

Efficient of Adsorption and Desorption of Zinc Ion by using Multi-Walled Carbon Nanotube

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Abstract: In the present work was used functionalized multi walled Carbon nanotube (fMWCNTs) as an adsorbent for zinc ion (Zn^{2+}) in the batch of adsorption and desorption systems. The characterization of multi-walled Carbon nanotube (MWCNTs-COOH) was performed by X-Ray diffraction (XRD) and Raman spectroscopy. Here, zinc sulphate ($ZnSO_4 \cdot 7H_2O$) was used as sources of zinc ion at different concentrations (0, 10, 20, 30, 40 and 50 mg/l) in adsorption batch and used the diethylene triamine pentaacetic acid (DTPA) as the elution reagent to extracted adsorbed of Zn^{2+} in desorption experiments. In this study, the different parameters such as pH of adsorbate, contact time, adsorbent (FMWCNTs) dosage, agitation speed and temperature were fixed at 7, 12 h, 0.05 gm, 180 rpm, and 25 °C, respectively. The results show that the maximum adsorption efficiency of Zn^{2+} onto MWCNTs increases with the increase of concentration until 40 (mg/l) and then decreased was started. While, the maximum desorption capacity (84%) at low concentration (10 mg/l). According to the correlation coefficient values (R^2) of the equilibrium isotherm models the adsorption data was a better fitted in Freundlich isotherm compared with Langmuir isotherm.

Keywords: Adsorption, Desorption, Mwcnts, Zn^{2+} , Freundlich and Langmuir Isotherm.

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I. INTRODUCTION

The environmental pollution with some heavy metals such as cadmium, copper, lead, and zinc is an undesirable change in the properties of air, water, and soil. The unwanted change in the environment it may cause a harmful for living organisms both animal and plants (Ansari et al., 2012). In general, the heavy metals are present in trace amounts in the environment and many of them are toxic even at very low concentration. Recently, increasing of pollution in environmental resources due to discharging of industries waste containing heavy metals it is a big problem worldwide.

Zinc (Zn^{2+}) is one of most important of heavy metals that was characterized by slow mineralization process and the extensive potential for pollution (Alloway, 2013; Ansari et al., 2012). On another hand, Zinc element is a necessary for the plant's growth in form of minor quantities as an essential micronutrient (Alloway 2008b). Moreover, it is considered that zinc has a major role in the many functions of metabolism (Hansch and Mendel, 2009).

Thus, the removal and/or reducing the toxicity by limiting his availability in the environment it's needed more modern technique and effective treatment methods.

Adsorption-desorption technique has been outperforming compared with other methods (Kuo, 2008).

In recent years, Carbon nanotubes (CNTs) have studied as new adsorbents materials, due to their unique properties such as large surface area and high reactivity (Ansari et al., 2012). CNTs demonstrated alternative applications to remove organic and inorganic contaminants and trace pollutants such as lead, cadmium, fluoride (Kosa et al. 2012; Abdel Salam et al. 2011). However, up to now, research studies on the adsorption of heavy metals with CNTs is still needed. In this work, we investigated the adsorption and re-desorption efficiency of zinc onto functionalized multi-walled carbon nanotubes (F-MWCNTs). For this purpose, we used Langmuir and Freundlich Isotherm models. In addition, the structures and the surface morphology of the F-MWCNTs and Zn^{2+} have been analysed using, X-Ray diffraction (XRD) and Raman spectroscopy measurements.

II. MATERIALS AND METHODS

➤ Multi-Walled Carbon Nanotubes (fMWCNTs)

Functionalized MWCNTs with carboxylic groups were purchased from Nanografi Co. Ltd., (Turkey) with outside and inside diameters are 10–20 nm and 5–10 nm,

respectively, (5-10 nm) in length, and >95% purity, with content (2.2 wt %) of carboxylic (COOH) groups will be used as adsorbent.

➤ *Preparing the Stock Solution of Zn²⁺*

For the study adsorption process, firstly a stock solution of Zn²⁺ (1000 mg/l) was prepared by dissolving 4.43 gm of zinc sulphate (ZnSO₄·7H₂O) in deionized water and completed the volume to 1000 ml. This stock solution was then diluted with deionized water to specified concentrations. The pH of the stock solution was adjusted by the addition of a small amount of 0.1 M HCl or 0.1 M NaOH solutions.

➤ *Adsorption Experiments*

Batch adsorption experiments were conducted by using a 50 mL plastic bottles containing 0.05 g of the adsorbent (FMWCNTs) and 10 mL of the Zn²⁺ solution with different initial concentrations (C₀) from 10 to 50 mg/l. The plastic bottles were sealed with a stopper, then were mounted on a shaker within a temperature control box (Model CH502, Chin Hsin, Taipei, Taiwan) and operated at (25 °C/180 rpm/12 h). After then, the FMWCNTs-sorbents were separated from the zinc solution by centrifuge (12000rpm/30 mint) and filtration through the filter paper (Whatman grade 42). The experiments were carried out by varying concentrations of initial Zn²⁺ solution (0, 10, 20, 30, 40, and 50 mg/l), in three replications. The initial and final concentrations of zinc were determined by using Inductively Coupled Plasma (ICP).

- *The Removed Percentage (%) and Adsorption Capacity (q_e) of Zn²⁺ was Calculated by the Following Equation (C. Lu and H. Chiu, 2006):*

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) V/m \quad (2)$$

Where q_e is the amount of Zn²⁺ adsorbed by FMWCNTs (mg/g); C₀ and C_e (mg/l) are the initial and final concentrations of the Zn²⁺, respectively; V is the initial solution volume (l) and m is the amount of adsorbent (g) added.

➤ *Desorption of Zn²⁺ Experiments*

The desorption of Zn²⁺ was studied on a sample obtained from the adsorption in the case of initial different concentrations as mentioned above. The experiment was done by adding 10 ml of diethylene triamine pentaacetic

acid (DTPA) (0.005 M DTPA + 0.01 M CaCl₂ + 0.1 M TEA at pH=7.3) as the elution reagent to extracted of Zn²⁺ adsorbed onto FMWCNTs (Zn-FMWCNTs). Then, the concentration of the desorbed Zn²⁺ in the solutions were analysed by using ICP.

- *The Desorption Rate was Calculated by the Following Equation:*

$$\text{Desorption (\%)} = (C_{\text{des}} / C_{\text{ads}}) \times 100 \quad (3)$$

Where C_{des} is the amount of the Zn²⁺ desorbed by DTPA from FMWCNTs, and C_{ads} is the amount of the Zn²⁺ adsorbed onto FMWCNTs.

➤ *Isotherm Models*

The experimental data for Zn²⁺ adsorption onto FMWCNTs were fitted to Langmuir and Freundlich isotherm models (N. A. Kabbashi, et al., 2009; Dastgheib S. A. and Rocktraw D. A. 2002)

$$q = \frac{abC_e}{1+bC_e} \quad (4)$$

$$q = K_f C_e^n \quad (5)$$

Where C_e is the equilibrium concentration of Zn²⁺ (mg/l); a and b are Langmuir constants and K_f and n are Freundlich constants.

III. RESULTS AND DISCUSSION

➤ *Characterization of FMWCNTs*

- *Raman Spectroscopy*

Raman spectroscopy has provided an exceedingly powerful technique to track surface modification, vibrational properties and electronic structures of CNT (Cui et al., 2011). Fig.1 shows Raman spectra of functionalized multi-walled carbon nanotube (MWCNTs-COOH). It is seen that the main peaks are D band located at 1303.60 cm⁻¹ which is related to disordered sp²-hybridized carbon atoms of nanotubes. The peak located at 1601.39 cm⁻¹ it is called G band which is related to the graphite E_{2g} symmetry of the interlayer mode and it reflects the structural integrity of sp²-hybridized carbon atoms of the nanotubes (Wang et al., 2012). The G' band at 2608.70 cm⁻¹ is an overtone of the D band. The D and G (I_D/I_G) bands ratio can be used to evaluate the defect density of the CNT structure (Alexander et al.,2018; Zhang et al.,2018).

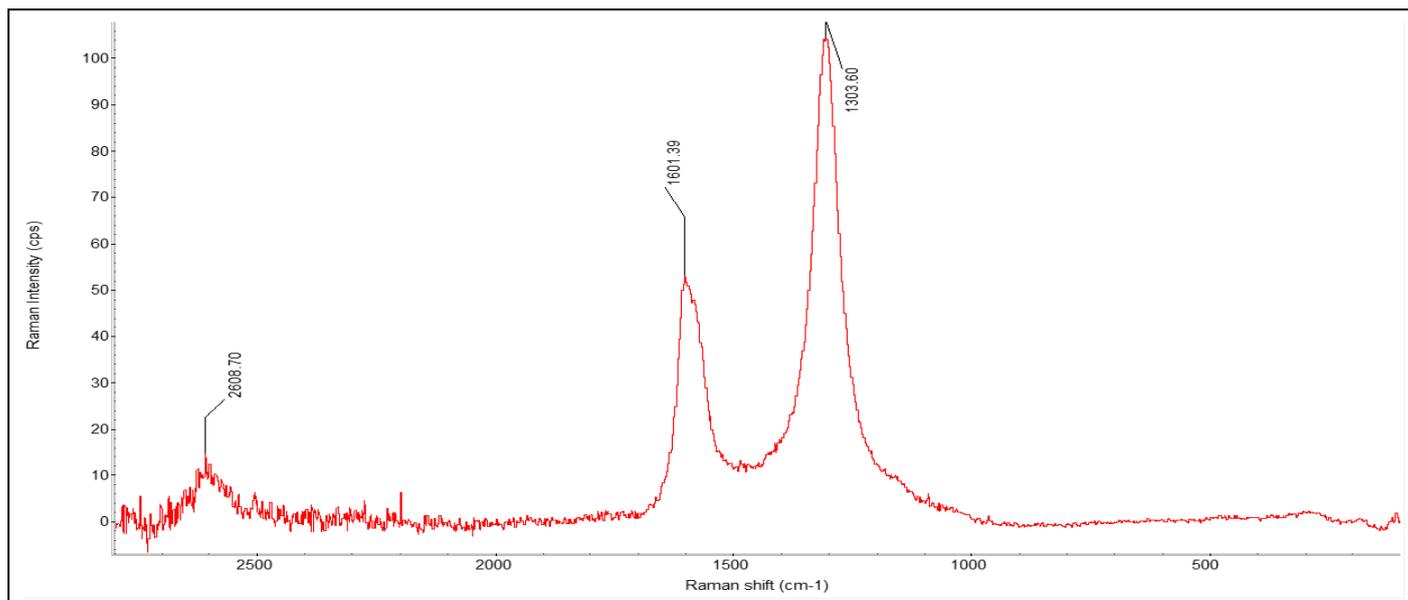


Fig 1 Raman Spectra of MWCNT-COOH

• *X-Ray Diffractions (XRD)*

The XRD analysis was performed to characterized crystallinity of the FMWCNTs. Here, the X-ray incident wavelength was 0.15418 nm by using Cu-K α (1.541874 Å) to obtain intense X-ray beams without K α_1 / α_2 separation. From Fig. 2, it can be seen that the diffractogram of FMWCNTs exhibits a typical and sharpest peak at 25.85^o

and less intense peak at 42.83^o which labeled as d (002) and (100), respectively. Besides, there is also observed the distribution of small diffraction within 2 θ . This could be explained by fact that the oxidation of MWCNTs can increase the interference between tubular structures as resulting in a change in the crystalline structure of MWCNTs (Al Mgher and Abdulrazzak 2016).

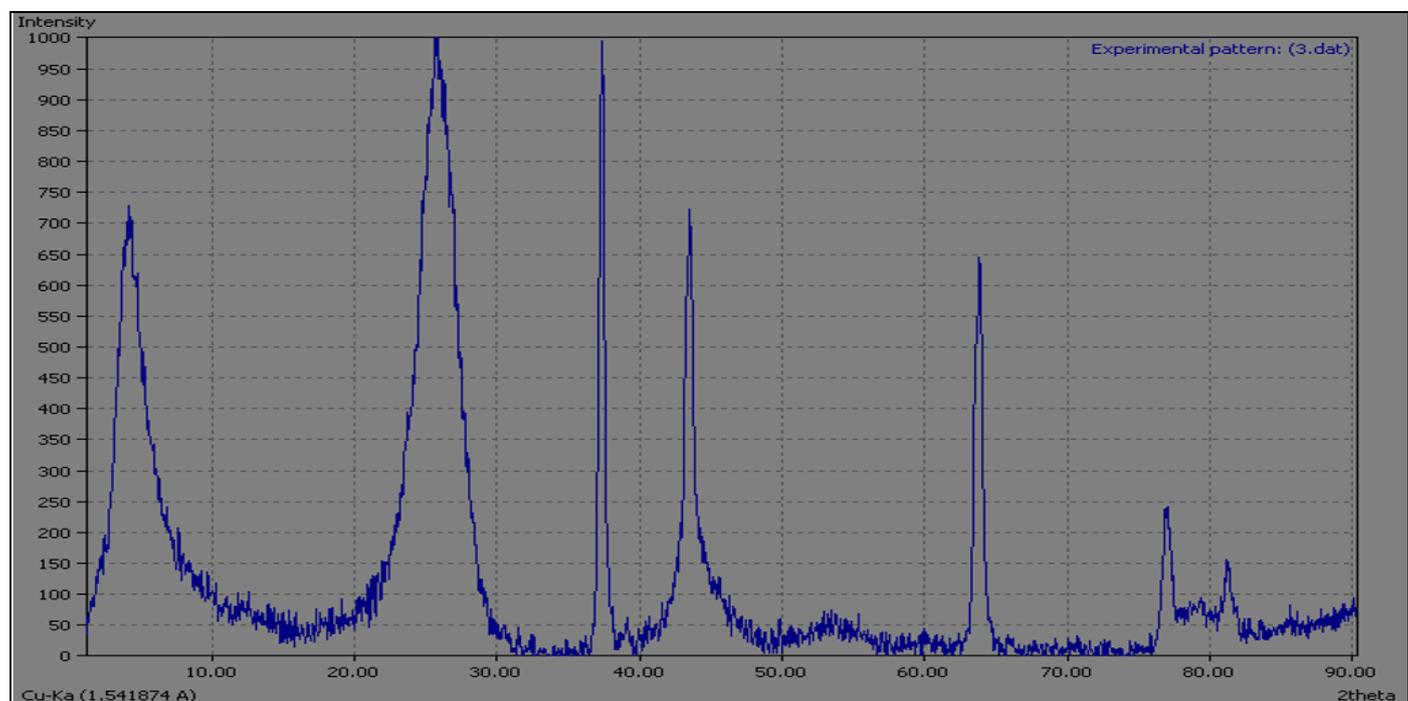


Fig 2 X-Ray Diffractions (XRD) of MWCNT-COOH

➤ *Adsorption of Zinc Ion (Zn²⁺) Onto F-MWCNTs*

The batch adsorption experiments were carried out by using different initial zinc concentrations ranging from 10 to 50 (mg/L), while the pH, contact time, amount of FMWCNTs, agitation speed and temperature were fixed at 7, 12 h, 0.05 gm, 180 rpm, and 25 °C, respectively (Tehrani et al., 2013). Adsorption of Zn⁺² onto FMWCNTs was

increased according to concentration and after 40 mg/l be closer to the equilibrium point as shown in Fig. 3. The carboxylic function groups (-COOH) on MWCNTs surface increase the adsorption capacity due to the strong interaction between negative charges of functional groups and positive charges of the ion (Atieh, 2011).

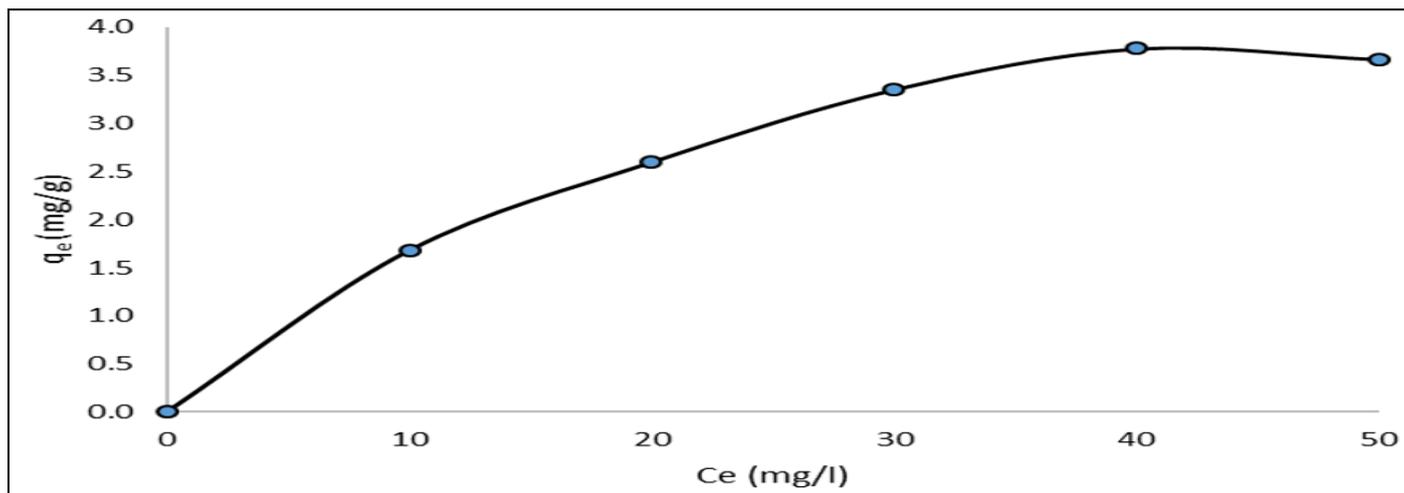


Fig 3 Adsorption Capacity of Zn²⁺ Onto FMWCNTs

➤ *Adsorption Isotherms*

The most common isotherm mathematical models used to express the adsorption of metal ions between adsorbent and liquid phases, based on a set of assumptions are namely; Langmuir and Freundlich (Wu, 2007). The equilibrium adsorption data of Zn²⁺ were simulated with the Langmuir and Freundlich isotherm models. Here, the Langmuir model assumes that the presence of monolayer coverage of the adsorbate on the adsorbent surface and there is no

interaction between the adsorbate molecules. The Freundlich model is an empirical relationship originated from the multilayer adsorption model and describing adsorption of solutes in liquid on the solid surface with several adsorption energies are involved (Dastgheib and Rocktraw, 2002). The Langmuir and Freundlich adsorption isotherms of zinc ion (Zn²⁺) onto MWCNTs-COOH are shown in Fig. 4 (a & b). The adsorption parameters of Langmuir and Freundlich for zinc are calculated and listed in Table 1.

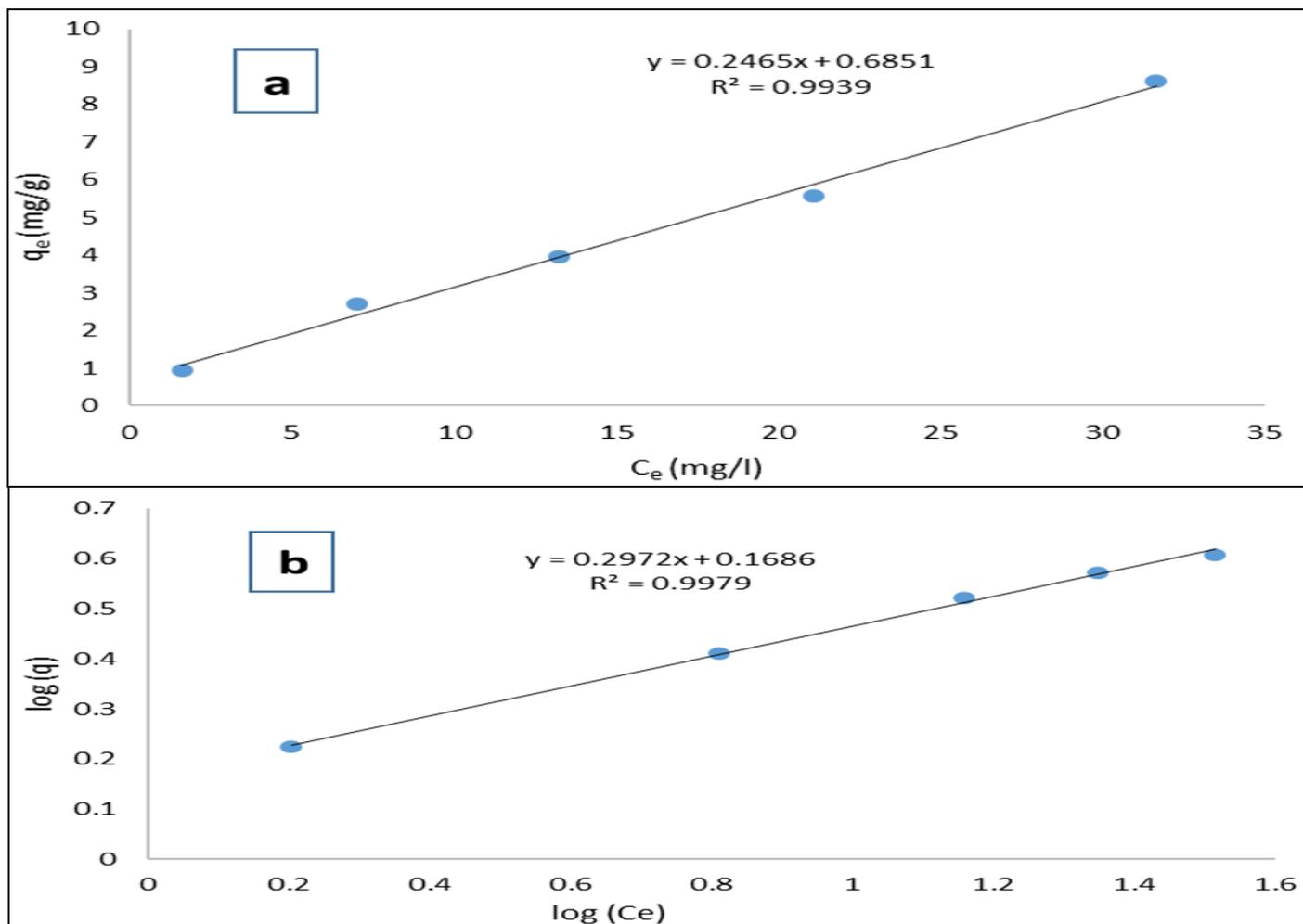


Fig 4 Langmuir (a) and Freundlich (b) Isotherms for Zn²⁺ Adsorption Onto fMWCNTs.

Table 1 Isotherm Parameters for the Adsorption of Zn^{+2} Onto fMWCNTs Surface.

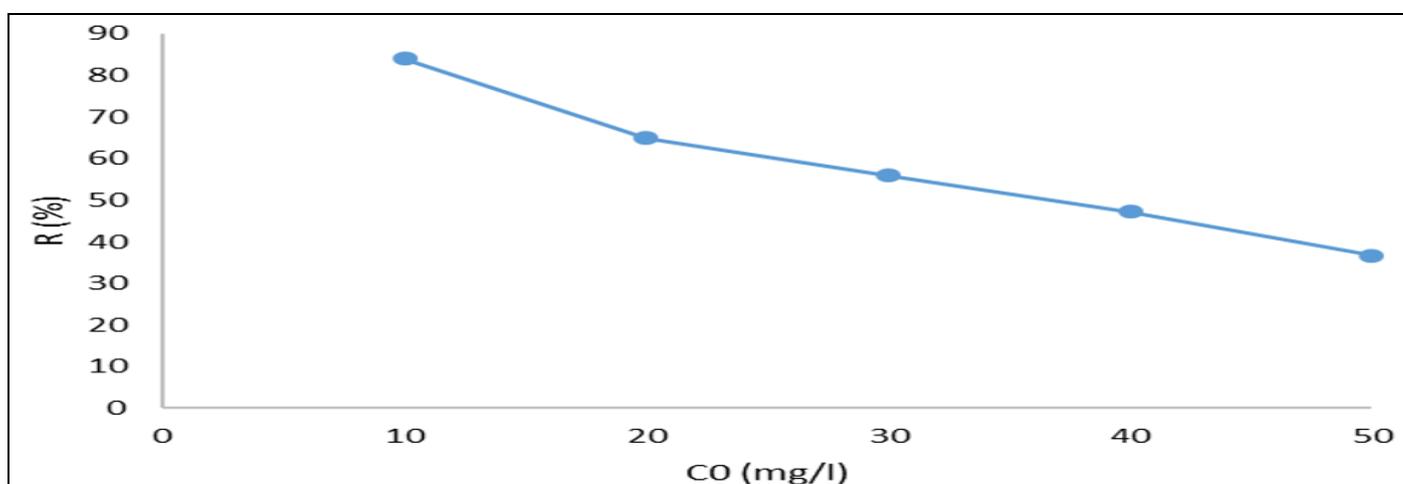
Langmuir			R^2	Freundlich		
q_m (mg/g)	b	K_L (L/mg)		1/n	K_F	R^2
3.778	4.057	0.3596	0.9939	0.297	1.686	0.9979

According to results the correlation coefficient values (R^2) for the Freundlich isotherm best fits the adsorption data rather than the Langmuir isotherm (Ahmed A. Moosa et al., 2016). Therefore, adsorption of Zn^{2+} onto FMWCNTs it takes place on the multilayer adsorption model. Also, the value of b is higher than k and that is an indicator of a good affinity between the sorbent (MWCNTs) and sorbate (Zn^{2+}).

➤ Desorption of Zinc Ion (Zn^{+2}) from F-MWCNTs

Desorption of zinc ions (Zn^{2+}) is a reversible process of adsorption, and the zinc ions need to be released from FMWCNTs. The desorption experiments were done at the

same plastic bottles used at adsorption experiment with different initial Zn^{2+} concentrations (similar to the batch method described above). When adsorption experiment completely occurred, the FMWCNT-Zn was dried at $40^\circ C$ for 4 h and then, 10 ml of DTPA was added to samples. After completed desorption process to removal Zn^{2+} from FMWCNTs, the amount of zinc was estimated in the extract by ICP-MO. (Fig. 5) showed that the efficiency of zinc removal was around 85 %. It is clearly shown that the study of adsorption and desorption efficiency was more effective at the low concentration level (Atieh, 2011).

Fig 5 The Removal of Zn^{+2} from FMWCNTs (%)

IV. CONCLUSION

Overall, the functional groups (COOH) improved ion-exchange capabilities of MWCNTs and increased Zn^{2+} adsorption capacities correspondingly. The adsorption of Zn^{2+} onto MWCNTs increases with the increase of solution concentration until (40 mg/l) and then started decreases, while the maximum desorption capacities at the concentration of (10 mg/l), in general the adsorption and desorption of Zn^{2+} onto fMWCNTs is more efficiency at low concentrations according Langmuir and Freundlich isotherm models.

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