

# Chitosan/Carbon Nanotube Composite Beads: Preparation, Characterization, and Cost Evaluation for Mercury Removal from Wastewater of Some Industrial Cities in Egypt

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**ABSTRACT:** Composite beads composed of chitosan (CS) with different carbon nanotubes (CNTs) were prepared by the incorporation of single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), and carboxylic multiwalled carbon nanotubes (MWCNT-COOHs). A protected crosslinking method was used for the preparation of the CS/CNTs beads by the reaction of the beads with Hg(II) as the protector. Scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis were used to characterize the prepared beads. The adsorption performance of the prepared beads was investigated for the removal of Hg(II). The results show that beads prepared by the protected crosslinking technique removed 2.5 times more Hg(II) from solution than beads prepared by normal crosslinking. The maximum Hg(II) removal values were 148.7, 183.2, 167.5, and 172.7 mg/g by CS, MWCNT-COOH-impregnated CS beads, MWCNT-impregnated CS

beads, and SWCNT-impregnated CS composite beads, respectively. The optimum removal conditions were pH = 4, contact time = 40 min, and temperature = 70°C. The equilibrium adsorption isotherm data of the beads exhibited a better fit to the Langmuir isotherm model. The reusability of Hg(II) sorption by the prepared beads was investigated to evaluate their repeated availability performance in water treatment. Quantitative removal of mercury from industrial wastes was demonstrated. A statistical analysis of the replacement cost of these sorbents revealed that SWCNTs, MWCNTs, and MWCNT-COOH could possibly be cost-effective sorbents in water treatment, regardless of their high unit cost at this time. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E93–E101, 2012

**Key words:** adsorption; blends; crosslinking; nanotechnology

## INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of metal ions has been causing worldwide concern. Wastewater from many industries, such as the metallurgical, tannery, chemical manufacturing, mining, and battery manufacturing industries, contains one or more toxic metal ions.<sup>1</sup> Mercury is one of the common pollutants of water; it results from the burning of coal by power plants and the inappropriate disposal of batteries, paints, lights, and industrial byproducts.<sup>2</sup> Mercury poisoning remains an infrequently considered clinical syndrome, even though mercury is the second most common cause of heavy-metal poisoning.<sup>3,4</sup> Mercury poisoning is becoming more important because of

the extensive contamination of water and fish and the increasing consumption of fish in the human diet.<sup>5</sup> Mercury is cytotoxic, exerting its effect by depleting thiol reserves in the mitochondria, which results in cell death. It is extremely neurotoxic and leads to dizziness, irritability, tremors, depression, and memory loss.<sup>6</sup>

The removal of metal ions, especially mercury, from wastewaters before they are released into the environment has become a must because there is the possibility of the entry of toxic metal ions into the food chain through waste discharge into water bodies. There are many conventional methods that are being used to remove metal ions, including oxidation, reduction, precipitation, membrane filtration, ion exchange, and adsorption. Nowadays, adsorption has been recognized as the most popular treatment process for the removal of metal ions from aqueous solution because of its simplicity, high efficiency, easy recovery, and reusability of the adsorbent.<sup>7,8</sup>

Carbon nanotubes (CNTs), a fascinating new member of the carbon family, have attracted strong

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research interest since their discovery<sup>9</sup> because of their unique morphologies and various potential applications as well as their remarkable mechanical properties. CNTs have been proven to possess excellent adsorption capacity in the removal of organic and inorganic pollutants because of their hollow and layered nanosized structures that have a large specific surface area.<sup>10–12</sup> Earlier studies suggested that CNTs may be promising adsorbents for treating wastewater for such ions as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cr}^{6+}$ .<sup>13</sup> Moreover, CNTs have been reported to be more adsorbent than activated carbon for dioxin removal because of the strong interactions between dioxins and CNTs,<sup>10</sup> and recently, CNTs have been used for the absorption of dye molecules.<sup>14</sup> However, their inherent insolubility in most organic and inorganic aqueous solutions has limited the manipulation of CNTs in the solution phase, which greatly hinders the application of CNTs in real work.<sup>15,16</sup> Therefore, studies have been extended recently to include the modification of CNTs to enhance their adsorption capacity.

Nanocomposites, in which polymers serve as hosts for inorganic particles of nanoscale dimensions, have attracted scientific and technological interest.<sup>17,18</sup> These materials promise to be excellent candidates for sensors, mechanical damping devices, and other technologies requiring functional materials with flexible properties. Nanocomposites can exhibit properties that substantially differ from those of the neat polymer, and nanocomposites may also prove to be useful for molecular separation, including chemical separation and bioseparation.<sup>19,20</sup> However, the fabrication of homogeneous nanocomposites with loadings of CNTs remains a technical challenge because their poor solubility makes chemical manipulation difficult.<sup>21,22</sup> The dispersion problem caused by low-solubility dispersions does not depend on solubility because a solution of CNTs must be solved to allow the mechanical reinforcement properties to be fully used.

Chitosan (CS), the deacetylated product of chitin, exhibits a high adsorption capacity toward metals because of its multiple functional groups, biocompatibility, and biodegradability.<sup>23</sup> CS-based adsorbents are versatile materials in view of their use in different forms, from flake, powder, or bead to hydrogel fiber types. However, the CS hydrophilic character and, consequently, its poor mechanical properties in the presence of water and humid environments limit its application. Chemical crosslinking,<sup>24</sup> carboxy alkyl substitution,<sup>25</sup> and polyamination<sup>26</sup> have been reported to increase the mechanical strength of CS hydrogels. These methods may not satisfactorily improve the mechanical stability and sometimes cause a significant decrease in the adsorption capacity.<sup>27</sup> Because amine groups are the most active sorption sites of CS, this crosslinking

reduces the number of active sites of sorbent. Therefore, the protection of active sites of CS before the crosslinking reaction may result in an increase in the sorption capacity. Also, different nanofillers, such as clay and silica nanoparticles, have been used to reinforce the base material CS in polymer nanocomposites.<sup>28</sup> Recently, CNTs have been used as a promising nanofiller for the preparation of CS/CNT nanocomposites because of their excellent mechanical, electrical, and thermal properties.<sup>29–32</sup> Also, because CS is a natural, linear polysaccharide polymer, it has been shown to interact with CNTs to form stable dispersions.<sup>33</sup>

In this study, we prepared four different types of beads: neat CS beads (CS), multiwalled-carbon-nanotube-impregnated chitosan (CS/MWCNT) beads, carboxylic-multiwalled-carbon-nanotube-impregnated chitosan (CS/MWCNT-COOH) beads, and single-walled-carbon-nanotube-impregnated chitosan (CS/SWCNT) beads. A protected crosslinking method was used for the preparation of the CS/CNTs beads. The prepared beads were characterized with scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). In addition, the sorption characteristics of Hg (II) onto the prepared beads were studied. Quantitative removal of mercury from industrial wastes was demonstrated. A statistical analysis of the replacement cost of these sorbents was also done.

## EXPERIMENTAL

### Materials

CS (weight-average molecular weight = 100,000–300,000) was supplied by Acros Organics, USA. Multiwalled carbon nanotubes (MWCNTs) and carboxylic multiwalled carbon nanotubes (MWCNT-COOHs) were supplied from NanoTechLabs, Inc. The single-walled nanotubes were a product of Alfa Aesar. Glutaraldehyde (GA; 50 wt % in distilled water) were supplied by Fisher Scientific. All of the other reagents we used were analytical-reagent grade.

### Preparation of the CS/CNT composite beads

First, 1.25 g of CS was dissolved in a sufficient amount of a 2.5 wt % acetic acid aqueous solution. CNTs were then dispersed in the CS solution with sonication for 2 h; then, another 1.25 g of CS was added to the dispersion solution to achieve a final CS concentration of 2.5%. The final weight ratio of CNTs to CS in all of the experiments was approximately 1%. A control CS was also prepared with regard to the previous method but without the addition of the CNTs. The freshly prepared dispersed solution was then injected through a 0.2-mm-diameter syringe at a

200  $\mu\text{L}/\text{min}$  flow rate into a coagulation solution bath ( $\text{H}_2\text{O}/\text{MeOH}/\text{NaOH} = 4 : 5 : 1$  w/w/w) at room temperature for 24 h with continuous stirring. The coagulated beads were then washed several times with deionized water.

### Protected-crosslinked bead synthesis

A protected-crosslinking method with  $\text{Hg}(\text{II})$  as a protector ion was used. In brief, active sites of CS were protected by the reaction of CS with excess  $\text{Hg}(\text{II})$  ions before it was crosslinked with glutaraldehyde. The reaction was carried out at room temperature for 24 h. Crosslinking was produced by the immersion of the resulting beads in 25% glutaraldehyde (w/v in water) for 24 h, followed by several washings with deionized water. The deprotection of the beads was achieved by an  $\text{HNO}_3$  solution (0.1M) at room temperature, which was stirred magnetically for 2 h. Then, the mixture was left standing for 24 h. The mixture suspension was filtered, and the  $\text{Hg}(\text{II})$  concentrations in the leaching filtrate was analyzed with inductively coupled plasma, iCAP 6500, ThermoScientific, UK. The precipitated residue was washed with water until it was neutral. The obtained beads were dried in an oven at  $70^\circ\text{C}$  until a constant weight was reached.

### Characterization of the composite beads

The surface morphology of the beads was examined with SEM (model FEI XL30 SEM-Field Emission Gun (FEG), FEI Co., Holland). The beads were initially dried in air at ambient temperature for 5 days before they were analyzed. The dried beads were sputter-coated for 200 s. The surface of the sample was scanned at the desired magnification to study the morphology of the beads. The presence of functional groups of the prepared beads was observed by the use of FTIR spectroscopy (Nicolet 8700, ThermoScientific). The IR spectra of the beads were recorded in transmittance mode over a wave number range of  $4000\text{--}400\text{ cm}^{-1}$  at  $25^\circ\text{C}$ . A Shimadzu TGA system (type TGA-50) under a nitrogen atmosphere (20 mL/min) was used in this study. The temperature range was from ambient to  $800^\circ\text{C}$  at heating rate of  $10^\circ\text{C}/\text{min}$ .

### Adsorption of $\text{Hg}^{2+}$

#### Batch procedure

The adsorption of  $\text{Hg}^{2+}$  from aqueous solutions was investigated in batch experiments. The tests were done in 100-mL polyethylene bottles, which were previously cleaned with deionized water, dilute nitric acid, and finally, deionized water again. In all of the experiments, the bead concentration was kept constant at 10 mg/25 mL with magnetic stirring at 600 rpm. The effects of the contact time, pH of the

medium, initial  $\text{Hg}^{2+}$  concentration ( $C_0$ ; ppm), and temperature of the medium on the removal were studied. The suspensions were brought to the desired pH by the addition of 0.1M NaOH and 0.1M  $\text{HNO}_3$ . The concentration of the metal ions in the aqueous phases after desired treatment periods was measured with Inductively Coupled Plasma (ICP). The experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. The adsorption capacity values ( $q_e$ 's; mg/g) were calculated as the difference in the  $\text{Hg}^{2+}$  ion concentration of the preadsorption and postadsorption solutions divided by the weight of dry beads according to the following equation:

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

where  $C_e$  is the final or equilibrium  $\text{Hg}^{2+}$  concentration (ppm),  $V$  is the volume of the  $\text{Hg}^{2+}$  solution (mL), and  $W$  is the weight of the beads (g).

The linear model, which describes the accumulation of solute by sorbent as directly proportional to the solution concentration, is presented by the following relation:

$$q_e = K_D C_e \quad (2)$$

The constant of proportionality or distribution coefficient ( $K_D$ ) is often referred to as the *partition coefficient*.

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and has been successfully applied to a wide range of systems that exhibit limiting or maximum sorption capacities. The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface.

The Langmuir isotherm is given by

$$q_e = \frac{Q_e K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $Q_e$  and  $K_L$  are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. Equation (3) is usually linearized by inversion to obtain the following form:

$$C_e/q_e = 1/(Q_e K_L) + (1/Q_e)C_e \quad (4)$$

Equation (4) is equally used to analyze the batch equilibrium data by plotting  $C_e/q_e$  versus  $C_e$ , which yields a linear plot if the data conform to the Langmuir isotherm.

The Freundlich isotherm is the most widely used nonlinear sorption model and is given by the general form:

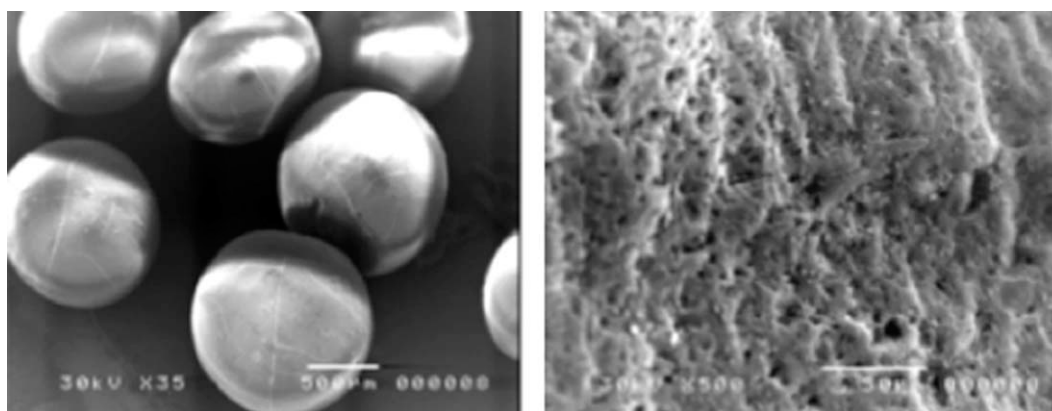


Figure 1 SEM micrographs of the CS/MWCNT-COOH composite beads.

$$q_e = K_F C_e^{1/n} \quad (5)$$

where  $K_F$  relates to the sorption capacity and  $n$  relates to the sorption intensity.

The logarithmic form of eq. (5) given below is usually used to fit data from batch equilibrium studies:

$$\text{Log } q_e = \text{Log } K_F + (1/n)(\text{Log } C_e) \quad (6)$$

## RESULTS AND DISCUSSION

### Preparation and characteristics of different CS/CNT composite beads

Compared to surface-functionalized CNTs with short chemical groups, polymer-modified CNTs are much more attractive as they provide better solubility in solvents, higher compatibility with polymers, and more reactive sites for further modifications.<sup>31</sup> Moreover, unmodified CNTs have a tendency to aggregate in water and other solvents because of strong van der Waals forces.<sup>34</sup> However, CNTs functionalized with CS can form a homogeneous black dispersion in aqueous solution. There would be an electrostatic interaction between the positively charged polycation of CS and the negatively charged CNTs, and it would decrease the van der Waals forces among CNT bundles by wrapping the CNTs in polymer chains.<sup>34</sup> For this reason, we prepared four different types of composite beads: neat CS beads, CS/MWCNT beads, CS/MWCNT-COOH beads, and CS/SWCNT beads (Fig. 1).

The IR spectra of the CS and CS with different CNTs are shown in Figure 2. The typical peaks of the CS included a broad band at 3000–3500  $\text{cm}^{-1}$ , which was the stretching vibrations of N–H and O–H. The peaks at about 1578 and 1377  $\text{cm}^{-1}$  could be assigned to the bending vibrations of N–H and

C–H. The strong peak at 1230  $\text{cm}^{-1}$  was due to the stretching vibrations of the C–O bond. However, it could be seen from Figure 2(b–d) that CNTs had no other groups, except C=C at 1650  $\text{cm}^{-1}$ .

Figure 3 presents the comparative thermogravimetric studies of the different synthesized solid-state beads. As can be seen in Figure 3, the thermal decomposition of pure CS involved the depolymerization and decomposition of glucosamine units of CS at about 200–400°C, whereas the CS/CNT composite sample decomposed within a temperature range of about 200–550°C. Meanwhile, the thermal decomposition of CS or CS/CNTs was followed by the oxidative decomposition of the residues in a temperature ranges of about 400–790°C.<sup>35</sup> Therefore, the data reflect that the TGAs of the CS/CNTs were slightly more stable than that of CS.

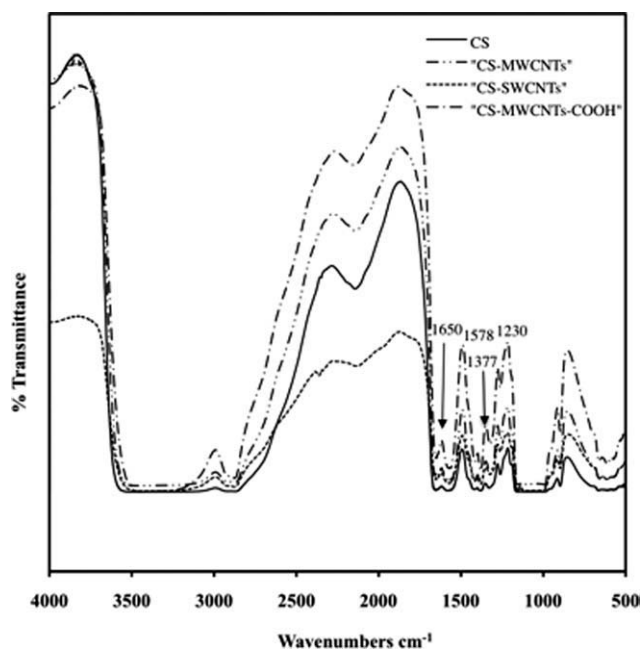


Figure 2 FTIR spectra of the prepared beads.



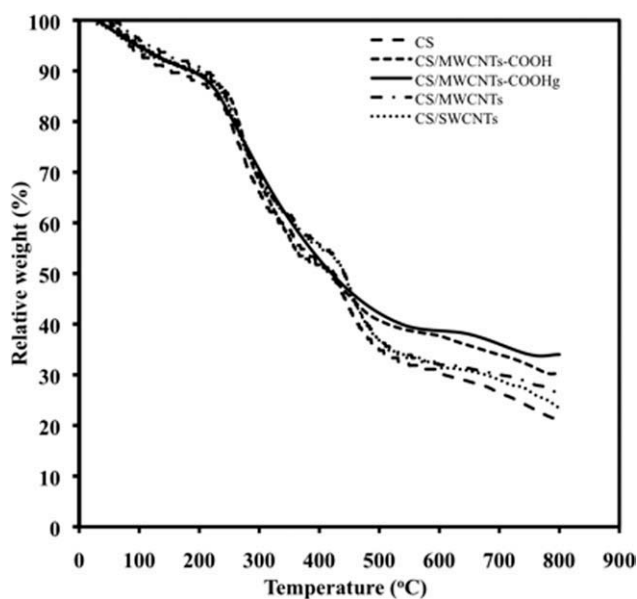


Figure 3 TGA curves of the different prepared beads.

### Adsorption of $\text{Hg}^{2+}$ by the prepared beads

#### Effect of the preparation technique

Because amine groups are the most active sorption sites of CS, normal crosslinking will reduce the number of active sites of sorbent. Therefore, the protection of active sites of CS in different beads was done by reaction with  $\text{Hg}(\text{II})$  as a protector before the crosslinking reaction. After that, deprotection of the sorbent was done by the release of mercury ions with 0.1M  $\text{HNO}_3$ . Table I shows that CS beads prepared by the protected crosslinking technique removed almost 2.5 times more  $\text{Hg}(\text{II})$  from solution than CS beads prepared by normal crosslinking. After deprotection treatment for the different synthesized beads,  $\text{HNO}_3$  could release 93–98% of  $\text{Hg}(\text{II})$  ion protector, as shown in Table II.

#### Effect of the pH

The pH value of the aqueous system is one of the most important parameters affecting the sorption behavior, as it determines the metal-ion speciation and the sorbent surface charge. In this study, we changed the pH range between 1.0 and 5.0. The effect of pH on  $\text{Hg}(\text{II})$  sorption by the different pre-

TABLE I  
Hg(II) Removal with Normal CS without Protected Crosslinking (I) and with Protected Crosslinking (II)

	Hg(II) removal (mg/g)
I	59.4
II	148.7

Initial concentration, 1000 mg/L; pH, 4; temperature, 25°C.

TABLE II  
Percentage of the  $\text{Hg}(\text{II})$  Released by 0.1M  $\text{HNO}_3$  from the Different CS Beads

	Hg(II) released (%)
CS	98.4
CS/MWCNT-COOHs	96
CS/MWCNTs	94
CS/SWCNTs	93

pared beads is shown in Figure 4. As seen here, the removal of mercury ions increased with increasing pH and then reached almost a plateau value around pH 4.0. At low pH values, hydrogen ions were likely to compete with mercuric ions and thus lower the amount of  $\text{Hg}(\text{II})$  removed. Thus, the greater  $\text{Hg}(\text{II})$  sorption taking place at higher pH could be attributed to a decrease in competition between  $\text{H}^+$  and  $\text{Hg}^{2+}$  at the same sorption site of the beads. Furthermore, the surface of the CNTs was more negatively charged at higher pH, which caused a greater electrostatic attraction of  $\text{Hg}^{2+}$ .<sup>1</sup> In general, the results indicate that the adsorption was highly pH dependent.

#### Effect of the time

The rapid adsorption of metal ions by the adsorbent is important for practical use, shortening the treatment time of water during purification. The change in the amount of adsorbed metal ions with times for different beads is shown in Figure 5. It was observed that the adsorption process was fast at first and then slowed down until saturation was reached (at nearly 40 min). The result suggested that at the beginning of the process, the adsorption occurred on the bead

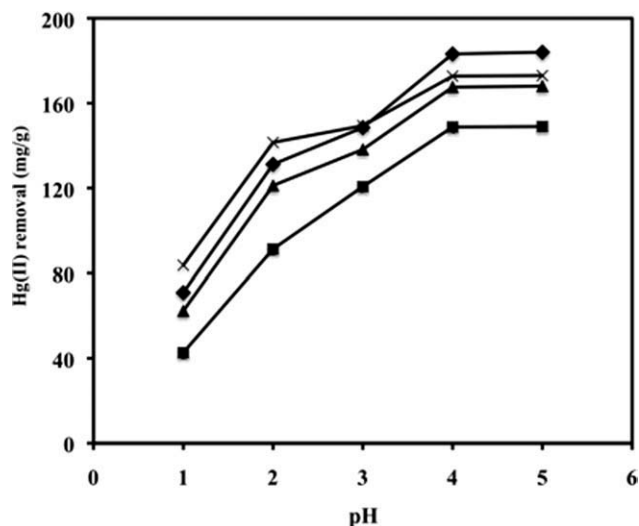
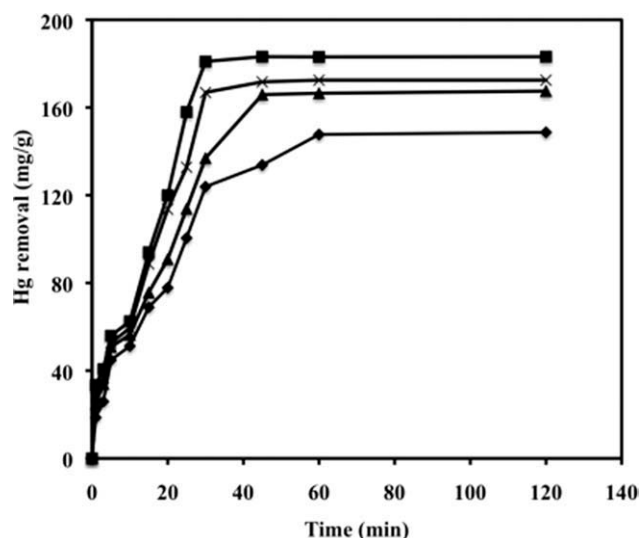


Figure 4 Effect of pH for the removal of  $\text{Hg}(\text{II})$  ions onto (■) CS, (◆) CS/MWCNT-COOH, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: initial concentration = 1000 mg/L, time = 2 h, and temperature = 25°C.



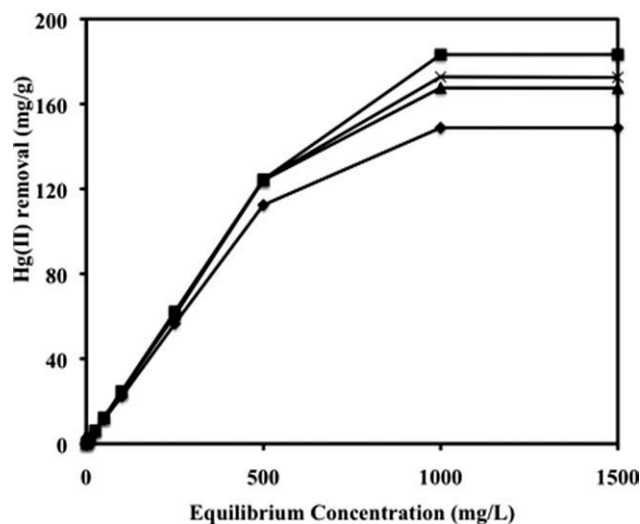
**Figure 5** Effect of the time on  $\text{Hg}^{2+}$  removal by (◆) CS, (■) CS/MWCNT-COOHs, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: pH = 4 and temperature = 25°C.

surface, so a fast adsorption rate was found. After that; the adsorption took place at the inner surface of the beads; thus, the adsorption rate was slow because of the pore diffusion of metal ions.

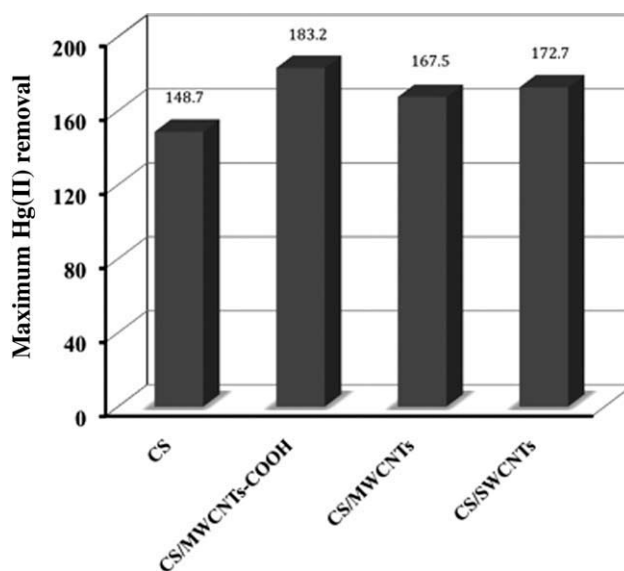
Effect of the equilibrium concentration of  $\text{Hg}^{2+}$  ions

Figure 6 shows the dependence of the equilibrium concentration of metal ions on the adsorbed amount of  $\text{Hg}^{2+}$  onto the beads. The adsorption values increased with increasing concentration of  $\text{Hg}^{2+}$  ions until a saturation value was achieved; this value represented the capacity of the beads.

The capacity of composite beads is an important factor for determining the amount of the beads



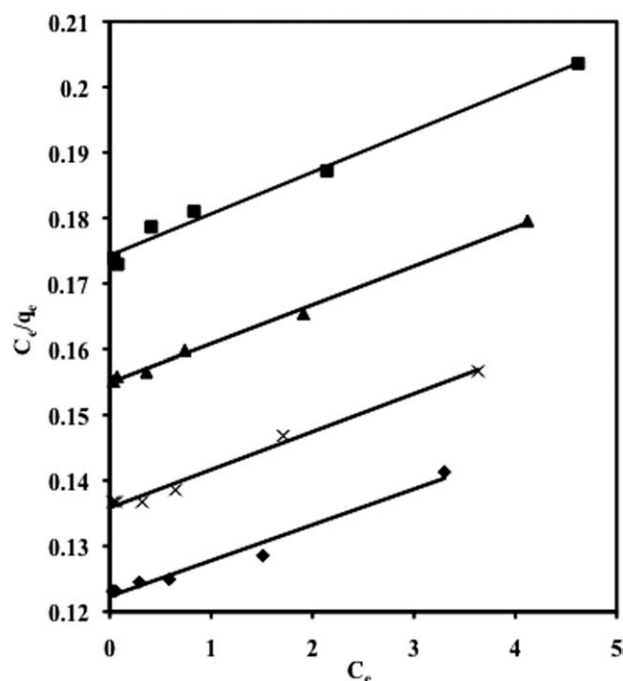
**Figure 6** Effect of the initial feed concentration on the removal of the  $\text{Hg}(\text{II})$  ions onto (◆) CS, (■) CS/MWCNT-COOHs, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: time = 2 h, temperature = 25°C, and pH = 4.



**Figure 7** Maximum  $\text{Hg}(\text{II})$  removal by the different prepared beads: pH = 4, time = 2 h, and temperature = 25°C.

required for the complete removal of a specific metal ion from a solution. The total sorption capacity of the different beads was determined by the determination of the amount of mercury ions sorbed per gram of beads at optimum pH and room temperature. Figure 7 shows the maximum sorption capacity of the different beads toward  $\text{Hg}(\text{II})$ . As is obvious in Figure 7, the maximum  $\text{Hg}(\text{II})$  removal values were 148.7, 183.2, 167.5, and 172.7 mg/g by the CS, CS/MWCNT-COOH, CS/MWCNT, and CS/SWCNT composite beads, respectively. The higher sorption by the CS/MWCNT-COOH beads could be explained by the fact that the COOH functional group could have caused a rise in the negative charge on the carbon surface, and the oxygen atoms in the functional groups donated a single pair of electrons to the metal ions, which consequently increased their cation-exchange capacity.<sup>1</sup> Also, Figure 7 reveals that the CS/SWCNTs showed better performance on the  $\text{Hg}^{2+}$  sorption than the CS/MWCNTs. Similar results have been reported in previous studies.<sup>1</sup>

During the batch experiments, adsorption isotherms, such as Langmuir and Freundlich isotherms, were used to evaluate the adsorption properties. These isotherms relate the metal uptake per unit weight of the adsorbent ( $q_e$ ) to the equilibrium adsorbate concentration in the bulk fluid phase ( $C_e$ ). Equations (4) and (6) were used for the analysis of the equilibrium batch experiment data with the assumption of Langmuir and Freundlich isotherms, respectively. Figure 8 presents the Langmuir isotherm plots of mercury(II) adsorption on the synthesized beads. The equilibrium data fit very well to the Langmuir isotherm. Calculation of the isotherm parameters with these plots gave the data presented in Table III.



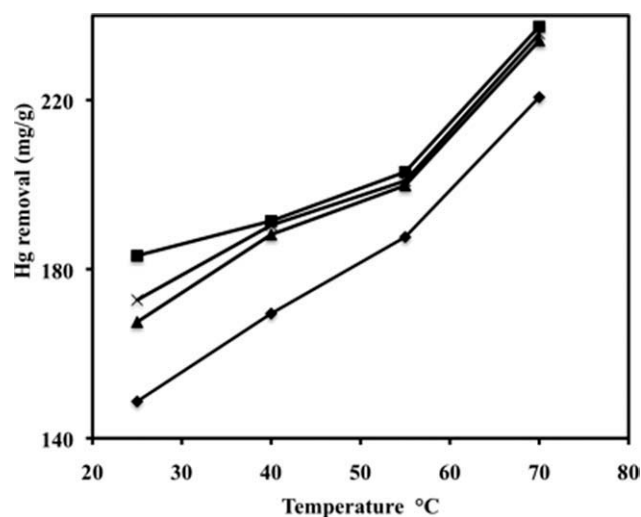
**Figure 8** Langmuir adsorption isotherm of Hg(II) ions onto (◆) CS, (■) CS/MWCNT-COOHs, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: time = 2 h, temperature = 25°C, and pH = 4.

#### Effect of the temperature

The temperature at which a sorption process is carried out will influence both the sorption rate and the degree to which sorption takes place. Figure 9 displays the influence of the temperature on the sorption capacity of the sorbent for Hg(II) by the different beads. The data of Figure 9 reveals a general trend of the sorption capacity of Hg<sup>2+</sup> ions to increase remarkably with a rise in temperature; this indicated an endothermic reaction. This increase may have been due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores of the beads.

#### Desorption and repeated use

The regeneration of the adsorbent was likely to be a key factor in improving the process economics. Desorption of the Hg<sup>2+</sup> ions from the different synthe-



**Figure 9** Influence of the temperature on the Hg<sup>2+</sup> removal by (◆) CS, (■) CS/MWCNT-COOHs, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: pH = 4 and time = 2 h.

sized beads was performed in a batch experimental setup. In this study, the desorption time was found to be 60 min. To determine the reusability of the beads, the adsorption–desorption cycles (*n*) were repeated 10 times with the same beads. The adsorption capacity of the recycled beads could still be maintained at a 78% level in the case of pure CS and at a 90–95% level in the case of the CS/CNTs in the 10th cycle (Fig. 10). We concluded that the CS/CNTs beads could be used many times without a significant decrease in their adsorption capacity.

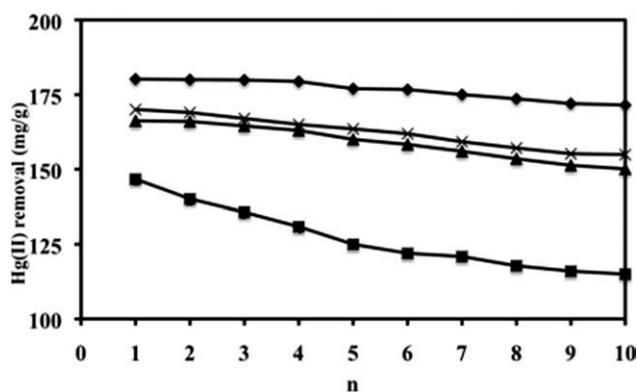
#### Removal of Hg(II) from wastewater

Four water samples collected from the industrial cities Abu Rawash and El-Obour near the capital Cairo in Egypt were found to contain 0.05–1.6 µg/mL Hg(II). Then, 100 mL of these wastewater samples were immersed into 500 mg of CS/MWCNT-COOH beads. The treatment process was continued for 2 h at room temperature. Generally, the treatment must provide water of better quality. Assays of mercury in the final effluents indicated 98–99.5% removal of the original mercury concentration. The

**TABLE III**  
Regression Coefficients of the Equilibrium Models for Hg(II) Removal by the Different Prepared Beads

	Experimental <i>q</i> (mg/g)	Langmuir constants			Freundlich constants		
		<i>Q<sub>c</sub></i> (mg/g)	<i>K<sub>L</sub></i> (L/mg)	<i>R</i> <sup>2</sup>	<i>n</i>	<i>K<sub>F</sub></i>	<i>R</i> <sup>2</sup>
CS	148.7	156.2	0.036	0.98	1.03	7.2	0.99
CS/MWCNT-COOHs	183.2	181.8	0.005	0.97	1.01	8.8	0.99
CS/MWCNTs	167.5	169.4	0.038	0.99	1.02	7.8	0.99
CS/SWCNTs	172.7	172.4	0.042	0.98	1.02	8.3	0.99

pH, 4; temperature, 25°C.



**Figure 10** Adsorption-desorption cycle of Hg(II) ions by (◆) CS, (■) CS/MWCNT-COOHs, (▲) CS/MWCNTs, and (×) CS/SWCNT composite beads: time = 2 h and temperature = 25°C.

data also showed a high efficiency of the beads for metal removal, even at very low concentrations.

#### Cost-evaluation analysis

The typical costs of the employed single-walled carbon nanotubes (SWCNTs), MWCNTs, MWCNT-COOH, and CS were US\$441.85/g, US\$48/g, US\$70/g, and US\$25/25 g, respectively. Therefore, the application of different CNTs as adsorbents is not convenient because of their high production costs. Recent advancements in carbon nanotechnology will markedly reduce the production cost of CNTs. Despite that, the direct use of CNTs as adsorbents is still expensive because many lower cost sorbents are available with good adsorption capacities. For this reason, we improved the adsorption capacity of CS beads by the addition of different CNTs, and the cost might not change significantly with such addition because the added CNT amounts were well below the CS amount (1 wt %) in the beads.

If the regeneration of CS/CNTs is performed, the CS/CNTs should be able to be reused through over hundreds of water treatment and regeneration cycles, and then, they can possibly be cost-effective sorbents.<sup>36</sup> To evaluate the replacement costs of CS, CS/MWCNTs, CS/SWCNTs, and CS/MWCNT-COOH in water treatment, a statistical analysis based on the best fit regression of  $q_e$  versus  $n$  of Figure 10 was conducted, and the results are expressed as eqs. (7)–(10), respectively:

$$q_e = 146.23n^{-0.349} \quad (7)$$

$$q_e = 169.74n^{-0.197} \quad (8)$$

$$q_e = 172.31n^{-0.182} \quad (9)$$

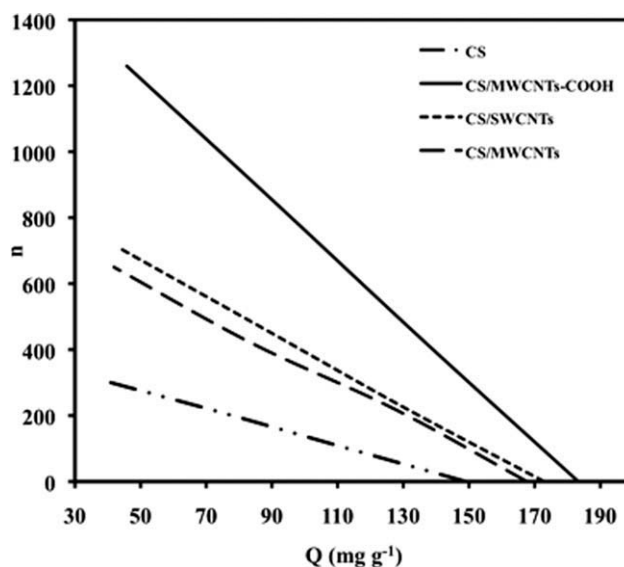
$$q_e = 182.51n^{-0.108} \quad (10)$$

The  $R^2$  values of these equations were from 0.96 to 0.99.

Figure 11 shows the predicted  $n$  values for the different synthesized beads with  $q_e$  values of 75, 50, and 25% of the original sorption of Hg(II). As observed, the predicted  $n$  values of the beads decreased with a rise in  $q_e$ . Also, it was apparent that the CS/CNTs could be reused for the removal of Hg<sup>2+</sup> through a large number of water treatment and regeneration cycles. This is the key factor for whether an expensive sorbent can be accepted by the field or not. It is expected that the unit cost of different CNTs can be further reduced in the future<sup>36</sup> so the CS/MWCNT-COOHs, CS/SWCNTs, and CS/MWCNTs appear possibly cost-effective Hg<sup>2+</sup> sorbents for water treatment. It should be noted that the predicted  $n$  was estimated on the basis of a  $q_e$  of only 10 cycles of water treatment and regeneration because it was quite time-consuming to perform hundreds of tests. Furthermore, the bead weight loss was neglected in the estimation of  $n$ . Thus, a departure of the predicted results from real conditions may possibly occur, and a prolonged test of the sorption performance of regenerated CNTs is required.<sup>36</sup>

#### CONCLUSIONS

In this work, we found that CS/CNT beads prepared by a protected crosslinking technique removed 2.5 times more Hg(II) from solution than beads prepared by normal crosslinking. The study revealed that the maximum Hg(II) removal by CS/CNTs was higher than that by CS. Mercury removal by the prepared beads increased with increasing pH and temperature of the feed solution and reached its maximum after 40 min of contact time. The Langmuir isotherm fit well. From the results, the beads



**Figure 11** Predicted  $n$  of different beads under various  $Q_e$  values.



could be recycled and used several times for the removal of Hg(II). The applicability of using such prepared beads for the removal of mercury from actual wastewater samples was investigated. Regardless of their high unit cost at this time, the data showed that such CS/CNTs beads could possibly be cost-effective sorbents in water treatment.

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