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Removal of Chromium (III) Ions from its Aqueous Solution on Adsorbent Surfaces: Charcoal, Attapulgite and Date Palm Leaflet Powder

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Abstract

In the present work, a study is carried out to remove chromium (III) from aqueous solution by: activated *charcoal*, *attapulgite* and *date palm leaflet powder (pinnae)*. The effect of various parameters such as contact time, and temperature has been studied. The isotherm equilibrium data were well fitted by Freundlich and Langmuir isotherm models. The adsorption capacity of chromium (III) that was observed by activated *charcoal*, *attapulgite* and *date palm leaflet powder (pinnae)* increased with the rise of temperature when the concentrations of Cr (III) were 600, 700 and 100mg/L respectively. The greatest adsorption capacity ofactivated *charcoal*, *attapulgite* and *date palm leaflet powder (pinnae)* at 10°C was 7.51, 5.39 and 0.77mg.g^{-1} respectively and reaching 9.99, 8.82 and 1.43mg.g^{-1} at 37.5°C. The thermodynamics study showed that the chromium (III) ions adsorption is endothermic and spontaneous with the increase of randomness at the solid-solution interface that involves adsorption and absorption mechanism.

Keywords: Chromium (III), Adsorption capacity, Freundlich and Langmuir isotherm

إزالة إيونات الكروميوم الثلاثي من محاليل مائية على سطوح مازة : الفحم المنشط التجاري ، أتابلكايت ، مسحوق سعف النخيل

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الخلاصة

تتناول هذه الدراسة إزالة أيون الكروميوم الثلاثي من محاليله المائية على: الفحم المنشط التجاري ، اتابلكايت (طين عراقي) ، ومسحوق سعف النخيل المتوافر محلياً في العراق . حيث تم دراسة عوامل الإتزان كتأثير الزمن و درجة الحرارة ؛ لتطبيق ايزوثرمات التوازن لإمتزاز أيونات الكروميوم الثلاثي التي تنطبق على ايزوثرمات فريندلش ولانكماير . أن سعة إمتزاز أيونات الكروميوم الثلاثي الممتز على الفحم المنشط ، اتابلكايت ، و مسحوق سعف النخيل تزداد بإرتفاع درجة الحرارة عند المدى (10–37.5) درجة مئوية بالتراكيز 600 و 700 و 100 ملغم/لتر على التوالي . وإن أعلى سعة إمتزاز لكل من الفحم المنشط ، اتابلكايت و مسحوق سعف النخيل في 10درجة مئوية كانت 7.51 , 5.39 , 0.77 ملغم/غم على التوالي في حين كانت سعة الإمتزاز 9.99 و 8.82 و 1.43 ملغم/غم بدرجة الحرارة 37.5 درجة مئوية . ومن دراسة التوازن الثرموداينميكي فإن إمتزاز ايونات الكروميوم الثلاثي يكون مصحوباً بعملية الامتصاص ، كما إن

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العملية تلقائية ، وعشوائية ، وماصة للحرارة عندما يتم التداخل ما بين المحلول و دقائق السطح الماز الذي ينتج عنه عمليتي الإمتزاز والإمتصاص معاً .

Introduction:

Interfaces are the boundary regions that separate different bulk regions of matter. They have special chemical, physical, and biological properties that have fascinated and drawn the attention of scientists and engineers from many different fields[l].

Adsorption implies the presence of excess concentration of substances in surfaces of a solid or a liquid. The substances that are adsorbed are termed as adsorbate, and the material that adsorbs is called adsorbent. The adsorbate may be solid, liquid or gas [2]. Adsorption can occur at any type of interface, although the distinct characteristics of solid versus liquid interfaces make the analysis of each case somewhat different. For that reason, the discussion of each situation is best presented in the context of specific interfaces [3].

Adsorption from Solution generally follows the same principles as laid down for adsorption of gases by solid and is subject to the same factors [4]. The molecules on the surface of a liquid have a different environment and therefore the surface has a different free energy from the bulk of the material [5]. Adsorption of surfactants on minerals from aqueous or organic solutions is often a complex process since it can be influenced by all components of the system: solid, solvent, and solute. Several interactions such as electrostatic attraction, covalent bonding, hydrogen bonding or nonpolar interactions between the adsorbate and the adsorbent species, and lateral interaction between the adsorbed species as well as their desolvation can contribute to the adsorption process.

Adsorption can be considered to be a process of selective partitioning of the adsorbent species to the interface in preference to the bulk and is the result of interactions of such species with the surface species on the solid. The interactions responsible for adsorption can be either physical or chemical in nature. Therefore, adsorption can be broadly classified into two categories, physical adsorption or physisorption and chemical adsorption or chemisorption, depending on the nature of the forces involved [6]. The basic concepts behind the factors governing the adsorption of surfaceactive molecules at interfaces has already been mentioned several times in terms of the Gibbs adsorption isotherm, which relates the surfaces excess concentration of the adsorbed species to the surface or interfacial tension of the system [3]. There are several factors controlling adsorption which also influence the mechanisms governing the adsorption process. These have been reviewed by Parfitt and Rochester [7]:

1- Nature of the surface.
2- Chemical structure of the solute and its interactions with the solvent.
3- Nature of the solvent.
4- Nature of the interactions between the surface and the adsorbed solute.
5- Temperature.

The adsorption of surface-active materials onto a solid surface from solution is an important process in many situations, including those in which we may want to remove unwanted materials from a system (detergency), change the wetting characteristics of a surface (coating and waterproofing), or stabilize a finely divided solid system in a liquid where stability may otherwise be absent (dispersion stabilization) [3].

Chromium is used in several industries, including metallurgy (steel, ferro-and nonferrous alloys), refractory (chrome and chrome-magnesite), and chemical manufacturing (pigments, electroplating, tanning and other), involving numerous commercial processes including electroplating, leather tanning, pulp production, milling, mining (ore refining), and wood preservation[8]. The properties of Cr are highly dependent on the molecular structure of the Cr compound, particularly on the oxidation state (or oxidation number) of the Cr[9]. Both valences of chromium (III, VI) are potentially harmful but hexavalent chromium has a greater risk due to its carcinogenic properties [10]. Dissolved concentrations of total Cr in groundwater from natural processes are typically below 10 mg/L [11]. One author stated that fish are sometimes more sensitive to Cr^{+3} than to Cr^{+6}[12]. It is poisonous only at high concentration. The removal or reduction of Cr (VI) to Cr (III) serve as a key process for removal of Cr(VI)-contaminated water and wastewater[13, 14].

In this work, it has been removing of chromium (III) ions from its aqueous solution on different adsorbent surfaces: charcoal, attapulgite and date palm leaflet powder that borne from a thesis [15].

Experimental Part

The Analar chemical compounds [$Cr(NO_3)_3.9H_2O$], Riedel - DE Haen AG, Seelze -Hannover, Germany; which are used in this work and their suppliers , are used in these experimental. A standard stock solution of Cr(III) 2000mg/L was prepared by dissolving 15.3916g of Chrom(III)-Nitrat-9-Hydrat in volumetric flask 1000mL in distilled water. All working solutions were prepared by diluting the stock solution with distilled water. Solutions of different concentrations 5, 10, 20, 30, 40, 50, 75, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000mg/L of Cr(III) were prepared by serial dilution from the standard stock solution 2000 mg/L. Deionized water was used to dilute the stock solution in order to get the desired concentration.

The absorbance at λmax= 303nm was measured for the blue greenly colored solution after 10 minutes ageing by a UV–Visible Spectrophotometer double Beam CECIL, CE 7200, (190 – 900)nm, England, to draw a calibration curve in the range of 5 to 2000 mg/L, and chemical analyses were carried out by Atomic Absorption Spectrophotometer/ Philips–Pye Unicam SP9, England;

- Chromium Hollow Cathode Lamp / Pye Unicam Ltd Cambridge, England.
- Principle Line 357.9nm
- Band Pass 0.2- 0.5nm
- Flame air / acetylene, fuel rich
  C_2H_2 : SP9 47-50, PU9000 4.1- 4.5min-1
- Lamp current maximum 7.5mA

, at λmax= 359.5nm in range of 5 to 100mg/L by plotting absorbance versus concentration of chromium after treating with the Least Square Method. The curve has indicated applicability of Beer-Lambert‘s Law over the region 5 to 2000mg/L and straight line equation.

Preparation of Adsorbent Surfaces:

Activated Charcoal:

Activated carbon is a black solid substance resembling granular or powdered charcoal. It is a processed carbon material with a highly developed porous structure and a large internal specific surface area. Activated carbon is defined as a carbonaceous material with a large internal surface area and highly developed porous structure resulting from the processing of raw materials under high temperature reactions. It is composed of 87% to 97% carbon but also contains other elements depending on the processing method used and raw material it is derived from. Activated carbon’s porous structure allows it to adsorb materials from the liquid and gas phase [16].

Commercial activated *charcoal* is packed for servicing industry.

Attapulgite:

Attapulgite (palygorskite) is a naturally occurring non-swelling clay mineral of needles, fibers or fibrous cluster morphology, it is composed of hydrous magnesium – aluminum silicate, having a theoretical formula of $Mg_5Si_8O_{20}(OH)_2(OH_2)_4.4H_2O$, where significant substitution of Mg^{+2} by Al^{+3} and Fe^{+3} occur in the octahedral position and Ca^{+2}, Na^+ and K^+ occur as interlayer cations [17,18]. The clays of *attapulgite* were supplied in a powder form. *Attapulgite* were first dispersed in a deionised water and then stirred. They were washed seven times with deionised water to remove excess adsorbents, filtered, and dried in an oven at 50-60 °C. The drying clays grounded and sieved by the available sieves to particle size of 75, 150 and 250 micrometers by using 200, 100 and 60 meshes sieves respectively and then stored in an air tight containers.

Date Palm Leaflet Powder (Pinnae):

Natural materials such as Palm Tree are available in large quantities in Iraq and are considered to be an important product for industrial, agricultural, and domestic uses [19]. At the tip of the leaf, there may be a single terminal leaflet or two leaflets forming a V figure 1.

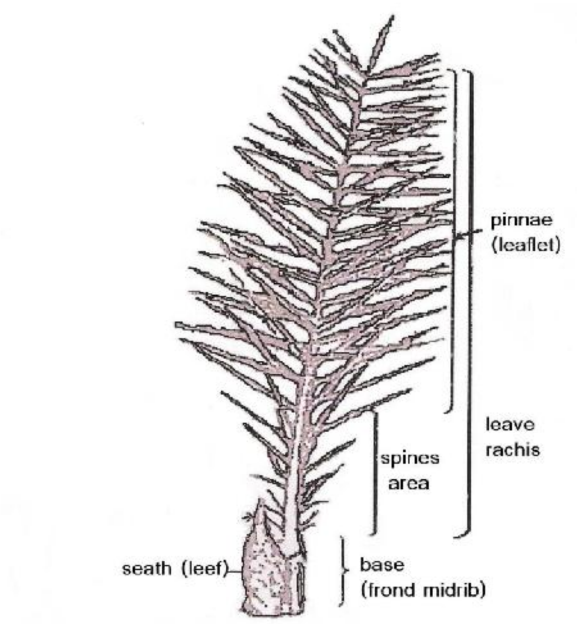


Figure 1-The Parts of the *leaves* of Palm Tree; [20].

The *date palm leaflet powder (pinnae)* was taken from a 10 years old khastawi palm tree, which was obtained from Al-Kadhumiya area in Baghdad city of Iraq. The *leaflets* were cut from the leaves of a palm tree and were cleaned to remove the dust, and then were covered with a light cover and left to dry in an air for 10 days, divided into small sections and grounded. Then, they were used for experiments without washing or any other physical or chemical treatments. The particles of size 150μm were used in all experiments throughout this work.

Equilibrium Study:

The equilibrium study that gives the capacity of adsorbent was carried out by varying parameters such as contact time and temperature. The volume of 10mL of chromium solution with some different concentration was placed in a 100mL volumetric flask for adsorption by three surfaces *charcoal*, *attapulgite*, and *date palm leaflet powder (pinnae)*. A series of such volumetric flasks were then shaken at a constant speed of 60 cycles per minute in a shaking water bath (thermostatically controlled shaker) with temperatures 10, 25 and 37.5°C. After shaking the flasks for optimum time, the adsorbate surfaces were separated after centrifugation at 5500 rpm for 5 minutes, and filtered using (42) Whatman filter paper ashless, and analyzed for the remaining chromium ions concentration by an UV-Vis spectrophotometry for *charcoal* and *attapulgite* and an Atomic Absorption Spectrometer (AAS) used for *date palm leaflet powder (pinnae)* analysis. All experiments were conducted at room temperature keeping ***pH*** of the solution constant. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms.

The amount of chromium ions adsorbed onto three surfaces (Q) was calculated by using the following expression; [21] as shown in equation (1):

$$Q = \frac{X}{m} = \frac{V(C_o - C}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where:

($\frac{X}{m}$) or (Q) = the adsorption capacity of chromium adsorbed on unit mass of three surfaces: *charcoal*, *attapulgite* and *date palm leaflet powder (pinnae)* (mg/g).

$X =$ the quantity adsorbed (mg)

$V =$ total volume of solution of substance adsorbed (0.01L)

C_o= initial Cr(III) concentration in solution (mg/L)

C = Cr(III) concentration in solution at any time (mg/L)

m = weight of three adsorbent [*charcoal*, *attapulgite* and *date palm leaflet powder (pinnae)*] (0.3000g).

Adsorption reactions have been described using a variety of models such as the Langmuir and Freundlich equations; [22].

Langmuir (1916) derived a simple adsorption isotherm based on theoretical considerations. Langmuir made the following assumptions.

1. The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.
2. The adsorbed layer is uniform all over the adsorbent.

   There is no interaction between the adjacent adsored molecules; [4].

The Langmuir model shows in Equation (2):

$$\frac{x}{m} = Q_e = \frac{abC_e}{1+aC_e} \quad \text{……………………………..…...……………………….. (2)}$$

The a and b are Langmuir constants which correspond to the maximum adsorption capacity (mg/g) of adsorbent and energy of adsorption, respectively. The parameter C_e corresponds to the remaining metal ion concentration in the solution and Q_e refers to the amount of metal ions sorbed per unit weight of adsorbent; [23].

Equation (2) is often rearranged to the liner form to permit easy verification of whether data conform to the Langmuir model as shows in equation (3) :

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{b} \quad \text{…………………………...………………………..……….....….. (3)}$$

If adsorption data conform to the Langmuir equation, a plot of $\frac{C_e}{Q_e}$ versus C_e yields a straight line with a slope $\frac{1}{b}$ and intercept $\frac{1}{ab}$. The Langmuir constant a is obtained by dividing the slope by the intercept $\frac{1}{ab}$.

Freundlich found that adsorption data for many dilute solutions could be fitted to an expression of the form in equation (4) :

$$Q_e = K\, C_e^{\frac{1}{n}} \quad \text{……..……………......................……………………..…..…..…….. (4)}$$

Where K and n are empirical constants and the other terms are as defined previously. The amount was originally empirical, without a theoretical foundation. The linear form of the Freundlich equation is shown in equation (5):

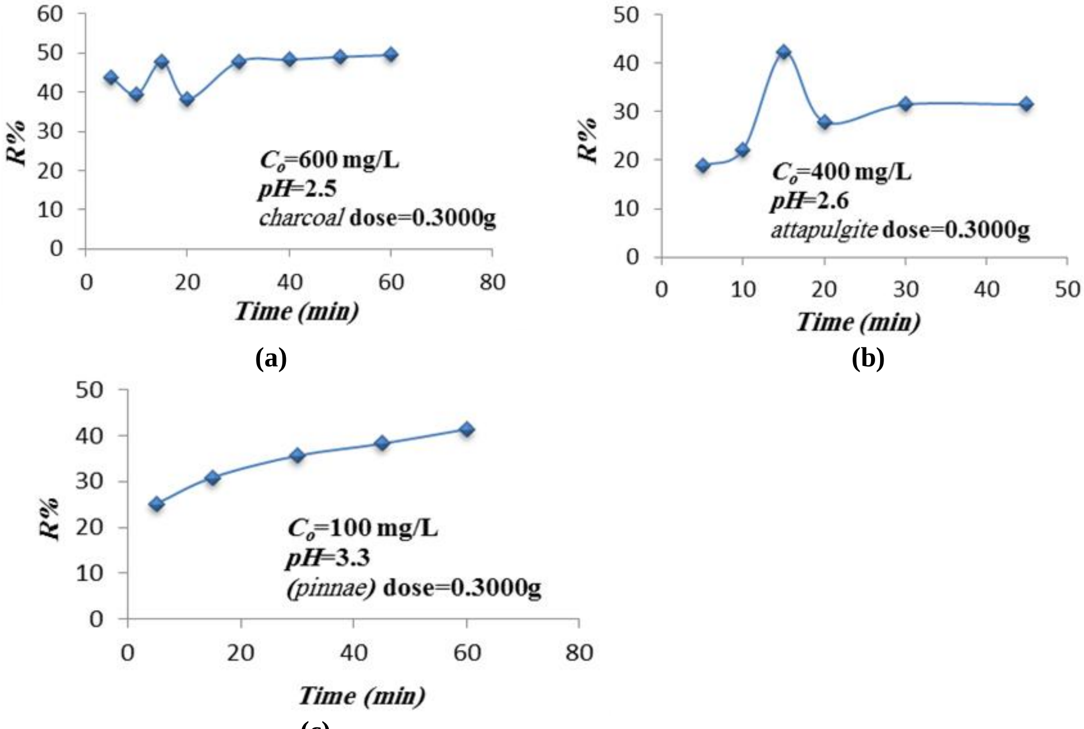
$$\log Q_e = \frac{1}{n} \log C_e + \log k \quad \text{……………………..……..................………… (5)}$$

The constants k and n are also related to the strength of the adsorptive bond and bond distribution, respectively; [24]. It has been shown mathematically that n can be regarded a measure of heterogeneity of adsorption sites [25].

Results & Discussions

Effect of Time on Cr(III) Adsorption Percentage :

The contact time is one of the effective factors in the adsorption process. In this stage, all of adsorbents (*charcoal*, *attapulgite* and *date palm leaflet powder*) and Cr (III) solution (adsorbate) sufficient for the adsorption process to reach equilibrium were studied at different periods (5 to 120 minutes) if other parameters like initial concentration, temperature, were kept constant. Figures 2: (a), (b) and (c) show the variation of adsorption percentage with a contact time and the time required by [Cr(III)~*charcoal*], [Cr(III)~*attapulgite*], and [Cr(III)~*date palm leaflet powder*] systems to attain equilibrium. .



(a) (b)

(c)

Figure 2-Variation of Adsorption Percentage with Time for Cr(III) Ions Removal by: (a) *Charcoal* Surface, (b) *Attapulgite* Surface and (c) *Date Palm Leaflet Powder* Surface at 37.5°C

Chromium(III) removal increases with increasing contact time at 600, 400 and 100mg/L Cr(III) concentrations and approximately 49%, 31.5% and 41% of maximum Cr(III) removed from *charcoal*, *attapulgite* and *date palm leaflet powder* and the time attained about 30, 45 and 60 min respectively. No further increase in adsorption was noticed up to 120 min.

Adsorption Isotherm:

In order to model the adsorption behavior, adsorption isotherms have been studied. The adsorption isotherm (***Q_e*** versus ***C_e***) shows the equilibrium between the concentration of chromium (III) in the aqueous solution and its concentration on the solid (mass of chromium(III) per unit mass of *charcoal*, *attapulgite* and *date palm leaflet powder*. It is evident that adsorption capacity increases with increasing equilibrium chromium (III) concentrations, as showen in figures 3, 4 and 5.

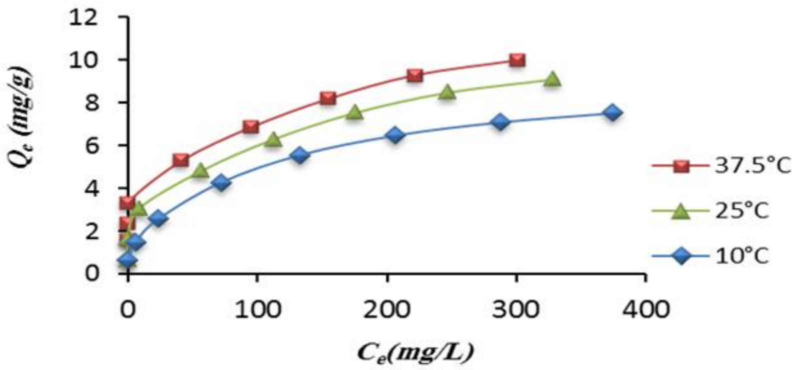


Figure 3-Adsorption Isotherm for Cr(III) Ions Removal on *Charcoal* Surface at different Temperatures

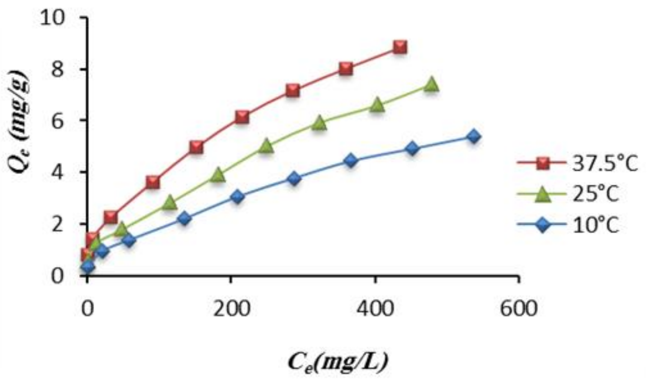


Figure 4-Adsorption Isotherm for Cr(III) Ions Removal on *Attapulgite* Surface at different Temperatures

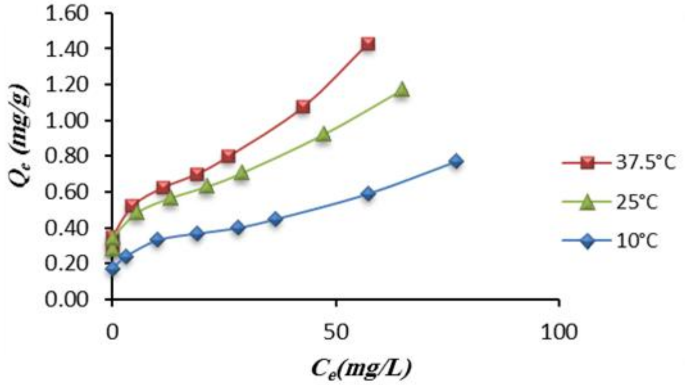


Figure 5-Adsorption Isotherm for Cr(III) Ions Removal on *Date Palm Leaflet Powder* Surface at different Temperatures

Further, the adsorption capacity increased with the rise of temperature. At 10°C, the maximum adsorption capacity of *charcoal*, *attapulgite* and *date palm leaflet powder* was 7.51, 5.39 and 0.77mg/g respectively; and, as the temperature increased to 37.5°C, the maximum amount rose to 9.99, 8.82 and 1.43mg/g respectively. This fact implies that the adsorption on *charcoal*, *attapulgite* and *date palm leaflet powder* for chromium (III) ions is favored at high temperature; [26, 27].

The adsorption of an ionic active site at solid-liquid interface is strongly influenced by charged site on the surface and increasing with an increase in surface area; [4].

Figure 6 shows that the equilibrium adsorption capacity of *charcoal* and *attapulgite* has a maximum value.

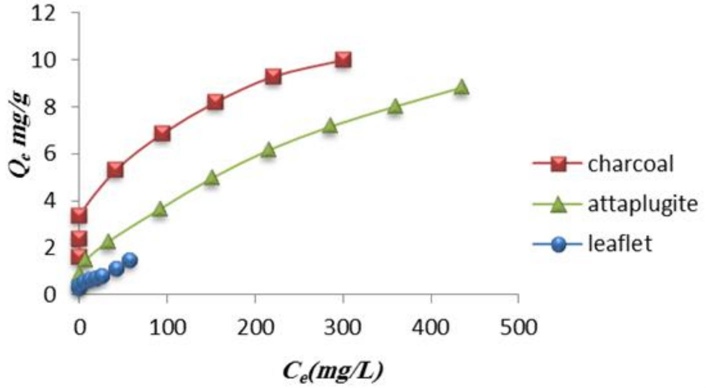


Figure 6-Adsorption Isotherm for Cr(III) Ions Removal by *Charcoal*, *Attapulgite*, and *Date Palm Leaflet Powder* at 37.5°C

Activated carbon adsorption seems to be an attractive choice for chromium removal both for its exceptionally high surface areas and well-developed internal microporosity structure [28]. For this reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewater. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability [29]. The enhancement of adsorption capacity of the commercial activated *charcoal* at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

On the other hand, the extremely large surface area of attapulgite makes it very sorptive in its natural form. Both external and internal structures contribute to this surface area. The internal bundles, or haystacks, aid the external surface area in achieving great amounts of adsorption. Attapulgite can take up water to 200% of its own weight. During calcinations, the haystack structure of the clay becomes very porous. The creation of this porous structure is believed to be more important to sorptive capability than the high surface area of attapulgite [30].

Two models (Frendlish and Langmuir) were used to determine adsorption of chromium on *charcoal*, *attapulgite* and *date palm leaflet powder*. The Frendlish isotherm is better fitted than the Langmuir isotherm with *charcoal*, *attapulgite* and *date palm leaflet powder*, as was evident from the values of correlation of determination (r^2). The results are illustrated of Frendlish and Langmuir equations in figures 7 and 8 which summarized the results in table 1 .

Figures 9 and 10 summarized the results in table 2 ; and figures 11 and 12 summarized the results in table 3. The isotherm constants were calculated from the slope and intercept of these figures and they are presented in tables 1, 2 and 3.

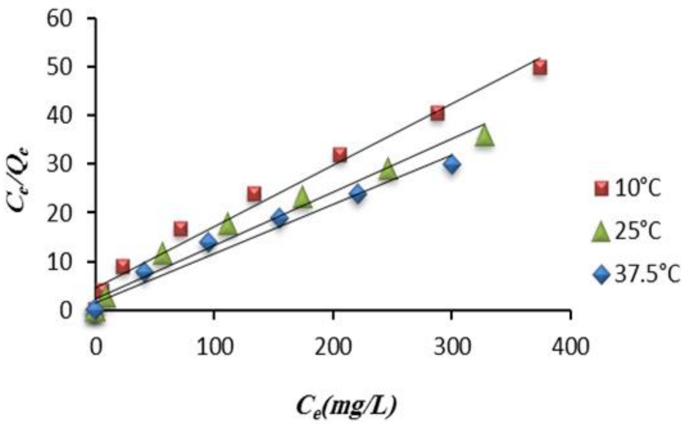


Figure 7-Langmuir Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Charcoal* Surface

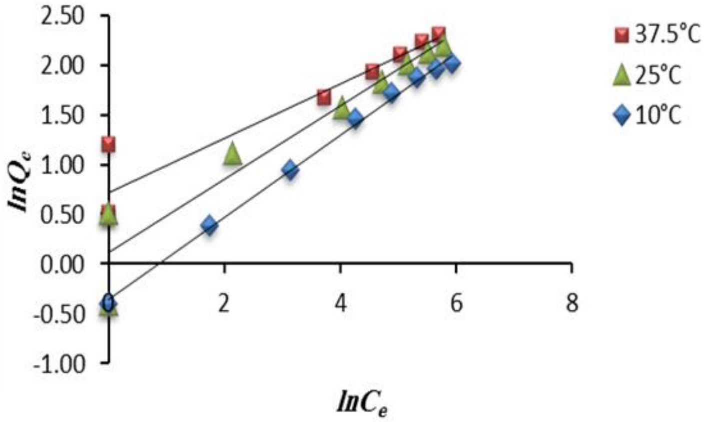


Figure 8-Freundlish Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Charcoal* Surface

Table 1-Langmuir and Frendlish Adsorption Isotherm values on *Charcoal* Surface

Temp. (°C)	**Langmuir Isotherm**			**Frendlish Isotherm**		
	Constants		**Correlation of determination (r^2)**	**Constants**		**Correlation of determination (r^2)**
	b **(L/mg)**	***a*** **(mg/g)**		***n***	***k***	
10	7.9239	0.0274	0.9787	2.4137	0.6967	0.9973
25	9.1241	0.0455	0.9701	2.7152	1.1218	0.9194
37.5	9.8522	0.0680	0.9739	3.6738	2.0565	0.9099

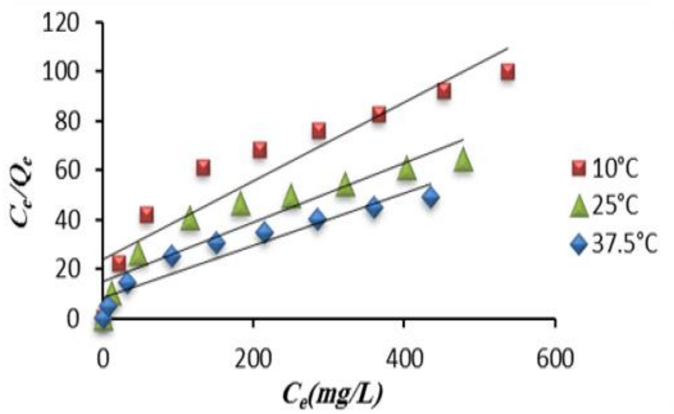


Figure 9-Langmuir Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Attapulgite* Surface

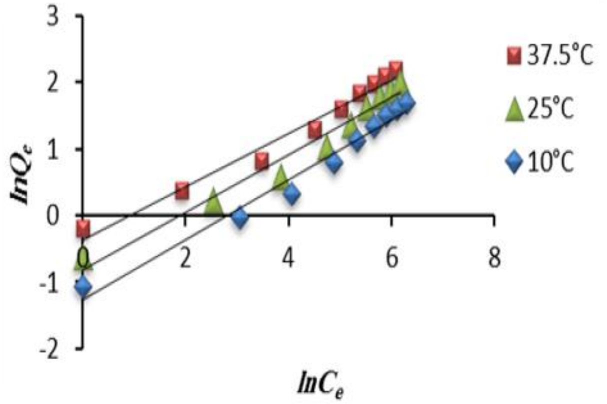


Figure 10-Freundlish Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Attapulgite* Surface

Table 2-Langmuir and Frendlish Adsorption Isotherm values on *Attapulgite* Surface

Temp (°C)	Langmuir Isotherm			Frendlish Isotherm		
	Constants		Correlation of determination (r^2)	Constants		Correlation of determination (r^2)
	b (L/mg)	a (mg/g)		n	k	
10	6.2933	0.0066	0.8646	2.2316	0.2851	0.9739
25	8.3612	0.0078	0.8462	2.3310	0.4458	0.9675
37.5	9.5511	0.0012	0.9070	2.5038	0.6974	0.9769

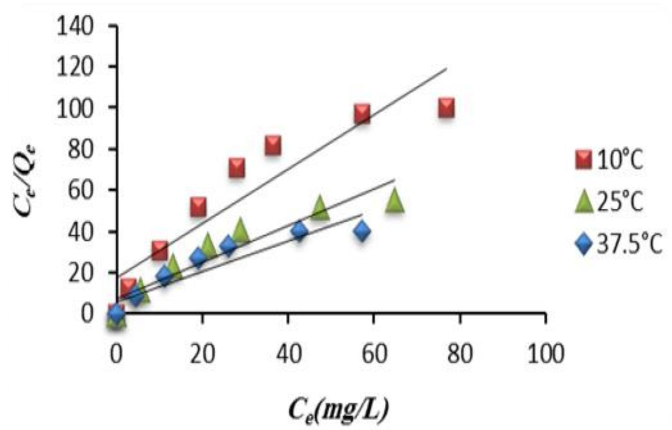


Figure 11-Langmuir Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Date Palm Leaflet Powder* Surface

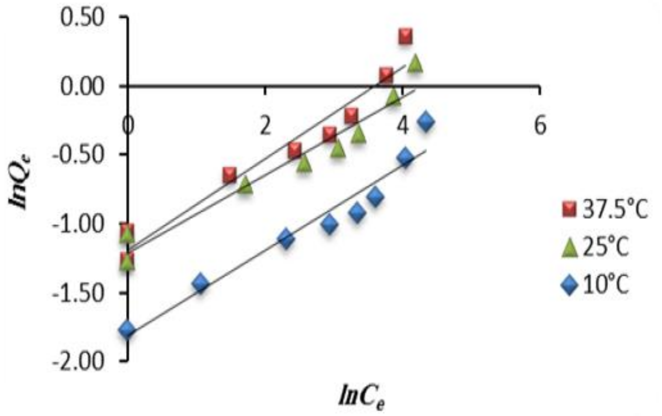


Figure 12-Freundlish Adsorption Isotherm for the Adsorption of Chromium(III) Ions by *Date Palm Leaflet Powder* Surface

Table 3-Langmuir and Frendlish Adsorption Isotherm values on *Date Palm Leaflet Powder* Surface

Temp (°C)	Langmuir Isotherm			Frendlish Isotherm		
	Constants		Correlation of determination (r^2)	Constants		Correlation of determination (r^2)
	b (L/mg)	a (mg/g)		n	k	
10	0.7605	0.0750	0.8675	3.2383	0.1629	0.9454
25	1.1271	0.1276	0.8992	3.5026	0.2959	0.9461
37.5	1.3519	0.1253	0.8644	2.0111	0.3030	0.9485

The values of correlation of determination r^2 obtained were higher in Frendlish isotherm than those in the Langmuir isotherm for *charcoal*, *attapulgite* and *date palm leaflet powder* which indicates that the adsorption process is well represented by the Frendlish equation. This may confirm the heterogeneous nature of the adsorbent surfaces. Linear plots of Frendlish isotherm lnQ_e versus lnC_e shows that the adsorption of chromium(III) ions follows the Frendlish isotherm figures 8, 10 and 12.

The found values of k and n have been given in tables 1, 2 and 3 which show that the increase in negative charges on the adsorbent surfaces *charcoal*, *attapulgite* and *date palm leaflet powder* makes electrostatic force like Vanderwaal's between: *charcoal*, *attapulgite* and *leaflet* powder surfaces and chromium(III) ions. This force increases the adsorption of chromium(III) ions. The higher atomic weight, the large size and radii of the chromium ion have limits the possibility of the adsorption of chromium ion onto adsorbents in higher concentration. However, the values clearly show the dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between chromium ion and adsorbent and of the possibility of slight chemisorptions rather than physisorption of chromium ion. The possibility of multilayer adsorption of chromium ion through the percolation process may be possible. The values of n are greater than the one indicating the adsorption is much more favorable; [31]. The values of $1 < n < 10$ showed favourable adsorption of Cr(III) on three surfaces *charcoal*, *attapulgite* and *date palm leaflet powder* which indicate that the bond energies increase with surface density, and the increase in negative charge on the adsorbent surface, that makes electrostatic force like Vanderwaal's between the surface and chromium ion; [29, 32].

Effect of Temperature:

The effect of temperature on the adsorption extent of chromium(III) on *charcoal*, *attapulgite* and *date palm leaflet powder* surfaces has been studied by varying the temperature in the range 10 to 37.5ºC as shown in tables 4, 5 and 6. Thermodynamic parameters such as change in free energy (ΔG)$\mathrm{kJ.mol^{-1}}$ change in enthalpy (ΔH)$\mathrm{kJ.mol^{-1}}$ and change in entropy (ΔS) $\mathrm{kJ.mol^{-1}.K^{-1}}$ was determined as the following:

The adsorption equilibrium constant, K_{ads} is described thermodynamically by Van't Hoff equation as shown in equation (6):

$$lnK_{ads} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{……………………………………………………..} (6)$$

The adsorption equilibrium constant, (K_{ads})L.g^{-1}, were calculated at different temperatures which is given by the equation (7):

$$K_{ads} = \frac{Qe}{Ce} \quad \text{…………………………………………………………………..} (7)$$

K_{ads} : is the thermodynamic equilibrium constant [33].

The value of the Gibbs free energy (ΔG) of a reaction or free energy change can be calculated by using the equation (8):

$$\Delta G = -RT\ lnK_{ads} \quad \text{……………………………………………………} (8)$$

The effect of temperature on adsorption depends on the enthalpy change [34].

The values of ΔH and ΔS were determined from the slope and intercept of lines respectively. ΔG was calculated from equation (9):

$\Delta G = \Delta H - T\Delta S$…………………………………….........................……..…. (9)

Table 4- Vales of thermodynamic function for the adsorption of Cr(III) ions on Charcoal surface different temperatures (contact time=30min)

C_o (mg/L)	K_{ads} $L.g^{-1}$			- ΔG $kJ.mol^{-1}$			ΔH $kJ.mol^{-1}$	ΔS $kJ.mol^{-1}.K^{-1}$	r^2
	Temperature								
	283.0 K	**298.0 K**	**310.5K**	**283.0 K**	**298.0 K**	**310.5K**			
20	0.000	0.000	0.000	00.00	00.00	0.000	0.0000	0.0000	-
50	0.259	0.000	0.000	34.43	36.25	37.78	0.0372	0.1218	0.8148
100	0.111	0.362	0.000	53.03	55.85	58.19	0.0583	0.1876	0.9988
200	0.060	0.086	0.128	13.45	14.16	14.76	0.0202	0.0476	0.9883
300	0.042	0.056	0.072	7.076	7.452	7.765	0.0146	0.0251	0.9988
400	0.031	0.043	0.053	5.777	6.084	6.340	0.0139	0.0205	0.9983
500	0.025	0.034	0.042	5.513	5.806	6.050	0.0142	0.0195	0.9956
600	0.020	0.028	0.033	4.342	4.573	4.765	0.0135	0.0154	0.9931

Table 5-Values of Thermodynamic Function for the Adsorption of Cr(III) Ions on *Attapulgite* Surface at different Temperatures (contact time=45min)

C_o (mg/L)	K_{ads} $L.g^{-1}$			- ΔG $kJ.mol^{-1}$			ΔH $kJ.mol^{-1}$	ΔS $kJ.mol^{-1}.K^{-1}$	r^2
	Temperature								
	283.0 K	**298.0 K**	**310.5K**	**283.0 K**	**298.0 K**	**310.5K**			
10	0.000	0.000	0.000	0.000	0.000	0.000	0.0000	0.0000	-
50	0.046	0.099	0.210	33.01	34.76	36.22	0.0404	0.1168	0.9956
100	0.024	0.038	0.069	18.96	19.96	20.80	0.0279	0.0671	0.9760
200	0.016	0.024	0.040	13.51	14.23	14.83	0.0233	0.0478	0.9810
300	0.015	0.021	0.033	11.19	11.78	12.28	0.0212	0.0396	0.9874
400	0.013	0.020	0.029	10.34	10.89	11.35	0.0206	0.0366	0.9993
500	0.012	0.018	0.025	8.944	9.419	9.815	0.0194	0.0317	1
600	0.011	0.013	0.022	8.420	8.867	9.240	0.0191	0.0298	1
700	0.010	0.015	0.020	7.964	8.387	8.739	0.0188	0.0282	0.9971

Table 6-Values of Thermodynamic Function for the Adsorption of Cr(III) Ions on *Date Palm Leaflet Powder* Surface at different Temperatures (contact time=60min)

***C_o* (*mg/L*)**	**K_{ads} L.g^{-1}**			**- *ΔG* kJ.mol^{-1}**			***ΔH* kJ.mol^{-1}**	***ΔS* kJ.mol^{-1}.K^{-1}**	***r*^{2}**
	Temperature								
	283.0 K	**298.0 K**	**310.5 K**	**283.0 K**	**298.0 K**	**310.5 K**			
5	0.000	0.000	0.000	0.000	0.000	0.000	0.0000	0.0000	-
10	0.083	0.000	0.000	63.57	66.94	69.75	0.0688	0.2249	0.8148
20	0.033	0.088	0.118	26.88	28.31	29.50	0.0348	0.0951	0.9509
30	0.019	0.043	0.055	19.31	20.34	21.19	0.0285	0.0683	0.9526
40	0.014	0.030	0.037	15.95	16.80	17.51	0.0259	0.0565	0.9495
50	0.012	0.024	0.031	14.55	15.33	15.97	0.0248	0.0515	0.9601
75	0.010	0.019	0.025	13.34	14.05	14.64	0.0241	0.0472	0.9742
100	0.010	0.018	0.025	13.68	14.41	15.02	0.0248	0.0454	0.9927

As depicted in tables 4, 5 and 6 the change in temperature affected the adsorption of chromium(III) on *charcoal*, *attapulgite* and *date palm leaflet powder* surfaces differently. The adsorption of chromium(III) increased with increasing temperature from 283.0 to 310.5K.

The effect of temperature on the adsorption depends on the enthalpy change. The values of ΔH are within the range of 0.069 to 0.013 kJ.mol^{-1} and this indicates the physisorption [31]. Positive values of ΔH, and higher removal capacities at elevated temperatures, indicated that adsorption of chromium(III) was endothermic in nature. At higher temperatures the energy of system seemed to facilitate the chromium(III) attachments onto adsorbent surfaces.

This means that the interaction between sorbents and Cr(III) requires an appreciable energy in order to take place. Endothermic Cr(III) uptake may also be interpreted as a consequence of possible absorption process, in which the ions diffuse inside the crystal lattice of sorbent and the diffusing speed increases with the increasing in temperature. This behavior is attributed to sorption process, which means that absorption process may occur accompanied with adsorption process [35].

The calculated values of K_{ads} presented in the tables 4, 5 and 6 indicate that K_{ads} values decreases with the increase in the concentration of the metal ion and increases with the increase in temperature [36].

The values of ΔG calculated using the K_{ads} were negative for the sorption of chromium ions onto *charcoal*, *attapulgite* and *date palm leaflet powder* surfaces at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the sorption.

The positive value of ΔS reflects the affinity of the *charcoal*, *attapulgite* and *date palm leaflet powder* surfaces for the chromium(III) ions and it suggests some structural changes in adsorbate and sorbent [37]. In addition, the positive value of ΔS shows the increasing randomness at the solid/liquid interface during the sorption of chromium ions on *charcoal*, *attapulgite* and *date palm leaflet powder* surfaces [31].

Conclusions:

The present study of the adsorptive behavior of chromium(III) ions in *charcoal, attapulgite* and *date palm leaflet powder* suspensions demonstrates the following facts :

- Removal of Cr(III) ions from aqueous solution was possible using several abundantly available low-cost adsorbents like *attapulgite* and *date palm leaflet powder* in addition to activated *charcoal*,.
- The equilibrium time for the adsorption of Cr(III) ions on *charcoal*, *attapulgite* and *date palm leaflet powder* was found to be 30, 45 and 60min respectively.
- There are three major factors which determine the adsorption capacity of the various adsorbent systems and the nature of their isotherms: the nature of the cation-Cr(III) interaction, the effect of the saturating cation on the aggregation state of the adsorbent suspension, and the effect of the limited water solubility of Cr(III) ions. There are indications that the bonding mechanism may involve an H bonded water bridge between the Nitrate of Chromium ion and the exchangeable cation.
- The adsorption process of Cr(III) ions is described by Frendlish isotherm and Langmuir isotherm.
- Adsorption of Cr(III) ions on *charcoal*, *attapulgite* and *date palm leaflet powder* yielded a maximum adsorption capacity of 9.99, 8.82 and 1.43mg.g^{-1} at 37.5ºC when the Cr(III) ions concentration was 600, 700 and 100mg/L respectively; that means *charcoal* has the highest value of adsorption capacity.
- The enhancement of adsorption capacity of the *charcoal*, *attapulgite* and *date palm leaflet powder* at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surfaces.
- The values of ***ΔH***, ***ΔS***, and ***ΔG*** results show that the *charcoal*, *attapulgite* and *date palm leaflet powder* employed have a considerable potential as an adsorbent for the removal of chromium(III) ions, and suggest that the adsorption of chromium(III) ions on the three surfaces was occur accompanied with absorption process.

Extensive studies are, however, required to evaluate *date palm leaflet powder* in terms of its competitive adsorption properties and reaction chemistry for situations when other cations and anions are also present in the solution. While there are drawbacks to traditional treatments, there are some benefits that make them widespread and in some cases the preferred alternative. A relatively good treatment is expected for *charcoal* removal in water as well. But the need to import this product from the foreign countries is at a relatively high cost. Yet, it is feasible to make this product in any part of the country using natural product in Iraq.

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