Carbonaceous Nanofiber Membrane Functionalized by beta-Cyclodextrins for Molecular Filtration

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ABSTRACT In this paper, we report the fabrication of carbonaceous nanofiber (CNF) membranes functionalized by beta-cyclodextrins (CNF-β-CD membrane) and their application for molecular filtration. The chemically synthesized carbonaceous nanofibers were first functionalized by β-CD, and the free-standing CNF membrane can be prepared by a simple filtration process. The membrane shows a remarkable capability to function as an ideal molecular filter through complexation of phenolphthalein molecules with the cyclodextrin molecules grafted on the CNFs. As a typical dye pollutant, fuchsin acid can also be effectively removed from the solution through such a membrane. Engineering the surface of this carbonaceous nanofiber membrane may allow it to be used for other applications such as chiral separation and drug delivery.

KEYWORDS: carbonaceous nanofibers · functionalization · free-standing membrane · beta-cyclodextrins · molecular filter performance

The release of the organic pollutants has become a global concern due to their overall environmental toxicity.[1−4] Cyclodextrins (CDs) have played a very important role in the removal of the organic pollutants.[5−7] The most significant characteristic of the CDs is their ability to form inclusion complexes in aqueous media with a wide variety of organic substrates, including many organic pollutants.[5,8,9] Some CD-functionalized materials have been researched for water purification purposes.[10−13] Research shows that CDs have extensive applications in many fields, such as pharmaceutical science, food science, and analytical science.[14,15] β-CD is one of the most common CDs.

In recent years, novel carbonaceous materials have already shown promising applications in many fields such as water purification, fuel cell catalysis, energy storage, bioimaging, drug delivery, and gas sensors.[16−21] Titirici and co-workers reported carbonaceous materials loaded with carboxylic groups using hydrothermal carbonization (HTC) of glucose in the presence of acrylic acid. The materials show high adsorption capacity for removal of heavy metals from aqueous solutions.[22] Previously, we reported that well-defined carbonaceous nanofibers (CNFs) can be synthesized from glucose by the HTC process[23] that have several remarkable characteristics, such as a highly porous, interconnected open pore structure, good flexibility, and large surface area. Recently, we have prepared a new type of free-standing filtration membrane made of CNFs that has a very narrow pore size distribution and is capable of filtration and separation of nanoparticles with different sizes from solution by a simple filtration process.[24] The CNF membrane is very flexible and mechanically robust enough for filtration operation under a high applied pressure. It has been demonstrated that the free-standing films with well-defined nanostructures have great potential for many applications such as separation of nanoparticles, sensors, and catalysts.[25−29]

In this paper, we report the fabrication of a carbonaceous nanofiber membrane functionalized by β-CD (CNF-β-CD membrane). The molecular filter performance of the membrane for filtration of phenolphthalein (Php)[30,31] has been examined. In addition, the capability of such a membrane to remove fuchsin acid from solution, which is a typical dye pollutant,[32,33] has also been studied.

RESULTS AND DISCUSSION

As shown in Scheme 1, functionalization of a carbonaceous nanofiber membrane by β-CD includes three steps. The first step involves the formation of the epoxy group onto the CNF by reacting epichlorohydrin with −OH on the CNF in alkaline conditions. The product was CNF-O. In the second step, the β-CD reacted with CNF-O to obtain the final product, CNF-β-CD. Finally, the functional nanofiber membrane was prepared by a simple filtration method.

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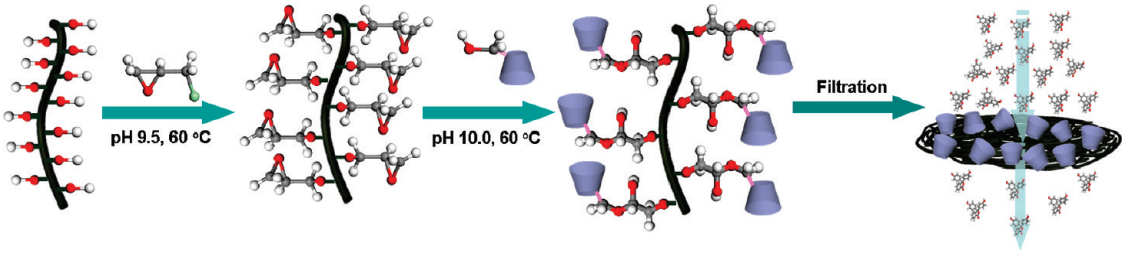

Scheme 1. Schematic illustration of the functionalization of a carbonaceous nanofiber membrane by β-CD and molecular filtration application.

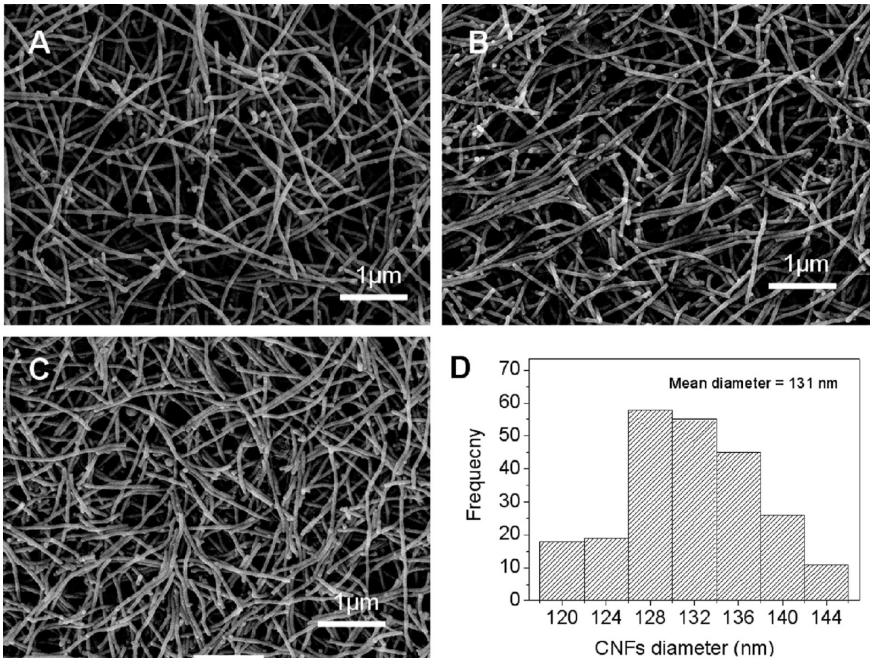

Figure 1. SEM images of CNF (A), CNF-O (B), and CNF-β-CD (C), and the diameter distribution of CNF-β-CD (D).

The morphologies of the as-obtained products are observed by SEM. Figure 1A shows representative SEM images of the CNF. Figure 1B and C depict representative SEM images of the intermediate (CNF-O) and final product (CNF-β-CD), respectively. From Figure 1A, B, and C, the fiber morphologies show that the fibers look uniform and have a relatively narrow size distribution. The CNF-β-CD showed an average diameter of 131 nm (shown in Figure 1D) and no obvious difference from that of the CNF. We believe that the whole reaction process did not affect the fibrous morphology.

Functionalization of the CNF by β-CD was confirmed by FTIR spectroscopy. Figure 2A shows the FT-IR spectra of CNF-O, CNF, and CNF-β-CD in the 400−4000 cm^{-1} wavenumber range. The peak at 3396 cm^{-1} in spectrum b can be assigned to the −OH stretching vibration arising from surface hydroxyl groups of CNF. The spectrum of CNF-O shows the characteristic peaks at 751 and 1265 cm^{-1}, indicating the formation of the epoxy group onto CNF. The peak at 1033 cm^{-1} in the spectrum of CNF-β-CD was assigned to the C−O and C−O−C stretching vibration. The increase in the band intensity at around 1033 cm^{-1} can be attributed to β-CD. Therefore, it can be concluded that β-CD has been grafted successfully on the surface of CNF. X-ray photoelectron spectroscopy (XPS) was used to quantitatively obtain information on the surface composition of the CNF-β-CD. Figure 2B shows the C_{1s} and O_{1s} XPS for CNF-β-CD, CNF, and β-CD. The results clearly demonstrated that the surface of the CNF-β-CD has a higher oxygen content than that of the CNF.

Wang *et al.* reported the plasma-induced grafting of β-CD onto multiwall carbon nanotube/iron oxides with a grafted β-CD content of 16.6 mg/g.[12] Chen *et al.* synthesized the CD-citrate-gum arabic-modified magnetic nanoparticles, and the amount of β-CD grafted on the nanoparticles is 28.7 mg/g.[34] Herein, we measured the content of β-CD in the CNF-β-CD sample according to the reported method,[30,35] and the amount is 205.0 mg/g. Therefore, a high content of β-CD grafted onto CNF can be realized by the present method. There are two reasons for this. First, our recent research work showed that the CNF contains a high density of surface functional groups, such as the −OH group, because of

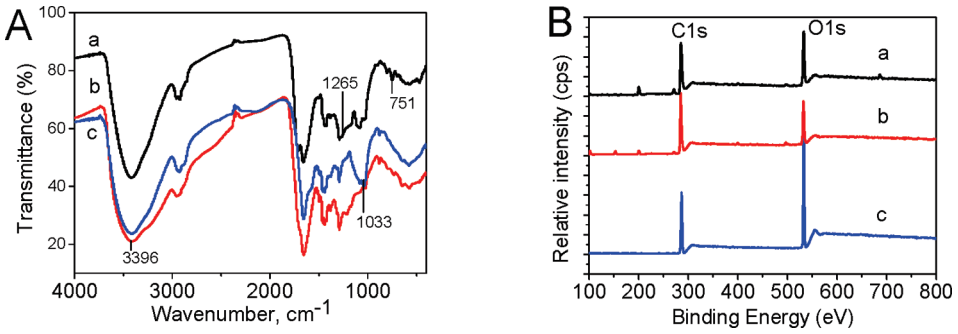

Figure 2. (A) FT-IR spectra of CNF-O (a), CNF (b), and CNF-β-CD (c); (B) C_{1s} and O_{1s} XPS for CNF-β-CD (a), CNF (b), and β-CD (c) (C_{1s} at 284.85 eV and O_{1s} at 532.05 eV).

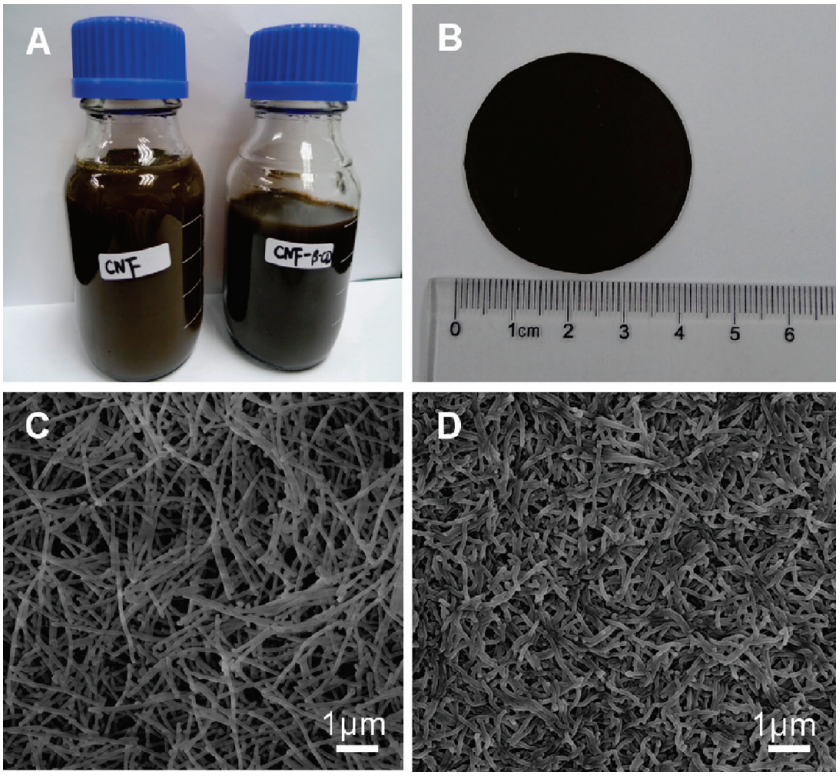

Figure 3. (A) Photographs of the CNF and CNF-β-CD aqueous dispersions. (B) Photograph of the CNF-β-CD membrane. (C) SEM image showing surface morphology of the CNF-β-CD membrane. (D) SEM image of the CNF-β-CD membrane after the filtration process of Php.

carbonization at low temperature.[23] These functional groups can supply the active sites for functionalization. Second, the CNF-β-CD has a relatively large surface area per unit volume. The BET surface area of the CNF and CNF-β-CD were obtained from N_2 adsorption–desorption isotherms measured using a surface area and porosity measurement system (TriStar II 3020 V1.03, Micromeritics Instrument Corporation). The BET surface area of the CNF and CNF-β-CD is 22.68 and 18.49 m^2/g, respectively.

The CNF-β-CD free-standing membrane was fabricated according to the filtration method,[28,36,37] which provides a simple and easy way to prepare large-scale free-standing membranes. The CNF and CNF-β-CD aqueous dispersions were used to prepare such a membrane, respectively. Photographs of the CNF and CNF-β-CD aqueous dispersions are shown in Figure 3A. A certain volume of the CNF-β-CD or CNF aqueous dispersion was filtered, and suction filtration was performed at decreasing pressure and usually completed within 5 min. Then, the CNF-β-CD or CNF free-standing membrane was obtained. A photograph of the membrane is shown in Figure 3B. Figure 3C shows the SEM images of the CNF-β-CD membrane. Figure 3C reveals that the membrane is made up of abundant randomly oriented nanofibers. The membrane has a highly porous, interconnected open pore structure and a large surface area. The thickness of the membrane depends on the volume of the filtered solution and the size of the filtration funnel. In our experiment, a 3.5 cm funnel was used to

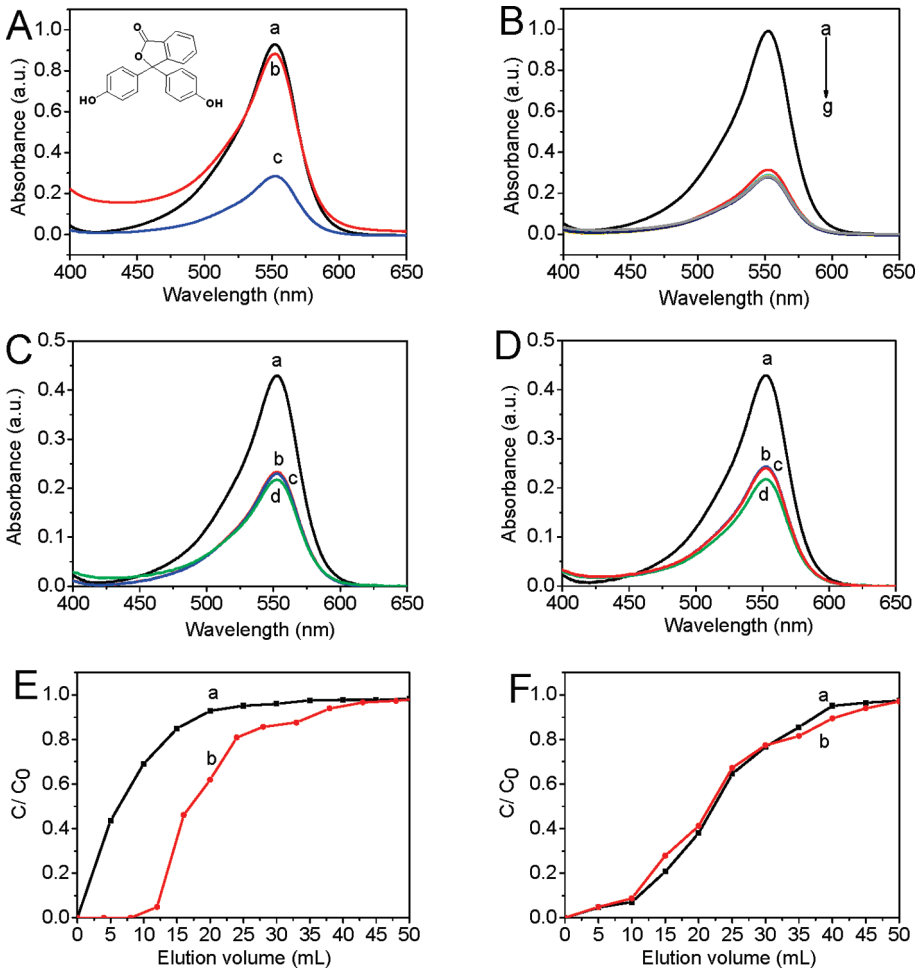

Figure 4. (A) UV−vis spectra of Php (*c* = 12 mg/L) solution after 4 h: (a) pure Php solution, (b) Php solution treated by CNF, (c) Php solution treated by CNF-β-CD. The inset is the structural formula of Php. (B) UV−vis spectra of Php (*c* = 12 mg/L) solution: (a) pure Php solution, (b−g) Php solution treated with CNF-β-CD (at 2 min, 5 min, 15 min, 90 min, 4 h, and 10 h). (C) UV−vis spectra of Php (*c* = 6.0 mg/L) solution after 15 min: (a) pure Php solution, (b) Php solution treated with CNF-β-CD dispersed in ethanol, (c) Php solution treated with CNF-β-CD dispersed in acetone, (d) Php solution treated with CNF-β-CD dispersed in deionized water. (D) UV−vis spectra of Php (*c* = 6.0 mg/L) solution after 15 min: (a) pure Php solution, (b) Php solution treated with CNF-β-CD after three recycles, (c) Php solution treated with CNF-β-CD after two recycles, (d) Php solution treated with CNF-β-CD. (E) Breakthrough curve of Php through the CNF-β-CD membrane (b) and CNF membrane (a). (F) Breakthrough curve of Php through the CNF-β-CD membrane after two (a) and three recycles (b).

prepare the free-standing membrane. Figure 3D shows a typical SEM image of the CNF-β-CD membrane after the filtration process of the Php. From Figure 3C and D, we observed that the membranes kept their fibrous structure after the filtration process.

Uptake of the Php was tested because Php is a model organic molecule and can form inclusion complexes with β-CD. The CNF-β-CD was dispersed into Php solution, and the change in absorbance of Php was recorded. Figure 4A shows the UV−vis spectra of Php solution treated with CNF and CNF-β-CD after 4 h, respectively. Curve a in Figure 4A shows the result of the control group. Figure 4A indicates that the absorbance of Php solution decreased significantly in the presence of CNF-β-CD, because of the removal of Php from the solution by complexation with the CDs functionalized on CNF-β-CD. Figure 4B shows the change in absorbance of Php as a function of time. It was observed that the removal of Php from solution by the complexation with the CDs was mainly complete within 2 min, and the saturation point was reached after approximately 5 min. That is to say, it is very quick that the β-CDs grafted on the CNF-β-CD form inclusion complexes in aqueous media with Php. From Figure 4A and B, the β-CD molecules grafted on the CNF still have the ability to form a complexation with Php. Interestingly, CNF-β-CD shows the ability to quickly take up Php from the solution.

CNF-β-CD is stable in organic solvent, such as ethanol and acetone. The uptake of Php by CNF-β-CD was used to test the stability of the CNF-β-CD in ethanol and acetone. The same amount of CNF-β-CD was dispersed in ethanol, acetone, and deionized water for 60 min, respectively. After removal of the organic solvent, CNF-β-CD was used to take up the Php solution. These results show that CNF-β-CD dispersed in ethanol or

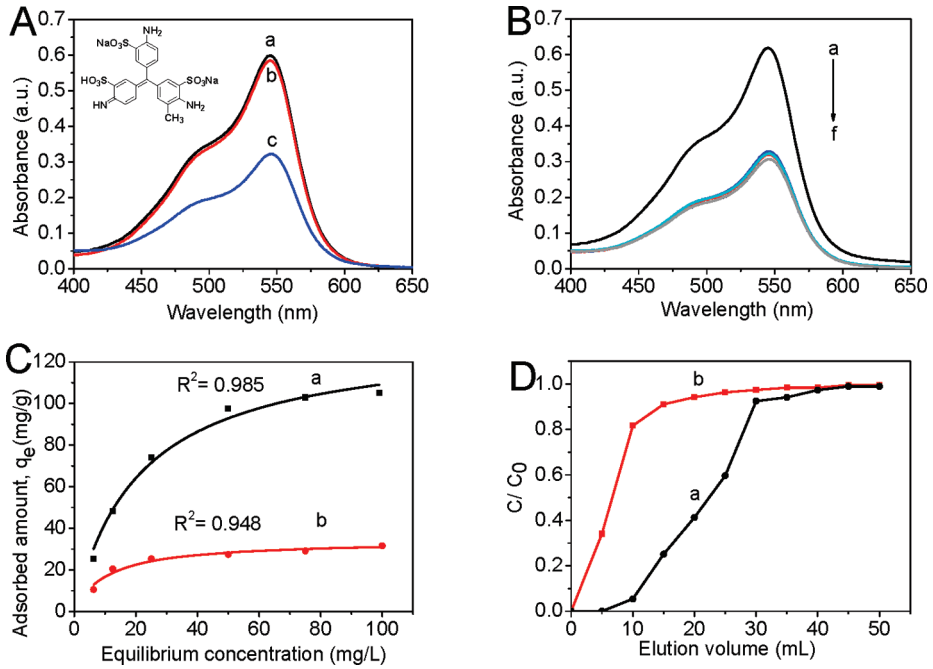

Figure 5. (A) UV−vis spectra of fuchsin acid solution (*c* = 40 mg/L) after 4 h: (a) fuchsin acid solution, (b) fuchsin acid solution treated with CNF, (c) fuchsin acid solution treated with CNF-β-CD, The inset is the structural formula of fuchsin acid. (B) UV−vis spectra of fuchsin acid solution: (a) fuchsin acid solution, (b−f) fuchsin acid solution treated with CNF-β-CD (at 2 min, 5 min, 15 min, 4 h, and 10 h). (C) Adsorption isotherms of fuchsin acid on CNF-β-CD (a) and commercial granular active carbon (b). (D) Breakthrough curve of fuchsin acid through the CNF-β-CD membrane (a) and CNF membrane (b).

acetone has the same ability to take up Php from the solution as CNF-β-CD dispersed in deionized water (Figure 4C). That is to say, beta-CD-modified CNF is stable in organic solvent, such as ethanol and acetone. The uptake of Php by CNF-β-CD was used to quantifiably test the repeated availability of CNF-β-CD. Ethanol was used to reuse the CNF-β-CD as shown in Figure 4D. The results indicate that CNF-β-CD was kept at about 92% availability after three recycles, showing the good reusability of the as-prepared CNF-β-CD.

Molecular filter performance of the CNF-β-CD membrane has been tested. A breakthrough curve of the Php through the CNF-β-CD membrane (one layer) was obtained. Figure 4E shows the breakthrough curves of the Php solution through the CNF membrane and the CNF-β-CD membrane. In the curve a, the outlet concentration (*C*) reached the feed concentration rapidly, indicating that the CNF membrane does not have the ability to capture Php, whereas in curve b, due to the capture of Php by the membrane, the outlet concentration increased slowly and reached the feed concentration when the elution volume became 44 mL (Figure 4E). The reusability of the CNF-β-CD membrane was also evaluated. Ethanol was used to pass through and recycle the membrane. Figure 4F shows the breakthrough curve of the Php through the CNF-β-CD membrane (one layer) after two and three recycles. It has been found that the decline in efficiency was not very obvious after reusing many times. In this system, the flow rate is 18 mL/h, and the effective area of the membrane is 4.1 cm^2. Figure 4E and F show that Php molecules can be filtered very quickly and effectively by the CNF-β-CD membrane. The CNF-β-CD membrane has a highly porous, interconnected open pore structure and a large surface area (Figure 3C). The XPS spectra indicate that there is β-CD present on the surface of the CNF. Therefore, β-CD on the membrane can quickly and effectively form inclusion complexes in aqueous media with Php.

Php is a model organic molecule and can form inclusion complexes with β-CD. The most significant characteristic of β-CD is its ability to form inclusion complexes in aqueous media with a wide variety of organic substrates, including many organic pollutants. Therefore, the membrane has potential applications for filtration of many organic pollutants. In addition, β-CD has the ability to form inclusion complexes with drugs and many other molecules, and CNF-β-CD is stable in organic solvent, such as ethanol and acetone. The membrane will also be very important in other fields such as chiral separation and drug delivery.

Fuchsin acid is a well-known, typical dye pollutant. The structural formula is shown in Figure 5A. Uptake of fuchsin acid was measured by immersing the CNF-β-CD membrane into fuchsin acid solution and the change in absorbance of fuchsin acid was recorded. Figure 5A shows the UV−vis spectra of fuchsin acid solution treated with CNF and CNF-β-CD membranes for 4 h, respectively. Curve a in Figure 5A shows the result of the control group. The results show that CNF-β-CD has the ability to complex with fuchsin acid molecules

(Figure 5A); however, bare CNF has no such ability. Figure 5B shows the change in absorbance of fuchsin acid as a function of time. Commercial granular active carbon (GAC) was tested for comparison. The results show that fuchsin acid molecules were quickly removed by CNF-β-CD and GAC exhibited adsorption kinetics much slower than CNF-β-CD. This indicated that the complexation of CNF-β-CD with fuchsin acid was mainly very fast, which is important for molecular filtration applications of the assembled CNF-β-CD membrane. Figure 5C shows adsorption isotherms of the fuchsin acid on CNF-β-CD and GAC.

The adsorption behavior was described by Langmuir isotherms,[38] expressed by the Langmuir function $q_e = q_m bC_e/(1 + bC_e)$, where q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m (mg/g) refers to the maximum adsorption capacity corresponding to complete monolayer coverage, C_e (mg/L) is the equilibrium solute concentration, and b (L/mg) is the equilibrium constant. From Figure 5C, the experimental data fit the Langmuir adsorption isotherm well. According to the Langmuir model, the estimated maximum uptake of fuchsin acid on CNF-β-CD and GAC was 132.43 and 34.20 mg/g, respectively. Compared with commercial GAC, CNF-β-CD exhibited extraordinarily high adsorption capacity for fuchsin acid. The estimated maximum uptake of fuchsin acid on CNF-β-CD was also much higher than that reported in the literature.[32]

The capability of the CNF-β-CD membrane to remove fuchsin acid from solution has been examined. The free-standing CNF membrane was also studied for comparison. The breakthrough curve of fuchsin acid through the CNF-β-CD membrane (one layer) is shown in Figure 5D. Curve b in Figure 5D indicates that the CNF membrane does not have the ability to capture Php. Curve a in Figure 5D shows that when the elution volume became 40 mL, complete adsorption of fuchsin acid in the early filtration stage occurred. The feed concentration was 10 mg/L, the flow rate was 50 mL/h, and membrane flux was 125 L/(m^2 h). The results indicate that the CNF-β-CD membrane has the ability to effectively remove fuchsin acid from a polluted solution.

Although some functionalized nanomaterials by β-CD have been prepared to remove pollutants, extra consumption of energy and time was needed for separation and recovery of adsorbents after the process by high-speed centrifugation because of the small sizes of these nanomaterials. Recently, there have been some reports on nanomaterials functionalized by β-CD and magnetic nanoparticles to remove pollutants. However, in those studies, a magnetic separation process was needed to separate the pollutants from the solution because of their small sizes.[12,39] For effective removal of pollutants, developing more effective, lower-cost methods to obtain clean water is of great importance. Membrane adsorption processes are probably the most attractive methods in wastewater decontamination.[1,40] Therefore, the as-prepared CNF membrane functionalized by β-CD provides a new candidate for removal of organic pollutants from water.

CONCLUSION

In summary, a new kind of CNF membrane functionalized by β-CD has been fabricated by using a simple surface modification procedure and a film casting technique, which shows remarkable capability to effectively filter Php from a solution. Compared with commercial granular active carbon, CNF-β-CD exhibited a high adsorption capacity for fuchsin acid, indicating that such a membrane can also be used for fast removal of fuchsin acid from solution. Further engineering of the surface of the CNFs will allow it to be used for other potential applications in chiral separation, drug delivery, and so on.

METHODS

All reagents are of analytical grade and used without further purification.

Synthesis of CNFs. CNFs were synthesized according to the method reported.[23,24] Briefly, 30 mL of acetone was added into 10 mL of the prepared dispersion of Te nanowires to precipitate the product before centrifuging at 6000 rpm, which was then dispersed into 80 mL of glucose solution (5 g glucose) with vigorous magnetic stirring for 15 min. Hydrothermal treatment of the mixed solution at 160 °C for different times could result in Te@C nanocables in a Teflon lined autoclave with a volume of 100 mL. After removal of the Te cores by chemical etching, pure CNFs can be obtained.

Synthesis of CNF-β-CD. In a typical process, a preweighed CNF was dispersed in 50 mL of distilled water, and a 10 wt% NaOH solution was added to adjust the pH (9−11). Then, 5.0 mL of epichlorohydrin was added. The mixture was stirred magnetically at 60 °C for 6 h. The solid product was separated by centrifugation and washed with distilled water several times. Then, 30 mL of distilled water was added to the product to disperse the CNFs. A 0.7 g amount of β-CD was added to the CNFs, the mixture was stirred magnetically, and a 10 wt% NaOH solution was added to adjust the pH (9−11). The mixture was stirred magnetically at 60 °C for 6 h. The solid product was separated by centrifugation and washed with distilled water several times, and the CNF-β-CD was obtained.

Fabrication of the CNF-β-CD Membrane. The free-standing CNF-β-CD membrane was fabricated according to the method reported.[26] A certain volume of the CNF-β-CD or CNF aqueous dispersion was filtered, and suction filtration was performed at decreasing pressure and usually completed within 5 min. Then, the free-standing CNF-β-CD or CNF membrane can be prepared.

Characterization. SEM was carried out with a field emission scanning electron microanalyzer (JEOL-6700F). UV−vis spectra were recorded on a UV-2501PC/2550 at room temperature (Shimadzu Corporation, Japan). The FTIR spectra were characterized on a Bruker Vector-22 FT-IR spectrometer from 4000 to 500 cm^{-1} at room temperature. X-ray photoelectron spectra were obtained on an X-ray photoelectron spectrometer (ESCALab

MKII), using Mg KR radiation (1253.6 eV) as the exciting source. The BET surface area was obtained from N_2 adsorption−desorption isotherms measured using a surface area and porosity measurement system (TriStar II 3020 V1.03, Micromeritics Instrument Corporation).

Batch Uptake Experiments. A 12.0 mg/L Php solution was prepared in absolute ethanol and distilled water, and the pH of the solution was adjusted to pH 10.5. For the uptake of Php by CNF-β-CD, about 10 mg of CNF-β-CD was placed in the Php solution in the flask. Then, the CNF-β-CD was removed and the absorbance spectra of the Php solution were recorded. A 10 mg sample of CNF was also placed in the Php solution for testing. The concentration of Php was determined using a UV-2501PC/2550 at room temperature. It was observed that the pH of the solution was unchanged at the end of the experiments.

Molecular Filtration Performance of the CNF-β-CD Membrane. The filtration experiments were conducted with a dead-end stirred cell (model 8010, Millpore Co., USA). The volume capacity was 10 mL, and the effective area of the membrane was 4.1 cm^2. A piece of the film was cut into a round shape with a diameter of 25 mm and then placed in the cell. A 8.0 mg/L Php solution was forced to filtrate through the film (35 mg of CNF-β-CD) at a flow speed of 18 mL/h. The concentration of the outlet Php solution was tested by optical absorption at 551 nm. The concentration of the outlet Php solution was plotted against the elution volume to obtain the breakthrough curve. A 35 mg amount of CNF membrane was used as the control group, and the breakthrough curve test was also performed. For the reuse, 50 mL of ethanol was used to pass through and recycle the membrane.

Removal of Fuchsin Acid from Solution. A fuchsin acid solution was prepared in distilled water. For the batch uptake of fuchsin acid by CNF-β-CD, about 10 mg of CNF-β-CD was placed in the fuchsin acid solution (40 mg/L) in a flask. Then, the CNF-β-CD was removed and the absorbance spectra of the fuchsin acid solution were recorded. The concentration of fuchsin acid was determined using a UV-2501PC/2550 at room temperature.

To obtain the isotherms, adsorption tests were conducted on each substance with a series of initial concentrations. CNF-β-CD samples were agitated for a contact time of 4 h at room temperature, while GAC was agitated for a contact time of 12 h for equilibrium adsorption. For the removal of fuchsin acid by the membrane, a 10.0 mg/L fuchsin acid solution was forced to filtrate through the film (35 mg of CNF-β-CD) at a flow speed of 50 mL/h. The filtration experiments were conducted with a dead-end cell. The concentration of the fuchsin acid solution was tested by optical absorption at 544 nm. The concentration of the outlet acid fuchsin solution was plotted against the elution volume to obtain the breakthrough curve. A breakthrough curve test was also performed for the control group (35 mg of CNF).

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