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ADSORPTION OF CR(VI) FROM AQUEOUS SOLUTION USING LOW COST ADSORBENT: EQUILIBRIUM STUDY

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Abstract:

The present investigation deals with the utilization of pine cone(PC) as adsorbent for the removal of chromium Cr(VI) from aqueous solution. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial Cr(VI) concentration, contact time, and adsorbent dosage, were considered. The optimal pH values of Cr(VI) removal by pine cone was 1.0. The time required for equilibrium was found to be about 100 minutes. The initial Cr(VI) concentration and adsorbent dosage was found to have large effect on the adsorption of Cr(VI). The equilibrium data were tested using several isotherm models, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) equations. The maximum adsorption capacities Qm at different dose, it was 37.594mg/g.

Key words: *Adsorption, pine cone, Cr (VI), kinetic, adsorption, isotherm, equilibrium.*

Introduction

Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining ores, dyeing ,fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic (Cieslak-Golonka, 1996). Its concentrations in industrial wastewaters range from 0.5 to 270 mg/l (Patterson, 1985). The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/l (EPA, 1990). In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels. The commonly used procedures for removing metal ions from effluents include chemical precipitation, coagulation, solvent extraction, membrane separation, reverse osmosis, ultra filtration, electrochemical deposition, ion-exchange and adsorption (Rao and Rehman, 2010; Sharma, 2003) have been reported as the common methods for removal of Cr(VI) from aqueous solutions and effluents. However, considering the high cost, long operation time and sludge generation, it is necessary to find out a more effective and economically viable process for the removal of Cr(VI). Among these methods, adsorption is generally considered to be simple, relatively low-cost and effective in removing Cr(VI) from water and wastewater (Gupta et al., 2010; Karthikeyan et al., 2005, Sharma et al., 2007). The feasibility of several low cost, non-conventional adsorbents obtained from agricultural and industrial wastes was explored Many papers have appeared on the production of low-cost adsorbent using cheaper and readily available materials (Tariq and suhad, 2009). The objective of the present study is to evaluate the capacity of pine cone powder as adsorbent using the batch adsorption process. Several isotherm models were used to evaluate the adsorbent. Condition parameters such as contact time, pH, initial metal ion concentrations, and adsorbent concentration were considered.

2. Materials and Methods

2.1 Preparation of pine powder

Pine cone were collected from northern part of Iraq ,dried and milled ,then shaked with distilled water to remove the soluble materials , this process was repeated about ten times or until we get rid of all colored or soluble materials ,then dried and sieved with a sieve(150µm). Finally the adsorbent was dried in air oven at (80°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 K2Cr2O7 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 pine cone was determined by adjusting the pH values of Cr(VI) solution to 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 with 0.1M HNO3 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 orbital Shaker model (IKAS130).The residual chromium in the sorption solutions was determined by atomic adsorption spectrophotometer type (AAnalyst200Perkin Elmer).

2.4 Effect of contact time on adsorption

The effect of contact time on adsorption of Cr(VI) onto pine cone were carried out by mixing solution with pH 1.0, by using 0.1 g of pine cone with 50ml of Cr(VI) of 10ppm at (19°±1C°) and shaked with160 rpm . At the end of each experiment the solution was filtered and residual Cr(VI) concentration was determined.

2.5 Effect of initial concentration of chromium ion on adsorption

The effect of initial concentration of Cr(VI) on adsorption onto pine cone, where carried out by mixing solution with pH 1.0 by using 0.1g of pine cone with 50ml of Cr (VI) (10, 30, 50, 80, 120) ppm at (18°±1C°) and shacked with 240 rpm for 100minutes. At the end of each experimental the solution was filtered and residual Cr (VI) concentration was determined.

2.6 Effect of adsorbent dose

The adsorption experiment at initial chromium concentration 10ppm were also performed with pine cone doses (1, 4, 8 and 10g/L) with pH 1.0 at (19°±1C°) and shaked with 240 rpm for 100minutes.

2.7 Adsorption Isotherm

Adsorption isotherm experiments were carried out at different adsorbent dose (1, 4, 8 and 12g/L) and different Cr(VI) concentrations (20, 40, 80 and 100ppm). At each adsorbent dose, each solution was shaked for 100 minutes at pH1.0 and temperature 18°C. The amount of Cr (VI) adsorbed onto the pine cone qe , was calculated using the following equation:

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

Where C0 and Ce 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 pine cone used (g).

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

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

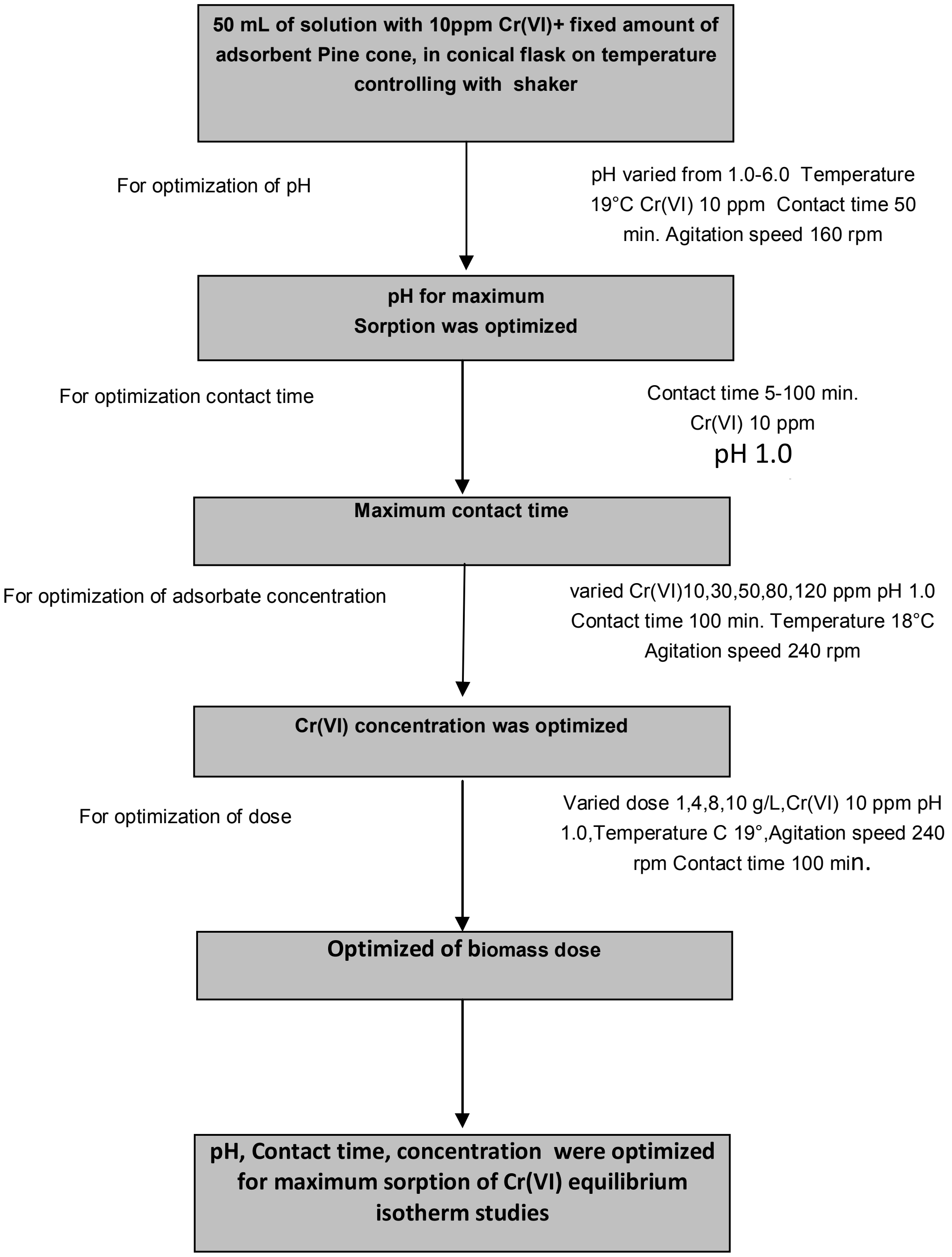


Figure 1. Full experimental diagram for execution of adsorption experiments.

3. Results and Discussion

It was found that the maximum removal of chromium from aqueous solution using (2g/L) pine cone as adsorbent occurred at pH 1.0, and the required time for equilibrium was 100 minutes at 18±°C.

So all batch sorption experiments were done at these conditions. The FTIR Spectrum of pine cone in Figure 2, revealed that the presence of phenolic, carboxylic, ketonic and aldehyde groups could be responsible for binding of metal ions.

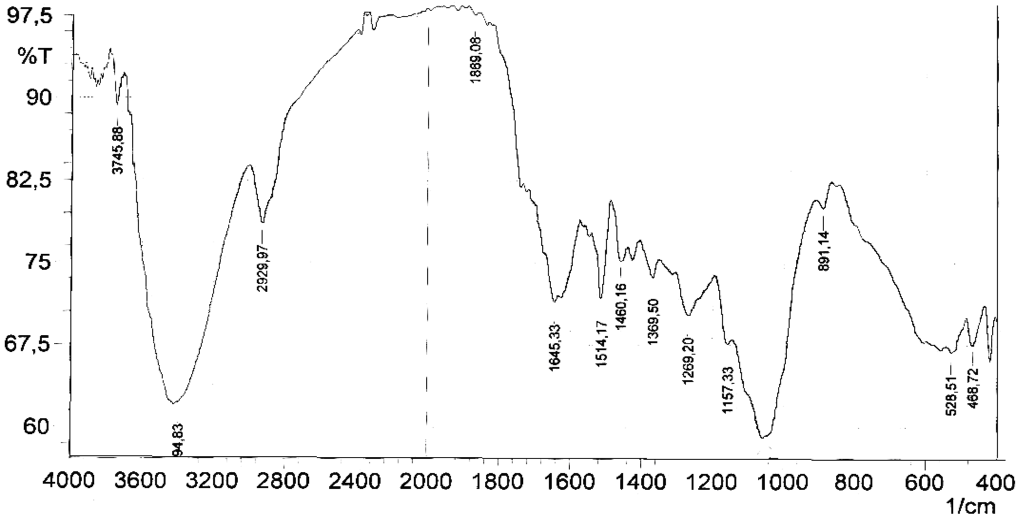


Figure 2: FTIR Spectrum (PC) before adsorption.

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. Plot of pH versus the adsorption capacity (qe) is shown in Figure 3. The optimum pH was found to be 1.0. The maximum removal of chromium ion at this pH is 59.38%. The surfaces of the pine cone become highly protonated under acidic conditions that favored the adsorption of Cr (VI) in the anionic form. The increase in pH value caused a decrease in protonation of the surface, which led to a decrease in the net positive surface potential of sorbent. This decreased the electrostatic forces between sorbent and sorbate, leading to reduced sorption capacity.(Li y.,et al.,2009).

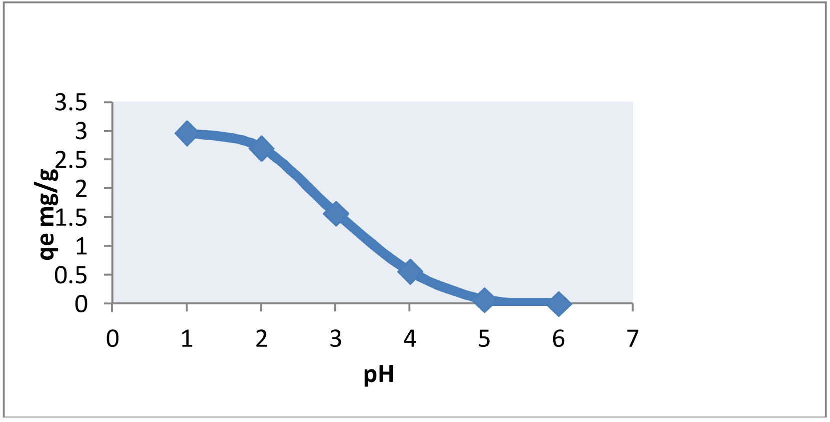


Figure 3: Effect of pH on the adsorption of Cr(VI) 10 mg/L onto (PC) 2g/L.

3.2 Effect of time and adsorbent dose

Effect of time for removal of Cr (VI) by pine cone with a dose of 2g/L concentration is shown in Figure 4. There was a rapid adsorption in the first 5 minutes,then decreased and little change occurred with time. The percent removal was 34.48% in the first 5 minutes and maximum removal was 51.01 % at 100 minutes. The effect of adsorbent dose (1, 4, 8 and 10g/L) was shown in Figure 5. The adsorpent capacity qe decreases as the adsorbent concentration increases, from 4.670 mg/g to 0.678 g/g, while the percent removal increases as the adsorbent dose increases, from 46.70% to 67.75%, these findings was in agreement with other researcher (El Nemr,2007).

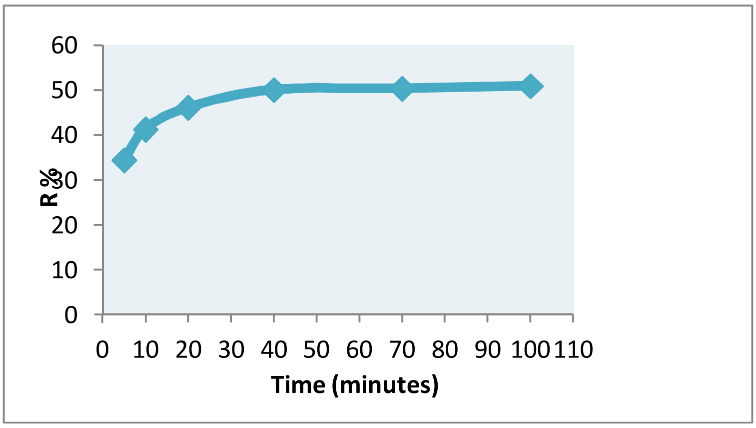
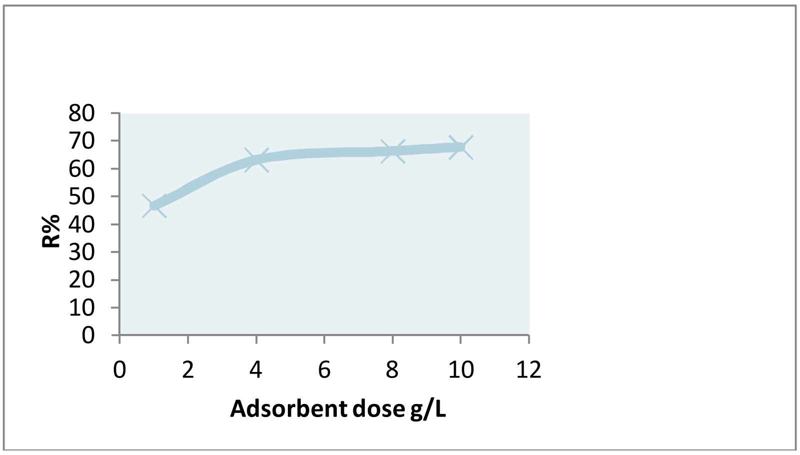


Figure 4: Time vs. R% of adsorption of Cr(VI) onto (PC).



Figure(5) : Adsorbent dose vs. R% of adsorption of Cr(VI) onto (PC)

3.3 Effect of initial concentration of Cr (VI)

The effect of initial Cr (VI) ion concentration is studied by using (10, 30, 50, 80 and 120 ppm) of chromium and adsorbent dose of 2g/L pine cone. The adsorption capacity qe was plotted against the concentration of Cr (VI). The relation is shown for different initial concentration in Figure 6. It revealed that, qe increases with increase of concentration of Cr (VI) (Baral,2007).

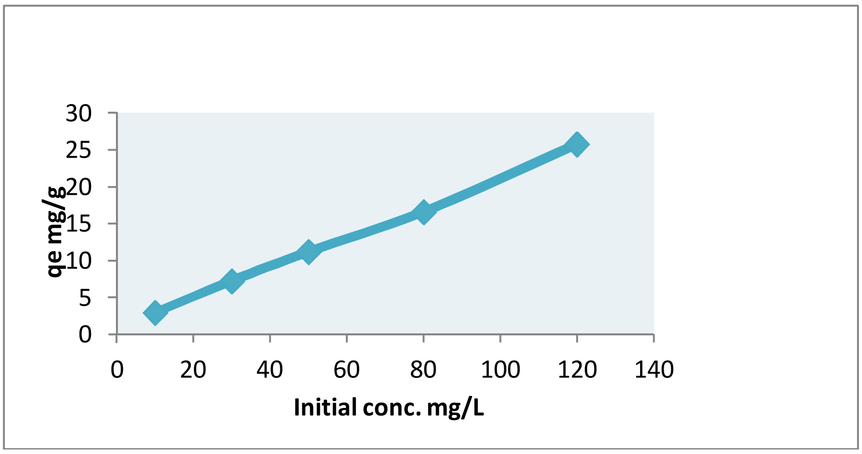


Figure 6: Relation between, q_e, and initial concentration.

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, (Langmuire,1916)

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

Ce is the equilibrium concentration in solution (mg/L), qe the amount of metal ion adsorbed (mg/g), Qm is the maximum monolayer capacity of the adsorbent (mg/g) and KL is an adsorption equilibrium constant (Lmg-1). Plot of 1/qe versus1/Ce is presented in Figure 7. The values of Langmuir isotherm constants and correlation coefficients are presented in Table 1.

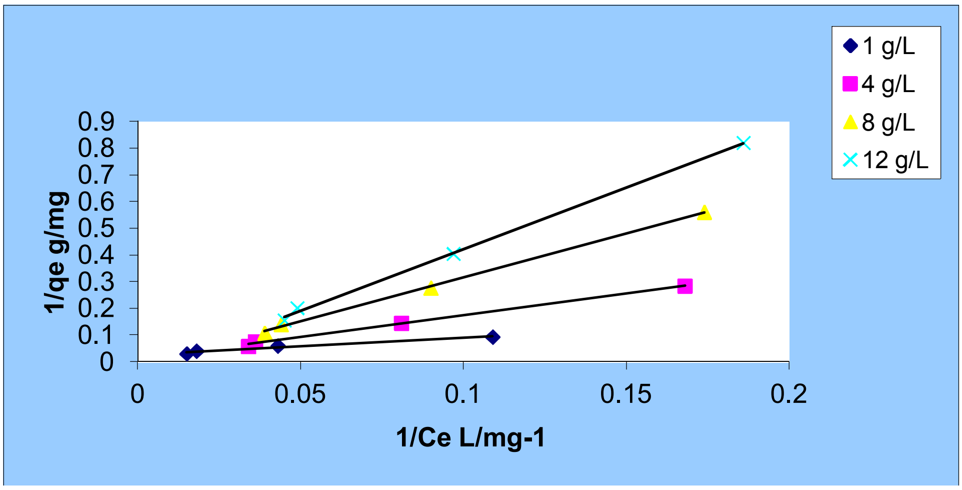


Figure 7. Langmuir isotherm for adsorption of Cr(VI) onto (PC), pH 1.0, contact time=100min

The linear form of Freundlich equation is (Freundlich,1906):

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

Where KF (Lmg-1) and n are constants indicating to the capacity and intensity of the adsorption, respectively. The linear plots of log qe versus log Ce at all adsorption dose were found to fit the Freundlich equation as illustrated in Figure 8, the values of Freundlich constants and correlation coefficientsa re listed in Table1.

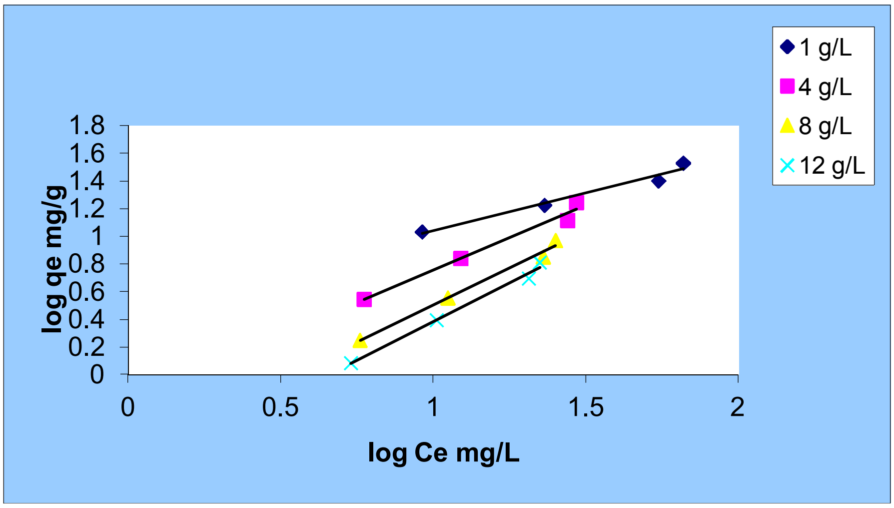


Figure 8. Freundlich isotherm adsorption of Cr (VI) onto (PC) at different dose.

The linear equation of Tempkin model can be written as follows (Tempkin M.,1940).

$$q_e = B_T \ln A_T + B_T \ln C_e \; ... (5)$$

Where BT is related to heat of adsorption, AT is the equilibrium binding constant (Lmg-)corresponding to maximum binding energy.The plot of qe versus lnCe at studied adsorbent doses is given in Figure 9, while values of Tempkin constants are given in Table 1.

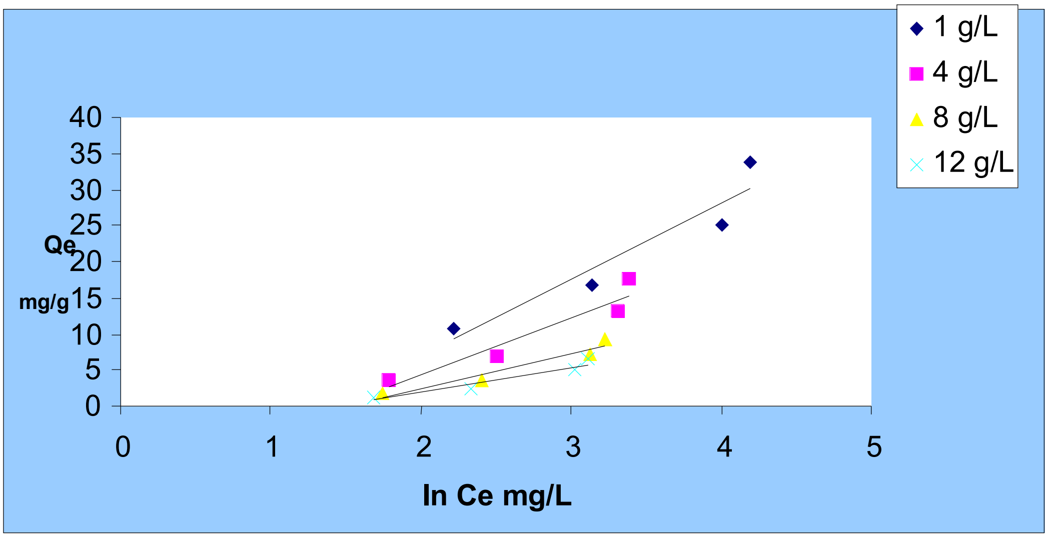


Figure 9. Tempkin plot of Cr (VI) adsorption onto (PC) at different dose.

The linear form of D-R isotherm equation can be expressed as follows (Dubinin M.,1947).

$$\ln q_e = \ln Q_m - K_{D-R} \varepsilon^2 \quad (6)$$

where Qm is the theoretical monolayer saturation capacity (mg g-1), KD-R is the D-R constant (mol2KJ-2). ε is the polanyi potential and is equal to:

$$\varepsilon = RT \ln[1 + \frac{1}{C_e}] \quad (7)$$

The mean energy of adsorption, E (KJmol-1) is related to KD-R as (Dubinin M.,1960):

$$E = \frac{1}{\sqrt{2K_{D-R}}} \quad (8)$$

The D-R constants are given in Table 1.

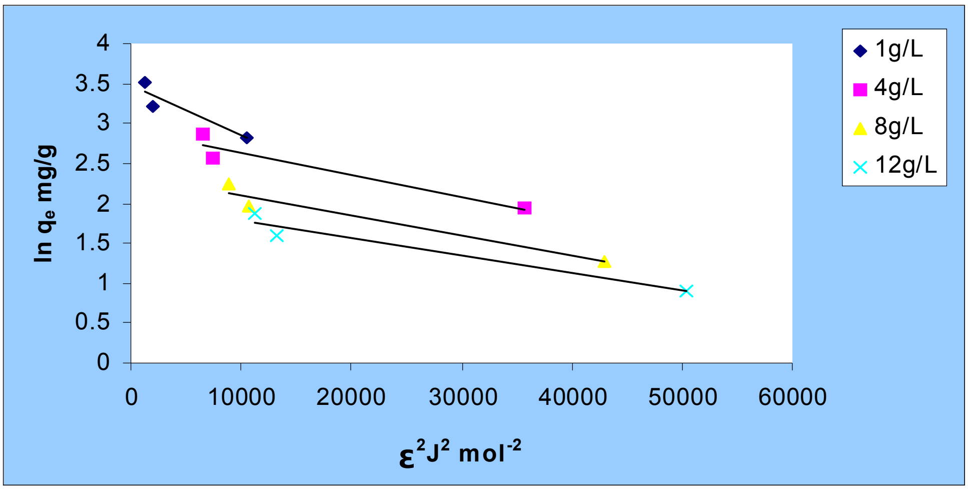


Figure 10. D-R isotherm for the adsorption of Cr(VI) onto(PC) at different dose.

Adsorption data fitted well with the Langmuir model. langmuir displayed a better fitting model than other models because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of the Cr (VI) ion on the surface of adsorbent.

Table 1. Comparison of the coefficients isotherm parameters from chromium (20, 40, 80, 100 mg/L) adsorption onto (PC) at different dose, at 18±1 °C.

Isotherm model	**Isotherm parameter**	**Dosage g/L**			
		1	4	8	12
Langmuir	Q_m (mg / g)	37.594	101.01	65.36	25
	K_L L mg $^{-1}$	0.043	0.006	0.005	0.009
	R^2	0.968	0.9959	0.9987	0.9984
Freundlich	K_F	3.155	0.657	0.272	0.181
	N	1.843	1.066	0.934	0.890
	R^2	0.9719	0.9821	0.9909	0.9913
Tempkin	A_T	0.263	0.235	0.228	0.240
	B_T	10.542	7.918	4.572	3.415
	R^2	0.9005	0.9059	0.9254	0.9246
D-R	Q_m mg/g	32.492	18.447	10.437	7.417
	$K_{D-R} \times 10^{-5}$ mol^2 J^{-2}	6	3	2	2
	E KJmol^{-1}	0.0913	0.129	0.158	0.158
	R^2	0.8632	0.9189	0.9457	0.9494

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كورتى

صنوبر ۆ روومزيـني كروم Cr (VI) لەگيراوەى ئاوى هاتيه لێكولين ژ چەنديا تاڤيكردني هەلمژينا Cr(VI) هاتيه دياركردن به پشن بەستني ب چەنديا رووەمزيـن , پەيتي سەرەتايى, وپەيوەندى كاتى. چەنديا تاڤيكردنى هاتيه جێ به جيى كردن ل سروشتيا گيراوەي pH وبه نەگوراني پلەى گه رمى 25C° ب كارئينانا رێكخەري گەرمى دهێته ب كارئينان خيرايیا ل تاڤيكردنا داتلى ئايسوسيرمى هاتيه شيكاركردن ب كارئينان (Langumir ,Freundlich, D-R,Tempkinp) رووەمزيـن ئايسوسيرمى دكه ڤێه هەمى شێويت خاندنى وشيانا بلنداهيا رووەمزيـن (Q_m mg/g=37.594).دهێته ديتن.

الخلاصة

يتضمن هذا البحث , دراسة قابلية استخدام مطحون مخروط الصنوبر لامتزازالكروم السداسي من المحاليل المائية ,واشتمل ايضا على دراسة العوامل المؤثرة على كفاءة الامتزاز مثل الداله الحامضيه ,والتركيز البدائي للكروم وتركيز المادة المازة وزمن التماس ونسبة الازالة. وكل التجارب تم اجرائها بداله حامضيه مقدارها 1.0 و درجة حرارة ثابتة باستخدام منظم حراري و جهاز رج, وتم اختبار النتائج العملية باستخدام عدة ايزوثرمات (Freundlich, Langmuir, Tempkin, D-R) و والحد الاقصى لسعة الامتزاز (37.594mg/ g).