Magnetic MFC aerogel for heavy metal ions separation

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Keywords: MFC aerogel; Fe3O4; metal ions separation.

Abstract. Magnetic micro-fibrillated cellulose(MFC) aerogel used as heavy metal ions absorbent was researched in the paper. It was expressed great separation capacity. The absorbent had little effect on contact time in 20-120min range. But it was dependent on ion initial concentration. 4 kinds of ions removal rate were ranked Cd2+>Zn2+>Pb2+~Cr6+ at same ions initial concentration of 100mg/l; and removal rate ranked Zn2+>Cd2+~Cr6+>Pb2+ at 60min contact time and higher initial separation concentrations. Magnetic MFC aerogel is a good absorbent of heavy metal ions in aqueous solution.

1. Introduction

The removal of heavy metal ions from natural waters and industrial wastewaters is a critical technology due to the environmental strict standard and the more attention to people health. For example, the Word Health Organization (WHO) has announced a maximum Hg(II) uptake of 0.3 mg/w and a maximum acceptable Hg(II) concentration of 1 μg/L in drinking water and the maximum copper limit of 1.0 mg/L [1–5]. The heavy metal ions removal research has widely been investigated such as chemical precipitation, solvent extraction, ultra filtration, ion exchange and adsorption[6–8]. Adsorption method appears to be the most effective, especially for effluents with moderate and low concentration. Though different types of polymer or mineral adsorbents were developed [9–13], and biopolymer adsorbents gained more attention due to avoiding the secondary pollution. [14,15].

In the current work, we prepared a novel absorbent with magnetic nanoparticles loaded MFC aerogel. SEM and TEM were scanned to observe the particle morphology. The hybrid aerogel application in heavy metal ions separation like Cr(VI), Pb(II), Cd(II) and Hg(II) was conducted in detail.

2. Experiments

Magnetic MFC aerogel preparation was described in our previous work elsewhere. The aerogel morphology was scanned in SEM and TEM, and was conducted TGA shown in Figure 1 and Figure 2.

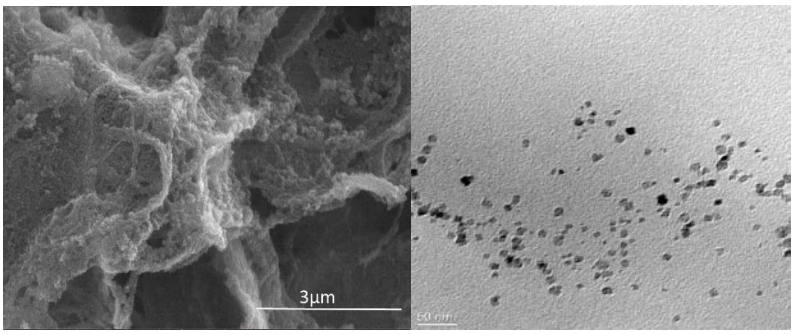

Fig 1 Magnetic MFC aerogel SEM(left) and TEM(right) images

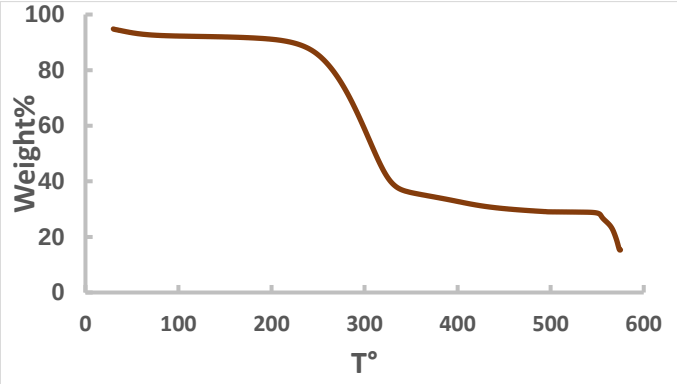

Fig 2 Magnetic MFC aerogel TGA for thermal stability

TGA was conducted in nitrogen air before 500° C, then in oxygen air between 500-575ºC. The aerogel residual was 15.3% and Tg was around 263 ºC which shows the aerogel good stability. This is close to the 18.3% magnetic ferrite content loaded in hydrogel [16]. The difference is the magnetic aerogel was prepared in 0.05 M Fe(II) and 0.1 M Fe(III) mixture for 1h before soaking into 0.2N NaOH solution for 1h at 60ºC and Freezer drying, the magnetic hydrogel was prepared in 0.25 M Fe(II) and 0.5 M Fe(III) mixture for 12 h before soaking into 0.5 M 250 mL sodium hydroxide solution, and dried in vacuum oven at 40 °C. 5mg aerogel was taken to absorb heavy metal ions in its 25mL aqueous solution. 4 kinds of metal ions, Cr6+, Zn2+,Cd2+ and Pb2+, were applied. The separation test was conducted as: 5mg of dry aerogel in 25 mL of metal solution for some time at stable pH value of 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. 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.

3. Results and discussion

4 kinds of metal ions solution were separated by the magnetic 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 3. 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, Cd2+ removal rate is close to 100%, the residual ion concentration less than 5mg/L; Zn2+ was removed the second most to 20mg/L; Cr6+ and Pd2+ were removed the least to near 50%. The magnetic MFC 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 Cd2+ and Zn2+ here. 4 kinds of ions were ranked Cd2+>Zn2+>Pb2+~Cr6+ by removal rate in Fig.3.

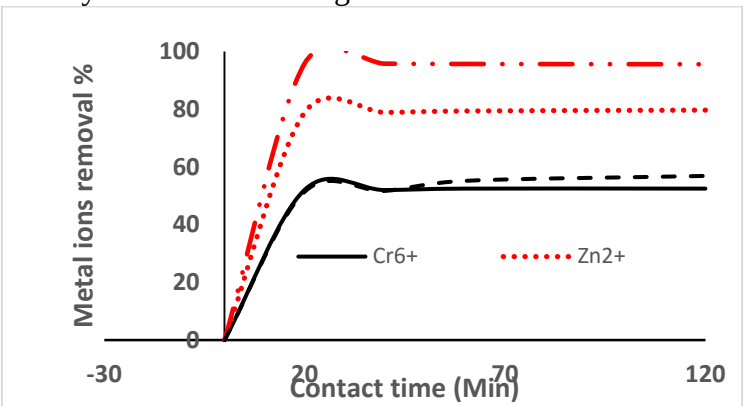

Fig 3 Effect of contact time on heavy metal ions removal by magnetic MFC aerogel.

Figure 4 is different initial metal ions concentration effect on removal percent using 5mg aerogel and 60min contact time. 4 kinds of ions performed differently. Cr6+ and Zn2+ ions removal rate had little effect on initial concentrations since their curves are almost flat in Figure 4.But Zn2+ was removed around 80%, much more than Cr6+ ,over 50% removal rate by the aerogel. Cd2+ and Pd2+ 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.4.

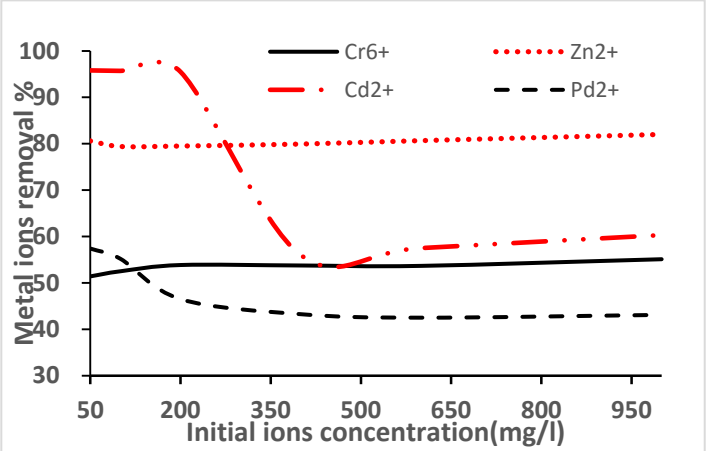

Fig. 4. Effect of initial metal ions concentration on percent removal by magnetic aerogel

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

$$q_e = \frac{(C0 - Ce)V}{W} \quad (1)$$

where C0 and Ce 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 qe was calculated in Table 1.

Tab 1 Experimental qe Values (mg/g)

Initial Con. mg/L	Cd2+ qe	Zn2+ qe	Pb2+ qe	Cr6+ qe
50	479	403	287	257
100	478.5	397	276	262.5
200	477.5	397.5	232.5	269.3
400	280	399.6	216.3	268.8
600	287.5	403.3	212.5	268.3
1000	301.5	410	215.5	275.5

*Contact time 60min, pH=6

In Tab 1, 4 kinds of ions had very higher qe values, much higher than other similar magnetic absorbent, which Cd2+ of 119.45mg/g and Pb2+ of 118.56mg/g were reported[16].

4. Conclusions

The magnetic MFC aerogel was applied in 4 kinds of metal ions separation successfully. The aerogel could absorb the ions fast. 4 kinds of ions removal rate were ranked Cd2+>Zn2+>Pb2+~Cr6+ at same ions initial concentration of 100mg/L. The contact time has little effect on ions removal rate. The ions initial concentration has effect on their removal rate. With 60min contact time,4 kinds of ions removal rate ranked Zn2+>Cd2+~Cr6+>Pb2+ at higher initial separation concentrations. The magnetic aerogel had very high absorbent capacity.

Acknowledgement

The research was assisted by Dr. Juliana Da Silva. Prof. Orlando Rojas of North Carolina State University (Raleigh, NC 27695, USA

) gave constructive suggestions and support in order to complete the work. The author are grateful to them.

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