A study of Adsorption of Lead (II) and Chromium (III) ions from Aqueous Solution on local Chaff

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Abstract

In the present study, Chaff was used as an adsorbent for removing Pb(II) and Cr(III) ions from aqueous solutions. The amounts of adsorbed ions were estimated were carried out by using flame atomic absorption spectrophotometer. The effects of initial metal ions concentration, pH, existing salt and temperature were studies.

The adsorption isotherms are of L-curve type according to Giles classification and the experimental data were best fitted to Langmuir and Freundlich isotherm models.

The adsorption phenomenon was examined as a function of temperature (25, 40 and 55^{o}C) and various thermodynamic parameters (ΔH^{o}, ΔS^{o} and ΔG^{o}) have been calculated. The thermodynamic parameters of metal ion-chaff systems indicated the adsorption processes is a non-spontaneous.

The results indicated that the adsorption extent of metal ions onto chaff increased with increasing the pH of solution and it was decreased with increasing ionic strength of solution.

Introduction

Water pollution is serious problem of the environment. The increasing in the use of major 20 heavy metals from over the past few decades has inevitably resulted an increasing flux of metallic substances in natural source of water [1]. The presence of toxic heavy metal ions in industrial wastewater has generated considerable concern in recent years. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries [2]. Among the toxic heavy metal ions which present potential danger to human health are copper, lead, cadmium, chromium and mercury[3]. These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [4]. All lead compounds are considered cumulative poisons. Acute lead poisoning can affect nervous system and gastrointestinal track[5]. Chromium has been considered as one of the top 16th. toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern[6].

A number of methods for the removal of heavy metals from aqueous solutions are available, including a reduction process, ferrous chloride treatment, biological treatment, biosorption and ion exchange followed by chelating resin[7]. Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material, the use of low-cost adsorbents is more suitable. A large number of low-cost adsorbents such as bentonite clay[8,9], mango peel waste[10], wheat bran[11,12], waste of olive-oil production[13], rice husk[14-18], oil palm shell[19], have been treated for heavy metals removal.

The aim of this work in to investigate the capability of locally available chaff for the removal lead and chromium ions from aqueous solution in different conditions of temperature, pH and ionic strength and to calculate the thermodynamic functions at equilibrium conditions.

Materials and Methods

Instruments:

1- Atomic Absorption spectrophotometer, Shimadzu. AA-6300, Japan.

2- Shaker water bath, K&K Scientific, Korea.

3- Centrifuge, CL008, Belgium.

4- Electronic Balance, Sartorius Lab. L420 B, +0.0001g.

5- pH-Meter, HM-73, TDA Electronic Ltd.

6- Vortex, Hook and Tuker, Mst.Ltd., Gallenkamp.

Materials:

Hydrochloric acid and sodium chloride were supplied by Fluka, lead nitrate and chromium nitrate were supplied by BDH. Chaff was obtained from "Al- diwaniyah Grain silo".

Methodology

Chaff in powder forms was washed with excessive amounts of distilled water; several washings were performed to remove dust and soluble materials. The powder was then dried under sunlight and then in an oven at 120^{o}C for a period of 1.5 hour and kept in airtight containers. Chaff surface was ground and sieved to a particle size of 150μm.

Adsorption Isotherm

Solutions of metal ions (10 ml) of known concentrations (50-500ppm) were added to stoppered flasks containing 0.2g of chaff. The flasks were shaken in a thermostatically controlled water bath at a speed of 150 rpm. till equilibrium is attained (60min for Pb(II) and 90 min for Cr(III)). These times are sufficient for the adsorption process to reach equilibrium in each case. After the equilibrium time elapsed, the suspensions were centrifuged at 3000 rpm for 20 min. The clear supernatants were assayed for metal, after appropriate dilution, spectrophotometrically by using Atomic Absorption spectrophotometer. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of metal adsorbed was calculated according to the following equation [20]:-

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \qquad \text{..(1)}$$

Where:

Q_e: sorption capacity (mg/g).

x : the quantity adsorbed (mg).

m : weight of adsorbent (g).

C_o : initial concentration (mg/L).

C_e : equilibrium concentration (mg/ L).

V : volume of solution (L).

Effect of Temperature

Adsorption experiment was repeated in the same manner at different temperatures 25, 40 and 55 ^{o}C to estimate the basic thermodynamic functions of the process.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of metals ions. Hydrochloric acid and sodium hydroxide were used to adjust the pH in the range from 2.7 to 6.8. The pH of the suspensions at the commencement o f the adsorption was measured as well as at the end of experiment using pH-meter.

Effect of Ionic Strength

The effect of the addition (0.1-0.3g) of sodium chloride to solutions containing fixed concentration of metal ions equilibrated with 0.2 g of chaff were investigated under the same experimental conditions described before.

Results and Discussion

The equilibrium uptake for metal ions Pb(II) and Cr(III) onto chaff are shown in Figure (1) as a function of the initial ion concentration at 25°C. Figure (1) shows adsorption capacity (Q_e) versus equilibrium concentration (C_e). An increase in the concentration increased the adsorption capacity.

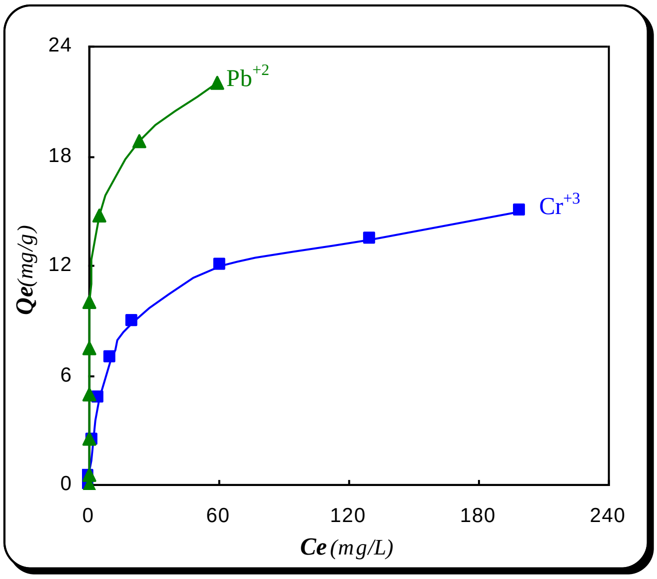

Figure (1) Adsorption isotherms of Metals ions on Chaff at 25°C

The shapes of metal ions isotherms can be considered as L-type according to Giles classification[21]. The L-type indicates that the interaction of sorbate-sorbent is much stronger than solvent-sorbent at the adsorption sites. The cell wall of chaff has carboxyl, hydroxyl and amidogen, which may be responsible for binding metal ions. When biosorption occurs, ion-exchange occurs in the same time, hydrogen ions in these groups were replaced by metal ions[22].

The removal of metals ions can be mathematically expressed in terms of adsorption isotherm. The Langmuir and Freundlich models are the most frequently employed models to describe the experimental data of adsorption isotherms.

The Langmuir isotherm can be expressed as follows[23]:

$$Q_e = \frac{q_m . K_L . C_e}{(1 + K_L . C_e)} \qquad \text{..................... (2)}$$

Where

Q_e: amount adsorbed per unit weight of adsorbent at equilibrium (*mg/g*).

C_e: equilibrium concentration of adsorbate in solution after adsorption (*mg/L*).

q_m (*mg/g*) and K_L (*L/mg*) are the Langmuir isotherm constants.

The Langmuir isotherm constants are evaluated through linearization of Eq.(2).

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + (\frac{1}{q_m}).C_e \qquad \text{.....................} (3)$$

The linear plot of C_e/q_e against C_e shows that the adsorption of two ions onto chaff seems to follow the Langmuir model (Figure (2) and Table (1)).

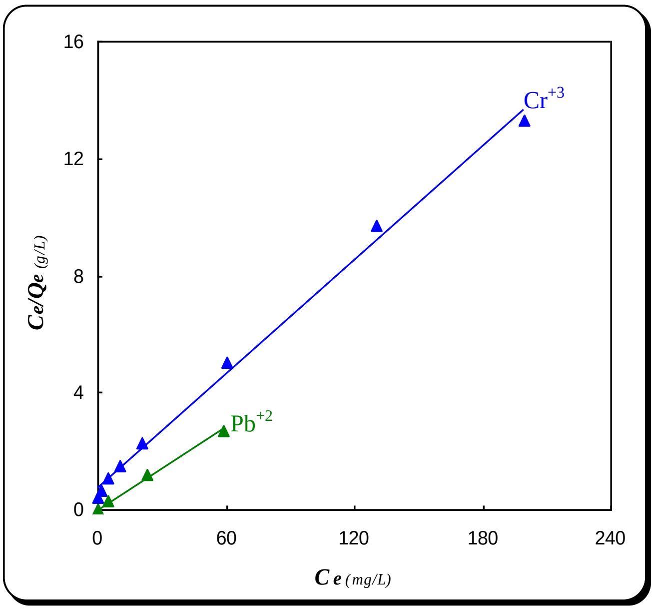

Figure (2) Linearized Langmuir isotherms of Metal ions adsorption onto chaff at 25°C

The Freundlich adsorption isotherm [24] was also applied for the removal of Cr(III) onto chaff.

$$Q_e = kC_e^{1/n} \qquad \text{..} (٤)$$

Where Q_e is the quantity adsorbed in mg/g, C_e is the equilibrium concentration in *mg/L*, *n* and *k* are constants for the given adsorbent and solute.

The applicability of Freundlich isotherm is indicated by using the linear from of Freundlich equation:

$$\log Q_e = \log k + \frac{1}{n}\log C_e \qquad \text{...} (٥)$$

A plot of *log* C_e versus *log* Q_e (Figure (3)) shows that the adsorption of Cr (III) seems to follow the Freundlich isotherm model as well as Langmuir isotherm. The value of Freundlich constants and correlation coefficient are presented in Table (1). The fact that the adsorption of Cr(III) onto chaff seems to follow both the Langmuir and Freundlich isotherm models indicates that a monolayer coverage is formed on the surface of the adsorbent[7]. The magnitude of n (n=2.106) shows favorable adsorption of Cr (III) onto chaff. As indicated from the value of correlation coefficient in Table (1), the adsorption of Pb(II) onto chaff was not follow the Freundlich isotherm.

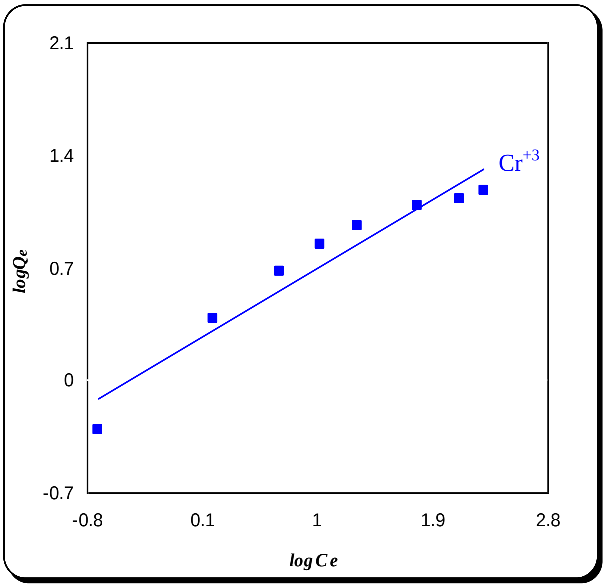

Figure (3) Linearized Freundlich isotherm of chromium ions adsorption onto Chaff at 25°C

Table (1) Freundlich and Langmuir isotherm constants for metals ions uptake by chaff

Metal ion	*Langmuir equation*			*Freundlich equation*		
	K_L	q_o	R^2	K_F	n	R^2
Pb^{+2}	1.563	21.834	0.9953	-	-	0.4389
Cr^{+3}	0.084	15.432	0.9953	0.597	2.106	0.9333

The general shapes of metal ions adsorption isotherms at three different temperatures are given in Figure (4).

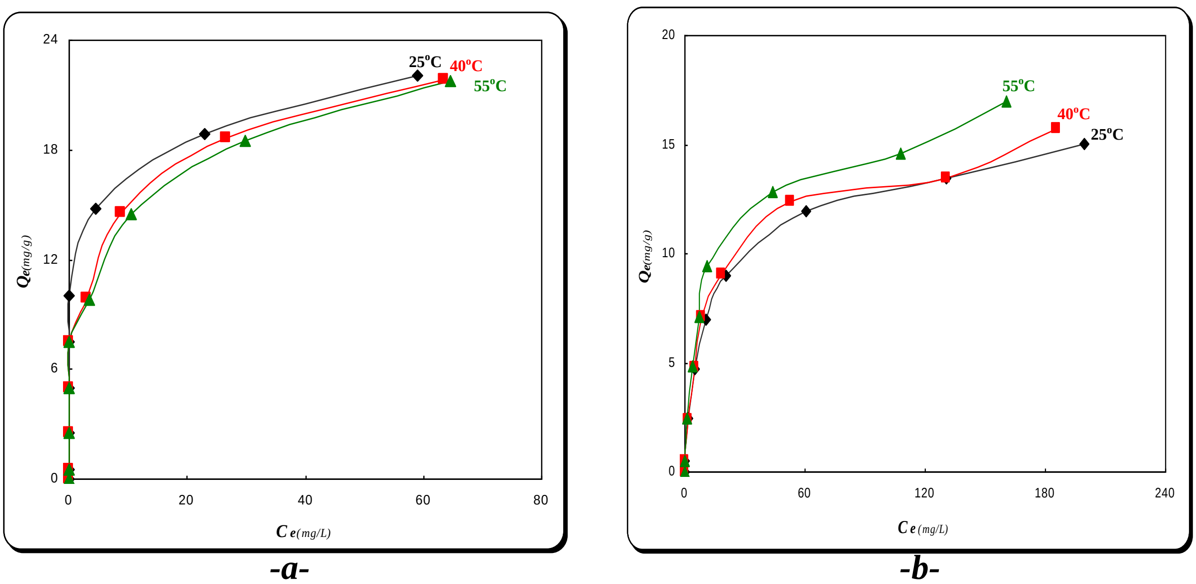

Figure (4) Adsorption isotherms of metal ions: a- Lead Ions b- Chromium ions onto chaff at 25°C

The results showed a decrease in the amount of Pb(II) adsorbed onto chaff with increasing temperature; hence the adsorption process appeared exothermic. Whereas the adsorption extant of Cr(III) onto chaff increase with increasing temperature; this suggests endothermic reaction. Endothermic metal uptake can be attributed to the possibility, that the metal ions are well solvated in aqueous solutions and the adsorption process requires an appreciable energy [25].

The basic thermodynamic quantities of adsorption of metal ions onto chaff were estimated through calculating X_m values at different temperatures. The heat of adsorption (ΔH) may be obtained from Van't Hoff equation: $\ln X_m = \frac{-\Delta H}{RT} + constant$, the change in free energy (ΔG) could be determined from equation ($\Delta G = -RT\ln K$) and the change in entropy (ΔS) was calculated from Gibbs equation: ($\Delta G = \Delta H - T.\Delta S$). Table (2) and Figure (5) demonstrate these calculations [26].

Table (2) Effect of temperature on the maximum adsorbed quantity for adsorption of Metal ions onto chaff

T °C	**T** K	*1000/T K⁻¹*	Pb^{+2}		Cr^{+3}	
			C_e =23		C_e =43.75	
			X_m	$\ln X_m$	Xm	$\ln X_m$
25	298	3.36	18.8	2.936	11.0	2.397
40	313	3.19	18.1	2.898	11.8	2.468
55	328	3.05	17.4	2.856	12.8	2.549

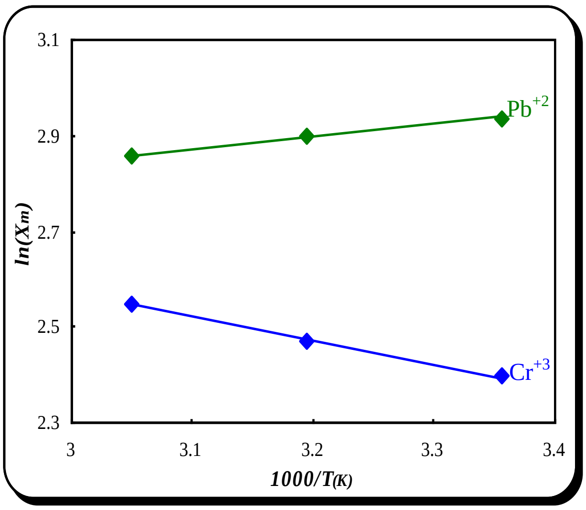

Figure (5) Plot of ln X_m against reciprocal absolute temperature for adsorption of metal ions onto chaff

Table (٣) shows the basic thermodynamic values of adsorption of metal ions on chaff. An adsorption of van der Waals type is suggested to take place as indicated by these values.

Table (3) Values of thermodynamic functions of adsorption process of metal ions on chaff at 25°C

Pb(II)			***Cr(II)***		
ΔH *kJ.mol*$^{-1}$	***ΔS*** *J.mol*$^{-1}$*.k*$^{-1}$	***ΔG*** *kJ.mol*$^{-1}$	***ΔH*** *kJ.mol*$^{-1}$	***ΔS*** *J.mol*$^{-1}$*.k*$^{-1}$	***ΔG*** *kJ.mol*$^{-1}$
-2.164	-6.929	+15.988	+4.097	-4.001	+27.177

The positive value of ΔG^o indicates non-spontaneous process. The negatives value of ΔS^o for adsorption of metal ions, reveal the decrease randomness at the solid-solution interface during the fixation of the ions on the active sites of the adsorbent.

The percentage of ions removal by chaff has been found to be dependent on pH of the solution (Figure (6)), which increased with increase in pH.

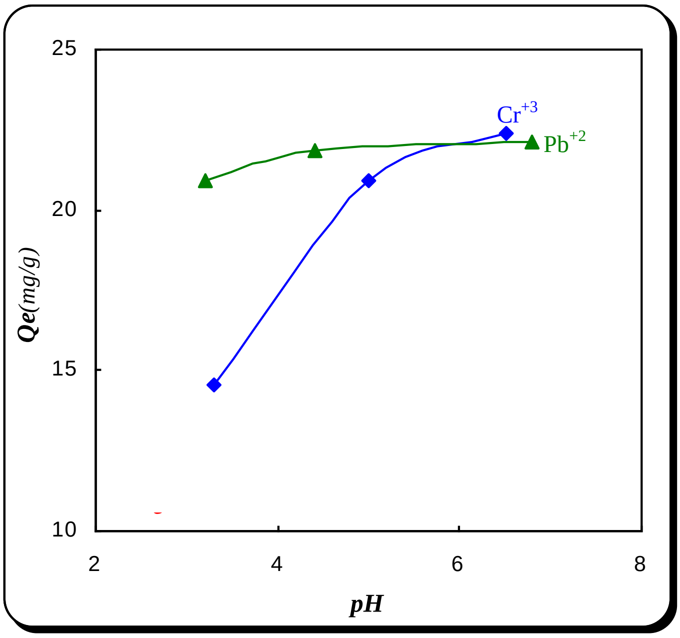

Table (6) Effect o f pH on the adsorption of Metal ions onto Chaff at 25°C

The behaviour of metal ions in aqueous solution is complex in the sense that it may be present as ions of different compositions and show different degree of activity. At low pH the chromium and lead exist as Pb(II) and Cr(III) ions in aqueous solution. Above pH 6.5, the ions start to get hydrolysis resulting in the formation of insoluble metal hydroxides such as $Pb(OH)^+$ and $Cr(OH)^{+2}$ (7,8). In the acidic pH, a high concentration of H^+ ions, resulting in the suppression of ions adsorption on the ion exchangeable sites of chaff and metal ions adsorption decreases(8).

The effect of ionic strength on adsorption uptake of metal ions onto chaff was studied at variable concentration of sodium chloride (Table (4) and Figure (7)).

The adsorption extent of metal ions has decreased in the presence of electrolyte. Competition between the metal ions and the sodium cation of the medium, for site available for metal binding is thought to be the main reason for the observed ionic strength effects. So the adsorption will decrease as a result of the reduced electrostatic attraction between the metal ions and surface of adsorbent [27].

Table (4) Effect o f Sodium chloride on the adsorption of dyes onto Chaff at 25°C

% NaCl (w/v)	Pb^{+2}	Cr^{+3}
	Q_e (mg/g)	Q_e (mg/g)
0.0	21.846	15.027
1.0	15.469	11.125
1.5	14.975	9.989
2.0	14.932	5.795
2.5	14.593	4.420
3.0	14.525	1.072

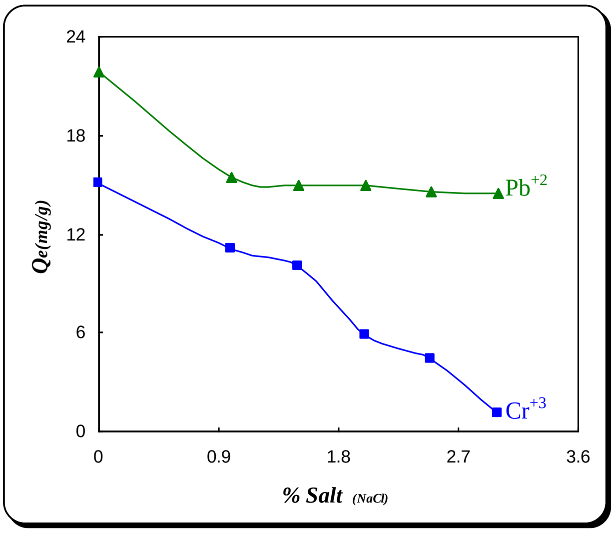

Figure (7) Effect of different concentrations of sodium chloride on the adsorption of metal ions at 25 °C

Conclusions:

On the basis of the experimental results of this investigation, the following conclusions can be drawn:

1- Chaff as adsorbent can be used for the removal Pb(II) and Cr(III) ions from solution.

2- The adsorption capacity of chaff was higher for Pb(II) than Cr(III) ions.

3- Langmuir isotherm model adequately described the adsorption of Pb(II) than Cr(III) ions onto chaff.

4- Thermodynamic studies confirmed that adsorption process of Pb (II) onto chaff was exothermic, while the adsorption of Cr(III) onto chaff was endothermic. The thermodynamic values of ΔG are positive for both systems, indicating a non- spontaneous process.

5- The percentage removal of metal ions was dependent on pH solution and ionic strength of sodium chloride solution.

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دراسة امتزاز ايونات الرصاص(II) والكروم(III) من محلولها المائي على سطح قشور الحنطة

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الخلاصة:

في هذه الدراسة استخدمت قشور الحنطة كسطح ماز لازالة ايونات الرصاص(II) والكروم (III) من محاليلها المائية. وقد تم استخدام تقنية الامتصاص الذري اللهيبي لتقدير الكميات الممتزة، كما درس تاثير تركيز الايون الفلزي ودرجة الحرارة والدالة الحامضية والقوة الايونية لمحلول الامتزاز.

بينت الدراسة ان ايزوثيرمات امتزاز الايونين هي من نوع (L) طبقا لتصنيف Giles وان عملية الامتزاز تتبع ايزو ثيرم لانكماير وفريندلش.

تم دراسة عملية امتزاز الايونين على سطح قشور الحنطة عندة درجات حرارية مختلفة (25^oC, 40 , 55)، كما حسبت الدوال الثرموديناميكية (ΔH^o, ΔS^o , ΔG^o) لعملية الامتزاز. وقد وجد ان عملية امتزاز كلا الايونين على السطح غير تلقائية.

اظهرت النتائج ان كمية ايون الرصاص والكروم الممتزة على هذا السطح تزداد مع زيادة الدالة الحامضية ونقصان القوة الايونية للمحلول.