Carbohydrate Polymers 163 (2017) 146–152

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Water-resistant cellulosic filter containing non-leaching antimicrobial starch for water purification and disinfection

Solmaz Heydarifard [a,b], Yuanfeng Pan [c,*], Huining Xiao [a,*], Mousa M. Nazhad [d], Oleg Shipin [e]

[a] Dept. of Chemical Eng., University of New Brunswick, Fredericton, NB, Canada
[b] Pulp and Paper Technology, Asian Institute of Technology, Bangkok, Thailand
[c] Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
[d] Pulp and Paper Center, The University of British Columbia, Vancouver, BC, Canada
[e] WHO Collaborating Centre for Water Supply, Asian Institute of Technology, Bangkok, Thailand

ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form 15 January 2017
Accepted 17 January 2017
Available online 20 January 2017

Keywords:
Cellulose foam paper
Water filter paper
Antibacterial
Guanidine polymer
Antibacterial thermoplastic starch
Viability of bacteria

ABSTRACT

Water-resistant cellulose foam paper was developed in this work in an attempt to improve the antimicrobial activity of cellulose foam paper for capture and deactivation of pathogenic microorganisms existed in water. Results indicated that the cellulose foam paper could significantly improve household water quality by incorporating guanidine-based polymer modified with starch or called antibacterial thermoplastic starch (ATPS) into fibre network in the presence of proper amount of fiber fines. Ring diffusion testing demonstrated that no ATPS diffused around or underneath of samples, verifying that cellulose foam filter added by ATPS were of non-leaching type. Furthermore, the viability of bacteria before and after filtering and the structure of cellulose foam paper were analyzed via fluorescence microscopy and scanning electron microscopy images. The findings further proved the effectiveness of antimicrobial cellulose foam in deactivating pathogens, *E.coli* in particular.

1. Introduction

Water is the main ingredient for survival of all life forms on earth. However, only less than 1% of the fresh water is drinkable and still at least one billion people around the world do not have access to potable and microbiologically safe purified water (Dankovich & Gray, 2011; Kumar et al., 2014). Annually, over 1.6 million of human being dies because of diarrhea from waterborne diseases. It is estimated that the lack of safe drinking water causes 6–60 billion cases of gastrointestinal illness per year (Cabral, 2010; Caslake et al., 2004). Generally, surface water and ground water are impacted by different contaminations. The presence of bacteria, Escherichia coli (*E.coli*) originated in fecal contamination in particular, is the main indication of water contamination. Owing to this increasing concern about global water borne diseases associated with drinking water, finding an affordable and suitable way of water treatment is of great importance (Jain & Pradeep, 2005; Smith, Gordon, Madani, & Stratton, 2005).

In today's technology, conventional water treatment methods are mostly chemically and operationally intensive, non-renewable, costly, time consuming and ineffective. Thus, there is a pressing need for cleaning water with effective, low cost and most importantly environmentally-friendly technique (Chong, Jin, Chow, & Saint, 2010; Cabral, 2010; Kumar et al., 2014). Water filtration is a promising technique for water purification. Water filtration membrane is a semipermeable membrane allows the fluid to pass through while holding back the particulate contaminants. The retention of the contaminants is accomplished within the porous media by different operations like sieving mechanism (Foglarova, Prokop, & Milichovsky, 2009; Huang & Paul, 2010; Zhang, Causserand, Aimar, & Cravedi, 2006). High water quality with easy maintenance, excellent filtration efficiency and low chemical sludge effluent are some noticeable advantages of water filtration process (Lee et al., 2000; Lee, Elam, & Darling, 2016; van Halem, van der Laan, Heijman, van Dijk, & Amy, 2009). Nowadays, most of water filtration membranes are made of synthetic polymers derived from non-renewable resources. Negative factors like climate change, many different environmental pollutants, reduction of oil resources give a rise to increase the demand of biodegradable products over non-renewable resources (Huck, Peldszus,

* Corresponding authors.
E-mail addresses: panyf@gxu.edu.cn (Y. Pan), hxiao@unb.ca (H. Xiao).

http://dx.doi.org/10.1016/j.carbpol.2017.01.063
0144-8617/

Haberkamp, & Jekel, 2009; Riggi, Santagata, & Malinconico, 2011; Ulbricht, 2006). Cellulose is one of the natural and most abundant renewable, biodegradable and compatible polymers, which can be a promising substitute for water filter due to its biocompatibility, easy fabrication into a variety of shapes with adjustable interconnecting porosity (Klemm, Heublein, Fink, & Bohn, 2005; Marques-marinho & Vianna-soares, 2013; Miyamoto, Takahashi, Ito, Inagaki, & Noishiki, 1989; Xing et al., 2010). In the current research, a novel cellulose derivative so called cellulose foam paper was developed and fabricated as water filter. 3D honeycomb structure, very high porosity, light weight, recyclable and very low cost of cellulose foam paper make it suitable for using as water filter. The main drawback of this material is its too low wet strength properties to use as water filtration membrane. Thus, the improvement of wet strength performance was reported previously (Heydarifard, Nazhad, Xiao, Shipin, & Olson, 2016).

Conventional water filter membranes not only lead to block the passage of deleterious solids, but also can trap some microorganisms inside the water (Kulikove & Zakharov, 2013). Very finely pored filter can be a promising way for capturing all microorganisms effectively. But, these membranes require high pressure drop and also have a short durability (Pall, Degen, Joffee, Foss, & Gsell, 1988). Hence, the research on using antimicrobial agents for improving the antimicrobial performance of water filtration membrane to repel and/or deactivate waterborne pathogenic microorganism has attracted tremendous interest. There are several compounds used as the antimicrobial agents for cellulose fibers in order to deactivate the waterborne microorganisms, such as phenols, halogens (e.g. iodine), heavy metals (e.g. silver nanoparticles (Mpenyana-Monyatsi, Mthombeni, Onyango, & Momba, 2012; Tankhiwale & Bajpai, 2009;), zinc oxide nanoparticles (Miao et al., 2014), copper (Vincent, Hartemann, & Engels-Deutsch, 2016) or gold (Qian, Pretzer, Velazquez, Zhao, & Wong, 2013)), phosphonium salts, and quaternary ammonium salts (Roy, Knapp, Guthrie, & Perrier, 2008) and cationic polymers especially guanidine-based cationic polymers (Wang, Wei, Zheng, & Xiao, 2015; Wei, Ziaee et al., 2015).

Guanidine-based polymers have been found a broad application in medicine, paper industry, water treatment and food and crop protection. Polyhexamethylene guanidine hydrochloride (PHGH) is one of the most representative guanidine-based polymers exhibits low mammalian toxicity and strong cytotoxicity toward both Gram negative and Gram positive bacteria, viruses and fungi. PHGH has too low molecular weight to apply directly on cellulose fibers due to poor stability and retention and easy volatility, thus modification of PHGH with starch enhance the polymer's molecular weight that ease the covalently attaching of PHGH on substrate without leaching and migration effects (Guan, Qian, Xiao, & He, 2008). PHGH modified starch or antibacterial-modified starch (ATPS) is a water-soluble antimicrobial polymer formed by grafting PHGH onto starch in the presence of an appropriate coupling agent. ATPS shows excellent antibacterial activity with theminimum inhibitor concentration (MIC) around 4–16 ppm (Wang, Wei, Zheng, & Xiao, 2015; Wei, Ziaee et al., 2015). The lethal function of ATPS is due to the irreversible cytological and physiological cell changes which culminate in the death of cell (Guan et al., 2008). Starch addition is not only affective for retention of antibacterial agent in the paper, but also in several articles it has been considered as fixative in paper dry strength (Balan, Guezennec, Nicu, Ciolacu, & Bobu, 2015; Lim, Liang, & Seib, 1992; Ulbrich, Radosta, Kießler, & Vorwerg, 2012).

The key objective of the current work was to develop the cellulose foam paper as antimicrobial water filter for water disinfection. To convert the conventional cellulose foam filter into an antibacterial one, the ATPS was added to pulp slurries as a functional wet-end additive prior to forming the cellulose foam filter. ATPS modified filter achieved excellent growth inhibition toward *E.coil*, especially when the foam pulp was combined with fiber fines.

2. Materials and methods

2.1. Materials

Commercially bleached Spruce Pine Fir (SPF) pulp sheet was obtained from Prince George Canfor Company in Canada. Fiber fines were obtained from refining of SPF pulp with specific energy of 1400 kwh/t by LC refiner. Cationic polyacrylamide (C-PAM) with high molecular weight was provided by Kemira Water Solution, Inc (Canada). Sodium olefin sulfonate (SDS) was purchased from Fisher Scientific (Canada). The corn starch was kindly provided by Ingredion (Montreal Canada). PHGH-modified starch or ATPS was prepared based on the procedures reported elsewhere (Wang, Wei, Zheng, & Xiao, 2015; Wei, Ziaee et al., 2015); and the number average molecular weight of was PHGH 720 Da.

For antibacterial tests, phosphate buffered saline (PBS) and LB Agar were purchased from Sigma-Aldrich. Escherichia coli (*E. coli*) bacteria (ATCC11229) were cultured at 37 °C in Agar solution prior to use. Fluorescein isothiocyanate (FITC) and propidium iodide (PI) as staining dyes were obtained from Sigma-Aldrich.

2.2. Fabrication of cellulose foam filter

To fabricate cellulose foam paper, pulp was diluted to 2000 mL (1.2% consistency) and disintegrated with a standard disintegrator (LABTEC Model 500-1) at 3000 rpm until fiber bundles are dispersed. The pulp was further diluted to 1% consistency. Then, 4 wt.% C-PAM (wt on dry fibre) and 6 wt.% SDS were added to pulp, and the pulp suspension was mixed using a mechanical stirrer (SCILOGEX OS20-S) at 2000 rpm for 20 min. Afterwards, a certain amount of foam pulp was poured into the Bückner funnel under the pressure 9.8 kPa and drained to remove the main portion of liquid and extra foam inside the foam pulp. The target air content and grammage of foam formed paper were set at 30% and 250 g/m^2, respectively. At last, the wet samples were dried at room temperature for 24 h.

2.3. Preparation of antibacterial foam paper

To render cellulose foam paper antibacterial, ATPS aqueous solution was added into the foam pulp suspension before draining with different dosages of 0.2, 0.5, 0.8, 1, 3, 5 wt.%. Fig. 1 shows the schematic of preparing antibacterial cellulose foam filter in sequence.

2.4. Assessment of cellulose foam filter antibacterial activity

The antibacterial activity of cellulose foam paper embedded with ATPS was tested against freshly cultured Escherichia coli (*E.coli*, ATCC 11229). For investigating the antibacterial susceptibility of the cellulose foam paper treated with ATPS, the bacterial pre-inoculum cultures were grown overnight at 37 °C in LB (Luria-Bertani) broth made of: 10 g/L casein enzymic hydrolysate, 5 g/L yeast extract and 10 g/L sodium chloride. Then, the antibacterial activity was checked using cellulose foam paper as water filter at gravity flow rate. A bulk solution of *E.coli* with the load of ~10^6 CFU/mL was prepared. The solution was passed through the cellulose foam paper samples treated with 0, 0.2, 0.5, 0.8, 1, 3, 5 wt.% PHGH-modified starch via wet-end addition, respectively. The cellulose foam paper without ATPS was used as a control. The bacterial solution (40 mL) was passed through the cellulose foam paper and output water samples were taken in sterilized conical flask. Then, the plating was performed with bacteria solution after filtering by serial dilution method for 10^5, 10^4, 10^3 and 10^2 CFU/mL with PBS