

Highlights

- Novel MWCNTs/SiO₂/β-CD composites were fabricated with excellent stability properties.
- The composites are characterized by FTIR, XRD, SEM and TGA techniques.
- Over 95% parabens removal efficiency was achieved by composites via adsorption.
- The composites are cost-effective adsorbents with high regeneration efficiency.

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4 **Fabrication of β -Cyclodextrin modified mesostructured silica coated multi-**
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7 **walled carbon nanotubes composites and application for paraben removal**
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4 **Abstract**
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7 In this work, the novel β -cyclodextrin modified mesostructured silica coated multi-walled
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9 carbon nanotubes (MWCNTs/SiO₂/ β -CD) composites were synthesized and applied for the
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11 removal of parabens in aqueous solution. The prepared MWCNTs/SiO₂/ β -CD composites were
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13 characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD),
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15 scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The effects of the
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17 amount of adsorbent, pH and elution solvents on the removal efficiency of parabens from water
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19 solutions were investigated and optimized. Under the optimized conditions, over 95% removal
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21 efficiency was achieved and the solution pH has no influences on the removal efficiency.
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23 Furthermore, the stability and reusability studies demonstrated that the prepared
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25 MWCNTs/SiO₂/ β -CD composites are cost-effective adsorbents for the removal of parabens from
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27 water with high regeneration efficiency. The composites fabricated in this study could become an
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29 attractive way as promising candidate for water purification.
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38 **Keywords:** Multi-walled carbon nanotube; β -cyclodextrin modified mesostructured silica;
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40 Parabens; Adsorption
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1. 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 anti-microbial and anti-fungal properties [1-4]. However, it has been recently reported that parabens are one class of endocrine disrupting chemicals (EDCs) and may cause endocrine disorders in the organisms [5,6]. Previous studies have reported that excessive use of parabens in cosmetics can cause contact dermatitis [7,8], breast cancer [9], endocrine system interference [10,11] and reproductive hormones disruption during pregnancy [6]. Due to the widespread use, the parabens are often detected in water, soil and even in human body [12-20]. Thus, it is necessary to develop the method of paraben removal from the wastewater. Currently, the methods of removing parabens from wastewater include adsorption, photodegradation, biodegradation and microwave elimination [21-25]. 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 [21]. 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 [26-28] due to their high specific surface area, high thermal and electrical conductivity, high stability, high chemical inertness and low density. 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

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4 gas and water purification, or as a solid phase extraction adsorbent to extract parabens in the
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6 cosmetics [30]. The adsorption mechanisms of carbon nanotubes involve Van der Waals force,
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8 π - π bond, electrostatic force and other hydrophobic interactions [29]. On the other hand, silica is
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10 an important mineral in nature and has been widely used in various industries as additives,
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12 catalyst carrier, bleaching agent, matting agent, rubber supplements, plastic fillers, insulating
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14 adiabatic fillers, ink thickeners, metal soft polish, senior household cosmetics packing and
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16 spraying materials, etc. [31]. The chemical properties of silica are relatively stable, with the
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18 advantages of heat resistance and low toxicity. Furthermore, mesoporous silica has mesoporous
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20 structure that enhances adsorption capacity. Thus, silica is often used as a modifier to enhance
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22 the stability of other materials. For example, Wang et al. reported that $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was used to
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24 remove organic pollutants from wastewater [32]. On the other hand, the molecular shape of
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26 cyclodextrins, a family of cyclic oligosaccharides, is like a cone with a cavity in the center. The
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28 surface of the cyclodextrin is hydrophilic induced by the primary and secondary hydroxyl groups
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30 and the interior of the cavity is hydrophobic [33]. Due to its external hydrophilic and internal
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32 hydrophobic cavity structure, cyclodextrins can be complexed with organic molecules, providing
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34 the possibility of removing organic contaminants from the wastewater. Topuz et al. reported that
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36 cyclodextrin functionalized mesostructured silica nanoparticles were used to remove polycyclic
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38 aromatic hydrocarbons [34]. To date, cyclodextrins are widely used in various fields such as drug
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40 delivery, molecular recognition, self-assembly, extraction of cholesterol from food,
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42 electrochemical applications, cosmetics, biosensors and adsorption of environmental pollutants
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55 In this paper, the β -cyclodextrin modified mesostructured silica coated multi-walled carbon
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57 nanotube ($\text{MWCNTs}/\text{SiO}_2/\beta\text{-CD}$) composites were synthesized to remove the parabens in
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4 aqueous solutions. The prepared composites were characterized by Fourier transform infrared
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7 thermogravimetric analysis (TGA). The effects of the amount of adsorbent, pH of solutions and
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9 the types of eluted solvent on the performance of adsorbents for parabens removal from aqueous
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11 solutions were investigated. Furthermore, the stability and reusability of prepared composites
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13 were evaluated.
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21 **2. Materials and methods**

22 **2.1 Chemical and standards**

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24 Multi-walled carbon nanotubes (MWCNTs) and the standards including methyl-, ethyl-,
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26 propyl-, and butyl-parabens (MP, EP, PP and BP) were purchased from TCI Chemical.
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28 Cetyltrimethyl ammonium chloride (CTAC), Tetraethyl orthosilicate (TEOS) and β -cyclodextrin
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30 (β -CD) were obtained from Aladdin Industrial Corporation (Shanghai, China). Sodium
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32 hydroxide was purchased from Xilong Science Corporation (Guangdong, China). Ethanol,
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34 acetonitrile and acetone were purchased from Tianjin Fine Chemicals Co., Ltd. (Tianjin, China).
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36 Chromatographic grade of acetonitrile and methanol were received from Merck, Germany.
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38 Concentrated nitric acid (68%) was purchased from Zhejiang Zhongxing Chemical Reagent Co.,
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40 Ltd. (Zhejiang, China). Stock mixture standard solutions of MP, EP, PP and BP were prepared in
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42 MeOH at the concentration of 1 mg/mL and stored in the refrigerator at 4 °C. Working standard
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44 solutions (1.0, 5.0, 10, 25 and 50 μ g/mL) were freshly prepared by diluting the stock solutions
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46 before use. Precautions have always been taken to minimize sample contamination. All
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48 containers, glassware, and filtration devices were thoroughly soaked with 0.1M HNO₃ solution
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50 for 24 h and rinsed twice with ultrapure water.
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2.2 Synthesis of MWCNTs/SiO₂/β-CD composites

The pristine MWCNTs were treated with concentrated nitric acid by refluxing the MWCNTs/HNO₃ mixture for 6h 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 dispersed in 100 mL of distilled water and were ultrasonically treated for 30 min to form a homogeneous dispersion. Then, 50 mL of distilled water and 1 mL of 1 M NaOH solution were added and ultrasonically treated for 5 min and kept at 60 °C for 0.5 hours while being stirred. Later, 1.50 g of β-CD was added followed by the slow addition of 4 mL mixed solution (TEOS/ethanol, v/v=1:4) and the obtained mixture was heated for 24 h at 60 °C while being stirred. Afterwards, the MWCNTs/SiO₂/β-CD composites were isolated by centrifugation and washed with methanol. The MWCNTs/SiO₂/β-CD composites were then dried at 50 °C in a vacuum drying oven for 12 h. For the synthesis of mesostructured silica coated multi-walled carbon nanotubes (MWCNTs/SiO₂), the synthesis step was the same as above without the addition of β-CD.

2.3 Characterization of MWCNTs/SiO₂/β-CD composites

The SEM (FEI, Nova Nano SEM 200, USA) was used for the morphological observation of the prepared MWCNTs/SiO₂/β-CD composites. TGA analysis 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°.

2.4 Paraben sorption experiments

The paraben sorption experiments were carried out in 3-mL of plastic cylinder tubes which were uniformly filled with prepared MWCNTs/SiO₂/β-CD composites. Prior to sorption experiments, the adsorption capacity of prepared MWCNTs/SiO₂/β-CD composites was investigated. 40 mg of the composites was 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 was 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/SiO₂/β-CD was calculated by following equation:

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

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 - Amount of the MWCNTs/SiO₂/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/SiO₂/β-CD composites may have limited capacity to adsorb the paraben molecules from aqueous solution. Different amounts of MWCNTs/SiO₂/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

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4 solutions were loaded into the tubes filled with the prepared composites at the rates of 5.0
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6 mL/min. Finally, the adsorbed parabens in tubes were washed out by 1.0 mL of organic elution
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8 solvents. The sample solutions containing parabens before and after passing through the
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10 adsorbents-filled tubes were injected into the HPLC system for analysis. For evaluating the
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12 effects of washing solvent on the elution efficiency of adsorbed parabens from the adsorbents,
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14 the parabens were washed using 1.0 mL of different organic solvents such as methanol,
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16 acetonitrile, methanol/acetonitrile (1:1 v/v), acetone and ethanol. The pH of sample solutions
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18 were adjusted by 0.01 M NaOH and HCl solutions. The removal efficiency was examined by
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20 parabens sorption percent, which is calculated by the following equation:
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$$\text{Sorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100\%$$

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29 C_0 -- Initial concentration of paraben in sample ($\mu\text{g/mL}$)

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32 C_e -- Concentration of the paraben in sample after sorption ($\mu\text{g/mL}$)
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34 **2.5 HPLC analytical methods**

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

3.1 Characterization

The morphologic properties of MWCNTs and MWCNTs/SiO₂/β-CD composites were characterized by SEM as shown in Fig. 1. The SEM image of MWCNTs (Fig. 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 (Fig. 1.B) shows a layer of substance covering the surface of carbon nanotubes.

TGA curves (Fig. 2) of MWCNTs and MWCNTs/SiO₂/β-CD composites were obtained under a 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 350 °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.

The material composition of MWCNTs and MWCNTs/SiO₂/β-CD composites were characterized by XRD (Fig. 3). An obvious diffraction peak at about $2\theta = 26^\circ$ was observed, which is indicative of MWCNTs. The weaker and broader band was found on the MWCNTs/SiO₂/β-CD composites curve at $2\theta = 20^\circ$ - 25° , indicating that the amorphous silica

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4 was successfully coated on MWCNTs [42]. In addition, the weak peak about $2\theta = 18^\circ$ may be
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6 related to β -CD [43].
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9 The FTIR spectra of oxidized MWCNTs and MWCNTs/SiO₂/ β -CD composites are shown
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11 in Fig. 4. Oxidized MWCNTs exhibit C=O and C-O stretching vibration at $\sim 1600\text{ cm}^{-1}$ and
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13 $\sim 1045\text{ cm}^{-1}$, respectively. For MWCNTs/SiO₂/ β -CD composites, the band at $\sim 1100\text{ cm}^{-1}$
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15 corresponds to Si-O-H and Si-O-Si stretching vibration, which demonstrates that the silica is
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17 coated on the surface of carbon nanotubes. In addition, the band intensity at $\sim 1029\text{ cm}^{-1}$ can be
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19 attributed to β -CD. These observations strongly demonstrate that the MWCNTs/SiO₂/ β -CD
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21 composites were successfully synthesized.
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25 26 27 28 **3.2 Removal of parabens by sorption** 29

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31 The adsorption capacity of prepared MWCNTs/SiO₂/ β -CD adsorbents was calculated
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33 following the procedures and arithmetic operation described in Part 2.4. The results indicated
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35 that the adsorbed quantity of parabens with 40 mg of MWCNTs/SiO₂/ β -CD increased with the
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37 increase of the added volume of sample solution. However, the adsorbed quantities of all four
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39 types of parabens kept stable when the added volume of 1.0 $\mu\text{g/mL}$ paraben mixtures was more
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41 than 30 mL. It suggested that the prepared MWCNTs/SiO₂/ β -CD composites have similar
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43 adsorption capacity for all four parabens and the maximum adsorption capacity was around 0.75
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45 $\mu\text{g/mg}$ based on the calculated results according to the adsorption capacity equation.
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50 51 **3.2.1 Effect of the amount of the MWCNTs/SiO₂/ β -CD composites** 52

53 To save the consumption of the MWCNTs/SiO₂/ β -CD adsorbents during the process for
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55 parabens removal from aqueous solution, the effect of the amount of adsorbents on the parabens
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57 sorption efficiency from 60 mL of 0.5 $\mu\text{g/mL}$ parabens mixture solutions was investigated.
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4 Different amounts of the MWCNTs/SiO₂/β-CD composites (10, 20, 30, 40 and 50 mg) were
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6 examined. As shown in Fig. 5, the sorption percentage of parabens increased when the amount of
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8 the adsorbents increased from 10 mg to 40 mg. This can be explained by the fact that more
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10 adsorbents will provide larger surface area and more sorption sites. The sorption rate of parabens
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12 reached a plateau (95%) when 40 mg of adsorbent was used to remove the parabens in 60 mL of
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14 0.5 μg/mL, and no significant increase was observed when 50 mg of adsorbent was used.
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16 Therefore, the 40 mg was the minimum amount of MWCNTs/SiO₂/β-CD adsorbents to remove
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18 the parabens from 60 mL of 0.5 μg/mL parabens solutions. It also further indicated that the
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20 parabens sorption capacity of the prepared adsorbents were around 0.75 μg/mg.
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26 **3.2.2 Effect of the elution solvent type**

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28 To achieve the high removal efficiency of parabens for recycling the adsorbents, it is
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30 essential to select the appropriate elution solvent to wash the adsorbed parabens on adsorbents
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32 after sorption process. In this study, five types of elution solvent, i.e., methanol, acetonitrile,
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34 methanol/ acetonitrile (1:1 v/v), acetone and ethanol were tested on a 40 mg of adsorbent
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36 following the procedures as per section 2.4. As illustrated in Fig. 6, when acetonitrile was
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38 selected as the elution solvent, the desorption percentage of parabens was below 80%. By
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40 contrast, when methanol was used as the elution solvent, the desorption percentage of parabens
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42 was close to 100%. Similarly, when ethanol and methanol/acetonitrile (1:1 v/v) were selected as
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44 the elution solvent, the elution efficiency was around 90%. However, the desorption rate was
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46 quite low (<80%) when acetone is used as the elution solvent due to its relatively low polarity.
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48 Therefore, methanol was the optimal elution solvent for wash the adsorbed parabens from the
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50 composites.
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3.2.3 Effect of sample pH

The pH of the sample solution is one of the most important factor 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 $\mu\text{g/mL}$ 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 Fig. 7, 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 be 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 values for common wastewaters.

3.3 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.

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/SiO₂/ β -CD composites in the removal of parabens was

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4 evaluated by using 40 mg of the adsorbents to adsorb the parabens in 60 mL of 0.5 µg/mL
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6 parabens solutions followed by washing with methanol solvents to ensure that the adsorbent has
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8 no residual parabens. As shown in Fig. 8, the parabens sorption percentage was over 85% after
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10 five cycles, indicating that MWCNTs/SiO₂/β-CD composites can be easily recycled for the
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12 removal of parabens. This reusability study shows that MWCNTs/SiO₂/β-CD composites have
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14 excellent regenerative capacity and can be used as effective materials in the treatment of
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16 paraben-containing wastewater.
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23 **3.4 Comparison with other adsorbents**

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26 Comparison of the parabens removal efficiency from aqueous solutions by using various
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28 adsorbents including of MWCNTs/SiO₂/β-CD composites, MWCNTs and MWCNTs/SiO₂ was
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30 performed by following the same procedures as previously described. As shown in Fig. 9, it is
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32 obvious that the sorption percentage of parabens with the MWCNTs/SiO₂/β-CD composites was
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34 significantly higher than the other two adsorbents, demonstrating its superiority in applications
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36 regarding paraben removal from wastewater.
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43 **4. Conclusion**

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46 The MWCNTs/SiO₂/β-CD composites were successfully synthesized and applied to remove
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48 the parabens by sorption from aqueous solutions. The in-tube conditions such as the adsorbent
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50 amount consumed, elution solvent type and pH of sample solutions were evaluated and
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52 optimized. The study showed that the coating of silica can improve the performance and stability
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54 of adsorbents. In addition, by using this synthesized composites, the parabens can be quickly and
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56 easily removed from the aqueous solutions and the composites could be recycled without a
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4 significant decrease of removal efficiency, which is beneficial for the practical applications in a
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6 larger scale. In summary, the prepared MWCNT/SiO₂/β-CD composites is a promising material
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9 for the efficient removal of parabens from the wastewater.
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4 **Figure Captions**
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7 **Fig. 1.** SEM images of (A) MWCNTs and (B) MWCNTs/SiO₂/β-CD composites
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9 **Fig. 2.** TGA of MWCNTs and MWCNTs/SiO₂/β-CD composites under the nitrogen atmosphere
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11 **Fig. 3.** XRD patterns of oxidized MWCNTs and MWCNTs/SiO₂/β-CD composites
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13 **Fig. 4.** FTIR spectra of oxidized MWCNTs and MWCNTs/SiO₂/β-CD composites
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15 **Fig. 5.** The sorption percentage of parabens with different amount of MWCNTs/SiO₂/β-CD
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17 composites from 60 mL of 0.5 μg/mL parabens aqueous solutions
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19 **Fig. 6.** Desorption efficiency of parabens with different types of elution solvents
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21 **Fig. 7.** Sorption efficiency of parabens from the sample solutions at different pH values
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23 **Fig. 8.** Recycling of parabens sorption on MWCNTs/SiO₂/β-CD composites
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25 **Fig. 9.** Comparasion of parabens sorption efficiency by using different adsorbents
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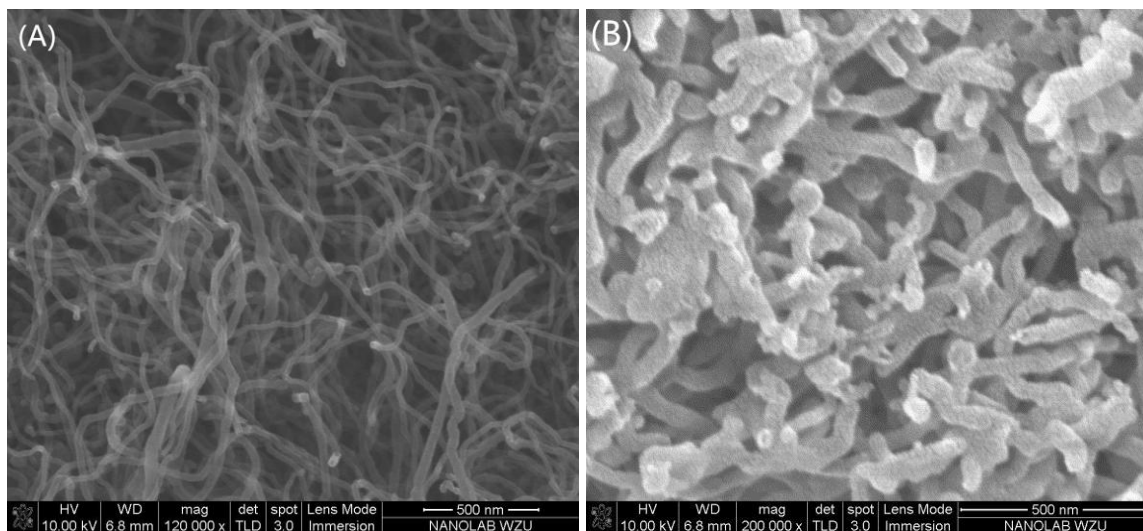


Fig. 1. SEM images of (A) MWCNTs and (B) MWCNTs/SiO₂/β-CD composites

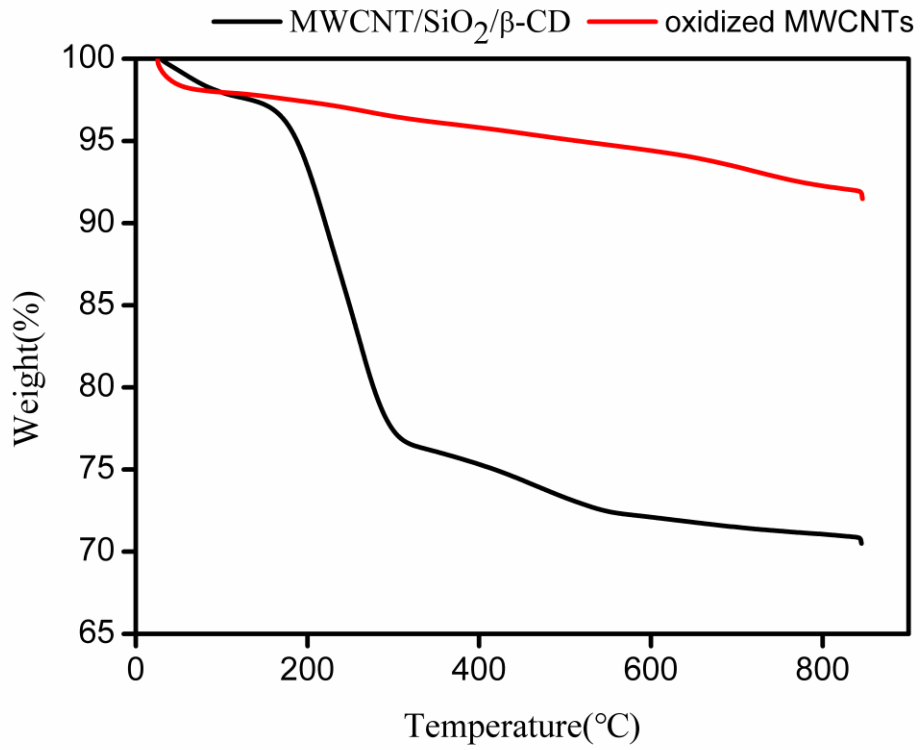


Fig. 2. TGA of MWCNTs and MWCNTs/SiO₂/β-CD composites under the nitrogen atmosphere

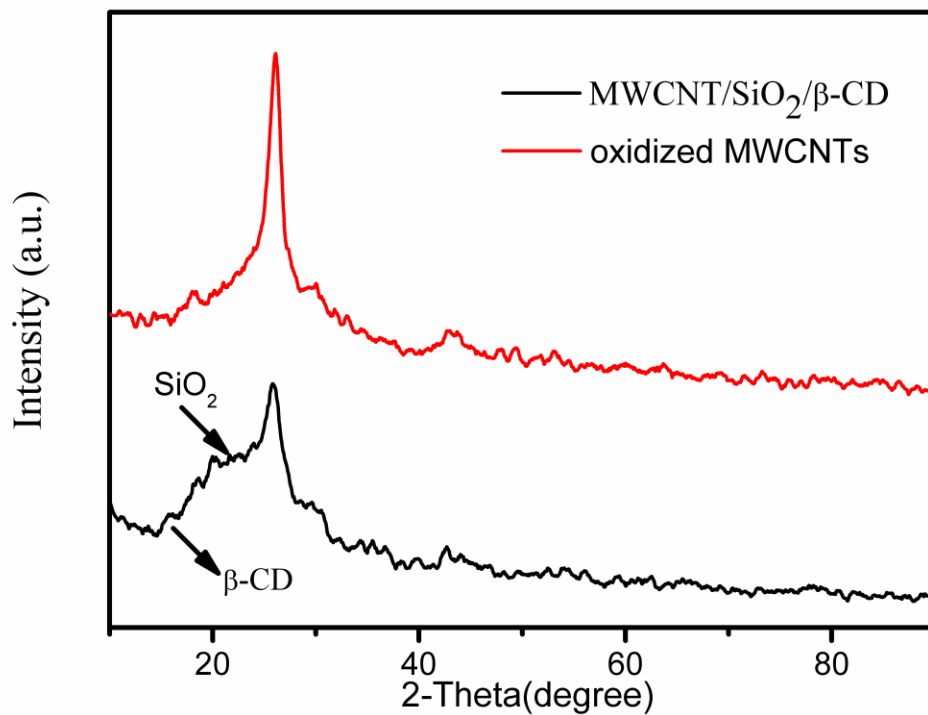


Fig. 3. XRD patterns of oxidized MWCNTs and MWCNTs/SiO₂/β-CD composites

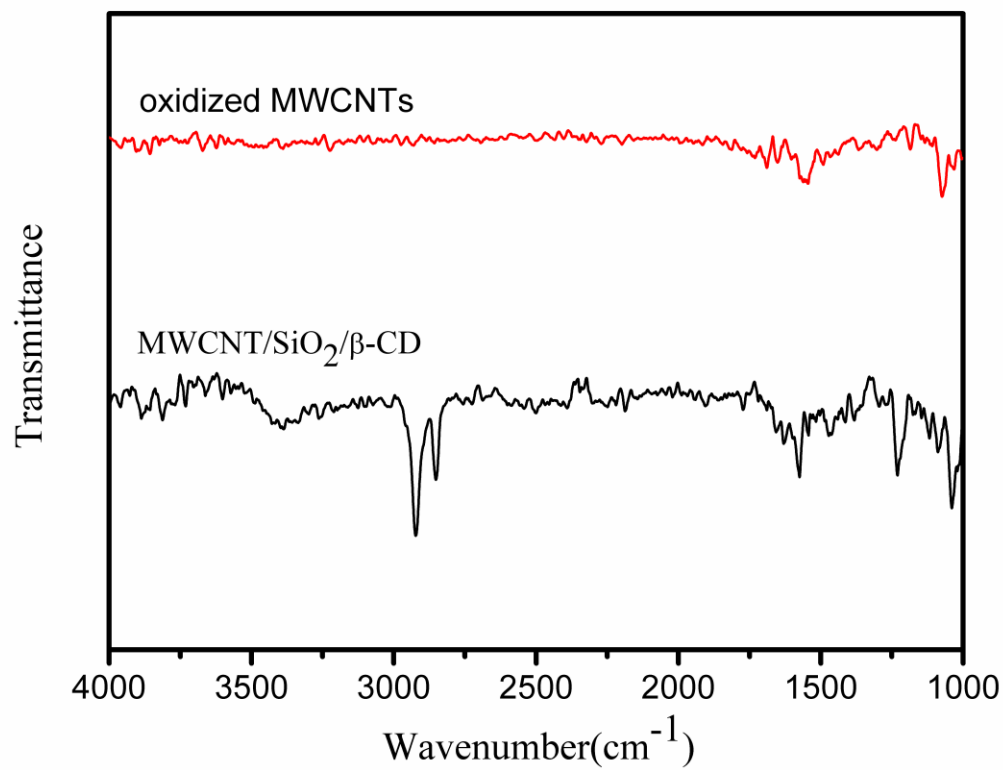


Fig. 4. FTIR spectra of oxidized MWCNTs and MWCNTs/SiO₂/β-CD composites

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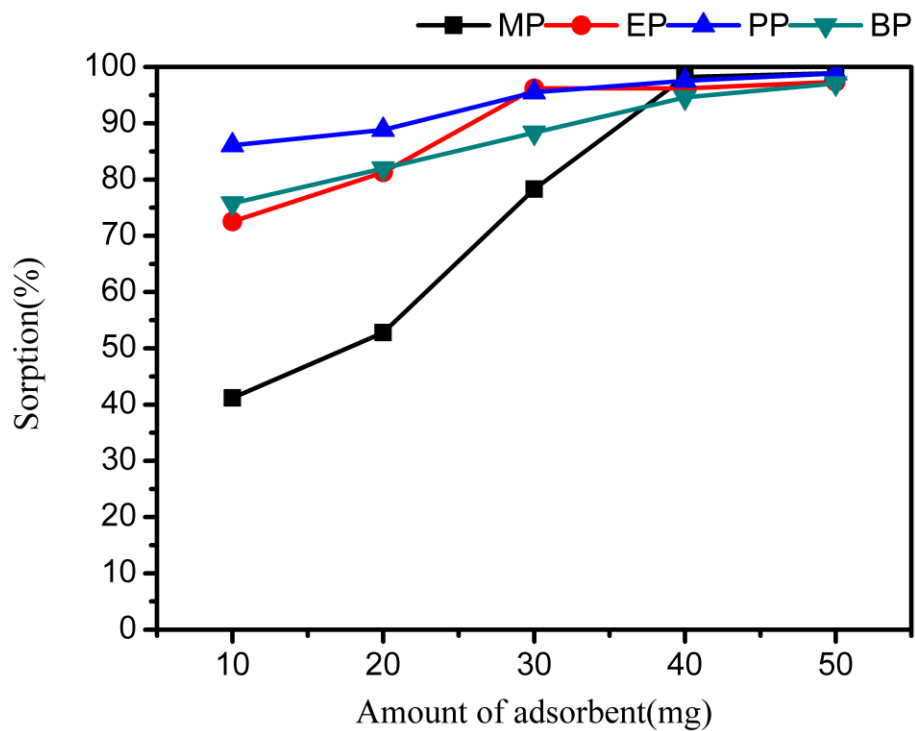


Fig. 5. The sorption percentage of parabens with different amount of MWCNTs/SiO₂/β-CD composites from 60 mL of 0.5 μg/mL parabens aqueous solutions

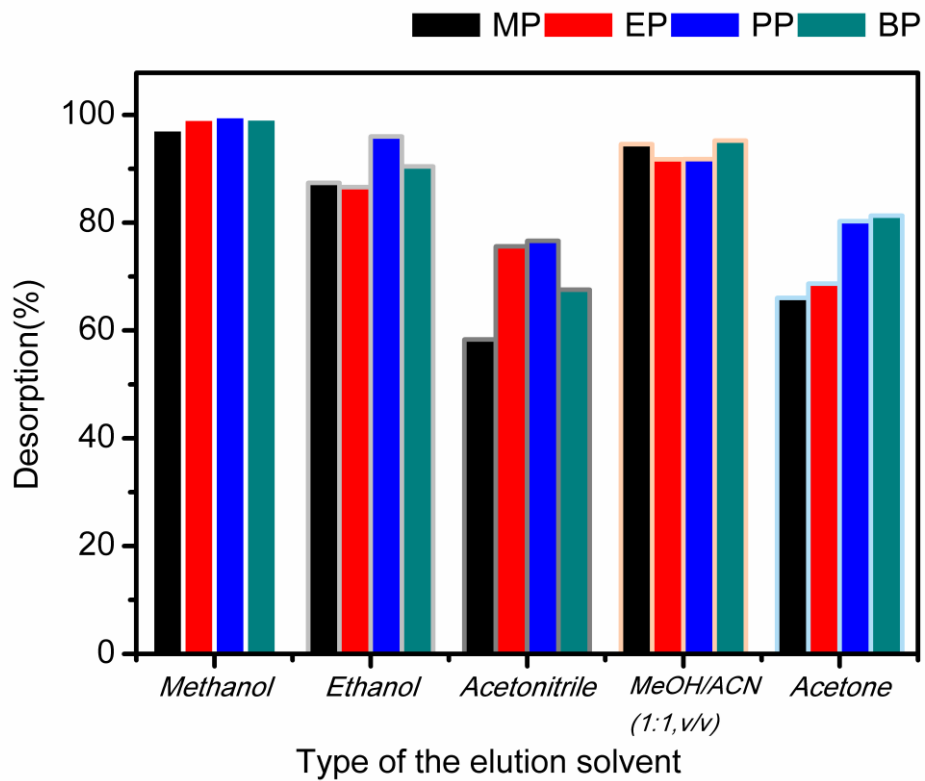


Fig. 6. Desorption efficiency of parabens with different types of elution solvents

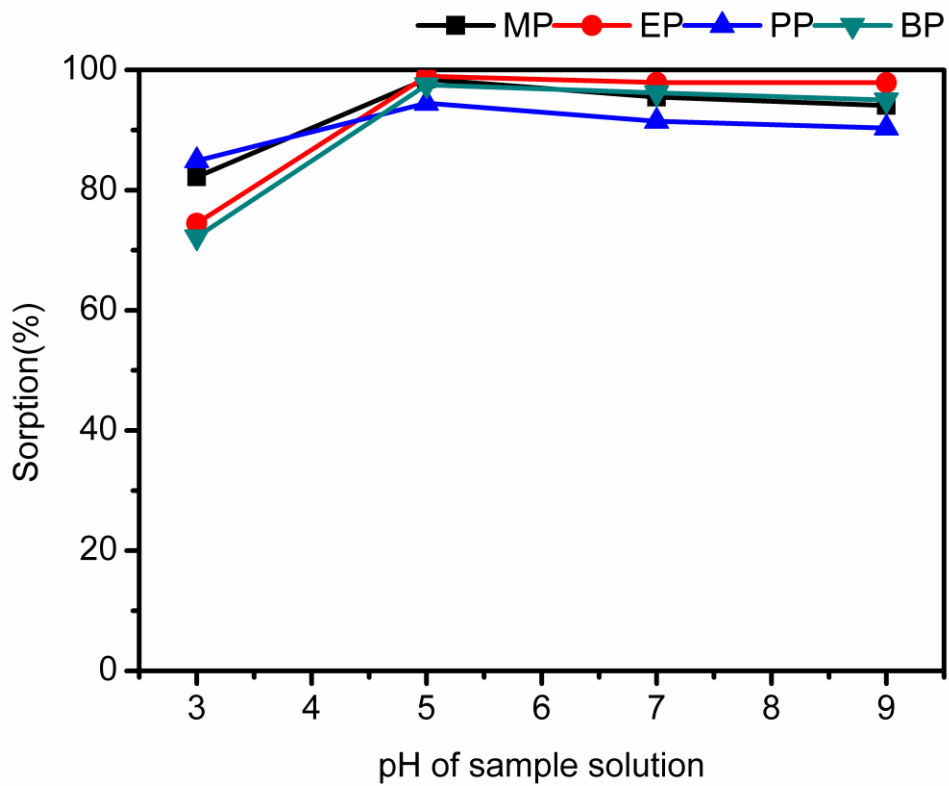


Fig. 7. Sorption efficiency of parabens from the sample solutions at different pH values

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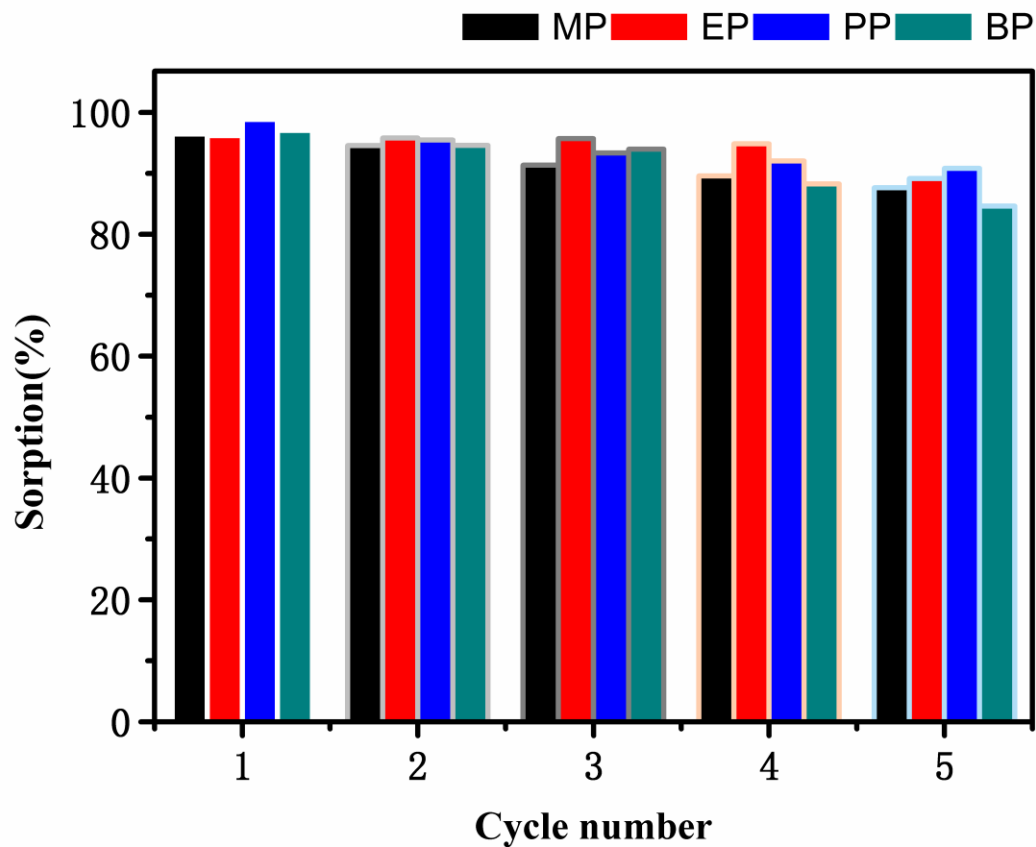


Fig. 8. Recycling of parabens sorption on MWCNTs/SiO₂/β-CD composites

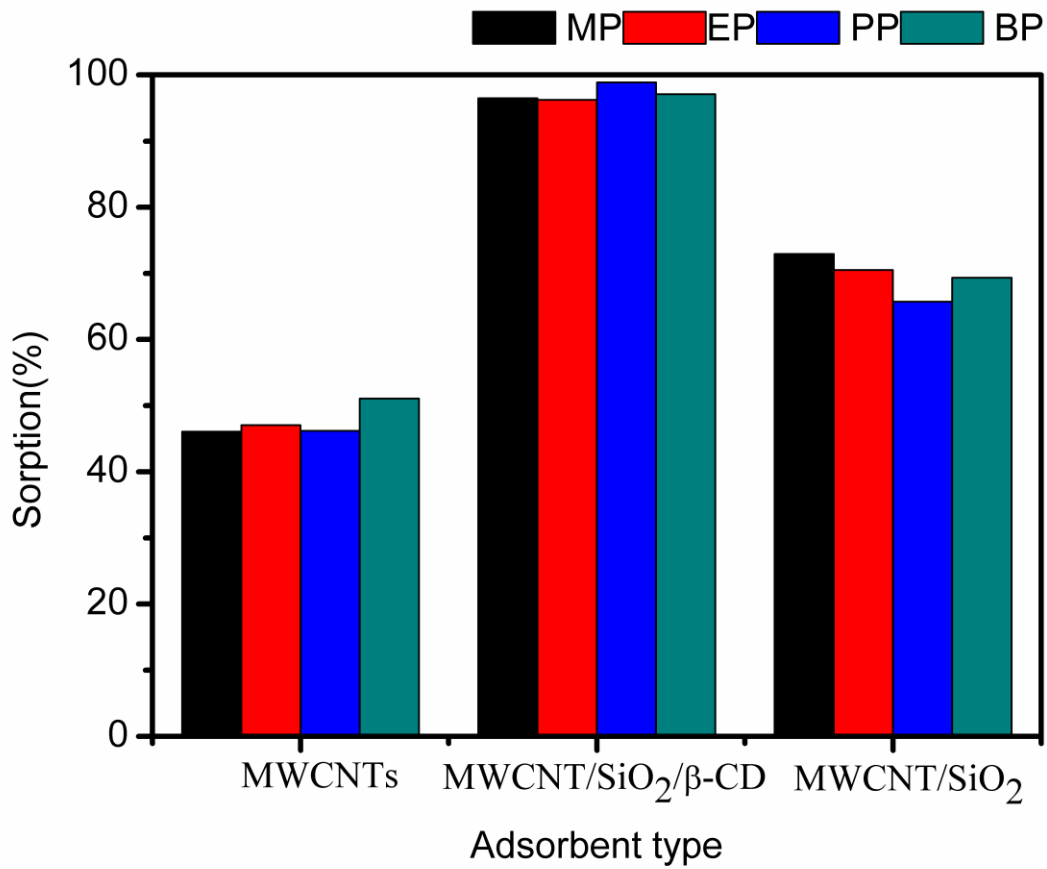


Fig. 9. Comparasion of parabens sorption efficiency by using different adsorbents