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Short communication

Polyaniline/cellulose fiber composite prepared using persulfate as oxidant for Cr(VI)-detoxification

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ABSTRACT

Cellulose fibers were engineered by in situ oxidative polymerization of aniline using ammonium persulfate as oxidant/initiator. The polyaniline/cellulose fiber composite was used for the treatment of Cr(VI)-contaminated water, and its effect was evaluated. Under the conditions studied, the composite exhibited very high water detoxification efficiency, as a result of reduction of Cr(VI) to Cr(III) in combination with adsorption of the Cr(III) onto the cellulosic substrate. Cellulose fibers used in the study served two purposes simultaneously, i.e., carrier of polyaniline and the adsorbent for Cr(III). The complexation of polyaniline with cellulose fibers provided synergistic effects on Cr(VI)-detoxification.

1. Introduction

The availability of fossil resources on the earth is limited, and these resources are nonrenewable and depleting. Therefore, there is an urgent need to develop chemicals, materials, and energy from renewable bioresources, such as lignocellulosic materials.

Cellulose fibers are renewable in that they are produced from lignocellulosic bioresources. Engineering of cellulose fibers or their networks is a useful strategy for upgrading the qualities of cellulosic products (Aracri, Valls, & Vidal, 2012; Fatehi & Xiao, 2010; Li, Li, & Lu, 2010), or providing special functions (Cha, Wang, He, & Ni, 2012; Hou, Liu, Liu, Duan, & Bai, 2008) for new uses.

Chemical modification of cellulose fibers by in situ polymerization of aniline has been reported to be effective for the fabrication of conductive paper (Qian, Shen, Yu, & An, 2010), which has a lot of potential applications, such as antistatic packaging. As a typical conducting polymer, polyaniline is effective in converting the highly toxic Cr(VI) to much less toxic Cr(III) in an aqueous medium (Ruotolo & Gubulin, 2005); however, the Cr(III) remained in the system still needs to be further detoxified. Interestingly, the current study showed that polyaniline/cellulose fiber composite prepared by in situ oxidative polymerization using the well-known ammonium persulfate as oxidant was quite effective in reducing Cr(VI) to Cr(III) and adsorbing the Cr(III) onto the composite.

2. Experimental

2.1. Materials

Aniline of analytical grade used for the in situ polymerization was freshly distilled under reduced pressure (−0.1 MPa), and was then stored in a refrigerator at 4 °C. The cellulose fibers, i.e., fully bleached chemical pulp derived from softwood, were provided by Mudanjiang Hengfeng Paper Co. Ltd., China, and were refined to a beating degree of 40° SR using a Valley beater. Ammonium persulfate, hydrochloric acid, sodium hydroxide, and potassium bichromate, were of analytical grade, and were used without further purification.

2.2. Preparation of polyaniline/cellulose fiber composite

After adding hydrogen chloride solution to cellulose fibers, under continuous stirring, aniline and ammonium persulfate were added. The in situ polymerization reaction was stopped after a given time, and the mixture was filtered. The filter cake, i.e., polyaniline/cellulose composite, was sufficiently washed using tap water.

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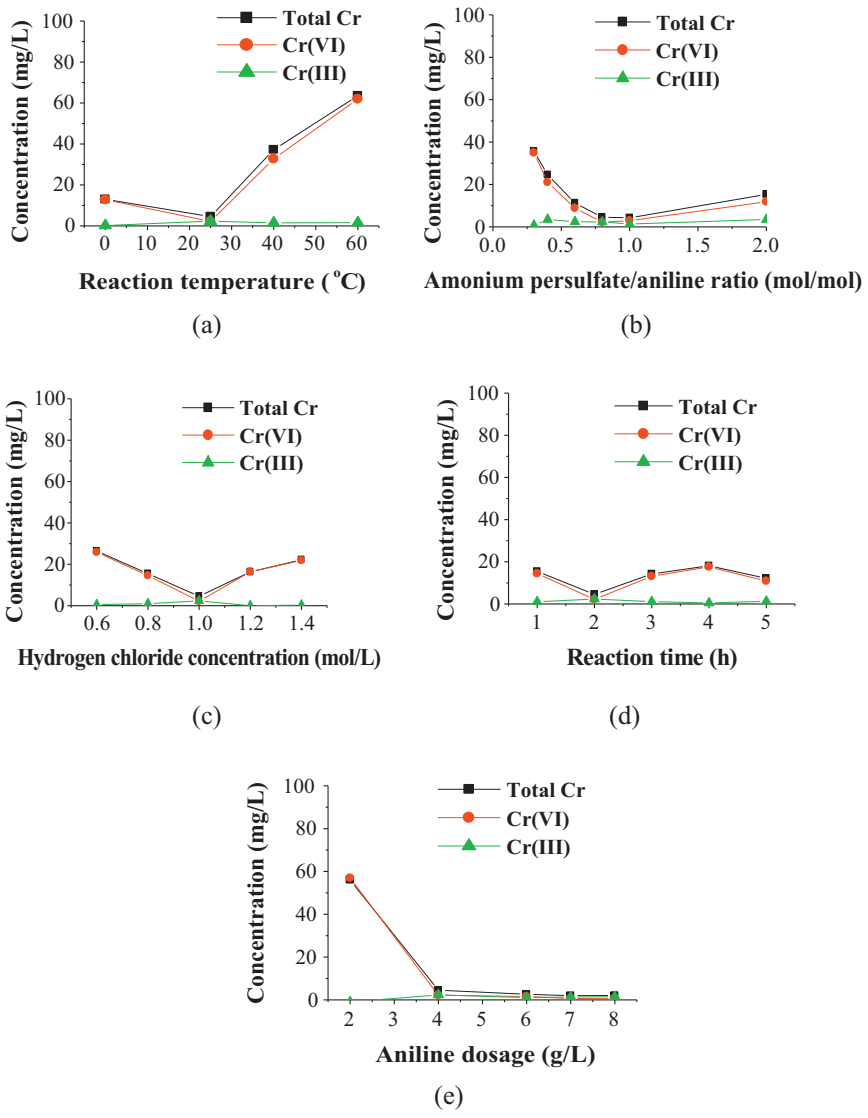

Fig. 1. Influence of process conditions in preparation of polyaniline/cellulose fiber composite on total Cr, Cr(VI), and Cr(III) concentrations in the treated water: (a) reaction temperature (aniline concentration: 4 g/L; ammonium persulfate/aniline molar ratio: 0.8 mol/mol; hydrogen chloride concentration: 1 mol/L; reaction time: 2 h); (b) ammonium persulfate/aniline molar ratio (aniline concentration: 4 g/L; reaction temperature: 25 °C; hydrogen chloride concentration: 1 mol/L; reaction time: 2 h); (c) hydrogen chloride concentration (aniline concentration: 4 g/L; reaction temperature: 25 °C; ammonium persulfate/aniline molar ratio: 0.8 mol/mol; reaction time: 2 h); (d) reaction time (aniline concentration: 4 g/L; reaction temperature: 25 °C; ammonium persulfate/aniline molar ratio: 0.8 mol/mol; hydrogen chloride concentration: 1 mol/L); (e) aniline concentration (reaction temperature: 25 °C; ammonium persulfate/aniline molar ratio: 0.8 mol/mol; hydrogen chloride concentration: 1 mol/L; reaction time: 2 h). Note that 6 g cellulose fibers (on a dry-weight basis) were used in the preparation of the composite.

2.3. Treatment of Cr(VI)-contaminated water

At room temperature, polyaniline/cellulose fiber composite with dry weight of 1 g was added to 100 ml of 100 mg/L Cr(VI) solution (pH 4.8), and the mixture was stirred at 350 rpm for 2 h. After treatment, the mixture was filtered through a medium speed filter paper. The filtrate, i.e., the treated water, was then collected.

2.4. Determination of chromium concentration

The concentrations of Cr(VI), Cr(III), and total Cr (on the chromate basis) were determined using a spectrophotometric method (Ansari, 2006). The detailed procedures were reported by Lei, Qian, Shen, and An (2012). In each test, four times were conducted, and the number was averaged.

3. Results and discussion

Our previous work showed that the use of cellulose fibers for the treatment of Cr(VI)-contaminated water only gave negligible detoxification effect (Lei et al., 2012). In an aqueous system, polyaniline can convert the highly toxic Cr(VI) to less toxic Cr(III) (Ruotolo & Gubulin, 2005). Therefore, it is possible that the use of polyaniline/cellulose fiber composite can detoxify Cr(VI)-contaminated water via a reductive/adsorptive mechanism (Lei et al., 2012), i.e., Cr(VI) is reduced to Cr(III) followed by adsorption of the Cr(III) onto the composite. To examine this assumption, the detoxification effect of polyaniline/cellulose fiber composite on Cr(VI)-contaminated water (Cr(VI) concentration: 100 mg/L) was evaluated.

Fig. 1(a) shows the effect of reaction temperature in preparation of polyaniline/cellulose fiber composite on total Cr, Cr(VI), and Cr(III) concentrations of the treated water. With the increase of

reaction temperature, i.e., in the range of 0–60 °C, water detoxification efficiency first increased and then decreased. At a temperature of 25 °C, Cr(VI)-contaminated water was substantially detoxified, and Cr(VI) concentration decreased by almost 100%. It is interesting to note that at different reaction temperatures, Cr(III) concentration of the treated water was only negligible, indicating that once Cr(VI) was converted to Cr(III), the Cr(III) was effectively adsorbed onto the composite, which is in agreement with the above-mentioned reductive/adsorptive concept.

Ammonium persulfate is a frequently used oxidant for polymerization of aniline in an acidic medium (Keivani, Zare, Aghaie, Aghaie, & Monajjemi, 2010). As shown in Fig. 1(b), with the increase of ammonium persulfate/aniline molar ratio, water detoxification efficiency first increased and then slightly decreased. At an ammonium persulfate/aniline molar ratio of 1 mol/mol, water detoxification efficiency generally reached a maximum. At above 1 mol/mol, the decreased efficiency may be explained by over-oxidation of aniline, making it less effective in functioning as a reductant.

Acid-doping is important for controlled adjustment of the redox state of polyaniline (Hatchett, Josowicz, & Janata, 1999), which is likely to influence the water detoxification efficiency of polyaniline/cellulose fiber composite. In this study, hydrogen chloride was used as an acid-doping agent, and its effect on water detoxification was examined, and the results are shown in Fig. 1(c). Expectedly, water detoxification efficiency was dependant upon hydrogen chloride concentration. At a hydrogen chloride concentration of 1 mol/L, water detoxification efficiency reached a plateau.

For polymerization of monomers in the presence of oxidant/initiator, reaction time may influence the degree of polymerization/oxidation of the monomers. As shown in Fig. 1(d), a reaction time of 2 h resulted in the highest detoxification efficiency. Again, prolonged reaction time may make the polyaniline over-oxidized, impairing its effectiveness as a reductant.

At a given amount of cellulose fibers (6 g, on a dry-weight basis), aniline concentration had an impact on the coated amount of polyaniline (data not shown), thereby influencing the water detoxification efficiency of polyaniline/cellulose fiber composite. Increasing aniline concentration from 2 to 4 g/L resulted in a significant increase in detoxification efficiency, and further increase of aniline concentration only gave a very minor effect (see Fig. 1(e)).

For all of the data points in Fig. 1, one unanimous fact is that the numbers of total Cr concentration are all very close to those of Cr(VI) concentration, and Cr(III) concentration is always around 0, which is in good agreement with the above-mentioned reductive/adsorptive concept. Cellulose fibers and polyaniline exhibited synergic effect on water detoxification, and a major function of cellulose fibers was its mechanical support in terms of Cr(III) adsorption. Also, similar to polypyrrole/cellulose fiber composite (Lei et al., 2012), a encouraging advantage of polyaniline/cellulose fiber composite in comparison to the common reductants is that it can potentially be reused upon desorption treatment.

4. Conclusions

Polyaniline/cellulose fiber composite was prepared via in situ oxidative polymerization of aniline using ammonium persulfate as oxidant. The influence of process variables in preparation of the composite including aniline concentration, reaction temperature, ammonium persulfate/aniline molar ratio, hydrogen chloride concentration, and reaction time, on detoxification of Cr(VI)-contaminated water, was examined. Under controlled conditions, the composite was highly effective in water detoxification through the reductive/adsorptive synergy as a result of the complexation of polyaniline with cellulose fibers.

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References

Ansari, R. (2006). Application of polyaniline and its composites for adsorption/recovery of chromium(VI) from aqueous solutions. *Acta Chimica Slovenica*, *53*(1), 88–94.

Aracri, E., Valls, C., & Vidal, T. (2012). Paper strength improvement by oxidative modification of sisal cellulose fibers with laccase–TEMPO system: Influence of the process variables. *Carbohydrate Polymers*, *88*(3), 830–837.

Cha, R., Wang, D., He, Z., & Ni, Y. (2012). Development of cellulose paper testing strips for quick measurement of glucose using chromogen agent. *Carbohydrate Polymers*, *88*(4), 1414–1419.

Fatehi, P., & Xiao, H. (2010). Effect of cationic PVA characteristics on fiber and paper properties at saturation level of polymer adsorption. *Carbohydrate Polymers*, *79*(2), 423–428.

Hatchett, D. W., Josowicz, M., & Janata, J. (1999). Acid doping of polyaniline: Spectroscopic and electrochemical studies. *The Journal of Physical Chemistry B*, *103*(50), 10992–10998.

Hou, Q., Liu, W., Liu, Z., Duan, B., & Bai, L. (2008). Characteristics of antimicrobial fibers prepared with wood periodate oxycellulose. *Carbohydrate Polymers*, *74*(2), 235–240.

Keivani, M. B., Zare, K., Aghaie, M., Aghaie, H., & Monajjemi, M. (2010). Synthesis of nano conducting polymer based polyaniline and it's composite: Mechanical properties, conductivity and thermal studies. *E-Journal of Chemistry*, *7*(1), 105–110.

Lei, Y., Qian, X., Shen, J., & An, X. (2012). Integrated reductive/adsorptive detoxification of Cr(VI)-contaminated water by polypyrrole/cellulose fiber composite. *Industrial & Engineering Chemistry Research*, *51*(31), 10408–10415.

Li, B., Li, Y., & Lu, R. (2010). Effect of modified nano TiO_2 on the properties of coating and coated paper. *CIESC Journal*, *6*(1), 228–234.

Qian, X., Shen, J., Yu, G., & An, X. (2010). Influence of pulp fiber substrate on conductivity of polyaniline-coated conductive paper prepared by in situ polymerization. *Bioresources*, *5*, 899–907.

Ruotolo, L. A. M., & Gubulin, J. C. (2005). Chromium (VI) reduction using conducting polymer films. *Reactive & Functional Polymers*, *62*, 141–151.