



Biocompatible microcrystalline cellulose particles from cotton wool and magnetization via a simple in situ co-precipitation method



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ABSTRACT

This investigation describes the preparation of magnetically doped degradable microcrystalline cellulose (MCC) nanocomposite particles with application potential in biotechnology, solid support for biomolecule/water purification, oil recovery from water and beyond. MCC was first extracted from cotton wool, the most abundant biocompatible polymer, by sulfuric acid hydrolysis and the effect of acid strength was examined. The size of the elongated fiber structure was reduced with increasing acid strength. MCC particles extracted by treatment with 70% sulfuric acid were used to prepare magnetic MCC nanocomposite particles. The nanocomposite particles named as MCC/Fe₃O₄ were prepared via in situ co-precipitation of Fe⁺³/Fe⁺² from their alkaline solution. The precipitated Fe₃O₄ nanoparticles are expected to be bonded with MCC particles via hydrogen bonding. The nanocomposite dispersion was colloidally stable and the particles responded when external magnetic field was applied. It was possible to control the magnetic property by regulating the content of iron oxide.

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1. Introduction

Cellulose is a naturally occurring most abundant renewable polymer on earth. This can be used as one of the most promising organic raw/bioengineered materials because of its easy availability, biodegradability, biocompatibility, non-toxic, environment friendly nature, protein rejecting ability, low cost and so on (Namazi & Jafarirad, 2008; Oksman et al., 2016; Reza et al., 2015; Zhu, Ma, Li, Pan, & Dai, 2015). It is a polysaccharide carbohydrate consisting of β -D-glucopyranose units joined by β -1,4 glycosidic linkages in a linear arrangement along with varied amounts of hemicelluloses and lignin (Gurgel, Junior, Gil, & Gil, 2008; Oksman et al., 2016; Reza et al., 2015; Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008; Zhu et al., 2015). In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups. Due to absence of side chains or branching, cellulose chains are associated into an ordered structure called fibrils/microfibrils depending on the state of intra- and inter-molecular hydrogen bonding. Therefore, overall cellulose is a semicrystalline polymer that is it

contains both crystalline and amorphous phases. It is the crystalline building-blocks of cellulose that have been used to prepare suspensions of micro/nanoparticles in water (Chen et al., 2014; Yang, Han, Zheng, Dong, & Liu, 2015). Over the past few years researchers are showing much interest on the synthesis of micro/nanoparticles from cellulose for applications in food engineering, water purification, targeted delivery of drugs, polypeptides, proteins, vaccines, nucleic acids, genes, cosmetics and other field (Ahmad, Ahmed, Swami, & Ikram, 2015; Liu, Jiao, Wang, Zhou, & Zhang, 2008; Lee et al., 2014; Raj & Saurabh, 2012; Yang et al., 2015).

The objective of the present investigation is to synthesize microcrystalline cellulose (MCC) nanocomposite particles with superparamagnetic properties. Considering the non-toxic, biodegradable and biocompatible nature of cellulose matrix, these magnetic nanocomposite particles can be useful as a green product for catalysis, designing drug delivery systems and adsorbents for water and biomolecule purifications (Arantes et al., 2017; Dias, Hussain, Marcos, Roque, 2011; Luo & Zhang, 2009; Mulinari & Da Silva, 2008; Nogueira, Trovó, Da Silva, Villa, & De Oliveira, 2007; Přikryl, Lenfeld, Horak, Ticha & Kucerova, 2012; Rubinstein, 2000; Shukla & Tiwari, 2012). The applications of magnetic MCC nanocomposite materials have also been suggested in magneto graphic printing, electromagnetic shielding, transparent films

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for magneto-optical applications, functional cellulose composites, magnetic filters and magnetic aerogels (Carrazana-García, Lopez-Quintela, & Rivas-Rey, 1997; Galland et al., 2013; Li et al., 2013; Liu, Zhou, & Zhang, 2011; Olsson et al., 2011; Small & Johnston, 2009; Wu, Jing, Gong, Zhou, & Dai, 2011). So far magnetic cellulose materials have been prepared by incorporating iron oxides (Wu et al., 2011), cobalt ferrites (Olsson et al., 2011; Nypelö, Rodríguez-Abreu, Rivas, Dickey, & Rojas, 2014) into the cellulose matrix. In some cases the iron oxide is preformed and then mixed with cellulose materials (Li et al., 2013; Xiong, Lu, Wang, Zhou, & Zhang, 2013). In another work magnetic nanoparticles modified microfibrillated cellulose particles were prepared by mixing the transparent cellulose solution with commercially supplied zero-valent iron nanoparticles (Hokkanen, Repo, Lou, & Sillanpää, 2015). The in situ preparation of nanosized magnetic microcellulose particles is also carried out on limited scale. In one such report the preparation was carried out by in situ oxidation followed by complexation of ferrous iron within the insoluble cellulose matrix (Marchessault, Bremner, & Chauve, 2006). Most of these studies used nanofibrillated cellulose and only few records are available on the magnetization of commercially available microcrystalline cellulose via in situ precipitation of iron oxide nanoparticles (Marchessault et al., 2006; Dimitrov, Herzog, & Nenkova, 2013).

The present work is aimed at the synthesis of the magnetically modified MCC nanocomposites particles named as MCC/Fe₃O₄. These nanocomposite particles were typically synthesized by the co-precipitation of ferrous and ferric salts under alkaline conditions in the presence of MCC particles. The MCC particles were first prepared by the hydrolysis of cotton wool with sulfuric acid. The size, structure and magnetic properties of the resultant MCC/Fe₃O₄ nanocomposite particles were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and, vibrating sample magnetometer (VSM). The non-toxic and degradable nature with magnetic responsive character would make MCC/Fe₃O₄ nanocomposite particles useful for application in drug delivery, cell treatment, magnetic filters, magnetic printing, magnetic paper and as adsorbent for wastewater purification.

2. Experimental

2.1. Preparation of microcrystalline cellulose (MCC) particles

MCC particles were extracted by sulfuric acid (Thomas Baker, India) hydrolysis of cotton wool (N. R. Surgical & Repacking Company, Bangladesh). The cotton wool (3 g) as supplied was first bleached with 30% hydrogen peroxide (150 mL) for 1 h at room temperature. The bleached pulp was washed repeatedly with distilled deionized water. About 3 g of bleached pulp (dried under vacuum at room temperature) was taken in a beaker containing about 120 mL distilled water and the pulp-water mixture was magnetically stirred at 250 rpm for 20 min. The cellulose dispersion was then subjected to hydrolysis by the addition of sulfuric acid and the overall acid concentration in the beaker was adjusted to 40%, 50%, 55%, and 70% respectively with the total volume being fixed to 300 mL. The hydrolysis was continued in the beaker covered with aluminum foil under continuous stirring for 4 h at 50 °C. The obtained cellulose dispersion was washed repeatedly with distilled water by centrifugation and decantation until the final pH was around ~6–7. MCC powder was then obtained by simple drying under vacuum at 50 °C.

2.2. Preparation of Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were prepared by the co-precipitation of Fe²⁺ (0.8619 g) and Fe³⁺ (1.0 g) from their aqueous solutions (molar ratio 1:2) containing 25% NH₄OH (17.29 g). The volume of the reaction mixture was 50 mL and the reaction was carried out in a three necked round bottomed flask under a nitrogen atmosphere for 2 h. The yield of Fe₃O₄ nanoparticles was gravimetrically 2.0 g.

2.3. Preparation of magnetic microcrystalline cellulose nanocomposite particles

Magnetic MCC (MCC/Fe₃O₄) nanocomposite particles were prepared by in situ co-precipitation of Fe²⁺ and Fe³⁺ ions in an alkaline solution. MCC powder (1 g) obtained by acid (70%) hydrolysis was taken in a 250 mL three necked round bottomed flask dipped in a thermostat water bath at 60 °C and dispersed in 30 mL distilled water by magnetic stirring at 200 rpm. The MCC dispersion was heated to 60 °C and then required amount of FeSO₄·7H₂O and FeCl₃ (molar ratio 1:2) aqueous solutions were added. The total volume was adjusted to 50 mL. The reaction mixture was magnetically stirred for another 10–20 min and finally calculated amount of NH₄OH (25%) was added to start the precipitation of iron oxide nanoparticles. The reaction was continued under a nitrogen atmosphere for 2 h. The white colored of MCC dispersion turned black at the end of the reaction. Three different MCC/Fe₃O₄ nanocomposite particles with various iron oxide contents (0.1, 0.2 and 0.3 g) were prepared and the iron oxide content in the recipe was optimized from the yield of the previous experiment.

The preparation scheme of magnetic MCC/Fe₃O₄ nanocomposite particles is detailed in Fig. 1.

2.4. Characterization

The particle size distribution and morphology were examined by SEM (JSM-6510, JEOL, Tokyo, Japan) image analysis. The solid content of the dispersion for SEM observation was adjusted to around 0.5% relative to water. A drop of diluted sample was dropped onto mica sheet and dried in a vacuum dryer. The dried samples were gold coated before SEM observation at an accelerating voltage of 20 kV. FTIR analysis was carried out by FTIR spectrophotometer (Perkin Elmer, FTIR-100, UK). Prior to the measurements all samples were washed and dried at low temperature (~50 °C). The sample was mixed with KBr and pressed into pellets before scanning over the range between 4000 and 400 cm⁻¹ in deflection mode. The XRD patterns of the powder samples were recorded by scanning XRD (Bruker D8 Advance, Germany) using Cu K α radiation (λ) 1.5406 Å, tube voltage of 33 kV, and tube current of 45 mA. The intensities were measured at 2-theta values from 10 to 90° at a continuous scan rate of 10°/min. The crystallinity index was calculated from the following equation (Segal et al., 1959).

$$\text{Cryst. Index}(\%) = [(I_{002} - I_{am})/I_{002}] \times 100 \quad (1)$$

where I_{002} is the maximum intensity of the (002) lattice diffraction at two theta value of about 22.8° and I_{am} is the intensity diffraction at two theta value of around 18°. The surface composition of MCC and MCC/Fe₃O₄ nanocomposite particles were evaluated by an XPS (PHI X-tool, ULVAC-PHI, Japan) equipped with a monochromatic Al K α radiation (1486.6 eV) at 104 W and 20 kV and an X-ray current of 20 (micro)A. Before the measurement the dispersion (purified by repeated decantation and separation employing magnetic field and centrifugation) was dried onto carbon/indium tape and dried at room temperature. The pressure in the measurement chamber was ca. 8.0 10⁻⁷ Pa. The step size was 0.25 eV for the survey (pass energy 280 eV). TGA measurements were carried out on a TGA (STA 8000, Perkin Elmer, Netherland) to confirm the inclusion of inorganic iron

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