



## Thermodynamic Study of Cr<sup>+3</sup> Ions Removal by “MnO<sub>2</sub>/MWCNT” Nanocomposite

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### ABSTRACT

In this research “MnO<sub>2</sub>/MWCNT” nanocomposite was prepared firstly and then it was used as an adsorbent for Cr<sup>+3</sup> ions removal from aqueous solutions. Our results showed that the prepared nanocomposite from modified multi-wall carbon nanotube and MnO<sub>2</sub> has a good capacity for Cr<sup>+3</sup> removal from aqueous solution. Morphology and Crystallinity of the modified MWCNT before and after deposition on MnO<sub>2</sub> were examined by SEM and XRD. In turn, the experimental results were examined according to the Langmuir, Freundlich and Temkin Isotherms and Freundlich isotherm represented our experimental results.

**Key words:** Adsorption; Adsorbent; Isotherm; MnO<sub>2</sub>/MWCNT.

### INTRODUCTION

Main reason causes environmental problems are toxic metal ions. Chromium is one of the most hazardous heavy metals<sup>1</sup>. It affects on human health, some problems that caused by chromium (III) are as follow; lung cancer, kidney and liver damage, skin rashes and also it affects human physiology<sup>2</sup>. Although chromium (III) has use in so many industries like leather tanning, paints, glass manufacture and etc<sup>3</sup>. But the most significant point about chromium (III) is, it can be oxidized to Chromium (VI) that cause serious health

risks<sup>4,5</sup>. Also admissible amount of chromium (III) in wastewater is 5mg/l<sup>6</sup>. So the elimination of chromium (III) from wastewater actuate tremendous attempt. There are prevalent methods for chromium (III) removal from the industrial wastewater consist of coagulation<sup>7</sup> and adsorption<sup>8</sup>, but among these physicochemical<sup>9</sup> wastewater treatment; adsorption is a promising way for water reuse requirements. There are divers materials used as adsorbents but activated carbon is the most effective adsorbent for this application<sup>10</sup>. The amount of Chromium is very rarely in environmental water samples, so very sensitive techniques are used for the determination

of chromium in water samples such as flame atomic absorption spectrometry (FAAS)<sup>11</sup>, inductively coupled plasma-atomic emission spectrometry (ICP-AES)<sup>12</sup>, graphite furnace atomic absorption spectrometry (GFAAS)<sup>13</sup> and inductively coupled plasma-mass spectrometry (ICP-MS)<sup>14</sup>. The purpose of this research is to extend advantages over other wastewater purification processes and characterizing major factors.

## MATERIALS AND METHODS

Multi-wall carbon nanotube (MWCNT, Outer diameter: 8-15 nm, Length: 50  $\mu\text{m}$ ) were purchased from Neutrino, the initial solution and after adsorption were analyzed by Perkin Elmer Analyst 200, and pH

meter (ABTGP353). A stock solution was prepared by dissolving 0.256 g  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 50 cc distilled water. The pH values of the solution were adjusted to the desired values with either 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. All chemicals were of analytical grade (AR) provided from Merck.

### Preparation of $\text{MnO}_2/\text{MWCNT}$ nanocomposite

The preparation process for the  $\text{MnO}_2/\text{MWCNT}$  nanocomposite was a co-precipitation method that before described by Zheng *et al.*<sup>5</sup>.

We synthesis  $\text{MnO}_2/\text{MWCNT}$  nanocomposite. First of all we modify pure MWCNT by dispersing MWCNT in  $\text{HNO}_3$  65 wt% for 24 h under stirring then rinsed with deionized water and dried in the air

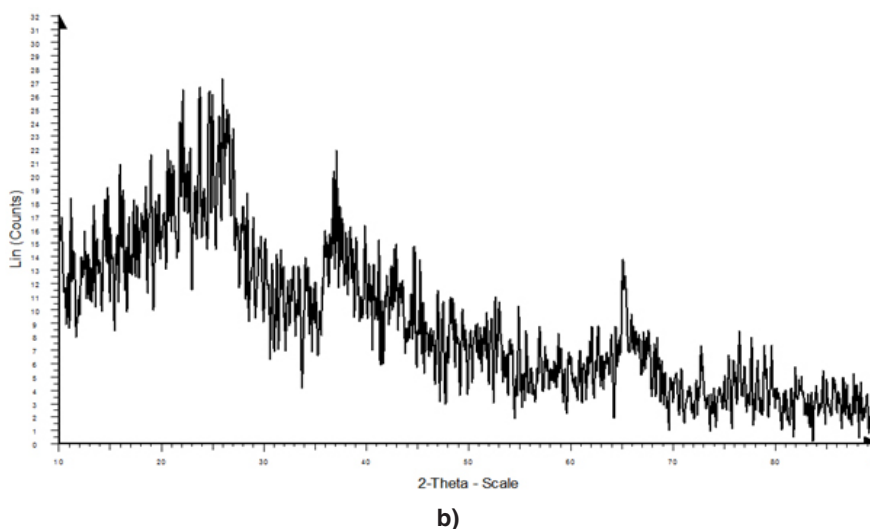
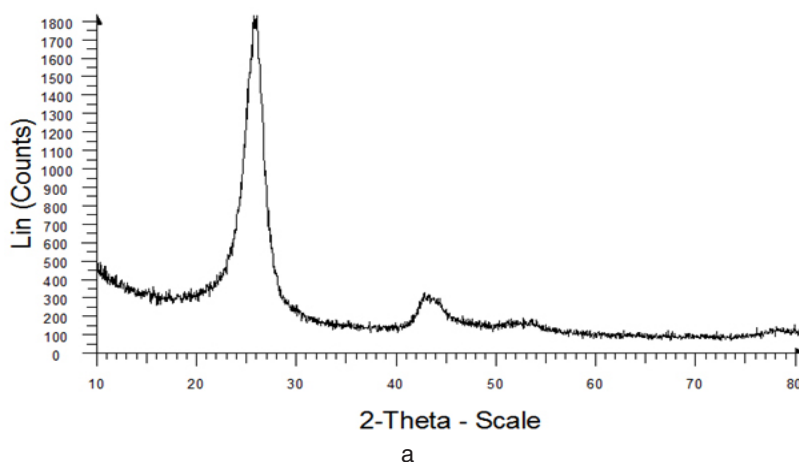


Fig. 1: XRD patterns of (a) activated MWCNT, (b)  $\text{MnO}_2/\text{MWCNT}$  nanocomposites

at 100° C<sup>16</sup>. Afterwards, about 0.1 g of the treated MWCNT was dispersed into 160 ml of 0.1M KMnO<sub>4</sub> solution under vigorous stirring at 40 °C for 2 h and 20 ml MnSO<sub>4</sub> (0.5 M) solution was added dropwise on the above suspension with intensive stirring and then the reaction mixture was kept at 40 °C for 24 h. Then the suspension was filtered washed several times with deionized water and alcohol, and the precipitation were collected and dried in an oven under 100 °C about 12 h.

#### Characterization of the treated MWCNT and MnO<sub>2</sub>/MWCNT nanocomposite

In order to determine crystallization and

surface morphology, we used XRD diffraction and SEM techniques.

It can be describe the XRD patterns of the treated MWCNT and the synthesized nanocomposite show the obvious peaks that refer to the formation of nano MnO<sub>2</sub> onto MWCNT. The treated MWCNT shows a sharp peak at around 26° and a broad weak peaks at around 43° and 53° (Fig. 1a), which can be well assigned to the (0 0 2), (1 0 0) and (0 0 4) planes of graphite carbon<sup>17</sup>. Fig. 1b showed the two typical broadening patterns of the MnO<sub>2</sub>/MWCNT samples of 2° at around 65.5 that can be ascribed the crystal planes of (0 2 0) in β-MnO<sub>2</sub><sup>18,19</sup>. And it is obvious after

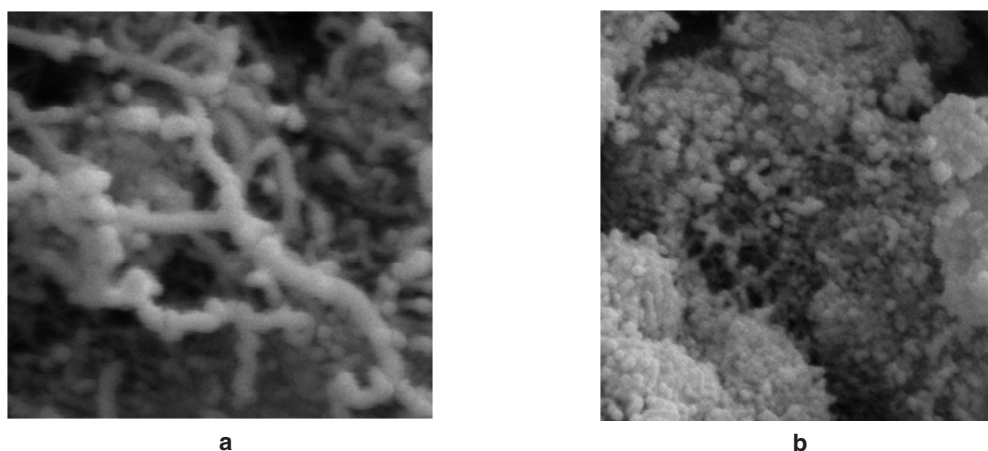


Fig. 2: SEM photographs of (a) activated MWCNT and (b) MnO<sub>2</sub>/MWCNT nanocomposite

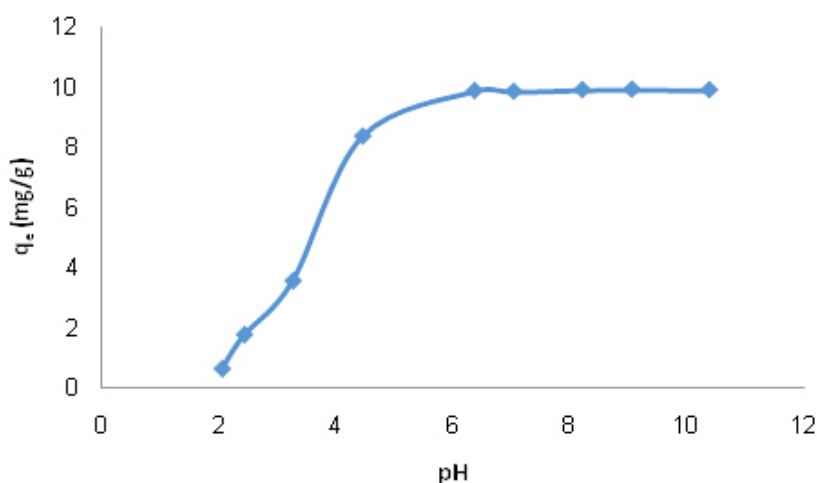


Fig. 3: Effect of pH on Cr (III) adsorption onto MnO<sub>2</sub>/MWCNT nanocomposite (adsorbent: 0.01 g/10 cc, initial Cr(III) conc.: 10 mg/L, temp.: 25°C, contact time: 40 min)

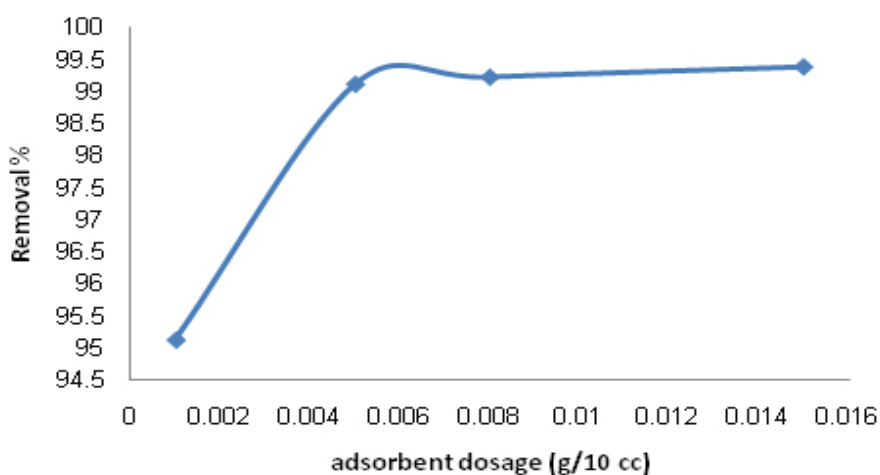
deposition of  $\text{MnO}_2$ , all surface of treated MWCNT completely covered by the nanoflakes of  $\text{MnO}_2$  (Fig. 2) The deposited  $\text{MnO}_2$  onto treated MWCNT exhibits a core-shell structure composed of many nanoflakes with a highly porous structure<sup>15,20</sup>

The adsorbed amount of chromium (III) onto the  $\text{MnO}_2/\text{MWCNT}$  nanocomposite were calculated by the following equations<sup>21,22</sup>:

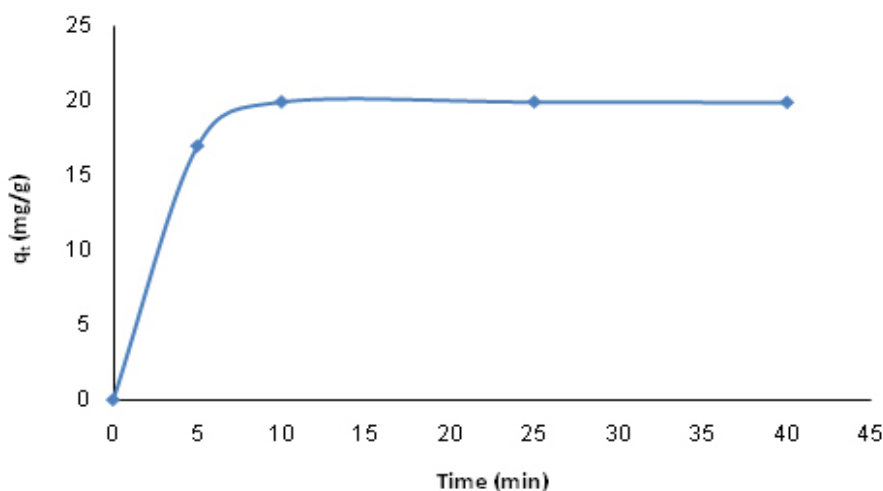
$$q_t = \frac{(C_0 - C_t) V}{M} \quad \dots(1)$$

$$q_e = \frac{(C_0 - C_e) V}{M} \quad \dots(2)$$

Where  $C_0$  is the initial concentration (mg/L),  $C_t$  is the amount of concentration (mg/L) at any time  $t$  and  $C_e$  the amount of concentration (mg/L) in equilibrium,  $V$  is solution volume (L); and  $M$  is  $\text{MnO}_2/\text{MWCNT}$  nanocomposite mass (g).



**Fig. 4: Effect of MnO<sub>2</sub>/MWCNT nanocomposit on Cr(III) adsorption (pH: 5, initial Cr(III) conc.: 10 mg/L, temp.: 25°C, contact time: 40 min)**



**Fig. 5: Effect of contact time on Cr(III) adsorption onto MnO<sub>2</sub>/MWCNT nanocomposite (adsorbent dose: 0.005 g/10 cc, pH: 5, initial Cr(III) conc.: 10 mg/L, temp.: 25°C).**

## RESULTS AND DISCUSSIONS

### pH optimization

In this research, the pH of solution influences the distribution of active sites on the surface of MnO<sub>2</sub>/MWCNT, to find out the effects of solution pH on adsorption capacity; Cr(III) adsorption was examined by adding different amounts of 0.1 M HCl or 0.1 M NaOH to obtain different pHs. In Fig. 3, it can be described that the amount of Cr(III) adsorbed on MnO<sub>2</sub>/MWCNT increased by increasing pH at 5, so we carry out the rest of experiment in this condition.

### Dose of adsorbent

In the next step, we identify the best adsorbent dosage, as we declare the less amount of adsorbent is also much profitable. Then we were measuring this parameter in 5 different dosage. We choose the adsorbent doses in 0.001g, 0.005 g, 0.008 g, 0.01 g, 0.015 g and we realize in a very low amount of adsorbent can reach to high level of removal too. Therefore we continue the rest of the reaction by using about 0.005 g of adsorbent. These results indicate that MnO<sub>2</sub>/MWCNT nanocomposite is promising candidate as highly effective adsorbent (Fig. 4).

### Contact time

To demonstrate the optimum contact time 0.005 g of MnO<sub>2</sub>/MWCNT nanocomposite was

added to 10 ml of Cr(III) solution with concentration of 10 mg/L at 25 °C. the pH of solution was 5 and we carried out this parameter in four different period time, samples were taken in 10 min, 25 min, 40 min (Fig. 5). So we find out even at the initial period contact time, the removal of Cr(III) was very fast, but by increasing contact time we reach to the much more removal of Cr(III).

### Effect of temperature

To identify the effect of temperature, 0.005 g of MnO<sub>2</sub>/MWCNT nanocomposite was added to 10 ml of Cr(III) solution with concentration of 10 mg/L at PH 5 and the experiments were carried out at temperatures of 35, 45, 55 °C. according to our investigations, the adsorbent amount of Cr(III) on MnO<sub>2</sub>/MWCNT nanocomposite decreases with the increasing temperature. Fig. 6 shows the effect of temperature on removal of Cr(III).

### Influence of initial ion concentration on Cr(III) adsorption

The initial ion concentration provide significant driving force in adsorption process, it can noted that the adsorption percent of Cr(III) decrease by increasing chromium concentration (Fig. 7, Fig. 8). We carried out our experiment in 10 to 50 mg/L.

### Adsorption isotherm study

In order to investigate the mechanism of Cr(III) adsorption on adsorbent and for declaring the

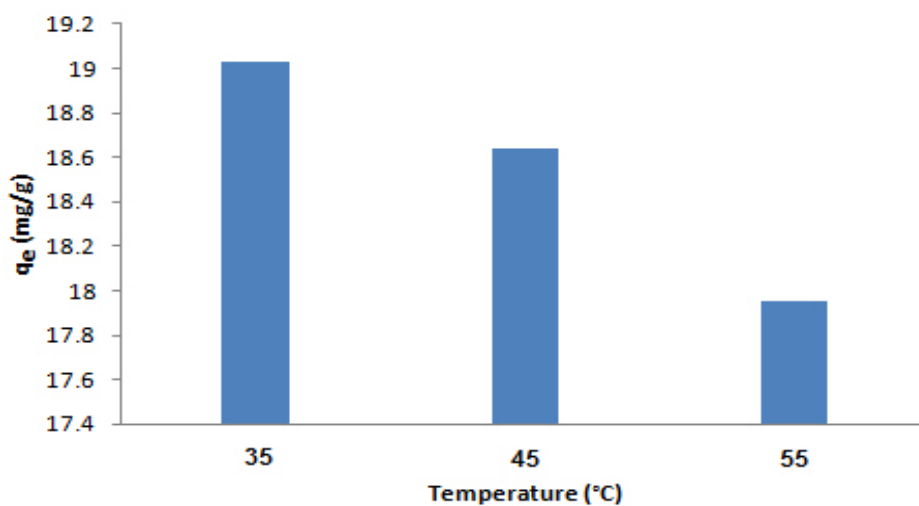


Fig. 6: Effect of temperature on contact Cr(III) adsorption onto MnO<sub>2</sub>/MWCNT nanocomposite (adsorbent dose: 0.005 g/10 cc, pH: 5, initial Cr(III) conc.: 10 mg/L, contact time: 40 min).

chemical equilibrium between Cr(III) and adsorbent, Langmuir and Freundlich and also Temkin isotherms were studied to describe equilibrium. Adsorption isotherm studies were carried out with various initial Cr(III) concentrations ranging from 10 to 50 mg/L.

The linearized form of Langmuir adsorption isotherm equation is as follow:

$$\frac{1}{q_e} = \left( \frac{1}{K_L q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$$

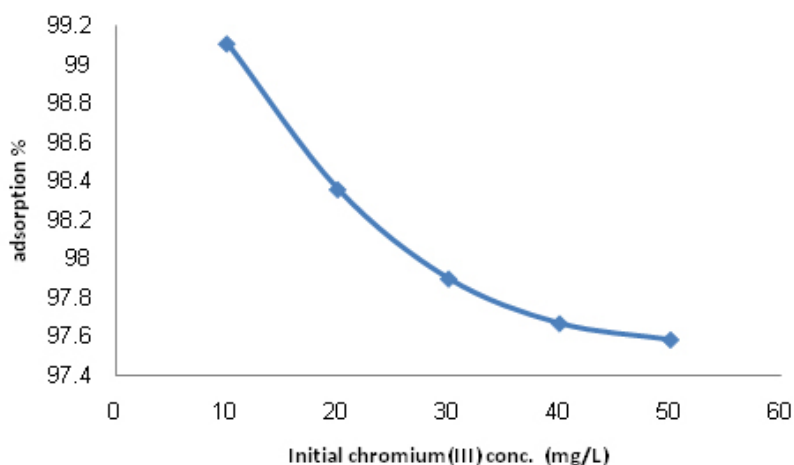
OR

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \dots(3)$$

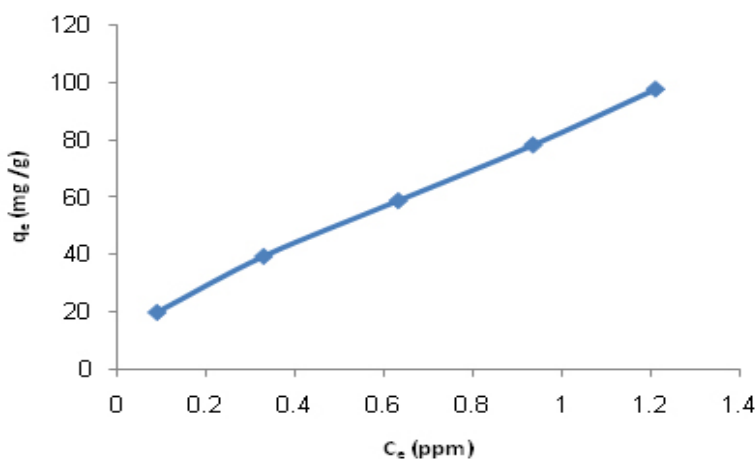
The linearized form of Freundlich adsorption isotherm equation:

$$\ln q_e = \left( \frac{1}{n} \right) \ln C_e + \ln K_F \quad \dots(4)$$

The linearized form of Temkin adsorption isotherm equation:



**Fig. 7: Effect of Cr(III) initial conc. On its adsorption onto MnO<sub>2</sub>/MWCNT nanocomposite (adsorbent dose: 0.005 g/10 cc, pH: 5, temp.: 25 °C, contact time: 40 min).**



**Fig. 8: Effect of Cr(III) initial conc. On its adsorption onto MnO<sub>2</sub>/MWCNT nanocomposite (adsorbent dose: 0.005 g/10 cc, pH: 5, temp.: 25 °C, contact time: 40 min).**

$$q_e = B_1 \ln C_e + B_1 \ln K_T \quad \dots(5)$$

Where  $C_e$  (mg/L) is the equilibrium concentration of Cr(III),  $q_e$  (mg/L) is the amount of Cr(III) adsorbed at equilibrium,  $q_m$  (mg/g) is the maximum adsorption at monolayer and  $K_L$  (L/mg) is the Langmuir constant including the affinity of binding sites.  $K_F[(\text{mg/g})(\text{L/mg})^{1/n}]$  and  $n$  are Freundlich constants indicating adsorption capacity and intensity, respectively.

$K_T$  (L/g) and  $B_1$  are the Temkin constants ( $K_T$  is the equilibrium binding constant and  $B_1$  is related to the heat of adsorption). The amounts of Langmuir, Freundlich and Temkin parameters were calculated from the slope and intercept of linear plots of  $1/q_e$  versus  $1/C_e$ ,  $\ln q_e$  versus  $\ln C_e$  and  $q_e$  versus  $\ln C_e$ , respectively<sup>23,24,25</sup>. Further we display the adsorption isotherms plots (Fig. 9).

It can be concluded from isotherm plots that the reaction process is much more compatible by Freundlich isotherm than others. The isotherm constants also listed in table 1.

In this work, also the thermodynamic parameters were calculated to evaluate the nature of adsorption process<sup>26,27</sup>. Thermodynamic parameters such as Gibbs free energy change ( $\Delta G^\circ$ , KJ/mol), enthalpy change ( $\Delta H^\circ$ , KJ/mol) and entropy change ( $\Delta S^\circ$ , J/mol.k) can be estimated as following:

$$K_c = \frac{C_0 - C_e}{C_e} \quad \dots(6)$$

$$\Delta G^\circ = -RT \ln K_c \quad \dots(7)$$

$$\ln K_c = -\left(\frac{\Delta H^\circ}{RT}\right) + \frac{\Delta S^\circ}{R} \quad \dots(8)$$

Where  $K_c$  is the equilibrium constant of the adsorption process,  $C_0$  and  $C_e$  are the initial and equilibrium concentration of Cr(III). In table 2 we also demonstrate thermodynamic parameters.

We can conclude this reaction is exothermic and spontaneous because Cr(III) adsorption decrease by increasing temperature. The value of " $S^\circ$  (J/mol K) indicates Cr(III) molecules reach to the arrangement in this adsorption.

## CONCLUSION

In this work we investigated the optimization conditions for removal of Cr(III) ions by  $\text{MnO}_2/\text{MWCNT}$  nanocomposite that we reach to a fairly good results. We investigated the adsorption in a wide range of pH to identify the best range. So we found that the pH = 5 is better. Therefore we did our measurements in this pH. We also investigated the best dosage of adsorbent, contact time, and also various concentrations have been studied. In lower concentration we got better results, and then we estimated thermodynamic parameters. As we found the studied adsorption was exothermic and spontaneously. Also we compare our experimental results with our calculation results. We concluded, the our results are better comparable with Freundlich isotherm.

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