



Renewable hybrid nanocatalyst from magnetite and cellulose for treatment of textile effluents



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ARTICLE INFO

Article history:

Received 17 November 2016

Received in revised form

27 December 2016

Accepted 4 January 2017

Available online 7 January 2017

Keywords:

Magnetite

Catalyst

Cellulose

Nanofibrils

Crystallite

ABSTRACT

A hybrid catalyst was prepared using cellulose nanofibrils and magnetite to degrade organic compounds. Cellulose nanofibrils were isolated by mechanical defibrillation producing a suspension used as a matrix for magnetite particles. The solution of nanofibrils and magnetite was dried and milled resulting in a catalyst with a 1:1 ratio of cellulose and magnetite that was chemically and physically characterized using light, scanning electron and transmission electron microscopies, specific surface area analysis, vibrating sample magnetometry, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, catalytic potential and degradation kinetics. Results showed good dispersion of the active phase, magnetite, in the mat of cellulosic nanofibrils. Leaching and re-use tests showed that catalytic activity was not lost over several cycles. The hybrid material produced was tested for degradation of methylene blue dye in Fenton-like reactions resulting in a potential catalyst for use in degradation of organic compounds.

Published by Elsevier Ltd.

1. Introduction

Cellulose has been studied and applied as a precursor of new bio-engineered materials (Oksman et al., 2016; Reza et al., 2015; Zhu et al., 2015) and is organized at a macromolecular level into fibrils consisting of glucose units in a linear and crystalline arrangement, along with hemicellulose and lignin (Fengel & Wegener, 1984; Zugenmaier, 2008). Cellulose fibers are made up of basic crystalline building-blocks or nanofibrils that can form suspensions in water when isolated (Chen et al., 2014).

The isolation process, typically by chemical or physical methods, can affect the properties of the resulting cellulose nanofibrils (Wang, Li, Yano, & Abe, 2014). Mechanical defibrillation is a physical process where cellulose fibers pass through a mill that reduces their

dimensions by friction. At a certain size range, the nanofibrils form a gel-like suspension (Bufalino et al., 2015; Fonseca et al., 2016). Defibrillation is a physical method that requires no chemicals in the isolation of cellulose nanofibrils, thus, reduces processing steps and pollution.

Cellulose nanofibrils can be used to prepare a multitude of useful commercial materials, such as aerogels, xerogels, hydrogels, beads and specialty biomaterials (including medical grafts) (Abe & Yano, 2011; Baetens et al., 2011; Chin, Binti Romainor, & Pang, 2014; Eichhorn et al., 2010; Gericke et al., 2013; Wan & Li, 2015). Aerogels have low density, high strength and a large surface area (Innerlohinger, Weber, & Kraft, 2006) and are produced by supercritical drying of cellulose nanofiber suspensions which allows them to maintain a structured gel (Heath & Thielemans, 2010). Air drying of nanofiber suspensions causes the gel structure to collapse resulting in a xerogel (Baetens et al., 2011). Depending on the final application, a xerogel may have the same benefits of an aerogel without the high costs of supercritical drying.

Aerogels and xerogels made from cellulose can serve as fixed supports for Fe ions in the production of chemical catalysts (Small & Johnston, 2009). These Fe-hybridized aerogels can be expected

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to be used in a number of industrial applications as they have superparamagnetic properties, remarkable mechanical strength, are lightweight, flexible, highly porous and have a large surface area that provide a huge number of reactive sites (Liu, Yan, Tao, Yu, & Liu, 2012). In addition to being produced from readily renewable resources, such as wheat straw, an agricultural residue, aerogels may be prepared using green chemical methods which further extends their usefulness and acceptability as a green product (Wan & Li, 2015). Olsson and coworkers used highly flexible and porous hybrid aerogels as templates to construct solid and stiff nanocomposites by compaction (Olsson et al., 2010). Fe ions may be used to catalyze Fenton-like reactions for the generation of hydroxyl radicals using strong oxidizing agents, such as H_2O_2 , as a precursor. Hydroxyl radicals have high oxidation potential and can degrade organic molecules, such as dyes generated in textile effluents (Nogueira, Trovó, Da Silva, Villa, & De Oliveira, 2007).

The use of iron-based catalyst systems is advantageous because iron is a naturally-occurring, abundant compound that is non-toxic, environmentally safe and readily renewable and sustainable. Some forms of iron oxide have magnetic properties facilitating the removal of reactants so that they can be readily reused (Luo & Zhang, 2009). Magnetite, a dark colored iron oxide, with the molecular formula Fe_3O_4 , provides magnetic properties to materials and supplies Fe ions to catalyze Fenton-like reactions.

The aim of this study was to evaluate the catalytic efficiency of a magnetic catalyst produced by impregnating cellulose nanofibrils with magnetite and applied to the degradation of methylene blue dye in a Fenton-like reactive process.

2. Materials and methods

2.1. Production and characterization of the cellulose suspension

The fibers of commercial eucalyptus kraft pulp (Jacareí/SP, Brazil) were immersed in distilled water for 48 h at 1% (w/w) concentration before defibrillation. Cellulose nanofibrils were obtained by mechanical defibrillation of the fiber cell wall using a Super-Masscolloider MKCA6-3, (Masuko Sangyo Co., LTD, Japan), operated at 1500 rpm, with a 0.01 mm opening between disks and applying 35 passages through the defibrillator (Bufalino et al., 2015; Tonoli et al., 2016). The resulting nanofibril suspensions were characterized morphologically using a Nikon Eclipse E200 (Japan) compound microscope by randomly selecting 10 areas on a slide for image analysis. Glass slides were prepared with 0.05 mL of sample mounted in glycerin.

Scanning electron microscopy (SEM) was performed using a Hitachi S4700 field emission SEM (Hitachi High-Technologies, Japan). The freeze-dried samples were adhered to aluminum specimen stubs using double-sided adhesive-coated carbon tabs (Ted Pella, Inc., Redding, CA). The samples were then sputter-coated with gold-palladium in a Denton Desk II sputter coating unit (Moorestown, NJ). SEM images were captured at a resolution of 2650×1920 pixels.

Transmission electron microscopy (TEM) was used to visualize the cellulose nanofibrils by mixing the suspended samples with uranyl acetate to make the cellulose particles electron dense in order to provide contrast in the TEM. A drop of the nanofibril suspension was placed onto a 400-mesh carbon-formvar grid (Ted Pella, Inc., Redding, CA) held at the edge with double-adhesive tape. The grids were allowed to air-dry and then were observed and photographed in a FEI Tecnai 12 TEM (FEI Company, Hillsboro, OR) operated at 120 kV. The average diameter of the micro/nanofibrils was determined by digital image analyses (ImageJ 1.48 v, National Institutes of Health, USA) on TEM micrographs. A minimum of 100 measurements were collected for analyses.

2.2. Production and characterization of the magnetic hybrids

The synthesis of magnetic material was performed using the methodology adapted from Schwertmann & Cornell (2000). Fe^{2+} and Fe^{3+} salts (6.314 g FeCl_3 and 2.343 g FeCl_2) were dissolved in 200 mL of an aqueous suspension of cellulose nanofibrils under nitrogen flow. NH_4OH was added until pH 11 was attained to precipitate both magnetite and cellulose from solution. The precipitate was washed with water until pH ~ 7 , oven-dried at 60°C , and milled in a ball mill. The mass ratio of cellulose:magnetite was 1:1 (cel:mag). To obtain the ratio, the experimental sample was compared to a sample of pure magnetite (magnetite) prepared by a similar method.

Surface areas were determined via N_2 adsorption at -196°C in an Autosorb-1 Quantachrome system (Quantachrome Instruments, Boynton Beach, FL). The samples were previously degassed at 110°C for 10 h, and the specific area was calculated using the Brunauer-Emmett-Teller (BET) model. Magnetic properties of the materials were measured by vibrating sample magnetometry (VSM) using an ADE/DMS Model 880 Vibrating Sample Magnetometer (MicroSense, LLC, Lowell, MA). Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60AH TGA (Shimadzu Corporation, Kyoto, Japan). Samples (approximately 10 mg) were heated under synthetic air atmosphere in the range of $25\text{--}800^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$ and a gas flow rate of 30 mL min^{-1} . Fourier transform infrared spectroscopy (FTIR) was performed using a Shimadzu spectrophotometer IRAffinity system, with KBr pellets containing 1% sample, in the spectral range of $400\text{--}4000\text{ cm}^{-1}$, 4 cm^{-1} resolution with 32 scans. X-ray diffraction (XRD) was performed using a Shimadzu XRD-6000 equipped with a graphite crystal as monochromator to collimate $\text{Cu-K}\alpha_1$ radiation at $\lambda = 1.5406\text{ \AA}$ with a step of 0.02° s^{-1} and an angular range (2θ) of $4^\circ\text{--}70^\circ$.

2.3. Catalytic tests

Assays of the catalytic decomposition of H_2O_2 by cel:mag were performed, under stirring, using 30 mg of the cel:mag catalyst, 5 mL of water and 2 mL of H_2O_2 . The volume of oxygen produced was monitored by displacement of water in a column over 30 min. A comparative reaction was also run using 30 mg of catalyst, 5 mL of methylene blue (50 ppm) and 2 mL of H_2O_2 . For leaching tests, 60 mg of the cel:mag catalyst were stirred with 10 mL of water for 180 min; then, decomposition of H_2O_2 was measured using 5 mL of the supernatant. For the dye tests, catalytic properties were assayed via kinetic degradation of methylene blue dye using 10 mg of the cel:mag catalyst, 9.9 mL of 50 ppm methylene blue solution and 0.1 mL of H_2O_2 . Reactions were monitored by spectrophotometry in UV-vis at 665 nm at 0, 15, 30, 60, 90, 120 and 180 min. All tests were performed using either the cel:mag or the magnetite catalytic formulations. Moreover, the degradation kinetics were also performed for pure cellulose.

3. Results and discussion

3.1. Morphology of the cellulose nanofibrils

One feature that determines the presence of nanofibrils is the formation of an increasingly gel-like suspension with successive passages through the defibrillator (Nakagaito & Yano, 2004). When the solution containing cellulose fibers passes through the defibrillator, disintegration of the cell walls occur, thus modifying the dimensions and surface structure of the fibers. Structural modification results in viscosity changes due to the breaking and reformation of chemical bonds. The crystallinity index and degree

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