

# Adsorption of Cu<sup>2+</sup> Ions From Aqueous Solutions Using Oxidized Multi-Walled Carbon Nanotubes

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Copper ion (Cu<sup>2+</sup>) is one of the heavy metal ions that cause environmental pollution specifically in water. Copper ion cations are not biodegradable and tend to cumulate in living organisms. Consequently, the removal of Cu<sup>2+</sup> in environmental samples plays an important role in environmental pollution monitoring. The purpose of the present work was to prepare oxidized Multi-Walled Carbon Nano Tubes (MWCNTs) for removal of Cu<sup>2+</sup> ions from aqueous solutions. This study was conducted under laboratory conditions. Multi-Walled Carbon Nano Tubes were oxidized and characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and the Brunauer, Emmett, and Teller (BET) methods. The effects of various factors, such as solution pH (3-9), adsorbent dose (0.006-0.06 g) and contact time (10-120 minutes) were investigated. Results showed that the suitable pH for Cu<sup>2+</sup> ions removal was about 6.0, and the optimal dose was 0.03 g. Isotherm studies indicated that the Langmuir model fits the experimental data better than the Freundlich model. Maximum Cu<sup>2+</sup> adsorption capacity was calculated as 200 mg g<sup>-1</sup>. The kinetics of the adsorption process was tested for the pseudo-first-order and pseudo-second-order models. The comparison among the models showed that the pseudo-second order model best described the adsorption kinetics. The results showed that oxidized MWCNTs can be used as a low cost adsorbent for the removal of Cu<sup>2+</sup> ions from aqueous solutions.

**Keywords:** Adsorption; Copper; Oxidized Multi-Walled Carbon Nanotube; Removal Efficiency

## 1. Introduction

Heavy metals are contaminants with potential toxicity for living organisms, when present above their permissible concentrations. In developing countries where industries such as metal plating, mining, tanning, and the manufacturing of fertilizers, batteries, paper and pesticides are growing, it is common for wastewaters containing heavy cations to be expelled into the environment. These ions are a hazard to public health and the environment when discharged inappropriately (1-3). Copper is one of the most significant heavy metals, often found in different effluents (4). Conventional methods for removal of heavy metals ions from aqueous solutions principally include chemical precipitation, ion-exchange, reverse osmosis and adsorption (5, 6). Adsorption is a simple, effective, and economical method for contaminants remediation (7). Activated carbon is a commonly used adsorbent for the removal of pollutants present in ground water and wastewaters. In spite of its effectiveness in the removal of heavy metals from wastewaters, the high cost of activated carbon has restricted its widespread use (8).

Recently, Carbon Nanotubes (CNTs) have been increasingly applied for environmental protection as novel materials due to their strong adsorption affinity for heavy metals (9, 10). Carbon Nanotubes mainly include Single-Walled (SWCNTs) and Multi-Walled (MWCNTs)

Carbon Nanotubes. These CNTs are considered a superior adsorbent for potential environmental remediation due to their large surface area and high reactivity (11-13). The adsorption capacity of CNTs can be improved by oxidation with KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, NaOCl or HNO<sub>3</sub>, which removes impurities, increases the surface area, and introduces oxygen-containing functional groups, thus altering adsorption characteristics (14).

The aim of the present work was to investigate the removal of Cu<sup>2+</sup> ions from aqueous solutions by adsorption with oxidized MWCNTs from a kinetic and equilibrium point of view. The effects of pH, adsorbent dose and contact time on the adsorption efficiency were studied as well.

## 2. Materials and Methods

All chemicals used in this study were of analytical reagent grade purchased from Merck (Darmstadt, Germany). Multi-Walled Carbon Nanotubes with length of 5-15 μm, outer diameter of 50-80 nm, inner diameters of 5-10 nm, and purity of ≥95 were purchased from Sigma-Aldrich (Madrid, Spain). Stock solution (1000 mg L<sup>-1</sup>) of Cu<sup>2+</sup> were prepared by dissolving Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in double-distilled water. Working standard solutions were prepared by diluting the stock solution in appropriate proportions.

The concentration of metal ions was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (JY138 ulttrace, France). A Metrohm model 713 pH-meter (Swiss) was used for pH measurements.

Morphology and structure of the oxidized MWCNTs was characterized by a scanning electron microscope (SEM-EDX, XL30, Philips Netherland). Fourier Transform Infrared Spectroscopy (FTIR) (4000 – 400  $\text{cm}^{-1}$ ) in KBr were recorded on Perkin Elmer, spectrum100, FTIR spectrometer. The specific surface area was defined by  $\text{N}_2$  adsorption-desorption porosimetry (77 K) using a porosimeter (Bel, Japan, Inc., Tokyo).

### 2.1. Oxidation of Multi-Walled Carbon Nanotubes

For oxidation, 2 g of MWCNTs were placed in a 1 L round bottom flask with reflux condenser and 300 mL of concentrated nitric acid (65%) was added. The mixture was refluxed for 48 hours at 120°C, cooled to room temperature, diluted with 500 mL of double-distilled water, and vacuum-filtered through filter paper (3 mm porosity, Whatman, Maidstone, UK). Washing was repeated until the pH became neutral, followed by drying in a vacuum oven at 100°C (15).

### 2.2. Batch Adsorption Experiments

Batch adsorption experiments were performed by adding 0.03 g of oxidized MWCNTs to 15 mL of  $\text{Cu}^{2+}$  solution (50 – 400  $\text{mg L}^{-1}$ ) in 25 mL stoppered conical flask. The pH of the solution was adjusted to optimum values using 0.1 mol  $\text{L}^{-1}$  HCl and/or 0.1 mol  $\text{L}^{-1}$  NaOH. The mixture was shaken for 75 minutes and the  $\text{Cu}^{2+}$  ions-loaded oxidized MWCNTs were separated and the concentrations of the metal, which remained in the solution was determined by Inductively Coupled Plasma Spectrometry (Verian710-Es Australia) and the concentration of the  $\text{Cu}^{2+}$  ions that remained in the adsorbent phase ( $q_e$ ,  $\text{mg g}^{-1}$ ) was calculated using the Equation:

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

Where  $C_0$  and  $C_e$  are the initial and equilibrium  $\text{Cu}^{2+}$  concentration in solution, respectively ( $\text{mg L}^{-1}$ ),  $V$  (L) is the volume of solution and  $W$  (g) is the weight of adsorbent. Finally, the  $\text{Cu}^{2+}$  removal efficiency was calculated by the Equation:

$$(2) \quad R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

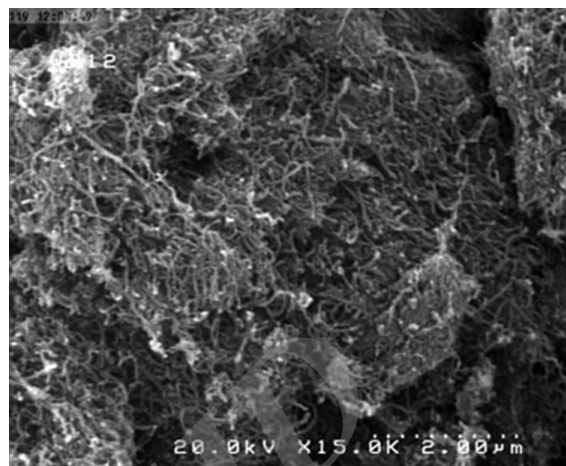
Where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) were the initial and final  $\text{Cu}^{2+}$  concentrations.

## 3. Results and Discussion

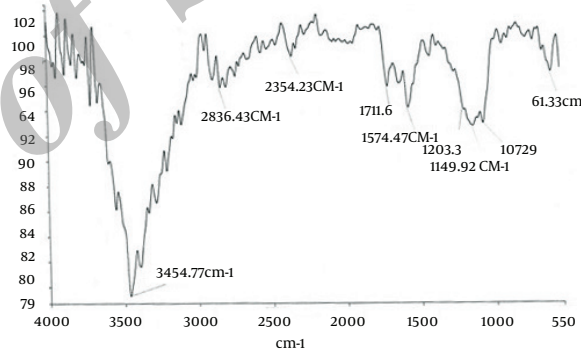
Figure 1 shows the morphological structure of oxidized MWCNTs. Figure 2 shows the FTIR spectrum of oxidized MWCNTs.

The effect of initial pH on the  $\text{Cu}^{2+}$  ions removal was studied at a pH range of 3.0 – 9.0 with initial metal concen-

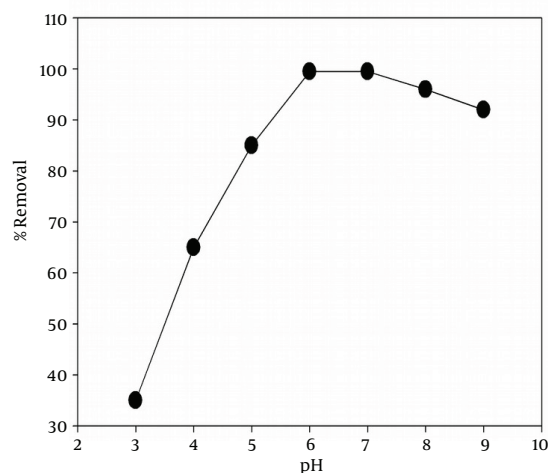
tration of 50  $\text{mg L}^{-1}$  and adsorbent dose of 0.03 g. The results are shown in Figure 3. As can be seen from the figure,



**Figure 1.** Scanning Electron Microscope Image of Oxidized Multi-Walled Carbon Nanotubes



**Figure 2.** Fourier Transform Infrared Spectroscopy Spectrum of Oxidized Multi-Walled Carbon Nanotubes



**Figure 3.** Effect of pH on the Removal of  $\text{Cu}^{2+}$  From Aqueous Solution by Oxidized Multi-Walled Carbon Nanotubes  $C_0 = 50 \text{ mg L}^{-1}$ , contact time = 75 minutes, dose of oxidized MWCNTs = 0.03 g, temperature = 25°C.

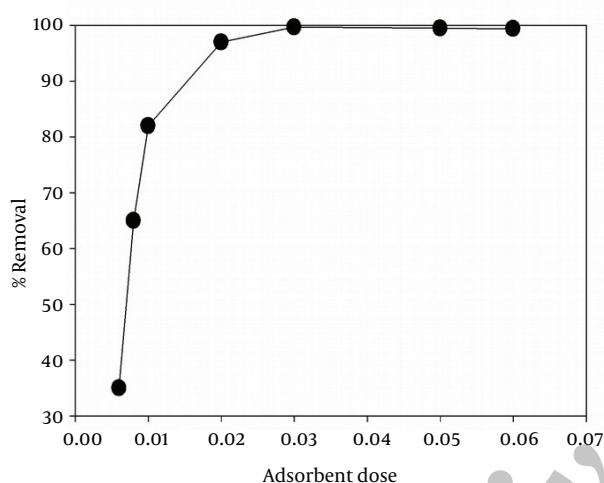
adsorption amount of the metal ions increased with increase of pH values up to 6.0, and then reduced gradually.

The effect of the adsorbent dose (varying from 0.006 to 0.06 g) on  $\text{Cu}^{2+}$  ions removal was investigated at  $25^\circ\text{C}$  (Figure 4). The results showed that the adsorption effectiveness increased with an increase in the adsorbent dose from 0.006 to 0.03 g. Therefore, 0.03 g was chosen as the optimum adsorbent dose for the following experiments.

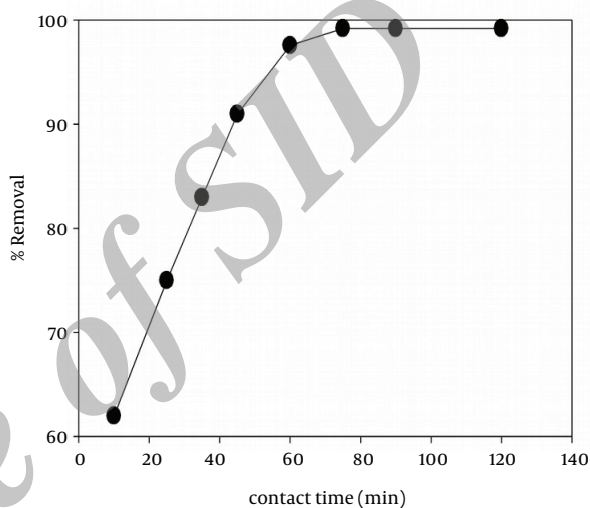
The effect of contact time was investigated in the time range of 10 - 120 minutes under pH 6.0 at  $25^\circ\text{C}$ . Figure 5 shows the effect of contact time on the removal of  $\text{Cu}^{2+}$  ions. The figure reveals that increased agitation time

increased the uptake of  $\text{Cu}^{2+}$  and attained equilibrium after 75 minutes.

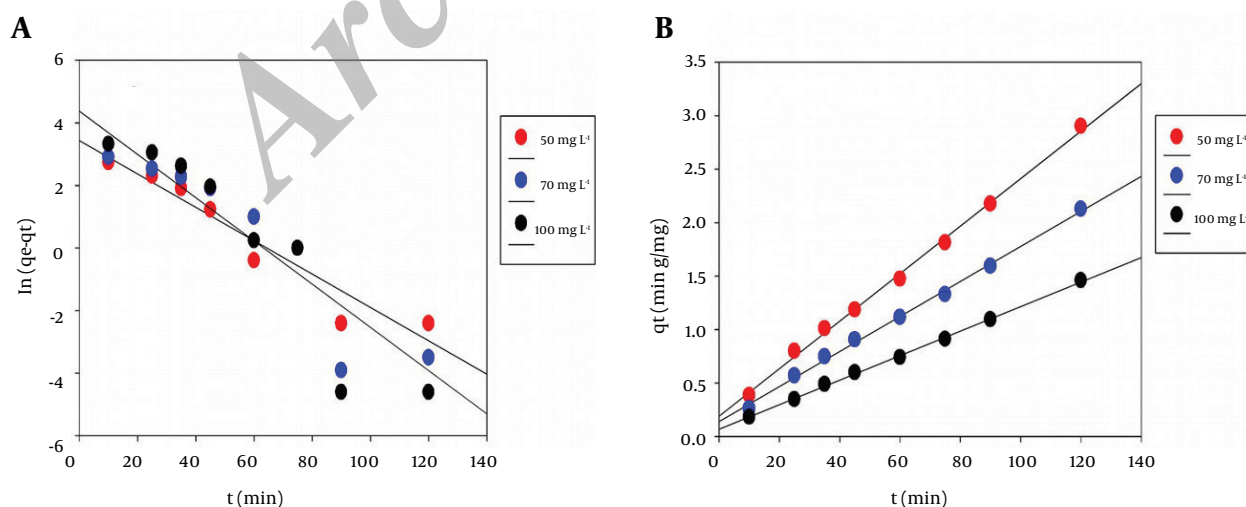
A kinetic study for adsorption is very important because it provides information about efficiency and the possibility of the expansion of a process. To investigate the kinetics of adsorption, three different initial concentrations of  $\text{Cu}^{2+}$  ions were chosen, 50, 70 and  $100 \text{ mg L}^{-1}$ . In this study, two kinetic models (pseudo-first order equation and pseudo-second order equation) were applied. Figure 6 shows the adsorption kinetic data of  $\text{Cu}^{2+}$  ions onto oxidized MWCNTs. The obtained data and the correlation coefficients,  $r^2$ , are given in Table 1.



**Figure 4.** Effect of Dose of Oxidized Multi-Walled Carbon Nanotubes on the Removal of  $\text{Cu}^{2+}$   $C_0 = 50 \text{ mg L}^{-1}$ , initial pH = 6.0, contact time = 75 minutes, temperature =  $25^\circ\text{C}$



**Figure 5.** Effect of Contact Time on the Removal of  $\text{Cu}^{2+}$  by Oxidized Multi-Walled Carbon Nanotubes  $C_0 = 50 \text{ mg L}^{-1}$ , initial pH = 6.0, dose of oxidized MWCNTs = 0.03 g, temperature =  $25^\circ\text{C}$



**Figure 6.** A, Pseudo-First-Order Kinetic Plot and B, Pseudo-Second-Order Kinetic Plot for the Adsorption of  $\text{Cu}^{2+}$  Ions Onto Oxidized Multi-Walled Carbon Nanotubes at  $25^\circ\text{C}$

In order to obtain insight into the possible mechanisms for removing  $\text{Cu}^{2+}$  ions from aqueous solution onto oxidized MWCNTs, the adsorption equilibrium data were analyzed using Langmuir and Freundlich models. The fitting parameters of these two models are shown in Table 2. The Langmuir and Freundlich adsorption isotherms are presented in Figure 7.

Figure 1 shows the morphological structure of oxidized MWCNTs. Scanning Electron Microscope clearly suggests the crystalline tubular structure of nanotubes. Figure 2 shows the FTIR spectrum of oxidized MWCNTs, indicating that the acid treatment process introduces new functional groups. The peak at  $3464.22\text{ cm}^{-1}$ ,  $1574.47\text{ cm}^{-1}$  and  $1711.6\text{ cm}^{-1}$  are attributed to the hydroxyl groups, carboxyl groups and carbonyl groups. These functional groups provide a large number of chemical adsorption sites and

thereby can increase the adsorption capacity of oxidized MWCNTs.

Specific surface areas are commonly reported as BET surface areas obtained by applying the theory of Brunauer, Emmett, and Teller (BET) to nitrogen adsorption/desorption isotherms measured at 77 K. This is a standard procedure for the determination of the specific surface area of a sample. The specific surface area of a sample is determined by physical adsorption of a gas on the surface of the solid and by measuring the amount of adsorbed gas corresponding to monomolecular layer on the surface. The data were treated according to the BET theory (16, 17).

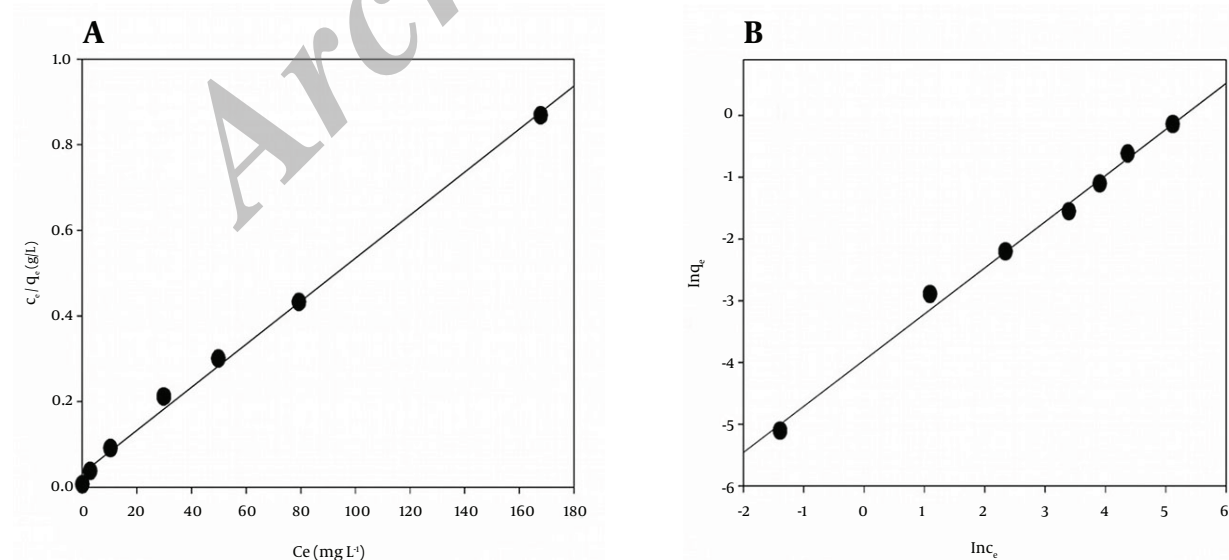
The results of the BET method showed that the specific surface areas (SSA) of MWCNTs and oxidized MWCNTs were  $115\text{ m}^2\text{ g}^{-1}$  and  $158\text{ m}^2\text{ g}^{-1}$ , respectively.

**Table 1.** Pseudo-First Order and Pseudo-Second Order Kinetic Model Parameters for the Adsorption of  $\text{Cu}^{2+}$  ions Onto Oxidized Multi-Walled Carbon Nanotubes

$\text{C}_0, \text{mg L}^{-1}$	Pseudo-first-Order Kinetic Model				Pseudo-Second-Order Kinetic Model		
	$q_{e, \text{exp}}, \text{mg g}^{-1}$	$q_{e1}, \text{mg g}^{-1}$	$k_1, \text{min}^{-1}$	$r^2$	$q_{e2}, \text{mg g}^{-1}$	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	$r^2$
50	42.34	31.15	0.053	0.918	45.04	0.002	0.997
70	57.36	79.67	0.069	0.8663	60.97	0.000	0.997
100	82.11	161.7	0.084	0.894	86.95	0.001	0.998

**Table 2.** Isotherm Parameters of Adsorption of  $\text{Cu}^{2+}$  ions Onto Oxidized Multi-Walled Carbon Nanotubes

	Langmuir			Freundlich		
	$B, \text{L mg}^{-1}$	$q_m, \text{mg g}^{-1}$	$r^2$	$K_f, \text{g}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$	$n$	$r^2$
$\text{Cu}^{2+}$	0.153	200	0.996	60.94	1.32	0.986



**Figure 7.** A, Langmuir and B, Freundlich Isotherms for  $\text{Cu}^{2+}$  Adsorption Onto Oxidized Multi-Walled Carbon Nanotubes

Pore size distributions of MWCNTs and oxidized MWCNTs were measured using the Barrett, Joyner and Halenda (BJH) method. The average pore diameter, and pore volume were 29 nm and  $0.17 \text{ cm}^3 \text{ g}^{-1}$  for MWCNTs, and 36 nm and  $0.24 \text{ cm}^3 \text{ g}^{-1}$  for oxidized MWCNTs, respectively.

The results indicated that the pore volume and average pore diameter of MWCNTs were less than oxidized MWCNTs. This can be comprehended considering the structure change of oxidized MWCNTs with nitric acid, which can easily break up the MWCNTs into smaller pieces with large amounts of defects on their surface, and open the tips and probe the holes through the MWCNTs.

The initial pH of the solution is one of the important factors controlling the adsorption of metal ions onto suspended particles by affecting the surface charge of the adsorbents as well as the degree of ionization of the adsorbate. It can be seen from Figure 3 that the removal of metal ions increases with an increase in pH of the solution to attain a maximum at pH 6.0 and thereafter it decreases when pH of the solution reaches up to 7.0. The maximum removal of  $\text{Cu}^{2+}$  at pH 6.0 was found to be 99.5%. The zero point charge ( $\text{pH}_{\text{zpc}}$ ) for the oxidized MWCNTs was determined around 5.0. This phenomenon appears to be due to the fact that at  $\text{pH} > \text{pH}_{\text{zpc}}$  the surface charge of oxidized MWCNTs becomes negative and the electrostatic interactions between the metal ions and adsorbent become stronger. Also the increase in  $\text{Cu}^{2+}$  ions removal with an increase in pH can be explained on the basis of a decrease in competition between protons and  $\text{Cu}^{2+}$  cations for the same functional groups. The decrease in adsorption at higher pH (above pH 7.0) is probably because the pH may affect the ionization degree of the adsorbate and the surface property of the adsorbent. Similar results have been found by Mariussen et al. (18).

The adsorbent dose is another important parameter because it has a direct relationship with the uptake capacity of an adsorbent for a given concentration of metal at the optimum conditions. As can be observed from Figure 4, removal efficiency was increased from 35% to 99.6%, by increasing the amount of oxidized MWCNTs from 0.006 to 0.03 g. This observation can be explained by the greater number of adsorption sites made available at greater oxidized MWCNTs dosages. A similar phenomenon has also been shown in the adsorption of Cu (II) from water with amino-functionalized mesoporous  $\text{Fe}_3\text{O}_4$  nanoparticles (19).

Contact time is one of the significant parameters for successful use of the adsorbents for practical applications. As can be seen from Figure 5,  $\text{Cu}^{2+}$  ions adsorption increases with contact time and gradually reaches equilibrium after 75 minutes. Rapid adsorption is observed within 60 minutes due to the availability of a large number of vacant sites. Subsequently, the diminishing availability of active sites and the decrease in the driving force lead to a slow adsorptive process. Similar results were observed by Zhao who investigated the effect of contact time on removal of  $\text{Cu}^{2+}$  from aqueous solution by Gra-

phene sponge and indicated that adsorption increases with increasing contact time (20).

The prediction of adsorption rate gives crucial information for designing sustainable batch adsorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch processes. In order to evaluate the kinetic mechanism that controls the adsorption process, the experimental data was analyzed using pseudo-first-order and pseudo-second-order models. The pseudo-first-order model and pseudo-second-order model Equations are presented in Equations (3) and (4), respectively (21, 22).

$$(3) \quad \ln(q_e - q_t) = \ln(q_e) - \frac{k_2 t}{2.303}$$

$$(4) \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where  $q_e$  and  $q_t$  are the amount of  $\text{Cu}^{2+}$  ions adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and time  $t$  (minutes);  $k_1$  is the rate constant of pseudo-first-order ( $\text{minute}^{-1}$ );  $k_2$  is the rate constant of pseudo-second-order ( $\text{g mg}^{-1} \text{ minute}^{-1}$ ) for adsorption. The correlation coefficients ( $r^2$ ) for pseudo-second-order model are all higher than for the pseudo-first-order model (Figure 6) and the experimental data fit the pseudo-second-order model better than the pseudo-first-order model (Table 1). Also  $q_e$  value agreed with the calculated values ( $q_{e\text{exp}}$ ), indicating a good fit of the adsorption process to this model. The results indicate that chemical adsorption might be the rate-limiting step.

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. The equilibrium data was fitted by conventionally and traditionally known models such as Langmuir (Equation 5) and Freundlich (Equation 6). The linear Equations were as follows (23, 24):

$$(5) \quad \frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b_1}$$

$$(6) \quad \ln q_e = \frac{1}{n} \ln C_e + \ln K_f$$

Where  $c_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{Cu}^{2+}$  ions in solution,  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorption capacity of oxidized MWCNTs,  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity of oxidized MWCNTs for monolayer coverage,  $b$  ( $\text{L mg}^{-1}$ ) is a constant related to the adsorption free energy,  $K_f$  ( $\text{mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}$ ) is a constant related to adsorption capacity, and  $n$  is an empirical parameter related to adsorption.

The correlation coefficients ( $r^2$ ) for Langmuir and Freundlich model were 0.996 and 0.986, respectively. The good agreement between the adsorption data and Langmuir model implies that the adsorption of  $\text{Cu}^{2+}$  on oxidized MWCNTs occurred as a single monolayer.

## 4. Conclusion

In summary, we have successfully prepared oxidized MWCNT for Cu<sup>2+</sup> ions removal from aqueous solutions. The results demonstrated that the adsorption of Cu<sup>2+</sup> on oxidized MWCNT was strongly dependent on pH and the amount of adsorption increased with an increase of adsorbent dose. The equilibrium data well fitted the Langmuir adsorption isotherms and the maximum adsorption capacity of Cu<sup>2+</sup> reached 200 mg g<sup>-1</sup> for oxidized MWCNT indicating that adsorption occurs on a homogeneous surface by monolayer adsorption without interaction between the adsorbed ions. Also, the kinetic study showed that the pseudo-second-order model was appropriate to describe the adsorption process.

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## References

1. Sheela T, Nayaka YA, Viswanatha R, Basavanna S, Venkatesha TG. Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. *Powder Tech.* 2012;**217**:163–70.
2. Gupta VK, Nayak A, Agarwal S, Chaudhary M, Tyagi I. Removal of Ni (II) ions from water using scrap tire. *J Mole Liquid.* 2014;**190**:215–22.
3. Wang H, Yuan X, Wu Y, Huang H, Zeng GM, Liu Y, et al. Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution. *Appl Surface Sci.* 2013;**279**:432–40.
4. Wang XS, Zhu L, Lu HJ. Surface chemical properties and adsorption of Cu (II) on nanoscale magnetite in aqueous solutions. *Desalination.* 2011;**276**(1-3):154–60.
5. Guo W, Meng X, Liu Y, Ni L, Hu Z, Chen R, et al. Synthesis and application of 8-hydroxyquinoline modified magnetic mesoporous carbon for adsorption of multivalent metal ions from aqueous solutions. *J Indust Engin Chem.* 2015;**21**:340–9.
6. Kaprara E, Seridou P, Tsiamilis V, Mitrakas M, Vourlias G, Tsiaoussis I, et al. Cu-Zn powders as potential Cr(VI) adsorbents for drinking water. *J Hazard Mater.* 2013;**262**:606–13.
7. Boparai HK, Joseph M, O'Carroll DM. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *J Hazard Mater.* 2011;**186**(1):458–65.
8. Hameed BH, El-Khalary MI. Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K<sub>2</sub>CO<sub>3</sub> activation and subsequent gasification with CO<sub>2</sub>. *J Hazard Mater.* 2008;**157**(2-3):344–51.
9. Yu F, Ma J, Wu Y. Adsorption of toluene, ethylbenzene and m-xylene on multi-walled carbon nanotubes with different oxygen contents from aqueous solutions. *J Hazard Mater.* 2011;**192**(3):1370–9.
10. Chiang YC, Wu PY. Adsorption equilibrium of sulfur hexafluoride on multi-walled carbon nanotubes. *J Hazard Mater.* 2010;**178**(1-3):729–38.
11. Gupta VK, Agarwal S, Saleh TA. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J Hazard Mater.* 2011;**185**(1):17–23.
12. Gong JL, Wang B, Zeng GM, Yang CP, Niu CG, Niu QY, et al. Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *J Hazard Mater.* 2009;**164**(2-3):1517–22.
13. Madrakian T, Afkhami A, Ahmadi M, Bagheri H. Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. *J Hazard Mater.* 2011;**196**:109–14.
14. Sheng GD, Shao DD, Ren XM, Wang XQ, Li JX, Chen YX, et al. Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. *J Hazard Mater.* 2010;**178**(1-3):505–16.
15. Atieh MA, Bakather OY, Al-Tawbini B, Bukhari AA, Abuilaiwi FA, Fettouhi MB. Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. *Bioinorg Chem Appl.* 2010:603978.
16. Walton KS, Snurr RQ. Applicability of the BET method for determining surface areas of microporous metal-organic frameworks. *J Am Chem Soc.* 2007;**129**(27):8552–6.
17. Brunauer S, Emmett PH, Teller E. Adsorption of Gases in Multimolecular Layers. *J Am Chem Society.* 1938;**60**(2):309–19.
18. Mariussen E, Johnsen IV, Stromseng AE. Selective adsorption of lead, copper and antimony in runoff water from a small arms shooting range with a combination of charcoal and iron hydroxide. *J Environ Manage.* 2015;**150**:281–7.
19. Xin X, Wei Q, Yang J, Yan L, Feng R, Chen G, et al. Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *Chem Engin J.* 2012;**184**:132–40.
20. Zhao L, Yu B, Xue F, Xie J, Zhang X, Wu R, et al. Facile hydrothermal preparation of recyclable S-doped graphene sponge for Cu<sup>2+</sup> adsorption. *J Hazard Mater.* 2015;**286**:449–56.
21. Azizian S. Kinetic models of sorption: a theoretical analysis. *J Colloid Interface Sci.* 2004;**276**(1):47–52.
22. Venkatesha TG, Viswanatha R, Arthoba Nayaka Y, Chethana BK. Kinetics and thermodynamics of reactive and vat dyes adsorption on MgO nanoparticles. *Chem Engin J.* 2012;**198-199**:1–10.
23. Langmuir I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J Am Chem Society.* 1918;**40**(9):1361–403.
24. Freundlich H, Heller W. The Adsorption of cis- and trans-Azobenzene. *J Am Chem Society.* 1939;**61**(8):2228–30.