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Immobilization of Chitosan onto Carbon Nanotubes for Lead Removal from Water

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Abstract: Carbon nanotubes (CNTs) are interesting materials which are being researched intensively in the past few years. Application of CNTs in water treatment with their unique properties has attracted the attention of many scientists and engineers. Moreover, manipulation of CNTs with other polymers has been done for different applications. This study describes the use of carbon nanotubes with attached Chitosan for lead removal from aqueous solution. The CNTs were functionalized with chitosan via covalent link. The immobilization was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscope (FESEM). The obtained nanocomposite was used as an adsorbent material for lead removal from aqueous solutions and its removal capacity was tested. The results show an optimum removal percentage (98.4%) at the center point conditions.

Key words: Carbon nanotubes, chitosan, immobilization, nanocomposite, lead

INTRODUCTION

Carbon nanotubes (CNTs) are found to be promising materials in various applications (Iijima, 1991). Many researches investigating the physical, chemical and electrical properties CNTs have been conducted. Moreover, the manipulation of CNTs with other polymers and functional groups became an attractive field as it offers solutions for overcoming the difficulties of insolubility of CNTs and obtaining new composites with unique properties (Balasubramanian and Burghard, 2005). Carbon nanotubes have been manipulated for applications in water treatment and the removal of heavy metals from water. It has been used for many types of heavy metals and proved effective removal (Hsieh and Horng, 2007).

Chitosan (CS) is a cationic polysaccharide with a dominant positive charge and high molecular weight ($=10^6 \text{ g mol}^{-1}$). The common sources of Chitosan are the shells of crabs and lobsters, from which chitin is obtained and then deacetylated to produce chitosan (Okuyama *et al.*, 2000). The reactivity of Chitosan is due to the presence of the amino group and primary and secondary hydroxyl groups at the positions C-2, C-3 and C-6, respectively, which made chitosan an

effective polymer for many applications especially water treatment (Hong and Samuel, 2000; Divakaran and Pillai, 2002; Chi and Cheng, 2006). Many works have been done to immobilize chitosan onto carbon nanotubes for applications such as biosensors, gene and drug delivery (Ke *et al.*, 2006; Liu *et al.*, 2005; Wu *et al.*, 2007). The attachment of chitosan onto the surface of CNTs has been done through covalent and noncovalent linkages. In this work we report the covalent immobilization of raw chitosan onto CNTs and its first application for removal of lead metal from water. The obtained nanocomposite was characterized by Fourier transform infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM) and the removal efficiency was measured using Atomic Adsorption Spectrometry (AAS).

MATERIALS AND METHODS

Materials: Multiwall carbon nanotubes produced by chemical vapour deposition (95% purity, $0.04\text{-}0.05 \text{ g cm}^{-3}$ bulk density, with an outer diameter of 10-20 nm and inner diameter of 5-10 nm and length 10-30 μm) was purchased from Chinese science academy. Chitosan with 88% degree of deacetylation was provided by department of

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biotechnology engineering, IIUM. Nitric acid (65%), sulphuric acid (98%), NaOH pellets, 99% acetic acid, thionyl chloride (>99%), anhydrous tetrahydrofuran THF and anhydrous dimethyl formamide DMF were all purchased from MERK, Germany. 50 mg L⁻¹ Lead stock solution from HACH was used. pH adjustments were done using 0.1 M hydrochloride and/or 0.1 M sodium hydroxide.

Instruments: FESEM (JEOL, JSM-6700F) and FTIR (Bruker, TENSOR 27) were used for the characterization of the nanocomposite. Atomic Adsorption Spectroscopy (AAS) was used for measurement of the residual lead concentrations.

Methods

Preparation of the nanocomposite: CNTs were first functionalized with carboxyl group by sonication at 40 °C for 2 h in acid mixture (65% HNO₃ and 98% H₂SO₄, ratio 1:3 (v/v)). The oxidized carbon nanotubes (MWCNT-COOH) were suspended in a solution of thionyl chloride in order to activate the carboxylic groups by conversion into acyl chloride groups so that amidation can occur with the chitosan. The solution was stirred for 24 h at 70°C in a necked flask with a reflux condenser and then separated by membrane filtration and the obtained solid was washed with THF and then dried in the oven to get acyl chloride functionalized nanotubes (MWCNT-COCl). Chitosan was mixed with MWCNT-COCl in DMF. The mixture was stirred at 120 °C for 96 hours under nitrogen atmosphere. After reaction, the mixture was filtered through a 0.22 µm polyether sulfone membrane. Finally, the product was dried in the oven to get chitosan immobilized multiwall carbon nanotubes MWCNT-CS.

Moreover, the morphology of raw MWCNTs, carboxyl-functionalized MWCNTs, MWCNT-CS and the chitosan were examined using FTIR. In addition, FESEM along with Energy Dispersive X-ray (EDX) analysis were performed for raw, oxidized and chitosan immobilized MWCNTs in order to confirm the functionalization and attachments.

Adsorption experiments: Adsorption experiments were carried out at room temperature by shaking the series of bottles containing the desired dose of adsorbent (20-60 mg L⁻¹) with predetermined concentration of lead (0.1-0.5 mg L⁻¹). The pH (5-7) was adjusted using 0.1 M hydrochloric acid and/or 0.1 M sodium hydroxide. At the end of the run time (20-100 min) the samples were filtered and the residual concentrations were measured by Atomic Adsorption Spectroscopy (AAS).

RESULTS AND DISCUSSION

Immobilization: Figure 1 shows the FTIR spectra of (a) the raw MWCNTs, (b) the MWCNT functionalized oxidation in acid mixture, (c) the chitosan and (d) the MWCNT-CS nanocomposite. It can be observed that very weak peaks appear in Fig. 1 (a) in the range 1850-2000 and 1750-1845 cm⁻¹ corresponding to the C = O (Kim *et al.*, 2006). However, new peaks appear at 2970, 1738, 1434, 1365 and 1216 cm⁻¹ in (b), the first peak corresponds to the -OH stretching, while the other peaks correspond to the -COOH (Wu *et al.*, 2007). These results indicate that the oxidation resulted in sufficient peaks for the immobilization to occur. Figure 1 also shows the FTIR spectrum of chitosan. The peak at 1645 cm⁻¹ (-NH₂) and the small band at 1587 cm⁻¹ assigned to N-H and amide groups of chitosan were replaced by new bands at 1633 and the sharp band at 1538 cm⁻¹, suggesting that some amino groups were converted into amide groups. Moreover, the bands at 1150, 1021 and 894 cm⁻¹ (d), corresponding to the glucopyranose rings of chitosan, implying the attachment of chitosan to the CNTs. Furthermore, the small band at around 1335 cm⁻¹ suggests that the primary hydroxyl groups partially participated in the reaction. Also the wide O-H and N-H absorption bands of CS at around 3287 cm⁻¹ (c) shifted to 3328 cm⁻¹ and became broader (d) suggesting the above conclusion as well (Ke *et al.*, 2006).

Figure 2 shows the FESEM of raw, oxidized and Chitosan immobilized CNTs. The raw CNTs have a snake-like shape with very smooth surface (Fig. 2a). The oxidized MWCNT (Fig. 2b) appear shorter than the raw MWCNT. Moreover, the surface of the raw MWCNT is smoother than the oxidized one due to the damage to the surface caused by the acid treatment. In addition, the oxidation

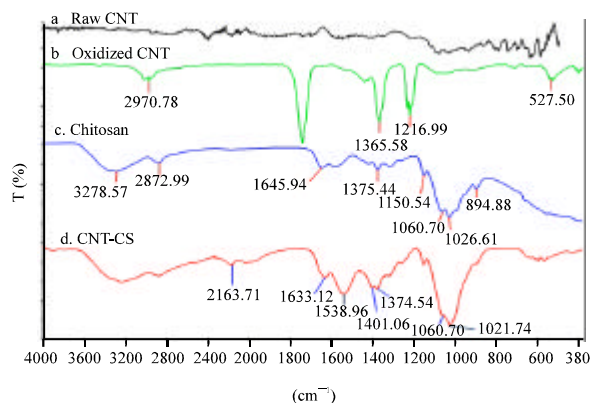


Fig. 1: FTIR of (a) raw MWCNT, (b) oxidized MWCNT, (c) chitosan and (d) the chitosan-MWCNT nanocomposite

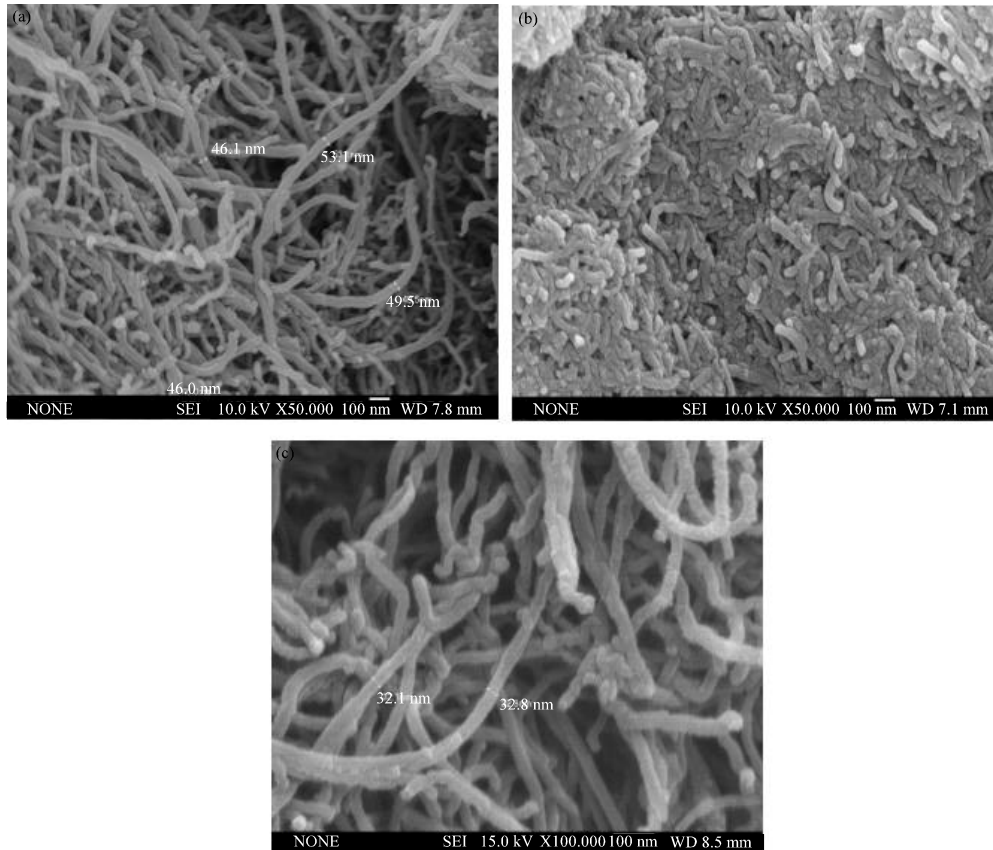


Fig. 2: FESEM of (a) Raw MWCNTs (b), MWCNT-COOH (c) and MWCNT-CS

resulted in reduction of the MWCNT diameter; the average diameter of the pristine CNT is 50 nm while the oxidized one is around 30 nm. Figure 2c shows the chitosan immobilized MWCNT.

Adsorption: Based on the ANOVA analysis of residual concentrations after the adsorption runs, a quadratic model was selected for the fitting of the data. The model in Eq. 1 describes the effect of each factor beside the interactions between the factors. The model is considered significant with p-value less than 0.05 for most of the parameters of the model. The correlation factor R^2 value of the model is 78.45%.

The regression equation in terms of the actual factors:

$$\begin{aligned} \text{Residual} = & -0.97204 + 0.75963 * \text{lead conc} + 0.013821 * \\ & \text{Dosage} + 0.12702 * \text{pH} + 5.12160\text{E-}003 * \text{contact time} + \\ & 1.46455\text{E-}003 * \text{agitation speed} - 4.69933\text{E-}003 * \text{lead conc} \\ & * \text{agitation speed} - 2.54381\text{E-}003 * \text{Dosage} * \text{pH} + 5.45018\text{E-} \\ & 005 * \text{Dosage} * \text{contact time} - 1.01195\text{E-}003 * \text{pH} * \text{contact} \\ & \text{time} \end{aligned} \quad (1)$$

The regression equation shows that as pH for example, increases the residual concentration of lead decreases, this would be due to the protonation of the -NH group of the chitosan that is immobilized in the surface on the MWCNTs which lead to better chelating of the metal ion and thus a reduction in the residual concentration.

From the analysis the optimal values are 0.3 mg L⁻¹ for lead initial concentration, 40 mg L⁻¹ for the CNT-CS dosage, pH 6 and 150 rpm agitation speed. Those values correspond to the center point and gave the maximum removal (98.4%).

CONCLUSION

A novel MWCNT-CS nanocomposite was prepared through the immobilization of the chitosan polymers onto the surface of the carboxyl oxidized MWCNTs. The attachment of chitosan to MWCNT-COOH was verified by FTIR and FESEM. The obtained nanocomposite was used as an adsorption material for lead removal from aqueous solutions to achieve water quality standard of 0.05 mg L⁻¹ as stated by the Malaysian department of

environment (DOE). The optimal conditions corresponding to the maximum removal percentage were those which correspond to the center point of the design values. In addition, the achieved residual concentration (0.008 mg L^{-1}) is much less than the Malaysian DOE requirement for the waste water (0.05 mg L^{-1}) and it is even less than the maximum allowable concentration for the drinking water (0.01 mg L^{-1}). A quadratic empirical model showing the interaction of the parameters and their effect on the residual concentration has been obtained by analysis using design expert.

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