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Short communication

Aerogels from quaternary ammonium-functionalized cellulose nanofibers for rapid removal of Cr(VI) from water

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ABSTRACT

An efficient heavy metal adsorbent from quaternary ammonium-functionalized cellulose nanofiber aerogels was successfully developed. The highly porous aerogel could well retain its large specific surface area, which allowed rapid and effective removal of Cr(VI) from contaminated water. The aerogel adsorbent became mechanically robust after chemical crosslinking. It could be easily separated from water after adsorption without complicated centrifugation or filtration process. With only 1 g of aerogel, more than 99% of Cr(VI) in 1 L of 1 mg/L solution could be removed in 50 min. Besides, the aerogel also exhibited excellent reusability.

1. Introduction

Water contamination by heavy metals, such as mercury, cadmium and chromium, has attracted considerable attentions as it poses a serious threat to human health and the environment (Kampalanonwat & Supaphol, 2010; Li et al., 2013). Various techniques, including chemical precipitation, biological treatment, membrane technology, electrolytic reduction, ion exchange and adsorption, have been developed to tackle this problem (Kampalanonwat & Supaphol, 2010; O'Connell, Birkinshaw, & O'Dwyer, 2008). Among these treatments, adsorption is considered to be one of the most effective and economic methods. The fabrication of adsorbent materials with enhanced adsorption capacity and reduced operation costs is a continuing goal of environmental remediation efforts. Owing to the large specific surface area and excellent adsorption capacities, nanomaterials have been widely used for the removal of pollutants from water (Badruddoza, Shawon, Daniel, Hidajat, & Uddin, 2013; Bell et al., 2006). For example, carbon nanotubes (CNTs) have been confirmed to possess great potential for pollutant removal from water (Liu, Li, & Yan, 2008; Wang et al., 2012). However, due to the high price and the difficulties for chemical modifications, it is unlikely for their large scale applications.

Cellulose is the most abundant and renewable biopolymer on earth and its utilization for assorted applications has seen a renaissance in research development (He et al., 2014; Pan & Ragauskas, 2012; Pirani & Hashaikeh, 2013). Cellulose nanofibers (CNFs) have been electronspun from cellulose derivatives and then chemically modified by Stephen, Catherine, Brenda, Andrew, and Leslie (2011) for heavy metal adsorption. In fact, CNFs readily exist in the cell walls of plants with matrix substances such as hemicellulose and lignin. They can be isolated from plant fibers by simple mechanical shearing processes (Littunen, Hippi, Saarinen, & Seppälä, 2013; Zhao et al., 2013, 2014). Besides, CNFs can also be created by some kinds of bacterials (Klemm et al., 2009). Previously, bacterial CNFs have been modified for the adsorption of Cu^{2+} and Pb^{2+} (Chen et al., 2009). It is important to note that the conventional drying process used to obtain the powdery cellulose will decrease the specific surface area of nanocellulose and thus limit the access of heavy metal ions to the grafted functional groups. Moreover, a complex separation step is required to remove the nanocellulose from solutions after adsorption (also for other powdery nano-adsorbents like CNTs), which raises the costs for water treatments. If the nanomaterials can be connected with each other to form macroscopic three-dimensional (3D) materials while retaining their large specific surface area, they would become excellent adsorbents with less demand on the separation process.

In this communication, it was demonstrated for the first time that freeze-dried and quaternary ammonium-functionalized aerogels from softwood CNFs could become an outstanding adsorbent for heavy metal ions of Cr(VI). Quaternary ammonium groups

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have long been recognized to exhibit strong affinity to oxyanions through electrostatic interactions (Gurgel, Perin de Melo, de Lena, Gil, 2009) and various kinds of adsorbents bearing quaternary ammonium groups have been developed to tackle Cr(VI) pollutions (Barassi et al., 2009; Wang et al., 2010). In order to stabilize the 3D structure during water treatment, the aerogel was covalently crosslinked. The low density, high porosity properties of aerogel together with its large specific surface area enabled the fast and effective removal of Cr(VI) from water.

2. Methods

2.1. Preparation of native CNFs

Commercial bleached softwood kraft pulp was used as the starting material for preparing CNFs. The dry pulp board was soaked in deionized water for 1 day and then dispersed using a mechanical disintegrator for 10 min to get a consistent fiber suspension. After that, the obtained cellulose fiber suspension was diluted to 0.6 wt% concentration by adding deionized water and then subjected to the mechanical defibrillation process using a high shear homogenizer (T18 basic, Ultra Turrax, IKA Works Inc., USA) at 20,000 rpm for 2 h.

2.2. Preparation of quaternary ammonium-functionalized CNFs

Quaternary ammonium-functionalized CNFs were prepared through a chemical reaction between CNFs and 2,3-epoxypropyltrimethylammonium chloride (Sigma–Aldrich) under an alkali environment. Sodium hydroxide was added to the CNFs water suspension at a concentration of 1 wt%. After dissolution of sodium hydroxide, a certain amount of 2,3-epoxypropyltrimethylammonium chloride was added to the system, and the reaction was controlled at 85 °C for 6 h. The modified CNFs were centrifuged for 3 cycles to remove sodium hydroxide, and then neutralized by hydrochloride. The products were further purified by centrifugation for at least 5 cycles. Weighted amount (2.5% of the solid weight of modified CNFs) of crosslinker Kymene™ (polyamide-epichlorohydrin resin, Ashland Hercules Inc., USA) was added to the suspension under mechanical stirring and finally treated in an ultrasonic bath for 10 min to obtain a gel-like suspension with a CNFs content at around 1 wt%.

2.3. Preparation of quaternary ammonium-functionalized CNFs aerogels

Plastic centrifuge tubes (50 mL) were used as the mold to produce aerogels. After transferred into the mold, the modified CNFs aqueous gels with crsosslinker were frozen at −20 °C in a low temperature refrigerator. The frozen samples were freeze-dried in a lyophilizer (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. Sponge-like samples were obtained after drying. The crosslinking of aerogels was realized by curing the freeze-dried samples containing the crosslinker in a vacuum oven at 120 °C for 3 h.

2.4. Analytical methods

2.4.1. Field-emission scanning electron microscopy

The surface morphology of samples was examined on a LEO 1530 scanning electron microscopy at an acceleration voltage of 10 kV. Samples were coated with Au prior to SEM observation.

2.4.2. Elemental analysis

The nitrogen content of the modified CNFs was analyzed on an Euro EA3000 analyzer (Euro EA3000, Euro Vector, Milano, Italy).

2.4.3. Titration for surface charge density

The surface charge density was measured by a PCD-Titrator. 0.001 N poly (N,N-diallyldimethylammonium chloride) (DADMAC) and 0.001 N potassium poly(vinyl sulfate) (PVSK) from Nalco company were used as the standard solutions. Back titration method was used, i.e., polyelectrolyte (either poly DADMAC or PVSK) with opposite charge of CNFs was first added into the suspension and fully stirred, and then the other polyelectrolyte was added to neutralize CNFs suspension. The concentration and volume of the CNF suspension, poly DADMAC, PVSK were recorded.

2.4.4. Batch adsorption studies

pH adjustment was done using 0.01 M NaOH and HCl solutions (both from Aldrich). The stock solution of Cr(VI) (100 mg/L) was prepared by dissolving a certain amount of AR grade $K_2Cr_2O_7$ (from Merck) in 1000 mL purified water from Millipore™ purification unit. A series of standard metal solutions were prepared by diluting the stock metal solution. A typical adsorption experiment was conducted as follows: 25 mg aerogel was added to 50 mL Erlenmeyer flask containing 25 mL 1 mg/L Cr(VI) solution and magnetically stirred at 120 rpm. At each pre-determined time interval, 1 mL of the solution was suctioned off by a syringe with a 0.22-μm syringe-end filter. The concentrations of Cr(VI) during adsorption tests were analyzed by spectrophotometry (Agilent 8453 UV–vis dissolution testing system, Aglient, USA) at the wavelength of 540 nm, using diphenylcarbazide as the chromogenic reagent (Wei, Li, Huang, Huang, & Wang, 2013).

2.4.5. Desorption of aerogel

The regeneration of aerogel was conducted using 0.1 M NaOH solution as the desorbing agent. The desorption lasted for 4 h under constant magnetic stirring (120 rpm), followed by repeatedly rinsing with deionized water to neutral pH.

3. Results and discussion

3.1. Modification of CNFs and construction of CNFs aerogels

Softwood pulp fibers with diameters in the range of 20–50 μm (Fig. S1a) were used as the starting material to produce CNFs. During the high shear homogenization process, CNFs could be gradually isolated from the pulp fibers due to the repeated shear forces. After 120 min processing, CNFs with diameters mostly ranging from 10 nm to 40 nm were obtained (Fig. S1b). CNFs were then chemically modified to graft quaternary ammonium functionalities on the surface. Because CNFs were insoluble in this modification solution (1% NaOH solution), only the surface molecules on CNFs would be reacted. Therefore, the morphology of CNFs would not be affected, as shown in Fig. S1c. The FTIR spectra of CNFs and modified CNFs were compared in Fig. S2. Both samples exhibited almost the same adsorption profiles, suggesting the mild chemical modification did not change the bulk chemical structure of CNFs. However, for the modified CNFs, a new weak peak at 1403 cm^{-1} appeared, which was assigned to the N—H stretching vibration absorption (Yan, Tao, & Bangal, 2009). In addition, C—O stretching vibration absorption at 1360 cm^{-1} noticeably enhanced after reaction, indicating ether bonds formed between CNFs and 2,3-epoxypropyltrimethylammonium chloride (Yu, Huang, Ying, & Xiao, 2007). Elemental analysis revealed a nitrogen content of 1.61% was achieved for the chemically modified

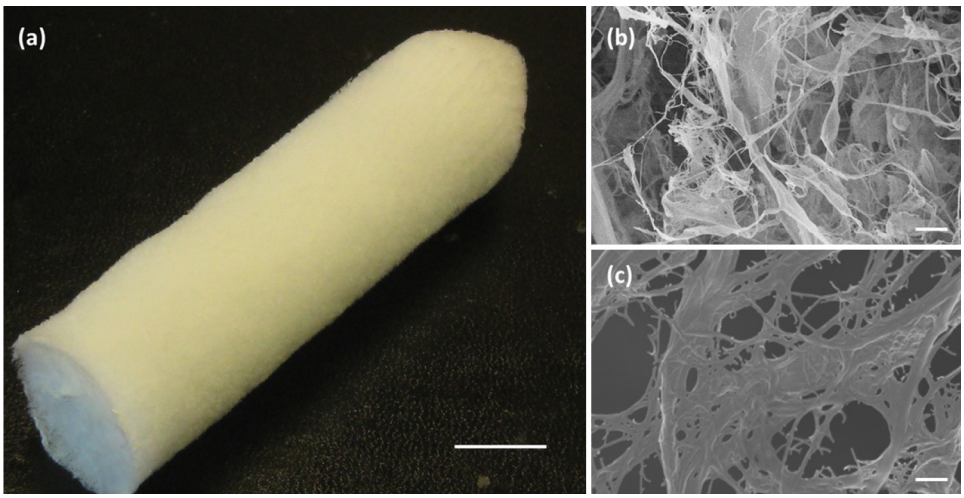

Fig. 1. (a) Digital camera picture of aerogel from quaternary ammonium-functionalized CNFs, scale bar is 2 cm, (b) and (c) SEM images of aerogel at different magnifications, and scale bars are 3 μm and 300 nm, respectively.

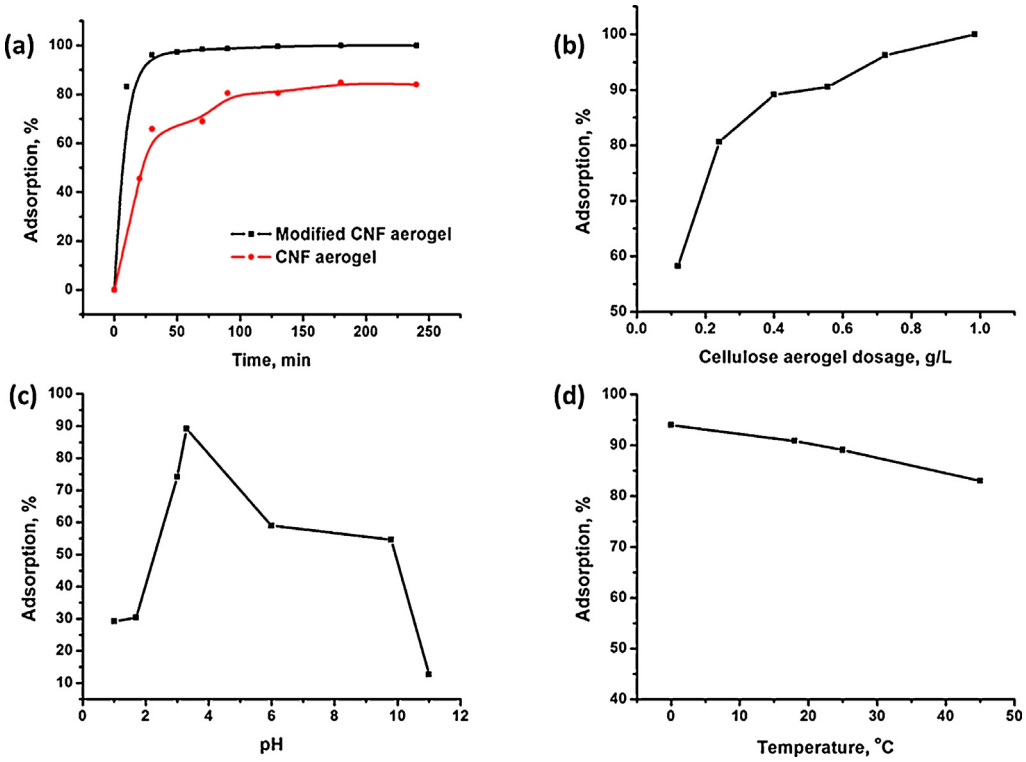

Fig. 2. (a) Comparison of adsorption of Cr(VI) from solutions to modified CNF aerogel and CNF aerogel as a function of contact time, Cr(VI) concentration = 1 mg/L; m(aerogel)/V(solution) = 1.0 g/L; pH = 3.0; temperature = 25 °C. (b) Effect of adsorbent dosage on the adsorption of Cr(VI), Cr(VI) concentration = 1 mg/L; temperature = 25 °C; pH = 3.0; adsorption time = 4 h. (c) Effect of pH on the adsorption of Cr(VI) by modified CNF aerogel, Cr(VI) concentration = 1 mg/L; m(aerogel)/V(solution) = 0.4 g/L; temperature = 25 °C; adsorption time = 4 h. (d) Effect of temperature on the adsorption of Cr(VI) by modified CNF aerogel, Cr(VI) concentration = 1 mg/L; m(aerogel)/V(solution) = 0.4 g/L; pH = 3.0; adsorption time = 4 h.

CNFs (with 34.79% and 6.29% for C and H, respectively). Moreover, charge titration experiment demonstrated the modified CNFs had a charge density of +80.4 μequiv./g, whereas the value was −40.3 μequiv./g for unmodified CNFs. All these results consistently confirmed that quaternary ammonium functionalities were successfully bonded to the surface of CNFs after this etherification reaction.

Fig. 1a shows a photography of a typical CNFs aerogel produced in a plastic centrifuge tube. In order to improve its water resistance, the aerogel was chemically crosslinked with the crosslinker Kymene™ which was formulated with polyamide-epichlorohydrin (PAE) resin and commonly used as wet strength additives in paper industry. The chemical reaction was initiated and proceeded under the reaction mechanism reported previously (Zhang, Zhang, Lu, & Deng, 2012). Fig. 1b and c gave the SEM images of the aerogel. The aerogel had a large amount of voids inside. The void size varied from place to place. Some large sheets, from the aggregation of CNFs, were interconnected to form micrometer voids. Meanwhile, some individual CNFs inside the sheets generated voids of several tens to hundreds of nanometers. This unique structure could

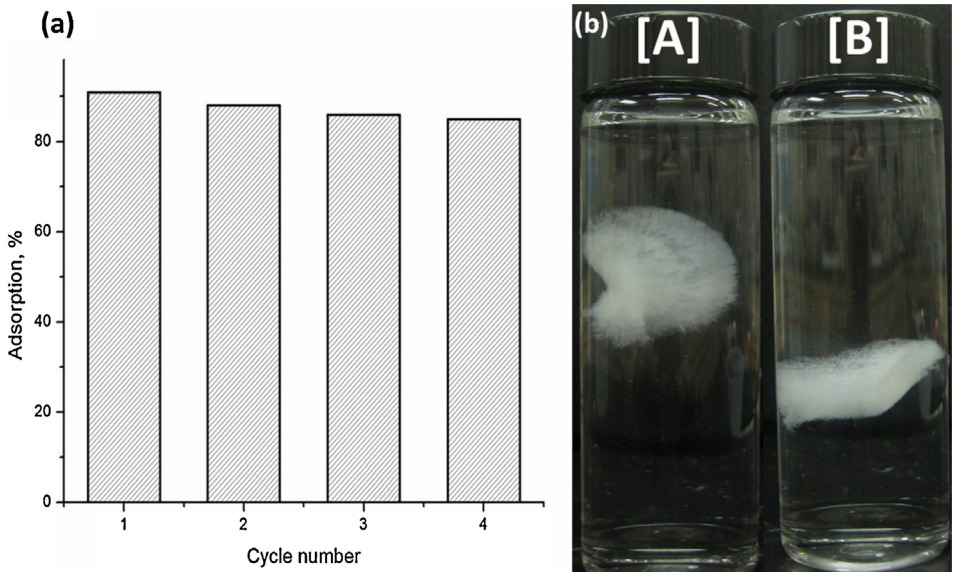

Fig. 3. (a) Adsorption of Cr(VI) from solutions to modified CNF aerogel in recycle studies, Cr(VI)concentration = 1 mg/L; m(aerogel)/V(solution) = 0.4 g/L; pH = 3.0; contact time = 4 h; temperature = 18 °C. (b) Stability of the 3D structure of crosslinked modified CNF aerogel before (A) after 4 cycles of adsorption/desorption (B).

promote access of heavy metal ions to the grafted functional groups on the aerogel, thus improving the metal adsorption capacity as well as the adsorption speed.

3.2. The effects of adsorption time, CNFs aerogel dosage, temperature, and pH on the removal of Cr(VI)

To manifest the adsorption efficiency of the aerogel, Cr(VI) was used as the model heavy metal for the adsorption tests. Fig. 2a shows the effect of agitation time on Cr(VI) removal using both the modified and unmodified aerogel. Both samples exhibited increased adsorption rate with the increase of agitation time. The amount of adsorbed Cr(VI) increased sharply in the first 20 min, indicating there were plenty of readily accessible sites available for a fast adsorption. The adsorption performance was remarkably improved by surface modification of CNFs with quaternary ammonium functionalities. The equilibrium adsorption time was estimated to be 50 min and nearly 100% of Cr(VI) could be removed from water after adsorption. Whereas, for unmodified aerogel, the equilibrium adsorption time was 180 min, and only 84% of Cr(VI) was removed. The adsorption of Cr(VI) onto aerogel was further confirmed by energy dispersive X-ray spectroscopy (EDS). Fig. S3a and b was EDS analysis of modified CNFs aerogel before and after water treatment, respectively. The new peak of Cr(VI) at 5.4 keV confirmed the successful adsorption of Cr(VI) on aerogel (Anandkumar & Mandal, 2009).

The adsorption isotherm of Cr(VI) on the modified CNFs aerogel was shown in Fig. S4. The experimental data were simulated by Langmuir model ($C_e/q_e = C_e/q_{max} + 1/(q_{max}K_L)$), where C_e is the equilibrium concentration mg/L, q_e is the amount of adsorbed material at equilibrium (mg/g), q_{max} is the adsorption capacity of adsorbent (mg/g) and K_L is a Langmuir constant related to energy. The maximum adsorption capacity of Cr(VI) calculated from Langmuir model was 17.66 mg/g (K_L = 2.24 L/mg, R^2 = 0.9903). This value was approaching that of commercial quaternary ammonium functionalized anion exchangers (20.8 mg/g for Lewatit^{TM} MP62, and 21.3 mg/g for Lewatit^{TM} MP610) (Gode & Pehlivan, 2005), and significantly higher than that of oxidized CNTs(4.26 mg/g) (Hu, Chen, Zhu, & Wang, 2009). Moreover, it took almost 30 h for CNTs to adsorb Cr(VI) to reach adsorption equilibrium (Hu et al., 2009).

The effects of aerogel dosage, pH and temperature of the solutions were crucial for Cr(VI) adsorption. An increased Cr(VI) adsorption was observed with the increase of aerogel dosage (Fig. 2b), ascribing to the fact that a higher amount of aerogel brought more active functional groups to the system, which trapped more Cr(VI) ions from water. pH of the solution strongly influenced the adsorption of Cr(VI). As can be seen from Fig. 2c, the maximum adsorption was reached when pH was 3.0. Either high pH or low pH would lead to reduced adsorption of Cr(VI). It is well known that the Cr(VI) may be represented in different forms such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ in the solution depending on the pH and concentration (Lee, Hong, Shin-Ya, & Kajiuchi, 2005). When pH = 3.0, $HCrO_4^-$ was the predominant form of Cr(VI) (Li, Gong, Li, Zhang, & Gong, 2012). Such a monovalent anion only exchanged one Cl^- from the quaternary ammonium functionalities on aerogel. When pH increased, divalent forms of Cr(VI) such as CrO_4^{2-} and $Cr_2O_7^{2-}$ became the majorities, which required to exchange two Cl^-. Therefore, the adsorption decreased. When pH increased to 11, the adsorption significantly decreased, owing to the fierce competition between anions to bind the ammonium groups in the presence of a large quantity of OH^- ions. When pH was as low as 1–2, H_2CrO_4 was the predominant form, leading to the reduced adsorption of Cr(VI). The adsorption of Cr(VI) was also temperature-dependent. Fig. 2d shows that the adsorption decreased almost linearly when the temperature increased from 0 °C to 45 °C. Because the adsorption of Cr(VI) onto aerogel adsorbent was an exothermal process, water treatment at a lower temperature would thermodynamically favor the adsorption.

3.3. Reusability of the CNFs aerogel

The reusability of adsorbent materials is important for a cost-effective water treatment. In this study, cyclic adsorption–regeneration tests were carried out for the aerogel adsorbent. Fig. 3a shows that after 4 cycles of adsorption–regeneration, the percentage adsorption just decreased from 90.9% to 84.9%, suggesting a good reusability of the adsorbent. More interestingly, the 3D structure of aerogel could be well kept during the water treatment. As shown in Fig. 3b, the aerogel did not show noticeable changes of the 3D network structure even after 4 cycles of adsorption–regeneration with constant magnetic stirring

(120 rpm), indicating the chemical crosslinking of nanofibers inside the aerogel was strong enough to withstand exterior forces. For most nanosized adsorbent materials, usually repeated high-speed centrifugation or filtration process had to be applied for their separation after adsorption. But for the aerogel adsorbent in this study, its robust and stable macroscopic structure made the separation process very easy. This advantage may greatly benefit the water treatment by minimizing the separation procedure and reducing costs.

4. Conclusions

In summary, a very efficient heavy metal adsorbent from quaternary ammonium-functionalized CNFs aerogel was demonstrated. The aerogel could well retain the large specific surface area, in combination with the unique porous structure, leading to the rapid and effective removal of Cr(VI) from water. The aerogel adsorbent became mechanically robust through chemical crosslinking. It could be easily separated from water after adsorption without complicated centrifugation or filtration process. Moreover, it also exhibited excellent reusability, showing great potential for future water treatments at industrial scale.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.05.020.

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