



Removal of heavy metals from aqueous solutions by multi-walled carbon nanotubes modified with 8-hydroxyquinoline

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were modified with 8-hydroxyquinoline and used for the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions. Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy showed the successful modification of the MWCNTs with 8-hydroxyquinoline. The adsorption parameters, such as the amount of MWCNTs used, temperature, pH, ionic strength, metal ion concentration, and competition among metal ions, were studied and optimized. The results showed that most of the metals were removed from aqueous solution using 250 mg of MWCNTs at pH 7.0 and 298 K in 0.01 M KNO₃ after 10 min of adsorption. The results also showed that the competition between the target heavy metals was in the order of Cu(II) > Pb(II) ≈ Zn(II) > Cd(II) for % adsorption. The recycling, desorption and regeneration of the MWCNTs were evaluated and the results demonstrated that most of the metal ions desorbed at pH values lower than 2.0, and the MWCNTs could be used for up to three cycles of adsorption/desorption without losing efficiency. The pristine and modified MWCNTs were used to remove the target heavy metals from two real samples collected from the Red Sea and a wastewater treatment plant. Both pristine and modified MWCNTs were capable of removing the heavy metals from the real samples. In general, the modification of MWCNTs with 8-hydroxyquinoline significantly enhanced the removal of heavy metals from aqueous solution.

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1. Introduction

Although carbon nanotubes exhibit great potential for the adsorption of heavy metal ions from aqueous solutions, the removal efficiency, selectivity, and sensitivity remain limited. The modification of carbon nanotubes is therefore considered to be an important route for the enhancement of removal efficiency, selectivity, and sensitivity of heavy metals. The surfaces of multi-walled carbon nanotubes (MWCNTs) can be modified in a variety of ways, such as chemical bond formation between the modifying species and MWCNTs surfaces or physical adsorption of the modifier to MWCNTs surface [1]. Many studies have focused on the removal of heavy metal ions by modified carbon nanotubes, including cadmium [2], nickel and strontium [3], lead [4], chromium [5], uranium [6], copper [7], and copper, zinc, cadmium, and nickel [8] ions from aqueous solutions.

The small molecule 8-hydroxyquinoline (8-HQ), also known as 8-quinolinol or oxine, is a monoprotic, bidentate chelating agent. It contains an oxygen donor atom and a nitrogen donor atom that

can both bind to metal atoms. Different adsorbents have previously been modified by 8-HQ to enhance the adsorption and removal of heavy metal ions from aqueous solutions. For example, 8-HQ was immobilized onto bentonite for the adsorption of Pb(II) ions [9] and Cu(II) ions [10] from aqueous solutions. Additionally, 8-HQ was chemically bonded to vinyl polymer resin for the removal of different metal ions [11] and was chelated with chitosan resin for the pre-concentration and determination of zinc [12]. Also, 8-HQ was used for the synthesis of surface-imprinted nanospheres for the selective removal of uranium from simulants of Sambhar Salt Lake and ground water [13].

In this study, multi-walled carbon nanotubes with average diameters of 10–20 nm (MWCNTs (10–20)) were physically modified through the immobilization of 8-HQ onto CNTs surfaces for the first time. The produced adsorbent was characterized using Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and specific surface area measurements. Then, the modified MWCNTs (8-HQ-MWCNTs (10–20)) were used for the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions. The adsorption parameters were also studied, and a comparison between pristine and modified carbon nanotubes was made. Recycling and regeneration of the used MWCNTs were studied, and desorption conditions were optimized. Finally, the pristine and

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modified MWCNTs were applied for the removal of target heavy metal ions from two different environmental water samples: sea-water and wastewater.

2. Experimental

2.1. Chemicals

Pristine multi-walled carbon nanotubes (MWCNTs) of 10–20 nm diameters were purchased from Shenzhen Nanotech Port Co., Ltd. The MWCNTs were stored dry at 25 °C. Analytical grade cadmium, lead, copper and zinc nitrate (Fluka) (Ion Standard Solution of 1000 mg/L) were employed to prepare stock solutions containing 100 mg/L of Cd(II), Pb(II), Cu(II) and Zn(II), respectively. The stock solutions were then further diluted to the desired concentrations. All other chemicals were of analytical grade and obtained from Sigma–Aldrich. The experiments were performed using ultrapure water with resistivity not less than 18.2 MΩ cm obtained with a Millipore Milli-Q system (Billerica, USA).

The modification of CNTs was performed using 8-hydroxyquinoline (8-HQ). A saturated solution of 8-HQ was prepared by adding an appropriate quantity in 1000 mL of ultrapure water, sonicating for 2 h and then stirring with a magnetic stirrer for 2 h. The solution was then filtered to remove the undissolved 8-HQ by filtration through Whatman filter paper. Next, 10.0 g of MWCNTs was added to the saturated solution of 8-HQ and put over the stirrer for 2 days. MWCNTs were separated by filtration through a 0.45-μm filter membrane and washed with deionized water to remove excess 8-HQ until the filtrate became colorless. The final product 8-hydroxyquinoline MWCNTs (8-HQ-MWCNTs) were dried in an oven at 110 °C overnight.

All glassware used in this work was rinsed with 10% nitric acid (suprapure, 69%) to remove all impurities that might be present and to prevent further adsorption of heavy metals to the walls of the glassware.

2.2. Characterization studies

Scanning electron microscope (SEM) measurements were taken using an FEI-Field Emission Scanning Electron Microscope (FISEM) (Quanta FEG 450, Netherlands). The specific surface area of the different MWCNTs was determined from nitrogen adsorption/desorption isotherms measured at 77 K using a model NOVA 3200e automated gas sorption system (Quantachrome, USA). Fourier transform-infrared (FT-IR) spectroscopy measurements were performed using an FTIR-8400 S (Shimadzu, Japan) and the same amount for each sample was employed. X-ray photoelectron spectroscopy (XPS) was performed using a Leybold MAX200 spectrometer with unmonochromatized Al Kα & Al-Kα X-rays at 100 W power. The source was operated at 15 kV and 20 mA with a take-off angle $\theta=0^\circ$ (relative to the sample normal). The binding energy scale was calibrated with respect to the C1s (284.5 eV). Spectra of Fe 2p_{3/2} and Cr 2p_{3/2} were recorded. The oxygen containing acidic functional groups on MWCNTs were qualitatively and quantitatively determined by Boehm titration by the previously reported method [14].

2.3. Analytical procedure

Differential pulse anodic stripping voltammetry (DPASV) was used for the determination of heavy metal ion concentrations in aqueous solution using a deposition potential of –1.23 V, a scan rate of 0.005 V/s, and a deposition time of 30 s with a Metrohm797 VA computrace (Switzerland instrument). This setup included a three electrode system with hanging mercury (HMDE) as the working electrode with a small size (size 1), a platinum plate as the

counter electrode, and Ag/AgCl (3.0 mol/L KCl) as the reference electrode.

2.4. Adsorption procedure

The optimization of adsorption parameters was performed by mixing certain amounts of CNTs with 20 mL solutions containing Cu(II), Pb(II), Cd(II) and Zn(II) together at room temperature. After a certain time interval, the solution was filtered through 0.45-μm Millipore filter paper, and the concentration of the metal ions in the filtrate was measured using DPASV. The amount of metal ion adsorbed on the MWCNTs was determined by the difference of the initial concentration (C_0) and the equilibrium concentration (C_e). The percentage removed of Cd(II), Pb(II), Cu(II) and Zn(II) ions from the solution was calculated using the following relationship:

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

All the experiments were repeated three times, and the reported values represent the averages. A parallel experiment was conducted in the absence of the CNTs to determine metal ion loss during the adsorption due to the glassware or any of the experimental equipment and found to be insignificant.

2.5. Desorption procedure

Adsorption experiments were conducted by shaking 0.25 g of CNTs with 20 mL of 0.5 ppm Cu(II), Pb(II), Cd(II) and Zn(II) solutions for 2 h at room temperature. After the metal ions adsorbed on the CNTs, the solution was filtered, and the filtrate was used to determine the % adsorption for each metal ion. For the desorption study, 0.25 g of CNTs containing the adsorbed metal ions was stirred in 20 mL deionized water adjusted at different acidic pH values and time intervals at room temperature. The fraction of metal ion desorbed from the MWCNTs was calculated using Eq. (2):

$$\% \text{ Desorption} = \frac{\text{Amount Released To Solution (mg/L)}}{\text{Total Adsorbed (mg/L)}} \times 100 \quad (2)$$

2.6. Real water samples

Red Sea water (RSW) and wastewater samples were used to evaluate the efficiency of the MWCNTs for the removal of the target heavy metals. The Red Sea water was collected from the Red Sea in front of Jeddah City, Saudi Arabia (Latitude deg. North 21.49555, Longitude deg. East 39.16655). The wastewater sample (MBR 6000 STP) was collected from the Membrane Bio-Reactor Technology Waste Water Treatment Plant – King Abdulaziz University (KAUWW), Jeddah City (Latitude deg. North 21.487954, Longitude deg. East 39.236748). The RSW and KAUWW samples were filtered through 0.45-μm Millipore filter paper and kept in Teflon® bottles at 5 °C in the dark. Some of the characteristics of the RSW and KAUWW are listed in Table 1.

3. Results and discussion

3.1. Characterization studies

Scanning electron microscope imaging was used to study the morphology of the pristine and modified MWCNTs. There was not a significant difference between the two types of carbon nanotubes. Representative images are shown in Fig. 1 for MWCNTs (10–20) and modified 8-HQ-MWCNTs. Clearly, both types of MWCNTs are rope-like, curved and highly tangled tubes with diameters between

Table 1
Analysis of wastewater and Red Sea water samples.

	KAUWW	RSW
Date of collection	26/3/2011	5/3/2011
pH	7.01	7.6
TDS	796 mg/L	39,000 mg/L
Conductivity	1593 $\mu\text{S}/\text{cm}$	78,000 $\mu\text{S}/\text{cm}$
TSS	Nil	2 mg/L
Turbidity	Nil	3 FAU
Ammonia	0.08 mg/L	3.2 mg/L
COD	6 mg/L	184 mg/L
BOD	3.5 mg/L	36.3 mg/L
K ⁺ (mg/L) ^a	7.866	568.59
Na ⁺ (mg/L) ^b	246.2	15360
Ca ²⁺ (mg/L) ^b	66.57	665.6
Mg ²⁺ (mg/L) ^b	12.36	2000

^a Measured with an AAnalyst™ 800 atomic absorption spectrophotometer (PerkinElmer®).

^b Measured with an Optima 4300™ DV ICP-OES (PerkinElmer®).

20 and 40 nm and with average lengths of hundreds of nanometers. Due to intermolecular forces, MWCNTs of different sizes and directions formed aggregated structures.

The infrared spectra of 8-HQ, the pristine MWCNTs (10–20) and the modified 8-HQ-MWCNTs (10–20) were recorded to investigate the successful modification of MWCNTs with 8-HQ, and the spectra are presented in Fig. 2. The presence of the –OH absorption band at 3433 cm^{-1} was clear for 8-HQ, the pristine MWCNTs (10–20) and the modified 8-HQ-MWCNTs (10–20). The intensities of the peaks were more pronounced for 8-HQ and the modified 8-HQ-MWCNTs (10–20) than the pristine MWCNTs (10–20). An obvious peak was observed at 1730 cm^{-1} and could be attributed to conjugated C=O stretching vibrations. This peak was pronounced for 8-HQ and the modified 8-HQ-MWCNTs (10–20), while it was absent for the pristine MWCNTs (10–20). The peaks that were clearly observed at 1637 cm^{-1} could be attributed to the C–O stretching modes for 8-HQ, pristine MWCNTs (10–20) and modified 8-HQ-MWCNTs (10–20). Additionally, the intensities of these peaks were more pronounced for 8-HQ and the modified 8-HQ-MWCNTs (10–20) compared to the pristine MWCNTs (10–20). The infrared band found at 1380 cm^{-1} could be assigned to the ring stretching vibration of 8-HQ, and similar but less pronounced peaks were observed for both pristine and modified MWCNTs. The characteristic absorption of the aryl C–OH stretching vibration at 1280 cm^{-1} was observed for 8-HQ and was less pronounced for both pristine and modified MWCNTs.

The concentrations of the oxygen-containing acidic functional groups (carboxylic, lactonic and phenolic groups) on the surface of the pristine MWCNTs (10–20) and 8-HQ-MWCNTs (10–20) were determined qualitatively and quantitatively using an acid–base neutralization method. This was done by immersing the MWCNTs in very dilute solutions of NaOH, NaHCO_3 or Na_2CO_3 , as described elsewhere [14]. The titration showed that the concentrations of oxygen-containing acidic functional groups for the pristine MWCNTs (10–20) were insignificant ($0.01 \pm 0.01\text{ mmol g}^{-1}$, $0.00 \pm 0.00\text{ mmol g}^{-1}$, and $0.02 \pm 0.01\text{ mmol g}^{-1}$ of carboxylic, lactonic and phenolic groups, respectively). These same groups were found to be $0.02 \pm 0.02\text{ mmol g}^{-1}$, $0.00 \pm 0.00\text{ mmol g}^{-1}$, and $0.06 \pm 0.03\text{ mmol g}^{-1}$, respectively, for the 8-HQ-MWCNTs (10–20). This slight increase in the phenolic group concentration for the 8-HQ-MWCNTs (10–20) compared with the pristine MWCNTs (10–20) might have been due to the presence of the 8-HQ on the MWCNTs (10–20) surface.

X-ray photoelectron spectroscopic (XPS) analysis was performed on the 8-HQ-MWCNTs sample to confirm the successful modification of MWCNTs with 8-HQ. It was clear from Fig. 3(a) that the XPS spectrum of 8-HQ-MWCNTs displayed three different

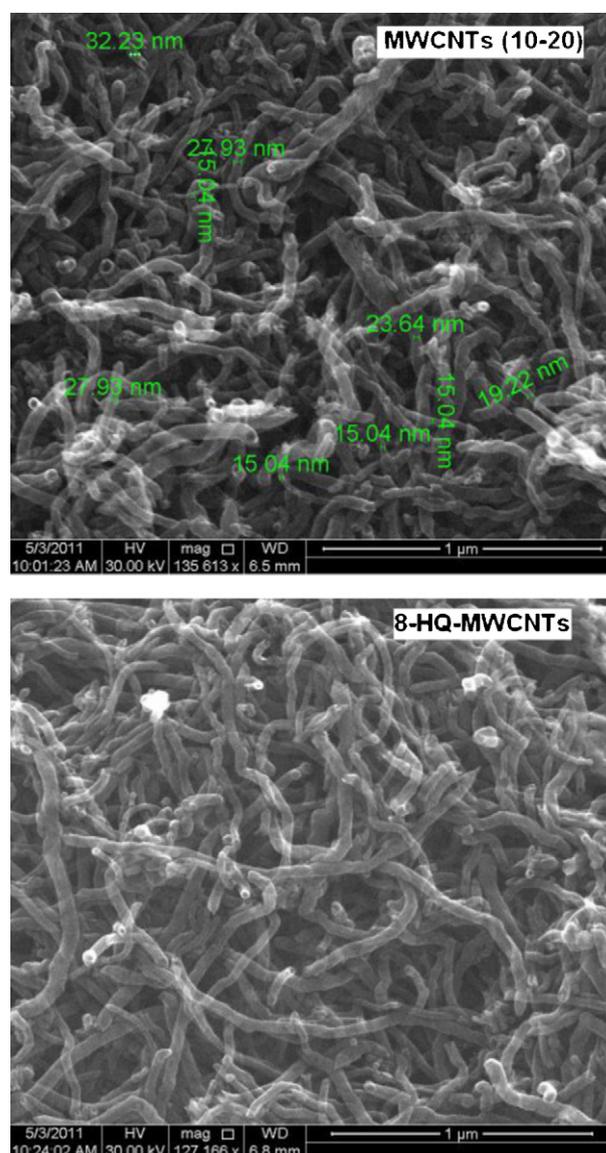


Fig. 1. Scanning electron microscope images of pristine MWCNTs (10–20) and modified 8-HQ-MWCNTs.

peaks for C1s, N1s, and O1s. The asymmetric strong peak at a binding energy (BE) of 284.0 eV for C1s was resolved into three peaks: peak 1 (BE = $282.5\text{--}286.4\text{ eV}$) could be attributed to the carbon from MWCNTs; peak 2 (BE = $283.0\text{--}287.0\text{ eV}$) could be attributed to the

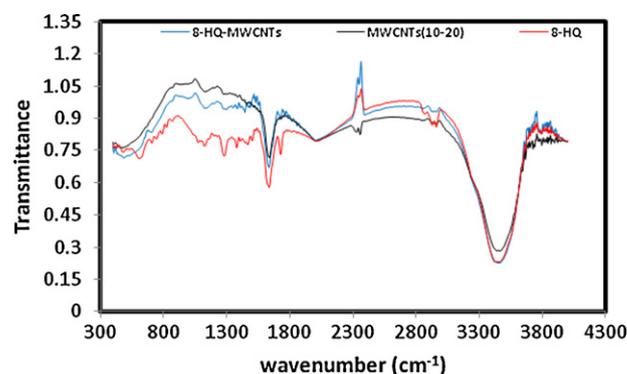


Fig. 2. FT-IR spectra of 8-HQ, pristine MWCNTs (10–20) and modified 8-HQ-MWCNTs (10–20).

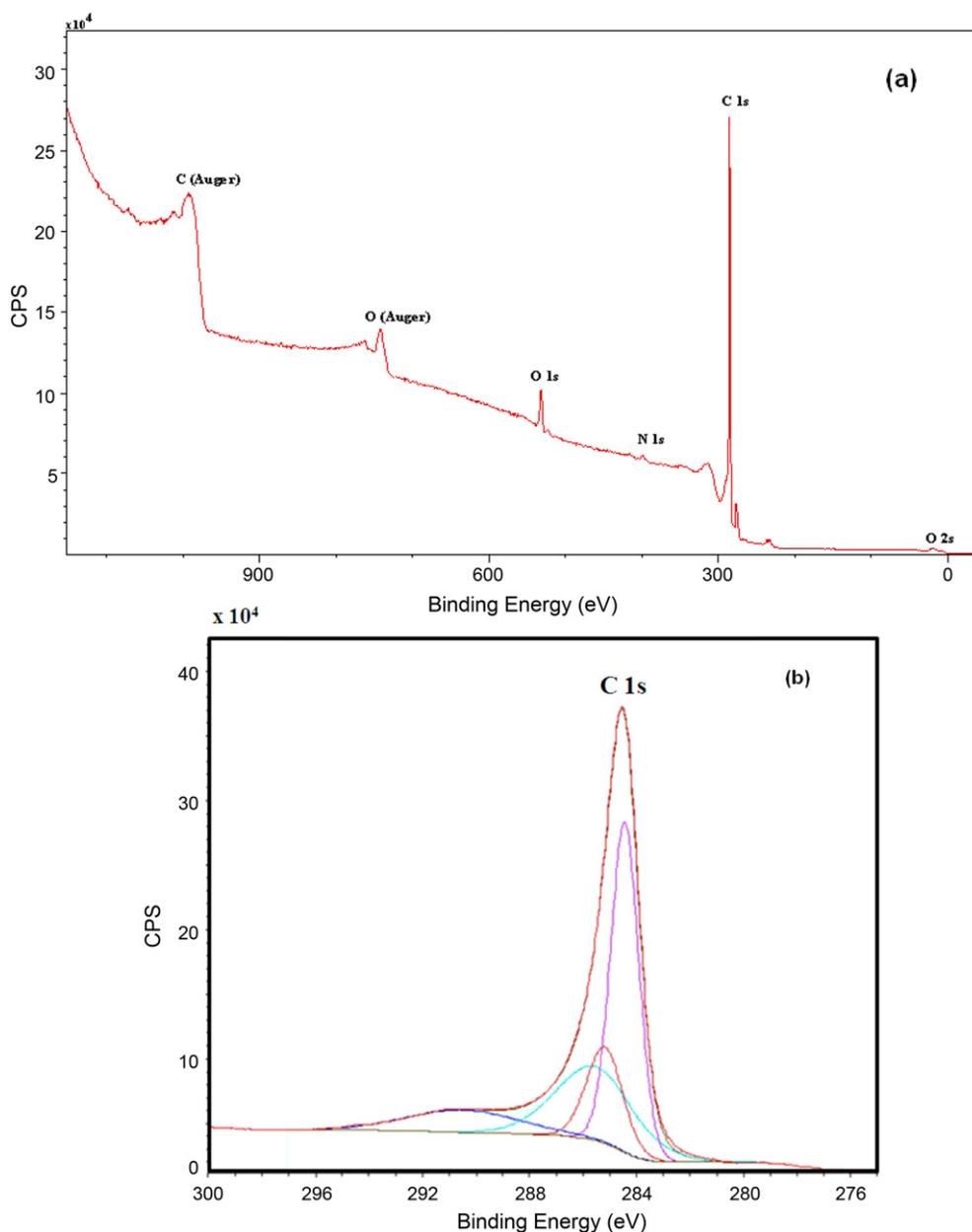


Fig. 3. (a) C1s, N1s and O1s XPS spectra of the 8-HQ-MWCNTs (10–20) and (b) C1s core spectrum.

carbon present in phenolic groups from both MWCNTs and 8-HQ; and peak 3 (BE=281.0–290.0 eV) could be attributed to the carbon present in the C=N groups from 8-HQ. In addition, the XPS survey showed a peak for N1s, which arose from the 8-HQ present on the MWCNTs surface. A strong indication of the presence of both N and O from the 8-HQ was clear from the spectrum and strongly indicated that 8-HQ was covalently bonded to the MWCNTs.

Nitrogen adsorption/desorption isotherms for the pristine and modified 8-HQ-MWCNTs were determined from N_2 adsorption isotherms measured at 77 K (Fig. 4). A hysteresis was observed for both MWCNTs, and this hysteresis could be attributed to well-known capillary condensation due to the intertubular structure [15]. According to the original IUPAC classification [16], the isotherms obtained from the different samples were classified as type IV isotherms with H3 type hysteresis loops. However, according to the extended classification of adsorption isotherms [17], the isotherms were classified as type IIb isotherms. The BET specific

surface areas were found to be 69.1 m^2/g and 76.2 m^2/g for the pristine MWCNTs (10–20) and modified 8-HQ-MWCNTs, respectively.

3.2. Adsorption study

The adsorption of metal ions from aqueous solution by carbonaceous adsorbents is well established. It is thus important to comprehensively investigate the adsorption of metal ions by carbon nanotubes for efficient remediation. Different factors that affect the adsorption process, such as pH, ionic strength, temperature, and competition among metal ions, must be optimized first. Also, it is important to study the effects of the modification of MWCNTs by 8-HQ on the adsorption behavior of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions.

3.2.1. Effect of contact time

The time needed for the interaction between the adsorbate and adsorbent is crucial (*i.e.*, the faster the removal, the better the

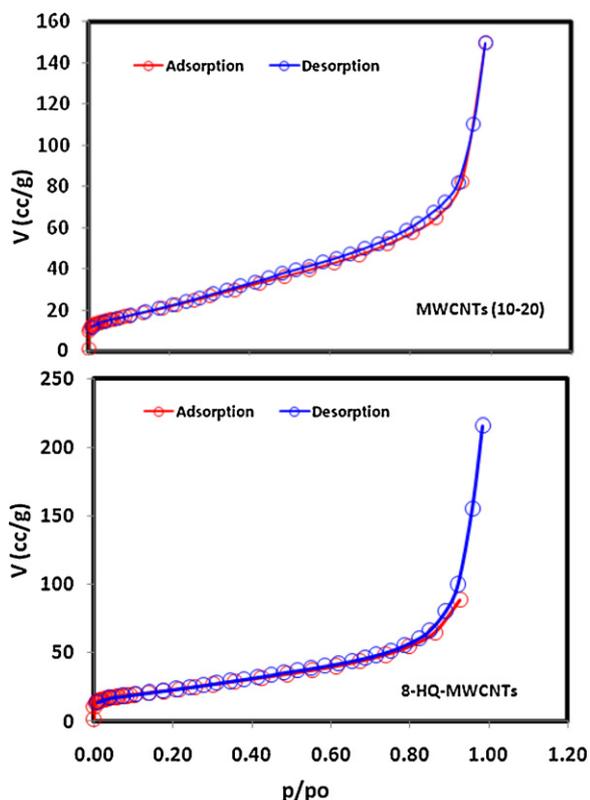


Fig. 4. N_2 adsorption/desorption isotherms of pristine MWCNTs (10–20) and 8-HQ-MWCNTs.

adsorbent). Hence, it is important to study the effect of contact time on the removal of the target heavy metals with both pristine and modified MWCNTs. Fig. 5 shows the effect of contact time on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) onto MWCNTs (10–20) and 8-HQ-MWCNTs from aqueous solutions. In general, the % adsorption of metals ions increased significantly within the

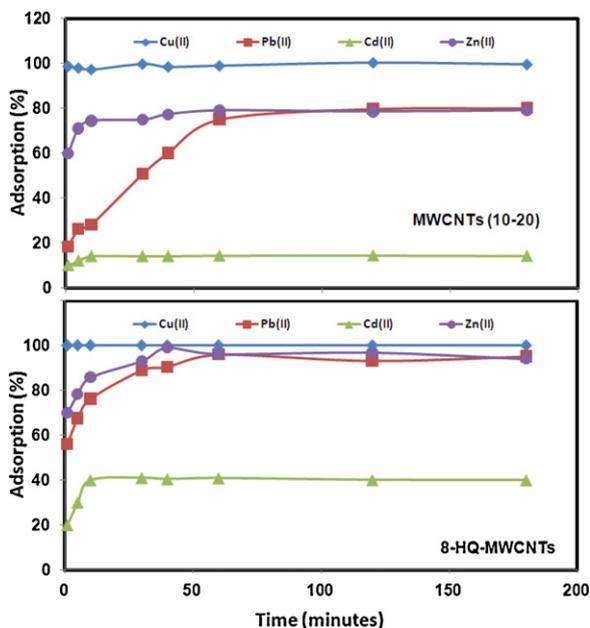


Fig. 5. Effect of contact time on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solution by MWCNTs (10–20) and 8-HQ-MWCNTs. Experimental conditions included a solution pH of 5, 0.25 g MWCNTs/20 mL solution, an ionic strength of 0.1 M KNO_3 , and a metal ion concentration of 1 mg/L.

first 10 min. Cu(II) adsorbed completely within the first minute and reached 100% for both MWCNTs (10–20) and 8-HQ-MWCNTs. For Pb(II), it took approximately 60 min to reach equilibrium with 75% and 95% adsorption for the MWCNTs (10–20) and 8-HQ-MWCNTs, respectively. The modification of MWCNTs with 8-HQ enhanced the adsorption of Pb(II) here by 27%. For Cd(II), it took approximately 10 min to reach equilibrium with 14.1% and 40.0% adsorption for the MWCNTs (10–20) and 8-HQ-MWCNTs, respectively. This indicated the advantage of modifying the MWCNTs with 8-HQ, which enhanced the adsorption by 185%. For Zn(II), it took approximately 10 min to reach equilibrium with 79% and 96% adsorption for the MWCNTs (10–20) and 8-HQ-MWCNTs, respectively. This further indicated the advantage of modifying the MWCNTs with 8-HQ because it enhanced the adsorption of Zn(II) by 21.5%. Based on these results, the equilibrium time was set at 120 min for the remaining experiments to be confident that equilibrium was achieved.

The fraction of metal ions that were adsorbed onto MWCNTs (10–20) reached 99.53%, 80%, 14.1% and 78.47% for Cu(II), Pb(II), Cd(II) and Zn(II) after 120 min, respectively. The fraction of metal ions that were adsorbed onto 8-HQ-MWCNTs reached 99.9%, 95.1%, 40.0% and 94.0% for Cu(II), Pb(II), Cd(II) and Zn(II), respectively. This meant that Pb(II) adsorption increased by 19% (from 80% to 95.1%), Cd(II) adsorption increased by 185% (from 14.1% to 40%), and Zn(II) adsorption increased by 20% (from 78.47% to 94.0%) upon the modification of MWCNTs with 8-HQ. However, this modification did not change the adsorption of Cu(II), as the % adsorption was almost 100% already. Based on these results, the calculated adsorption capacities were found to be 0.080 mg g^{-1} , 0.064 mg g^{-1} , 0.011 mg g^{-1} , and 0.063 mg g^{-1} for Cu(II), Pb(II), Cd(II) and Zn(II), respectively, when pristine MWCNTs (10–20) was used, and 0.080 mg g^{-1} , 0.076 mg g^{-1} , 0.032 mg g^{-1} , and 0.075 mg g^{-1} , for Cu(II), Pb(II), Cd(II) and Zn(II), respectively, when 8-HQ-MWCNTs was used. These values were lower than many other studies using different carbon nanotubes [18]. This might be attributed to the lower specific surface area of the pristine MWCNTs (10–20) and 8-HQ-MWCNTs, which were $69.1 \text{ m}^2/\text{g}$ and $76.2 \text{ m}^2/\text{g}$, respectively, compared with carbon nanotubes employed in previous studies [18].

3.2.2. Effect of CNT dose

The effect of the MWCNTs (10–20) and 8-HQ-MWCNTs dosage on the percentage of metal ions adsorbed from aqueous solutions was studied using metal ion concentrations of 1 mg/L (Fig. 6). The experimental results revealed that the removal efficiencies of metal ions increased gradually with increasing amounts of MWCNTs. Increasing the masses of MWCNTs (10–20) from 0.05 g to 0.25 g sharply increased the % adsorption of Zn(II) from 71.6% to 97.28%, Pb(II) from 42.44% to 93.17%, and Cu(II) from 70% to 100%, while no Cd(II) adsorbed onto MWCNTs (10–20). The 8-HQ-MWCNTs exhibited good performance in the removal of the targeted heavy metals. The % adsorption increased from 6.58% to 97.68% for Zn(II), from 19.23% to 97.34% for Pb(II), from 0% to 39% for Cd(II), and from 99.83% to 99.94% for Cu(II) over the same mass range. This increase in % adsorption might have been attributed to the fact that increasing the adsorbent dose provided a greater surface area or more adsorption sites for the metal ions [19]. Additional increases in the amount of MWCNTs used from 0.25 g to 0.30 g did not significantly affect the removal percentage of metal ions.

3.2.3. Effect of ionic strength

The influence of ionic strength on the adsorption of metal ions is critical because it can create different adsorption situations by which electrostatic interactions between the MWCNTs surfaces and the metal ions are either attractive or repulsive. The effect of ionic strength on the adsorption of the target metals with pristine

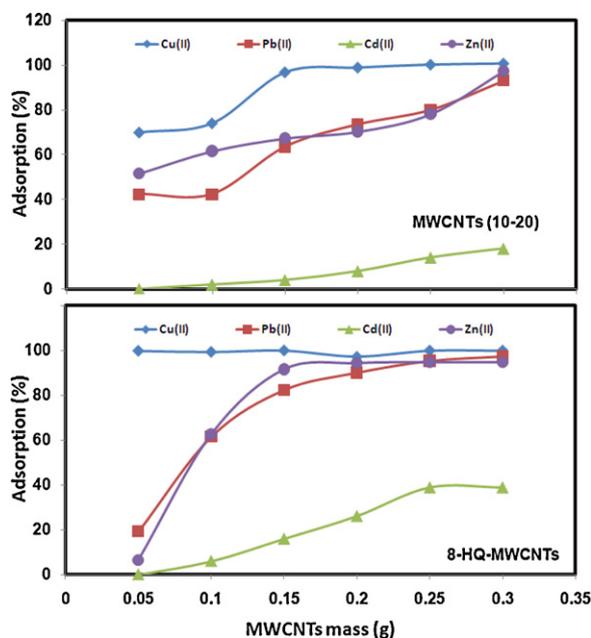


Fig. 6. Effect of the dose of MWCNTs on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solution. Experimental conditions included a solution pH of 5, a contact time of 2 h, an ionic strength of 0.1 M KNO_3 , and a metal ion concentration of 1 mg/L.

and modified MWCNTs was therefore investigated. The adsorption experiments were conducted by changing the ionic strength using KNO_3 concentrations of 0.001, 0.01, 0.1 and 1.0 mol/L. Fig. 7 shows the effects of ionic strength on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) by pristine MWCNTs (10–20) and modified 8-HQ-MWCNTs. For the pristine MWCNTs, no significant effect on the adsorption of Cu(II) was observed after modifying the ionic strength. For the other metal ions, the % adsorptions were gradually increased with increasing ionic strength up to 0.1 mol/L with % adsorptions of 94.0%, 14.1%, and 78.5% for Pb(II), Cd(II) and Zn(II), respectively. Increasing the ionic strength from 0.1 mol/L to

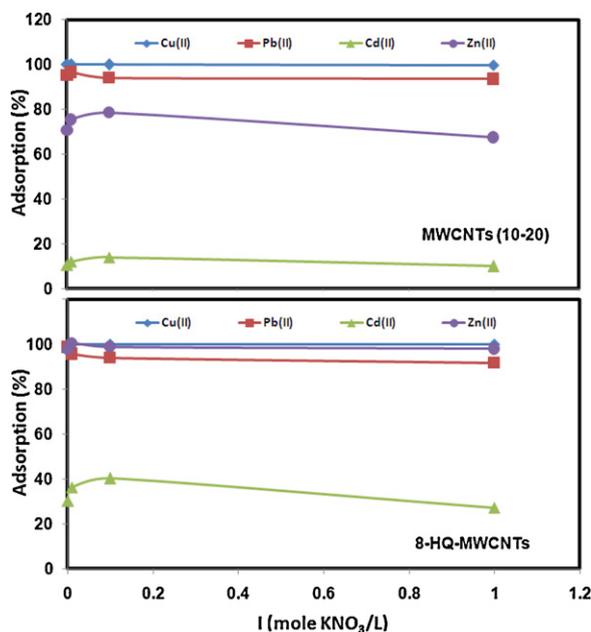


Fig. 7. Effect of ionic strength on metal ion adsorption onto pristine and modified MWCNTs. Experimental conditions included a solution pH of 5, a contact time of 2 h, 0.25 g MWCNTs/20 mL solution, and a metal ion concentration of 1 mg/L.

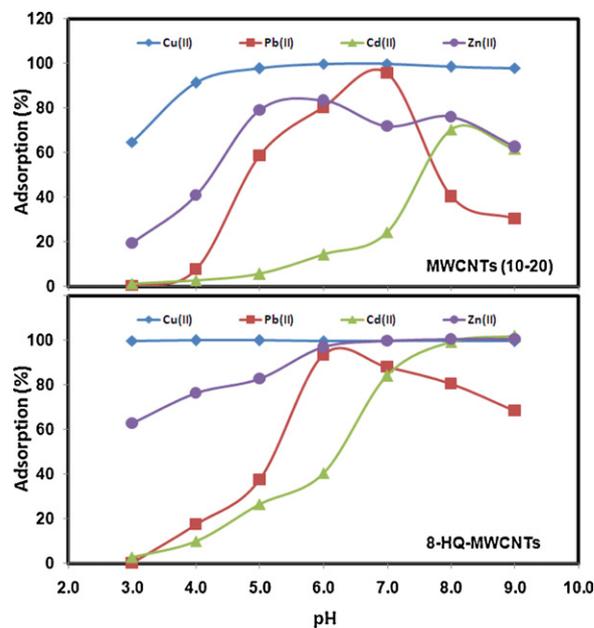


Fig. 8. Effect of solution pH on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solution by MWCNTs (10–20) and 8-HQ-MWCNTs. Experimental conditions included a contact time of 2 h, 0.25 g MWCNTs/20 mL solution, an ionic strength of 0.1 M KNO_3 , and a metal ion concentration of 1 mg/L.

1.0 mol/L decreased the % adsorptions to 93.0%, 10.0%, and 67.5% for Pb(II), Cd(II) and Zn(II), respectively. The same effect was observed when the modified 8-HQ-MWCNTs were used as the adsorbents for the removal of Cu(II), Pb(II), Cd(II) and Zn(II), except higher % adsorptions were achieved at a KNO_3 concentration of 0.1 mol/L (i.e., 100%, 94.1%, 40.2%, and 98.8% for Cu(II), Pb(II), Cd(II) and Zn(II), respectively).

The observed increases in the % adsorptions could have resulted from the attractive nature of the electrostatic interactions between the metal ions and both pristine and modified MWCNTs surfaces at lower ionic strengths (between 0.001 and 0.1 M). Further increases in the ionic strength from 0.1 to 1.0 M KNO_3 transformed this interaction into repulsive in nature and, as a result, decreased the adsorption. In other words, the adsorption process was hindered in part by excess K^+ in the solution. Metal ions usually form electric double layer (EDL) complexes with MWCNTs. It has been reported [20] that the presence of a cation, such as K^+ , decreases heavy metal ion interaction constants due to the accumulation of charge in the vicinity of the MWCNTs surfaces. The presence of these cations creates a localized potential that repels other cations, thus reducing the adsorption potentials of the MWCNTs. Additionally, the ionic strength affected the activity coefficients of Pb(II), Cd(II) and Zn(II) ions, which limited their transfer to the MWCNTs surfaces [21]. Moreover, an increase in ionic strength supplies more positive ions that compete with the heavy metal ions for adsorption sites on the MWCNTs.

3.2.4. Effect of solution pH

Solution pH is one of the main influences on the adsorption process, especially for heavy metal ions, such as Cu(II), Pb(II), Cd(II) and Zn(II), as they exist in different species depending on the pH. The effects of solution pH on the adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) by MWCNTs (10–20) and 8-HQ-MWCNTs were studied in the pH range of 3.0–9.0, and the results are presented in Fig. 8. In general, the removal of metal ions by MWCNTs was highly dependent on the pH of the solution. For all metals, the % adsorption increased gradually with increasing pH. For example, the removal of Cu(II) by MWCNTs (10–20) increased from 64.9% to 99.7%, from

0.0% to 80.5% for Pb(II), from 1.2% to 14.3% for Cd(II), and from 19.13% to 83.40% for Zn(II) when the pH increased from 2.0 to 6.0. However, the removal of Cu(II) by 8-HQ-MWCNTs did not change significantly because the adsorption was already close to 100.0. Adsorption increased from 0.26% to 93.65% for Pb(II), from 1.2% to 40.67% for Cd(II), and from 62.83% to 96.98% for Zn(II) when the pH increased from 2.0 to 6.0. The minimum adsorption observed at low pH values might have been due to the fact that the higher concentration and mobility of hydrogen ions (H^+) present at lower pH favored the preferential adsorption of hydrogen ions than metal ions. In addition, at low pH values the surfaces of the MWCNTs are predominantly covered by H^+ , which prevents metal ions from approaching the binding sites. This was also in agreement with the surface complex formation (SCF) theory, which states that an increase in the pH decreases the competition for adsorption sites between protons and metal species [22]. Moreover, lower positive surface charge leads to less Coulombic repulsion of the metal ions.

Further increases in the solution pH were shown to exhibit different effects on the adsorption process, especially in the basic region where deposition plays a predominant role in metal ion removal. Increasing the pH from 6.0 to 9.0 sharply increased the % adsorption of Cd(II) from 14.3% to 61.7% by MWCNTs (10–20) and from 40.67% to 100% by 8-HQ-MWCNTs. This increase in the % removal was mainly due to adsorption, as cadmium usually precipitates at higher pH values (see cadmium speciation diagram) [23]. According to the equations referenced by Dabrowski [24], the solubility (C_{Cd}) of $Cd(OH)_2$ at pH 5.5 is significant and reaches approximately $10^{3.45}$ M, so Cd(II) is the main species at this pH. At pH 9.0, however, the C_{Cd} of $Cd(OH)_2$ is only about 2.56×10^{-4} M. Further increasing the pH value to 12 decreased the C_{Cd} of $Cd(OH)_2$ to approximately 3.23×10^{-5} M. At this point, the main species in the solution was $Cd(OH)_2$.

When the pH of the solution increased from 6.0 to 9.0, the % adsorption of lead ions decreased from 80.45% to 30.32% with MWCNTs (10–20) and decreased from 93.65% to 68.6% with 8-HQ-MWCNTs. This decrease in the % adsorption at pH values higher than 6.0 could potentially be due to precipitation in the form of $Pb(OH)_2$ [23]. For Cu(II), there was not a significant pH effect from 6.0 to 9.0 because the % adsorption was approximately 100.0% for both pristine and modified MWCNTs. This could be attributed to both adsorption and precipitation processes due to the formation of $Cu(OH)_2$ at pH values higher than 6.0 [23]. For zinc ions, the % adsorption decreased from 83.4% at pH 6.0 to 62.6% at pH 9.0 with MWCNTs (10–20) and increased from 96.98% at pH 6.0 to 100% at pH 9.0 with 8-HQ-MWCNTs. This could be attributed to adsorption at the MWCNTs surface and/or the precipitation of zinc in the form of zincite (ZnO) and/or zinc hydroxides [25]. Leyva et al. stated that the main species of zinc were $Zn(OH)^{+1}$, $Zn(OH)_2$ and $Zn(OH)_3^{-1}$, and thus the removal of zinc was potentially accomplished through the simultaneous precipitation of $Zn(OH)_2$ and adsorption of $Zn(OH)^{+1}$ and $Zn(OH)_3^{-1}$ [26]. It is commonly agreed that the adsorption of metal ions increases with increasing pH because the metal ionic species become less stable in solution. However, at higher pH values (i.e., pH 6.0–10.0), the adsorption capacity decreased, which may have been due to the precipitation of copper, lead, cadmium and zinc.

3.2.5. Effect of metal ion concentrations

Metal ions that are present in contaminated environments exist in different concentrations depending on the sources of contamination. Thus, it is very important to study the effects of varying metal ion concentrations on their adsorption by pristine and modified MWCNTs. The effects of metal ion concentrations on the adsorption behavior of MWCNTs (10–20) and 8-HQ-MWCNTs were studied using a constant MWCNTs dose of 250 mg (Fig. 9). At very low concentrations (i.e., 0.05 mg/L), almost 100% of the Cu(II),

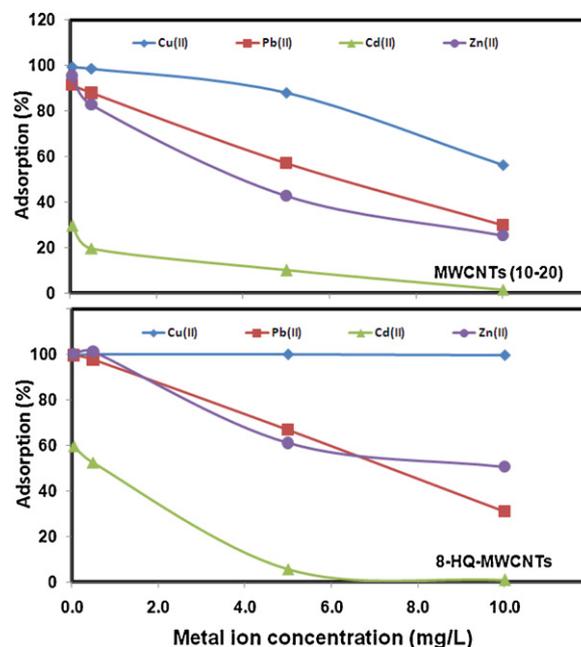


Fig. 9. Effect of metal ion concentration on adsorption by MWCNTs (10–20) and 8-HQ-MWCNTs from aqueous solution. Experimental conditions included a solution pH of 7, a contact time of 2 h, 0.25 g MWCNTs/20 mL solution, and an ionic strength of 0.1 M KNO_3 .

Pb(II), and Zn(II) was adsorbed by both types of MWCNTs. For Cd(II), 29.7% and 59.7% was adsorbed by MWCNTs (10–20) and 8-HQ-MWCNTs, respectively, at a Cd(II) concentration of 0.05 mg/L. Further increases in the metal ion concentration to 0.5, 5.0 and 10.0 mg/L were associated with a decrease in the fraction of metals adsorbed down to 56.4%, 29.8%, 1.5% and 25.37% for Cu(II), Pb(II), Cd(II), and Zn(II), respectively, with MWCNTs (10–20). For 8-HQ-MWCNTs, increasing the metal ion concentration from 0.05 to 10.0 mg/L did not affect Cu(II) adsorption, but the % adsorption of the remaining metals decreased with increasing metal ion concentration to 31.1%, 1.0%, and 50.71% for Pb(II), Cd(II), and Zn(II), respectively.

3.2.6. Effect of competition

Contaminated water commonly contains more than just one heavy metal, as metals co-exist and compete for binding to different ligands in the environment. It is therefore important to study the competition between Cu(II), Pb(II), Cd(II), and Zn(II) for adsorption onto MWCNTs (10–20) and 8-HQ-MWCNTs. Although the four metal ions are bivalent, each of them interacts with the surfaces of pristine and modified MWCNTs in different ways with different capacities.

There is a poor understanding of the order of binding of heavy metal ions by solid adsorbents like MWCNTs. Stafiej and Pyszynska [27] studied the adsorption characteristics of certain divalent metal ions (i.e., Cu, Co, Cd, Zn, Mn, and Pb) by MWCNTs and found that the affinity of metal ions for MWCNTs followed the order $Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II)$. Meanwhile, Li et al. [28] studied the competitive adsorption of Pb(II), Cu(II) and Cd(II) ions by oxidized MWCNTs and found that the adsorption capacities of MWCNTs for the three metal ions were in the order $Pb(II) > Cu(II) > Cd(II)$. In the present study, it was observed that binding to both MWCNTs followed the order $Cu(II) > Pb(II) \approx Zn(II) > Cd(II)$ for % adsorption.

Unfortunately, there is no consensus in the competitive adsorption of metal ions, as researchers have attributed their different affinities to different factors. These factors are related to the

properties of these ions in aqueous solution and could affect surface binding and interaction energies or the accessibility of surface centers, which can be linked to the size of the species adsorbed. Although Pb(II) and Cd(II) have the largest radii (1.33 Å and 0.97 Å, respectively), they show lower adsorption than Cu(II) and Zn(II), which have smaller ionic radii (0.72 Å and 0.74 Å, respectively). Thus, the smaller the ionic radius, the easier it is for a metal ion to penetrate through the boundary layer and adsorb onto the MWCNTs surface. Electronegativity (Pauling) is listed in the following order: Pb(II) > Cu(II) > Cd(II) > Zn(II) (i.e., 2.33, 1.90, 1.69, and 1.65, respectively). This order does not agree well with the experimental affinities for binding and adsorption by MWCNTs. The high adsorption and binding of Cu(II) to the MWCNTs compared with other metals can be explained. Because Cu(II) is predominantly specifically adsorbed (inner-sphere complexation), increasing the amount of more strongly bonded Cu is expected to reduce the number of sites available for Cd and Zn adsorption. Furthermore, Cu(II) is stabilized by the Jahn–Teller effect. The d^9 electronic configuration of this ion provides three electrons to two degenerate e_g orbitals and six electrons to the t_{2g} , leading to a doubly degenerate electronic ground state and a large energetic stabilization. A similar effect was observed in a multi-component system, where an increase in the Cu concentration resulted in a reduction of the uptake of other heavy metals [29]. Additionally, it was reported that high copper adsorption was caused by its ability to be reduced by the carbonaceous surface. Therefore, Cu(II) ions in close proximity to the MWCNTs surfaces are reduced after being attracted to cation exchange centers on the nanotube surfaces. The copper ions then vacate the cation exchange site for the adsorption of other ions [30]. Conversely, the lower adsorption of Cd(II) might be due to its lower tendency to form hydrolysis products and the fact that its ions do not compete effectively for variable charge surfaces, such as MWCNTs. As a result, its adsorption is restricted to permanently charged sites [31].

The difference in the adsorption affinities in this study compared with other studies could be attributed to the unique features of each of the carbon nanotubes produced by the vastly different production methods. Generally, the decrease in the % adsorption could be due to the saturation of the active sites of the MWCNTs (10–20) and 8-HQ-MWCNTs with metals ions at higher concentrations. The mechanism by which the Cu(II), Pb(II), Cd(II) and Zn(II) adsorbed on the surface of 8-HQ-MWCNTs is believed to be both electrostatic attraction between the positive metal ion and the delocalized π -electrons present at the carbon nanotubes surface, and ion exchange arising from the presence of 8-HQ molecules on the MWCNTs surface.

3.3. Desorption study

Recycling, regeneration and repeated availability are important factors for advanced adsorbents. Such adsorbents not only possess higher adsorption capabilities but also display better desorption properties. Better desorption significantly reduces the overall costs associated with adsorbate removal, especially when high costs currently limit their potential use [28]. To evaluate the recycling and reversibility of Cu(II), Pb(II), Cd(II) and Zn(II) adsorption by MWCNTs, optimum conditions for the efficient desorption of Cu(II), Pb(II), Cd(II) and Zn(II) from MWCNTs were studied.

3.3.1. Solution pH

Fig. 10 shows the Cu(II), Pb(II), Cd(II) and Zn(II) recovered from MWCNTs (10–20) at pH values ranging from 1.0 to 5.0. Desorption experiments were conducted for 2.0 h to ensure full desorption equilibrium. It was apparent that the % desorption increased with a decrease in solution pH, especially for Pb(II), Cd(II) and Zn(II) (% desorption reached 152.3%, 162.3% and 69.6% at pH 1.0, respectively).

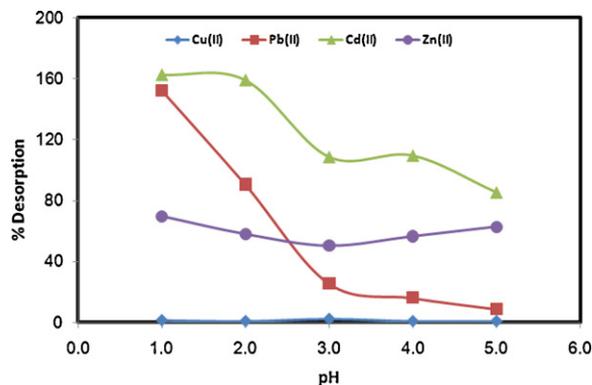


Fig. 10. Effect of solution pH on the Cu(II), Pb(II), Cd(II) and Zn(II) recoveries from MWCNTs (10–20). Experimental conditions included a solution temperature of 298 K, 0.25 g MWCNTs/20 mL solution, an ionic strength of 0.1 M KNO_3 , and a metal ion concentration of 0.5 mg/L.

The high percentage of desorption for Pb(II) and Cd(II) might be attributed to the use of Cd(II) and Pb(II) nanoparticles as catalysts for the production of MWCNTs (10–20) [32,33]. Surprisingly, the % desorption of Cu(II) was only 1.0%, which might be attributed to the stronger binding of Cu(II) to the MWCNTs surface than for the other ions. These results demonstrated that the heavy metal ions adsorbed by MWCNTs (10–20) could easily be desorbed. Therefore, it should be possible to employ MWCNTs (10–20) repeatedly in heavy metal wastewater management. Furthermore, this recovery of the metal ions also indicated that ion exchange was involved in the adsorption mechanism.

3.3.2. Desorption time

Fig. 11 shows the effect of time on the desorption of Cu(II), Pb(II), Cd(II) and Zn(II) from MWCNTs (10–20) at a constant pH of 2.0. Notably, the Cu(II), Pb(II), Cd(II) and Zn(II) recoveries from MWCNTs (10–20) achieved after the first minute of desorption (i.e., 0.72%, 124.1%, 142.2% and 68.9%, respectively) were nearly unchanged after 10.0 min of desorption. This demonstrated the rapid reversibility of the desorption process at low pH. A low recovery of Cu(II) was again observed (1% after 240 min).

3.3.3. Recycling of MWCNTs

The effect of frequent use on MWCNTs (10–20) as adsorbents is an important factor to consider before adsorbent choice. The effect of the number of adsorption cycles on the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solution by MWCNTs (10–20) was studied, and the results are presented in Fig. 12. It is clear

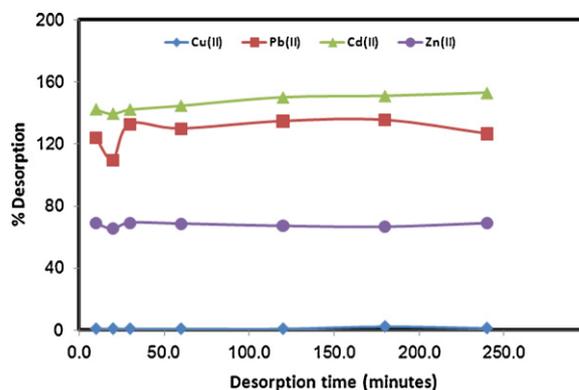


Fig. 11. Effect of regeneration time on the Cu(II), Pb(II), Cd(II) and Zn(II) recoveries from MWCNTs (10–20). Experimental conditions included a temperature of 298 K, a pH of 2, 0.25 g MWCNTs/20 mL solution, an ionic strength of 0.1 M KNO_3 , and a metal ion concentration of 0.5 mg/L.

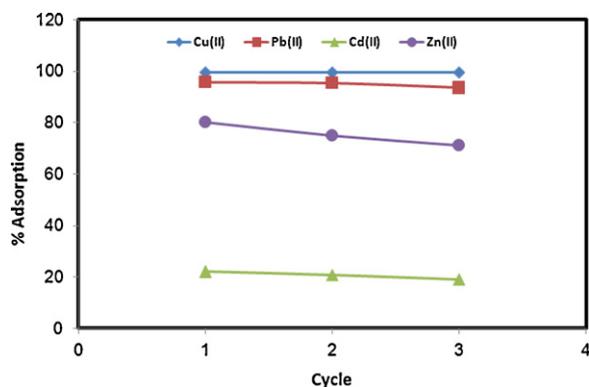


Fig. 12. Effect of the number of regeneration cycles on the Cu(II), Pb(II), Cd(II) and Zn(II) recoveries from MWCNTs (10–20). Experimental conditions included a temperature of 298 K, a pH of 7, 0.25 g MWCNTs/20 mL solution, an ionic strength of 0.1 M KNO₃, and a metal ion concentration of 0.5 mg/L.

from the figure that the four metal ions under investigation were efficiently removed until the third cycle, where the % adsorption values were 99.5%, 95.8%, 80.1% and 21.9% for Cu(II), Pb(II), Cd(II) and Zn(II), respectively. This represents another advantage of the use of MWCNTs for the removal of heavy metal ions from aquatic environments.

3.4. Environmental applications

One of the most important factors that should be considered when investigating porous or nanomaterials for the removal of any pollutant(s) from the environment is the application to real samples from the environment. In this study, two different samples were collected from two different environments: Red Sea water (RSW) and wastewater collected from the King Abdulaziz University Wastewater (KAUWW) Treatment Plant. Detailed analyses for both samples are presented in Table 1. Metal ion analysis using ASV showed that the concentrations of the metal ions under investigation were very low. To verify the applicability of the MWCNTs for the removal of heavy metals from real water samples, the samples were therefore spiked with 0.5 mg/L of Cu(II), Pb(II), Cd(II) and Zn(II). Adsorption experiments using pristine and modified MWCNTs were then performed. The effects of the addition of MWCNTs and 8-HQ-MWCNTs to RSW and KAUWW samples are presented in Table 2 and Figs. 13 and 14. The results show that both pristine and modified MWCNTs efficiently removed a considerable percentage of Cu(II), Pb(II), Cd(II) and Zn(II) for both RSW and KAUWW samples. For the RSW (Fig. 13), almost 100% of the Cu(II) was removed from the solution upon the addition of MWCNTs (10–20). Very low amounts of Pb(II), Cd(II) and Zn(II) were removed for both MWCNTs, although 8-HQ-MWCNTs were more efficient in this regard. This phenomenon might be attributed to the very high concentrations of the cations Na⁺, K⁺, Mg²⁺, and Ca²⁺ in RSW (Table 1). These

Table 2
Removal of the target heavy metal ions from wastewater and Red Sea water samples by pristine MWCNTs and 8-HQ-MWCNTs.

	Cu(II)	Pb(II)	Cd(II)	Zn(II)
Red Sea water sample				
Original concentration (mg/L)	0.035	0.010	0.002	0.007
% Adsorption with MWCNTs (10–20) ^a	97.6	0.255	0.6	8.02
% Adsorption with 8-HQ-MWCNTs ^a	98.1	2.68	1.1	9.90
KAU waste water sample				
Original concentration (mg/L)	0.000	0.000	0.000	0.016
% Adsorption with MWCNTs (10–20) ^a	99.0	44.5	0.3	45.7
% Adsorption with 8-HQ-MWCNTs ^a	99.2	51.4	5.77	83.2

^a After spike with 0.5 mg/L metal ions.

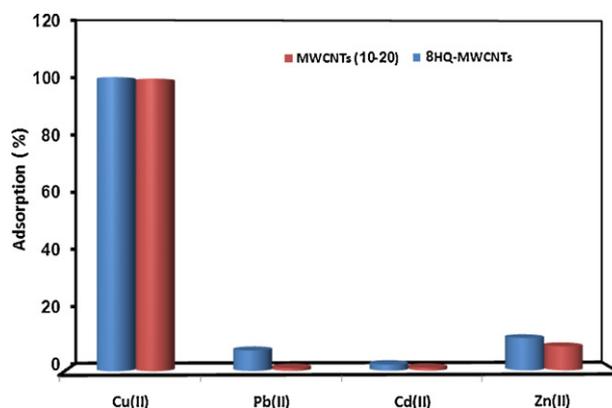


Fig. 13. Adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) by MWCNTs (10–20) and 8-HQ-MWCNTs from spiked Red Sea water. Experimental conditions included a temperature of 298 K, a pH of 7, 0.25 g MWCNTs/20 mL solution, and an ionic strength of 0.1 M KNO₃.

cations, when present at very high concentrations, compete for the MWCNTs active sites and consequently decrease the adsorption of heavy metals. Also, these positive ions form a positive layer around the MWCNTs that serves to decrease the electrostatic attractions between the MWCNTs surface and the heavy metal ions [34].

In the case of the KAUWW sample, it is clear from Table 2 and Fig. 14 that most of the metal ions were removed from the solution. When MWCNTs (10–20) were used, 99.0%, 44.5%, 0.3%, and 45.7% of Cu(II), Pb(II), Cd(II) and Zn(II), respectively, were removed from the KAUWW spiked samples. When 8-HQ-MWCNTs were used, 99.2%, 51.4%, 5.77%, and 83.2% of Cu(II), Pb(II), Cd(II) and Zn(II), respectively, were removed from the KAUWW spiked samples. The enhancement in the % adsorption was mainly due to the 8-HQ modification of MWCNTs.

A comparison between RSW and KAUWW samples showed that the efficiency of removal by MWCNTs was higher in the case of KAUWW spiked samples because larger amounts of the metal ions were removed. This could be attributed to the fact that the RSW sample contained excessive concentrations of Na⁺, K⁺, Mg²⁺, and Ca²⁺ compared with the KAUWW sample (Table 1). The presence of these ions at such high concentrations likely caused a screening effect that decreased the adsorption of the trace metal ions by MWCNTs. That was not the case for Cu(II) only because it formed strong complexes with MWCNTs, even in the presence of high concentrations of interfering cations. These same effects have been observed in other studies using other adsorbents [35,36].

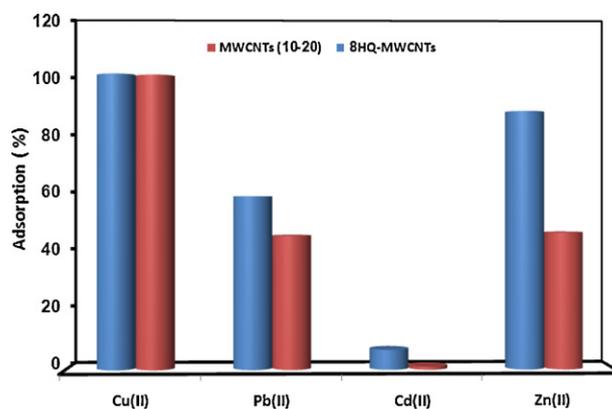


Fig. 14. Adsorption of Cu(II), Pb(II), Cd(II) and Zn(II) by MWCNTs (10–20) and 8-HQ-MWCNTs from spiked wastewater samples collected from the KAU wastewater treatment facility. Experimental conditions included a temperature of 298 K, a pH of 7, 0.25 g MWCNTs/20 mL solution, and an ionic strength of 0.1 M KNO₃.

4. Conclusions

The modification of MWCNTs with the well-known ligand 8-hydroxyquinoline was studied. Pristine and modified MWCNTs were characterized with FT-IR, XPS, surface area analysis and scanning electron microscopy. The pristine and modified MWCNTs were then used for the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions. The effects of adsorption parameters, such as the amount of MWCNTs used, temperature, pH, ionic strength, metal ion concentration, and competition among metal ions, were studied and optimized. The recycling, desorption and regeneration of the MWCNTs were evaluated and the results demonstrated that most of the metal ions desorbed at pH values lower than 2.0, and that the MWCNTs could then be used in up to three cycles of adsorption/desorption without losing efficiency. Two different environmental samples were collected and used to evaluate pristine and modified MWCNTs for Cu(II), Pb(II), Cd(II) and Zn(II) removal. The results revealed that modified MWCNTs had a greater potential for the removal of target metal ions from real water samples than pristine MWCNTs. In conclusion, the modification of MWCNTs with 8-hydroxyquinoline should be a successful strategy for enhancing the adsorption properties of MWCNTs in the removal of heavy metals from the environment.

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