

Reinforced MFC aerogel for heavy metal ions separation

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Abstract. Micro-fibrillated cellulose (MFC) aerogel was reinforced by chitosan. The reinforced MFC aerogel was used as heavy metal ions absorbent. The results showed that the aerogel had good absorption capacity of over 200mg/g for all 4 kinds of heavy metal ions, Cd²⁺, Zn²⁺, Pb²⁺ and Cr⁶⁺ in the initial concentration range of 50-1000mg/L. The aerogel had little effect on contact time, but showed dependence on ion initial concentration. The reinforced MFC aerogel is a novel and attractive absorbent for heavy metal ions separation.

Introduction

Micro-fibrillated cellulose (MFC) is isolated from natural cellulose fibers by basically mechanical action after enzyme or chemical pretreatment. MFC has been widely investigated recently due to its sustainable, renewable, and biocompatible nontoxic properties for relatively high physical-chemical stability materials [1-3]. These aerogels are based on the hydrogen bond formation between MFC [4]. Unfortunately, these hydrogen bonds can be easily destroyed by immersing the aerogels in water, which limited the application of the aerogels.

Chemical-crosslinking affords a method for the preparation of cellulose aerogels with high mechanical properties [4-6]. Although many efforts have been carried out for the improvement of the mechanical properties of cellulose aerogels, the substances that can provide safe, renewable, and biocompatible nontoxic are more desirable.

Regarding to the chemical nature, chitosan and cellulose have similar structure, with the same β -glycosidic linkages, being the main difference the presence of primary amino groups at most of the C-2 positions in chitosan, in place of the hydroxyl groups of cellulose. Much work has been devoted to the study of chitosan blends with cellulose [7-10], poly (vinyl alcohol) [11-13], gelatin [14], collagen [15] and others [7]. The evidence of some chitosan-cellulose interactions were found. The chemical reaction of the chitosan amino groups with cellulose carbonyl Groups was proved [3].

In the current work, we firstly reported a reinforced MFC aerogel and its application with the addition of chitosan. The aerogels showed mechanical properties improved. Using the reinforced aerogel as absorbent, 4 kinds of heavy metal ions separation were examined in different conditions. The aerogel will have strong potential in heavy metal ions removal.

Experiments

MFC and chitosan solution preparation were described in our previous work. MFC dispersion with chitosan mixture at 90/10 (MFC to chitosan weight) was mixed to 0.5% by adding DI water, by a high-shear mixer for 5min, followed by a magnetic bar stirring for 1h, and then sonication for another 30min. Then the mixture was centrifuged to remove water at a speed of 1.2×10^4 rpm for 1h. A gel was formed.

The gel was frozen by liquid nitrogen, then placed on freezer dryer (Labconco) for at least 48h. The aerogel morphology was monitored in SEM in Figure 1. Pure MFC aerogel has much open structure and very weak bonding strength, see Fig.1 Left; chitosan reinforced MFC aerogel has tight structure and more contacts of fibrils, see Fig.1 right. The properties were examined like density, strength and BET surface area. The aerogel density was measured by the volume and weight of 0.0397g/cm^3 . The strength was evaluated by its water stability which was conducted in water for

stirring at given time. The aerogel were soaked into water and kept under magnetic stirring at 610rpm for 4h, its shape and size were kept intact, while aerogel without chitosan was dispersed into water see Fig.2. The interaction between MFC and chitosan in aerogel was examined by FTIR in Figure 3. It is proved that the chitosan spectra disappeared 1650, 1560cm⁻¹, which were assigned to O-C=N, implying the chemical reaction between chitosan and cellulose[3]. MFC with chitosan aerogel BET surface area of 9.7m²/g were measured after 4h degassing at 105°C (Gemini VII Series Surface Area Analyzer, Micromeritics Instrument Corporation). The separation test was conducted as: 5mg of dry aerogel in 25 mL of metal ion solution for some time at pH 6 adjusted with HNO₃ (0.01 M) or NaOH (0.01 M) using a pH meter. The mixture was centrifuged and filtered. 10mL filtrate was taken to measure the residual ions concentration. 4 kinds of metal ions, Cr⁶⁺, Zn²⁺, Cd²⁺ and Pb²⁺, were selected. The Perkin Elmer 8000 ICP-OES was used to analyze the concentration of heavy metal ions. Different contact time and different initial concentration were conducted respectively. All measurements were repeated three times.

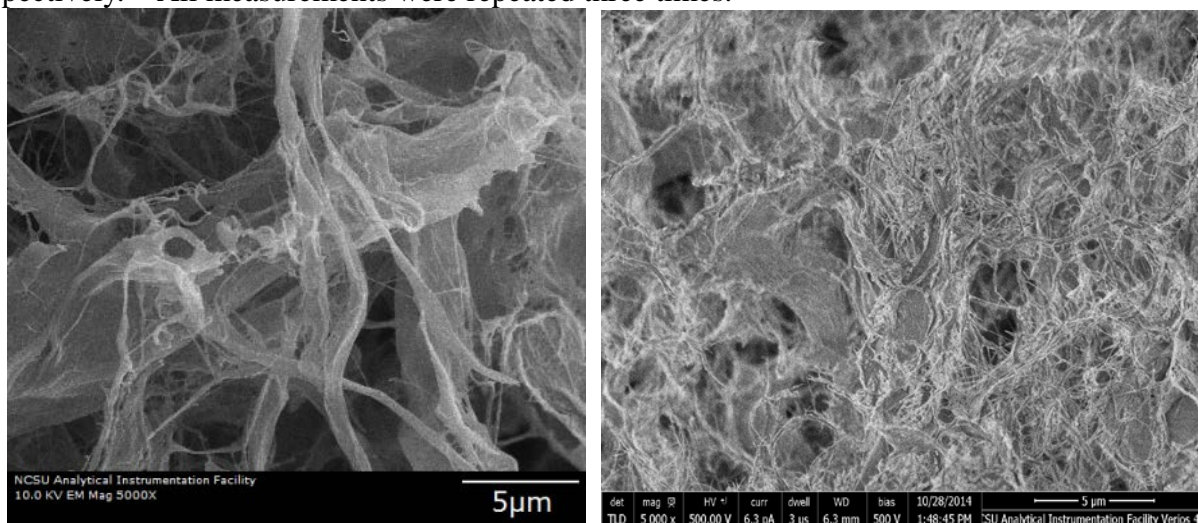


Fig .1 SEM images of MFC aerogel without chitosan (left) and with chitosan (right)

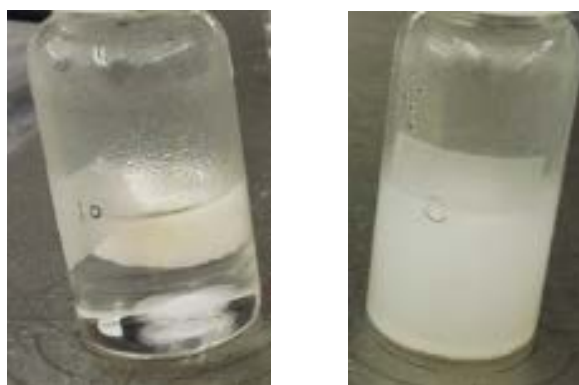


Fig.2 MFC aerogel water stability (left: chitosan reinforced MFC aerogel, right: pure MFC aerogel)

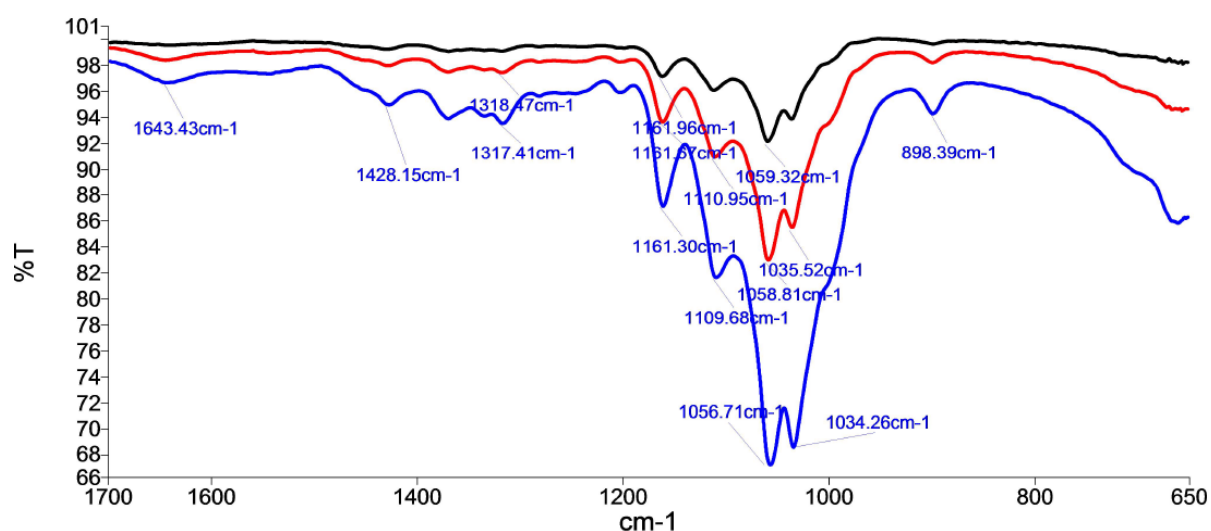


Fig 3 FTIR spectra of MFC aerogel without chitosan (black) and with chitosan 20%(red) and 30%(blue)

Results and discussion

4 kinds of metal ions solution were separated by the reinforced MFC aerogel using 20-120min different contact time range. The initial metal ions concentration are 100mg/L. After 5mg aerogel absorbent was applied, the residual metal ions concentration was measured and recorded in Figure 4. We can see that the contact time has little effect on all metal ions separation since the curves are near flat during 20-120min contact time test range. In other words, the aerogel absorbed the ions very quickly to its absorption equilibrium. Among these 4 ions, Cd^{2+} removal rate is close to 100%, the residual ion concentration less than 5mg/L; Zn^{2+} was removed the second most to 20mg/L; Cr^{6+} and Pd^{2+} were removed the least to near 50%. The aerogel performed as very good absorbent for heavy metal ions both good effectivity (short contact time) and high removal efficiency (high removal rate), typically for Cd^{2+} and Zn^{2+} here. 4 kinds of ions were ranked $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pd}^{2+} \sim \text{Cr}^{6+}$ by removal rate in Fig.4.

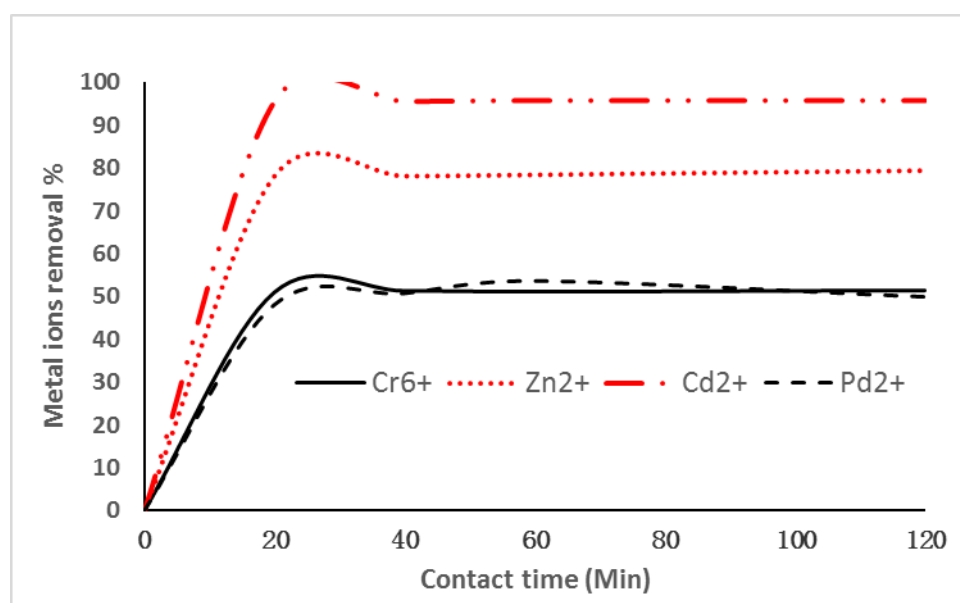


Fig 4 Effect of contact time on heavy metal ions removal by chitosan reinforced MFC aerogel.

Figure5 is different initial metal ions concentration effect on removal percent using 5mg aerogel and 60min contact time. 4 kinds of ions performed differently. Cr^{6+} and Zn^{2+} ions removal rate had little effect on initial concentrations since their curves are almost flat in Figure 4. But Zn^{2+}

was removed around 80%, much more than Cr6+, over 50% removal rate by the aerogel. Cd2+ and Pb2+ had better removal rate at lower initial concentration, typically below 100mg/L here. At higher initial concentration, both ions removal rate decreased, especially Cd2+. 4 kinds of ions removal rate ranked Zn2+>Cd2+~Cr6+>Pb2+ at higher initial separation concentration in Fig.5.

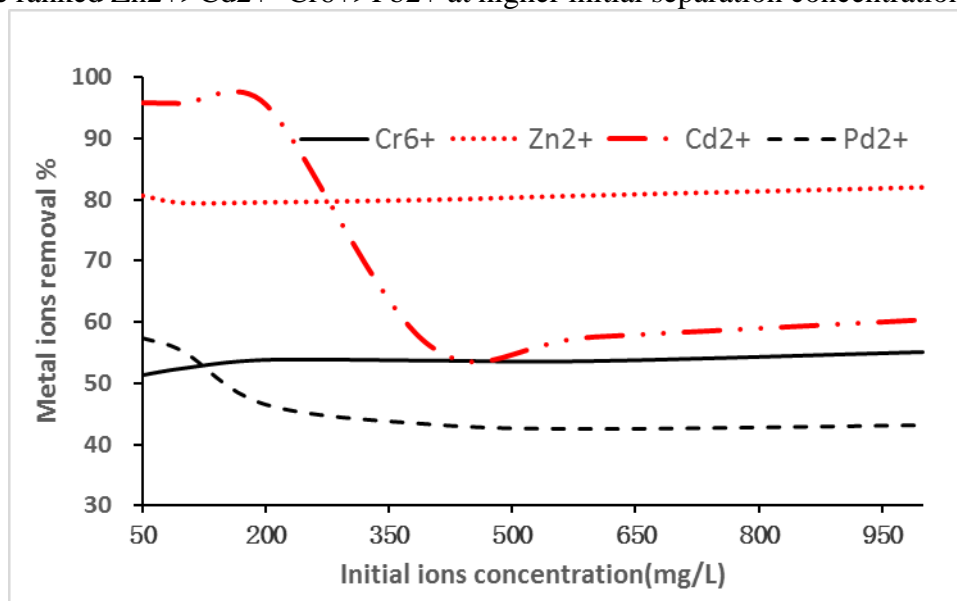


Fig. 5. Effect of initial metal ions concentration on percent removal by chitosan reinforced MFC aerogel

The amount of metal ion adsorbed on the aerogel, q_e (mg/g), was calculated according to eq (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg/L), V is the volume of the metal ion solution used in the adsorption experiment (mL), and W is the weight of the aerogel (mg), respectively. Different initial concentration q_e was calculated in Table 1.

Tab 1 Experimental q_e Values (mg/g)

Initial Con. mg/L	Cd2+ q_e	Zn2+ q_e	Pb2+ q_e	Cr6+ q_e
50	474	401	285	247
100	479.5	399	279	267.5
200	475.5	392.5	227.5	259.3
400	277.5	397.1	213.8	263.8
600	284.2	401.7	210	260
1000	297	407	215.5	272.5

*Contact time 60min, pH=6

In Tab 1, 4 kinds of ions had very high q_e values, much higher than reference [16]. The later using carbon aerogel for absorbent at 1-5mg/L initial concentration range, reported Cd2+, (400.8 mg/g), Zn2+ (1.84 mg/g), and Pb2+ (0.70 mg/g).

Conclusions

The chitosan reinforced MFC aerogel was prepared successfully. Its micro-structure is much tighter than pure MFC aerogel. The reinforced MFC aerogel has water stability. FTIR proved the chemical bonds between MFC and chitosan groups. The reinforced aerogel was used as heavy metal ions absorbent. This aerogel absorbent had good absorption capacity of over 200mg/g for all 4 kinds of heavy metal ions, Cd2+, Zn2+, Pb2+ and Cr6+ in the initial concentration range of 50-1000mg/L. The aerogel had little effect on contact time, but showed dependence on ions initial concentration. The reinforced MFC aerogel is a novel and attractive absorbent for heavy metal ions separation.

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