Fabrication of $\beta$-cyclodextrin modified mesostructured silica coated multi-walled carbon nanotubes composites and application for paraben removal

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ABSTRACT

In this work, the novel $\beta$-cyclodextrin modified mesostructured silica coated multi-walled carbon nanotubes (MWCNTs) composites were synthesized and applied for the removal of parabens in aqueous solution. The prepared MWCNTs/SiO$_2$/$\beta$-CD composites were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and thermogravimetric analysis. The effects of the amount of adsorbent, pH and elution solvents on the removal efficiency of parabens from water solutions were investigated. Under the optimized conditions, over 95% removal efficiency was achieved by using 40 mg of MWCNTs/SiO$_2$/$\beta$-CD adsorbents to absorb the parabens from 60 mL of 0.5 $\mu$g/mL parabens solutions. The solution pH in the range from 5 to 9 has no influence on the removal efficiency and the parabens sorption capacity of the prepared adsorbents were around 0.75 $\mu$g/mg. Furthermore, the stability and reusability studies demonstrated that the prepared MWCNTs/SiO$_2$/$\beta$-CD composites are cost-effective adsorbents for the removal of parabens from water with high regeneration efficiency. The composites fabricated in this study could become an attractive candidate for water purification.

Key words | adsorption, MWCNTs/SiO$_2$/$\beta$-CD, paraben removal, water treatment

INTRODUCTION

Parabens, including methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP) and butyl paraben (BP), are widely used in food and cosmetics because of their antimicrobial and anti-fungal properties (Haman et al. 2015). However, it has been recently reported that parabens are one class of endocrine disrupting chemicals and may cause endocrine disorders in the organisms (Liao et al. 2013; Ma et al. 2016). Previous studies have reported that excessive use of parabens in cosmetics can cause contact dermatitis, breast cancer, endocrine system interference and reproductive hormones disruption during pregnancy (Darbre et al. 2004). Due to the widespread use, the parabens are often detected in water, soil and even in the human body (Li et al. 2016; Sun et al. 2016; Wang & Kannan 2016). Thus, it is necessary to develop the method of paraben removal from the wastewater. Currently, the methods of removing parabens from wastewater include photodegradation, biodegradation, microwave/ultrasound elimination, and adsorption (Saleh 2015a, 2015b, 2017; Velegraki et al. 2015; Danmaliki & Saleh 2016; Papadopoulos et al. 2015; Saleh et al. 2016a, 2016b; Kumar et al. 2017; Wang et al. 2017). However, due to their high cost and severe operating conditions, the first three methods could only be used for small-scale processes. In contrast, the adsorption is considered as a promising method for removal of contaminants from wastewater due to its low cost, ease of operation, and stability (Sajid et al. 2018). The key in adsorption technique is the use of efficient adsorbents with high stability and reusability to improve the pollutant removal performance. Therefore, the preparation of novel adsorbent materials is crucial for the development of the adsorption technique.

Carbon materials are widely used in environmental purification due to their high specific surface area, high thermal and electrical conductivity, high stability, high chemical inertness and low density (Yu et al. 2016a, 2016b; Álvarez-Torrellas et al. 2017). The use of carbon nanotubes in the field of adsorption is promising in recent years because of
their large surface area, surface hydrophobicity and strong interaction capabilities for various compounds. Therefore, carbon nanotubes are often used as adsorbents for gas and water purification, or as a solid phase extraction adsorbent to extract parabens in the cosmetics (Saleh & Gupta 2012; Gupta & Saleh 2013; Saleh 2013). The adsorption mechanisms of carbon nanotubes involve Van der Waals force, π-π bond, electrostatic force and other hydrophobic interactions (Xu et al. 2018). On the other hand, silica is an important mineral in nature and has been widely used in various industries as additives, catalyst carrier, bleaching agent, matting agent, rubber supplements, plastic fillers, insulating adiabatic fillers, ink thickeners, metal soft polish, senior household cosmetics packing and spraying materials (Singh et al. 2014). The chemical properties of silica are relatively stable, with the advantages of heat resistance and low toxicity. Furthermore, mesoporous silica has mesoporous structure that enhances adsorption capacity. Thus, silica is often used as a modifier to enhance the stability of other materials. For example, it has been reported that Fe₃O₄@SiO₂ was used to remove organic pollutants from wastewater (Wang et al. 2016). In addition, the molecular shape of cyclodextrins, a family of cyclic oligosaccharides, is like a cone with a cavity in the center. The surface of the cyclodextrin is hydrophilic induced by the primary and secondary hydroxyl groups and the interior of the cavity is hydrophobic (Sherje et al. 2017). Due to its external hydrophilic and internal hydrophobic cavity structure, cyclodextrins can be complexed with organic molecules, providing the possibility of removing organic contaminants from the wastewater. Topuz et al. reported that cyclodextrin functionalized mesostructured silica nanoparticles were used to remove polycyclic aromatic hydrocarbons (Topuz & Uyar 2017). To date, cyclodextrins are widely used in various fields such as drug delivery, molecular recognition, self-assembly, extraction of cholesterol from food, electrochemical applications, cosmetics, biosensors and adsorption of environmental pollutants (Shen et al. 2015; D’Angelo et al. 2017; Dong et al. 2017).

In this paper, the β-cyclodextrin modified mesostructured silica coated multi-walled carbon nanotube composites were synthesized to remove the parabens from aqueous solutions by adsorption. The prepared composites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis. The effects of the amount of adsorbent, pH of solutions and the types of eluted solvent on the performance of adsorbents for parabens removal from aqueous solutions were investigated. Furthermore, the stability and reusability of prepared composites were evaluated.

**MATERIALS AND METHODS**

**Chemicals and materials**

Multi-walled carbon nanotubes (MWCNTs) and the standards including methyl-, ethyl-, propyl-, and butyl-parabens (MP, EP, PP and BP) were purchased from TCI Chemical. Cetyltrimethyl ammonium chloride (CTAC), tetraethyl orthosilicate (TEOS) and β-cyclodextrin (β-CD) were obtained from Aladdin Industrial Corporation (Shanghai, China). Sodium hydroxide was purchased from Xilong Science Corporation (Guangdong, China). Ethanol, acetonitrile and acetone were purchased from Tianjin Fine Chemicals Co., Ltd (Tianjin, China). Chromatographic grade of acetonitrile and methanol were received from Merck, Germany. Concentrated nitric acid (68%) was purchased from Zhejiang Zhongxing Chemical Reagent Co., Ltd (Zhejiang, China). Stock mixture standard solutions of MP, EP, PP and BP were prepared in MeOH at the concentration of 1 mg/mL and stored in the refrigerator at 4 °C. Working standard solutions (1.0, 5.0, 10, 25 and 50 μg/mL) were freshly prepared by diluting the stock solutions before use. Precautions have always been taken to minimize sample contamination. All containers, glassware, and filtration devices were thoroughly soaked with 0.1 M HNO₃ solution for 24 h and rinsed twice with ultrapure water.

**Synthesis of MWCNTs/SiO₂/β-CD composites**

The pristine MWCNTs were treated with concentrated nitric acid by refluxing the MWCNTs/HNO₃ mixture for 6 h at 120 °C. Afterwards, the oxidized MWCNTs were collected and neutralized to a pH close to 7.0 by rinsing with distilled water. Then the MWCNTs were dried at 50 °C in a vacuum drying oven for 12 h. In a 250 mL, three-neck, round bottom flask, 75 mg of carboxylation functionalized MWCNTs and 750 mg of CTAC were added to this flask. Then 100 mL distilled water was added to the flask. Subsequently, the above mixture was ultrasonically treated for 30 min to form a uniform dispersion. After 30 min, 1 M NaOH solution and 50 mL of distilled water were added to the mixture. The mixture was further ultra-sonicated for 5 min. Subsequently, the flask containing the mixture was placed in a 60 °C thermostatic oil bath and stirred for 0.5 h. Next, 1.50 g of β-CD was added to the flask. Then, 4 mL of the mixed solution...
(TEOS/ethanol (v/v = 1:4) was slowly added to the above mixture and the reaction was continued for 24 h at 60 °C with stirring. Afterwards, the MWNT/SiO$_2$/β-CD was isolated by centrifugation and washed with methanol. Then, the MWNT/SiO$_2$/β-CD was dried at 50°C in a vacuum drying oven for 12 h. For the synthesis of mesostructured silica coated multi-walled carbon nanotubes (MWNT/SiO$_2$), the synthesis step was the same as above, but the β-CD was not added.

**Characterization of MWCNTs/SiO$_2$/β-CD composites**

The SEM (FEI, Nova Nano SEM 200, USA) was used for the morphological observation of the prepared MWCNTs/SiO$_2$/β-CD composites. Thermogravimetric analysis (TGA) was carried out under a nitrogen environment with the heating rate of 10 °C/min by a STA7300 instrument (Hitachi High Technology Co. Ltd, Japan). The FTIR spectra were obtained from an instrument purchased from Thermo Fisher Scientific (NICOLET IS10). The XRD patterns were examined on a Bruker X-ray diffractometer (Bruker D8) in the 2θ range 10–90°.

**Paraben sorption experiments**

The paraben sorption experiments were carried out in 3-mL plastic cylinder tubes which were uniformly filled with prepared MWCNTs/SiO$_2$/β-CD composites. Prior to sorption experiments, the adsorption capacity of prepared MWCNTs/SiO$_2$/β-CD composites was investigated. In total, 40 mg of the composites were loaded into the tubes and activated by washing subsequently with methanol and distilled water. Then, the aqueous sample solutions containing paraben mixtures at the concentrations of 1.0 μg/mL were loaded into the tubes at the flow rate 5.0 mL/min. After sorption process, the concentration of parabens in water samples were determined by high-performance liquid chromatography (HPLC). The adsorption capacity of the MWCNTs/SiO$_2$/β-CD was calculated by following equation:

$$Q_t = \frac{(C_0 - C_t) \times V_s}{m_{adsorbent}}$$

where:
- $Q_t$ – Adsorption capacity (μg/mg)
- $C_0$ – Initial concentration of parabens in sample (μg/mL)
- $C_t$ – Concentration of the parabens in sample after adsorption (μg/mL)
- $V_s$ – Volume of spiked parabens water sample (mL)
- $m_{adsorbent}$ – Amount of the MWCNTs/SiO$_2$/β-CD composites (40 mg).

To achieve a higher parabens removal efficiency and better reusable capability of adsorbents, several parameters including of adsorbents amount, elution solvent and pH of sample solution were investigated and optimized to improve the sorption performance since the MWCNTs/SiO$_2$/β-CD composites may have limited capacity to adsorb the paraben molecules from aqueous solution. Different amounts of MWCNTs/SiO$_2$/β-CD composites (10, 20, 30, 40 and 50 mg) were filled into the tubes separately. The 60 mL of mixture solution containing 0.5 μg/mL of MP, EP, PP and BP standards were prepared in distilled water. Then the paraben solutions were loaded into the tubes filled with the prepared composites at the rates of 5.0 mL/min. Finally, the adsorbed parabens in tubes were washed out by 1.0 mL of organic elution solvents. The sample solutions containing parabens before and after passing through the adsorbents-filled tubes were injected into the HPLC system for analysis. For evaluating the effects of washing solvent on the elution efficiency of adsorbed parabens from the adsorbents, the parabens were washed using 1.0 mL of different organic solvents such as methanol, acetonitrile, methanol/acetonitrile (1:1 v/v), acetone and ethanol. The pH of sample solutions were adjusted by 0.01 M NaOH and HCl solutions. The removal efficiency was examined by parabens sorption percent, which is calculated by the following equation:

$$\text{Sorption(%) = } \frac{C_0 - C_e}{C_0} \times 100\%$$

where:
- $C_0$ – Initial concentration of paraben in sample (μg/mL)
- $C_e$ – Concentration of the paraben in sample after sorption (μg/mL).

**HPLC analytical methods**

The concentrations of parabens were analyzed by HPLC, Wufeng LC100 equipped with a UV-absorbance detector and a Waters symmetry-C18 column (5 μm, 150 × 3.9 mm). Mobile phases A and B were 5% acetonitrile and acetonitrile, respectively. The mobile phase composition initially was 50% A + 50% B, then changed to 5% A + 95% B by a linear gradient within 7 min. The flow rate was 1.0 mL/min and the detection wavelength was 255 nm. The parabens in samples were identified by matching retention times against that of the standards. All quantification was performed by the
calibration equation based on peak area method. The calibration curve was established by linear regression of the peak area and concentration of the standards.

**RESULTS AND DISCUSSION**

**Characterization**

The morphologic properties of MWCNTs and MWCNTs/SiO₂/β-CD composites were characterized by SEM as shown in Figure 1. The SEM image of MWCNTs (Figure 1(a)) clearly represents the disordered distribution of carbon nanotubes, with no covering on the surface. By contrast, the SEM image of MWCNTs/SiO₂/β-CD composites (Figure 1(b)) shows a layer of substance covering the surface of carbon nanotubes.

TGA curves (Figure 1(c)) of MWCNTs and MWCNTs/SiO₂/β-CD composites were obtained under an N₂ environment in the temperature range of room temperature to 800 °C. TGA curve of MWCNTs had a weight reduction of 9% from room temperature to 800 °C, which is attributed to the reduction of water molecules and the breakage of carboxyl groups. TGA curve of MWCNTs/SiO₂/β-CD composites had a weight reduction of 2% below 100 °C, which is attributed to the evaporation of water molecules. It is observed that the mass loss of MWCNTs/SiO₂/β-CD composites is mainly between 200 °C and 310 °C, which is caused by the decomposition of β-CD on the surface of SiO₂. The MWCNTs/SiO₂/β-CD composites continued to lose weight after 550 °C, which is attributed to the reduction in the number of oxygen-containing structure. Since the MWCNTs/SiO₂/β-CD composites contain silica and carbon nanotubes, the weight is almost unchanged after 550 °C (Saleh et al. 2018). The material composition of MWCNTs and MWCNTs/SiO₂/β-CD composites were characterized by XRD (Figure 1(d)). An obvious diffraction peak at about 2θ = 26° was observed, which is indicative of MWCNTs. The weaker and broader band was found on the MWCNTs/SiO₂/β-CD composites curve at 2θ = 20°–25°, indicating that the amorphous silica was successfully coated on MWCNTs (Kalapathy et al. 2000). In addition, the weak peak about 2θ = 18° may be related to β-CD (Liu et al. 2014). The FTIR spectra of oxidized MWCNTs and MWCNTs/SiO₂/β-CD composites are shown in Figure 1(e). Oxidized MWCNTs exhibit C=O and C-O stretching vibration at ~1,600 cm⁻¹ and ~1,045 cm⁻¹, respectively (Saleh 2013a, 2015b; Alswat et al. 2016; Balarak et al. 2017). For MWCNTs/SiO₂/β-CD composites, the band at ~1,100 cm⁻¹ corresponds to Si-O-H and Si-O-Si stretching vibration, which demonstrates that the silica is coated on the surface of carbon nanotubes. In addition, the band intensity at ~1,029 cm⁻¹ can be attributed to β-CD. These observations strongly demonstrate that the MWCNTs/SiO₂/β-CD composites were successfully synthesized.

**Evaluation and optimization of parabens removal by sorption with prepared composites**

The adsorption capacity of prepared MWCNTs/SiO₂/β-CD adsorbents was calculated following the procedures and arithmetic operation described earlier. The results indicated that the adsorbed quantity of parabens with 40 mg of MWCNTs/SiO₂/β-CD increased with the increase of the added volume of sample solution. However, the adsorbed quantities of all four types of parabens remained stable when the added volume of 1.0 μg/mL paraben mixtures was more than 30 mL. It suggested that the prepared MWCNTs/SiO₂/β-CD composites have similar adsorption capacity for all four parabens and the maximum adsorption capacity was around 0.75 μg/mg based on the calculated results according to the adsorption capacity equation.

To minimize the consumption of the MWCNTs/SiO₂/β-CD adsorbents during the process for parabens removal from aqueous solution, the effect of the amount of adsorbents on the parabens sorption efficiency from 60 mL of 0.5 μg/mL parabens mixture solutions was investigated. Different amounts of the MWCNTs/SiO₂/β-CD composites (10, 20, 30, 40 and 50 mg) were examined. As shown in Figure 2, the sorption percentage of parabens increased when the amount of the adsorbents increased from 10 mg to 40 mg. This can be explained by the fact that more adsorbents will provide larger surface area and more sorption sites. The sorption rate of parabens reached a plateau (95%) when 40 mg of adsorbent was used to remove the parabens in 60 mL of 0.5 μg/mL, and no significant increase was observed when 50 mg of adsorbent was used. Therefore, the 40 mg was the minimum amount of MWCNTs/SiO₂/β-CD adsorbents to remove the parabens from 60 mL of 0.5 μg/mL parabens solutions. It also further indicated that the parabens sorption capacity of the prepared adsorbents was around 0.75 μg/mg.

To achieve the high removal efficiency of parabens for recycling the adsorbents, it is essential to select the appropriate elution solvent to wash the adsorbed parabens on adsorbents after sorption process. In this study, five types of elution solvent, i.e. methanol, acetonitrile, methanol/acetone mixture (1:1 v/v), acetone and ethanol were tested on
40 mg of adsorbent following the procedures as described previously. As illustrated in Figure 3, when acetonitrile was selected as the elution solvent, the desorption percentage of parabens was below 80%. By contrast, when methanol was used as the elution solvent, the desorption percentage of parabens was close to 100%. Similarly, when ethanol and methanol/acetonitrile (1:1 v/v) were selected as the elution solvent, the elution efficiency was around 90%.

Figure 1 | Characterization of the oxidized MWCNTs and the prepared MWCNTs/SiO$_2$/β-CD composites: (a) and (b) SEM images; (c) TGA analysis; (d) XRD patterns; (e) FTIR spectra.
However, the desorption rate was quite low (<80%) when acetone is used as the elution solvent due to its relatively low polarity. On the other hand, the sorption of PP is the highest, and the sorption of MP is the lowest. As illustrated in the previous reports, the total hydrogen bond numbers, diffusion constant and solvent accessible surface of organic compounds affect their affinity to the carbon-based nanomaterials (Song et al. 2016; Yu et al. 2016a, 2016b; Yu et al. 2017). In this study, the PP has more methyl functional groups than that of MP, indicating higher sorption affinity of prepared MWCNT/SiO₂/β-CD for PP as compared to MP. Therefore, methanol was the optimal elution solvent to wash the adsorbed parabens from the composites.

The pH of the sample solution is one of the most important factors that might affect the adsorption rate of parabens, since the pH may affect the fraction distribution of paraben species and further interaction capability between parabens with the adsorbents. To study the effect of pH on the sorption rate of parabens, 60 mL of 0.5 μg/mL parabens solutions with different pH values (3, 5, 7 and 9) were prepared separately. The performance of parabens sorption with the prepared composites was evaluated. As shown in Figure 4, when the pH increased from 3 to 5, the parabens sorption rates increased and exhibited no significant change with the further increase of pH values. The reason could be that the parabens can be hydrolyzed in strong acidic solution. A slight decrease in basic solutions was observed that may have resulted from the alkaline hydrolysis of paraben. Thus, the pH of water sample solutions have no significant effects on the performance of adsorbents in the range from 5 to 9 which is the normal pH value for common wastewaters.

Stability and reusability study

A promising adsorbent should be stable under different conditions to ensure its effectiveness. To assess the stability of the prepared MWCNTs/SiO₂/β-CD composites, they were first dispersed in water at different pH values and then allowed to stand for 24 h followed by centrifugation and drying. It was found that the surface as well as the sorption percentage and capacity of the MWCNTs/SiO₂/β-CD composites were almost unchanged (Saleh et al. 2016a, 2016b; Jabli et al. 2017; Osb et al. 2017). Reusability is another important aspect for adsorbents, not only to reduce their cost in practical applications but also to meet the requirements of
green chemistry. In this work, the reusability of the fabricated MWCNTs/SiO$_2$/$\beta$-CD composites in the removal of parabens was evaluated by using 40 mg of the adsorbents to adsorb the parabens in 60 mL of 0.5 $\mu$g/mL parabens solutions followed by washing with methanol solvents to ensure that the adsorbent has no residual parabens. As shown in Figure 5, the parabens sorption percentage was over 85% after five cycles, indicating that MWCNTs/SiO$_2$/$\beta$-CD composites can be easily recycled for the removal of parabens. This reusability study shows that MWCNTs/SiO$_2$/$\beta$-CD composites have excellent regenerative capacity and can be used as effective materials in the treatment of paraben-containing wastewater.

**Comparison with other adsorbents**

Comparison of the parabens removal efficiency from aqueous solutions by using various adsorbents including MWCNTs/SiO$_2$/$\beta$-CD composites, MWCNTs and MWCNTs/SiO$_2$ was performed by following the same procedures as previously described. As shown in Figure 6, it is obvious that the sorption percentage of parabens with the MWCNTs/SiO$_2$/$\beta$-CD composites was significantly higher than the other two adsorbents, demonstrating its superiority in applications regarding paraben removal from wastewater.

**CONCLUSIONS**

The MWCNTs/SiO$_2$/$\beta$-CD composites were successfully synthesized and applied to remove the parabens by sorption from aqueous solutions. The in-tube conditions such as the adsorbent amount consumed, elution solvent type and pH of sample solutions were evaluated and optimized. The study showed that the coating of silica can improve the performance and stability of adsorbents. In addition, by using these synthesized composites, the parabens can be quickly and easily removed from the aqueous solutions and the composites could be recycled without a significant decrease of removal efficiency, which is beneficial for the practical applications in a larger scale. In summary, the prepared MWCNT/SiO$_2$/$\beta$-CD composites is a promising material for the efficient removal of parabens from the wastewater.

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**REFERENCES**


Saleh, T. A. 2017 Advanced Nanomaterials for Water Engineering, Treatment, and Hydraulics. IGI Global, Hershy.


Sun, Q., Li, M., Ma, C., Chen, X., Xie, X. & Yu, C. P. 2016 Seasonal and spatial variations of PPCP occurrence, removal and mass loading in three wastewater treatment plants located in different urbanization areas in Xiamen, China. *Environmental Pollution* 208, 371–381.

Topuz, F. & Uyar, T. 2017 Cyclodextrin-functionalized mesostructured silica nanoparticles for removal of polycyclic


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