Removal of Cr(VI) from Aqueous Solution Using A new Adsorbent

BANN A. DAWOOD
Department of Chemistry
Faculty of Science
University of Zakho

SUHAD A. YASIN
Department of Chemistry
Faculty of Science
University of Duhok

Received 21 / 12 / 2011
Accepted 09 / 04 / 2012

الخلاصة

يتضمن هذا البحث استخدام القرفة كمادة مازة جديدة لازالة الكروم السداسي من محلوله المائي بعد جمعها من السوق المحلية. واشتمل ايضا على دراسة العوامل المؤثرة على سعة الامتزاز مثل تأثير الدالة الحامضية, والتركيز الابتدائي للكروم السداسي وكمية المادة المازة وزمن التماس وكفاءته المتمثلة بنسبة الازالة. وتم اختبار النتائج العملية باستخدام عدة ايزوثرمات مثل Tempkin, Freundlich, Langmuir. وقد لوحظ ان بيانات الامتزاز العملية تنطبق تماما مع كافة الموديلات وقد لوحظ ان الحد الاقصى لسعة الامتزاز Qm باختلاف تركيز المادة المازة كان (13.8ملغرام/غرام) والذي تم الحصول عليه من تطبيق معادلة Langmuir. كما تم تحليل النتائج الحركية باستخدام ثلاث معادلات حركية وهي الرتبة الأولى والثانية و Elovich model ومن الواضح ان الرتبة الثانية وElovich model منطبقة تماما.

Abstract:

In the present study, Cinnamon (which is locally known as darseen) from local market was used as new adsorbent for removal of Cr (VI)from aqueous solution after it is collected. The research including study of the effect pH, initial Cr(VI) concentration, adsorbent dose and contact time on the adsorption capacity and percent removal were explored. The equilibrium data were tested using several isotherm models, Langmuir, Freundlich and Tempkin equations. The adsorption isotherm fit well with all models studied and the maximum adsorption capacity Q_m of different adsorbent dosage was (13.8mg/g), obtained from Langmuir model. When the experimental data were applied to the first-order, second-order and Elovich kinetic model, it was clear that second-order and Elovich models fitted well.

KEYWORDS: Cinnamon, kinetic, Isotherm, Adsorption

Introduction

Chromium (VI) is a common waste product generated from various industrial processes such as electroplating, wood preservation, metal finishing, chrome plating and leather tanning, and is highly toxic as compared to Cr(III) to biological activities [1]. The threshold value for Cr (VI) has been reported to be 0.1mg/L[2]. Because of high toxicity of Cr(VI) to living systems, it should be removed from wastewaters before its discharge into the enviroment. The chemistry of Cr(VI) is greatly dependent on pH of the solution. Cr(VI) normally exists in the anionic form, as $Cr_2O_7^{-2}$, $HCrO_4^{-1}$ or CrO_4^{-2} forms depending on pH and concentration. At pH value below 1, the predominant species is chromic acid (H_2CrO_4) with dissociation constant K_1=4.1, and K_2=1.2X10^{-6} respectively. In acidic media with pH value2-4, Cr(VI) exist, mostly in the form of dichromate ($Cr_2O_7^{-2}$) ions. At pH between 4 and 6, $Cr_2O_7^{-2}$ and $HCrO_4^{-1}$ ions exist in equilibrium, and in alkaline conditions(pH>8) it exists predominantly as chromate anion (CrO_4^{-2})

$$Cr_2O_7^{-2} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$$

The change in equilibrium is visible by a change from yellow (chromate)to orange(dichromate).

$$2CrO_4^{2-} \text{(yellow)} + 2H^+ \text{(aq)} \rightleftharpoons Cr_2O_7^{2-} \text{(red orange)} + H_2O$$

Cr (VI) in the form of dichromate (pH<6) is a relatively strong chemical oxidant. Its oxidative nature is a reason for its toxic and carcinogenic properties. Since it is readily diffused through the skin, it then reacts with the enzymes of the body or biological systems. After the oxidation reaction, it is reduced to Cr(III). The accumulation of Cr(III) in cells results in changing the structure of DNA molecule and disordering the metabolism activities [3]. The various treatment techniques available for the removal and recovery of Cr(VI) from wastewaters are reduction precipitation, ion-exchange, reverse osmosis, lime-coagulation, carbon adsorption, solvent extraction, chemical precipitation, evaporation and electrolytic reduction[4-7]. However, most of the methods suffer from drawbacks such high capital and operational cost of the disposal of the residual metal sludge. Many agricultural waste have been used for removal of Cr(VI) from aqueous solution like sugarcane biogases [5], oak sawdust [6], activated Neem leaves [7], Sunflower stem [8], and so many other agricultural materials have been used for Cr(VI) removal from aqueous solution.

In this project Cinnamon powder was used for removal of Cr(VI) from aqueous solution. Three isotherms were applied to experimental data, these are Langmuir, Freundlich and Tempkin models. The experimental data were also applied to three kinetic models.

2. Materials and Methods

2.1 Preparation of Cinnamon powder

Cinnamon flakes were grounded and sieved with a sieve (60μm). Then milled biosorbent was shacked 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 dried in air at 50°C for overnight.

2.2 Metal solution

Metal stock solution containing Cr(VI) with a concentration of 500mg/L was prepared by dissolving 1.4144g of $K_2Cr_2O_7$ in 1L of deionized water, this solution was used for further experimental solution preparation. Analytical grade reagents were used throughout this study.

2.3 Effect of pH

The effect of pH on adsorption of Cr(VI) onto Cinnamon was determined by adjusting the pH values of Cr(VI) solution to 1.0,2.0,3.0,4.0,5.0 with 0.1M HNO_3 and 0.1M NaOH. The pH values of Cr(VI) solution were measured by pH meter type Hana 301 instruments. All experiments were done by using Horizontal Shaker model LSb-015S.The residual chromium in the sorption solutions was determined by atomic adsorption spectrophotometer type (AAnalyst200Perkin Elmer).

2.4 Effect of contact time and initial concentration of chromium ion on adsorption

The effect of initial concentration of Cr (VI)and time on adsorption of Cr(VI) onto Cinnamon were carried out by mixing using solution with pH 2.0, by0.2 g of Cinnamon with 50ml of Cr(VI) of 10ppm at 25°C and shaked with140 rpm for(100) minutes. At the end of each experimental the solution was filtered and residual Cr (VI) concentration was determined.

2.5 Adsorption Isotherm

Adsorption isotherm experiments were carried out at different adsorbent dose (2,6,10 and 14g/L) and different Cr(VI) concentrations (10,20,30,40ppm). At each adsorbent dose, each solution was shaked for 120 minutes at pH2.0 and temperature 25°C. The amount of Cr (VI) adsorbed onto the Cinnamon(g) q_e, was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad \text{…………………(1)}$$

Where C_0 and C_e are the initial and equilibrium concentration (mg/L) of Cr(VI), respectively, V is the volume of experimental solution (L),M is the weight of the Cinnamon used (g).

The Cr (VI) percent removal R%(adsorption efficiency) was calculated using the following equation:

$$R\% = \frac{(C_\circ - C_e)}{C_\circ} \times 100 \quad \text{…………..(2)}$$

3. Results and Discussion

It was found that the maximum removal of chromium from aqueous solution using (2g/L) Cinnamon powder as adsorbent occurred at pH 2.0, and the required time for equilibrium was 120 minutes and temperature was 25°C.

So all batch sorption experiments were done at these conditions. The FTIR Spectrum of Cinnamon Figure (1) revealed that the presence of phenolic, Carboxylic, Ketonic and aldehyde groups could be responsible for binding of metal ions.

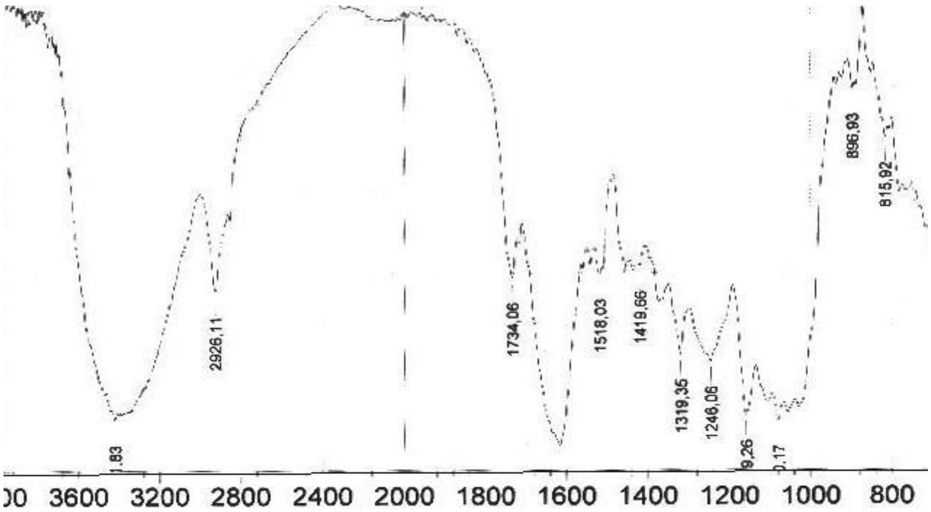
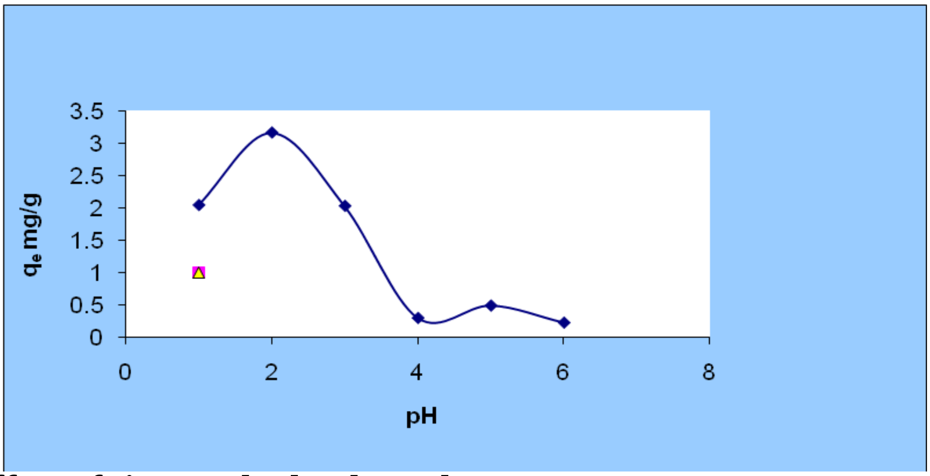


Figure1: FTIR Spectrum of Cinnamon

3.1 Effect of pH on Cr (VI) adsorption

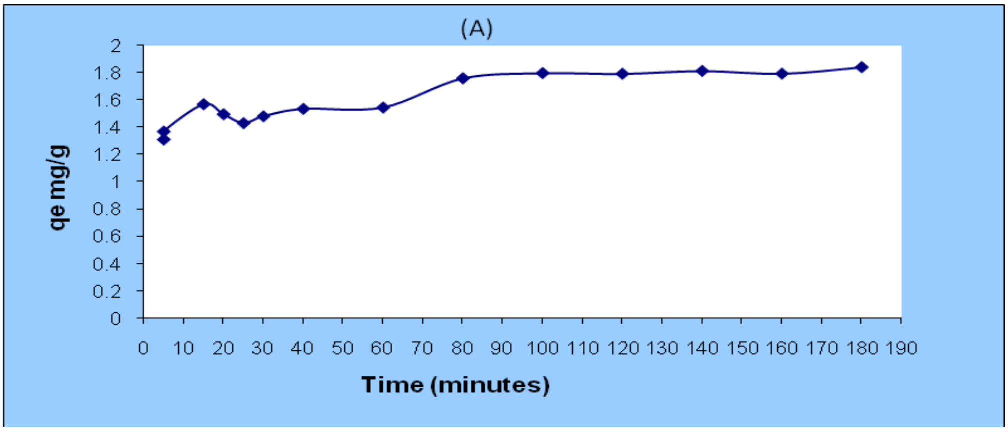
pH is an important parameter influencing heavy metal adsorption from aqueous solution. It affects both the surface charge of adsorbent and the degree of ionization of heavy metal in solution, [9]. Plot of pH versus the adsorption capacity (q_e) is shown in Figure(2). The optimum pH was found to be pH =2. The maximum removal of chromium ion at this pH is 63.3% which could be attributed to the electrostatic attraction between the positive charges present on adsorbent surface due to the acidic solution and the chromium ion in the form $Cr_2O_7^{2-}$ which is predominate at this pH.

Figure 2: Effect of pH on the adsorption of Cr(VI) onto Cinnamon.



3.2 Effect of time and adsorbent dose.

Effect of time for removal of Cr (VI) by Cinnamon with a dose of 2g/L concentration is shown in Figure (3). There was a rapid adsorption in the first 5 minutes, then decreased and little change occurred with time. The percent removal was 52.56% in the first 5 minutes and maximum removal was 70.41 % at 80 minutes. The effect of adsorbent dose (1,2,4,8 and 12g/L) was shown in Figure(4). The adsorpent capacity q_e decreases as the adsorbent concentration increased, from 3.182mg/g to 0.683g/g, while the percent removal increases as the adsorbent dose increases, from 31.8% to 82%, these findings was in agreement with other researcher[10].



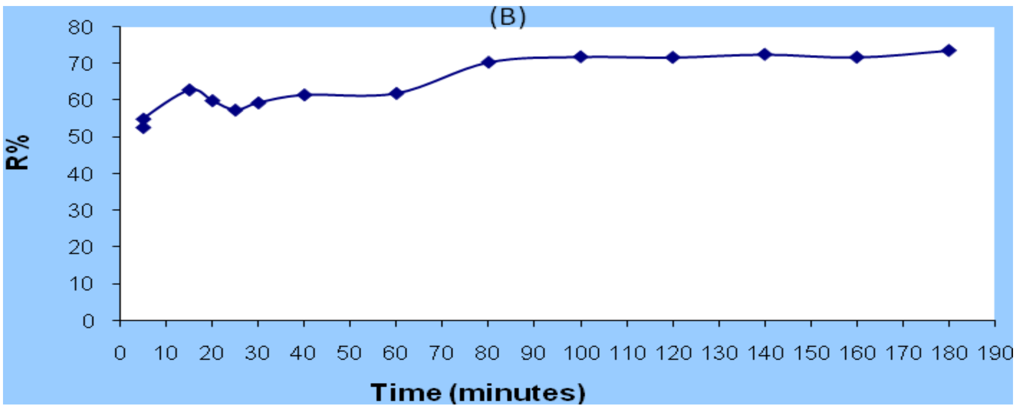
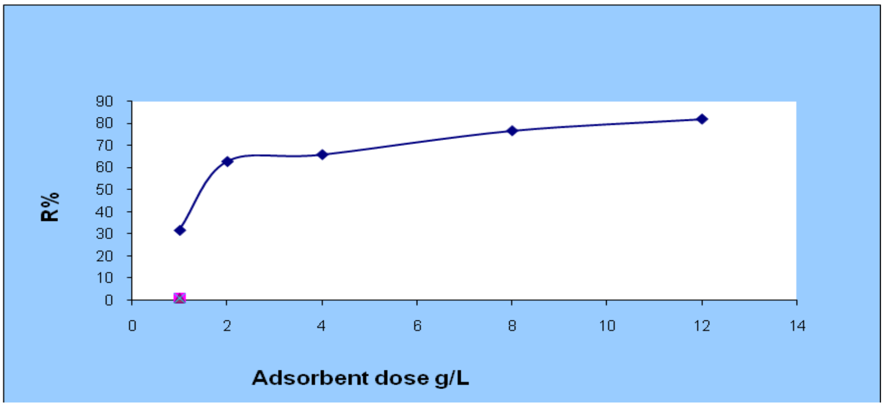


Figure 3: A) Effect of time vs. q_e, B) Effect of time vs. R%



Figure(4): Effect of adsorbent dose vs. R%.

3.3 Effect of initial concentration of Cr (VI)

The effect of initial Cr (VI) ion concentration is studied by using (10, 20, 30 and 40 ppm) of chromium and dose of 2g/L Cinnamon. The adsorption capacity q_e was plot against the concentration of Cr (VI).The relation is shown for different initial concentration in Figure(5). It revealed that, q_e increases with increase of concentration of Cr (VI)[13].

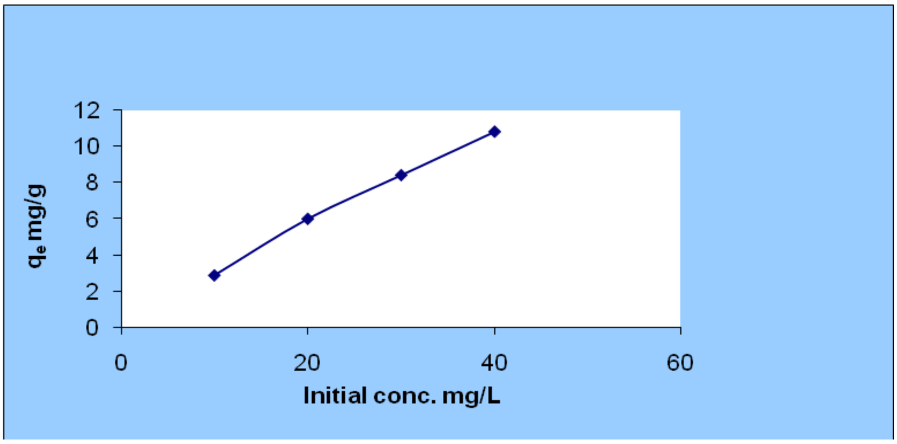


Figure 5: Relation between, q_e, and initial concentration.

3.4 Adsorption isotherm

Adsorption isotherm are essential for the description of how metal ion will interact with the adsorbent surface and are useful to optimize the adsorbent for the removal of Cr (VI) ions.The Langmuir model can be represented by the following linear equation, [11]

$$\frac{1}{q_e} = (\frac{1}{K_L Q_m})\frac{1}{C_e} + \frac{1}{Q_m} \cdots\cdots\cdots (3)$$

Ce is the equilibrium concentration in solution (mg/L), q_e the amount of metal ion adsorbed (mg/g), Q_m is the maximum monolayer capacity of the adsorbent (mg/g) and K_L is an adsorption equilibrium constant (Lmg-1).Plot of $1/q_e$ versus$1/C_e$ is presented in Figure (6).The values of Langmuir isotherm constants and correlation coefficients are presented in Table (1).

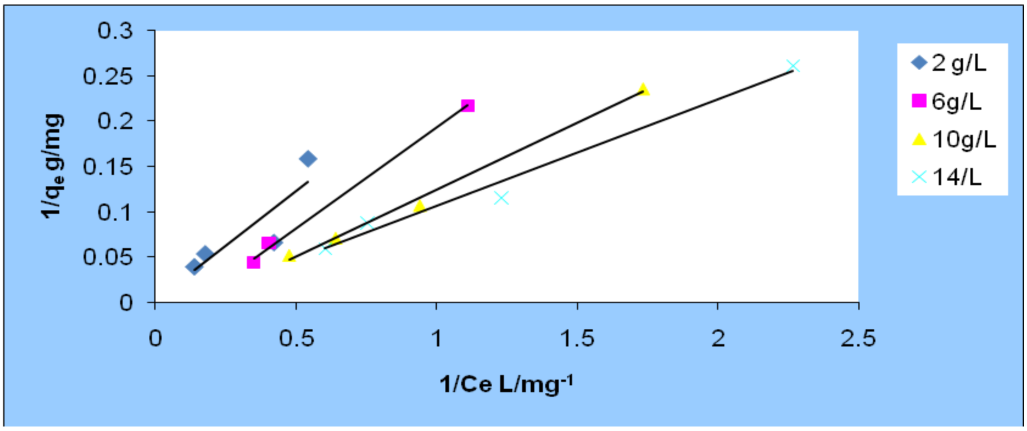


Figure (6): Langmuir isotherm adsorption of Cr (VI) onto Cinnamon.

The linear form of Freundlich equation is [12]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad \text{......................(4)}$$

Where K_F (Lmg^{-1}) and n are constants indicating to the capacity and intensity of the adsorption, respectively. The linear plots of log q_e versus log C_e at all adsorption dose were found to fit the Freundlich equation as illustrated in Figure (7), the values of Freundlich constants and correlation coefficients are listed in Table(1). All values of n are higher than one referring that the adsorption is favored physical process [13].

The linear equation of Tempkin model can be written as follows [14].

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad \text{........................(5)}$$

Where B_T is related to heat of adsorption, A_T is the equilibrium binding constant (Lmg^{-1}), corresponding to maximum binding energy. The plot of q_e versus lnC_e at studied adsorbent doses are given in Figure 8, while values of Tempkin constants are given in Table (1).

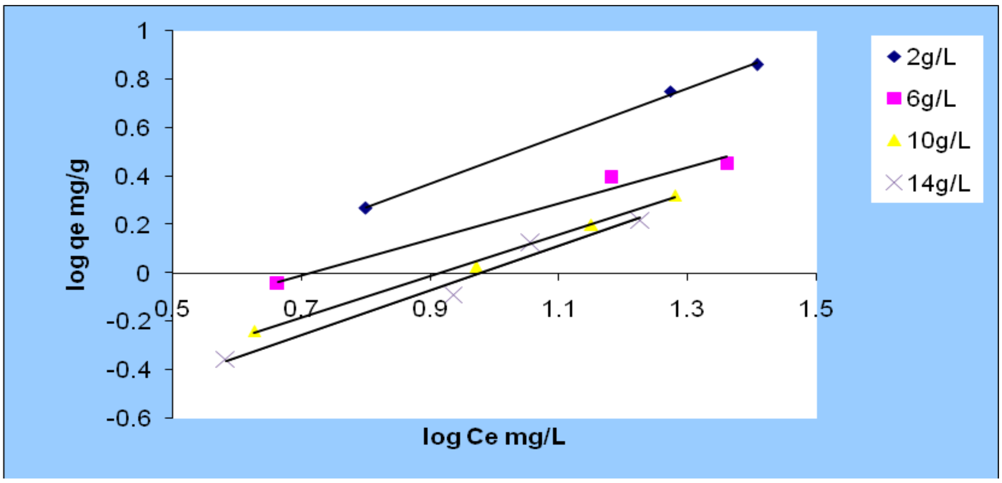


Figure (7): Freundlich isotherm adsorption of Cr (VI) onto Cinnamon.

Isotherm model	Values of Isotherm parameters	Dosage(g/L)			
		2	6	10	14
Langmuir	Q_m (mg / g)	13.8	7.5	6.0	8.26
	K_L(L mg $^{-1}$)	0.023	0.0296	0.0248	0.0145
	R^2	0.7522	0.9977	0.9947	0.9812
Freundlich	K_F	0.3	0.297	0.1643	0.126
	n	1.0	1.348	1.168	1.1

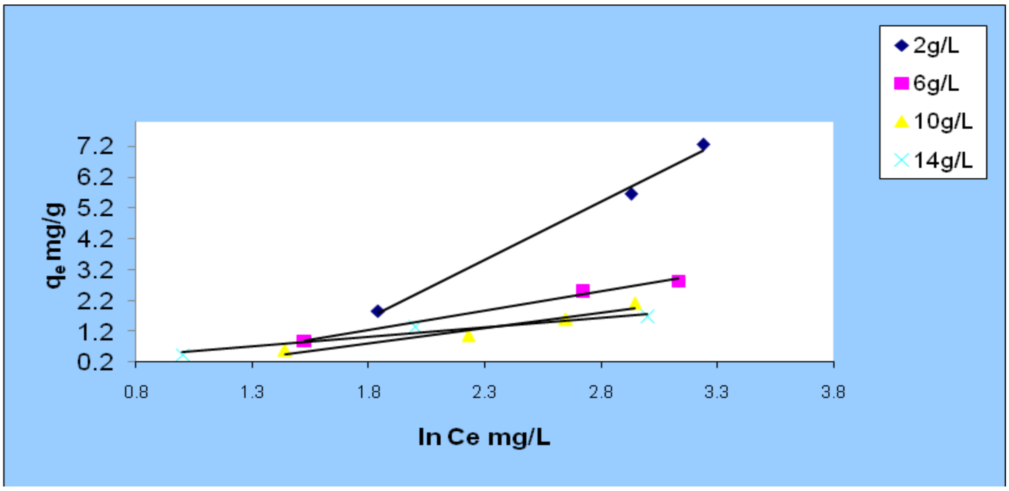


Figure (8): Tempkin plot of Cr (VI) adsorption onto Cinnamon

Table 1:- Isotherm parameters and correlation coefficients calculated for various Adsorption models at different doses for adsorption of Cr(VI) onto Cinnamon.

	R^2	0.9983	0.9792	0.9966	0.9719
Tempkin	A_T	0.48	0.278	0.35	0.287
	B_T	3.76	1.23	0.9759	0.8187
	R^2	0.9938	0.995	0.9442	1.00

3.5 Adsorption dynamic

Adsorption kinetic studies are crucial characteristics of the adsorption process which describe the adsorption rate. In order to understand the controlling mechanisms involved the adsorption of Cr (VI). The Kinetic of Cr (VI) adsorption onto Cinnamon were analyzed using Pseudo first-order, Second-order and Elovich kinetic models. The Pseudo first-order [15] is generally expressed in a linear from as follows.

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \cdots\cdots\cdots (6)$$

Where q_e and q_t are the adsorption capacities of Cr adsorbed (mg g^{-1}) at equilibrium and at any time t, respectively, and k_1 is the equilibrium rate constant of pseudo-first order adsorption (min^{-1}).

The correlation coefficient of plot of log (q_e-q_t) vs. t, indicated that, the first-order kinetic model do not describe the kinetic data of Cr (VI) adsorption. Moreover, the q_e(cal) do not agree with q_e(exp), Table (2).

The Pseudo second-order equation [16] is expressed in a linear form as follows:

$$t / q_t = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}(t) \cdots\cdots\cdots\cdots (7)$$

Where, k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of pseudo-second-order adsorption. The initial adsorption rate, h (mg g^{-1} min-) is expressed by the following equation.

$$h = k_2 {q_e}^2 \cdots\cdots\cdots\cdots\cdots\cdots (8)$$

Figure (9) represent the Second order plot, where the correlation coefficients is (0.999).

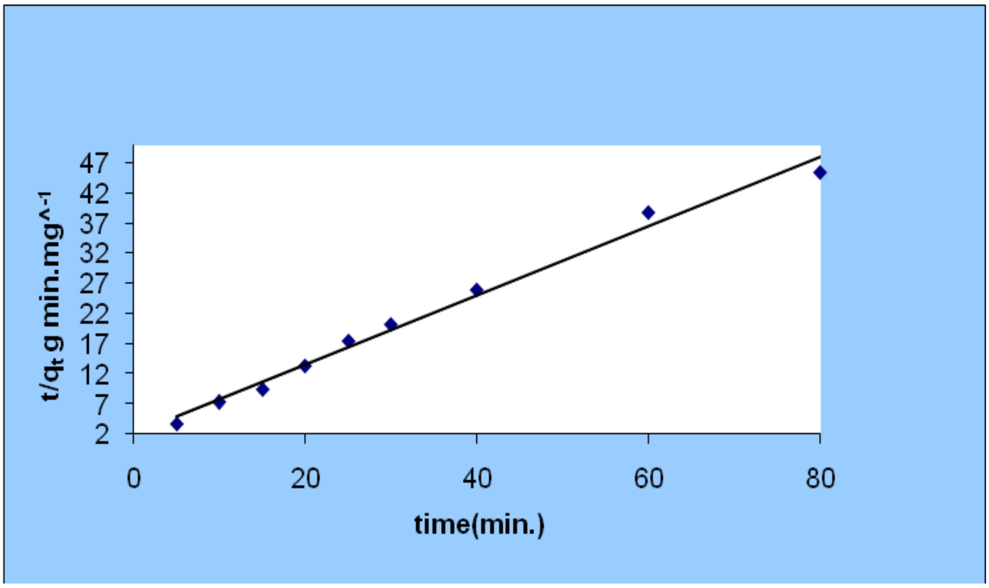
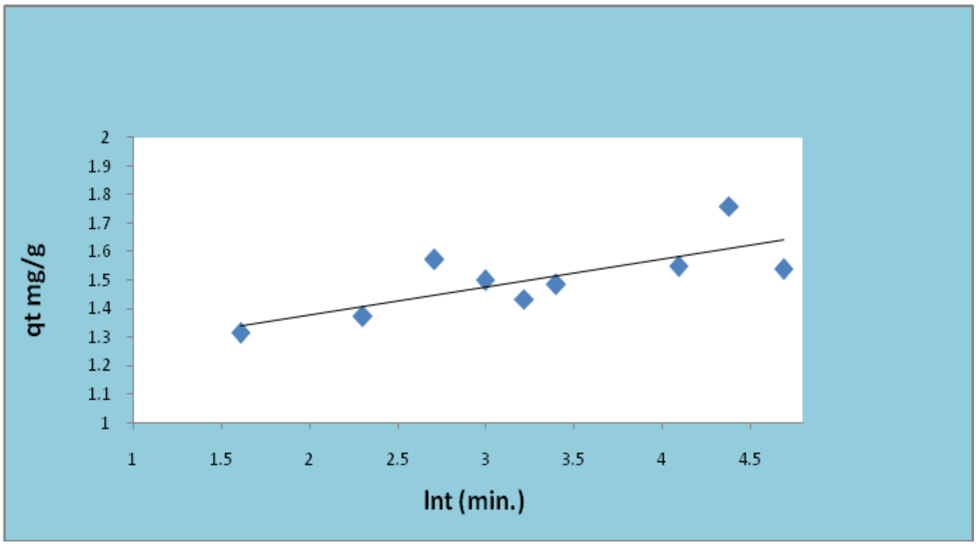


Figure (9): pseudo second order kinetic for the adsorption Cr(VI) onto Cinnamon 4g/L,at [10mg/L Cr(VI),pH2,150rpm,Temp.25°C,Cinnamon 0.2g/50ml].

Elovich model as modified by Chien and Clayton, which can be presented as in the linear form of Elovich equation is[17]

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \cdots\cdots\cdots\cdots (9)$$

Where, α is the initial adsorption rate and β is the desorption constant. Plot of q_t versus. ln (t) yield a linear relationship as shown in Figure (10), and the Elovich constants α and β were calculated and listed in Table (2).



Figure(10): Elovich kinetic for the adsorption of Cr (VI) onto adsorbent.

Table(2): Comparison of the first- order, Second- order, Elovich and calculated experimental q_e values for the adsorption of Cr(VI), 10mg/L, onto Cinnamon, 4g/L.

kinetic model	Parameter	
first- order kinetic model	$q_e$exp.(mg/g)	1.798
	q_e calc. (mg/g)	0.508
	k_1(min.$^{-1}$)	0.016
Second- order kinetic model	R^2	0.649
	k_2 (g mg^{-1} min^{-1})	0.149
	h (mgg^{-1} min^{-1})	1.032
	$q_e$calc.(mg/g)	2.632
Elovich model	R^2	0.999
	β (g mg^{-1})	6.579
	α (mg g^{-1} min^{-1})	141.458
	R^2	0.931

Conclusions

The present investigation showed that, the Cinnamon, is found to be very effective to remove Cr(VI) from aqueous solutions. The equilibrium data were analyzed using the Langmuir, Freundlich, and Tempkin isotherms. The maximum monolayer adsorption capacities were found to be (13.8), (7.5), (6.0) and (8.26) mg/g at Cinnamon dose 2g/L, 6g/L, 10g/L and 14g/L, respectively. Equilibrium data fitted very well to Tempkin isotherm equation. The kinetic analyses of the adsorption data of the studied system was found to follow the pseudo-second –order kinetic model.

References:-

1) Katz F., Salem H., ”The biological and environmental chemistry of chromium”. VCH Publisher, New York, p:51(1994).

2) Ajmal M., Ali Khan R. and Siddiqui B., Wat. Res., 30: 1478-1482(1996).

3) Ansari R., Acta Chim. Solv., 53: 88-94, (2006).

4) Metcalf and Eddy, “WASTEWATER ENGINEERING, TREATMENT, DISPOSAL AND REUSE”, 3rd. Edition, McGraw-Hill, (1993).

5) Rengaraj S., Yeon K., and Moon S., J. Hazard. Mater., B87: 273 (2001).

6) Sharma D, and Foster C., Bioresour technol., 47:257(1994).

7) Hassan S., Krishpajah A., Ghosh T.K., Visnanth D.S., Boddu V.M., Smith E.D., Sep.sci. Technol., 38:3775(2003).

8) Khan N.A. and Mohamad H., water and Wastewater Asia, 37-41(2007).

9) Argun M.E., Durun S., Ozdemin C. and Karatas M., J.Hazard Mat.,141:77-85(2007).

10) Babu B.v. and Gupta S., Adsorption, 14:85-92(2008).

11) Jain M., Grag V.K. and kadirvelu K., j. Hazard Mat.162,365-372(2009).

12) Aksu Z., Process Biochemistry, 40:997-1026(2005).

13) El-Nemr,J.Hazard. Mat., 161(1): 132-141(2009).

14) Langmuir I.,J.Am. Chem. Soc., 38:2221-2295 (1916).

15) Freundlich H. M. F., phys. Chem. (Leipzig), 57A: 385- 470(1906).

16) Grini G., Peindy H.N., Gimbert F., and Robert C., Separation and purification Technology, 53(1): 97-110 (2007).

17) Temkin M. J., and Pyzhev V., Acta physiochim. URSS,12: 217-222(1940).

18) Langergren S., Handlingar, 24:1-39(1898)

19) Ho Y.S., Mckay G., Wase DAJ and Foster CF., 18(7): 639-650(2000).

20) Chien S.H. and Clayton W.R., Soil Sci. Soc. Am. J., 44:265-268 (1980).