

## OXIDATION OF CARBON NANOTUBES USING FOR Cu(II) ADSORPTION FROM AQUEOUS SOLUTION

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**Abstract.** Carbon nanotubes (CNTs) synthesized via chemical vapour deposition without hydrogen were oxidized with 0.1 M potassium permanganate at 40 °C for 2 hours. The material exhibits a high Cu<sup>II</sup> adsorption capacity from the aqueous solution. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), scanning electron microscope (SEM), transmission electron microscope (TEM) and nitrogen adsorption/desorption isotherms were used to characterize the oxidized CNTs. After oxidizing, the obtained CNTs were used to remove Cu<sup>II</sup> from the aqueous solution. With Cu<sup>II</sup> initial concentration of 20 mg.L<sup>-1</sup>, at pH 4 and adsorbent dosage of 0.2 g.L<sup>-1</sup>, the oxidized CNTs exhibit a high Cu<sup>II</sup> adsorption ability with a maximum adsorption capacity of 174.4 mg.g<sup>-1</sup>.

**Keywords:** oxidized carbon nanotubes, Cu<sup>II</sup> adsorption capacity, Cu<sup>II</sup> adsorption, potassium permanganate, oxidized CNTs

### 1 Introduction

A considerable amount of heavy metal in wastewater from industrial processes including copper (Cu<sup>II</sup>), lead (Pb<sup>II</sup>), cadmium (Cd<sup>II</sup>), zinc (Zn<sup>II</sup>), chromium (Cr<sup>III</sup>), etc. may endanger human health [1]. Among such metals, copper is a noted contaminant that can cause many dangerous diseases such as liver and kidney damage, intestinal distress, and anaemia when it is accumulated in the human body for a longterm [2]. Adsorption is one of the effective methods used to remove heavy metals from aqueous solutions. The popular adsorbent can be activated carbon [3], bio-char [4], fly ash [5] or carbon nanotubes (CNTs) [6, 7].

CNTs are known as a good adsorbent of heavy metals after their surface are oxidized due to high surface area. This oxidation stage may

remarkably enhance the dispersion of CNTs in water or solvents due to the formation of polar functional groups containing oxygen, *e.g.*, -OH, -C=O, and -COOH [8, 9, 10]. Further, the electrostatic charge derived from such polar functional groups forms the attraction forces of metal ions, thereby enhancing the adsorption of heavy metals. Strong oxidants used for the treatment are usually HNO<sub>3</sub> [7], a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [10, 11], KMnO<sub>4</sub> [12], a mixture of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> [13], and NaClO [14].

Potassium permanganate is a strong oxidant that can split the C-C bond and separate tubes from bundles or open tubes. Therefore, the morphology and heavy metal adsorption ability of CNTs may vary, depending on the concentration of potassium permanganate and oxidation temperature/time [12, 15]. The oxidation of CNTs using potassium permanganate is not

extensively studied worldwide, especially in Vietnam. Regarding the removal of Cu<sup>II</sup> by CNTs, many studies conducted so far have shown comparatively low values of maximum Cu<sup>II</sup> adsorption capacity [2, 16, 17].

In this study, the suitable oxidation conditions of CNTs by potassium permanganate for the adsorption of Cu<sup>II</sup> from the aqueous solution are examined. Besides, the effects of pH and the dosage of sorbent on Cu<sup>II</sup> adsorption capacity onto oxidized CNTs were investigated.

## 2 Experimental

### 2.1 Materials

The starting CNTs were synthesized from liquefied petroleum gas (LPG) via the chemical vapour deposition (CVD) method, in which, LPG (Dung Quat, Quang Ngai, Vietnam) carried in a nitrogen flow was pyrolyzed at 800°C, using Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as a catalyst.

0.25 g of the resulting CNTs were suspended and sonicated in 25 mL of a mixture containing KMnO<sub>4</sub> (PA, China) and H<sub>2</sub>SO<sub>4</sub> (PA, China) at a definite temperature for a definite time. The obtained material was separated, washed with de-ionized water and dried at 80 °C until stable weight.

### 2.2. Methods

**Characterization of CNTs.** The atomic composition was identified using Energy-dispersive X-ray spectroscopy (EDS) (Model S-4800 (Hitachi, Tokyo, Japan)). Raman spectrum was employed to study the defects on the surface of the material using RAM HR800 (Horiba). The particle morphology was studied using a scanning electron microscope (SEM; Model S-4800 (Hitachi, Tokyo, Japan)), and a transmission electron microscope (TEM) being attached to the

SEM. The specific surface area was measured using nitrogen adsorption/desorption isotherms at 77 K (Model BELSORP-mini, MicrotrackBEL, Osaka, Japan).

**Adsorption studies.** All the working solutions of Cu<sup>II</sup> were prepared from solid CuSO<sub>4</sub>.5H<sub>2</sub>O (PA, China). The concentration of Cu<sup>II</sup> was determined using UV-VIS molecular absorption spectrometry. The adsorption capacity of Cu<sup>II</sup> was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $q_e$  is the Cu<sup>II</sup> adsorption capacity;  $C_0$  and  $C_e$  are the concentrations of Cu<sup>II</sup> before and after adsorption;  $m$  is the mass of oxidized CNTs;  $V$  is the volume of the Cu<sup>II</sup> solution.

To determine the effect of pH on the removal of Cu<sup>II</sup> from the aqueous solution, 10 mg of oxidized CNTs were dispersed in 50 mL of a 20 mg.L<sup>-1</sup> Cu<sup>II</sup> solution for 120 min with pH varied from 2 to 5. Cu(OH)<sub>2</sub> precipitation would appear at pH greater than 5. The effect of the adsorbent dosage from 0.08 to 0.1 g.L<sup>-1</sup> on Cu<sup>II</sup> adsorption was also studied.

The maximum Cu(II) adsorption capacity ( $q_m$ ) of the oxidized CNTs was determined from the isothermal data. A sample containing 50 mL of Cu(II) solutions with a concentration ranging from 10 to 60 mg.L<sup>-1</sup> was stirred at 30 °C for 80 min with 0.2 g.L<sup>-1</sup> of oxidized CNTs. The equilibrium amount of Cu(II) in the solution was determined after the adsorption.

## 3 Results and discussion

### 3.1. Oxidation of CNTs

**Effect of KMnO<sub>4</sub> concentration.** The morphology of CNTs and the number of functional groups containing oxygen vary according to the ratio of KMnO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> in the oxidizing solution and

therefore affecting the adsorption ability of CNTs. Nine samples of CNTs were ultrasonically oxidized at 40 °C for 2 hours with different  $\text{KMnO}_4$  concentrations from 0.05 to 0.5 M.

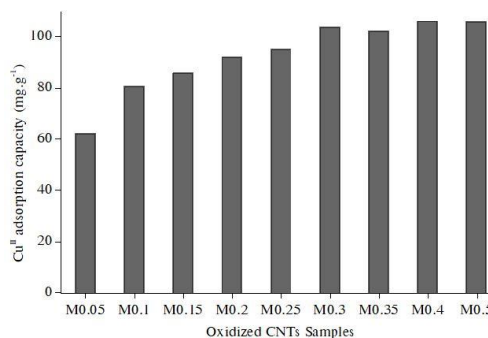
The  $\text{Cu}^{\text{II}}$  adsorption capacity of the adsorbent shown in Fig. 1 strongly increases from 62.1 to 103.7  $\text{mg}\cdot\text{g}^{-1}$  with the increase of  $\text{KMnO}_4$  concentration from 0.05 to 0.3 M, and then, remains practically stable around 103  $\text{mg}\cdot\text{g}^{-1}$  for higher  $\text{KMnO}_4$  concentration. This demonstrates that  $\text{KMnO}_4$  enables the formation of  $-\text{OH}$ ,  $-\text{C}=\text{O}$  and  $-\text{COOH}$  groups. Unlike oxidized CNTs, the bare CNTs exhibits much lower  $\text{Cu}^{\text{II}}$  adsorption capacity (7,6  $\text{mg}\cdot\text{g}^{-1}$ ). This indicates the importance of the oxidation stage when using CNTs as a heavy metal adsorbent.

The SEM images of oxidized CNTs indicate that the increase of  $\text{KMnO}_4$  concentration can destroy the tubes (Fig. 2). The obtained CNTs only retain the long tube structure when using  $\text{KMnO}_4$  concentration from 0.05 to 0.15 M; with 0.15M  $\text{KMnO}_4$ , some of the tubes were become very short and locate on the surface of long tubes. The tube structure is strongly destroyed when using the concentration of  $\text{KMnO}_4$  from 0.2 to 0.5 M.

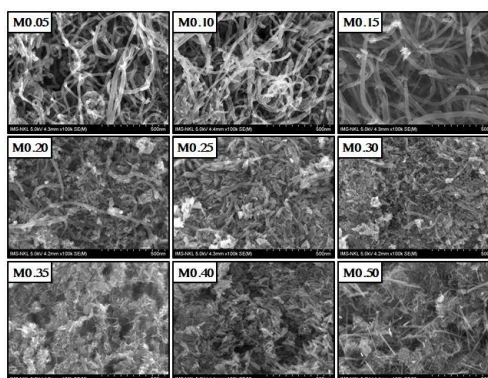
The XRD diagrams of bare CNTs and oxidized CNTs (M0.1 and M0.25) show that in the M0.25 sample, the crystal phase of carbon disappears and the micro crystal or amorphous carbon is observed (Fig. 3). With bare CNTs and the M0.1 sample, a characteris diffraction peak of the graphite phase appears at  $2\theta$  of 26,22 °, corresponding to the (002) plane (JCPDS card files, no 41-1487).

In conclusion, with  $\text{KMnO}_4$  concentrations from 0.2 to 0.5 M, the CNTs structure was collapses completely. Therefore, this range of  $\text{KMnO}_4$  concentration is not chosen as a suitable concentration for oxidizing CNTs despite high  $\text{Cu}^{\text{II}}$  adsorption capacity because the obtained materials from M0.2 to M0.5 convert into

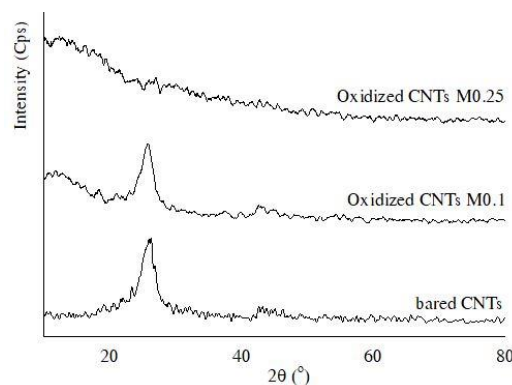
amorphous carbon. Therefore, 0.1 M  $\text{KMnO}_4$  was chosen for further experiments. Slobodian et al. [18] also used this concentration for oxidizing a CNTs network embedded in elastic polyurethane. However, in the study of Zhang et al. [12], 0.313 M  $\text{KMnO}_4$  solution was used to oxidize CNTs.



**Fig. 1.** Effect of  $\text{KMnO}_4$  concentration on  $\text{Cu}^{\text{II}}$  adsorption capacity of oxidized CNTs (*Experimental conditions*: mass of adsorbent is 0.01g; volume of  $\text{Cu}^{\text{II}}$  solution is 50 mL; ultrasonic time is 3 hours;  $\text{Cu}^{\text{II}}$  concentration is 20  $\text{mg}\cdot\text{L}^{-1}$ ).

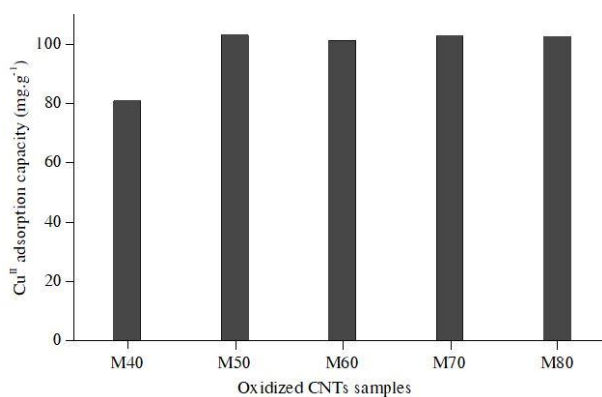


**Fig. 2.** SEM images of oxidized CNTs prepared with different  $\text{KMnO}_4$  concentrations.

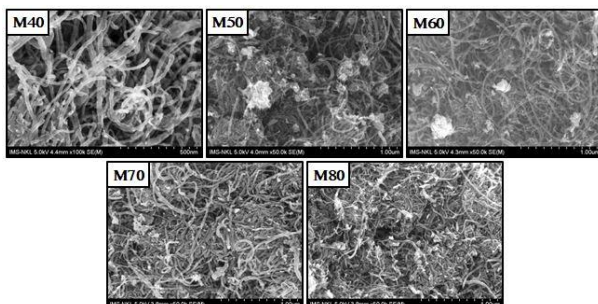


**Fig. 3.** XRD diagrams of bare CNTs, oxidized CNTs (M0.1 and M0.25).

**Effect of oxidation temperature and time.** The oxidation temperature was chosen through the investigation of five CNTs samples oxidized at different temperatures from 40 to 80 °C. The result shows that at temperatures from 50 to 80 °C, although the Cu<sup>II</sup> adsorption capacity of oxidized CNTs (Fig. 4) is equally high (around 102 mg.g<sup>-1</sup>), a large number of tubes are demolished, and the number of very short tubes increases with temperature (Fig. 5). At 40 °C, the material exhibits a rather high Cu<sup>II</sup> adsorption capacity (80.8 mg.g<sup>-1</sup>), and the tubes retain their length. Therefore, 40 °C was used for further CNTs oxidation.



**Fig. 4.** Effect of oxidation temperature on Cu<sup>II</sup> adsorption capacity of oxidized CNTs (*Experimental conditions:* mass of adsorbent is 0.01g; volume of oxidant is 25 mL; ultrasonic time is 3 hours; Cu<sup>II</sup> concentration is 20 mg.L<sup>-1</sup>).

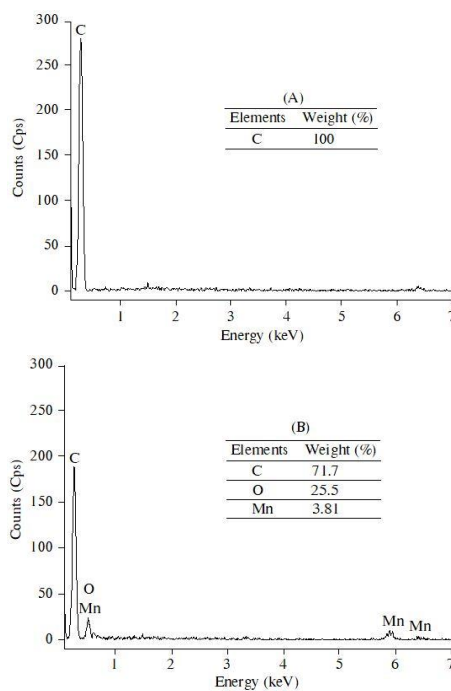


**Fig. 5.** SEM images of oxidized CNTs prepared at different oxidation temperatures.

With KMnO<sub>4</sub> concentration and at 40 °C, the obtained adsorbents exhibit a stable Cu<sup>II</sup> adsorption capacity (around 81 mg.g<sup>-1</sup>) when increasing ultrasonically treating time from 2 to 5 hours. Therefore, an ultrasonic treatment for 2 hours is used for oxidizing CNTs.

### 3.2. Characterization of oxidized CNTs

EDS analyses of bare and oxidized CNTs (Fig. 6) provide the evidence for the presence of carbon as the main component in the material, in which the bare sample consists of more carbon (100 %) than oxidized sample (71.7 %). This might be because oxygen and manganese appear in the oxidized sample. The amount of oxygen demonstrates that the functional groups containing oxygen appear on the surface of CNTs. A small amount of manganese might be a product of KMnO<sub>4</sub> reduction.



**Fig. 6.** EDS analyses of bare CNTs (A) and oxidized CNTs (B).

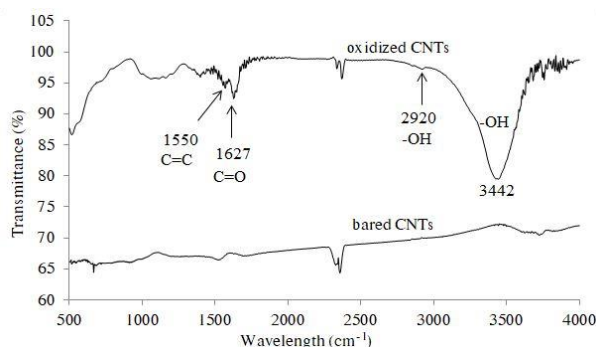


Fig. 7. FT-IR spectra of bare CNTs and oxidized CNTs

The formation of functional groups on CNTs was studied using FT-IR spectroscopy (Fig. 7). Many peaks/bands of oxygen-containing groups appear on the FT-IR spectrum. The band assigned to the -OH groups of carboxylic acid, alcohol and water appear at around 3442 and 2920  $\text{cm}^{-1}$ . Also, the C=O groups indicating the presence of -COOH appear at around 1627  $\text{cm}^{-1}$ . Li et al. [6], Moosa et al. [6] and Wang et al. [17] found the similar characteristic peaks/bands for the oxidized CNTs. A weak peak at around 1550  $\text{cm}^{-1}$  might be assigned to the C=C groups from graphite.

Fig. 8 and Fig. 9 show the FE-SEM and STEM images of bare CNTs and oxidized CNTs. The tube structure remains after the oxidation by acid. Unlike raw CNTs, some tubes become shorter reflecting partial damage by the oxidation of CNTs, which is also present in Raman spectra.

The Raman D band (D = disorder) locates at 1319  $\text{cm}^{-1}$  due to amorphous carbon and structural defects (Fig. 10); graphite structures are proved with G band (G = graphite) at 1567  $\text{cm}^{-1}$ . The G' band at 2642  $\text{cm}^{-1}$  is an overtone of the D band. The density of defects in the CNTs structure could be estimated via the ratio of integrated intensities of the D and G bands ( $I_D/I_G$ ). This means a larger value of the  $I_D/I_G$  and  $I_D/I_G$  ratios shows a higher defect density [9]. Fig. 10 shows that the values of  $I_D/I_G$  for the oxidized CNTs are larger than those for bare CNTs. As a result, the oxidation of CNTs surface indeed creates defects in its structure.

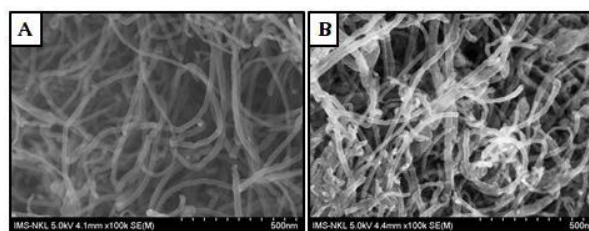


Fig. 8. SEM images of bare CNTs (A) and oxidized CNTs (B)

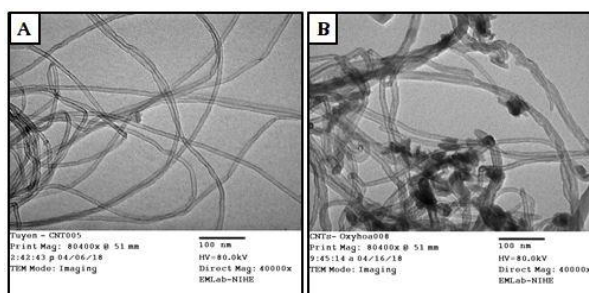


Fig. 9. TEM images of bare CNTs (A) and oxidized CNTs (B)

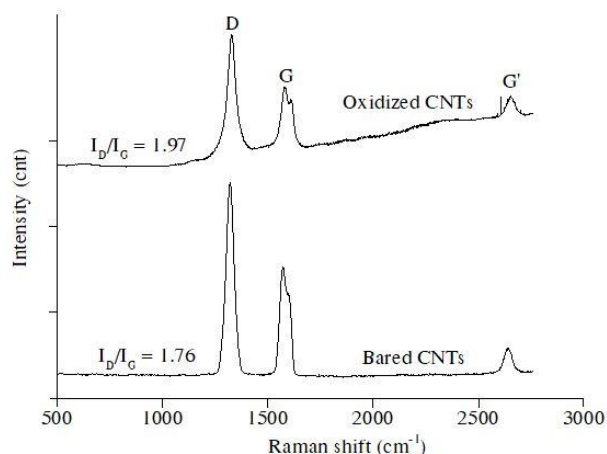


Fig. 10. Raman spectra of bare CNTs and oxidized CNTs.

The specific surface area of oxidized CNTs measured with the BET method is 137  $\text{m}^2\cdot\text{g}^{-1}$ , which is higher than that of raw CNTs (178  $\text{m}^2\cdot\text{g}^{-1}$ ). The rupture of CNTs indicates the formation of defects, for example, increased amounts of pentagon and heptagon defects, thereby enhancing the surface area [19].



### 3.3. Cu<sup>II</sup> adsorption onto oxidized CNTs

**Effect of pH.** The experimental data show that the increase of pH from 2 to 5 increases Cu<sup>II</sup> adsorption capacity from 52.4 to 84.7 mg·g<sup>-1</sup>. This trend might be the result of stronger acidity of –COOH and –OH groups locating on the surface of oxidized CNTs due to higher pH. This enhances the amount of H<sup>+</sup> dissociated from these groups and the surface of adsorbent is more negatively charged and favorable for attracting cations. The solution containing 20 mg·L<sup>-1</sup> Cu<sup>II</sup> has pH 4 and at this pH, Cu<sup>II</sup> adsorption capacity is rather high (80.2 mg·g<sup>-1</sup>) and comparable to that at pH 5 (84.7 mg·g<sup>-1</sup>). Therefore, pH 4 was kept for Cu<sup>II</sup> adsorption from aqueous solutions.

**Effect of oxidized CNTs (adsorbent) dosage.** The changes in Cu<sup>II</sup> adsorption efficiency depend on the CNTs dosage. With the Cu<sup>II</sup> initial concentration to 20 mg·L<sup>-1</sup>, a strong uptrend of Cu<sup>II</sup> adsorption efficiency is observed from 34.1 to 86.5 % when the dosage of oxidized CNTs increases from 0.08 to 0.2 g·L<sup>-1</sup>. Subsequently, Cu<sup>II</sup> adsorption efficiency rose slightly from 86.5 to 92.3 % when the dosage of oxidized CNTs increases to 1 g·L<sup>-1</sup>. Thus the suitable dosage of oxidized CNTs for Cu<sup>II</sup> removal is 0.2 g·L<sup>-1</sup>.

**Adsorption isotherm study.** The Langmuir and Freundlich isotherm models [15, 16] were used to evaluate the adsorption with non-linear equations as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

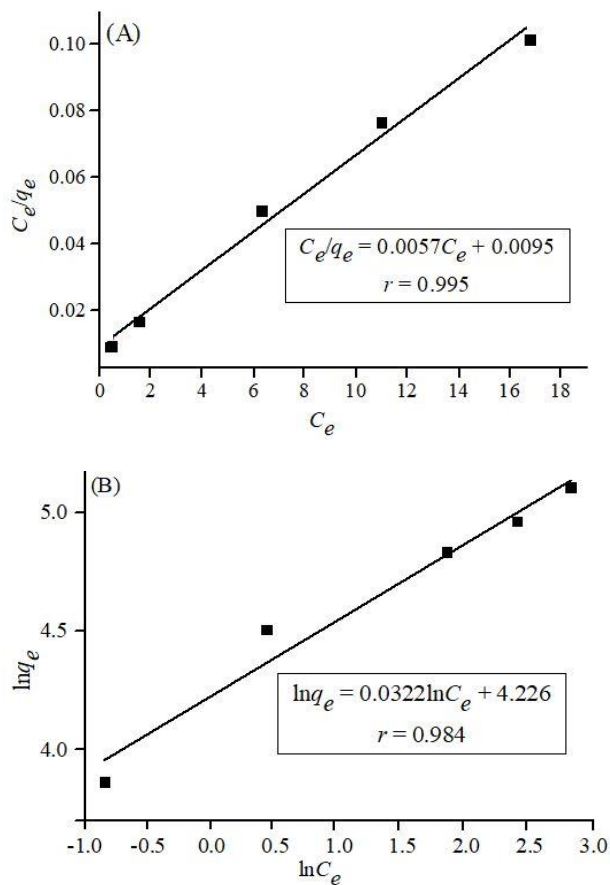
where  $C_e$  is the equilibrium concentration of Cu(II) in the solution after adsorption;  $q_e$  is the Cu(II) adsorption capacity of modified CNTs that is calculated from equation (1);  $q_m$  is maximum Cu(II) adsorption capacity;  $K_L$  is the Langmuir constant which is related to the strength of adsorption, an essential characteristic of

Langmuir isotherm can be expressed as a dimensionless constant called equilibrium parameter:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where  $C_0$  is the highest initial concentration of Cu(II); the value of  $R_L$  indicates the type of the isotherm;  $K_F$  and  $n$  are the Freundlich constants [20].

Fig. 11 illustrates the non-linear correlation between  $q_e$  and  $C_e$  corresponding to the Langmuir and Freundlich isotherm models. The correlation coefficient for the Langmuir model ( $r = 0.995$ ) is greater than that of the Freundlich model ( $r = 0.984$ ). This indicates that the adsorption is in the monolayer form, i.e., the experimental data are in agreement with the Langmuir model.



**Fig. 11.** Langmuir (A) and Freundlich (B) isotherm studies on Cu(II) adsorption

The equilibrium parameter ( $R_L$ ) value is 0.02 characterizing for the dimensionless constant calculated from the Langmuir model approximated to zero and is in the range from 0 to 1. The maximum Cu(II) adsorption capacity ( $q_m$ ) is 174.4 mg·g<sup>-1</sup>. The above result indicates that Cu(II) adsorption onto modified CNTs takes place favorably and irreversibly, with a good adsorption capacity for this sorbent.

## 4 Conclusions

Carbon nanotubes oxidized with KMnO<sub>4</sub> are a good sorbent for the removal of Cu<sup>II</sup> from aqueous solutions. The suitable conditions for ultrasonic oxidizing CNTs are 40 °C, 2 hours, KMnO<sub>4</sub> concentration of 0.1 M. The oxidation with KMnO<sub>4</sub> forms functional groups containing oxygen and increases the surface area and defects on the surface of CNTs, which is favourable for heavy metals adsorption. The obtained CNTs exhibit high Cu<sup>II</sup> adsorption with a maximum adsorption capacity of 174.4 mg·g<sup>-1</sup>.

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