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Novel AgNWs-PAN/TPU membrane for point-of-use drinking water electrochemical disinfection

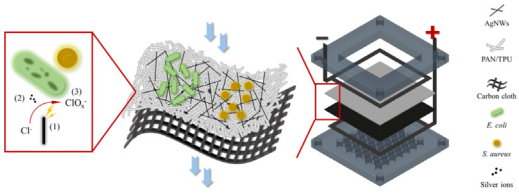
Xiaojun Tan [b,c], Chao Chen [b,c], Yongyou Hu [a,b,*], Junjie Wen [b,c], Yanzhe Qin [a,b], Jianhua Cheng [a,b], Yuancai Chen [a,b]

[a] School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China
[b] The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China
[c] School of Civil Engineering and Transportation, South China University of Technology, Guangzhou 510640, PR China

HIGHLIGHTS

- The AgNWs-PAN/TPU membrane achieved a complete removal of bacteria by filtration.
- The AgNWs-PAN/TPU membrane showed an excellent disinfection efficiency.
- Electrochemical disinfection achieved total inactivation in 20 min under 1.5 V.
- This disinfection voltage could be applied with commercially available dry cells.

GRAPHICAL ABSTRACT



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ABSTRACT

The safety of drinking water remains a major challenge in developing countries and point-of-use (POU) drinking water treatment device plays an important role in decentralised drinking water safety. In this study, a novel material, i.e. a silver nanowires-polyacrylonitrile/thermoplastic polyurethane (AgNWs-PAN/TPU) composite membrane, was fabricated via electrospinning and vacuum filtration deposition. Morphological and structural characterisation showed that the PAN/TPU fibres had uniform diameters and enhanced mechanical properties. When added to these fibres, the AgNWs formed a highly conductive network with good physical stability and low silver ion leaching (<100 ppb). A POU device equipped with a AgNWs-PAN/TPU membrane displayed complete removal of 10^5 CFU/mL bacteria, which were inactivated by silver ions released from the AgNWs within 6 h. Furthermore, under a voltage of 1.5 V, the bacteria were completely inactivated within 20–25 min. Inactivation efficiency in 5 mM NaCl solution was higher than those in Na_2SO_4 and $NaNO_3$ solutions. We concluded that a strong electric field was formed at the AgNW tips. Additionally, silver ions and chlorine compounds worked synergistically in the disinfection process. This study provides a scientific basis for research and development of silver nanocomposite membranes, with high mechanical strength and high conductivity, for POU drinking water disinfection.

1. Introduction

In developing countries, unsafe drinking water supply has caused high morbidity and mortality. According to 2017 WHO data, about 800,000 people, most of them are children in low-income countries, die of diarrhoea each year, and pathogens in water are the major causative agent (World Health Organization (WHO), 2017). The

* Corresponding author at: School of Environment and Energy, South China University of Technology, Guangzhou 510006, China.
E-mail address: ppyyhu@scut.edu.cn (Y. Hu).

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contamination of drinking water by pathogens occurs through several channels: (a) drinking water is obtained from surface water without further treatment, (b) leakage and contamination of the water pipe network, and (c) long-term storage of water in remote areas is easily contaminated (Clasen and Bastable, 2003). Therefore, disinfection of drinking water is critical and there is an urgent need to develop highly efficient terminal disinfection materials and techniques.

Point-of-use (POU) drinking water treatment is an inexpensive, self-sustaining, and decentralised method that can be combined with membrane filtration, thermal disinfection, and chemical disinfection techniques (Sobsey et al., 2008; Lui et al., 2014; Lui et al., 2016). Among them, POU devices with membrane filtration technology are the most widely used, as they do not require bleach nor produce disinfection by-products (DBPs) (Hunter, 2009; Fan et al., 2018). In recent years, electrochemical disinfection has also been developed as a promising alternative disinfection method. It destroys a wide variety of microorganisms rapidly and effectively. Moreover, it is low-cost and simple (Kerwick et al., 2005). Thus, electrochemical POU devices could be a promising terminal sterilisation technology.

Electrochemical POU electrode materials include stainless steel, platinum, and platinum-plated electrodes (Jeong et al., 2007), boron doped diamond (BDD) electrodes (Schmalz et al., 2009), activated carbon (Racyte et al., 2013), and carbon cloth (Matsunaga et al., 1992). Recent efforts have focused on developing electrode materials with improved efficiency and a combination of conductive, electro-oxidation, and adsorption properties. For example, a conductive nanosponge electrode (Liu et al., 2013), flake graphite intercalation compound adsorbent (Hussain et al., 2014), and Ti_nO_{2n-1} ceramic reactive electrochemical membrane electrode (Guo et al., 2016) were fabricated and evaluated for electrochemical disinfection. These novel materials exhibited disinfection effects at a lower voltage (<10.0 V), and the devices mentioned above demonstrated electrochemical disinfection that combined adsorption and filtration. Nevertheless, precursors of DBPs are produced in redox reactions of electrode materials. Some of these precursors, such as hypochlorous acid and hypochlorite, play a role in oxidation and increase disinfection efficiency (Jeong et al., 2006). Carcinogens such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) were generated through the reactions between DBP precursors and organic matter in water (Sadiq and Rodriguez, 2004; Doederer et al., 2014; D. Liu et al., 2016). The production of DBP precursors is impacted by the electrode materials, applied voltages, and electrolytes used. Hence, to control the production of DBP precursors, it is necessary to explore efficient disinfection with new electrode materials at low voltage to prevent the production of DBPs. Furthermore, in previous study, electrochemical disinfection devices required a continuous power supply, which increased operation costs. In this study, antibacterial nanofibres were included in the electrochemical disinfection system, achieving the function of entrapment and inactivation of bacteria even in the absence of an applied electric field.

Membranes with controllable porous structures have been successfully fabricated via electrospinning and used as an antibacterial substrate (Greiner and Wendorff, 2007). Given their excellent physicochemical stabilities, polyacrylonitrile (PAN) (Inagaki et al., 2012) and polyurethane (PU) (Chattopadhyay and Webster, 2009) are commonly used materials for filter membranes. In recent years, studies have shown that silver nanowires (AgNWs) have excellent optical properties, mechanical flexibility, and antibacterial properties (De et al., 2009; Sun, 2010). AgNWs provide increased numbers of binding sites for supporting materials (Schoen et al., 2010), conductive paths (Xu et al., 2015), as well as sustained release of silver ions from their tips (Scanlan et al., 2013). In addition, studies showed that under the applied voltage, silver ions were released from the tips and high charges accumulated at the tips, which is favourable for inactivation of microorganisms (Zhao et al., 2016). In our previous research on effective POU electrochemical disinfection systems for drinking water treatment, we synthesised and investigated a AgNWs-CC (silver nanowires carbon fibre cloth) nanocomposite (Hong et al., 2016a) and a PAN/PANI/AgNWs-CC (polyacrylonitrile/polyaniline/silver nanowires carbon fibre cloth) composite nanofibre membrane (Wen et al., 2017). The inactivation rate of bacteria of the AgNWs-CC nanocomposite was 99.999% at a voltage of 10.0 V. The PAN/PANI/AgNWs-CC composite nanofibre membrane achieved a similar rate at only 3.0 V, as it could completely retain the bacteria and displayed higher conductivity. However, the PAN/PANI/AgNWs-CC membranes were prepared by blending silver nanowires into electrospun substrates via co-electrospinning, that is, silver nanowires were encapsulated in nanofibres, and their electrical conductivity, tip electroporation, and release of silver ions were limited. Therefore, the emphasis of the current research was to remove these restrictions and improve the performance of electrochemical POU disinfection devices with silver nanomaterials.

We fabricated a hybrid nanofibre membrane using polyacrylonitrile (PAN) and thermoplastic polyurethane (TPU) via electrospinning, and then embedded AgNWs on the surface of the electrospun nanofibres through vacuum filtration deposition. Field emission scanning electron microscopy (FESEM), dynamic mechanical analysis (DMA), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and graphite furnace atomic absorption spectrometry (GFAAS) were used to analyse the physicochemical properties of the hybrid membrane. An electrochemical POU device was built with a AgNWs-PAN/TPU composite membrane. The effects of voltage, bacterial concentration, and salt solution were investigated to evaluate the membrane filtration and electrochemical disinfection performance. The mechanism of electrochemical disinfection and the strategy of reducing the precursors of DBPs are discussed in terms of the relationships among the release of silver ions, the change in surface morphology of the bacteria, and the precursors of DBPs. The purpose of this study is to provide a scientific basis for research and development of silver nanocomposites and the application of electrochemical POU devices with high efficiency and low consumption.

2. Materials and methods

2.1. Materials and chemicals

PAN with an average molecular weight (MW) of 150,000 was obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). TPU with an average Mw of 10,000 was purchased from BASF Polyurethane Specialties Co. Ltd. (Germany). 10 mg/mL AgNWs (diameter ~60 nm, length ~20 μm) dissolved in *N*,*N*-dimethylformamide (DMF) were acquired from Wei Xi New Materials & Technology Company (Changsha, China). Gram-negative *Escherichia coli* (*E. coli*, ATCC 25922) and gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC 6538) were obtained from the American Type Culture Collection (ATCC, USA). All chemicals used in the study were of analytical grade.

2.2. Preparation of PAN/TPU electrospun nanofibres

PAN was dissolved in DMF at 80 °C and magnetically stirred for 1 h. Then, TPU was added to the PAN solution and mixed via magnetic stirring at room temperature (~25 °C) for 12 h to acquire a homogeneous 10 wt% PAN/TPU electrospun solution. The blend ratios of PAN/TPU were 3:1, 2:2, and 1:3.

The electrospinning process was carried out using the Nanospider NS-200S electrospinning lab unit (Elmarco, Liberec, Czech Republic). The polymer solution was placed in the carriage containing the active electrode parallel to the collecting electrode. Then, the spinning solution was delivered 220 mm from the active electrode to the collecting electrode by applying a voltage of 70 kV, with the carriage moving at a speed of 200 mm/s, and the relative humidity and temperature at 35–45% and ~25 °C, respectively. The fibres were collected on a