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Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution

Mohamed Abdel Salam*, Mohamad S.I. Makki, Magdy Y.A. Abdelaal

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80200, Jeddah 21589, Saudi Arabia

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were modified with chitosan, and a homogenous nanocomposite was obtained. The morphological properties of the MWCNTs/chitosan nanocomposite were studied with scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and thermal gravimetric analysis (TGA). The morphological results indicate the successful modification and the formation of MWCNTs/chitosan nanocomposites. The MWCNTs/chitosan nanocomposite was packed inside a glass column and used for the removal of copper, zinc, cadmium, and nickel ions from aqueous solution. The MWCNTs/chitosan nanocomposite showed a great efficiency for the removal of the target metal ions from the aqueous solution. The results suggested that this novel MWCNTs/chitosan nanocomposite could be used for different environmental applications.

1. Introduction

Carbon nanotubes (CNTs) have captured much attention worldwide since the discovery of CNTs in 1991 [1]. Significant work has been done to reveal the unique structural, mechanical, electrical, electromechanical and chemical properties of CNTs and to explore the key applications of these novel materials. CNTs have unique size distributions, novel hollow-tube structures, high specific surface areas, electrical conductivity and semiconductivity. Carbon nanotubes have a wide range of length scales and are capable of being oxidized and forming carboxylic groups on their surfaces [2]. Different diameters and chiralities of carbon nanotubes give rise to various chemical, physical and mechanical properties [3–5]. These characteristics allow applications of CNTs in many fields such as photocatalysis [6], medicine [7], nanoscale electronics [8], hydrogen storage [9,10], mechanical systems [11], SEM probes [12] and electron field emission tips [13]. Many research studies have shown the capability of CNTs in the adsorption and removal of different pollutants such as virus from water [14], dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples [15], organophosphorous pesticides in wastewater sludge [16], nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples [17], atrazine from aqueous solution [18–20], polyhalogenated organic pollutants in environmental water samples [21–25], tetrabromobisphenol A [26], pharmaceuticals in spiked water samples [27], drugs in urine [28], ionizable organic compounds [29], poly aromatic hydrocarbons [30], thiamethoxam, imidacloprid, acetamiprid [31], polycyclic aromatic hydrocarbons in environmental water [32], different pesticides [33] and metal ions [34–39] from different environments. Recently, modification of CNTs with polymers has been of significant interest due to their exceptional properties and applications [24,25,40–42]. One of the common polymers that is used for the modification of carbon nanotubes is chitosan [43–45]. Chitosan, a polysaccharide biopolymer obtained from the deacetylation of chitin, has been widely used in medical applications because it can not only be economically processed from chitin but is also non-toxic, biocompatible, and biodegradable [46,47]. Chitosan is known to have good complexing ability through specific interactions of its amino groups with heavy metals from various waste waters [48–52]. Carbon nanotubes were modified with chitosan and used for different applications such as the adsorption of congo red [53], the determination of copper (II) by anodic stripping voltammetry [54], and biosensors for different molecules such as hydrogen peroxide [55] and cholesterol [56].

Both carbon nanotubes and chitosan can adsorb and remove heavy metals from aqueous environments, but, to the authors' knowledge, there are no studies exploring the potentiality of com-

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* Corresponding author. Tel.: +966 541886660; fax: +966 2 6952292.
E-mail address: masalam16@hotmail.com (M.A. Salam).

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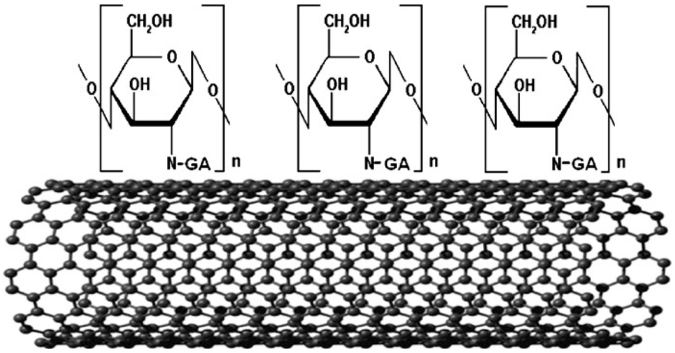

Fig. 1. Physical structure of MWCNTs/CS nanocomposite.

bining these two adsorbents in the form of a composite and using it for heavy metal removal from aqueous solution. In this study, for the first time, a nanocomposite made of carbon nanotubes and chitosan was prepared. The CNTs/chitosan nanocomposite was characterized using different techniques to verify the modification, and the nanocomposite was packed inside a glass column, where it was used for the adsorption/removal of copper, zinc, cadmium, and nickel ions from aqueous solution.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs), with diameters of 60–100 nm, were obtained from Shenzhen Nano-Technologies (China) and were used as received. High molecular weight chitosan (CS) was obtained from Aldrich (MWt 10,000.00). All other chemicals were purchased from Aldrich unless otherwise mentioned.

2.2. Experimental methods

2.2.1. Preparation of the MWCNTs/CS nanocomposite

An amount of 1.5 g of chitosan was sonicated for 2 h in 50 ml of deionized water in the presence of a few drops of acetic acid until the solution was homogenous. Approximately 0.5 g of MWCNTs were suspended separately in deionized water and sonicated for 2 h. The two suspensions were mechanically mixed, then sonicated for 4 h to increase the homogeneity and crosslinked with glutaraldehyde (GA), and the nanocomposite was left to dry overnight in a vacuum oven at 60 °C followed by mechanical grinding. The MWCNTs/chitosan nanocomposite is represented schematically in Fig. 1.

2.2.2. Characterization of MWCNTs/CS nanocomposite

Scanning electron microscope (SEM) images were taken using a JEOL JSM 6360 LV electron microscope. FT-IR spectrophotometric analysis was performed with the KBr disc technique using a Jasco model FT-IR 310 (Japan). Thermal gravimetric analysis (TGA) was performed with a model Perkin Elmer thermal analyzer system under N_2 flow at a heating rate of 10 °C/min. The surface area was determined at 77 K from nitrogen adsorption/desorption isotherms measured using a model NOVA 3200e automated gas sorption system (Quantachrome, USA). Prior to measurement, each sample was degassed for 6 h at 100 °C. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) equation [57].

2.2.3. Preparation of the metal ions solution

A stock solution containing 1 ppm (1 mg/L) of copper, cadmium, zinc and nickel ions was prepared from reference concentrated solutions using deionized water.

2.2.4. Analytical procedure

A known amount of MWCNTs/CS nanocomposite was packed inside a glass column as shown in Fig. 2, where 25 ml of the metal ion solution was allowed to flow inside the column with a flow rate of 5 ml/min. The metal ion concentration was determined before and after the treatment using inductively coupled plasma-optical emission spectrometry (ICP-OES Optima 4100 DV), Perkin Elmer, USA.

3. Results and discussion

3.1. Characterization of the MWCNTs/chitosan nanocomposite

The physical characterization of the nanocomposite is crucial to prove that the nanomaterial was well developed. Different techniques were used to study and validate the structure of the MWCNTs/CS nanocomposite.

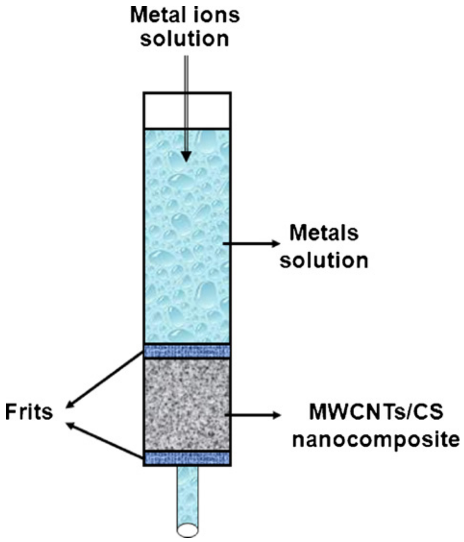

Fig. 2. MWCNTs/CS nanocomposite packed inside a glass column.

3.1.1. Scanning electron microscopy

Scanning electron microscopy was used to study the morphology and homogeneity of the MWCNTs/CS nanocomposite. The SEM images in Fig. 3 show the pristine MWCNTs, pure chitosan and MWCNTs/CS nanocomposite. Fig. 3(A) shows that pure MWCNTs were cylindrical in shape with an average diameter of 200 nm and tangled together, while pure chitosan samples had no common structure, as shown in Fig. 3(B). Fig. 3(C) shows the MWCNTs/CS nanocomposite where the MWCNTs were embedded and well dispersed within the chitosan matrix.

3.1.2. FT-IR spectroscopy

The FT-IR technique is one of the most important characterization techniques used to elucidate the changes in chemical structures. Fig. 4 shows the FT-IR spectrum of the MWCNTs/CS nanocomposite where the characteristic bands of chitosan at 1089 cm^{-1} indicate C–O–C bonds, 1559 cm^{-1} indicate the free NH_2 groups and 1658 cm^{-1} indicate the residual acetamide groups after the deacetylation of chitin during production process of chitosan. In addition, there is an absorption band at 2938 cm^{-1} attributed to C–H bonding. Fig. 4 shows the characteristic absorption bands of MWCNTs including the absorptions at 1380 cm^{-1} for CH bonding and at 1600 cm^{-1} for olefinic double bonds.

3.1.3. Thermal gravimetric analysis (TGA)

TGA analysis was performed to estimate the homogeneity of the MWCNTs/CS nanocomposite and its thermal stability. Fig. 5 shows the high thermal stability of pristine MWCNTs until 530 °C. Then, they decomposed in one stage until they are completely decomposed around 700 °C. Meanwhile, pure chitosan decomposed in different stages starting from 50 °C until complete decomposition at 530 °C. On the other hand, the thermal stability of the MWCNTs/CS nanocomposite stability, which was a mix of both the pristine MWCNTs and the pure chitosan, showed decomposition in two stages, but at higher temperature compared to pure chitosan and at a lower temperature compared with pristine MWCNTs. By comparing the TGA curves for the pristine MWCNTs, pure chitosan and MWCNTs/CS nanocomposite at 530 °C, where all the pure chitosan was decomposed and the pristine MWCNTs were still stable, the amount of MWCNTs in the nanocomposite was estimated to be

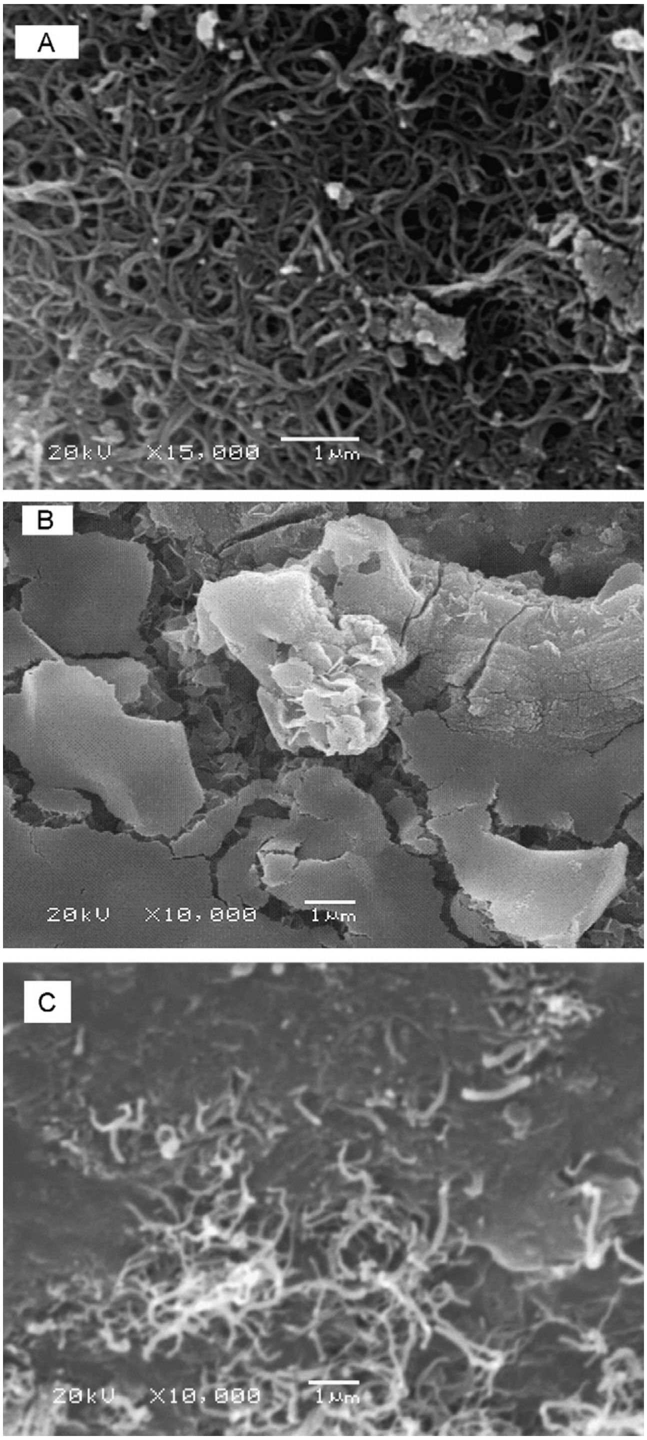

Fig. 3. SEM images for pure MWCNTs (A), pure chitosan (B) and the MWCNTs/CS nanocomposite (C).

25% (wt%) as it was originally prepared. This analysis was repeated three times with the same result, indicating the homogeneity of the MWCNTs/CS nanocomposite prepared.

3.1.4. *Surface area analysis*

The surface area of any adsorbent is one of the key factors in the adsorption/removal/exchange process of any pollutants from the environment. The surface area of the pristine and modified MWCNTs was determined from the nitrogen adsorption/desorption isotherms measured at 77 K using a model NOVA 3200e automated gas sorption system (Quantachrome, USA), and the results are presented in Fig. 6. The specific surface area, S_{BET}, was calculated with the Brunauer–Emmett–Teller (BET) equation [57]. The surface areas for the pristine MWCNTs and MWCNTs/CS nanocomposite were found to be 82.4 and 135.1 m^2/g, respectively, which indicated an increase of the surface area of the modified carbon nanotubes compared with the pristine ones due to the good dispersion of the MWCNTs within the chitosan matrix, which decreased the tangling and folding of the carbon nanotubes and, as a result, enhanced their accessibility for nitrogen adsorption. The isotherms obtained could be classified as a type IV isotherm with H3 type hysteresis loops according to the original IUPAC classification [58]. However, according to the extended classification of adsorption isotherms [59], the isotherms are type IIb isotherms.

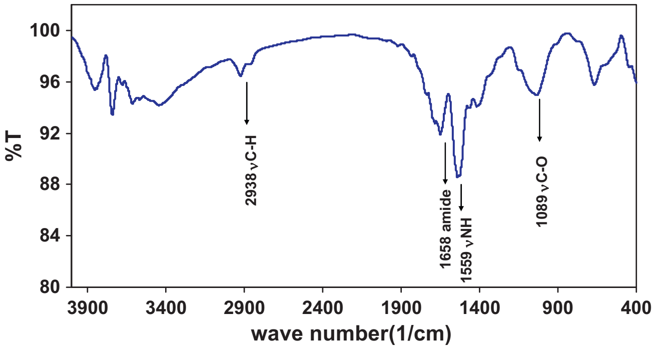

Fig. 4. FT-IR spectrum of the MWCNTs/CS nanocomposite.

3.2. *Environmental application of MWCNTs/CS nanocomposite*

Due to the high surface area of MWCNTs, they are customarily used for environmental remediation to remove different pollutants from the environment. In this study, the MWCNTs/CS nanocomposite was used for the removal of selected heavy metals, copper, zinc, cadmium, and nickel ions, which pose an environmental problem, from aqueous solution. The MWCNTs/CS nanocomposite was packed inside a glass column, as explained earlier in the experimental section, which was used for the removal of the target metal ions from aqueous solution.

The effect of different factors on the process of metal ion removal was studied, including the nanocomposite mass, solution pH, solution flow rate, and solution temperature. Different nanocomposite

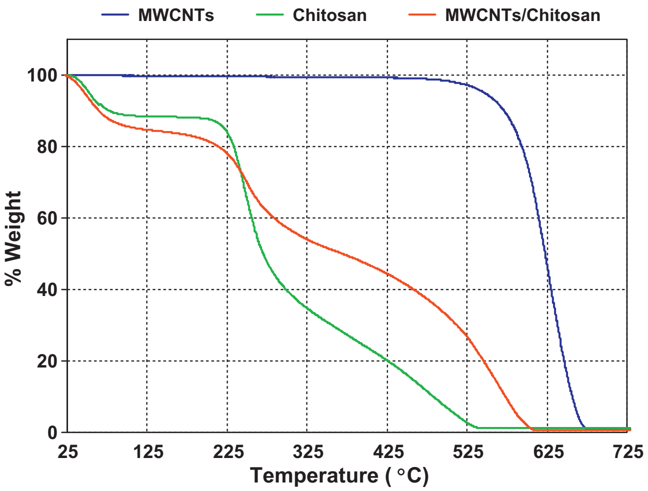

Fig. 5. Thermogravimetric analysis for MWCNTs, chitosan and the MWCNTs/CS nanocomposite.

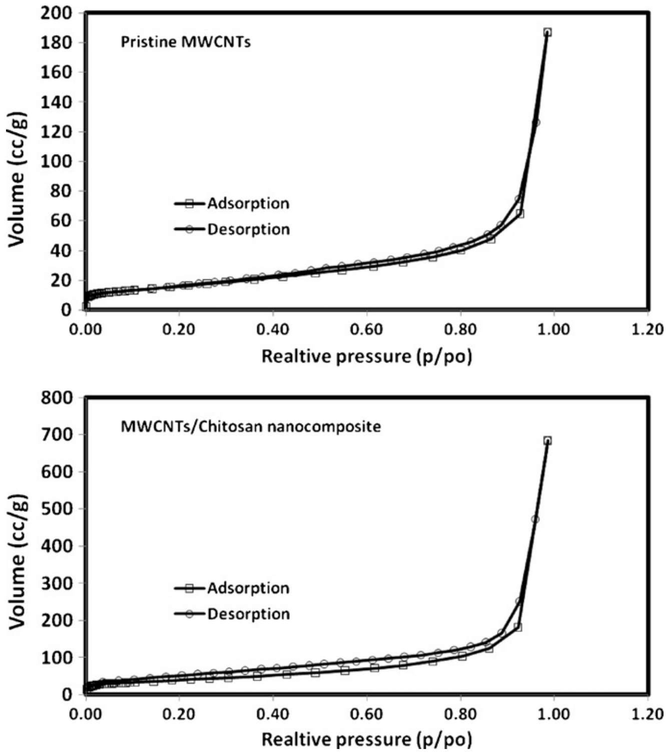

Fig. 6. Surface area analysis for pristine MWCNTs and the MWCNTs/CS nanocomposite.

masses were used, namely, 50, 100, 200, and 300 mg. Fig. 7 shows the effect of changing the MWCNTs/CS nanocomposite mass on the percent removal of the target metal ions (pH 7.0, flow rate 5.0 ml/min, and 298 K). The percent of metal ions removal from the solution increased up to more than 90% by increasing the nanocomposite mass up to 200 mg due to the increase of the active sites available for binding the metal ions as a result of increasing the MWCNTs/CS nanocomposite mass. There was a competition among the target metal ions for the binding of the active sites of the nanocomposite. Competitive adsorption is important in water and wastewater treatment because most metal ions to be adsorbed exist in solution with other metal ions. This competition was in the following order: Cu(II) > Cd(II) ≈ Zn(II) > Ni(II). This competition was responsible for the higher removal/adsorption of the copper ions compared with other metal ions, which may explained why Cu(II) forms much stronger complexes compared to the other ions due to the Jahn–Teller effect. The Jahn–Teller effect stabilized the d^9 Cu(II) complexes compared with the completely filled d orbital in the case of Cd(II) and Zn(II) ions. The same phenomenon was observed in other studies where there was a competition among the metal ions for the binding of different materials [49,60–63]. Another explanation for the higher adsorption of Cu(II) on the nanocomposite could be attributed to its ability to be reduced by the carbonaceous surface. Copper ions in the close vicinity of the surface are reduced after being attracted to active sites and accommodated on the nanotube surface and then leave the active site for the adsorption of another ion [39]. The same experiment was repeated using different solutions containing each of the target metal ions separately and 200 mg of the MWCNTs/CS nanocomposite. The results showed that most of the metal ions were removed from the aqueous solution, i.e., the percent removal was 100%, 98%, 99% and 100% for Cu(II), Cd(II), Zn(II), and Ni(II), respectively. Thus, the high adsorption ability of the MWCNTs/CS nanocomposite towards the target metal ions was demonstrated. This behavior was expected for metal ions such as Zn(II) and Ni(II), which had lower adsorption in the presence of other metal ions such as Cu(II) and Cd(II) due to the competition for the binding sites at the surface of MWCNTs/CS nanocomposite.

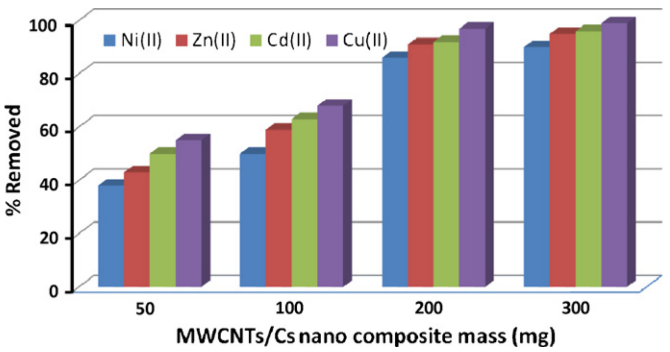

Fig. 7. The effect of the MWCNTs/CS nanocomposite mass on the removal of different metal ions from aqueous solution.

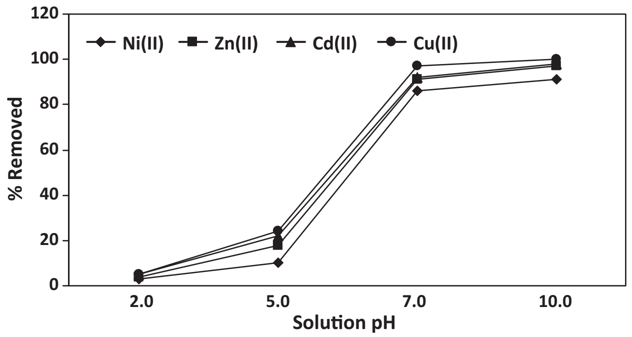

Fig. 8. The effect of the MWCNTs/CS nanocomposite mass on the removal of different metal ions from aqueous solution.

The effect of the solution pH on the removal of Cu(II), Cd(II), Zn(II) and Ni(II) from aqueous solution by the MWCNTs/CS nanocomposite was studied at different pH values (pH 2.0, 5.0, 7.0, and 10.0), and the results are shown in Fig. 8 (MWCNTs/CS nanocomposite mass 200 mg, flow rate 5.0 ml/min, and 298 K). It is clear that the pH of the solution plays an important role in the removal of the metal ions by the MWCNTs/CS nanocomposite. In general, the removal of the target metal ions was significantly lower at pH values between 2.0 and 5.0 due to the competition between protons (H^+) and the target metal ions for the active sites on the MWCNTs/CS nanocomposite. Increasing the pH to higher values enhanced the removal efficiencies for all the ions until it reached a maximum at pH 10.0. The increase of the percent removal of Cu(II), Cd(II), Zn(II) and Ni(II) by the MWCNTs/CS nanocomposite at higher pH values could be attributed to the hydrolysis of the metal ions.

The effect of the solution flow rate on the removal of Cu(II), Cd(II), Zn(II) and Ni(II) from aqueous solution by the MWCNTs/CS nanocomposite was studied, and the results are presented in Fig. 9 (MWCNTs/CS nanocomposite mass 200 mg, pH 7.0, and 298 K). Four different flow rates were chosen: 1.0, 5.0, 10.0, and 15.0 ml/min. Generally, increasing the solution flow rate was associated with a decrease in the percentage of the metal ions removed from the solution because the increase in the flow rate decreased the contact time between the metal ions and the active sites of the MWCNTs/CS nanocomposite, which reduced the percent removal of the metal ions from the aqueous solution. It was found that a flow rate of 5.0 ml/min was optimal because it is almost obtained the same percent removed as the 1.0 ml/min flow rate.

The effect of the solution temperature on the removal of Cu(II), Cd(II), Zn(II) and Ni(II) from aqueous solution by the MWCNTs/CS nanocomposite was studied, and the results are shown in Fig. 10

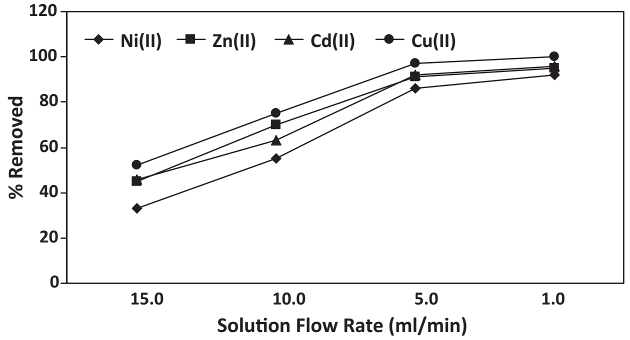

Fig. 9. The effect of the solution flow rate on the removal of different metal ions from aqueous solution by the MWCNTs/CS nanocomposite.

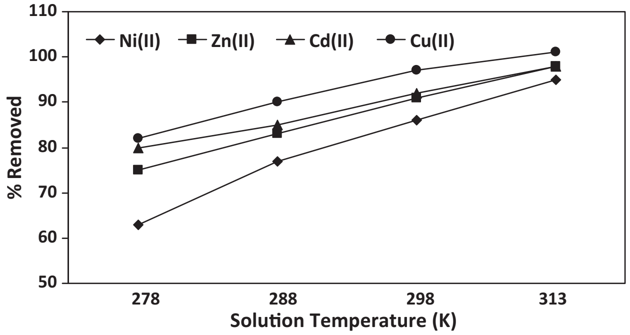

Fig. 10. The effect of the solution temperature on the removal of different metal ions from aqueous solution by the MWCNTs/CS nanocomposite.

(200 mg MWCNTs/CS nanocomposite, pH 7.0, and 5.0 ml/min). Four different solution temperatures were chosen, 5.0 °C (278 K), 15.0 °C (288 K), 25.0 °C (298 K), and 40.0 °C (313 K), which represent the normal temperatures of aqueous environments. It is clear from the figure that increasing the solution temperature increased the percent removal of the metal ions from the aqueous solution, indicating that the removal/adsorption process was endothermic in nature, which agrees with other studies [64–67].

4. Conclusions

A nanocomposite made of multi-walled carbon nanotubes and chitosan (25:75 wt%) was prepared. The MWCNTs/chitosan nanocomposite was characterized with scanning electron microscopy, and thermal gravimetric analysis confirmed the homogenous distribution of the MWCNTs within the chitosan matrix. The FT-IR indicated the presence of the characteristic functional groups of both MWCNTs and chitosan within the nanocomposite. The MWCNTs/chitosan nanocomposite was used for the removal of copper, zinc, cadmium and nickel ions from aqueous solution. The results showed that MWCNTs/chitosan nanocomposite could remove most of the metal ions from solution successfully. The results also revealed the competition among the metal ions under investigation. The order of metal ion removal from aqueous solution was Cu(II) > Cd(II) ≈ Zn(II) > Ni(II).

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