Chemosphere 167 (2017) 469–477

Contents lists available at ScienceDirect

Chemosphere

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

Antimicrobial filtration with electrospun poly(vinyl alcohol) nanofibers containing benzyl triethylammonium chloride: Immersion, leaching, toxicity, and filtration tests

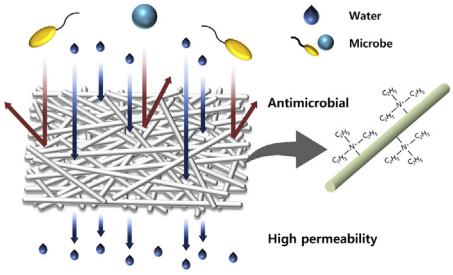
Jeong-Ann Park [a], Song-Bae Kim [b, c, *]

[a] Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
[b] Environmental Functional Materials and Water Treatment Laboratory, Seoul National University, Seoul 08826, Republic of Korea
[c] Department of Rural Systems Engineering/Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 08826, Republic of Korea

HIGHLIGHTS

- Antimicrobial BTEAC-PVA nanofibers were synthesized using electrospinning process.
- Water stability of BTEAC-PVA nanofibers was improved by heat-methanol treatment.
- Leached BTEAC was far below the toxicity level for *D. magna* immobilization.
- Bacteria removal could be enhanced by incorporation of BTEAC into PVA nanofibers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 May 2016
Received in revised form
22 September 2016
Accepted 10 October 2016
Available online 14 October 2016

Handling Editor: Jian-Ying Hu

Keywords:
Antimicrobial agent
Benzyl triethylammonium chloride
Electrospun nanofiber
Poly(vinyl alcohol)
Toxicity
Water filtration

ABSTRACT

Antimicrobial electrospun poly(vinyl alcohol) (PVA) nanofibers were synthesized by impregnating benzyl triethylammonium chloride (BTEAC) as an antimicrobial agent into PVA nanofibers. The BTEAC-PVA nanofibers were heat-methanol treated during the preparation for various tests. The BTEAC-PVA nanofibers became more hydrophilic than the PVA nanofibers due to incorporation of BTEAC. Through heat-methanol treatment, thermal property, crystallinity, and water stability of BTEAC-PVA nanofibers were improved considerably. The immersion test shows that heat-methanol treatment has an advantage over heat treatment to maintain BTEAC content in BTEAC-PVA nanofibers. The acute toxicity test demonstrates that the 24-h EC_{50} and 48-h EC_{50} values (EC_{50} = median effective concentration) of BTEAC to *Daphnia magna* were 113 and 90 mg/L, respectively. The leaching test indicates that the BTEAC concentration leached from BTEAC-PVA nanofibers was far below the concentration affecting the immobilization of *D. magna*. For antimicrobial filtration tests, the BTEAC-PVA nanofibers were deposited onto glass fiber filter. The antimicrobial filtration test was conducted against bacteria (*Escherichia coli*, *Staphylococcus aureus*) and bacteriophages (MS2, PhiX174), demonstrating that the BTEAC-PVA nanofibers could enhance the removal of *E. coli* and *S. aureus* considerably but not the removal of MS2 and PhiX174 under dynamic flow conditions.

1. Introduction

Electrospun nanofibers (ENs) are fabricated through electrospinning polymer solutions. ENs have been recently tested for

* Corresponding author. Environmental Functional Materials and Water Treatment Laboratory, Seoul National University, Seoul 08826, Republic of Korea.
E-mail address: songbkim@snu.ac.kr (S.-B. Kim).

http://dx.doi.org/10.1016/j.chemosphere.2016.10.030
0045-6535/

Nomenclature

a_n	apparent density of the nanofibers
b_n	bulk density of the polymer solution
BTEAC	benzyl triethylammonium chloride
EC_{50}	median effective concentration
ENs	electrospun nanofibers
GF	glass fiber filter
ΔH_f	heat (enthalpy) of fusion
J	pure water flux
LRV PC	log reduction value polycarbonate filter
PVA	poly(vinyl alcohol)
QACs	quaternary ammonium compounds
S	total permeation area
t	total permeation time
T_m	melting point
V	total permeation volume
X_c	degree of crystallinity

water filtration due to their high permeability with many small pores, interconnected pore structure, large surface to volume ratio, and flexibility (Jang et al., 2013; Nasreen et al., 2013; Homaeigohar and Elbahri, 2014). Water filtration application of ENs includes heavy metal removal, microbial removal, desalination, and filtration of organic materials/microparticles (Bazargan et al., 2011; Lev et al., 2012; Wang et al., 2012; Nasreen et al., 2013). Antimicrobial functionalized ENs are fabricated to enhance antimicrobial activity through incorporating antimicrobial agents into electrospun nanofibers (Nasreen et al., 2013). Polymers such as polyacrylonitrile (Zhang et al., 2011; Ma et al., 2012; Mei et al., 2012, 2014), polyamide (Bjorge et al., 2009; Daels et al., 2011; de Vrieze et al., 2012), polyvinylidene fluoride (Hong et al., 2013), polyurethane (Pant et al., 2014), and poly(vinyl alcohol) (PVA) (Gule et al., 2012; Adibzadeh and Bazgir, 2014; Mi et al., 2014; Dobrowsky et al., 2015) have been used for the synthesis of antimicrobial ENs for water filtration. Various antimicrobial agents such as silver (Ag) (Bjorge et al., 2009; Zhang et al., 2011; de Vrieze et al., 2012; Hong et al., 2013; Adibzadeh and Bazgir, 2014; Pant et al., 2014), quaternary ammonium compounds (QACs) (Daels et al., 2011; Dobrowsky et al., 2015), copper/zinc (Gule et al., 2012), graphene oxide (Hong et al., 2013), cellulose nanowhiskers (Ma et al., 2012), and polyhexamethylene guanidine hydrochloride (Mei et al., 2012, 2014) have been incorporated into electrospun nanofibers and evaluated for antimicrobial ENMs.

PVA has been widely used for the fabrication of antimicrobial nanofibers due to its inexpensiveness, biocompatibility, biodegradability, non-toxicity, and chemical/thermal stability, and obtained water stability through crosslinking (Linh et al., 2010; Liu et al., 2012; Rwei and Huang, 2012; Abbasizadeh et al., 2013; Gule et al., 2013). However, limited studies have been performed for the application of functionalized PVA ENs for antimicrobial water filtration (Gule et al., 2012; Adibzadeh and Bazgir, 2014; Dobrowsky et al., 2015). Gule et al. (2012) have prepared antimicrobial PVA ENs using AquaQure, which mainly contains copper and zinc ions, as an antimicrobial agent. During the fabrication of PVA/AquaQure ENs, heat treatment was used to enhance water stability of the ENs through crosslinking. The authors performed filtration tests to examine antibacterial efficiency (up to 5.0 log reduction) of PVA-AquaQure ENs against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, and *Salmonella typhimurium*. Adibzadeh and Bazgir (2014) have fabricated antimicrobial PVA/Chitosan ENs containing silver nanoparticles with heat treatment as a crosslinking method. The authors conducted antibacterial water filtration tests to determine the bacterial removal efficiency (1.5 log reduction) of PVA/Chitosan-Ag ENs against *E. coli*.

QACs are cationic surface-active agents. They are known to be most useful antiseptics and disinfectants with a broad spectrum of antimicrobial activity (McDonnell and Russell, 1999). QACs could be easily electrospun with PVA polymers (Kanazawa et al., 1993; Voigt, 2009; de Britto et al., 2011). Benzyl triethylammonium chloride (BTEAC) is a one of QACs (Gliścińska et al., 2012). During the electrospinning of nanofibers, BTEAC has been incorporated into polymer solution in two respects. The first is related to change the electrical conductivity and surface tension of the solution and to increase spinnability during the electrospinning of nanofibers (You et al., 2006; Wang et al., 2008; Arumugam et al., 2009; Seo et al., 2009; Tong and Wang, 2010; Lu et al., 2012; Suslu et al., 2014). The second concerns its use as an antimicrobial agent to enhance antimicrobial activity of electrospun nanofibers. BTEAC can be embedded as a biocide into the matrix of electrospun nanofibers (Kim et al., 2007; Daels et al., 2011). As membrane-active agents, QACs can adsorb onto the bacterial cell surface and disrupt the cytoplasmic membrane of bacteria, leading to the release of K^+ ions and other cytoplasmic constituents (Kawabata and Nishiguchi, 1988). The inactivation mechanisms of the unenveloped virus by QACs are not clear but are presumably related to the denaturation of the capsid (Hegstad et al., 2010). For the enveloped virus, which has a lipid layer around the nucleocapsid (nucleic acid + capsid), the inactivation mechanism is the release of the nucleocapsid due to the disruption of the viral envelope by QACs (Tsao et al., 1989).

In our previous study (Park and Kim, 2015), the BTEAC-PVA nanofibers were prepared through electrospinning to examine their antimicrobial characteristics using minimum inhibitory concentration, agar diffusion, intimate contact, and dynamic contact methods. The antimicrobial properties of BTEAC-PVA nanofibers were further investigated in this study through immersion, leaching, toxicity, and water filtration tests. Electrospun BTEAC-PVA nanofibers were prepared with heat-methanol treatment. The immersion test was performed for BTEAC-PVA nanofibers with no treatment, heat treatment, and heat-methanol treatment to evaluate the water stability of the nanofibers and to quantify the amount of BTEAC in the immersed nanofibers. The leaching test was performed to determine the releasing amount of BTEAC from the nanofibers. The acute toxicity test was conducted to examine the potential toxicity of BTEAC to *Daphnia magna*. The antimicrobial water filtration test was conducted to examine the removal of bacteria (*E. coli* and *S. aureus*) and bacteriophages (bacteriophages MS2 and PhiX174) from water by BTEAC-PVA nanofibers deposited onto glass fiber filter (GF).

2. Materials and methods

2.1. Fabrication of BTEAC-PVA nanofibers

PVA (M.W. = 85,000–124,000, 99% hydrolyzed) and BTEAC ($C_6H_5CH_2N(Cl)(C_2H_5)_3$) were purchased from Sigma Aldrich. A PVA solution (8 wt. %) was prepared by dissolving PVA powder in deionized water at 80 °C for 16 h and then cooling the solution at room temperature. The as-prepared PVA solution (8 wt%) was placed in a 25-mL syringe with a metal needle (inner diameter = 0.51 mm) that was connected to the positive terminal of a high-voltage power supply. The PVA nanofibers were collected on a rotating cylinder (diameter = 9 cm; speed = 1000 rpm) on a negative terminal. Electrospinning of PVA nanofibers was