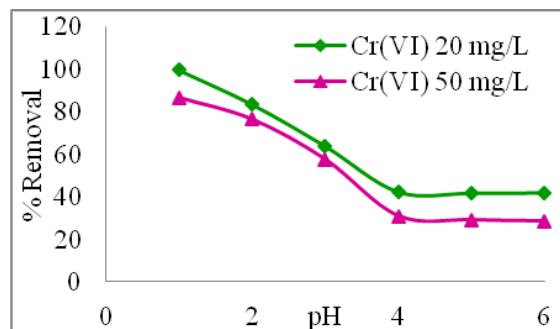


Fig. 2: Effect of pH for the Cr(VI) adsorption onto C-GCh

The parameters of Langmuir, Freundlich, Temkin and Redlich- Peterson equations obtained were given in table 1.

High k_L values indicate high adsorption affinity. From the Langmuir equation, the maximum adsorption capacity for Cr(VI) was found to be 32 mg/g. The magnitude of k_f showed a high Cr(VI) adsorptive capacity of C-GCh from aqueous solution studied. Table 1 also indicated that the values of $1/n$ and b_R lies between 0 and 1 indicating that Cr(VI) is favourably adsorbed by C-GCh at all studied parameters.

Table 1: Parameters of isotherms for Cr(VI) adsorption

Isotherm modes	Parameters			RMSE	χ^2
Langmuir	q_m (mg/g)	K_L (L/mg)		4.77	3.86
	32	0.90			
Freundlich	K_F (L ⁿ /g)	1/n		0.83	0.10
	14.28	0.27			
Temkin	K_T (L/g)	b_T (J/mol)		2.54	0.96
	21.95	493.5			
Redlich-Peterson	$K_R \cdot 10^3$ (L/g)	$a_R \cdot 10^3$ (L/mg)	b_R	1.56	0,56
	-360.9	-280.9	0,70		

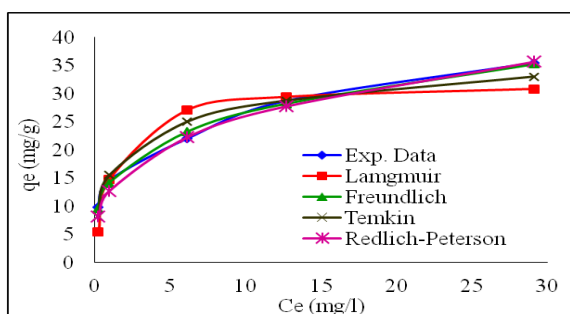


Fig. 3: Nonlinear adsorption isotherms for adsorption of Cr(VI) ions on C-GCh at 302 K

3.3. Thermodynamic parameter

In this work, the effect of temperature on Cr(VI) ions removal efficiency onto C-GCh was studied in the range of 293-323 K. The initial Cr(VI) concentrations were studied in the range of 20-100 mg/L, while pH, adsorbent dosage, contact time were fixed at 1, 0.1 g, 720 min. It was found that removal efficiency of Cr(VI) increases with the increase of temperature from 303-323 K (as shown Fig. 4).

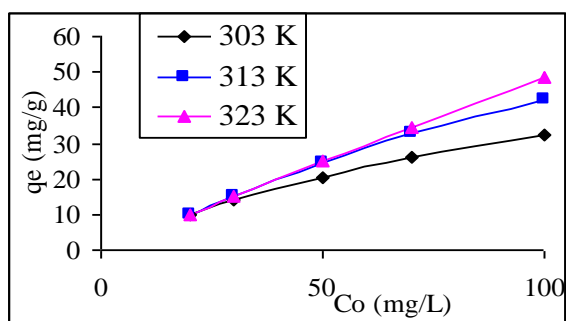


Fig. 4: Effect of temperature for Cr(VI) ions removal efficiency onto C-GCh

The maximum adsorption capacity of C-Gch for Cr(VI) was found to be 33.56, 43.48 and 50.25 mg/g at 303, 313 and 323 K, respectively. The adsorption capacity obtained of the C-Gch for Cr(VI) was much higher than the one that has been reported for chitosan flakes (20.93 mg/g) [16]. Thus, the presence of citric acid in chitosan flakes increases significantly the adsorption capacity for Cr(VI) ions.

In order to evaluate isothermodynamic parameters of the adsorption process such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS), the equations were used [5, 8]:

$$\Delta G = -RT \ln KL \tag{3}$$

where KL is the Langmuir constant; T is solution temperature (K); R is the gas constant (8.314 J/mol K).

The enthalpy change (ΔH) and entropy change (ΔS) of the adsorption were calculated from the slope and intercept from the plot of $\ln(KL)$ versus $1/T$ according to the Van't Hoff equation at different adsorption temperatures:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{4}$$

The values of ΔH^0 , ΔS^0 and ΔG^0 parameters were summarized in the table 2.

Table 2: Change of thermodynamic with temperature

Temperature (K)	q_m (mg/g)	K_L (L/mg)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol)
303	33.56	0.314	-3.47	29.04	107.28
313	43.48	1.513	-4.54		
323	50.25	6.219	-5.61		

The positive value of ΔH^0 confirms that the biosorption process of Cr(VI) is endothermic. The negative value of ΔG^0 at various temperatures indicates the feasibility and spontaneity of the biosorption process. The increase in ΔG^0 with the temperature indicates that the biosorption is more favorable at high temperatures. The positive value of ΔS^0 shows the affinity of biosorbent for Cr(VI) and it also confirms an increase in the randomness at the solid-solution interface during the biosorption process.

The maximum adsorption capacities (q_m) increased from 33.56, 43.48, 50.25 mg/g for 303, 313 and 323 K, respectively. The values of K_L were increased with increasing the temperature of solution. High K_L values indicate high adsorption affinity.

3.4. Adsorption kinetic

Kinetic models have been used to investigate the mechanism of sorption to find out the stage which plays a decisive role to the adsorption reaction rate. In this research, the adsorption kinetic data obtained from different concentrations. The pH, temperature, adsorbent dosage were fixed at pH 1, 309K and 0.1g. Kinetic models used for fitting experimental data are pseudofirst-order (6) and pseudo-second order (7) [1, 8].

$$\text{Log}(q_e - q_t) = \text{log}q_e - \frac{k_1}{2.303} t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where, k_1 , k_2 are the pseudo-first-order constant (min^{-1}) and the pseudo-second-order constant ($\text{g/mg}\cdot\text{min}$), q_t , q_e are amount adsorbed at time t and equilibrium (mg/g). The plots of $\text{log}(q_e - q_t)$ from Eq.(5) and t/q_t from Eq.(6) against t give a linear relationship. which allow to calculate k_1 , k_2 and predict q_e . The linear plots for the pseudo-second-order models at different initial concentration of Cr(VI) are presented in Fig. 5 respectively. The values of the parameters and correlation coefficients are also presented in table 3 and It can be seen in the Fig. 5.

The values of parameters of the pseudo second-order model were found to be near unity for all concentrations ranging from 20 to 100 mg/L, indicating that the experimental data are good fitted with the pseudo-second-order model. These results are very significant in the adsorption of polluted water containing high concentrations of Cr(VI) by using the C-GCh.

Table 3: Adsorption kinetic model rate constants at different concentrations of Cr(VI)

C^0 (mg/L)		20	50	100
e. exp		9.96	21.84	39.68
Pseudo first order	k_1	0.001	0.002	0.003
	R^2	0.650	0.865	0.635
	qe. cal	1.89	3.53	5.28
Pseudo second order	$k_2 \cdot 10^2$	0.1	0.04	0.02
	R^2	0.997	0.995	0.995
	qe. cal	11.11	24.39	45.45

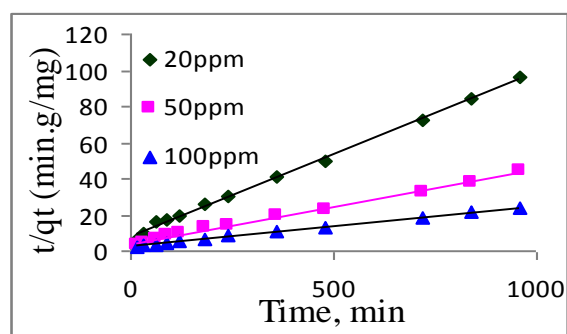


Fig. 5: Plots of pseudo-second-order equation for Cr(VI) adsorption

Table 4: Comparison of adsorption capacity of Cr (VI) with other adsorbents

Type of adsorbent	Adsorption capacity (mg/g)	pH	Reference
Sawdust	3.3	6.0	[13]
Coconut shell activated carbon	20	2.5	[1]
Sugar beat pulp	17.2	2.0	[12]
Maize cob	13.8	1.5	[12]
Sugar cane bagasse	13.4	2.0	[12]
Coconut husk fibers	29.0	2.1	[14]
Palm pressed-fibers	15.0	2.0	[14]
Pinus sylvestris bark activated by 0.05 N NaCl	19.5	4.5	[2]
Chitosan cross-linked withy glutaraldehyde	20.9	1.0	[16]
C-GCh	32.0	1.0	Present study

4. CONCLUSION

The main aim this study is to find optimum conditions to removal Cr(V) simultaneously from aqueous solutions by studying the effect of various process parameters. The optimum conditions found were: pH = 1, contact time 720 min, temperature 323 K, and at this condition the maximum adsorption capacities (mg/g) were 33.56, 43.48, 50.25 mg/g for 303, 313 and 323 K, respectively. Thermodynamic calculations indicate that the adsorption of Cr(VI) onto C-GCh was spontaneous and endothermic. Two models were used to study the adsorption kinetics. It was found that pseudo-second-order equation provided the best correlation to the data.

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Corresponding author: **Ho Thi Yeu Ly**

Ho Chi Minh City University of Technical Education
1, Vo Van Ngan Street, Thu Duc District, Ho Chi Minh City
E-mail: yeulyvn@gmail.com; Telephone: 0985321371.