

Removing of Hexavalent Chromium from Aqueous Solutions Using Dried Yogurt, and Studying Isotherm, Kinetic and Thermodynamic Parameters

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Abstract:

In this study, Yogurt was dried and milled, then shaken with distilled water to remove the soluble materials, then again dried and milled. Batch experiments were carried out to remove hexavalent chromium from aqueous solutions. Different parameters were optimized such as amount of adsorbent, treatment time, pH and concentration of adsorbate. The concentrations of Cr⁶⁺ in solutions are determined by UV-Visible spectrophotometer. Maximum percentage removal of Cr⁶⁺ was 82% at pH 2. Two equilibrium adsorption isotherms mechanisms are tested Langmuir and Freundlich, the results showed that the isotherm obeyed to Freundlich isotherm. Kinetic models were applied to the adsorption of Cr⁶⁺ ions on the adsorbents, pseudo-first-order, the pseudo second-order respectively. Results showed that pseudo second-order kinetic model was applicable to the experimental data well. The thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated. ΔH° , ΔS° and ΔG° for this study were negative indicating that the process is exothermic, while negative values of ΔG° indicate spontaneous process.

Key words: Adsorption, Adsorption isotherms, Adsorption kinetics, Hexavalent chromium, Yogurt.

Introduction:

Metals pollution is one of the modern challenges due to the wide using metals in the industries which caused serious increase of releasing the metals into the environment. There are at least twenty metals classified as toxic substances. Half of these toxic metals are spread in the environment in quantities that pose a danger to human health by causing cancer diseases (1).

There are many sources for metal pollution in the environment, for example chemical and refractory processing, tanning, and mining electroplating. Many metals such as chromium, cadmium, zinc, lead, mercury, and copper are used in various industries (2, 3). These industries release solid or liquid wastes polluted by metals into the environment, which leads to increasing levels of environmental pollution. There are two basic valences of chromium tri and hexa valence chromium (Cr³⁺ and Cr⁶⁺), The World Health Organization (WHO) recommends a maximum appropriate concentration of Cr⁶⁺ as 0.02 mg/L in wastewater which is discharging outside (4).

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It has shown that the hexavalent chromium compounds cause genetic mutations by penetrating cell membranes due to differences in physiochemical properties (5).

Adsorption process can be used for treatment and removal of contaminants as an effective method to reuse contaminated water again. Adsorption technique to remove the toxic metal ions from polluted water is a preferable approaches due to low cost compared with other methods such as chemical precipitation, ion exchange, membrane processes, and liquid extraction (6). One of other advantage is the availability of natural surfaces sources that can be used as adsorbent surfaces, such as clays, agricultural, and organic wastes (7).

This research aims to evaluate the drying yogurt as adsorption surface and optimize the conditions to remove hexavalnce chromium from aqueous solutions, and also study the thermodynamic of adsorption process.

Material and Methods:

Dry yogurt samples were collected from local market in Baghdad (natural yogurt produced in rural homes without any industrial additives). Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) were purchased from sigma Aldrich and used as

received. Potassium dichromate ($K_2Cr_2O_7$) of analar grade purchased from (BDH).

UV-Visible spectrometer, CARY 100 con Australian made, water bath shaker type lab companion BS- 11, digital scale KERN-ABBS and pH meter type trans BP 300 were used in this work.

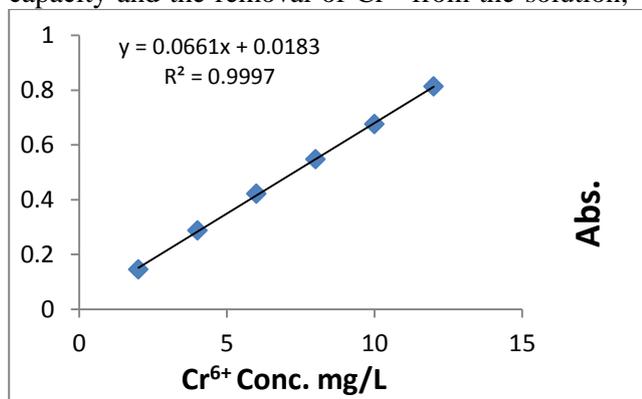
Experimental

The yogurt was dried over night at 80°C, then rinsed with distilled water for 8 hours and dried in an air oven at 80°C for overnight. The resulted dried yogurt was passed through 150 μm sieve after being milled with agate mortar. Dry yogurt is ready to use as adsorption surface. 1000 mg/L stock solution of chromium ion Cr^{6+} was prepared by dissolving 0.2827 g in 100mL distilled water, wavelength of maximum absorption peak (λ_{max}) was detected at wave length 372 nm and stabilized for all subsequent measurements, calibration curve was built using UV-Vis absorbance measures for series of concentrations prepared by multi dilution of stock solution. To study different parameters, adsorption experiments were carried out using 50 mL of series of concentrations. Solutions were prepared by dilution of stock solution for different experiments then using calibration curve to calculate the concentrations for definite time intervals. The percentage of removal Cr^{6+} (R%) was calculated by equation 1.

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \dots \dots (1)$$

Where, C_i and C_e represent the metal ions concentrations (Cr^{6+} mg/L) at initial and final experiment.

To optimize conditions of the best adsorption capacity and the removal of Cr^{6+} from the solution,



(a)

effect of different parameters on adsorption capacity were studied in this work such as time, pH, and initial concentration of yogurt, adsorbent dosage and temperature of adsorption. Adsorption capacity was calculated by equation 2

$$q_e = \frac{(C_i - C_e) \times V}{M} \dots \dots \dots (2)$$

Also, the adsorption capacity (q_t) at time t was determined using the Equation 3 (8).

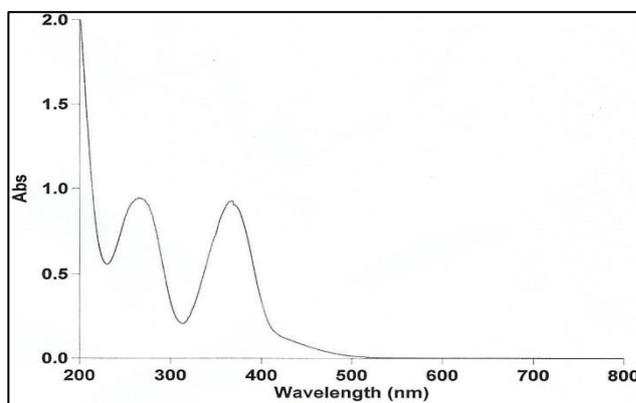
$$q_t = \frac{(C_0 - C_t) \times V}{M} \dots \dots \dots (3)$$

Where C_0 , C_e and C_t are the metal ions concentrations (mg/L) at initial, equilibrium and at time t, V is the solution volume (mL) of metal ions at initial concentration and M is adsorbent mass used (g). Kinetic studies of adsorption and adsorption isotherms are carried out in this work to determine reaction order and type of isotherm.

Results and Discussion:

Removal of metal ions by adsorption depends on several parameters such as contact time, temperature, pH, and adsorbate concentration. Increasing the initial concentration of adsorbate leads to increase the amount of adsorbed q_e (mg/g), and this is due to increase driving force of concentration gradient (9). Also, pH of the solution has important influence in this process (10).

Calibration curve was built between different concentrations of Cr^{6+} (2, 4, 6, 8, 10 and 12 mg/L) and the UV-Vis absorbance, calibration curve showed very good linearity and correlation coefficient (R^2) of 0.9997 as shown in Fig. 1.



(b)

Figure 1. (a) Calibration curve of Cr^{6+} Concentration vs Absorbance (b) UV-Vis Absorbance spectrum

This calibration curve was used in all calculations in this work.

Effect of Contact Time

Ten experiments with different contact time between 10 to 100 minutes and, effect of adsorption

contact time on Cr^{6+} removal are shown in Fig. 2. It can be noticed from the figure that the chromium removal percentage increased with increasing time to about 60 minutes, with the removal rate almost 80%. The maximum Cr^{6+} removal percentage was 82.12% at 100 min.

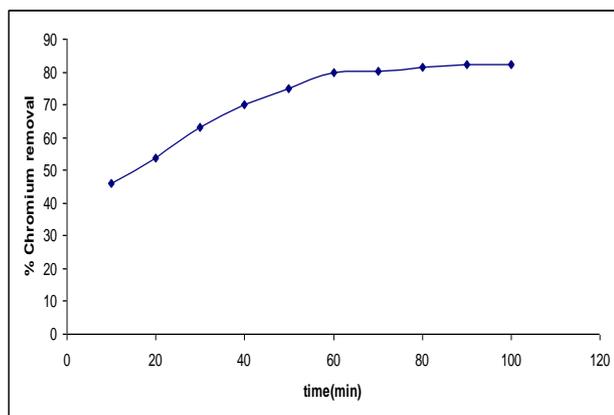


Figure 2. Effect of contact time on adsorption of Cr⁶⁺

Effect of pH

Effect of pH on the Cr⁶⁺ adsorption by waste yogurt was studied over pH range of 1 to 8. Different pH conditions were maintained by sodium acetate buffer. Maximum removal conc. of Cr⁶⁺ was observed at pH 2 as shown in Fig. 3. The removal of Cr⁶⁺ significantly increased from 1 to 2 pH, and then decreased with increasing the pH of the solution. The chromium removal percentage increased from 31.45% at pH 8.0 to 82.12% at pH 2.0. The maximum adsorption that was observed at pH 2.0 as shown in Fig. 3 may be attributed to the competition between adsorption sites and hydroxyl groups on Cr⁶⁺ ions. These results agree with previous studies of chromium adsorption by banana peel and date palm seed (11).

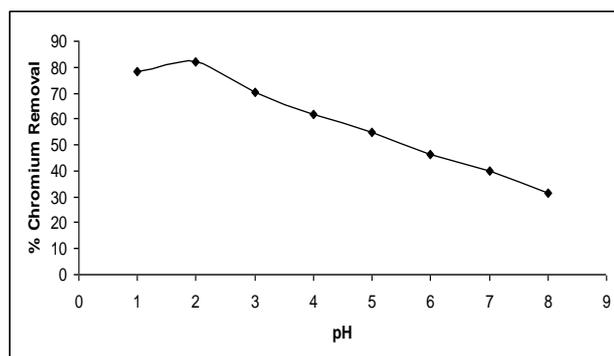


Figure 3. Effect of pH on adsorption of Cr⁶⁺

Effect of Initial Chromium Ion Concentration.

Series of initial concentrations of Cr⁶⁺ between (10 to 60 mg/L) were tested to determine the effect of initial concentration on adsorption. The relation between concentration and calculated adsorption capacity (q_e) was plotted as shown in Fig. 4. The adsorption capacity q_e (mg/g) increases with

increasing the initial concentration of the adsorbate, and this can be attributed to the increase in driving force of the concentration gradient with increase in concentration of chromium (8).

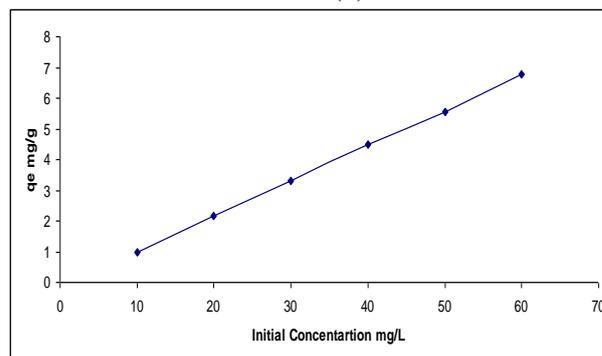


Figure 4. Effect of initial concentration on adsorption of Cr⁶⁺

Effect of Adsorbent Dosage

50 ml of the Cr⁶⁺ solution was exposed for 80 minutes to a dose ranging from 0.05 to 0.5 g of adsorbent and then the removal percentage for each dose was calculated. Removal percentage was plotted against dosage of adsorbent as shown in Fig. 5; this Figure shows increasing of removal percentage from 0.05 g with 30% percentage removal then it reached the maximum value with 84.6% removal at 0.4 g (12).

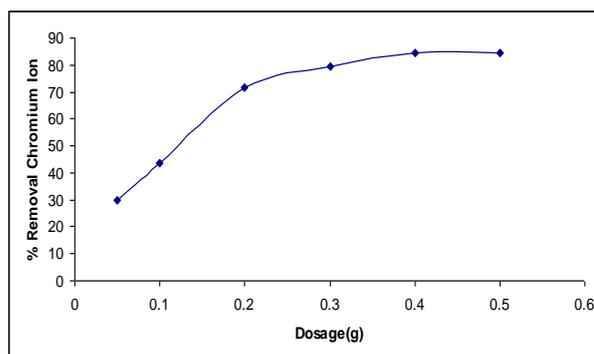


Figure 5. Effect of adsorbent Dosage on removal percentage

Adsorption Isotherms

There are several equilibrium adsorption isotherms mechanisms to understand the sorption process; two mechanisms have been tested in this work, Langmuir and Freundlich isotherms. Table 1 shows Langmuir and Freundlich constants for this study.

Table 1. Values of the Langmuir and Freundlich constants for the adsorption of Cr⁶⁺ onto drying Yogurt

Isotherm model	Isotherm parameter	Temperature °C		
		25	35	45
Langmuir	Q _m (mg / g)	6.459	23.98	40.00
	K _L (L/g)	0.462	0.713	0.150
	R ²	0.9062	0.9395	0.9246
Freundlich	K _F (L/g)	0.275	0.333	0.683
	n	0.5	1.09	0.735
	R ²	0.978	0.993	0.896

The Langmuir isotherm assumes that the adsorption occurs on a single layer of the adsorbent on identical limited sites (13). Using Langmuir equation 4:

$$\frac{1}{q_e} = \left(\frac{1}{K_L Q_m} \right) \frac{1}{C_e} + \frac{1}{Q_m} \dots (4)$$

Where: K_L = Langmuir equilibrium constant for adsorption (L/mg), Q_m = maximum adsorption capacity (mg/g), q_e = amount adsorbate equilibrium (mg/g), C_e = equilibrium concentration (mg/L).

By plotting 1/q_e versus 1/C_e Fig. 6, it is clear that there is an agreement between the experimental data at high value of correlation factor R², while the values of Q_m are higher than expected which indicates the incompatibility with the Langmuir model.

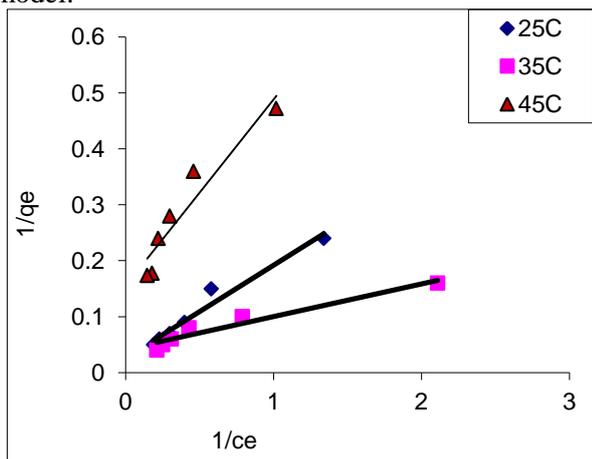


Figure 6. Relationship between 1/q_e and 1/C_e in Langmuir model

Freundlich equilibrium adsorption isotherm model assumes that the adsorption occur by one layer of heterogeneous surface and gives a linear Freundlich equation (14).

$$\log q_e = \log K_F + 1/n \log C_e \dots (5)$$

K_F and n are the isotherm constants of the Freundlich equation. Plotting of logq_e versus logC_e at different temperature, the linear plot indicates that adsorption follows Freundlich isotherm as shown in Fig. 7.

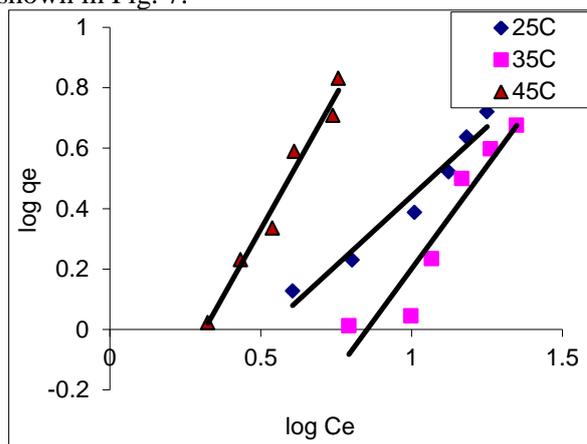


Figure 7. Relationship between logq_e and logC_e in Freundlich model

There are two different types of adsorption, chemical and physical. Value of n in Freundlich equation can be used to determine the type of adsorption. If n value is less than one, this means the adsorption is chemical, while if value of n is more than one, this indicates that the adsorption process is physical (15). As shown in table 1, the adsorption process is physical at temperature of 35 °C, while the adsorption at both 25 and 45 °C is chemical process.

Kinetics of Adsorption

Studying the kinetics is very important for understanding the adsorption reaction. This is done by suggesting kinetic models and studying their applicability to experimental adsorption data. Parameters of first and second order reaction are listed in table 2.

Table 2. Kinetic parameters for the adsorption

Kinetic Model	Parameter	Temperature °C		
		25	35	45
First- Order Kinetic Model	q _e exp (mg/g)	0.533	0.316	0.372
	k ₁ ×10 ² (min. ⁻¹)	0.029	0.048	0.023
	q _e calc. (mg/g)	3.418	3.998	3.182
	R ²	0.9748	0.9709	0.9246
Second- Order Kinetic Model	k ₂ ×10 ² (g mg ⁻¹ min. ⁻¹)	0.126	0.015	0.166
	q _e calc.(mg/g)	3.484	4.80	3.226
	R ²	0.9983	0.9889	0.9983

Equation 6 is a model of the pseudo first order (16):

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

Where, q_e and q_t represent the concentration of the adsorbed metal ion (mg g⁻¹) at time t and at solid phase equilibrium respectively, and k₁ is the first order constant of the adsorption (min⁻¹). Plotting of log (q_e-q_t) vs. t give a straight line and the constant of the rate can be calculated from the slope of the straight line Fig. 8.

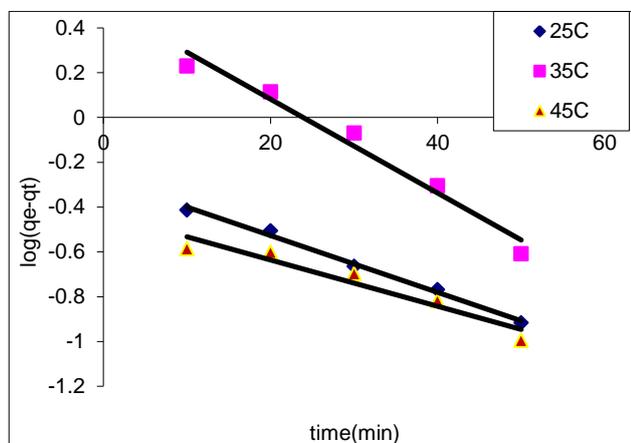


Figure 8. First order plot of adsorption of Cr⁶⁺ on Drying Yogurt.

Equation 7 represents the pseudo second order reaction of Cr⁶⁺ on drying yogurt (16).

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

Where k₂ constant rate of pseudo-second order adsorption (g mg⁻¹ .min⁻¹), plotting of t/q_t vs time should be straight-line as shown in Fig. 9.

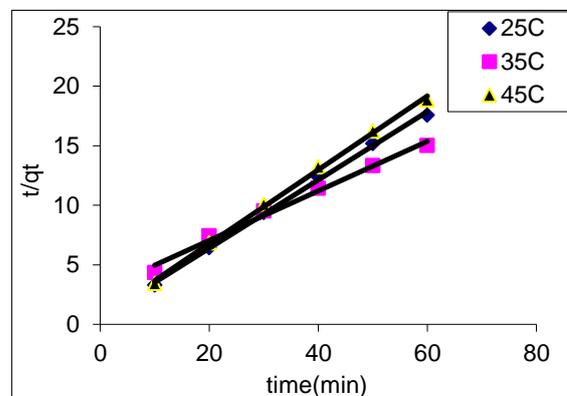


Figure 9. Second order plot of adsorption of Cr⁶⁺ onto Drying Yogurt.

Linearity of plotting of two kinetic models shows the reaction follow the second order mechanism more than the first order mechanism.

Thermodynamic Parameters of Adsorption

Some thermodynamic parameters such as changes in enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) were calculated in this study from the following equations (17).

$$K_{eq} = C_{solid}/C_{liquid} \dots\dots\dots (8)$$

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (9)$$

$$\Delta G^\circ = -RT \ln K_{eq} \dots\dots\dots (10)$$

Where K_{eq} equilibrium constant, C_{solid}, C_{liquid} are the equilibrium adsorbate concentrations at solid and liquid phase (mg/L), T is the absolute temperature of the reaction (°K) and R is the gas constant (8.314 Jmol⁻¹K⁻¹). ΔH° and ΔS° are determined by using Vant Hoff equation (eq. 9) and calculated intercept and slop of plotting K_e vs 1/T Fig. 10.

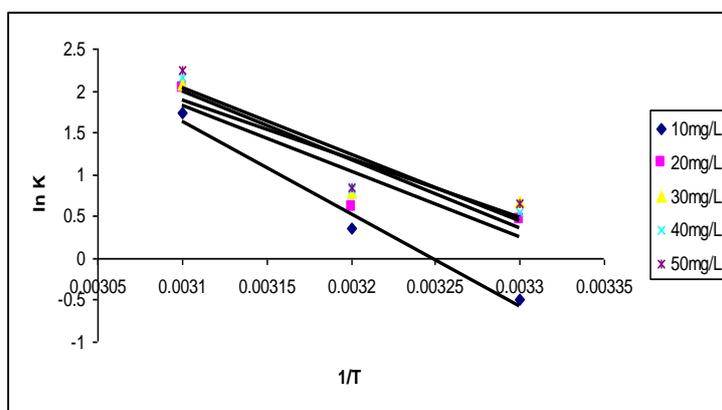


Figure 10. Vant Hoff Equation plot at different concentration.

Calculated thermodynamic parameters are shown in table 3.

Table 3. Calculated values of thermodynamic parameters

Cr ⁶ Con. mg/L	ΔH° KJmol ⁻¹	ΔS° Jmol ⁻¹ k ⁻¹	ΔG° KJmol ⁻¹			R ²
			25°C	35°C	45°C	
10	-1.140	-43.55	-2.096	-2.302	-2.945	-0.8793
20	-10.018	-40.175	-2.088	-2.565	-2.865	-0.9671
30	-9.519	-38.629	-2.125	-2.565	-2.873	-0.9754
40	-9.020	-36.683	-2.118	-2.289	-2.834	-0.897
50	-8.76	-33.98	-1.987	-2.023	-2.451	-0.948

In this study, the calculated values of ΔH° are negative, and this means the adsorption was exothermic process, while the calculated values of (ΔS°) were negative as well, which means that the molecules are more ordered in liquid-solid interphase compared to liquid phase. The free energy values (ΔG°) of adsorption process were measured and show positive values, which indicated the non-spontaneous nature of the adsorption process (18).

Acknowledgments :

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Conclusion

Drying yogurt can be used as an effective absorbent material for hexavalent Chromium ion and possibly other metal ions as well. Drying yogurt can remove more than 80% of hexavalent chromium from waste water. Drying yogurt could be used in waste water purification.

Conflicts of Interest: None.

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إزالة الكروم السداسي من المحاليل المائية باستخدام اللبن الزبادي المجفف، دراسة الأيزوثيرم والحركية والعوامل الترموديناميكية

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الخلاصة:

في هذه الدراسة، تم تجفيف الزبادي وطحنه، ثم شطفه بالماء المقطر بالهزاز لإزالة المواد الذائبة وتجفيفه وطحنه ثانية. أجريت مجموعة تجارب لإزالة الكروم السداسي التكافؤ من المحاليل المائية. تم دراسة تأثير عوامل مختلفة على النسبة المئوية لإزالة الكروم السداسي مثل كمية المادة المازة والزمن ودرجة الحموضة وتركيز المادة الممتزة. حسب تركيز الكروم السداسي في المحاليل بواسطة مطياف الأشعة فوق البنفسجية - المرئية. أعلى نسبة مئوية لإزالة الكروم السداسي كانت 82٪ عند الرقم الهيدروجيني 2. تم اختبار اثنين من ايزوثيرمات الاتزان وهي لانكماير وفريندلج، اظهرت نتائج دراسة ايزوثيرم الاطاعة بشكل اكبر لنموذج فرينلج. كما تم تطبيق نموذجين لحركية إمتزاز أيونات الكروم السداسي على المادة المازة وهما الرتبة الأولى الكاذبة والرتبة الثانية الكاذبة على التوالي. اظهرت نتائج دراسة الحركية ان الرتبة الثانية الكاذبة اكثر إنطباقاً على البيانات التجريبية. وتم احتساب بعض القيم الترموديناميكية مثل التغيرات في الطاقة الحرة والانتالبي والانتروبي وكانت قيم التغيرات في الانتالبي والانتروبي لهذه الدراسة سالبة يشير ذلك إلى أن العملية طاردة للحرارة، بينما تشير القيم السلبية للتغير في الطاقة الحرة إن العملية تلقائية.

الكلمات المفتاحية: الامتزاز ، ايزوثيرمات الامتزاز ، حركية الامتزاز ، الكروم السداسي، الزبادي