

## Removal of Copper (II) from Wastewater Using Modified Carbon Nanotubes

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### ABSTRACT

In the present work, carbon nanotubes were prepared by Chemical Vapor Deposition (CVD) method, acetylene gas was used as a carbon source. In CVD system, a catalytic growth of CNTs is carried out by decomposition of acetylene ( $C_2H_2$ ) at a temperature of  $750\text{ }^\circ\text{C}$  for one hour, argon is used as an oxidation protection gas. The carbon nanotubes produced are purified to remove impurities such as metal catalyst and then functionalized by treating with  $HNO_3$ . Scanning Electron Microscopy (SEM), FT-IR spectra and BET for Surface Area measurement technique were used for characterization of CNTs. CNTs with about 30 nm in diameter and with length of several microns were obtained. The effects of initial concentration of metal (ppm), pH, carbon nanotube (CNT) dosage (mg) and contact time (min) on the adsorption of  $Cu^{+2}$  ion were studied.

The results show that the pH of aqueous solution is one of the major parameters that control the adsorption of ion at the solid-water interfaces. Maximum removal percentage of  $Cu^{+2}$  species is achieved at pH 8, CNT dosage of 50 mg/L and initial concentration of 50 mg/L and it is 98.39%. The constants of Langmuir and Freundlich models are obtained from fitting the adsorption equilibrium data. The correlation coefficients of Langmuir and Freundlich models are 0.75 and 1, respectively, indicating that the Freundlich model is more appropriate to describe the adsorption characteristics of  $Cu^{+2}$  onto CNTs.

**Keys words:** Carbon Nanotube, Heavy Metals, and Adsorption.

### ازالة النحاس (II) من فضلات الماء بأستخدام الكربون النانوي المعدل

#### الخلاصة

في هذا العمل فأن انابيب النانوكاربون قد تم تحضيرها بطريقة الترسيب الكيميائي (CVD)، واستخدم غاز الاستيلين كمصدر للكربون. في منظومة (CVD) فقد تم انماء الانابيب النانوكربونية بتفكيك غاز الاستيلين بمساعدة عامل مساعد بدرجة حرارة  $750\text{ }^\circ\text{C}$  ولمدة ساعة واحدة، كما استخدم غاز الاركون كمادة مانعة للتأكسد. ان الانابيب النانوكاربونية المنتجة قد تم تنقيتها وتوظيفها كيميائيا بمعاملتها مع حامض النتريك. استخدمت تقنيات المجهر الالكتروني الماسح ومطياف

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الاشعة تحت الحمراء وتقنية قياس المساحة السطحية (BET). لتشخيص انابيب النانوكاربون حيث تم الحصول على انابيب ذات اقطار بحدود ٣٠ نانومتر واطوال تصل الى بضعة مايكرون. ان تأثير التركيز الابتدائي للمعدن (ppm), مقياس ال pH, كميات الكاربون النانوي (ملي غرام/لتر) و زمن التماس بالدقيقة على اداء عملية الامتزاز للكاربون النانوي لأزالة معدن النحاس من فضلات الماء قد تم دراستها.

اظهرت النتائج ان (pH) واحد من اهم المتغيرات المسيطرة على امتزاز الايون على سطح الصلب - ماء. اعلى نسبة امتزاز للنحاس (II) عند pH=8, كمية الانابيب النانوكاربونية 50 (ملي غرام/لتر) والتركيز الابتدائي ٥٠ (ppm) هو ٩٨,٣٩%. إن ثوابت موديل لانكماير و فرندلج اخذت من قراءات عملية الامتزاز, وجد منها (coefficients correlation) لموديل لانكماير = 0.75 ولموديل فرندلج = ١, يُشير بأن موديل فرندلج أكثر ملائمة لوصف خصائص امتزاز Cu<sup>+2</sup> في الكاربون النانوي.

## INTRODUCTION

The pollution of water resources due to the disposal of heavy metals has been causing worldwide concern [1]. Metal ions such as Cu (II); Pb(II); and Cd(II), etc have been included in U.S. Environmental Protection Agency's list of priority pollutants[2].

The effects of heavy metals such as copper, lead, zinc, mercury, chromium and cadmium on human health have been investigated extensively and have negative effects on water resources, Cu<sup>+2</sup> is found as a contaminant in food, especially shell fish, liver, mushrooms and nuts [3]. Several methods have been applied over the years for the elimination of metal ions in industrial waste waters. The traditional methods commonly used for the removal of heavy metal ions from aqueous solutions include ion-exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electro dialysis and adsorption [4].

Carbon nanotubes (CNTs) have come under intense multidisciplinary study because of their unique physical and chemical properties. They have been used as an adsorbent for hydrogen and other gases due to their highly porous and hollow structure, large specific surface area, light mass density and strong interaction between carbon and hydrogen molecules. Carbon nanotubes (CNTs) modified with chemical treatment is relatively new adsorbents that have proven very efficient for treating many kinds of trace pollutants such as copper and cadmium [5]. Muataz Ali Atieh[6] study was carried out to evaluate the environmental application of modified and non-modified carbon nanofiber through the experiment removal of zinc from water. Results of the study showed that raw (non-modified) CNFs have very poor efficiency in removing zinc from water by conventional adsorption mechanism. However, when CNFs were modified with carboxylic group, a significant improvement in the zinc removal efficiency was observed. Omid Moradi[7] investigated the interaction between some heavy metal ions such as of Pb(II), Cd(II) and Cu(II) ions from aqueous solution adsorbed by single walled carbon nanotube (SWCNTs) and carboxylate group functionalized single walled carbon nanotube (SWCNT-COOH) surfaces. The effect of contact time, pH, and initial concentration of ion, ionic strength and temperature on the adsorption of ion were investigated. Ch. Lu[8] studied commercial single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) purified by sodium hypochlorite solutions and employed as adsorbents to study the adsorption of zinc from water.

The aim of the present study is to prepare CNTs by CVD technique, functionalization of CNTs and use the CNTs to remove the Cu<sup>+2</sup> ions from

wastewater. It also provides the adsorption conditions in term of various system parameters such as initial concentration, pH, contact time and CNTs dosage. The study also aims to evaluate the adsorption isotherm of the experimental data.

## EXPERIMENTAL WORK

### Preparation of CNTs

The carbon nanotubes CNTs are produced by the pyrolysis of Acetylene gas on particles of catalyst ( $\text{Al}_2\text{O}_3$ ) in a chemical vapor deposition (CVD) with argon as inert gas. CNTs is produced by pyrolysis of acetylene gas under influence of high temperature  $750^\circ\text{C}$ .

### Purification of CNTs

One gram of CNTs produced was heated at  $350^\circ\text{C}$  for 30 min to remove amorphous carbon. After thermal treatment, half gram of CNTs was dispersed into a flask containing 20 ml of 70% sodium hypochlorite solution. The solution was then shaken in an ultrasonic cleaning bath, for 20 min and was heated at  $85^\circ\text{C}$  in a water bath for 3 hours to remove metal catalysts. After cooling, the CNTs were washed with deionised water until the pH of the solution reached 7. Finally, the solution was filtered by centrifugal filtration and dried in oven at  $200^\circ\text{C}$  for 2hr then the purified CNTs were obtained.

### Functionalization of CNTs

Carbon nanotubes were oxidized by nitric acid under optimal oxidation temperature. 0.1 g of dried CNTs powder was treated with 15 ml of  $\text{HNO}_3$  solution (2 M solution) for 1 hour at  $80^\circ\text{C}$  under refluxing. After oxidation, samples were recovered and washed thoroughly with distilled water until the pH was almost 7. Finally, carbon supports were filtered, washed with distilled water and dried at  $108^\circ\text{C}$  for 12 hours.

### Characterization of CNT

Scanning Electron Microscopy (SEM) (Type TESCAN) was used to observe the carbon nanotubes CNTs produced by CVD method after purification. FTIR measurements (Bruker –Tensor 27/ Germany), was used to analyze the chemical bonds and the functional groups grafted on to the carbon nanotubes. The specific surface area of CNTs was measured using instrument model Q-surf 9600 (USA), based on Brunauer, Emmett and Teller (BET).

### Batch Mode Adsorption

The standard solutions of fixed concentration of  $\text{Cu}^{+2}$  (10, 30, 50) ppm were prepared by dissolving the required amount of  $\text{Cu}^{+2}$  stock solutions with distilled water. The desired weight of CNTs adsorbent (10, 30 and 50 mg/L) was added to 100 mL flasks. Flasks are then agitated with the speed of (200 rpm) at room temperature using a mechanical shaker. The pH of each solution was adjusted using 0.1 M HCl or 0.1 M NaOH.

After the equilibrate time of (10, 20, 30, 40, 50 and 60 min) passed, CNTs were separated from the samples by filtering and the filtrates were analyzed using a U.V-1100 spectrophotometer (Chrom Tech-Chine).

## RESULTS AND DISCUSSION

### Characterization of CNTs

From the SEM image shown in Figure (1), two types of structure can be identified: CNTs with an average diameter of 30 nm and several micron in length. The observed CNTs are usually curve and have cylindrical shapes. Due to inter-

molecular force, the CNTs have different sizes and directions and form an aggregated structural solid.

FTIR spectra of functionalized CNTs are shown in Figure (2), the peaks which are identified at  $1701.22\text{ cm}^{-1}$ , characterize C=O which can be attributed to acidic group, like carboxyl. The peaks appearing at  $2945.3\text{ cm}^{-1}$  and  $3305.99\text{ cm}^{-1}$  are due to the carbon hydrogen bond stretch and hydroxyl group, respectively. The hydroxyl group can be attributed to the acid treatment of the CNTs after production to remove the metal catalyst for purification purpose. The results of FTIR confirm the growth of carbon structure due to the observation of stretching C-C bond at  $1554.63\text{ cm}^{-1}$ .

These results are in a good agreement with the results obtained by Ch. Lu[8]. The surface area of CNTs, as determined by the BET method was found to be  $53\text{ (m}^2\text{/g)}$ .

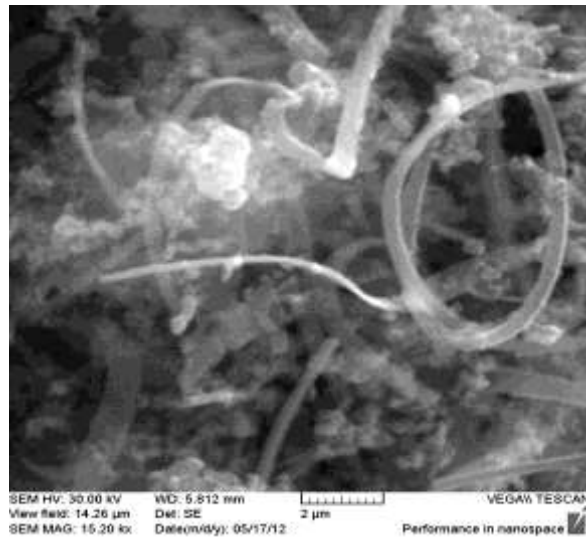


Figure (1) Scanning electron images of CNTs.

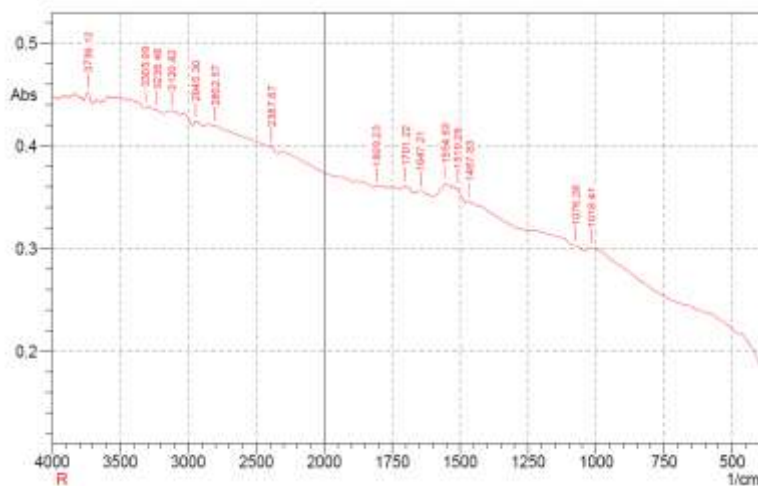


Figure (2) FTIR of the prepared CNTs.

**Effect of Different Parameters on Adsorption of Copper (II) by Modified CNTs**

**Effect of Contact Time**

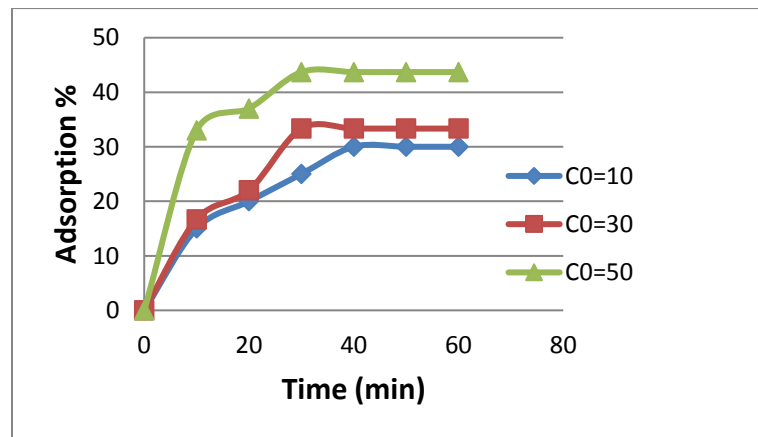
Figures (3,4 and 5), show the percentage of adsorbed ion  $Cu^{+2}$  on to CNTs surfaces as a function of contact time at  $T=298\pm 1^{\circ}K$ . It is noted that the adsorption of  $Cu^{+2}$  increases rapidly with time and then reaches equilibrium.

Two stages can be observed on the curve of contact time. Region stage one in which the adsorption of  $Cu^{+2}$  takes place rapidly within a short time; this is obvious from the fact that a large number of vacant surface sites are available for the adsorption during the initial stage and with the passage of time [8].

The second one is equilibrium stage. At equilibrium time there is no active site on the CNTs.

In Figure (6), the perfect results were obtained for  $Cu^{+2}$  ion: when the initial concentration was 50 mg /L at pH=8, equilibrium time was 3min and  $T=298^{\circ}K$ . In fact with time increase of ion concentration, the percentage of ion adsorption increased. This is due to the existence of free function group (- COOH) on the absorbent. This functional group causes a rise in the negative charge on the carbon surface. The oxygen atoms in the functional group denoted single pairs of electron to metal ion and consequently increase their cation exchange capacity.

These results are in good agreement with the results obtained by Ghasem Zolfaghari[9], who found that the adsorption percentage increases with increasing the contact time.



**Figure (3) the effect of contact time on percentage Removal of  $Cu^{+2}$  at initial concentration ( $C_0$ ) 10, 30 and 50 ppm, pH=5 and CNT =10(mg/ L).**

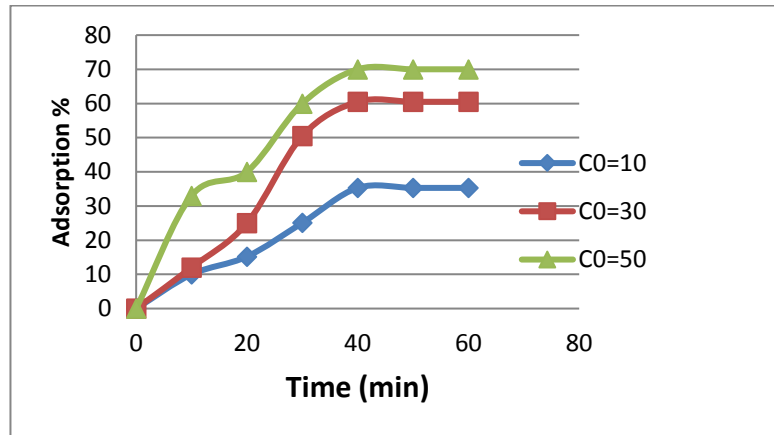


Figure (4) the effect of contact time on percentage removal of  $Cu^{+2}$  at initial concentration ( $C_0$ ) 10,30 and 50 ppm, PH=5 and CNT =30(mg/ L).

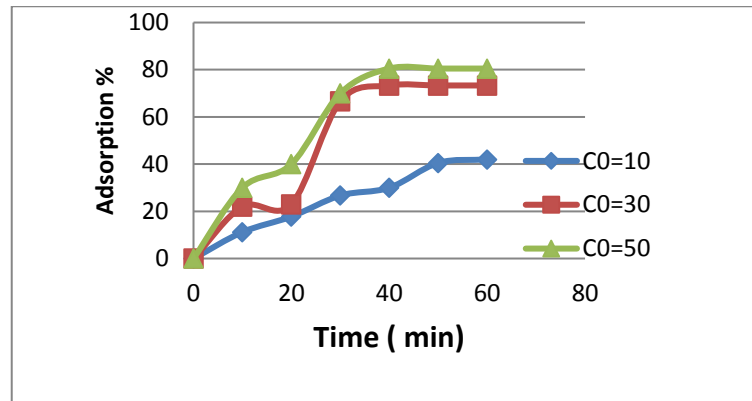


Figure (5) the effect of contact time on percentage removal of  $Cu^{+2}$  at initial concentration ( $C_0$ ) 10, 30 and 50 ppm, pH=5 and CNT =50(mg/ L).

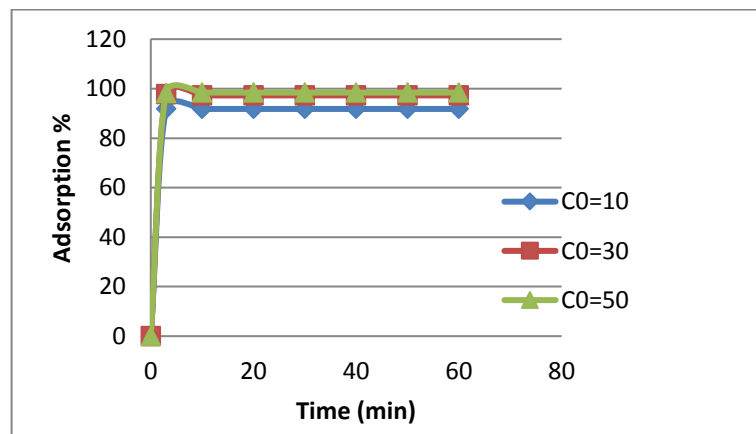


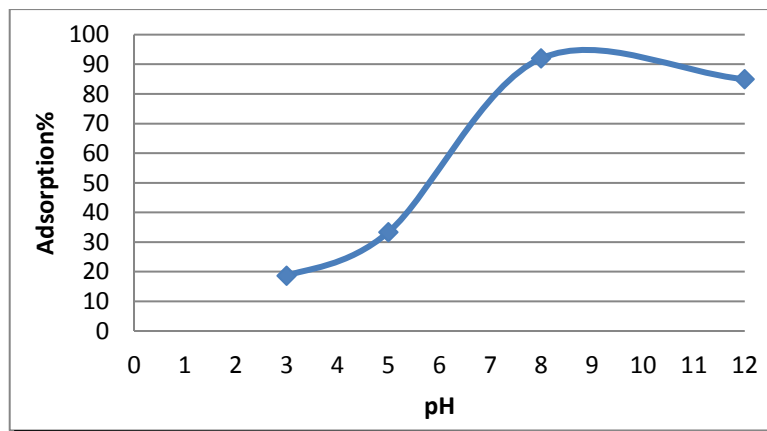
Figure (6) the effect of contact time on percentage removal of  $Cu^{+2}$  at initial concentration ( $C_0$ ) 10, 30 and 50 ppm , pH=8 and CNT = 50(mg/ L).

**Effect of pH on Ion Adsorption**

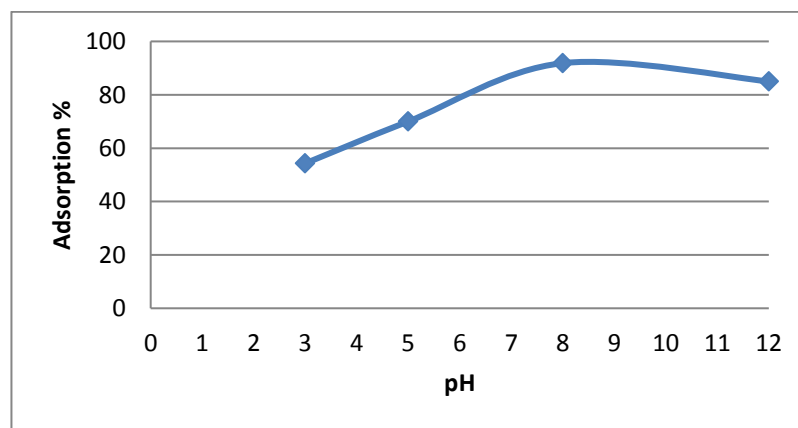
Figures (7), (8) and (9) show the effect of pH on the adsorption of Cu<sup>+2</sup> onto CNTs. As can be seen, the pH of the solution plays an important role in affecting the adsorption characteristics of Cu<sup>+2</sup> onto CNTs. With the C<sub>0</sub> of 10 ppm, the adsorption of Cu<sup>+2</sup> onto CNTs increases with the increase in pH range of 3–8, fluctuates is very little and reaches a maximum in the pH range of 8 and decreased at a pH of 12.

The ionic adsorption capability is known to be mainly determined depend on functional groups which are usually introduced by chemical treatments such as oxidation by HNO<sub>3</sub>. Appropriate treatments can introduce functional groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (>C=O), on the surface of CNTs. Introduction of functional groups on CNT enhances its ionic adsorption properties [9].

These results are in good agreement with the results obtained by Omid Moradi[7].



**Figure (7) The effect of pH on the percentage of adsorption of Cu<sup>+2</sup>, Initial concentration of metal ion is 10 ppm, CNTs dosage 10 mg/L and contact time 60 min and Temperature 298 K<sup>0</sup>.**



**Figure (8) The effect of pH on the percentage of adsorption of Cu<sup>+2</sup>, Initial concentration of metal ion is 10 ppm, CNTs dosage 3 mg/L and contact time 60 min Temperature 298 K<sup>0</sup>.**

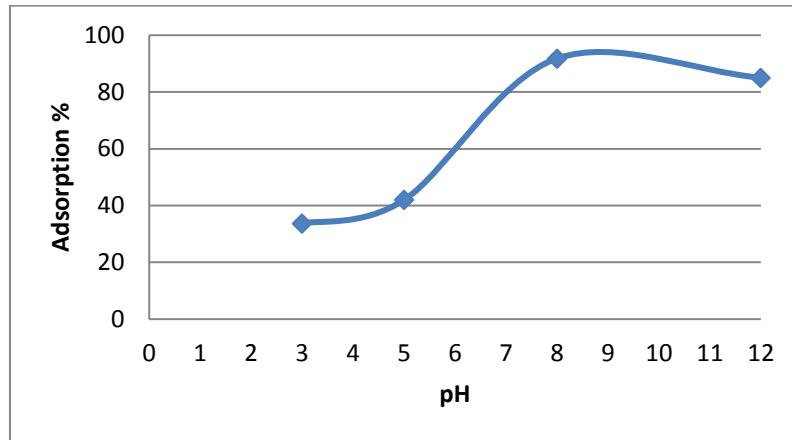


Figure (9) The effect of pH on the percentage of adsorption of Cu+2, Initial concentration of metal ion is 10 ppm, CNTs dosage 5 mg/L and contact time 60 min Temperature 298 K<sup>0</sup>.

#### Effect of CNTs Dosage

The amount of carbon nanotubes in the water is one of the major factors, which affect the adsorption capacity. The batch adsorption experiments were carried out by using various amounts of CNTs of 10,30 and 50 mg/L. Figures (10),(11) and (12) show the effect of CNTs dosage on percentage of adsorption of copper. As can be seen the amount of adsorption for copper increases with adsorbent dose. This increase in loading capacity is due to the availability of greater amounts of active sites of the adsorbent [10].

These results are in good agreement with the results obtained by Muataz Ali[6], who found that the adsorption percentage increases with increasing the amount of carbon nanotubes.

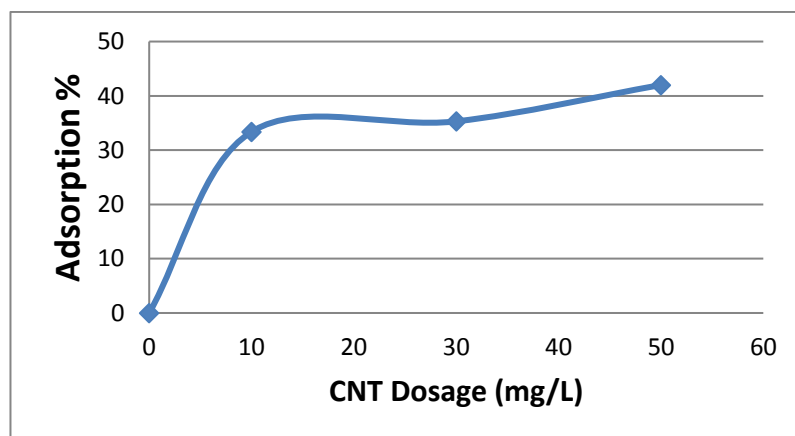


Figure (10) the effect of CNTs dosage on percentage of adsorption of copper at pH=5, C<sub>0</sub>= 10 ppm and time =60 min.



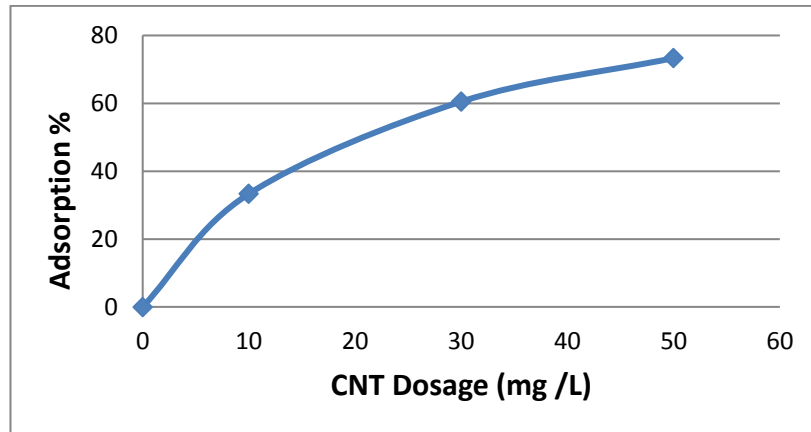


Figure (11) The effect of CNTs dosage on percentage of adsorption of copper at pH=5, C<sub>0</sub>= 30 ppm and time =60 min.

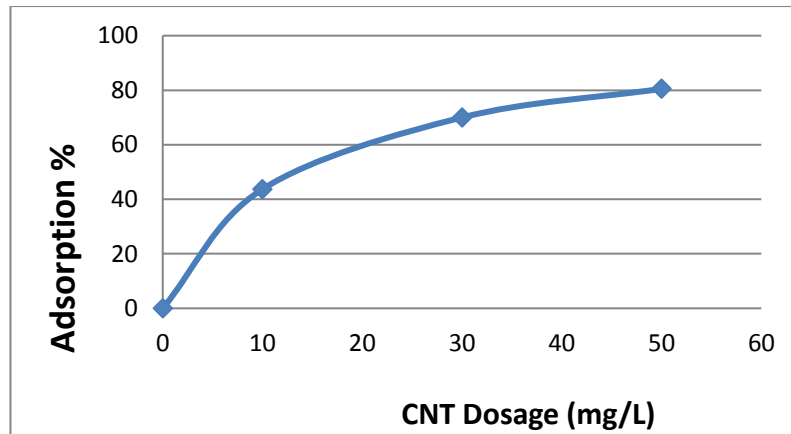


Figure (12) The effect of CNTs dosage on percentage of adsorption of copper at pH=5, C<sub>0</sub>= 50 ppm and time =60 min.

### Effect of Copper Concentration

Figures (13to 15) show the percentage removal of Cu<sup>+2</sup> at different concentration. It is clearly shown that the percentage removal of Cu<sup>+2</sup> increases by increasing the concentration using the same dosage of CNTs. More metal ions were left unadsorbed in the solution due to the saturation of the binding sites. Metal ion adsorption is attributed to different mechanisms of ion exchange as well as to the adsorption. This effect on ion adsorption can be explained, as follows at low metal ion/adsorbent ratios, metal ion adsorption involves more energy sites. As metal ion/adsorbent ratio increases, more energy sites are saturated and adsorption begins on fewer energy sites, resulting in low increasing of metal ion adsorption.

These results are in good agreement with the results obtained by Omid Moradi[7], who found that the adsorption percentage increases with increasing the initial concentration for copper .

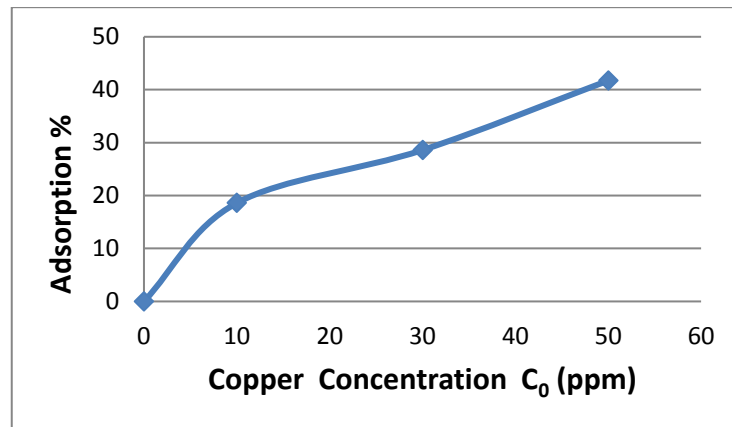


Figure (13) The percentage removal of  $Cu^{+2}$  at different concentrations (ppm), pH=3, contact time=60 min and CNT dosage=10 (mg/L).

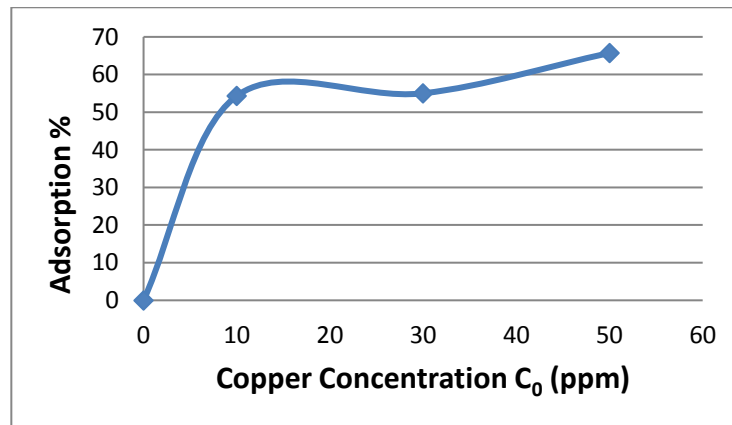


Figure (14) the percentage removal of  $Cu^{+2}$  at different Concentrations (ppm), pH=3, contact time=60 min and CNT dosage=30 (mg/L).

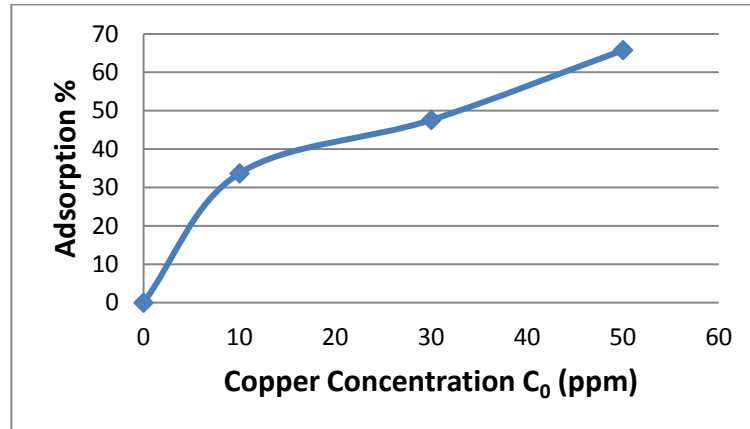


Figure (15) The percentage removal of Cu+2 at different Concentrations (ppm), pH=3, contact time=60 min and CNT dosage=30 (mg/ L).

### Adsorption Isotherms

The distribution of adsorbates between aqueous phase and adsorbent is a measure of the position of equilibrium in an adsorption process and can be investigated through various models such as the Langmuir and Freundlich isotherms. The linear forms of the two models are [11]:

$$\text{Langmuir} \quad \frac{C}{q} = \frac{1}{(K_L q_m)} + \frac{C}{q_m} \quad \dots (1)$$

$$\text{Freundlich} \quad \log q = \frac{1}{n} \log c + \log K_F \quad \dots (2)$$

The Langmuir isotherm equation is used to estimate the maximum adsorption capacity of the CNTs under the conditions of 298 °K, pH 8.0, 1hour contact time and 30 mg/L adsorbent dose while varying initial Cu<sup>+2</sup> concentration from 10 to 50 mg/L. The values of the isotherm constants and R<sup>2</sup> are given in Table (1). The linear plot of C/q versus C along with high value correlation coefficient indicates that Freundlich isotherm provides a better fit with the equilibrium data. The isotherm parameters as derived from the slope and intercept of the plots are listed in Table (1) [12].

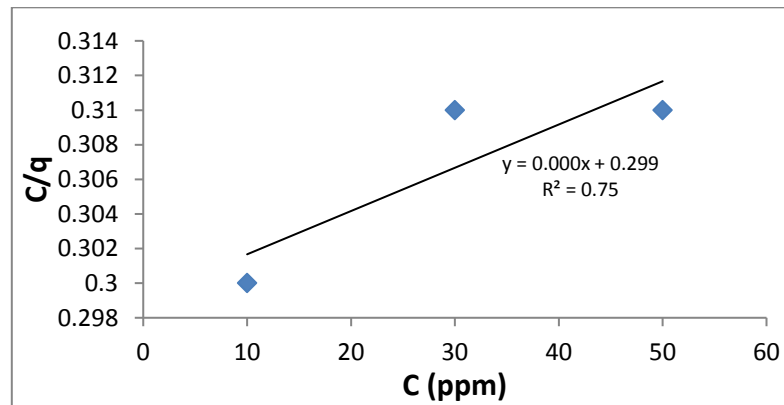
The values of the isotherm constants and R<sup>2</sup> are given in Table (1). The linear plot Figure (16) of C/q versus C along with high value correlation coefficient indicates that Langmuir isotherm provides a poor fit with the equilibrium data. The adsorption data when fitted to the Freundlich isotherm i.e. the plot of log q versus log C<sub>0</sub>, Figure (17) shows that Freundlich isotherm gives a better fit to the experimental data as compared to Langmuir isotherm.

When Langmuir and Freundlich isotherms are compared, Freundlich Isotherm shows better fitting model with higher correlation coefficient of ( R<sup>2</sup> = 1) compared Langmuir Isotherm of (R<sup>2</sup> = 0.75). Therefore, this indicates the applicability of monolayer coverage of Cu (II) ions to the surface of the adsorbent. This is due to the

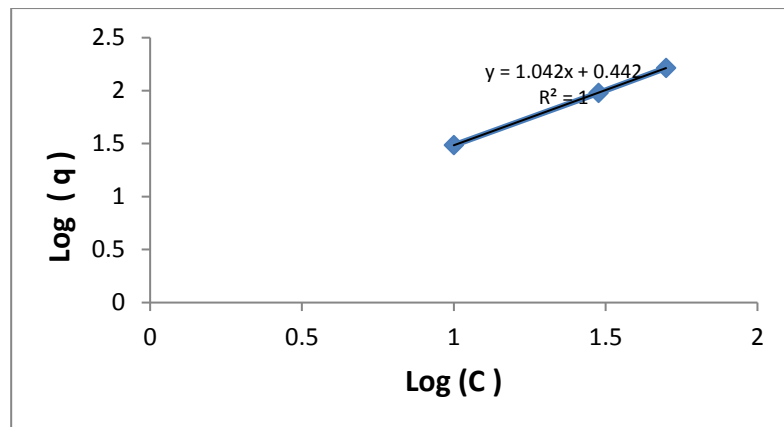
fact that CNTs have greater surface area for metal adsorption. The good correlation coefficient of Freundlich isotherm also indicates that Cu (II) ions strongly adsorb to the surface of CNTs. Therefore, it is verified that CNTs have great potential to be a good adsorbent for the removal of Cu (II) ions in water treatment [13].

**Table (1) Coefficients of Langmuir and Freundlich isotherms.**

Isotherm model	Correlation Coefficients(R <sup>2</sup> )	Constants
Langmuir	0.75	K <sub>L</sub> = 0.0015 ( Langmiur constant) (L/mg) q <sub>m</sub> = 2222 ( maximum adsorption capacity) (mg/g)
Freundlich	1	K <sub>F</sub> = 3.1( Freundlich constant) (mg/g)(mg/L)- 1/n n=1 (dimensionless)



**Figure (16) Adsorption isotherm Langmuir model for copper (II).**



**Figure (17) Adsorption isotherm Freundlich model for copper (II).**

**CONCLUSIONS**

From this study, the following main conclusions can be obtained:

1. The carbon nanotubes which was prepared in this study was found to be efficient for the adsorption of  $\text{Cu}^{+2}$  in aqueous solution.
2. Characterization of CNTs by SEM spectroscopy shows a domination of CNTs image.
3. Functionalization of CNTs identified by FTIR is show the presence of functional groups of (-COOH) at  $1701.22 \text{ cm}^{-1}$  as well as hydroxyl groups. Such groups offer free active sites and consequently increase cation exchange capacity.
4. In general, the adsorption of  $\text{Cu}^{+2}$ , onto CNTs increases with the increase in pH range from pH=1 to pH=8, reaches a maximum in the pH range of 8 and decreases at a pH of 12. The contact time to reach equilibrium is 60 min for CNTs. The percentage of removal increases with increase in the contact time. The maximum percentage of adsorption at pH= 8, CNT= 50 mg/L is 98.39%.
5. Removal percentage increases with increase in CNTs dosage and Initial concentration.
6. Freundlich adsorption model is better fitted for the adsorption of Cu (II), the good correlation coefficient of Freundlich isotherm indicates that  $\text{Cu}^{+2}$  ions are strongly adsorbed to the surface of CNTs.

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