Carbohydrate Polymers 136 (2016) 493–498

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Study on the sorption process of triclosan on cationic microfibrillated cellulose and its antibacterial activity

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ARTICLE INFO

Article history:
Received 6 August 2015
Received in revised form
18 September 2015
Accepted 19 September 2015
Available online 25 September 2015

Keywords:
Cationic microfibrillated cellulose
Triclosan
Sorption models
Functionalization
Antibacterial activity

ABSTRACT

Cationic microfibrillated cellulose (CMFC), as one kind of cellulose-based materials, is widely used in many fields. In this work, it was functionalized with a traditional antibacterial agent (triclosan, TCS). The sorption process of TCS onto CMFC was expressed by kinetic and isotherm models. The results showed that there was a high correlation coefficient ($R^2 > 0.9$) in the pseudo-second-order model and the isotherm models, indicating that CMFC had a good sorption capacity for TCS. The sorption type was chemisorption, and the reaction power was electrostatic interactions. The antibacterial activity of the assembled TCS/CMFC compound was tested by disk diffusion method, and it was found a higher antibacterial activity than CMFC alone (bigger inhibition zone diameters). Further, the functionalized TCS/CMFC compound was used in the fiber network during handsheets making, and it had a higher antibacterial rate than TCS alone (increase by 45.1% against *Escherichia coli* and by 54.8% against *Staphylococcus aureus*, respectively).

1. Introduction

Microfibrillated cellulose (MFC) is one kind of natural cellulose based materials. Due to its high surface energy, nano-scale dimensions, barrier properties and the ability to form a nanoporous network (Cha, He, & Ni, 2012; Jahan, Saeed, He, & Ni, 2011; Zaman, Xiao, Chibante, & Ni, 2012), MFC has been applied as a dispersion stabilizer, mechanical reinforce, and coating agent in film production, paper industry and manufacture of biocomposites (Andresen, Johansson, Tanem, & Stenius, 2006; Dutta et al., 2015; Shen, Song, Qian, Liu, & Yang, 2010; Siqueira, Bras, & Dufresne, 2010; Siró & Plackett, 2010). Recently, the antibacterial activities of these MFC-added products have been paid much attention. If MFC can be possessed antibacterial activity, the production processes of these antibacterial products (such as films, paper and plastics) can be achieved efficiently. Usually, the surface modification method is used to prepare antibacterial cellulose materials. For example, Martins et al. have assembled Ag nanoparticles on nanofibrillated cellulose for antibacterial paper products (Martins et al., 2012). Andresen et al. modified the surface properties of MFC by octadecyldimethyl (3-trimethoxysilylpropyl)-ammonium chloride (ODDMAC) to prepare nonleaching antibacterial films (Andresen et al., 2007). Compared with both antibacterial materials (Ag nanoparticles and ODDMAC), triclosan is cheaper and has more broad-spectrum and efficient antibacterial properties. Besides, cationic MFC not only has the properties of MFC, but also has the positive charge property, which can cause a good sorption ability to negative charge antibacterial agents (Zhu et al., 2014). Therefore, cationic MFC and TCS may be a good choice to prepare cellulose-based antibacterial agent.

The sorption isotherms, such as Langmuir and Dubinin–Radushkevich (D–R), are normally used to evaluate the sorption abilities of some adsorbents and to analyze the principles of different sorption processes. The surface properties, sorption mechanisms and affinities of the sorbents can be learned through the parameters which are obtained from those different models. Much important information could be provided for theoretical research and practical production (Khaled, El Nemr, El-Sikaily, & Abdelwahab, 2009). And the suitable model of the isotherm data can be used for process design (Ofomaja, 2008).

In this study, the sorption ability of TCS onto CMFC was evaluated by kinetic models and isotherm models. The sorption kinetic parameters of TCS sorption on CMFC were analyzed by pseudo-first-order and pseudo-second-order kinetic models to determine the sorption type between TCS and CMFC. Several isotherm models were chosen to analyze the sorption process of TCS on CMFC and to evaluate the sorption ability of CMFC to TCS. Furthermore, the antibacterial activity of TCS/CMFC compound was tested against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) to ensure that the antibacterial property of TCS was maintained after

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http://dx.doi.org/10.1016/j.carbpol.2015.09.060
0144-8617/

the sorption process. Finally, the antibacterial activities of handsheets, which were added TCS/CMFC compound, were tested by the developed Quine's method. All of these were to evaluate the sorption ability of CMFC to TCS, to verify the feasibility of preparing cellulose-based antibacterial agent (TCS/CMFC), and to determine the effectiveness of TCS/CMFC compound in fiber network.

2. Materials and methods

2.1. Materials

Cationic microfibrillated cellulose (CMFC) (charge density, 0.18 meq/g), in the form of water dispersion with 0.99 wt% content of dry CMFC, was prepared from the enzyme-treated hardwood sulfite-based dissolving pulp by chemical modification and high pressure homogeneous processing at Tianjin Key Laboratory of Pulp and Paper in China. More details regarding the CMFC can be learned in the published literatures (Zhu et al., 2014, 2015). Triclosan (99.0%) was obtained from a Tianjin Chemicals Company in China. Agar, beef extract and peptone were purchased from Tianjin local Chemicals Companies in China. Unbleached wheat straw pulp was provided by a pulp mill in Shandong province in China. Unless otherwise specified, the deionized water was used in all the experiments and other chemicals were analytical grade without further purification.

2.2. Methods

2.2.1. Sorption process of triclosan on CMFC

The data for the sorption process between TCS and CMFC were obtained following a published procedure (Hu, Zhao, & Wei, 2009). Firstly, the different amounts of TCS (4.0, 6.0, 7.6, 8.0, 8.4, 9.2, 10.0, 10.8 mg) were dissolved into 20 mL ethanol. Then, it was forwarded to 8.00 g (0.99 wt%) CMFC in a 250 mL Erlenmeyer flask following the addition of 60 mL deionized water, and the mixture was shaken at 20 °C and 200 rpm. Unless specified, the reaction time was fixed at 300 min. After that, 5 mL samples were taken from each Erlenmeyer flask and centrifuged at 15,000 rpm for 30 min. The filtrate was collected and analyzed by ultraviolet spectrophotometry. The sediments, marked as the TCS/CMFC compound, were washed and vacuum dried, following by the standard Fourier transform infrared spectrometer (FTIR) analysis (Liu, Lin, Chen, Huang, & Cao, 2014). The samples of CMFC and TCS were also prepared with potassium bromide for FTIR analysis. The amount of TCS adsorbed on CMFC in this sorption process can be calculated by Eq. (1).

$$q_e = \frac{[(C_0 - C_e) \times V]}{W} \quad (1)$$

where q_e (mg/g) is the amount of TCS adsorbed on CMFC, C_0 and C_e (mg/L) are the initial and equilibrium concentrations of TCS, respectively. V (mL) is the volume of whole reaction solution, and W (mg) is the oven dried mass of CMFC.

2.2.2. Antibacterial activity

The disk diffusion method was chosen to evaluate the antimicrobial activity of the TCS/CMFC compound, against the *E. coli* and *S. aureus* (Liu et al., 2013; Tang, Liu, Xia, Xue, & Wang, 2012). The TCS/CMFC compound from the procedure of sorption kinetics and the control (CMFC), were prepared into small compact discs. Then, the antibacterial activity of the samples was tested by disk diffusion method. First, 0.1 mL *E. coli* and *S. aureus* (10^5 CFU/mL) were inoculated on the beef-protein medium respectively, and then spread on the entire surface of the medium by sterile spatula. After that, the sample discs were placed onto the center of the beef-protein medium plates and the dishes were then kept in an incubator at 37 °C for 24 h. The inhibition zones around the discs, where no growth occurred, were measured in millimeters (Liu, Xu et al., 2014).

To determine the effectiveness of TCS/CMFC compound in fiber network, the developed Quine's method was chosen to measure the antibacterial activity of TCS/CMFC added handsheets and TCS added handsheets. A certain amount of TCS (0.2 mg/g, to oven dried fibers) was added directly into the handsheets during sheet-making as control, and the same amount of TCS was adsorbed by CMFC (16 mg/g, to oven dried fibers) under 20 °C and 200 rpm for 60 min before the TCS/CMFC compound was added into the handsheets. Then, these handsheets were cut into square chips (25 mm × 25 mm) and were tested against *S. aureus* and *E. coli* by the developed Quine's method. 0.5 mL *E. coli* and *S. aureus* (10^5 CFU/mL) were inoculated on the surface of experiment handsheet chips and the control group, respectively. Then, these chips were dried at 37 °C for 1 hr in a sterile environment. Subsequently, the dried chips were placed onto the center of the beef-protein medium plates and semisolid beef-protein medium were poured on the entire surface of these plates. The dishes were then kept in an incubator at 37 °C for 24 h. The amount of colonies on the square handsheets chips was counted, and the inhibition of the bacteria growth was calculated by the following equation:

$$AR = \frac{A_0 - A}{A_0} \times 100 \quad (2)$$

where AR is the abbreviation of antibacterial rate (%); A_0 is the area of whole square handsheet chips; and the value of A is the area of the colonies detected from the TCS added handsheets and TCS/CMFC added handsheets, respectively.

3. Results and discussion

3.1. Kinetic analysis of the TCS sorption on CMFC

In this study, in view of the high surface energy (Tang, Li, & Song, 2006) and positive charge of CMFC, pseudo-first-order and pseudo-second-order kinetic models (Ho, McKay, Wase, & Forster, 2000; Ofomaja, 2008; Tang, Li, & Chen, 2009) were used to determine the controlling mechanism of TCS sorption on CMFC.

Fig. 1 shows the sorption of TCS on CMFC as a function of time. Pseudo-first-order kinetic model was used to model the sorption process and was expressed as Eq. (3).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (3)$$

where q_e and q_t are the amounts of adsorbed TCS on CMFC (mg/g) at equilibrium and at reaction time t (min), respectively, k_1 (L/min) is the rate constant of pseudo-first-order kinetic model.

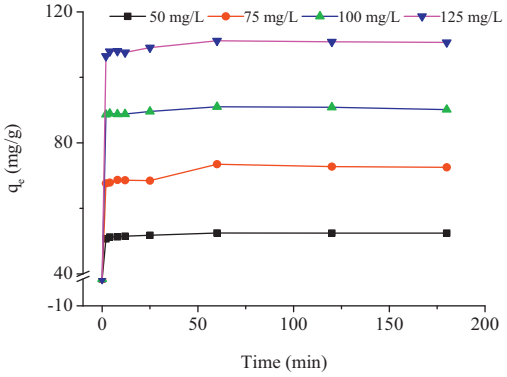

Fig. 1. Sorption of TCS on CMFC as a function of time (initial concentration of TCS in 50, 75, 100 and 125 mg/L).