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Magnetite nanoparticles decorated on multi-walled carbon nanotubes for removal of Cu^{2+} from aqueous solution

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ABSTRACT

Acid-functionalized multi-walled carbon nanotube (MWCNTs-COOH) was prepared by acid treatment followed by decoration with magnetite (Fe$_3$O$_4$) nanoparticles (Fe$_3$O$_4$/MWCNTs-COOH) by co-precipitation of Fe^{2+}/Fe^{3+} in the colloidal suspension of MWCNTs-COOH. The adsorption capacity and separation efficiency of these two adsorbents were investigated for the removal of Cu^{2+} ions in aqueous solution as water treatment adsorbents. The effect of reaction conditions, such as contact time, initial concentration of Cu^{2+} ions, and adsorbent dosage, on the adsorption capacity of MWCNTs-COOH was investigated. It was found that contact time of 10 min, adsorbent dosage of 0.2 g/L and 15 mg/L as initial concentration of Cu^{2+} ions are ideal conditions for maximum adsorption capacity (10.45 mg/g). The adsorption capacity of synthesized Fe$_3$O$_4$/MWCNTs-COOH containing different weight percent of Fe$_3$O$_4$ (10, 25, 50 wt%) was explored for removal of Cu^{2+} ions from aqueous solution and the best results achieved with 25 wt% Fe$_3$O$_4$/MWCNTs-COOH, which exhibited optimum adsorption capacity of 9.50 mg/g and 97% separation efficiency. Further, Langmuir and Freundlich isotherm models were applied to validate experimental data obtained in this work for Cu^{2+} adsorption.
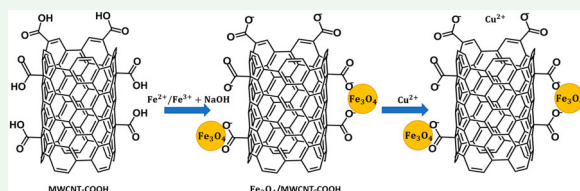
1. Introduction

The removal of heavy metal ions from industrial waste water is of great interest in the field of waste water treatment. Copper ion (Cu^{2+}) is one of the major heavy metal ions involved in an electroplating process and a greater chance of getting released into water as contaminants [1]. Several methods have been adopted commercially for the removal of metal ions such as chemical precipitation, ion-exchange, reverse osmosis, adsorption, etc [2]. Adsorption is a simple, effective, and economical way for the removal of toxic contaminants [3] using materials such as zeolites [4], metal-organic frameworks (MOFs) [5], and carbon-based nanomaterials [6]. Researchers continue to explore new adsorbents with higher adsorption capacities and efficiencies. Carbon nanotubes (CNTs) are considered as promising candidate due to their large surface area and strong adsorption affinity, which can be increased by a simple treatment with oxidizing agents [7] such

as KMnO$_4$, H$_2$O$_2$, and HNO$_3$. These oxidizing agents can remove impurities and introduce oxygen-containing functional groups [8]. However, CNTs cannot be easily separated from solution through conventional filtration and centrifugation processes, due to their small sizes. The use of magnetic separation method may offer an alternative way to solve this problem if CNTs is modified as magnetic adsorbent, which can be conveniently collected from wastewater by applying an external magnetic field [9]. Moreover, the magnetic separation method is an efficient, fast, and economical method for the separation of magnetic adsorbents from media after completing the adsorption treatment of pollutants [10], compared to filtration and centrifugation methods.

To improve the adsorption properties as well as separation efficiency, functional groups and/or metal and metal oxide nanoparticles attached to CNTs surfaces. In recent years, metal oxide/carbon nanotube

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nanocomposites have been extensively studied and found to be effective adsorbent for the removal of heavy metal ions from wastewater [11]. In addition, MOF–CNT composites have also been reported with enhanced adsorption capacity and reusability [12]. Among a wide variety of metal oxide nanoparticles, Fe_3O_4 nanoparticles are particularly attractive due to their unique magnetic properties [13]. Chen et al. reported a novel method of synthesis of magnetic nanoparticles (Fe_3O_4/CNTs) for efficient removal of Cr(VI) from aqueous solution. The Fe_3O_4/CNTs had high efficient magnetic separation at low magnetic field gradients [14]. Cun-Ku et al. reported a simple and effective chemical method to decorate acid-treated MWCNTs (AMWCNT) with Fe_3O_4 nanoparticles and explored the sorption property of AMWCNTs/Fe_3O_4 composites for the removal of 2,4-dichlorophenol (2,4-DCP) and Cu^{2+} ions from aqueous solution [15]. AMWCNTs/Fe_3O_4 exhibited greater efficiency in removal of Cu^{2+} ions due to the magnetism of Fe_3O_4 compared to pristine AMWCNTs. Suwattanamala et al. [16] prepared Fe_3O_4 nanoparticles decorated on acid-functionalized MWCNTs and investigated their sorption properties for the removal of methylene blue in aqueous solution. The experiments demonstrated that Fe_3O_4 /MWCNT nanoparticles can be conveniently employed for contaminant removal process efficiently. Yang et al. [17] also reported on the removal of Cu^{2+} ion by magnetic Fe_3O_4/CNTs, which were prepared by the co-precipitation method. The influence of percentage of Fe_3O_4 loading was investigated in the range 35.5–64.1 wt%. The results revealed that an optimum loading of Fe_3O_4 nanoparticles on the CNT support improved not only adsorption capacity but also regeneration efficiency.

The aim of the present work is to investigate adsorption properties and separation efficiency of Fe_3O_4 nanoparticles decorated on acid-functionalized MWCNT for the removal of Cu^{2+} ions from aqueous solution. The effect of reaction conditions, such as contact time between adsorbent and Cu^{2+} ions in aqueous solution, amount of adsorbent, and initial concentration of Cu^{2+} ions in aqueous solution, on adsorption capacity were also studied. Further, the effect of weight percent of Fe_3O_4 in Fe_3O_4/MWCNTs-COOH on adsorption capacity as well as separation efficiency was evaluated for optimizing Fe_3O_4 content. Further, to check the validity of experimental data in this work for Cu^{2+} adsorption, both Langmuir and Freundlich isotherm models were employed. Based on experimental results to arrive at optimum reaction conditions and wt% of Fe_3O_4 to achieve maximum adsorption capacity for removal of Cu^{2+} ions along with the easy and convenient separation of adsorbent from the aqueous solution.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) were purchased from Bayer material sciences. All reagents and solvents were used without further purification. Standard solution of Cu^{2+} ion (1000 ppm) was purchased from Carlo Erba.

2.2. Synthesis of acid-functionalized MWCNT (MWCNTs-COOH)

MWCNTs-COOH was prepared by oxidization of MWCNT in HNO_3. 1.0 g of MWCNTs was dispersed in 75 mL of concentrated HNO_3 and heated at 100°C for 8 h. The oxidized MWCNTs was filtered and washed until the filtrate became neutral. Finally, the obtained MWCNTs-COOH was dried in the oven at 100°C for 24 h.

2.3. Synthesis of Fe₃O₄ nanoparticles decorated on MWCNT-COOH (Fe₃O₄/MWCNTs-COOH)

Typically, 0.12 g of synthesized MWCNTs-COOH was dispersed in 12.5 mL of mixed solution of $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$. The suspension was stirred under N_2 atmosphere. Then, 50 mL of aqueous solution of sodium hydroxide (1 M) was slowly added into the suspension under stirring. After stirring for 2 h, the product was separated from the mixture using magnet. The black solid separated from the mixture was washed by distilled water several times until neutral pH. The obtained Fe_3O_4/MWCNTs-COOH was dried under N_2 atmosphere.

2.4. Characterization

The particle size and dispersion of Fe_3O_4 nanoparticles on MWCNTs-COOH nanotubes were investigated by Transmission Electron Microscope (TEM, Philips TECNAI 20). The percentage of Fe_3O_4 loading was determined by SEM/EDX analysis (LEO 1450 VP, Oxford Instrument). Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) was recorded on Perkin Elmer, Model 200. Magnetic properties were analyzed using a Vibrating Sample Magnetometer (VSM, VersaLab). The concentration of metal ions in aqueous solution was determined by Flame Atomic Absorption Spectrometer (PinAAcle 900F, USA) in the absorbance mode at $\lambda =$ 324.75 nm using air/acetylene. Each measurement was performed at least duplicate and the average values were presented.

2.5. Batch adsorption experiment

Batch adsorption experiment was employed to evaluate Cu^{2+} adsorption onto MWCNTs-COOH. The effect of various parameters such as contact time (0–60 min), amount of MWCNTs-COOH, i.e. adsorbent dose (0.05–0.4 g/L) and initial concentration of Cu^{2+} ions (2–20 mg/L) were on Cu^{2+} adsorption were investigated. In 250 mL stoppered conical flask, 0.020 g of MWCNTs-COOH was re-dispersed in 100 mL of water using an ultrasonic bath. Then, 10 mL of an aqueous solution of Cu^{2+} ions (of desired initial concentration) was added. The suspension was shaken at $25 \pm 1°C$ for different periods (i.e. contact time). The Cu^{2+} loaded-sorbents were separated from the solution by filtration using a membrane filter. The concentration of metal ions remained in the solution was determined by Flame Atomic Absorption Spectrometer.

The percent (%) Cu^{2+} removal after desired period of contact time is calculated by the following equation:

$$\%removal = \frac{(C_0 - C_t)}{C_0} \times 100$$

where C_0 and C_t (mg/L) are the initial and final Cu^{2+} concentrations, respectively.

The adsorption ability was determined by varying the amount of adsorbent at 0.05, 0.1, 0.2, and 0.4 g/L. The concentration of the Cu^{2+} ions that remained in the adsorbent phase at equilibrium (q_e, mg/g) was calculated using the following equation:

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

where C_0 (mg/L) is the initial concentration of Cu^{2+} in the suspension; C_e (mg/L) is the equilibrium concentration of Cu^{2+} in the supernatant solution after filtration; V (L) is the volume of solution and W (g) is the weight of adsorbent. The obtained adsorption data between the MWCNTs-COOH and Cu^{2+} ions were analyzed using Langmuir and Freundlich isotherm models.

3. Results and discussion

3.1. Decoration of Fe_3O_4 on MWCNT-COOH

Fe_3O_4 nanoparticles decorated on acid-functionalized MWCNTs were prepared using a simple one-pot strategy via in-situ growth of Fe_3O_4 magnetic nanoparticles onto the surfaces of MWCNTs. An aqueous solution of Fe^{2+} and Fe^{3+} ion precursors are mixed at specified molar ratios and then the acid-functionalized MWCNTs were introduced, yielding the Fe_3O_4 nanoparticles decorated on the surface of acid-functionalized MWCNTs in basic

solution. TEM images of Fe_3O_4/MWCNT-COOH nanocomposites are shown in Figure 1.

TEM image (Figure 1(a)) showed that Fe_3O_4 nanoparticles are attached on the surfaces of MWCNTs and also some agglomeration of nanoparticles. The stability of Fe_3O_4 nanoparticles decorated on MWCNTs-COOH is achieved through the interaction between Fe_3O_4 nanoparticles and surface of carboxyl groups (COOH) on MWCNTs [18]. Agglomeration of nanoparticles may originate from magnetostatic coupling between particles and this coupling would decrease the interaction between Fe_3O_4 and MWCNTs. The average size of Fe_3O_4 nanoparticles is 15.40 ± 0.36 nm, as shown in Figure 1(b). The weight percentage of Fe_3O_4 in Fe_3O_4/MWCNTs-COOH compositions was determined by SEM–EDX analysis and the results indicated that the amount of Fe_3O_4 loading was 3–5% higher than the theoretical calculation. This may be due to inhomogeneous dispersion [15] and/or few percent of Fe_3O_4, which has no interaction with nanotube, might have passed through the membrane during filtration.

The magnetic properties of the Fe_3O_4/MWCNTs-COOH were measured by Vibrating Sample Magnetometer. It is evident from Figure 2 that the synthesized 50wt% Fe_3O_4/MWCNT-COOH nanoparticles has superparamagnetic properties with saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) values of 40.1 emu/g, 0 emu/g, and 0 O_e, respectively. The separation ability of Fe_3O_4/MWCNTs-COOH was also evaluated under external magnetic field. As seen in Figure 2 (inset), the Fe_3O_4/MWCNTs-COOH nanoparticles dispersed in aqueous solution were attracted towards magnet rapidly demonstrating easy separation from the aqueous solution, whereas pristine MWCNTs and CNTs have the problem of separation issues from aqueous solutions.

Surface functional groups of acid oxidized MWCNT and their surface decoration with Fe_3O_4 were analyzed by FTIR spectroscopy as shown in Figure 3.

IR Spectrum of pristine MWCNTs (Figure 3(a)) shows the characteristic peaks of graphite structure at 1645 cm^{-1} and 1158 cm^{-1} corresponding to C=C and C–C stretching vibrations, respectively, and the peaks at 2855 and 2927 cm^{-1} corresponding to stretching vibration of CH_2 group located at the defect sites on the sidewall surface. IR spectrum of acid-treated MWCNTs (Figure 3(b)) shows a broad band at 3394 cm^{-1}, which can be assigned to O–H stretching of carboxyl (O=C–OH) and hydroxyl (C–OH) groups. The peaks at 1733 cm^{-1} and 1204 cm^{-1} can be attributed to the C=O and C–O stretching vibration mode of carboxylic groups, respectively [19], which indicates the carboxylic acid groups have been successfully introduced
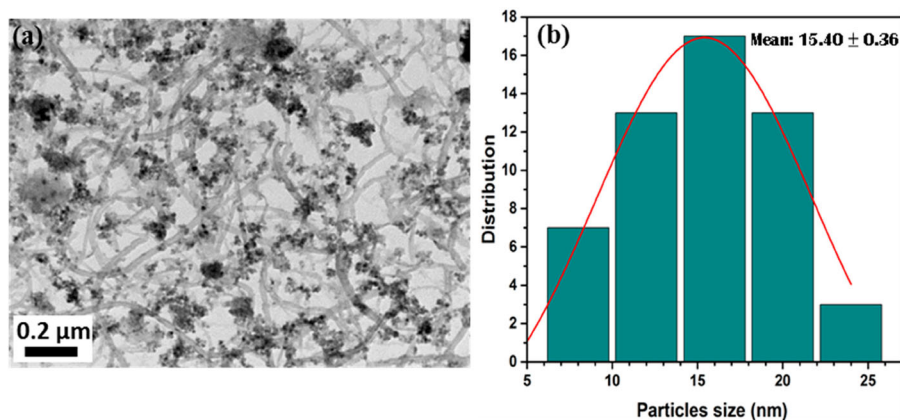
Figure 1. (a) TEM image of 50wt% Fe_3O_4/ MWCNTs-COOH nanocomposites and (b) size distribution histogram of Fe_3O_4 nanoparticles.

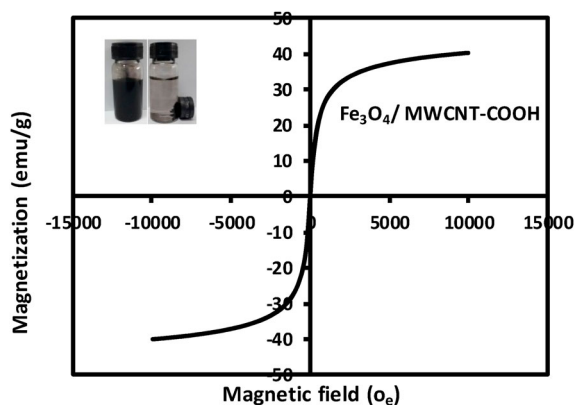**Figure 2.** Magnetic hysteresis loop of the synthesized 50wt% Fe_3O_4/MWCNTs-COOH at room temperature. The inset shows the separation of Fe_3O_4/MWCNTs-COOH in the presence of an external magnetic field.

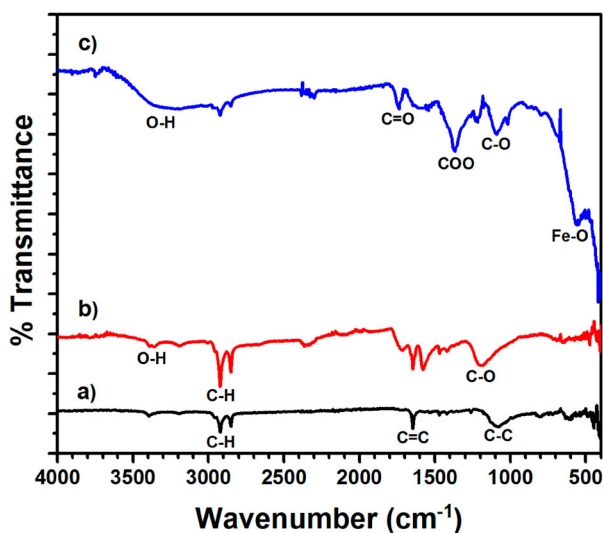**Figure 3.** FTIR-spectra of (a) pristine MWCNTs (b) MWCNTs-COOH and (c) Fe_3O_4/MWCNTs-COOH.

onto surfaces of MWCNTs. The IR spectrum of Fe_3O_4 decorated on MWCNTs-COOH (Figure 3(c)) shows peaks corresponding to the functional groups of MWCNT-COOH and Fe_3O_4. The characteristic peak observed at 580 cm^{-1} corresponds to the stretching vibration of Fe–O in Fe_3O_4 [20]. The peak at 1362 cm^{-1} can be assigned to symmetric and asymmetric COO stretching vibration of carboxylate group [21].

3.2. Adsorption study

The functionalized MWCNTs-COOH was employed as an adsorbent for the adsorption of Cu^{2+} ions. The effect of various parameters such as contact time, adsorbent dose, and initial concentration of Cu^{2+} on the adsorption process was investigated. Contact time between the adsorbent and aqueous solution containing metal ions is considered as an essential factor to understand the speed of adsorption process for the removal of metal ions. Therefore, at first the effect of contact time on the adsorption of Cu^{2+} ions onto MWCNTs-COOH is shown in Figure 4. It can be seen that % removal increases rapidly over a short period of time (5 min) and reaches equilibrium in 10 min. The rapid adsorption process in the initial period is probably due to the high concentration gradient between the adsorbate in solution and the number of available vacant sites on the surface of the adsorbent. The progressive slow adsorption process with further increasing contact time indicates difficulty in occupying the remaining vacant sites due to repulsion between the absorbate molecules in the bulk liquid phase and on the external surface of adsorbent [22,23].

The short time (less than 10 min) required to reach equilibrium indicating that the MWCNTs-COOH have a very high adsorption efficiency for Cu^{2+} ions. Large surface area and the negative charge of the MWCNTs-COOH surfaces could increase the interaction with Cu^{2+}
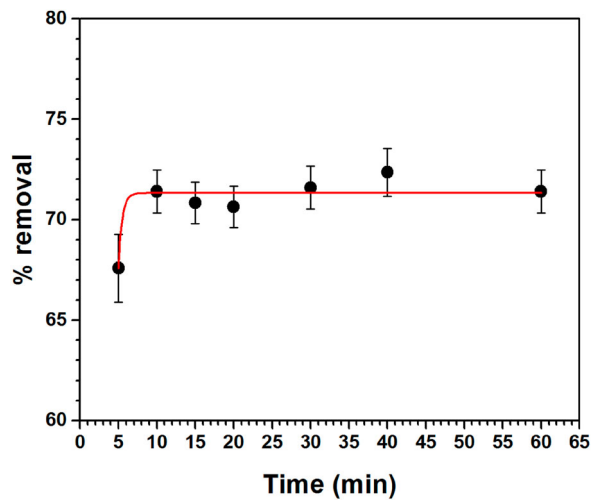
Figure 4. Effect of contact time on the adsorption of Cu^{2+} onto MWCNT-COOH. The reaction conditions: adsorbent dosage = 0.2 g/L, initial Cu^{2+} concentration = 15 mg/L, pH = 7 and T = 25℃.

Figure 6. Effect of initial concentration Cu^{2+} ions on the removal of Cu^{2+} by MWCNTs-COOH adsorbent. Reaction conditions: adsorbent dosage = 0.2 g/L, contact time 15 min, pH = 7 and T = 25℃

ions and improve their adsorption capacity [24]. Reduced amount of adsorbents are required for the removal of Cu^{2+} ions due to rapid removal process coupled with high adsorption efficiency indicating economics of this separation method [23].

Adsorption capacity is an essential factor to determine how much adsorbent is required quantitatively for interaction with Cu^{2+} ions effectively in a given solution. The effect of adsorbent dosage on Cu^{2+} adsorption by MWCNTs-COOH was studied by varying adsorbent content from 0.05 to 0.4 g/L and the results are presented in Figure 5. It can be seen from Figure 5 that the adsorption capacity increased with increasing
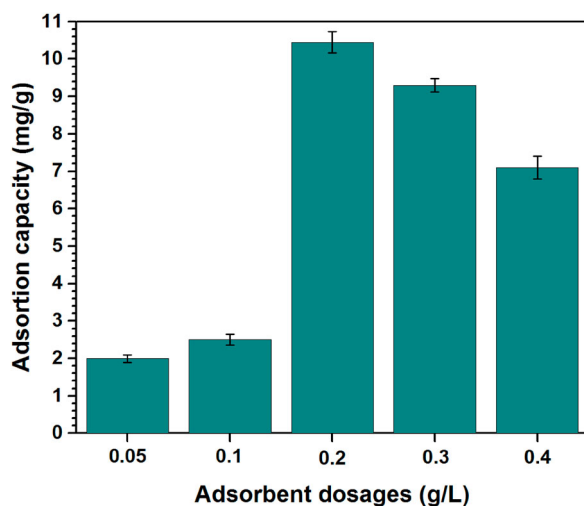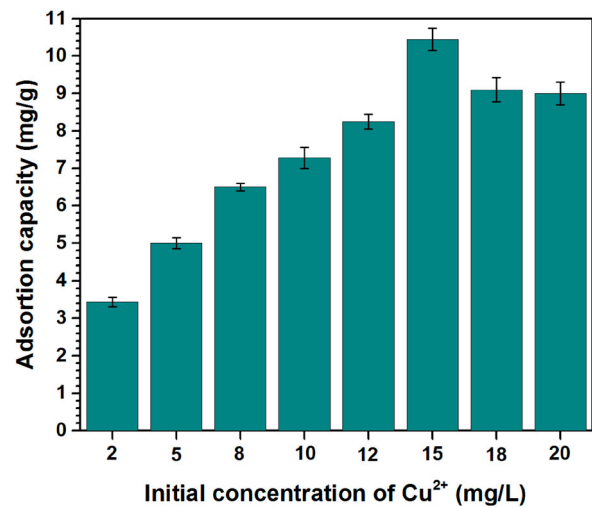

Figure 5. Effect of adsorbent dosage on Cu^{2+} adsorption by MWCNT-COOH. Reaction conditions: initial Cu^{2+} concentration = 15 mg/L, contact time 15 min, pH = 7 and T = 25℃.

adsorbent dose from 0.05 to 0.2 g/L and thereafter, adsorption capacity decreased with increasing dose. Maximum adsorption capacity of 10.45 mg/g was achieved with 0.2 g/L adsorbent dose. An increase in uptake ability of Cu^{2+} could be attributed to a greater surface area of adsorbent and more adsorption sites present on adsorbent surfaces, which increased the availability of adsorption. While a further increase in the adsorbent dose might cause aggregation of adsorbent and decrease the available adsorption sites [25]. Therefore, 0.2 g/L of adsorbent dose was selected as the optimum dose for all further experiments in this study as it exhibited high acceptable level of adsorption capacity.

The effect of initial concentration of Cu^{2+} ions on the removal of Cu^{2+} by MWCNTs-COOH (adsorbent dosage = 0.2 g/L) was studied at different initial Cu^{2+} concentrations ranging from 2 to 20 mg/L as presented in Figure 6. When the initial Cu^{2+} concentration is increased from 2 to 15 mg/L, the adsorption capacity of MWCNTs-COOH increased from 3.44 to 10.45 mg/g, which can be attributed to enhancement in the driving force of a concentration gradient to overcome the mass transfer resistance between the liquid–solid phases [26]. Further increase in initial concentration of Cu^{2+} ions, there was a reduction in adsorption capacity observed.

3.3. Freundlich and Langmuir Isotherms models

The Langmuir and Freundlich isotherm models were employed to check the validity of the present experimental data obtained for Cu^{2+} adsorption onto MWCNTs-COOH. The Langmuir isotherm model is

expressed by the following linear equation:

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

where C_e (mg/L) is the equilibrium Cu^{2+} concentration in solution; q_e (mg/g) is the equilibrium amount of Cu^{2+} absorbed per unit mass of adsorbent; q_m (mg/g) is the maximum adsorption capacity at saturation, and K_L (L/mg) is Langmuir constant related to the energy of adsorption [27–31].

The Freundlich isotherm model is represented by the following linear equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where n and K_F are Freundlich parameters. The value of n shows the favourable adsorption ability and K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$) relates to the adsorption capacity [27–31].

The experimental isotherm data for Cu^{2+} adsorption onto MWCNTs-COOH were analyzed using Langmuir and Freundlich models. Langmuir and Freundlich isotherm plots in linear forms of Cu^{2+} adsorption on MWCNT-COOH are shown in Figure 7.

The slope and the intercept of each linear plot in Figure 7 were used to calculate Langmuir and Freundlich parameters and their parameters are listed in Table 1.

The results demonstrated that Langmuir model with R^2 values up to ~0.995 is the best fit linearly for the adsorption of Cu^{2+} than Freundlich model. The validity of models can be determined by calculating the residual root mean squared error (RMSE) statistical parameter as below:

$$\text{RMSE} = \left(\sum (q_{e,exp} - q_{e,cal})^2 / n\right)^{1/2}$$

where $q_{e,exp}$ (mg/g) is the experimental data of the equilibrium adsorption capacity and $q_{e,cal}$ (mg/g) is the equilibrium adsorption capacity calculated from model calculation [31]. The smaller RMSE value revealed that

Table 1. Parameters of Langmuir and Freundlich adsorption isotherm models for Cu^{2+}.

Langmuir				Freundlich			
q_m (mg/g)	K_L (L/mg)	R^2	RMSE	n	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	R^2	RMSE
10.45	0.39	0.995	0.426	2.78	3.59	0.973	2.169

the Langmuir model fits the experimental isotherm result closer than the Freundlich model.

One essential parameter of the Langmuir isotherm equation can be defined in terms of the dimensionless factor R_L as known as the Hall separation factor or equilibrium factor, which is calculated using the following equation:

$$R_L = 1/(1 + K_L C_o)$$

where K_L (L/mg) is the Langmuir constant and C_o (mg/L) is the initial concentration of Cu^{2+} in the liquid phase. The value of R_L indicates the type of the isotherm shape and predicts whether a sorption system is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$) [23]. In this study, the obtained R_L values for the adsorption of Cu^{2+} onto the MWCNTs-COOH were found to be in a range of 0.116–0.567 for the initial concentrations varied in the range of 2.0–20.0 mg/L. These R_L values indicate that MWCNTs-COOH is favourable for adsorption Cu^{2+} from water under the conditions used in this study. The Langmuir model is based on the assumption that there is no interaction between the adsorbate molecules. This indicates that the adsorption of Cu^{2+} on MWCNTs-COOH occurred as a single monolayer and the binding energy presented on the surface of adsorbent is uniform [28]. Therefore, MWCNTs-COOH shows great potential to be a good adsorbent for the removal of Cu^{2+} ions in water treatment.

The value of the maximum adsorption capacities for the adsorption of Cu^{2+} obtained from the Langmuir
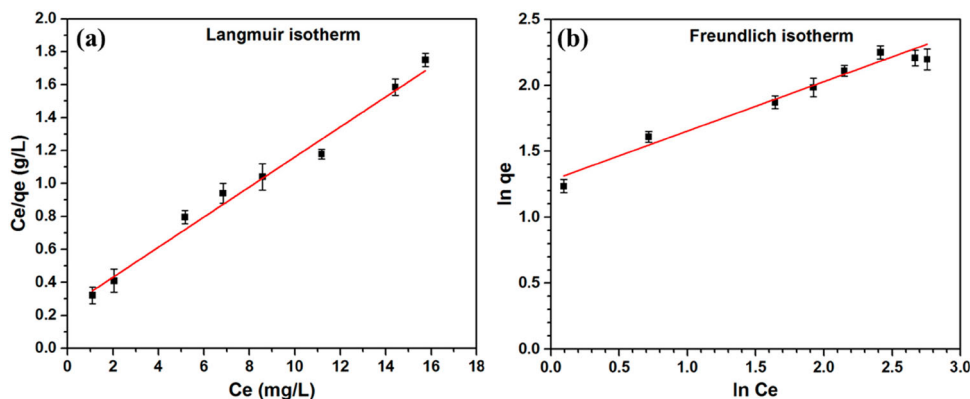

Figure 7. Adsorption isotherm model for Cu^{2+} (a) Langmuir and (b) Freundlich isotherm.

Table 2. Maximum adsorption capacity obtained the Langmuir isotherm model for Cu^{2+} on selected modified MWCNTs materials.

Adsorbents	Maximum adsorption capacity (mg/g) at given T (℃)	References
Treated MWCNTs (HNO_3)	12.34 (20℃)	[32]
Oxidized MWCNTs (HNO_3)	7.8 (room temp.)	[33]
Double oxidized MWCNTs (HNO_3/H_2SO_4)	14 (room temp.)	[33]
MWCNTs in the presence of humic acid	7.78 (20℃)	[34]
Chitosan/poly(vinyl)alcohol thin adsorptive membranes modified amino functionalized MWCNTs oxidized MWCNTs (HNO_3)	11.1 (20℃) 10.45 (25℃)	[35]
Fe_3O_4-decorated oxidized MWCNTs (HNO_3)	9.5 (25℃)	Present study

isotherm model on modified MWCNTs materials reported in the literature are summarized in Table 2 along with data from the present study. Though direct comparison is not appropriate due to different experimental conditions, but we can infer from these data that the maximum adsorption capacity of MWCNTs-COOH and Fe_3O_4-decorated MWCNTs-COOH observed in the present study are more or less similar to the reported values.

3.4. Adsorption and separation evaluation

Adsorption capacity of Cu^{2+} on Fe_3O_4 and Fe_3O_4/ MWCNTs-COOH were investigated. In addition, the separation ability of Fe_3O_4/MWCNTs-COOH from aqueous solutions using external magnetic field was also determined. The results are presented in Table 3.

It is clear from Table 3 that Cu^{2+} adsorption capacity of MWCNTs-COOH is nearly three times higher than that of pristine MWCNTs. The presence of functional groups on MWCNTs, introduced by acid treatment, increase Cu^{2+} adsorption capacity. Fe_3O_4 nanoparticles showed similar adsorption capacity of Cu^{2+} to MWCNTs, and furthermore, Fe_3O_4 adsorbent can be easily and completely

Table 3. The adsorption and separation properties of different adsorbents.

Adsorbents	Adsorption capacity (mg/g)[a]	% adsorbent removal[b]
MWCNTs	3.42	–
Fe_3O_4 (15.34 ± 0.36 nm)	3.37	100
MWCNTs-COOH	10.45	–
10 wt% Fe_3O_4/ MWCNTs-COOHMWCNTs-COOH	10.20	80 ± 2
25 wt% Fe_3O_4/ MWCNTs-COOHMWCNTs-COOH	9.50	97 ± 2
50 wt% Fe_3O_4/ MWCNTs-COOHMWCNTs-COOH	3.15	99 ± 2

[a]Initial concentration of Cu^{2+} ion 15 mg/$g_{adsorbent}$ at 25℃ for 15 min, adsorbent dosage = 0.2 g/L.
[b]The percentage of adsorbent separated from solution by external magnet.

separated from the reaction medium using an external magnet. The adsorption capacity of MWCNT-COOH decorated with Fe_3O_4 nanoparticles (Fe_3O_4/MWCNT-COOH) decreases with increasing percent weight loading of Fe_3O_4, though % adsorbent removal increases with increasing wt% of Fe_3O_4. In short, higher the decoration with magnetic particles, higher is the separation efficiency but lower the adsorption capacity. This decrease in adsorption capacity also implies that there is an interaction between carboxylate/hydroxide sites on the surface of the carbon nanotube and Fe_3O_4 nanoparticles causing blocking of few active sites for Cu^{2+} adsorption. It is also seen from Table 3 that Fe_3O_4 has lower adsorption capacity than MWCNTs-COOH and the adsorption capacity of MWCNTs-COOH decreases with increasing wt% of Fe_3O_4. The process of decoration Fe_3O_4 nanoparticles onto MWCNTs-COOH surfaces and Cu^{2+} adsorption sites are shown in Scheme 1.

Basically, Cu^{2+} ions are chemically adsorbed on carboxylate group of MWCNTs surfaces due to electrostatic interaction. In addition, it is possible that there is an interaction between Cu^{2+} and π -electron of a benzene ring on the surface of the nanotube. However, the interaction intensity of Cu^{2+} on the nanotube surface is lower than at the functionalized groups. With an increase in the electronic effect due to Fe_3O_4 nanoparticles, the adsorption capacity is expected to increase, but the reverse trend was observed. This may be due to binding of Fe_3O_4 with the number of carboxylate groups, which decreased active sites for the adsorption. In this study, it is confirmed that the adsorption capacity decreased with increasing Fe_3O_4 loading from 10 to 50 wt%, which directly indicates the fact that the increased blocking of sites with increasing concentration of Fe_3O_4 in Fe_3O_4/MWCNTs-COOH for Cu^{2+} adsorption. However, the biggest advantage of Fe_3O_4/MWCNTs-COOH adsorbent is that it can be easily separated from the reaction medium by the magnetic method after adsorption compared to pristine MWCNTs-COOH [12]. 25% Fe_3O_4 loading onto MWCNTs-COOH can be considered as the most suitable magnetic adsorbent for removal of Cu^{2+} ions from aqueous solutions based on its optimum adsorption capacity and separation efficiency.

4. Conclusion

Adsorption capacity and separation efficiency of adsorbents are important factors for identification and selection as suitable adsorbents for waste water treatment for the removal of metal ions. MWCNTs-COOH is a potential adsorbent for removal of Cu^{2+} ions in aqueous solutions but the separation of MWCNTs-COOH from the solution after adsorption is the major issue. In order to
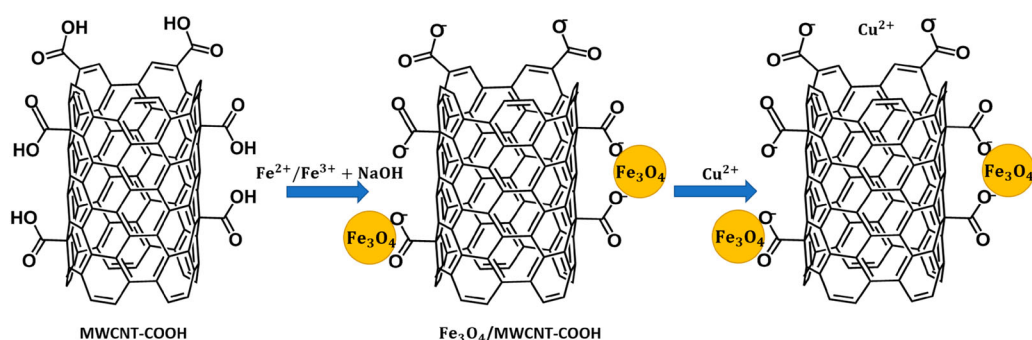
Scheme 1. Propose a reaction process of decoration Fe_3O_4 nanoparticles onto MWCNTs-COOH surfaces and adsorption of Cu^{2+} on Fe_3O_4/MWCNT-COOH nanocomposites.

improve the separation efficiency without compromising much on adsorption capacity of MWCNTs-COOH, the adsorbent is modified to improve separation efficiency. Initially, MWCNTs-COOH was prepared by acid treatment and subsequently, MWCNTs-COOH was decorated with Fe_3O_4 nanoparticles by co-precipitation of Fe^{2+}/Fe^{3+} in the colloidal suspension of MWCNTs-COOH. The adsorption capacity of MWCNTs-COOH was determined under different reaction conditions such as contact time between adsorbent and Cu^{2+} ions in aqueous solution, adsorbent dose, and initial concentration of Cu^{2+} ions in solution. The best adsorption capacity of MWCTNs-COOH (10.45 mg/g) was achieved with a reaction time of 10–15 min, adsorbent dose of 0.2 g/L and initial Cu^{2+} concentration of 15 mg/L. Further, Fe_3O_4/MWCNTs-COOH containing different concentrations of Fe_3O_4 in the adsorbent was investigated for adsorption capacity study for removal of Cu^{2+} ion in aqueous solution. It was found that the adsorption capacity decreased with increasing Fe_3O_4 nanoparticles through separation efficiency increased. Fe_3O_4/MWCNTs-COOH containing 10% Fe_3O_4 was found to have optimum adsorption capacity (9.50 mg/g) and magnetic separation efficiency of 97%. Further, the validity of experimental data obtained in this work for Cu^{2+} adsorption was verified by employing both Langmuir and Freundlich isotherm models. It can be concluded from this research work that 25%Fe_3O_4/MWCNTs-COOH nanocomposite can be considered as suitable magnetic adsorbent for removal of Cu^{2+} ions in aqueous solutions.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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