

Kinetic and thermodynamic study of Cr (II) and Mn (II) adsorption on some commercial adsorbents

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Abstract:

The present work deals with the adsorption of some heavy metal ions such as Cr (II) and Mn (II) on some commercial adsorbents namely commercial activated carbon (CAC) and commercial silica jell (CSJ). The effect of contact time and pH were investigated. The study disclosed that the adsorption capacity was increased with time until the equilibrium was reached, and the pH value =2 was the higher adsorption capacity. The adsorption of metal ions adsorption on the commercial adsorbents (CAs) and was found to follow a pseudo first order kinetics. Also, the thermodynamic functions such as ΔG , ΔH and ΔS were determined. The adsorption of metal ions on the studied adsorbent was found to be spontaneous due to the negative values of ΔG . The adsorption results of heavy metal ions were analyzed to Langmuire model of adsorption and was found fit to it, as well as the adsorption isotherm of heavy metal ions on the studied adsorbents were determined.

Keywords : Heavy metals adsorption; Commercial adsorbents, Adsorption; Kinetic, Thermodynamic.

1- Introduction:

Contamination of water by toxic heavy metals through wastewater discharge by industrial activity is major environmental issues. Rapid industrialization has seriously contributed to the release of toxic heavy metals in the water streams. Mining, electroplating, metal processing, textile and battery manufacturing industry are the main source of heavy metals contamination. Those activities polluted the water streams especially rivers and loss its potential value and beneficial use [1-2].

Heavy metals cannot be metabolized and bio-accumulated in organism body. These toxic metals can move up the biological chain, thereby reaching human being where they produce chronic and acute ailments. Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs. Presence of heavy metals in water streams and marine water causes a significant health threat to the aquatic community – most common being the damage of the gill of the fish [3].

There are many methods that can be used for heavy metals removal from water streams such as chemical precipitation, coagulation, ion-exchanger, sorption, osmosis and electrolysis [4]. Adsorption considers one of the practical processes to remove heavy metals from the waste water. Activated carbon, silica and zeolites are good adsorbents for heavy metals removal from waste water [4-5].

The present work studied the kinetics and thermodynamics of Cr (II) and Mn (II) ions adsorption from aqueous solution on some commercial adsorbents namely CAC and CSJ.

The adsorption of metal ions was found to fit the Langmuire model, also, the adsorption isotherms were found to fit the H-type of adsorption isotherms according to Giles classifications. The kinetic study of metal ions adsorption followed the pseudo first order kinetic, as well as the determination of thermodynamic functions was done.

2- Experimental:

In this study, commercial Activated carbon (CAC) and commercial silica jell (CSJ) were used as adsorbents for metal ions removal. These adsorbents were supplied from BDH and Fluka companies. The adsorbent were

ground at first and allowed to pass through 40 mesh sieve, then they were dried in oven at 110 °C for 5hrs. to remove any adsorbed humidity from atmosphere and then used.

The studied metal ions were Cr(II) and Mn(II). The salts of these metals were dissolved in DW to prepare a known initial solution namely (100 and 500 ppm) for Cr (II) and Mn (II) respectively. The salts were used without any further purification.

The adsorption experiments were conducted via shaking 0.1g of the adsorbent with 50 mL of different concentrations of the used metals using electrical shaker at 150 r/min, for Cr (II) the solution concentrations were from (10-100 ppm) and for Mn (II) from (20-500 ppm) until equilibrium was attained. The adsorbed quantity of metal ions were determined spectrophotometrically at (320 and 530 nm) for Cr and Mn respectively using UV-Visible Shimadzu model 1260 PC. The following equation was used for calculating the adsorbed quantity of metal ions .

$$Q_e = (C_o - C_e)V/W \quad (1)$$

Where Q_e is the adsorbed quantity in mg/g, C_o and C_e are the initial and equilibrium concentrations in mg/L, V is the used volume of solution and W is the weight of adsorbent in g.

There are many studies on the sorption of heavy metals from aqueous solution. Some studies analyzed their results according to Freundlich adsorption isotherm and others followed Langmuire adsorption isotherm. In this study the adsorption results were analyzed according to Langmuire models. The Langmuire model of adsorption can be expressed in the following equation:

$$C_e/Q_e = 1/Q_m K_L + C_e/Q_e \quad (2)$$

Where C_e is the equilibrium concentration in mg/L, Q_e is the adsorbed quantity at equilibrium and K_L is the Langmuire constant.

3- Results and Discussions:

3-1 The effect of contact time:

The effect of adsorption time is an important factor since it shows the optimum time for adsorption to reach equilibrium. The effect of adsorption time on the adsorption of Cr(II) and Mn(II) on CAC and CSJ are depicted in Figures 1 and 2 respectively.

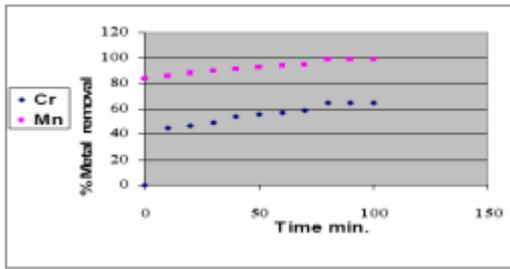


Figure 1: Effect of contact time on Cr (II) and Mn (II) adsorption on CAC at 305 K°

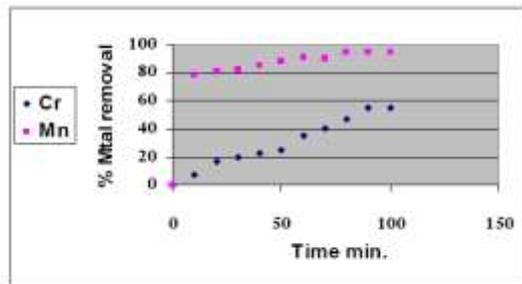


Figure 2: Effect of contact time on Cr (II) and Mn (II) adsorption on CSJ at 305 K°

These Figures showed that the adsorption increase with agitation time and reaches the maximum after 80 minutes in the case of *CAC* and 70 minutes in the case of *CSJ*. The explanation of these figures is that the curve is single, continuous and leading to saturation suggesting the possible monolayer coverage of the metal ions on the adsorbents surfaces.

It can be seen that the uptake of Mn (II) on both adsorbents were higher than Cr (II), this is due to large diameter of Cr (II) as compared to Mn (II) [6]. Also, the uptake of metal ions by *CAC* were higher than those of *CSJ*, this is due to the higher surface area of activated carbon in comparison with *CSJ*.

3-2: Effect of pH.

The adsorption of metal ions from aqueous solution via adsorption is highly dependent on the pH of the solution since it affects the surface charge of the adsorbent and the degree of ionization and the speciation of the adsorbate [7]. The adsorption experiments were conducted in different pH and showed that there was a change in removal % of metal ions when pH varied from 2-8. The effect of pH on the adsorption of Cr (II) and Mn (II) on both adsorbents are shown in Figures 3 and 4 respectively.

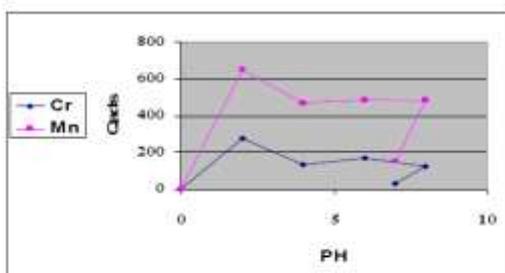


Figure 3: Effect of PH on Cr (II) and Mn (II) adsorption on CAC at 305 K°.

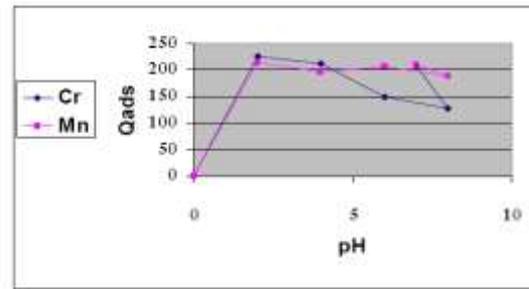


Figure 4: Effect of PH on Cr (II) and Mn (II) adsorption on CSJ at 305 K°.

From Figures 3 and 4 it can be seen clearly that the maximum adsorption was occurred at lower PH value namely (2), this may be due to the presence of large number of H⁺ ions which in turn neutralize the negatively charged adsorbent thereby reducing hindrance to the diffusion of chromate and manganate ions. The decrease at high PH may belong to abundant of OH⁻ ions causing hindrance to diffusion chromate and permanganate ions [8-9].

3-3 : Langmuire Linear isotherms:

Langmuire model of adsorption can be used to describe the distribution of metal ions between the liquid phase and the solid phase. Langmuire model is the most commonly used for liquid phase adsorption [10-14].

This model of adsorption describe the monolayer coverage that could happen on homogeneous surfaces. The linear plot of C_e versus C_e/Q_e gives the Langmuire constants Q_m and K_L . These constants are related to the adsorption capacity and energy of adsorption. The Langmuire linear isotherm of Cr (II) and Mn (II) on *CAC* and *CSJ* are shown in Figures 5 and 6 respectively. The Langmuire constants Q_m and K_L of Cr (II) and Mn (II) adsorption on *CAC* and *CSJ* are presented in Table1.

Table1. Langmuire constants for Cr (II) and Mn (II) adsorption on *CAC* and *CSJ*.

Adsorbent	Metal ion	Q_m	K_L	R^2
<i>CAC</i>	Cr (II)	152	0.02	0.9395
<i>CSJ</i>	Cr (II)	100	0.0003	0.9234
<i>CAC</i>	Mn (II)	417	0.046	0.9992
<i>CSJ</i>	Mn(II)	147	0.00128	0.9141

What can be seen from Table1 that is the maximum adsorption capacity Q_m of Mn (II) adsorption on both *CAC* and *CSJ* was higher than those of Cr(II) adsorption on *CAC* and *CSJ*, this is due to the diameter of metal ion and the ionic charge, both ions have the same ionic charge, but they are differ in diameter, therefore, the smaller the diameter is the higher the adsorption [14-15].

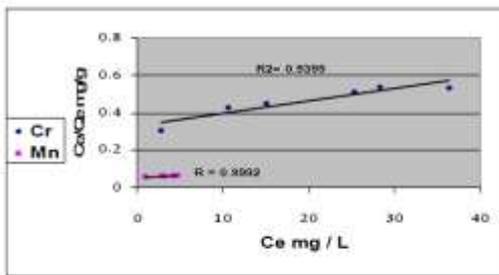


Figure 5: Langmuire linear plots of Cr (II) and Mn (II) on CAC at 305 K°.

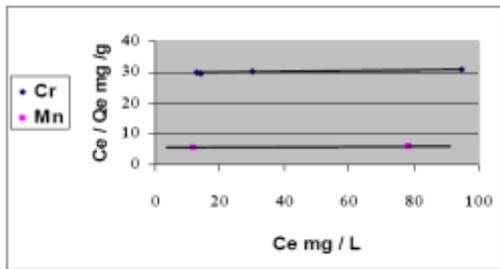


Figure 6: Langmuire linear plots of Cr (II) and Mn (II) on CSJ at 305 K°.

Also, from Table1 it can be seen that Q_m of both Cr(II) and Mn(II) on CAC was higher than those of CSJ, there are two explanations for this, the first one is the surface area of the adsorbent. The surface area of the adsorbents in this study was measured in term of iodine number which gave (1200 and 343 mg/g) for CAC and CSJ respectively.

The second reason belongs to the surface chemistry. It is well known that the surface chemistry plays a great role in the adsorption phenomena. In the case of CAC there are many oxygen surface groups such as acetone ,phenol, carboxyl and hydroxyl ,therefore there are many interactions with the metal ions via Vander walls attractions and other electronic forces since there will be more negative charges on the surface of CAC which in turn increases the adsorption of metal ions, while, in the case of CSJ there is only OH groups on the surface ,therefore there is less interactions with metal ions because the negative charge on CSJ surface is less,also,it seems that the ion-exchange is the dominate mechanism in adsorption [14].

3-4: Adsorption isotherm

The adsorption isotherm is the plot between the equilibrium concentration C_e and the quantity adsorbed on equilibrium Q_e . The adsorption isotherms of Cr(II) and Mn(II) on CAC and CSJ were determined and was found to fit H-type CAC according to Giles classifications of adsorption isotherms. These isotherms are shown in Figures 7 and 8 respectively.

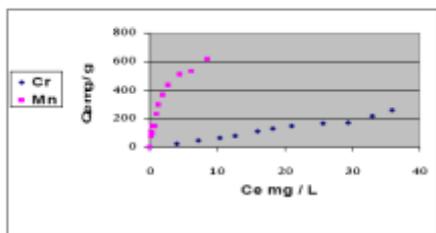


Figure 7: Adsorption isotherms of Cr (II) and Mn (II) on CAC at 305 K°.

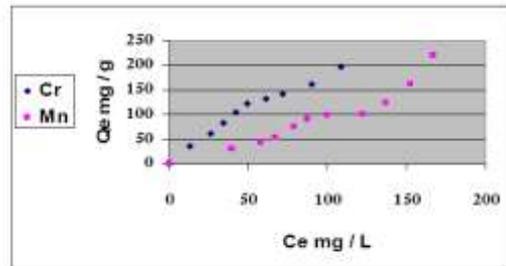


Figure 8: Adsorption isotherms of Cr (II) and Mn (II) on CSJ at 305 K°.

The H-type of adsorption isotherm exhibits a steep increase at low concentration which refers to that there is a good affinity between the solute and the adsorbent, where it shows an increase in the adsorbed quantity until it reaches a steady state and then goes back to increase which means that there are more site accessible for adsorption[11].

3-5: Kinetic and thermodynamic of adsorption:

The kinetic of adsorption describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption.

The kinetic study was achieved via agitating a known quantity of the adsorbent with solution of known concentration of metal ion ,after each ten minutes the concentration was calculated until a constant concentration value was obtained. The adsorption of metal ions from aqueous solution was applied on some kinetic orders as following.

Pseudo first order : $\text{Log} [C_e - C_t] = \text{log} C_e - K / 2.303 . t$ (4)

Pseudo second order : $t / q_t = 1 / K_s q_e^2 + t / q_e$ (5)

Figures 9 and 10 show the pseudo 1st and 2nd order of metal ions adsorption on the used adsorbents, while Figures 11 and 12 show 2nd order kinetic model.

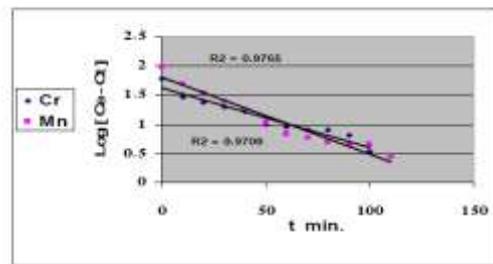


Figure 9. Pseudo 1st order of metal ions adsorption on CAC at 305 K°.

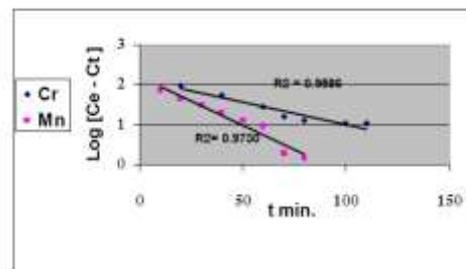


Figure 10. Pseudo 1st order of metal ions adsorption on CSJ at 305 K°.

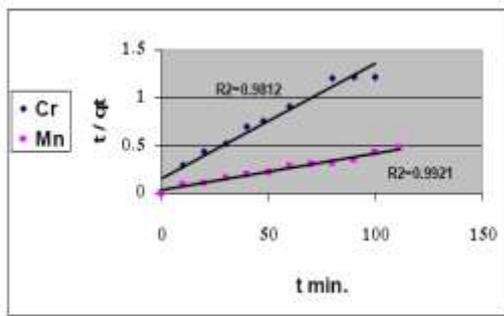


Figure 11. Pseudo 2nd order of metal ions adsorption on CAC at 305 K°.

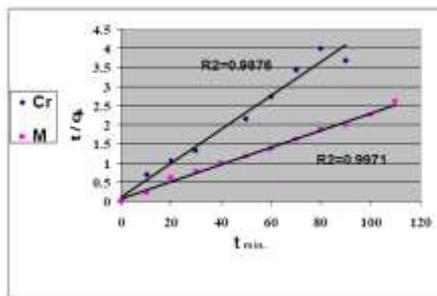


Figure 12: Pseudo 2nd order of metal ions adsorption on CSJ at 305 K°.

The pseudo-first order rate expression, popularly known as the Lagergren equation, is generally described by the following. What can be seen from the above Figures that both model of kinetics have given good straight line of high R^2 but the adsorption of metal ions on both adsorbents was followed pseudo 1st order since they gave higher R^2 values than 2nd order did [16].

The value of K_{ads} was determined according to the following equation [5]:

$$K_0 = C_{solid} / C_{liquid} \quad (6)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), respectively. The values of K_0 are given in table 2. values of metal ions adsorption on the studied adsorbents are presented in Table2.

Table 2. Thermodynamic equilibrium constants of metal ions adsorption on the studied adsorbents.

CAC				CSJ			
K_0 / Cr		K_0 / Mn		K_0 / Cr		K_0 / Mn	
305 K°	314 K°						
1.8	1.2	55	3.75	1.13	1.1	2.23	1.4

The thermodynamic functions of metal ions adsorption on both adsorbents were determined using the following equations:

$$\Delta G = - R T \ln K_{ads} \quad (7)$$

$$\ln K_1 / K_2 = - \Delta H / RT [1 / T_2 - 1 / T_1] \quad (8)$$

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

Where ΔH is the enthalpy change in KJ/mole, ΔG is the free energy change of adsorption in KJ/mole and ΔS is the entropy change in joul/mole. The values of thermodynamic functions of metal ions adsorption on the studied adsorbents are given in Table3.

Table3. Thermodynamic functions of metal ions adsorption on CAC and CSJ.

Cr / CAC				Mn / CAC					
ΔG	ΔH	ΔS		ΔG	ΔH	ΔS			
305 K°	314 K°	305 K°	314 K°	305 K°	314 K°	305 K°	314 K°		
- 1.5	- 0.9	- 0.4	5	3	- 10.16	- 3.5	- 2.6	31	10
Cr / CSJ				Mn / CSJ					
ΔG	ΔH	ΔS		ΔG	ΔH	ΔS			
305 K°	314 K°	305 K°	314 K°	305 K°	314 K°	305 K°	314 K°		
- 3.10	- 0.30	- 0.03	10	1	- 2.03	- 0.80	- 0.5	5	1

What can be seen from Table3 that the values of ΔG were negative which means that the adsorption process is

spontaneous and the adsorption of metal ions is highly favorable[12], while the values of ΔH were negative

which means the exothermic nature of the process and these results are contrary to the data given in the some literatures. This may mean that the energy released during the adsorption is higher than that needed for extracting the solvent molecules from the porous network of the adsorbents [18]. The positive values of ΔS indicates the increment of disorder and randomness at the solid solution interface of the adsorbent [6].

Conclusions:

The study disclosed that adsorption is an effective method for heavy metal ions removal from there aqueous

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solutions. Activated carbon and silica jell were found to be good adsorbents for this purpose for their ability on heavy metal ion removal from aqueous solutions. The results of this study indicated that the adsorption of heavy metal ions from aqueous solution was followed the pseudo 1st order kinetic, and the adsorption process was spontaneous. Also, Langmuire model of adsorption was found to be followed due to the higher R^2 values obtained from Langmuire linear plots which indicated the monolayer coverage of metal ions on the adsorbents surfaces.

الملخص:

الدراسة الحالية تضمنت دراسة امتزاز بعض ايونات المعادن الثقيلة مثل ايونات الكروم الثنائي والمنغنيز الثنائي على سطوح بعض المواد المازة التجارية مثل الفحم المنشط والسليكا جل. زمن الامتزاز وتأثير الدالة الحامضية على امتزاز ايونات المعادن المذكورة قد تم دراستها ووجد ان كمية المادة الممتزة تزداد مع الزيادة في زمن الامتزاز، اما تأثير الدالة الحامضية فلقد وجد بان القيمة التي $= 2$ قد اعطت أعلى سعة امتزازية. ولقد وجد بأن امتزاز أيونات المعادن المذكورة على سطوح المواد المازة المستخدمة يتبع حركية التفاعل من المرتبة الأولى الوهمية نظرا للقيمة العالية لمعامل الارتباط المستحصلة مقارنة بتلك المستحصلة من حركية المرتبة الثانية الوهمية. الدراسة أيضا تضمنت حساب بعض الثوابت الترموديناميكية مثل التغير في الطاقة الحرة والتغير في العشوائية اضافة الى التغير في المحتوى الحراري، ولقد وجد بأن امتزاز هذه اليونات على سطوح المواد المازة المستخدمة كان تلقائيا نظرا لقيم التغير في الطاقة الحرة السالبة. نتائج امتزاز المعادن الثقيلة المدروسة قد تم تحليلها طبقا لنموذج لانكماير للامتزاز ووجدت النتائج انها متطابقة مع هذا النموذج ،ايضا تم تعيين ايزوثرمات الامتزاز لايونات المعادن المذكورة.