

Multi-walled carbon nanotubes loaded chitosan for water treatment application

Abeer Abdulaziz H. Bukhari

Department of Chemistry, Faculty of Science, University of Tabuk, Saudi Arabia, email: a.bukhari@ut.edu.sa

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ABSTRACT

Chitosan-multi-walled carbon nanotubes nanocomposite (Ch-MWCNT) with ratio 2:1 was synthesized by the sonication process, characterized, and utilized in water treatment for heavy metals adsorption compared to pure multi-walled carbon nanotubes (MWCNT) under different adsorption conditions. The ability of Ch-MWCNT in removing heavy metals from an aqueous solution was studied and the results indicate the order of metal ion removal was $\text{Cu}^{2+} > \text{Pd}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The results also indicate the successful potential of chitosan to overcome the adsorption limitation of pure MWCNT in all studied adsorption conditions. Desorption study was studied by recovering the adsorbed metal ions from Ch-MWCNT under different desorption conditions and the results indicate that Cd^{2+} ion was the most desorbed metal ion from Ch-MWCNT at pH 2 after 2 h desorption time.

Keywords: Chitosan; Carbon nanotube; Heavy metals; Water treatment

1. Introduction

The water crisis is considered one of the greatest challenges nowadays. The main obstacle is found is pollution which exacerbates water shortage problems. Water resources are contaminated with heavy metals and distillate as regular pollutants of anthropogenic activities. Not all these pollutants can be removed from water efficiently by the traditional methods of water treatment [1,2]. Nanotechnologies based on carbon nanotubes (CNTs) are utilized in several fields of water treatment, including membranes, filters, catalysts, or sorbents [3]. The adsorption process is considered an efficient simple procedure for organic and inorganic compound elimination during potable water treatment [4]. CNT is an extremely studied material that possesses the ability to remove heavy metals and several organic contaminants from wastewater via the adsorption process [5]. The problems that limit applying CNTs as adsorbent are their separation difficulty, poor dispersion capability, as well as their small particle size [6]. The maximum adsorption tends to attribute to the surface carrying negatively charged CNTs functional groups

– leading to hydrated ion formation such as $\text{M}(\text{OH})^{+1}$ and $\text{M}(\text{OH})_2$. In solution with a pH more than 12, the dominant metal forms $\text{M}(\text{OH})_3^{-1}$, thus, the removal process of heavy metals is decreasing as a result of the competition between $\text{M}(\text{OH})_3^{-1}$ and OH^{-1} in addition to the repulsive force that occurs between $\text{M}(\text{OH})_3^{-1}$ and CNT surface carrying negative charges [7]. Chen et al. [8] found that using CNTs modified with different functional groups have a great affinity for heavy metals removal from wastewater. CNTs are used as an effective adsorbent for the removal of both organic and inorganic contaminants including lead, nickel, arsenate, fluoride, Cd^{2+} , Cu^{2+} , 1,2-dichlorobenzene, trihalomethanes [9].

Chitosan has excellent metal-binding capacities depending on the presence of electron pair on the amine nitrogen in chitosan molecule which is found to be important in up taking the metal cations by chelating; resulting in a reduction in toxin synthesis as well as microbial growth. Also, chitosan is capable of chelating a few elements as well as many essential nutrients required for bacterial and fungal growth [10–12].

The application of chitosan in water treatment and agriculture has great potential. Chitosan is capable of removing

* Corresponding author.

many toxic water pollutants like heavy metals, dyes, and phenol compounds [13].

Different polymeric and bio-polymeric materials, such as polyaniline and chitosan, are reacted by CNTs surface wrapping in addition to π - π stacking via the solubilized polymeric chain. Applying such functionalization techniques is providing various CNTs applications [14,15]. Polymer nanocomposites have been reinforced by nanoparticles that have a high surface area to volume ratio; for instance, carbon nanotubes, nanoplatelets, nanofibers, and nanoparticles. Recently CNTs are considered desirable fillers, due to the improvement of biopolymers properties. According to many studies, the researchers examined the effect of using CNT fillers within the chitosan matrix, then evidenced the suitable properties of chitosan-CNT nanocomposites and their high potential for several biomedical applications. The conjugation of CNTs and natural polymer chitosan is leading to hybrid materials that possess a mixture of desired properties that overcome any disadvantage that could affect individuals [16–18].

Kerdnawee et al. [19] were investigating the tetracycline adsorption onto each of the graphite, activated carbon (AC), and CNTs. They reported that the affinity of tetracycline adsorption was decreased in the order of; graphite > SWCNT > MWCNT > AC till equilibrium of the surface area of the adsorbent. The weak tetracycline adsorption onto AC proved that the accessibility of available adsorption sites had a great effect on the adsorption affinity. However, AC has more micropores; they are sometimes unavailable for the relatively large organic molecules access. The strong tetracycline adsorption onto CNTs could refer to the strong adsorptive combinations; including the cation- π bonding and van der Waals forces, with the graphene surface of CNTs.

Li et al. [20] investigated the trihalomethanes adsorption onto CNTs and powdered activated carbon (PAC) according to kinetics mechanism. CNTs achieved the adsorption equilibrium faster than the PAC did, due to the difference of porous structures in CNTs and PAC. The suitable CNTs pore structure is found to be proper for the pollutant's diffusion into the inner pores. While PAC is rich with micropores, which lead to trihalomethanes easily moving from the exterior surface into PAC inner pores till reaching the equilibrium.

Zhang et al. [21] studied the adsorption kinetics of both biphenyl and phenanthrene on CNTs and granular activated carbon (GAC). They found that the organic compound adsorption to CNTs was controlled by external mass transfer. In the case of GAC, the intraparticle diffusion was dominated by the adsorption process. So CNTs are more effective in sorption kinetics than GAC in well-mixed systems.

The conjugation of CNTs and natural polymer chitosan is leading to hybrid materials which possess a mixture of desired properties as well as overcoming any disadvantage that could affect individuals. It is proved that the attachment between natural polymer chitosan with multi-walled carbon nanotubes (Ch-MWCNT) leads to overcoming the toxicity of MWCNT. Also, MWCNT is shown to induce improvement in each of the mechanical, thermal and electrical properties of the original material [22]. So,

by adding MWCNTs that have excellent electrical properties to natural polymers, unique conductive MWCNT/polymer nanocomposites are produced.

The present work aims to compare the desorption capacity of MWCNT with the ability of the prepared Ch-MWCNT nanocomposite in removing four heavy metals from aqueous solutions under different adsorption conditions in order to elucidate the effect of the presence of chitosan to overcome the adsorption limitation of the carbon nanotubes.

2. Experiment setup

2.1. Materials

Multi-walled carbon nanotubes with diameter 7:15 nm and length 0.5:10 μ m were supplied from Sigma-Aldrich (Darmstadt, Germany). HNO_3 (67%) and H_2SO_4 (98%) were supplied from NEN Technologies Private Limited Company (Jaipur - India). Chitosan with mol. wt. 400.00 was supplied from Mallinckrodt, USA. All other used chemicals were provided from Merck (Darmstadt, Germany).

2.2. Characterization

The morphology and fracture surface of the polymer and its composite were examined by transmission electron microscope (TEM) analysis using a JEM 1230 electron microscope and operated at 60 kV (JEOL Ltd., Tokyo, Japan)

The Fourier-transform infrared (FTIR) spectra were obtained using a Bruker IFS 28 spectrometer 67 (Leipzig, Germany).

The residual concentration of the heavy metal ions in the solution will be analyzed and measured using the Perkin Elmer UV-Vis spectrophotometer (Massachusetts, USA) at its maximum absorption wavelength in the range between 200:600 nm.

2.3. Methods

2.3.1. Purification of CNT

Multi-walled carbon nanotubes were purified according to the literature procedure [23]. The CNTs (500 mg) were added to 98% H_2SO_4 and 67% HNO_3 mixture (3:1 v/v, 200 mL), irradiated by ultrasonic sonifier (400 W) under room temperature for 30 min, washed with ultra-pure water and filtered by a microporous filtration membrane, re-dispersed in 200 mL, 2 M HNO_3 and refluxed for 24 h, collected by filtration, washed with ultra-pure water and dried under vacuum at 50°C for 24 h (Fig. 1).

2.3.2. Preparation of Ch-MWCNT

20 mg of purified MWCNTs were dispersed in 40 mL chitosan solution (40 mg chitosan in 0.1 M aqueous acetic acid) and irradiated by ultrasonic sonifier (400 W) for 30 min. Stirred for 8 h at room temperature [23], the obtained Ch-MWCNTs were filtered and unbound chitosan was removed by ultra-centrifugation and washed with ultra-pure water and dried at room temperature.

2.3.3. Preparation of stock metal solutions

MWCNTs and modified-MWCNTs with chitosan (Ch-MWCNTs) have been used for increasing the effectiveness of divalent metal ions removal such as lead, zinc, copper, and cadmium from polluted industrial wastewater. For achieving a better understanding of the target of heavy metal ions adsorption on MWCNTs and Ch-MWCNTs in aqueous solution, the adsorption studying process should be accompanied by kinetic studies and adsorption behavior investigation.

Solutions of lead, zinc, copper and cadmium divalent metal ions were prepared from metal nitrates solutions with concentration 1,000 mg/L using tripled deionized water. The pH value of the prepared solutions was adjusted by HNO₃ and NaOH diluted solutions and measured by a pH-meter combined with a glass electrode. Metal concentrations estimated by Perkin Elmer UV-Vis spectrophotometer at its maximum absorption wavelength were in the range between 200–600 nm.

2.3.4. Adsorption experiments

Specific amounts (0.05–0.30 g) of MWCNTs and Ch-MWCNTs were added separately to 50 mL of each metal ion solution and stirred using a magnetic stirrer for 4 h at room temperature. The amount of adsorbed metal ion on both MWCNT and Ch-MWCNT was determined by UV-Vis spectrophotometer, and metal ion removal percentage was calculated by using the following equation [24]:

$$\% \text{Removal of metal ion} = \left[\frac{(C_0 - C_e)}{C_0} \right] \times 100 \quad (1)$$

where (C_0) is the initial metal ion concentration and (C_e) is the equilibrium metal ion concentration after the adsorption process.

The effect of initial metal ion concentration, adsorption time, pH value and ionic strength were also studied.

2.3.5. Desorption procedure

For the desorption study, 0.25 g of Ch-MWCNT containing each adsorbed metal ions were stirred in 20 mL deionized water at room temperature under different acidic pH values ranging from 2 to 6 and different time intervals between 5–240 min. The fraction of desorbed metal ion from the Ch-MWCNTs was determined by UV-Vis spectrophotometer and the desorption percentage was calculated using the following equation [25]:

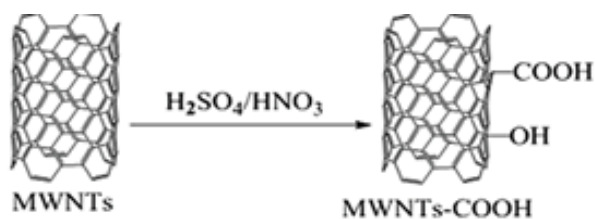


Fig. 1. Purification of MWCNT.

$$\% \text{Desorption} = \frac{\text{desorbed metal ion (mg/L)}}{\text{adsorbed metal ion (mg/L)}} \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization of the prepared Ch-MWCNT nanocomposite

3.1.1. Transmission electron microscope

Fig. 2 illustrates the TEM of pure CNT, modified MWCNT, chitosan, and Ch-MWCNT nanocomposite with ratio 2:1. From the figure, it is obvious that the purified MWCNT has a good homogeneity with a uniform distribution in the chitosan polymer surface. From the figure, it is also noticeable that the produced Ch-MWCNT has a smooth surface and MWCNT causes a trigger in the morphological features of the chitosan surface [26,27].

3.1.2. Fourier-transform infrared spectroscopy

The modification of pure MWCNT and the incorporation of MWCNT inside the chitosan has been confirmed by FTIR analysis of chitosan and prepared Ch-MWCNT which is illustrated in Fig. 3.

In CNT spectra, the intense and wideband at 3,220 cm⁻¹ is attributed to the vibration of –OH in the carboxyl group, the characteristic peaks at 1,513 and 1,040 cm⁻¹ are due to the vibration of C=O and C–O, respectively. In Ch-MWCNT spectra, the intense bands at 3,480 and 1,040 cm⁻¹ are attributed to the stretching vibration of N–H and C=O in –CONH, respectively, which confirm that the polymer was grafted onto MWCNTs via the amide linkage [27].

3.2. Adsorption study

The process of metal ions adsorption from aqueous solution has been determined by using carbonaceous adsorbents as CNT. The investigation of metal ions adsorption by the means of CNT is found to be efficient in the remediation process. For the success of the adsorption process, various factors like temperature, pH, ionic strength as well as the competition occurring between metal ions have to be optimized. The MWCNTs modification using chitosan and its effect on the adsorption behavior of Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ and from aqueous solutions have been studied.

3.2.1. Effect of solution pH

The heavy metal ions adsorption process is much affected by the solution pH. Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ can be found in different species according to the pH value of the aqueous solution, so it is examined of pH range from 3.0 to 9.0 and studied its effect on the adsorption process via Ch-MWCNTs and MWCNTs. The heavy metal removal is mainly dependent on the solution of pH that occurs via Ch-MWCNTs and MWCNTs. The results are found in Table 1. Generally, the adsorption percentage gradually increases associating to pH increase for all tested metals. The removal of metals by MWCNTs when the pH increases from 3.0 to 6.0 has been illustrated as; Cd²⁺ increase from 1.35% to 15.5%, while Pb²⁺ rise from 0% to 81.2%, Cu²⁺

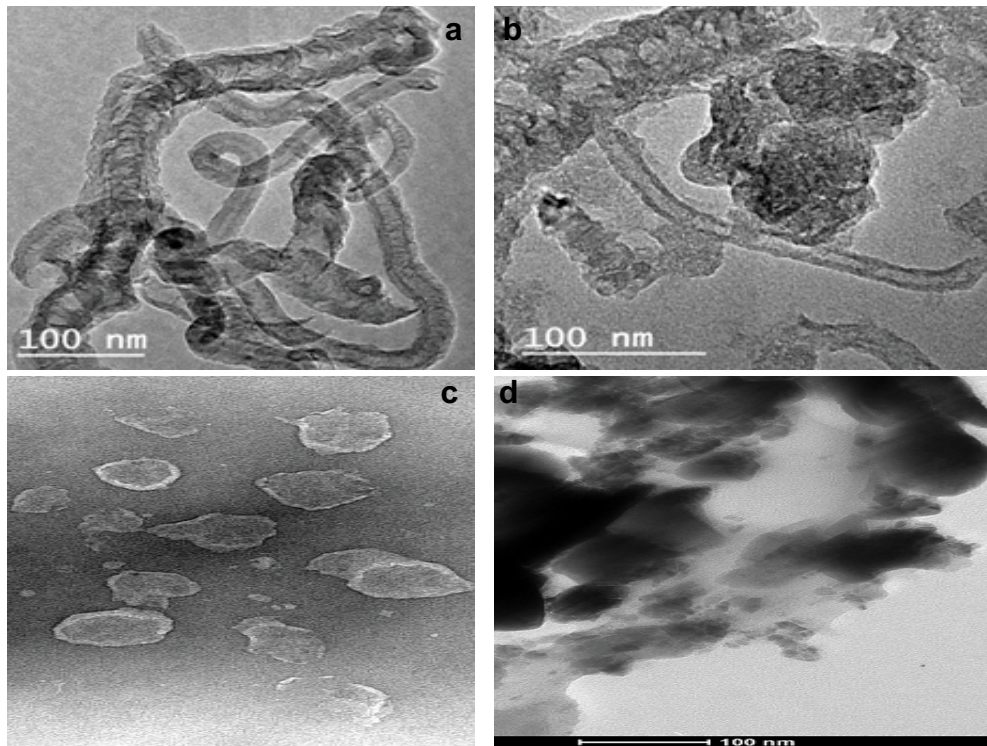


Fig. 2. Transmission electron microscope images of (a) pure CNT, (b) modified CNT, (c) pure chitosan, and (d) chitosan-CNT.

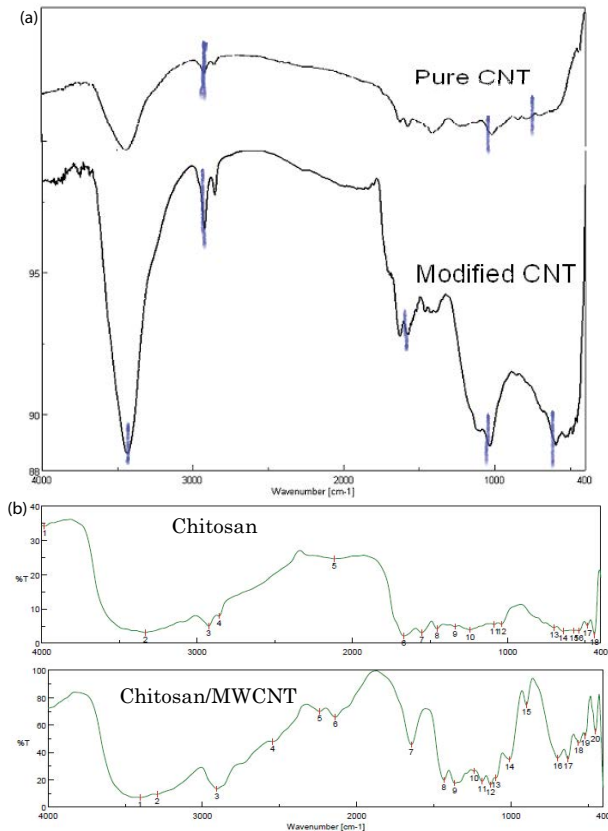


Fig. 3. Fourier-transform infrared spectroscopy of (a) pure CNT, purified CNT and (b) chitosan and Ch-MWCNT nanocomposite.

is also increased from 65.3% to 99.6% and finally Zn^{2+} rises from 20.1% to 84.6%.

In case of increasing pH from 3.0–6.0, the adsorption percentage is also increased as Cd^{2+} rises from 1.2% to 39.9%; Pb^{2+} increases reaching 0.37% to 94.8%, as well as Zn^{2+} rises from 63.8% to 97.7%. Although Cu^{2+} removal via Ch-MWCNTs has not significantly changed – as its adsorption is already about 100%.

At low values of pH, the adsorption process may be in minimum rate which is based on the fact that dealing with the higher concentration and mobility of hydrogen ions (H^+) found at lower pH is favorable to adsorb hydrogen ions rather than metal ions. Also, the MWCNTs surfaces are predominantly covered by H^+ at low pH values, which prevent the tested heavy metal to approach the binding sites [28].

While in a higher solution, pH rises from 6.0 to 9.0. In the case of Cd^{2+} ions, the adsorption percentages increase associating to the increase of pH value from 6–9 as being increased from 15.5% to 59% by MWCNT and via Ch-MWCNT adsorption percentages are 39.9% reaching 100%. The adsorption percentage of Pb^{2+} decreased from 81.2% to 29.9% by MWCNTs and 94.8% to 67.9% by Ch-MWCNTs. This minimizes the adsorption percentage when pH rises over 6.0. This can be referred to precipitation of Pb^{2+} ions as $Pb(OH)_2$ form. However, Cu^{2+} has not been significantly affected by the rise of pH till it reaches 9.0. This is due to the percentage of Cu^{2+} adsorption which almost reached 100% via Ch-MWCNTs and MWCNTs. The percentage of Zn^{2+} adsorption is found to decrease from 84.6% to 61.4% by MWCNTs, while it increases from 97.7% till reaching 100% using Ch-MWCNTs at pH 9.0.

Table 1

Effect of solution pH on the adsorption of Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ from aqueous solution by MWCNTs and Ch-MWCNTs

pH	Percentage of adsorption (%)			
	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺
MWCNTs				
3	1.35	0.00	65.3	20.1
4	7.48	17.44	85.37	40.11
5	10.02	60.00	98.80	75.60
6	15.5	81.2	99.6	84.6
7	20	62.72	100	65
8	67	40.50	100	70
9	59	29.9	100	61.4
Ch-MWCNTs				
3	1.2	0.37	98.54	63.8
4	5.22	15.10	98.90	80.33
5	20.75	30.89	99.95	85.27
6	39.9	94.8	100.00	97.7
7	80.25	80.66	98.90	98.00
8	100.00	72.91	99.00	98.55
9	100.00	67.9	99.50	100.00

Experimental conditions included a solution temperature of 25°C, 250 mg MWCNTs/50 mL aqueous solution, metal ion concentrations of 0.5 mg/L and ionic strength of 0.1 M KNO₃.

Such a suggestion agrees with the surface complex formation theory that is defined as increasing in pH decreases the competition between H⁺ and metal ions on adsorption sites [29]. Much more, the decrease in positively charged surfaces causes a lowering in metal ions Coulombic repulsion. In that case, Cu²⁺ was significantly unaffected by rising pH from 6.0 to 9.0 as adsorption percentage already reached approximately 100% via both Ch-MWCNTs and MWCNTs. The removal of Zn²⁺ increases from a solution of pH ranged 1–8, reaching its maximum at 8–11 pH range, then decreases when pH exceeds 12.

3.2.2. Effect of the dosage of MWCNT and Ch-MWCNTs

The percentage of adsorption of metal ions is affected by the dosage of Ch-MWCNTs and MWCNTs utilizing metal ion concentrations of 1 mg/L. Results in Table 2 represent the gradual increase in the metal ions removal associating with rising MWCNTs amounts.

As shown in Table 1, the adsorption percentage increases with the increase of the MWCNTs masses from 0.05 g to 0.25 g. As in that case, the Pb²⁺ increases from 42.44% to 93.17%, Zn²⁺ increases from 71.63% and reaches 97.28%, while the increase in Cu²⁺ is from 70.10% till achieving 100%. However, there is no Cd²⁺ that has been adsorbed via MWCNTs.

The heavy metals removal by the means of Ch-MWCNTs improves the removal performance. There is an increase in the adsorption percentage as Pb²⁺ increases from 59.23% to 97.34%. While in the case of Zn²⁺, the percentage increases from 76.58% to 97.68%, Cu²⁺ increases from 99.83% to 99.94%.

Table 2

Effect of concentration of MWCNT on the adsorption of different metal ions at pH 7

Concentration (g)	Percentage of adsorption (%)			
	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺
MWCNTs				
0.05	0.00	42.44	70.10	71.63
0.10	1.20	43.20	72.10	79.00
0.15	2.00	60.46	99.10	80.28
0.20	4.00	76.00	99.80	95.37
0.25	14.40	93.17	100.00	97.28
0.30	14.14	94.03	100.00	98.50
Ch-MWCNTs				
0.05	0.00	59.23	99.83	76.58
0.10	4.01	60.57	99.91	80.54
0.15	20.57	80.00	99.94	86.41
0.20	30.64	90.51	98.57	88.55
0.25	39.00	97.34	99.94	97.68
0.30	39.00	98.00	100.00	98.12

Experimental conditions included a solution pH of 7.0, a temperature of 25°C, metal ion concentrations of 1 mg/L in 50 mL aqueous solutions and ionic strength of 0.1 M KNO₃.

Cd²⁺ percentages rise from 0% reaching 39% over the same mass-range.

This adsorption percentage elevation could refer to the fact that increasing dose and concentration of adsorbent provide more surface area which promotes more adsorption sites required from target heavy metals [30].

3.2.3. Initial metal ion concentrations

The contaminated environments contain different metal ions concentrations that are affected by the contamination sources. As shown in Table 3, under a constant dose of MWCNTs (250 mg), the adsorption of metal ion concentrations has been affected by both Ch-MWCNTs and MWCNTs. Even with tiny metals concentrations as 0.05 mg/L, Ch-MWCNTs and MWCNTs can successfully adsorb almost all the Zn²⁺, Cu²⁺ and Pb²⁺. In the case of Cd²⁺ at 0.05 mg/L concentration, only Ch-MWCNTs can adsorb 59.7%, while 29.7% via MWCNTs. An inverse relationship occurs between the adsorption rate and concentration of metal ions. As in case of MWCNTs, the percentage of metals adsorbed decrease with increasing concentration of the metal ion as 0.5 (20.25%, 90%, 92.76% and 83.54%), 5.0 (10.01%, 65.44%, 87% and 40.22%) and 10.0 mg/L (1.5%, 29.8%, 56.4% and 25.37%) for Cd²⁺, Pb²⁺, Cu²⁺, and Zn²⁺. While for nanocomposite Ch-MWCNTs, the percentage of adsorption is decreasing associating with the increase in concentration of metal ions as 10.0 mg/L gives 1.0% 31.1% and 50.71% for Cd²⁺, Pb²⁺ and Zn²⁺ respectively. In the case of Cu²⁺, its adsorption was less affected than other tested metals from increasing the conc. from 0.05 (100%) to 10.0 mg/L (60.2%).

This decrease in percentage adsorption might have been attributed to the high metal ions concentration causing

Table 3

Effect of different concentrations of metal ion on its adsorption from aqueous solution using MWCNTs and Ch-MWCNTs at pH 7

Metal concentration (mg/L)	Percentage of adsorption (%)			
	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺
MWCNTs				
0.05	29.70	100.00	100.00	100.00
0.5	20.25	90.00	92.76	83.54
5.0	1.01	65.44	87.00	40.22
10.0	1.50	29.80	56.40	25.37
Ch-MWCNTs				
0.05	59.70	100.00	100.00	100.00
0.5	55.87	96.30	93.00	85.30
5.0	5.33	70.54	88.10	67.55
10.0	1.00	31.10	60.20	50.71

Experimental conditions included a solution pH of 7.0, a temperature of 25°C, 250 mg MWCNTs/50 mL aqueous solution and ionic strength of 0.1 M KNO₃.

limitation in their attachment upon MWCNT surface rather than in case of MWCNTs active sites have been saturated with the metal ions. Application of MWCNTs increases the heavy metals removal efficiencies referring to their high chance of forming a complex between target ions and modifiers [31].

3.2.4. Effect of contact time

Contact time is one of the main factors affecting the efficiency of adsorption of Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ via both MWCNTs and Ch-MWCNTs from aqueous solutions. As shown in Table 4, it indicates that the adsorption % of metals ions significantly increase in the first 10 min. Cd²⁺ takes approximately 10 min for reaching equilibrium but with an adsorption percentage of about 40.0% and 14.1% for Ch-MWCNTs and MWCNTs respectively. Pb²⁺ takes about 60 min for reaching equilibrium with an adsorption percentage of 95% and 79.7% via Ch-MWCNTs and MWCNTs, respectively. So, chitosan modification Ch-MWCNTs enhances the Pb²⁺ adsorption by 27.2%. Cu²⁺ completely adsorbed reaching 100% for Ch-MWCNTs and MWCNTs just during the first minute. In the case of Zn²⁺, it takes about 10 min for reaching equilibrium with 96% and 78.5% adsorption for the Ch-MWCNTs and MWCNTs, respectively. This also indicates the advantage of modification of MWCNTs by chitosan that could improve Zn²⁺ adsorption by 21.5%, proving the aim of chitosan modification of MWCNTs which increases the adsorption percentage by 185%. According to these results, the remaining experiments have been set for 120 min for being confident that equilibrium has been achieved. The adsorption capacity (q) (mg/g MWCNTs) was obtained as follows [7]:

$$q = \left[(C_0 - C_f) \frac{V}{m} \right] \quad (3)$$

Table 4

Effect of contact time of MWCNT and Ch-MWCNT on the adsorption of different metal ions at pH 7

Time	Percentage of adsorption (%)			
	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺
MWCNTs				
5	10.1	20.0	99.1	60.3
10	13.1	27.2	100	79.0
15	18.2	28.4	99.1	79.2
30	14.0	53.0	89.8	79.0
40	13.4	57.2	94.2	78.9
60	13.1	79.7	98.0	78.50
120	13.1	79.9	99.2	78.6
175	13.0	79.8	99.5	79.0
Ch-MWCNTs				
5	20.0	55.0	97.0	70.0
10	39.0	70.0	100.0	96.0
15	39.0	78.0	100.0	86.0
30	39.0	87.0	100.0	90.0
40	38.0	87.0	100.0	99.0
60	37.0	95.0	100.0	96.0
120	39.0	94.9	99.9	94.9
175	38.0	98.0	100.0	98.0

Experimental conditions included a solution pH of 7.0, a temperature of 25°C, 250 mg MWCNTs/50 mL aqueous solution, metal ion concentrations of 0.5 mg/L and ionic strength of 0.1 M KNO₃.

where C_0 and C_f are the initial and final concentrations (mg/L) of the metal ion in the aqueous solution, V is the volume of the metal ion solution and m is the weight of MWCNTs.

The results indicate that adsorption occurs rapidly within the first 10 min upon the surface of Ch-MWCNTs and MWCNTs. There is a great advantage from MWCNTs modification by chitosan, as it improves Zn²⁺ adsorption by 21.5% and 18.5% in the case of Cd²⁺. Thus, explaining the low adsorption rate associated with time increase refers to the long-range of metal diffusion through interlayer as well as inner cavities of MWCNTs [32]. According to the results, it takes 120 min to reach equilibrium, so we fix this time for the rest of the experiments to ensure reaching equilibrium.

After 120 min, MWCNTs can adsorb about 13.1%, 79.9%, 99.2%, and 78.6% for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ respectively. While Ch-MWCNTs adsorption percentages become about 39.0%, 94.9%, 99.9% and 94.9% for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺, respectively. The modification has not changed the percentage of Cu²⁺ adsorption as it is almost reached 100% already. So as given results, the adsorption % of Pb²⁺ increases by 19% (from 79.9% to 94.9%), and Zn²⁺ adsorption increases by 20% (from 78.6% to 95.0%) while Cd²⁺ increases by 185% (from 13.1% to 39%).

3.2.5. Effect of ionic strength

Studying the affected heavy metal as Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺, adsorption by the ionic strength factor uses both

Ch-MWCNT and MWCNTs as shown in Table 5. By using MWCNTs, the percentages of adsorbed metals increase directly with rising ionic strength till reaching 0.1 mol/L followed by decreasing till reaching 1.0 mol/L. For Pb^{2+} , the percentages increase to 93.8% then decrease to 92.5%. Zn^{2+} percentages differ from 79.6% to 66.9% with increasing the ionic strength from 0.1 to 1.0 mol/L. Adsorption percentages of Cd^{2+} are 15.1% and 9.8% at 0.1 and 1.0 mol/L of KNO_3 concentration respectively. In the case of Cu^{2+} , there is not any significant effect on the percentages of adsorption either from changing the ionic strength or using Ch-MWCNTs or MWCNTs in the adsorption process as its adsorption percentages are constant at 100%.

Using nanocomposite Ch-MWCNTs in heavy metal removal also has the same effect as MWCNTs. As at ionic strength 0.1 mol/L, the adsorption percentages are 41.1%, 95.3%, 100% and 97.9% for Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} respectively.

These increases in the adsorption percentages can be due to the attractive nature of the electrostatic interactions between Ch-MWCNTs or MWCNTs with the metal ions. By the further increase in the ionic strength from 0.1 to 1.0 M KNO_3 , the repulsive interaction in nature occurs resulting in decreasing the adsorption percentage of metal ions. By other means, excess K^+ in the solution cause blockage of the adsorption process. Metal ions usually form electric double layer complexes with MWCNTs.

When cations are present in solution, they lead to a decrease in the interaction constants of metal ions because of charge accumulation near the MWCNTs surface. These cations form localized potential which raises the repulsion to other cations causing a reduction in MWCNTs adsorption capability [33]. Furthermore, the activity coefficients of Pb^{2+} , Zn^{2+} and Cd^{2+} have been affected by ionic strength, leading to the limitation to be adsorbed upon MWCNTs surfaces [34]. Also increasing the ionic strength creates more positively charged ions which cause

competition between target metals for being adsorbed upon MWCNTs surfaces.

3.2.6. Effect of competition

One type of water pollution is contamination with heavy metals that cohabit and compete together to bind with several kinds of ligands found in the environment. This is tended to examine the effect of competition among Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} to be adsorbed via Ch-MWCNTs and MWCNTs. As the tested heavy metals are bivalent, each one can interact within various capacities to the surfaces of both Ch-MWCNTs and MWCNTs.

The competition between metal ions together is based on the behavior of such ions in an aqueous solution. Furthermore, it has effects on the binding surface, surface centers accessibility, and interaction energies that could bind to the probable size of the species adsorbed. Cu^{2+} and Zn^{2+} possess small radii of 0.72 Å and 0.74 Å, respectively, which lead to adsorption percentages much more than that of bigger ions as Pb^{2+} and Cd^{2+} of radii 1.33 Å and 0.97 Å, respectively. So as the ionic radius is smaller, as it is easier for penetration of metal ion through the boundary layer on the adsorbent surface. Also, a smaller radius facilitates the adsorption process by Ch-MWCNTs and MWCNTs.

The electronegativity (Pauling) has been listed as: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ (2.33, 1.90, 1.69, and 1.65, respectively). Unfortunately, this electronegativity order isn't agreeing with their affinities for interacting and adsorbed onto Ch-MWCNTs and MWCNTs.

Cu^{2+} has unique behavior compared to the other tested metals with the highest capacity for binding and adsorbed by both Ch-MWCNTs and MWCNTs with high rates. As Cu^{2+} is mainly adsorbed (inner-sphere complexation) the percentage of hardly attaching bonds caused by Cu^{2+} increases. This is expected from reducing the number of available sites during the adsorption process for other metal ions as Cd^{2+} and Zn^{2+} . This Cu^{2+} effect is also the same in the system with multicomponent, as with increasing Cu^{2+} concentration the adsorption of other tested metals is also being reduced.

The ability of Cu^{2+} to be reduced via the carbonaceous groups on the surface has been also reported to increase copper adsorption. So, Cu^{2+} that nearing enough to the nanotube has to be reduced after attracting to cation exchange centers on the MWCNTs surfaces. Cu^{2+} vacates the cation exchange site for being adsorbed by other tested heavy metals. Otherwise, the lower percentage of Cd^{2+} adsorption is referred to as its ions don't effectively compete for surfaces with variable charge as MWCNTs. However, in the case of Cd^{2+} , it is a lower tendency to form hydrolysis is also reducing its adsorption which is restricted to permanently charged sites.

The variability in the adsorption affinities among tested metal ions in our study compared to other studies may attribute to the unique features of each CNT that differs according to the different techniques of the production. In general, the lower adsorption percentage can base on the active sites' saturation of both Ch-MWCNTs and MWCNTs by tested ions with higher concentrations. The adsorption mechanism of Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} upon Ch-MWCNTs surface is due to the arising of ion exchange as a result of

Table 5
Effect of concentration of MWCNT on the adsorption of different metal ions at pH 7

KNO ₃ concentration (mol/L)	Percentage of adsorption (%)			
	Cd ²⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺
	MWCNTs			
0.001	10.0	87.4	100	70.3
0.01	11.0	92.1	100	77.0
0.10	15.1	93.8	100	79.60
1.00	9.8	92.5	100	66.9
	Ch-MWCNTs			
0.001	30.4	99	100	79.3
0.01	37.0	98	100	88.5
0.10	41.1	95.3	100	97.9
1.00	30.7	92.0	100	94.2

Experimental conditions included a solution pH of 7.0, a temperature of 25°C, 250 mg MWCNTs/50 mL aqueous solution, and metal ion concentrations of 0.5 mg/L.

chitosan molecules presence upon the surface of MWCNTs in addition to the electrostatic attraction between the positively charged metal ions with the delocalized π -electrons found on MWCNT surface [35].

3.3. Desorption study

The desorption is shown to reduce the overall costs associating with the removal of adsorbed metal ions, especially in case of limitation of being utilized due to their high costs. Evaluation of the reversibility and recycling of adsorption of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Zn^{2+} from Ch-MWCNTs have been studied using optimum conditions for getting efficiency desorption process [36].

3.3.1. Effect of solution pH

Table 6 represents the data that explains the desorption process. From the table it is clear that the Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} have been recovered from Ch-MWCNTs using different pH values ranged from 2 to 6. The desorption experiments took 2 h. For being ensured from reaching full desorption equilibrium. It has been noticed that the % desorption increase associating with the decrease in solution pH, particularly in cases of Pb^{2+} , Zn^{2+} and Cd^{2+} .

Cu^{2+} desorption percentage is only 0%, which referred to its strong attachment with Ch-MWCNTs surface compared to other tested ions. The results showed that the other adsorbed tested ions through Ch-MWCNTs can be desorbed easily. So, it is possible to repeatedly use Ch-MWCNTs in the removal of heavy metal, such as in the treatment of wastewater. The metal ions recovery had also indicated that the ion exchange has occurred during the adsorption process [37].

3.3.2. Effect of desorption time

Table 7 shows how the desorption of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} from Ch-MWCNTs is affected by time using constant pH of 2.0.

The recovery of Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} from Ch-MWCNT occurred after the first minute of desorption (as 142%, 126%, 0.8% and 70.2% respectively) have been much unchanged after ten min of desorption. These results proved the rapid reversibility of the desorption process even at low solution PH. Cu^{2+} has also shown a lower recovery tendency reached 1% after 240 min of desorption.

Table 6
Effect of pH of solution on the Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} recoveries from MWCNTs

pH	Percentage of desorption (%)			
	Cd^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}
2	163.5	155	0	70.2
3	154	93	0	50.8
4	100	21	0	45.5
5	97	10	0	43.0
6	83	5	0	39.2

Table 7
Effect of regeneration time on the Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} recoveries from Ch-MWCNTs

Time (min)	Percentage of desorption (%)			
	Cd^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}
5	142	126	0.8	70.2
10	140	120	0.7	66.8
15	152	135	0	72
60	158	133	0	72
120	160	138	0	72
180	160	138	0	72
240	166	124	1.00	76

4. Conclusion

According to the results of this study, it can be concluded that Ch-MWCNT (100:50) nanocomposite is prepared by modifying chitosan and functionalized MWCNT. The Ch-MWCNTs nanocomposite was characterized by TEM analysis confirming the MWCNTs homogeneously distributed in the chitosan matrix. The FTIR indicates that the characteristic functional groups of MWCNTs and chitosan are successfully present in the modified nanocomposite.

Applying Ch-MWCNT is effective in the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} from the solution. Results illustrated the ability of Ch-MWCNT to successfully removing most of the heavy metals within the solution. Furthermore, results showed there was competition among tested metals. The order of metal ion removal from aqueous solution was $\text{Cu}^{2+} > \text{Pd}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

The capacity of MWCNTs, as well as Ch-MWCNTs as an adsorbent for Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} removal from wastewater (WW) and industrial wastewater (IWW) samples, were evaluated. Comparing between samples results of WW and IWW illustrates the high MWCNTs powerful in heavy metals adsorption and removal especially for IWW as higher heavy metal concentrations have been removed.

In conclusion, MWCNTs modification with chitosan could form a successful strategy for improving the adsorption and dispersion properties of MWCNTs which are used in environmental cleanup and heavy metals removal.

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