

A Novel Degradable Adsorbent of the Hyperbranched Aliphatic Polyester Grafted Cellulose for Heavy Metal Ions

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A novel degradable adsorbent for the removal of heavy metal ions from waste water, a hyperbranched aliphatic polyester grafted cellulose (HAPE-Cell), was successfully prepared by the simple one-pot method for the first time. The hyperbranched aliphatic polyester was grafted from the surface hydroxyl groups of natural cotton fibers via the solution polycondensation of the AB₂ monomer, 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA), with the catalysis of *p*-toluenesulfonic acid (p-TSA). The HAPE-Cell was characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The adsorption properties of the HAPE-Cell towards the heavy metal ions (Cu(II), Hg(II), Zn(II), and Cd(II)) were also preliminarily investigated.

Key Words: Hyperbranched aliphatic polyester, graft, cotton fiber, adsorbent, heavy metal ions.

Introduction

Cellulose is an abundant, naturally occurring, and promising low-cost material. Its modification by grafting with different vinyl monomers gives new materials for selectively permeable membranes,¹ drug delivery,² outstanding sorption agents,^{3–5} and enzyme immobilization.⁶

The modification of cellulose fibers by the grafting of vinyl polymers has been achieved by the ready-made functional end-group terminated polymers, and with the surface groups of the fibers via grafting-onto methods,⁷ or grafting-from methods, from the surface polymerizable groups⁸ or the surface initiating groups.^{9–13} The other polymers have also been grafted from the surface of the natural fibers with ring-opening polymerization¹⁴ and direct condensation polymerization.¹⁵

Hyperbranched polymers are macromolecular compounds built from multifunctional monomers AB_n, where the function A can couple with the function B, as proposed¹⁶ and demonstrated.¹⁷ In the last decade, the study and use of novel hyperbranched polymers for applications at surfaces and interfaces has grown.^{18–20} Hyperbranched polymers have been fabricated from the flat surfaces or the surfaces of porous particles for many applications, including microcolumn packing for the on-line preconcentration and separation of the

noble metal ions,²¹ the chiral stationary phase in HPLC,²² effective catalysts for hydroformylation and Heck reaction by being complexed with Rh and Pd,²³ designable size exclusion chromatography columns,²⁴ corrosion-resistant coatings and chemical sensing,²⁵ photoacid-based lithography,²⁶ and electrostatic immobilization of glucose oxidase.²⁷

In the present work, the hyperbranched aliphatic polyester was successfully grafted for the first time from the surface hydroxyl groups of natural cotton fibers using the one-pot method via the solution polycondensation of the AB₂ monomer, 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA), with the catalysis of *p*-toluenesulfonic acid (p-TSA). The HAPE-Cell is a novel degradable adsorbent for the removal of heavy metal ions from waste water.

Experimental

Chemicals

The cotton fiber used was absorbent cotton obtained from Shanghai Medicine Chemical Co. (Shanghai, China) and was washed with methanol, acetone, deionized water, and then dried in a vacuum oven maintained at room temperature. *p*-Toluenesulfonic acid (pTSA) and 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA) were all analytical grade and were used as received from Tianjin Chemical Co. (Tianjin, China). Toluene, dimethyl formamide (DMF), and other solvents used were all analytical grade.

Preparation of HAPE-Cell

The HAPE-Cell was prepared with the following one-pot method, as previously reported:²⁸ 2.0 g of natural cotton fiber (bare Cell), 0.20 g of *p*-toluenesulfonic acid (pTSA), 1.0 g of bis-MPA, and 20 mL of dimethyl formamide (DMF) were mixed and refluxed for 6 h with N₂ bubbling throughout.

The product, a mixture of HAPE-Cell and non-grafted HAPE, was precipitated in water. The HAPE-Cell was separated from the non-grafted HAPE by extraction with DMF, after keeping the crude on a Soxhlet apparatus until constant weight was achieved. Then, the HAPE-Cell was washed with ethanol and dried in a vacuum oven maintained at room temperature. The ideal structure of the HAPE-Cell is shown in Figure 1.

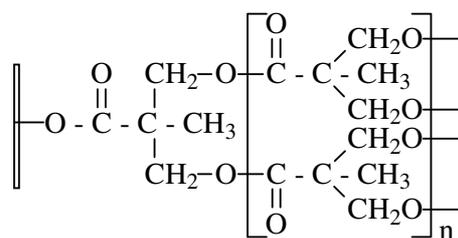


Figure 1. The ideal structure of the HAPE-Cell.

Characterization and analysis

Elemental analysis (EA) of C and H was performed on an Elementar Vario EL instrument. A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis. X-ray diffraction (XRD) analysis was carried out with a Shimadzu XRD 6000 with Cu K α radiation, operated at 50 kV and 80 mA over the range of 10° < 2 θ ° < 100°. The surface morphology of the fibers was observed using

scanning electron microscopy (SEM) (XL-20, Philips Corporation, the Netherlands), operating at 25 kV. The grafting parameters were estimated from the results of elemental analyses. The percentage of grafting (PG%) was calculated according to the following relationships:

$$\text{PG\%} = \text{HAPE grafted (g)/cotton charged (g)} \times 100\%$$

Competitive adsorption of the heavy metal ions

The heavy metal ions' competitive uptake capacities of the bare Cell and HAPE-Cell were determined preliminary as follows: 1.0 g of fiber (bare Cell or HAPE-Cell) was wetted separately with 5 mL of distilled water for 24 h. Then, 30 mL of heavy metal ion mixture solution (containing Cu(II), Zn(II), Cd(II), and Hg(II) with the same concentration of 1.0 mg/mL in HNO₃ media (pH 3.0)) was added and the mixture was shaken for 1 h at room temperature. Then, the supernatant solutions were taken out for the determination using ICP-OES performed with a Perkin-Elmer ICP/6500 inductively-coupled plasma spectrometer (RF power supply: 1100 w; Ar plasma gas flow: 14.0 L min⁻¹; Ar auxiliary gas flow: 0.5 L min⁻¹; Ar nebulizer gas flow: 1.0 L min⁻¹; viewing height: 11 mm; detection line: Cu 327.3 nm, Hg 194.2 nm, Zn 213.8 nm, and Cd 226.5 nm).

Results and Discussion

The hyperbranched polymers derived from 2,2-bis(hydroxymethyl)propionic acid were previously studied with multi-hydroxyl molecules, such as 2-ethyl-2-(hydroxymethyl)-1,3-propanediol,²⁸ 1,1,1-tri(hydroxyphenyl) ethane,²⁹ and Boltorn H40³⁰ as the core. Differing from those works, a degradable, natural, carbohydrate polymer cotton fiber was used as the core in the present work. In the condensation polymerization, the carboxyl groups of the monomers or oligomers reacted with the hydroxyl groups of the other monomers and oligomers, or the surface hydroxyl groups of the cotton fiber under acid-catalysis. The 2 esterification reactions were competitive reactions. The first one brought the hyperbranched aliphatic polyester and the latter conducted the grafting process. Thus, the HAPE-Cell, with the ideal structure shown in Figure 1, was produced, although the non-grafted free hyperbranched aliphatic polyester was the main product because of the large space hindrance on the surfaces of the cotton fibers.

The percentage of grafting (PG%), calculated with the weight method, was 17.4%, which is consistent with the 17.6% calculated from the C elemental analysis of the HAPE-Cell of 43.6%. In the FT-IR spectrum of the HAPE-Cell (Figure 2), the absorbance band at 1708 cm⁻¹ assigned to the C=O stretching of the ester groups was less than in the FR-IR spectrum of the bare cellulose, which indicated that the hyperbranched aliphatic polyester was successfully grafted from the natural cotton fibers with the proposed method.

It also could be concluded that the hyperbranched aliphatic polyester was successfully grafted from the surfaces of the natural cotton fibers based on SEM analysis (Figure 3). After the condensation polymerization of 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA), the surface morphology of the product did not like the smooth surfaces of the bare Cell. The main XRD patterns of the bare Cell did not shift after condensation polymerization, which indicated that the crystalloids of the natural cotton fibers had not changed in the polar solvent (DMF) at the high reacting temperature (about 140 °C) (Figure 4). Therefore, the monomer, 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA), could not enter into the crystals of the natural cotton

fibers and the hyperbranched aliphatic polyester was successfully grafted from the surfaces of the natural cotton fibers with the proposed method.

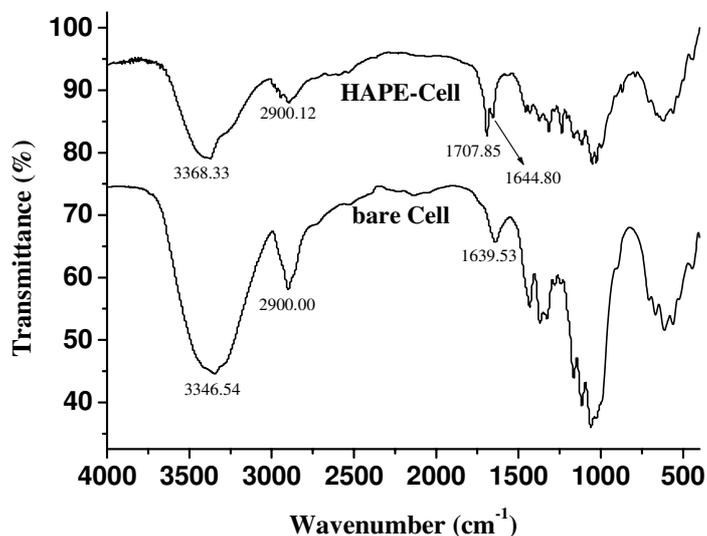


Figure 2. FT-IR spectrum of the bare Cell and HAPE-Cell.

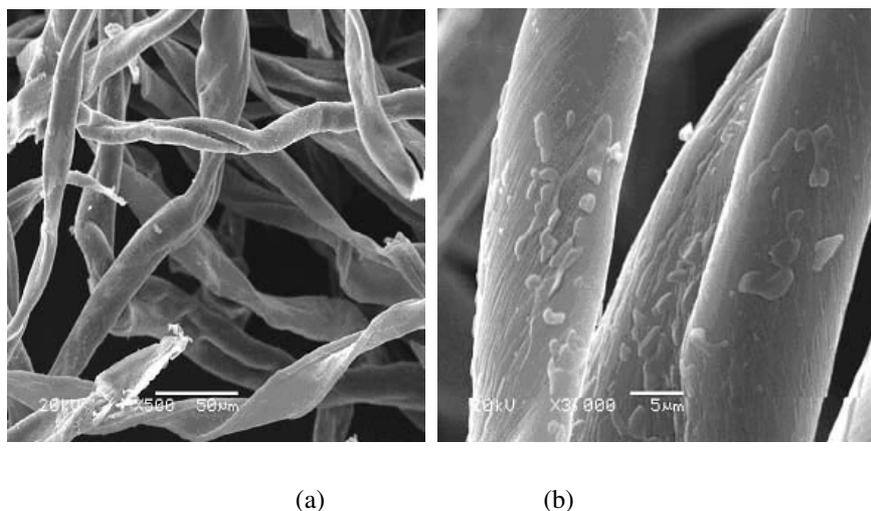


Figure 3. SEM image of the bare Cell (a) and the HAPE-Cell (b).

The heavy metal uptake abilities of the bare Cell and HAPE-Cell fibers were examined simply by soaking them (each of 1.0 g) in 30 mL of a heavy metal ion mixture solution (1.0 mg/mL each of Cu(II), Zn(II), Cd(II), and Hg(II), in HNO₃ media at pH 3.0) for 1 h. The heavy metal loading capacities were assayed by analysis of residual metal concentrations in the aqueous solution by direct ICP-OES detection, the results of which are given in Figure 5. After the surface modification with HAPE, the loading capacities increased markedly. Moreover, unlike most commercial adsorbents with synthetic polymers as the backbone, the HAPE-Cell is a degradable material that will not contribute to environmental pollution, either during or after use. It is therefore expected to be widely used for the removal of heavy metal ions from waste water.

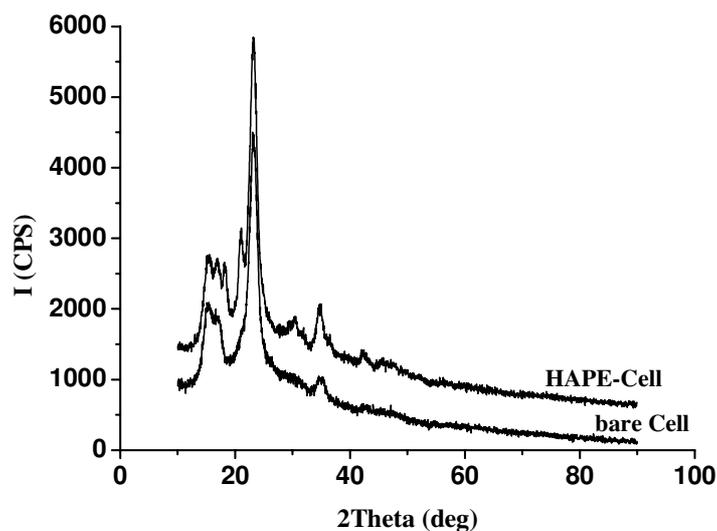


Figure 4. XRD pattern of the bare Cell and HAPE-Cell.

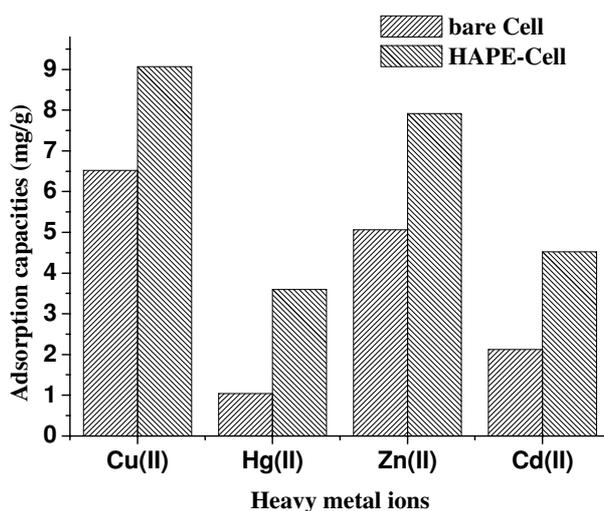


Figure 5. The adsorption capacity of the bare Cell and HAPE-Cell.

Conclusion

This report described a novel degradable adsorbent (HAPE-Cell) that was successfully prepared by grafting the hyperbranched aliphatic polyester from the surface hydroxyl groups of natural cotton fibers via the simple one-pot method. It is expected to be widely used for the removal of heavy metal ions from waste water.

Acknowledgments

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