

# Synthesis of Cyclodextrin-functionalized Cellulose Nanofibril Aerogel as a Highly Effective Adsorbent for Phenol Pollutant Removal

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Cellulose nanofibril (CNF) aerogels with grafted beta-cyclodextrin ( $\beta$ -CD) were prepared for the adsorption of phenol pollutants from water. Compared with regular wood fibers, CNF aerogel not only can immobilize more  $\beta$ -CDs, but also it provides higher porosity and a larger specific surface area for phenol absorption. The CNF-CD aerogel becomes mechanically robust through chemical crosslinking. It can be easily separated from water after adsorbing phenol pollutants without complicated centrifugation or filtration. A series of studies on phenol adsorption was conducted. The results indicated that the CNF-CD aerogel prepared with a suspension concentration of 3% (w/w) had the highest adsorption capability. In addition, the CNF-CD aerogel showed an excellent reusability. The results indicated that the CNF-CD aerogel is an environmentally friendly and promising adsorbent for removing phenol pollutants from water.

*Keywords:* Adsorption; Aerogel; Nanofibrillar cellulose; Beta-cyclodextrin; Phenol pollutants; Water treatment

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## INTRODUCTION

Water contamination by phenol pollutants generated in the production of plastics, medicines, pesticides, and the petrochemical industry has attracted considerable attention in recent years (Nadavala *et al.* 2014). Phenol pollutants have raised serious concerns about the aquatic ecosystem and human health because of the long-term accumulation of their single and combined toxicological effects. Numerous technologies, such as biodegradation, fluid extraction, photo-catalysis, and adsorption, have been developed to remove phenol pollution from water (Crini 2006; Chong *et al.* 2010; Sajab *et al.* 2014). Adsorption is one of the most efficient and popular methods for the removal of phenol compounds from waste water because of its efficiency and economy (Liu *et al.* 2013). Activated carbon is a widely used adsorbent for removing organic pollutants from water, but it is difficult to regenerate (Maugans and Akgerman 2003). Many new inorganic materials have been studied for the removal of phenols from contaminated water, such as carbon nanotubes, silica, and ceramic membranes (Phan *et al.* 2002; Allabashi *et al.* 2007; Salipira *et al.* 2008). However, because of their high price and the difficulties of their chemical modification, they are unsuitable for practical use on a large scale.

Cellulose is the most abundant biopolymer on earth. The hydroxyl groups on cellulose can be easily converted into different functionalities, making it a promising

candidate for biosorbent materials. However, the adsorption capacity of natural cellulose fibers is usually low without surface functionalization. Furthermore, the regular wood fibers have a low specific area. Therefore, using nano-sized cellulosic materials with effective functional groups could significantly improve adsorption performance. The  $\beta$ -CDs are truncated cone-structure molecules derived from starch, which have great complexation ability with organic guests, especially aromatic molecules. Furthermore,  $\beta$ -CDs have a lower price than  $\alpha$ -CDs and  $\gamma$ -CDs (Landy *et al.* 2012). To improve the adsorption ability of cellulose,  $\beta$ -cyclodextrin has been grafted onto its surface (Xia and Wan 2008; Zhao *et al.* 2010). The similar structures of cellulose and CD, which are both derived from polysaccharides, preserves the biocompatibility and biodegradability of these promising materials. Although there have been several reports on the synthesis of cellulose grafting  $\beta$ -CDs, a low grafting efficiency hinders their adsorption performance. Nano-sized cellulose has been widely used in research because of its large specific surface area and unique physical properties. The amount of  $\beta$ -CDs immobilized on cellulose nanocrystal (CNC) can reach up to 18% (w/w) (Lin and Dufresne 2013; Chen *et al.* 2014), but its small particle size and high dispersion properties in water make it difficult to separate from the pollutant solution. Furthermore, the gelation behavior of CNC at a concentration higher than 2% (w/w) limits its application as an adsorbent material. CNF with large amount of micro- and macro-sized pores can be isolated from the wood fibers by a simple mechanical shearing process, which exhibits low density (approximately 1.6 g/cm<sup>3</sup>), high specific strength and modulus, high surface area, and reactive surfaces containing -OH side groups (Qing *et al.* 2015). The phenol adsorption rate and capacity by conventional CD-based organic polymers including cellulose, chitosan, and starch particles are very low because powdery adsorbents usually have a small specific surface area and an absence of framework porosity (Crini and Peindy 2006; Li *et al.* 2009a; Bonenfant *et al.* 2010). CNF aerogels-sponge-like materials have attracted a great deal of interest because of their extremely low density and high specific surface area. CNF aerogels are porous structured materials with a large amount of micro- and macro-sized pores. These unique properties of CNF aerogels make them useful in water uptake and organic dye absorption (Jiang and Hsieh 2014). Interactions between chitosan-CD adsorbents and phenols through hydrogen bonding or Van der Waals forces have been proposed. Because of the high specific surface area and porous structure, it is expected that  $\beta$ -CDs-modified CNF aerogels could have great adsorption capacity and a fast adsorption rate. The aerogel adsorbent can become very robust after crosslinkage by a polyamide-epichlorohydrin resin, even in a harsh stirring environment (Cai *et al.* 2014), which makes it possible to reuse the material. The coupling between CDs and organic mesoporous silica has been investigated for the removal of organic pollutants, and, with open-framework structure and a high specific surface area, it allows for rapid and efficient adsorption (Bibby and Mercier 2003). However, the porous and high specific surface area of CD-natural-organic adsorbents such as CNF-CD aerogels has not been reported until now.

In the present study, CNF graft  $\beta$ -cyclodextrin was first synthesized using epichlorohydrin (EPI) as a coupling agent. Because of the high specific surface area of the CNF, more CDs can be immobilized on the surface of the CNF compared with regular wood fibers under the same reaction conditions. To stabilize the 3D structure of CNF-CD aerogel during waste water treatment, the aerogel was crosslinked with polyamide-epichlorohydrin resin in this study. The porous structure and specific surface area of CNF-CD aerogel adsorbent could be easily tuned by varying the concentration

of NCF-CD suspensions (Jin *et al.* 2004). The variously structured CNF-CD materials, including cast membranes from CNF-CD suspension and freeze-dried CNF-CD aerogels prepared with various concentrations (1%, 2%, and 3% w/w) of CNF suspensions, were prepared, and their adsorption properties were investigated. *p*-chlorophenol (C<sub>6</sub>H<sub>4</sub>OH, PCP) was selected as the model pollutant because PCP molecules can be adsorbed by hydrogen bonding and cavity interaction (Li *et al.* 2009b). Batch adsorption experiments were carried out to study the adsorption ability of PCP. The  $\beta$ -CD based CNF aerogel adsorbent showed fast and high adsorption capabilities for phenols. In addition, because CNF-CD aerogels can be easily separated from the pollutant water, they can be washed and reused without using centrifugation or filtration. Because of the unique properties of CNF aerogels, such as renewability, biodegradability, and low cost,  $\beta$ -CD modified CNF aerogels are attractive adsorbents.

## EXPERIMENTAL

### Preparation of Native CNF and Cellulose Fibers

Commercial bleached softwood kraft pulp was used as the starting material for preparing CNF and original cellulose fibers. The dry cellulose pulp board was soaked in deionized water for 24 h and then dispersed using a mechanical blender for 30 min to obtain a consistent fiber suspension. The native cellulose fiber was obtained. After that, the cellulose fiber suspension was subjected to the mechanical defibrillation process using a high-speed shear homogenizer (T18 basic, Ultra Turrax, IKA Works Inc., USA) at 20,000 rpm for 3 h to obtain the CNF.

### Preparation of CNF and Normal Cellulose Graft $\beta$ -Cyclodextrin

The  $\beta$ -CD was grafted onto the surface of CNF and native cellulose fiber using epichlorohydrin (EPI) under alkaline conditions. First, 25 mL of 4% (w/w) CNF or regular wood fiber suspensions were put into five conical flasks. Then 4.6 g NaOH was dissolved into each gel with frequent shaking by the shaker. Afterward, 3, 5, 8, 11, 13, 16, and 19 g of  $\beta$ -CD, respectively, were added to the flasks to form a homogeneous suspension, and were continuously shaken for 2 h. Two hours later, the desired amount of EPI was added into the reaction medium, and the reaction was allowed to proceed at 45 °C for 6 h. The EPI/CD molar ratio was controlled at nine for each sample (Zhao *et al.* 2010). After the reaction, the suspension was washed with acetone and distilled water through centrifugation until the suspension become neutral. The obtained  $\beta$ -CD-CNF and  $\beta$ -CD-celluloses were used to make the aerogels.

### Preparation of CNF-CD Aerogels and Membrane

Various concentrations (1%, 2%, and 3% w/w) of the grafted CNF were transferred to 50-mL plastic centrifuge tubes; then a set amount of the cross-linker Kymene™ (Polyamide-epichlorohydrin resin, Ashland Hercules Inc., USA) was added to the suspensions under mechanical stirring, and finally the mixture was treated with an ultrasonicator for 1 min to obtain the gels. The gels were rapidly frozen by merging into liquid nitrogen for 20 s. Then, the frozen samples were freeze-dried in a freeze dryer (VirTis Freezemobile 25EL Sentry 2.0, USA) at a condenser temperature of -84.5 °C. The samples were kept frozen during drying under a vacuum of 80 mTorr for four days. The membrane was prepared by casting 3% (w/w)  $\beta$ -CD-CNF gel on the plate and dried

at room temperature for three days. The cross-linking of aerogel and membrane was achieved by curing the dried samples containing the cross-linker in a vacuum oven at 120 °C for 3 h (Zhang *et al.* 2012).

## Characterizations

### *β-CD grafting efficiency measurement*

The content of β-CD in CD-grafted CNF and regular wood fibers was analyzed using the UV spectrophotometric method (Lin *et al.* 2013). First, 0.5, 1, 1.5, 2, and 2.5 mL of β-CD solution were added to 25-mL flasks, respectively; afterward, 10 mL of distilled water and 2 mL of phenolphthalein solution were added to each flask, which was shaken for 30 s. Then, 2 mL of sodium carbonate solution was added. The absorbencies of all those solutions were acquired at the characteristic wavelength of 552 nm (Hitachi Model U-3010, USA). The standard curve between the weight of β-CD and the absorbency of phenolphthalein was then obtained. A weighed amount of CD-cellulose was added to the phenolphthalein solution and stabilized for 20 h. The absorbency of phenolphthalein was measured at a wavelength of 552 nm. The grafting efficiency was determined by the weight of CD-cellulose and its absorbency according to the standard curve.

### *Fourier transform infrared spectroscopy (FTIR)*

The dried, powdery samples were prepared for FTIR measurement. Dried powder samples were obtained by grinding the freeze-dried CNF-CD in a grinding bowl. The spectra were recorded using Nicolet Magna-IR 550 equipment (Thermo Fisher Scientific Inc., USA) with a detector at 4 cm<sup>-1</sup> resolution from 600 to 4000 cm<sup>-1</sup> and 32 scans per sample.

### *Thermogravimetric analysis*

The thermal properties of the CNF-CD, CNF, and β-CD were tested on a Perkin Elmer STA 6000 thermal analyzer (PerkinElmer Inc., USA). Approximately 10 mg of powder sample was used for each test. The experiment was performed at a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen flow of 20 mL·min<sup>-1</sup>. The temperature range for TGA analysis was 30 to 600 °C.

### *Scanning electron microscope analysis*

Scanning electron microscopy (Zeiss LEO 1530 microscope, Zeiss/LEO Inc., USA) was used for the morphology characterization. The samples were attached to holders with conductive double-side carbon tape and sputter-coated with gold to avoid charging during the tests.

### *Bulk density*

The bulk density of the aerogel was determined by dividing the weight of the sample by the volume of the plastic centrifuge tube. The density of the membrane was determined by its weight and volume. The volume was calculated from the thickness of the membrane and its area.

### *Water uptake capacity*

The CNF-CD aerogel, cast CNF-CD membrane, and CNF-CD fibers were dried at 105 °C for several days until a constant weight was achieved. Approximately 1 g of dried

sample was weighed and then soaked in water. The wetted samples were wiped with a blotting paper and immediately weighed so that their water uptake capacity could be determined by their weight change (Cai *et al.* 2014).

#### *Adsorption and regeneration properties*

The CD-containing CNF aerogels/membranes/fibers formed as previously described were used to remove PCP pollutants in water. CNF-CD aerogels (1%, 2%, and 3% (w/w)) as well as CNF-CD regular fiber powder and CNF-CD membranes were cut into small pieces for adsorption experiments. PCP aqueous solutions with varying concentrations were prepared using purified water from a Millipore<sup>TM</sup> purification unit (EMD Millipore Corporation, USA).

Adsorption isotherms were measured as follows: for each CNF-CD aerogel, cast membrane, and  $\beta$ -CD-modified regular wood fiber sample, solutions containing 5, 10, 15, 20, 25, 30, 35, and 40 mg/L of *p*-chlorophenol (PCP) were used. The suspension was then filtered, and the residual solute concentration in the filtrate was measured using UV-Vis spectroscopy (Hitachi Model U-3010). The characteristic absorbed wavelength of PCP was 281 nm. The amount of PCP solute adsorbed by the CNF-CD was then determined by subtracting the concentration in the supernatant from that of the initial solution.

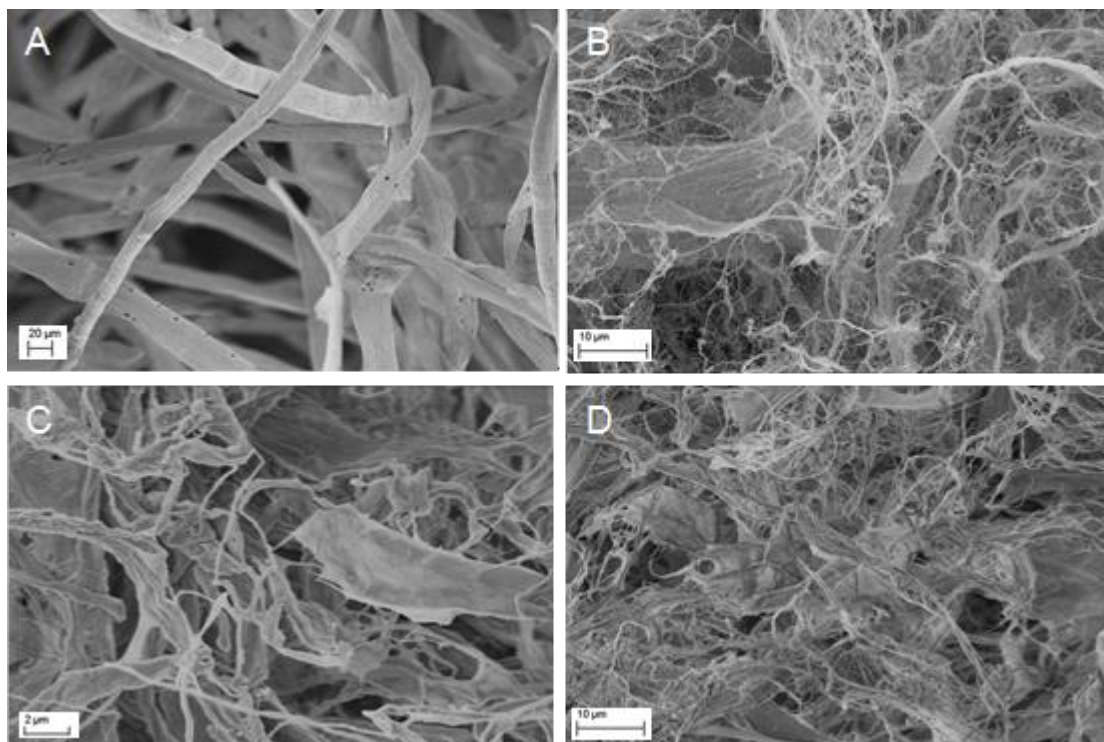
Adsorption kinetics was measured as follows: 3% (w/w) CNF-CD aerogel, coated CNF-CD membranes, and CD-modified regular wood fibers were used for adsorption kinetics measurements. Approximately 30 mg of each adsorbent was mixed and stirred into 40 mg/L PCP solutions at various temperatures. The adsorption values were measured by UV-vis spectroscopy at set times.

The effects of pH and temperature on adsorption were measured as follows: approximately 30 mg of 3% (w/w) CNF-CD aerogel was stirred into 50 mL of 40 mg/L PCP solution for 24 h. The pH adjustment was done using 0.01 M NaOH and HCl solutions. Temperature was controlled with a water bath. The regeneration of CNF-CD aerogel adsorbent was conducted using 1:1 ethanol water solution with agitation for 3 h. The reuse test was performed in 40 mg/L PCP solution.

## RESULTS AND DISCUSSION

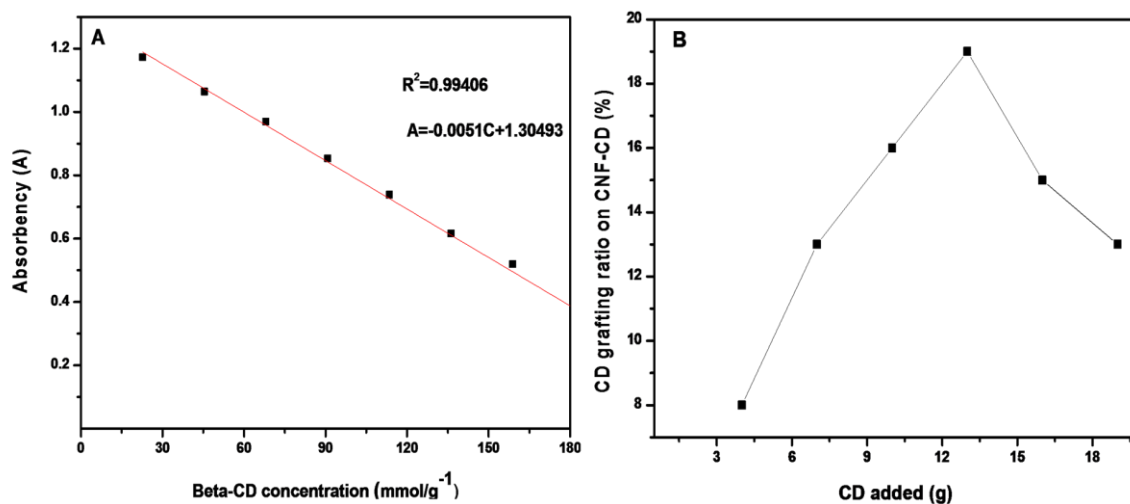
Softwood pulp fibers with diameters in the range of 20 to 50  $\mu\text{m}$ , as shown in Fig. 1(A), were used as the starting materials to produce CNF. During the high-speed shear homogenization process, CNFs were gradually isolated from the macroscopic pulp fibers because of the repeated shear forces. After 120 min, CNFs with diameters mostly ranging from 10 to 40 nm were finally obtained; however, some large-sized CMFs also were present. Figure 1 shows SEM images of the as-prepared CNF and CNF-CD aerogel at various magnifications.

CNF and regular wood fibers were grafted with  $\beta$ -CD using EPI as a coupling agent (Zhao *et al.* 2010). The grafting ratio was determined by the phenolphthalein-UV spectrophotometric method and weight measurement (Lin *et al.* 2013). Because the hydrophobic phenolphthalein molecule can be accommodated by the cavity of  $\beta$ -CD under alkaline conditions, a negative correlation between the concentration of  $\beta$ -CD and the absorbency of phenolphthalein can be obtained (Fig. 2(A)). The grafting efficiency was determined by the weight of CNF-CD and the absorbency according to the standard curve.



**Fig. 1.** SEM images of (A): regular wood fiber; (B): CNF; (C) and (D): CNF-CD aerogel at various magnifications

The amount of  $\beta$ -CD grafted on the regular wood fibers also can be calculated by the correlation equation. To measure the grafting efficiency using the gravimetric method, grafted CNF and regular fiber samples were weighed after washing and freeze-drying. The grafting efficiency of each sample measured by two different methods was repeated three times. The grafting ratios calculated by the two methods were similar. Because CNF has a large specific surface area, it can immobilize more CD (19.03%) than regular wood fiber (8.07%) under the same reaction conditions (1g CNF/regular wood fiber, 13 g (11.45 mmol) CD, 9.53 g (103.05 mmol) EPI).



**Fig. 2.** (A): Calibration curve of absorbency vs.  $\beta$ -CD concentration; (B):  $\beta$ -CD grafting efficiency on CNF with various amounts of CD and EPI (EPI /CD mole ratio controlled at nine)

The EPI/CD mole ratio was controlled at nine (below 10) to avoid the self-crosslinking of  $\beta$ -CD, as recommended by Zhao *et al.* (2010) and Lin and Dufresne (2013). Figure 2(B) shows the surface grafting analysis data. When the cellulose concentration remained constant, the grafting ratio increased up to a maximum value when the CD amount increased to 13 g (11.45 mmol), corresponding with 9.53 g (103.05 mmol) of EPI. However, when the amount of added CD increased to 16 g, the grafting ratio was reduced because, to a certain extent, increased viscosity inhibited the reaction.

The FTIR spectra of CNF,  $\beta$ -CD, and modified CNF are compared in Fig. 3. By magnifying the region of 650 to 1500  $\text{cm}^{-1}$ , it can be seen that after the grafting reaction, the peaks at 1163, 1113, and 1059  $\text{cm}^{-1}$  decreased compared with those of pure CNF. The decreased peaks indicated antisymmetric bridge oxygen stretching, antisymmetric in-phase ring stretching, and C-O stretching for cellulose. Moreover, the C-O stretching peak at 1031  $\text{cm}^{-1}$  became broad after the grafting reaction. These results are similar to other reports for CD-grafted cellulose (Zhao *et al.* 2010; Lin and Dufresne 2013).

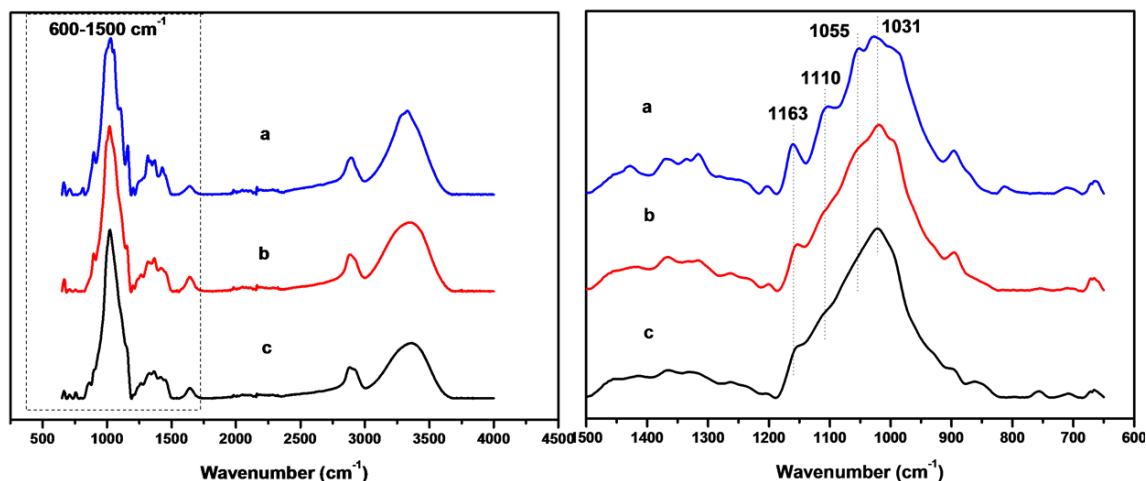


Fig. 3. FTIR spectra of (a) CNF; (b) regular wood fiber graft  $\beta$ -CD; and (c) CNF graft  $\beta$ -CD

The thermal stability of CNF-CD, CNF, and CD was studied using the DTG curves shown in Fig. 4.

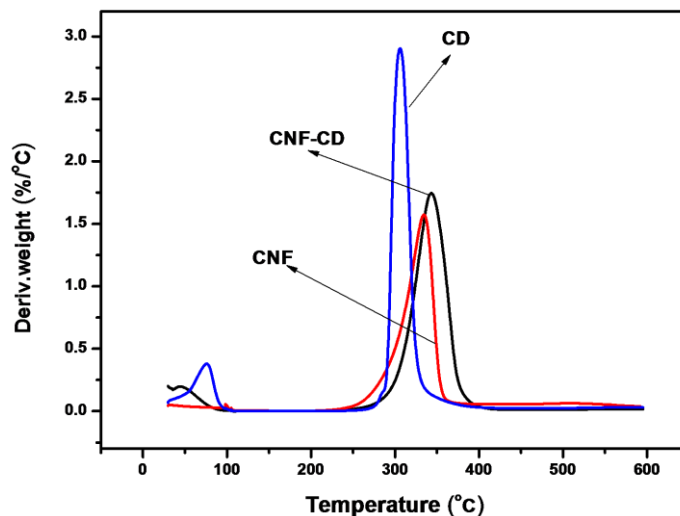


Fig. 4. DTG curves of CNF, CD, and CNF graft CD

The maximal weight loss rate shifted from 334.3 to 343.6 °C. A possible reason is that the crosslinking between cellulose-OH and CD-OH may cause increased compaction of the cellulose chains, resulting in an increase in the resistance for thermal treatment (Nada *et al.* 2008). However, once the ether bond cracked, the thermal degradation of CD molecules on the surface of CNF occurred, which resulted in a higher weight loss of CNF-CD than CNF at the maximal weight temperature.

Digital camera images of CNF graft  $\beta$ -CD membrane and aerogel can be seen in Fig. 6(D). The bulk density and water uptake capacity of those adsorbents are shown in Table 1. The bulk density of the aerogel was determined by dividing the weight of the sample by the volume of the plastic centrifuge tube. The volume of the prepared CNF aerogel remained the same as that of the centrifuge tube because the CNF-CD suspension was instantly frozen by liquid nitrogen. The bulk density of the CNF-CD aerogel increased almost linearly proportionally to the starting concentration of CNF-CD solution. This was in accordance with the previous observations by others. The water uptake capacity tests of the CNF-CD aerogels and the membrane indicated that aerogel adsorbent has superabsorbent properties compared with the membrane and showed that 1 g of CNF-CD aerogel could absorb more than 70 g of water; however, only 6 g of water could be absorbed by the CNF-CD membrane. The water uptake capacity of CNF-CD aerogel increased with increasing concentration of the CNF-CD suspension during the preparation process. This phenomenon was probably caused by the different pore structure of those aerogels. The water absorption ability was largely dependent on the storage of the nano- and microsized pores of the CNF-CD aerogels.

**Table 1.** Bulk Density and Water Uptake Capacity of Adsorbents

CNF-CD Adsorbents	Bulk Density (g/cm <sup>3</sup> )	Water Uptake Capacity (w/w)
1% (w/w) aerogel	0.03	58.53
2% (w/w) aerogel	0.02	65.83
3% (w/w) aerogel	0.01	75.54
membrane	0.77	6.02

The Langmuir adsorption isotherm was used to explain the different adsorption processes. The Langmuir equation and its rearranged form can be described as Eqs. 1 and 2 (Wu *et al.* 2008), where  $K_L$  is the Langmuir isotherm constant and  $q_m$  is the maximum adsorption capacity:

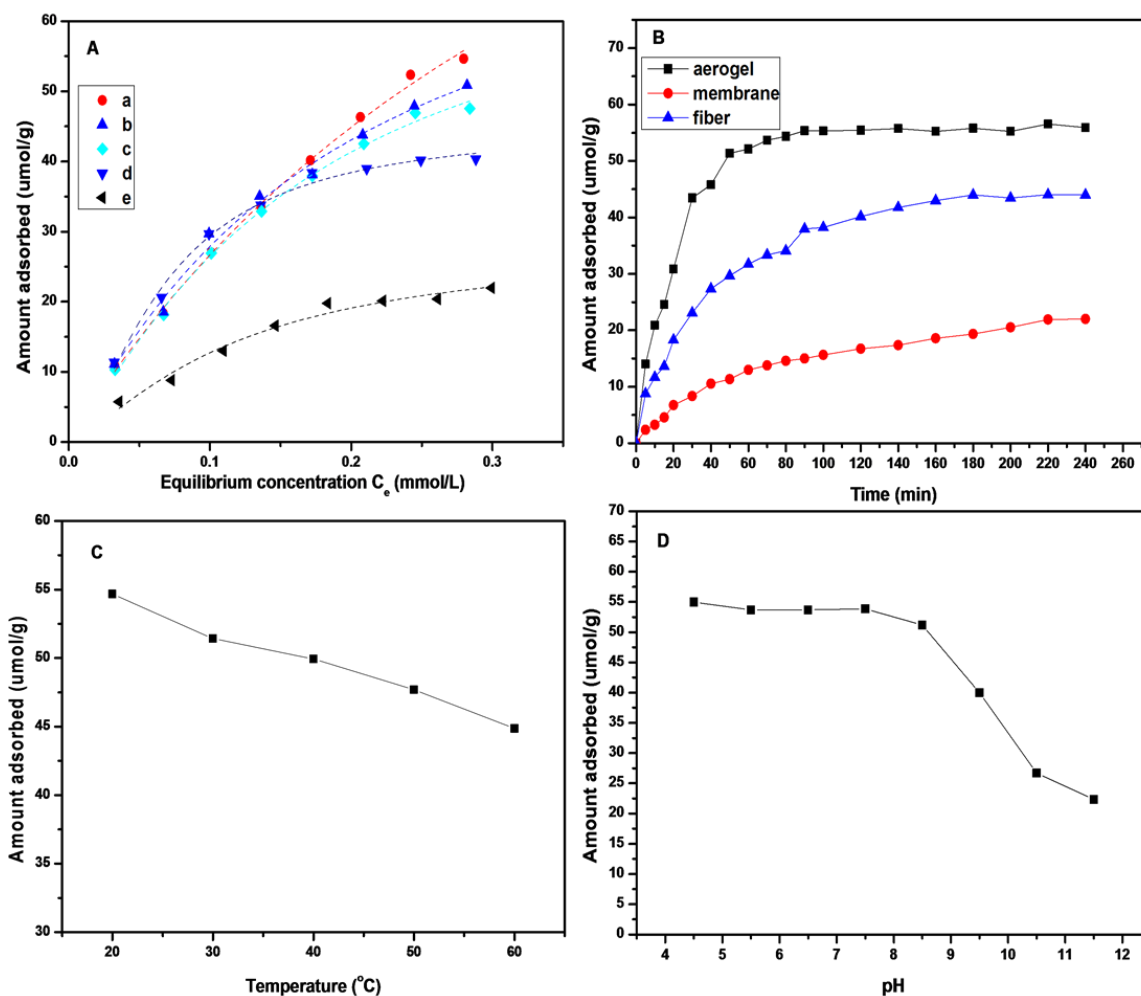
$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

The results in Fig. 5(A) indicate that the adsorption capacity increased with increasing equilibrium concentration of PCP solution for each sample. It has been reported that the diameter of the  $\beta$ -CD cavity is approximately 0.8 nm, which is suitable for containing phenols (Chen *et al.* 2007). A comparison between the adsorption isotherms shows a noticeable difference in performance among CNF-CD aerogels, the



CNF-CD membrane, and CD-modified CNF fibers, although they have a similar amount of CD groups grafted onto the CNF surface (168.28  $\mu\text{mol/g}$ ).



**Fig. 5.** (A) Adsorption isotherm of (a) 3% (w/w) CNF-CD aerogel; (b) 2% (w/w) CNF-CD aerogel; (c) 1% (w/w) CNF-CD aerogel; (d) CNF-CD powder; and (e) CNF-CD membrane at pH 7.0 and 20  $^{\circ}\text{C}$ . (B) Adsorption kinetics of PCP by 3% (w/w) CNF-CD aerogel; CNF-CD membrane and CNF-CD powder at pH 7 and 20  $^{\circ}\text{C}$ . (C) Effect of temperature on the adsorption of PCP onto 3% (w/w) CNF-CD aerogel at pH 7.0. (D) Effect of pH on the adsorption of PCP onto 3% (w/w) CNF-CD aerogel at 20  $^{\circ}\text{C}$

The Langmuir isotherm was successfully applied to those phenol adsorption tests ( $R^2 > 0.95$ ). The maximum adsorption capacity of CNF-CD aerogel ( $q_e$ ) obtained by extrapolating the curve to higher concentrations using Eq. 2 was 148  $\mu\text{mol/g}$ . However, the CNF-CD membrane and CD-modified CNF fibers could adsorb only 39  $\mu\text{mol/g}$  and 63  $\mu\text{mol/g}$ , respectively. These results clearly indicate that CNF-CD aerogel has a much higher adsorption capacity than the other samples because of its high specific surface area and abundant pores, which can be verified by the huge difference in water uptake capacities between the CNF-CD membrane and the aerogel. The compact structure of the CNF-CD membrane would hinder the interaction between the adsorbents and adsorbates. Many interactions between adsorbents and adsorbates have been proposed, including Van der Waals forces, hydrogen bonding, and hydrophobic interactions (Zhang *et al.* 2008).

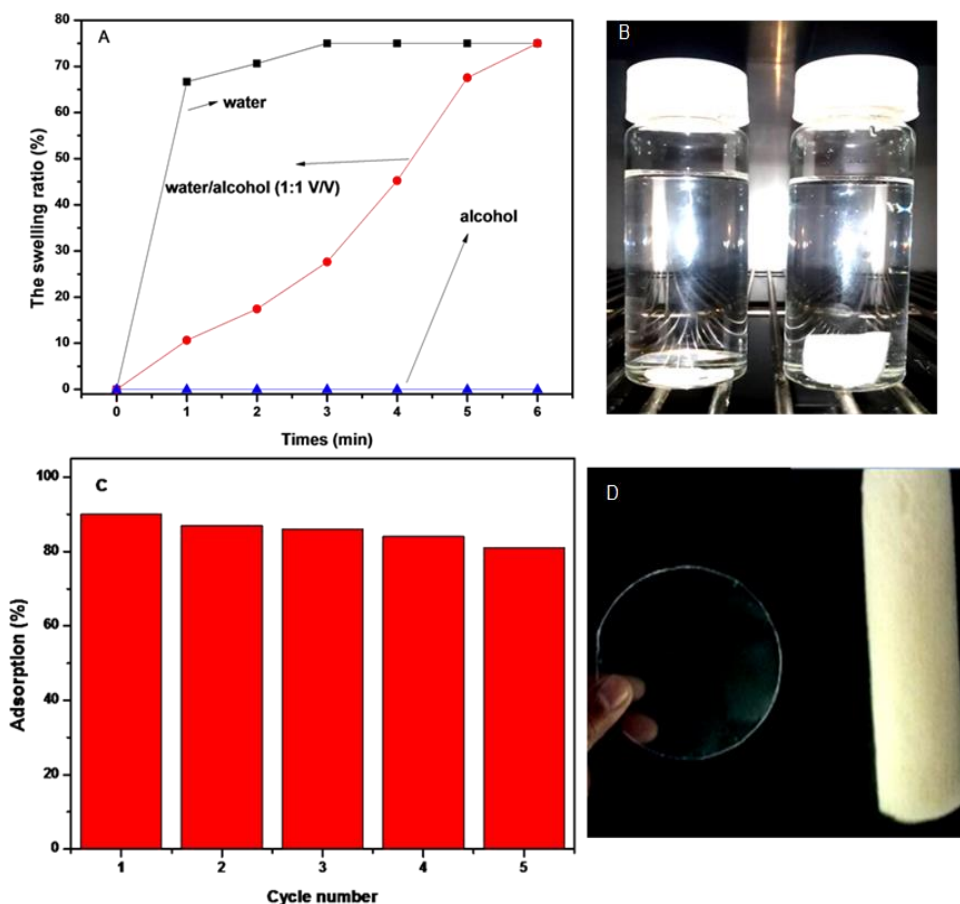
The adsorption mechanism of CNF-CD aerogel can be concluded to be as follows: First, the highly porous CNF-CD aerogel improves the phenol molecules' access to the cavity of  $\beta$ -CD grafted onto the surface of the NFC chains. Second, the hydrogen bonding taking place between the -OH groups of PCP molecules and the hydroxyl groups of CNF-CD aerogel is more effective because the specific surface area of the aerogel is much higher than that of the membrane and CD-modified CNF fibers. Finally, PCP molecules can be accommodated by the nanosized-pores of CNF-CD aerogel due to Van der Waals forces. The amount of pores and the surface area of the aerogel adsorbents were strongly dependent on the starting concentrations of CNF-CD during the aerogel preparation process (Jin *et al.* 2004). The amount of pores and specific surface area of the CNF-CD aerogels showed an almost linear growth with the starting concentration of CNF-CD. As a result, the PCP adsorption ability of the CNF-CD aerogels increased with increasing concentrations of the CNF-CD suspension during the preparation process. These results further confirmed that the highly porous and specific surface area structures of the aerogels are beneficial for the adsorption of phenol molecules.

For the kinetics experiment, 3% (w/w) CNF-CD aerogel, CNF-CD membrane, and CD-modified CNF fibers were mixed into 40 mg/L of the PCP aqueous solution, respectively. The results are shown in Fig. 5(B). It can be seen that both adsorbents showed increased adsorbed amount with time. The uptake speed of phenol molecules by 3% (w/w) CNF-CD aerogel (about 40 min) was the fastest to reach the maximum adsorption capacity, which was much higher than that of the CNF-CD membrane (more than 3 h) and CD-modified CNF fibers (about 2 h) under same adsorption experimental conditions. The fast adsorption performance exhibited by the CNF-CD aerogel can be attributed to the fast diffusion speed of PCP molecules in its open-framework structure. There are many pores inside the aerogel, varying from micrometers to nanometers, so PCP molecules could diffuse into the aerogel very quickly. However, the compact structure of the CNF-CD membrane makes it difficult for phenol molecules to access the cavity of the CD. The adsorption speed of CD-modified CNF fiber was faster than that of the CNF-CD membrane, but slower than that of the CNF-CD aerogel due to its low specific area and less porous structure.

The adsorption of phenol by 3% (w/w) CNF-CD aerogel is also dependent on temperature and pH, and the results are shown in Figs. 5(C) and (D). The adsorption capacity decreased almost linearly with the temperature increase from 20 to 40 °C, which is in agreement with the reported results (Álvarez *et al.* 2005). This confirmed that the interaction between the phenol molecules and the CNF-aerogel is an exothermal process. The phenol uptake efficiency can be strongly influenced by the pH of the solution. The adsorption capacity sharply decreased above a pH of 9. The reason is that when a solution is beyond  $pK_a$  under a high pH condition, phenolate anions become the majority, while they are neutral phenol molecules under  $pK_a$  (Rawajfih and Nsour 2006). The molecule form of PCP is more effectively absorbed by the CNF-CD aerogel.

The regeneration of saturated CNF-CD aerogel adsorbents was carried out in an ethanol-water solution. The robust, sponge-like aerogel adsorbent was suitable for isolation without filtration or centrifugation. The adsorbent could be well-kept during the regeneration and isolation processes. The squished and dewatered aerogel showed fast recovery ability and returned to its original shape and saturated swelling ability by putting it in water or 1:1 water-alcohol solution, as shown in Fig. 6(A). However, the swelling and shape recovering did not occur in alcohol. So it is reasonable to use 1:1 water-alcohol solution to remove the PCP from CNF-CD aerogel.

The aerogel was first squeezed onto the filter paper to remove free water, then it was placed in 1:1 water-alcohol solution. After 2 h of agitation, the regenerated aerogel was collected for an adsorption reuse test. As can be seen in Fig. 6(C), after five regeneration cycles, the CNF-CD adsorbent adsorbed 80% of the adsorbate compared with its first adsorption capacity, which suggests the high reusability of the CNF-CD aerogel as a pollution molecule removal adsorbent.



**Fig. 6.** (A) Swelling ratio of squished and dewatered CNF-CD aerogel absorbent in different solutions; (B) Shape recovery of squished and dewatered CNF-CD aerogel absorbent in alcohol (left) and 1:1 water/alcohol (right) for 1 h; (C) Adsorption efficiency as a function of the repeat cycle; (D) Digital camera pictures of the CNF graft  $\beta$ -CD membrane and aerogel

## CONCLUSIONS

1. In this work, CD functional CNF aerogels have been shown to be an effective new class of adsorbents for the removal of phenols such as PCP from water. The maximum adsorption capacity of CNF-CD aerogel was 148  $\mu\text{mol/g}$ . The large specific surface area and unique porous structure of the CNF-CD aerogel adsorbent allows for more interaction and bonding capability with PCP molecules compared with other adsorbents.

2. The open-frame structure also leads to the rapid adsorption process. The uptake of PCP molecules by the CNF-CD aerogel was shown to be very rapid, reaching the maximum adsorption capacity after about 40 minutes.
3. The mechanically robust aerogel-adsorbent could be easily separated from water after adsorption without centrifugation or filtration, showing promising potential for use under the harsh conditions of industrial waste water treatment applications.
4. Moreover, the natural, green adsorbent also exhibited excellent reusability, showing great potential for water treatments.

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