



Research article

Study on cellulose microfilaments based composite spheres: Microwave-assisted synthesis, characterization, and application in pollutant removal

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ABSTRACT

A novel study of synthesizing the temperature-responsive polymer grafted cellulose filaments/Poly (N-isopropylacrylamide) (NIPAM) spheres (P-MCCBs) was carried out for the removal of dyes and heavy metal ions. The novelty of the presented work consists of the application of the nano-sized pore-forming agent (Calcium Carbonate) and the introduction of a temperature-responsive monomer (NIPAM) while preparing the adsorbents. In addition, the spherical adsorbents were synthesized through an in-situ free radical polymerization using a microwave-assisted heating approach. The morphology, chemical structure, pH, and thermal sensitivity of P-MCCBs were characterized properly. The adsorption and desorption behaviors of dyes and heavy metal ions on P-MCCBs were also investigated. The results showed that P-MCCBs exhibited a fast adsorption rate, the adsorption equilibrium reached within 80 min and 40 min for MB and Pb²⁺, respectively (25 °C). Moreover, around 5–8% and 20% of adsorbed MB and Pb²⁺ were released at the temperature above 45 °C. The adsorption kinetics followed pseudo-second-order model, and the desorption process was fit well using Higuchi and Korsmeyer-Peppas models. These results indicated that P-MCCBs could be served as a novel material for controllable adsorption and desorption processes of various contaminants.

1. Introduction

The rapid economic development and the expanded industrial activities introduced the increased levels of hazardous dyes and heavy metal ions into hydrosphere, which has aroused enormous interest. These contaminants are hazardous and endanger humans even at low concentrations. Dyes and toxic heavy metal ions are utilized in various industrial fields including printing, leather, mining, textile, pulp mills, etc. (Crini, 2006; Zhang et al., 2017). The industrial effluent should be discharged with sufficient treatment due to the potentially risk to environment. However, the by-products are also toxic and carcinogenic and difficult to be degraded or destroyed (Mahajan and Bali, 2012). The adsorption using a solid adsorbent is promising among the conventional methods such as ion exchange, chemical precipitation, solvent extraction, etc., due to the advantages such as low cost, highly efficient, easy-operating, and no by-products (Garg et al., 2004). Various adsorbents

have been reported by researchers in recent years (Zhou et al., 2017; Lyu et al., 2018). To overcome the disadvantages of using activated carbon, various low-cost adsorbents, such as agricultural by-products (Pellera et al., 2012), bio-adsorbents (Li et al., 2018), kaolinite (Rosales et al., 2018), composite materials and hydrogels (Sharma et al., 2017a,b), have been investigated systematically. Particularly, cellulose, as a most-abundant natural material, can be utilized as a green approach for water treatment.

Recently, smart materials, thermo- and pH-responsive materials, were reported by some researchers (Jalili et al., 2017; Atta et al., 2017; Qian et al., 2017), which could be applied in various fields such as biotechnology and pharmaceutical. Poly (N-isopropylacrylamide) (Poly-NIPAM), with the lower critical solution temperature (LCST) at 32 °C, was water insoluble and usually used as the thermal-sensitive polymer (Liu et al., 2010). Pan et al. (2010) synthesized PNIPAM grafted thermo-responsive regenerated cellulose membranes using atom

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transfer radical polymerization (ATRP) and found the thermally modulated properties on the synthesized membranes. Yang et al. (2015) synthesized polymer (poly (N-isopropylacrylamide)) grafted cellulose (cellulose-g-PNIPAM), which exhibited obvious thermal-responsive property and might be utilized for some other biomedical applications, such as drug carrier and tissue engineering. In addition, the typical pH-sensitive polymers, such as poly (acrylic acid) (PAA) (Pal et al., 2016) and poly(4-vinylpyridine) (P4VP) (Behbahani et al., 2016), have been reported as competitive resources due to the properties such as stable and highly binding capacity compared to those species with relatively low molecular weight. Until now, the multi-functional materials with dual-responsive properties have been studied. Jin et al. (2018) prepared the core and shell hybrid composite for drug release, the copolymer poly(N-isopropylacrylamide)-co-poly(acrylic acid) [P(NIPAM-co-AA)] with pH- and thermal-sensitive properties was investigated to control the drug release on the composite. Thermal- and pH-sensitive NIPAM nanogels were synthesized by copolymerization of acrylic acid (AA) using different micro-emulsion polymerization, the responsive nanogels had excellent drug release properties (Pruettiphap et al., 2017). Furthermore, some researchers have studied the microwave-assisted polymerization due to the disadvantages of the conventional methods, such as the reaction rate is uncontrollable, the reaction time is long, and the by-products might affect the application of products. This technique has been reported in step-growth polymerizations (Komorowska-Durka et al., 2015), free radical polymerizations (Zhang et al., 2007), and ring-opening polymerizations (Singla et al., 2014).

In this study, we aim to synthesize temperature-responsive polymer grafted cellulose filaments/Poly (N-isopropylacrylamide) spheres (P-MCCBs) via microwave-assisted synthesis. The precipitated cellulose/CF composite spheres were firstly prepared, followed by the graft modification on the spheres using a microwave-assisted synthesis. The temperature responsiveness was added on the spheres through free radical polymerization using N, N'-methylenebisacrylamide (MBA) as the crosslinker and potassium persulfate (KPS) as the initiator. The P-MCCBs were characterized using FTIR, TGA, and SEM. Finally, the P-MCCBs were utilized for the adsorption of methylene blue (MB), as a representative of dyes, and lead Pb^{2+} ions, as a representative of heavy metal ions, from aqueous solutions.

2. Material and methods

2.1. Materials and reagents

Cellulose (filter paper, Qualitative P4) was purchased from Fisher Scientific. Cellulose microfilaments (CFs) were supplied by FPIInnovations Canada (Pointe Claire, QC, Canada). NaOH (solid), $CaCO_3$ (≤ 30 nm), maleic anhydride (MA), urea, methylene blue, Lead (Pb (II)) nitrate, N-isopropylacrylamide (NIPAM), were all purchased from Sigma-Aldrich Chemical Co., N, N'-methylenebisacrylamide (MBA), N, N, N, N-tetramethylethylenediamine (TEMED), and potassium persulfate (KPS) were all of analytical grade (Sigma-Aldrich).

2.2. Microwave-assisted synthesis of polymer grafted precipitated cellulose/CFs composite spheres

The synthesis of polymer grafted precipitated cellulose/CFs composite spheres (P-MCCBs) were carried out as follows: cellulose and CFs were used as the raw material for the preparation of precipitated cellulose/CFs composite spheres. Dried cellulose was dissolved by using the matrix solution (7 wt% NaOH/12 wt% urea) at the temperature of -10 °C, and then the CFs and the pore forming agent (Nano-sized $CaCO_3$) were dispersed in the matrix solution using a homogenizer (High-speed shear, Stanfen, Germany) for 5 min to obtain a constant CFs suspension. Afterwards, the CFs suspension was added into 1 mol/L HCl solution dropwise. The precipitated cellulose/CF composite spheres were formed, at the mean time, the pore forming agent was dissolved in

Table 1
The recipe of preparation (P-MCCBs).

Sample	MCCBs (g)	NIPAM (g)	KPS (g)	MBA (g)
P1-MCCBs	20	1	0.02	0.03
P2-MCCBs	20	2	0.04	0.06
P3-MCCBs	20	3	0.06	0.09

HCl solution. The as-prepared spheres (CCBs) were then washed with distilled water and acetone for several times and finally dried through a vacuum drying process.

The preparation of carbonylated CCBs (MCCBs) was reported in our previous work (Li et al., 2017). The polymer grafted MCCBs (P-MCCBs) were prepared by concurrent crosslinking and free radical polymerization of NIPAM on the MCCBs using a microwave-assisted heating technique. First, prior to make a uniform solution, the monomer NIPAM, the crosslinking agent MBA and initiator KPS were added and dissolved in distilled water by gently stirring. Different concentrations of NIPAM were applied by 5, 10, and 15% of the weight of MCCBs, respectively. The concentrations of MBA and KPS were 3% and 2% based on the weight of NIPAM; and the detailed information is shown in Table 1. After that, the dried MCCBs were soaked in the solution mentioned above. The adsorbents were saturated by shaking at 130 rpm using the shaker (SWB25, Thermo Electron Corporation, Germany). The excess solution was then removed, and the adsorbents were transferred into the baker containing paraffin oil and an emulsifier span 80. The spheres were fully dispersed by vigorous stirring and then transferred into the microwave reactor. The optimal conditions were used for the polymerization (70 °C and 100 w). With the polymerization at different time, the P-MCCBs composites were washed with excessive distilled water and finally with acetone several times. The sample-MCCBs were then dried using a vacuum-drier. The corresponding samples were named P1-MCCBs, P2-MCCBs, and P3-MCCBs according to the concentrations of NIPAM in the preparation.

2.3. Characterization

The samples were analyzed by Fourier transform infrared spectroscopy (FTIR). The test was carried out using NEXUS 470 spectrophotometer (Nicolet Thermo Instruments, Canada) from 500 to 4000 cm^{-1} with a detector at 1 cm^{-1} resolution and 16 scans per sample. Thermal property of the adsorbents was tested using a Thermogravimetric Analyzer (TGA, Q600, TA Instruments, USA). Approximately 10–15 mg of the adsorbents was used per test. The experiment was carried out under nitrogen flow of 100 $mL\ min^{-1}$ at a heating rate of 10 °C min^{-1} . Scanning electron microscopy (SEM, JEOL JSM-6400, Japan) was applied to show the morphological characterization. Samples were attached on the holder and being coated with gold before test. The measurement of bulk density was carried out by adding 1 g of each sample into a measuring cylinder accurately, and then the volume of the sample could be obtained. The bulk density was calculated by dividing the weight (g) with the volume (cm^{-3}) measured. The graft efficiency and weight gain were calculated by weighing the samples before and after polymerization. The graft efficiency could be obtained using the weight of the monomer consumed (g) divided by the weight of the monomer added (g).

2.4. Adsorption of MB and Pb^{2+}

To study the effects of shaking time, temperature, and pH systematically, the batch mode adsorption was carried out. The stock solutions (1000 $mg\ L^{-1}$ MB and Pb^{2+}) were prepared by adding a certain amount of MB and $Pb(NO_3)_2$ into the distilled water and the working solutions were obtained by diluting the stock solutions accurately. The procedures are as follows: 1 ± 0.0001 g MB and 1.5986 ± 0.0001 g Pb

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