Materials Science and Engineering C 48 (2015) 179–187

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Silver nanoparticle-doped zirconia capillaries for enhanced bacterial filtration

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ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 17 October 2014
Accepted 1 December 2014
Available online 3 December 2014

Keywords:
Ceramic capillary membrane
Macroporous
Immobilized silver nanoparticles
Bactericide membrane surface
Silver leaching

ABSTRACT

Membrane clogging and biofilm formation are the most serious problems during water filtration. Silver nanoparticle (Ag_{nano}) coatings on filtration membranes can prevent bacterial adhesion and the initiation of biofilm formation. In this study, Ag_{nano} are immobilized via direct reduction on porous zirconia capillary membranes to generate a nanocomposite material combining the advantages of ceramics being chemically, thermally and mechanically stable with nanosilver, an efficient broadband bactericide for water decontamination. The filtration of bacterial suspensions of the fecal contaminant *Escherichia coli* reveals highly efficient bacterial retention capacities of the capillaries of 8 log reduction values, fulfilling the requirements on safe drinking water according to the U.S. Environmental Protection Agency. Maximum bacterial loading capacities of the capillary membranes are determined to be 3×10^9 bacterial cells/750 mm^2 capillary surface until back flushing is recommendable. The immobilized Ag_{nano} remain accessible and exhibit strong bactericidal properties by killing retained bacteria up to maximum bacterial loads of 6×10^8 bacterial cells/750 mm^2 capillary surface and the regenerated membranes regain filtration efficiencies of 95–100%. Silver release is moderate as only 0.8% of the initial silver loading is leached during a three-day filtration experiment leading to average silver contaminant levels of 100 μg/L.

1. Introduction

Water purification technologies play an important role in reducing the risk of the dissemination of waterborne diseases or epidemic outbreaks that are caused by pathogenic microorganisms and viruses. Bacteria such as pathogenic serovars of *Salmonella* and *Vibrio cholerae* are responsible for severe diseases such as typhoid fever and cholera, and *Escherichia coli* serves as an important indicator organism for fecal contaminations. Today, more than 250 serotypes of *E. coli* are known ranging from harmless gut commensals to severe pathogens [1], such as the virulent enterotoxigenic (ETEC), enteropathogenic (EPEC), and enterohemorrhagic (EHEC) *E. coli*. Furthermore, viral infections can be spread via drinking water contaminations and highly infectious diseases are for example hepatitis A, poliomyelitis caused by the poliovirus or the severe acute respiratory syndrome (SARS) which is caused by the coronavirus.

Because bacterial contaminations in drinking water are nowadays the main reason for most of the upcoming diseases [2], the removal and inactivation of pathogenic coliforms and other microorganisms are therefore a field of great interest for both, industries and local authorities. These institutions are obliged to fulfill the requirements on water containing 0 fecal and total coliform counts in 100 mL of water intended for drinking [3]. Hence, small-sized water filtration systems that can be easily transported and provide sufficient amounts of purified water are of global interest [4].

Different filtration materials have been described for the use in water purification, such as polymeric materials like cellulose acetate (CA) [5], polysulfone (PS) [6], polyacrylonitrile (PAN) [7] or polyvinylidene fluoride (PVDF) [8], while polyethersulfone (PES) is the most commonly used material for membrane applications [9]. In contrast to polymeric filter materials, ceramics feature outstanding positive properties because they are usually bio-inert, do not undergo swelling, are chemically and thermally stable, and withstand high mechanical stress enabling the cleaning and reuse of the filter after heat or acid/base treatment for decontamination [10,11]. These excellent properties result in an increased membrane service life compensating the higher costs of ceramics in comparison to polymeric materials.

The most common problem during bacteria filtration is the formation of biofilms on the membrane surface leading to pore clogging and consequently, a reduction of the filter performance is given. These clustered bacterial communities are attached to the membrane surface and protect themselves against environmental influences. Bacteria produce extracellular polymeric substances (EPS) to form complex macroscopic

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http://dx.doi.org/10.1016/j.msec.2014.12.001
0928-4931/

structures that increase their resistance against e.g. toxic chemicals and antimicrobial agents. The removal of biofilms from the membrane surface is challenging and results in both cost- and time-intensive membrane regeneration procedures. Therefore, the reduction of the initial physical attraction of bacteria to the membrane surface, which can be attributed to a reversible attachment [1], plays a key role in inhibiting the formation of biofilms and several antibacterial surfaces have already been proposed [12,13]. Especially, immobilized nanosilver can act as an efficient antibacterial agent by killing retained bacteria directly on the membrane surface.

The decoration of filtration membranes with nanomaterials [14] have come into spotlight for water decontamination, catalysis and environmental remediation exploiting their unique surface chemical activities. Though the use of silver as an antimicrobial agent is known for about 7000 years [15], upcoming with the urgent need to eradicate antibiotic-resistant bacteria and with new insights into the mechanism of action [16], the use of silver has regained an emerged interest along with new interesting fields of applications [17]. Silver displays a broad antibacterial spectrum against Gram-positive and -negative bacteria [18] and nanosilver is one of the safest and mildest antibacterial agents for mammalian cells [19].

In recent years, silver nanoparticles (Ag_{nano}) have been embedded into various materials to generate antibacterial composites [20–23] and especially polymeric nanocomposite membranes are produced for water filtration purposes [6,14,24–27], since nanoparticles feature advantages in comparison to bulk silver: i) very small amounts of silver are needed due to the high specific surface area of silver nanoparticles, ii) when compared to silver ions, the bactericidal effect of Ag_{nano} is long-lasting because zerovalent (metallic) Ag_{nano} are not inactivated by complexation and precipitation [28] and iii) a controllable release of Ag^+-ions from the particles [29] compose them a cost-effective material for surface coatings. Most of the studies investigated the antibacterial properties of the nanocomposite membranes by describing the effect of the physical contact between silver nanoparticles and bacterial cells, but experiments were not performed under filtration conditions with special focus on antibacterial efficiency and silver leaching [27].

In our study, we present an advanced water filtration system based on ceramic capillary membranes which are subsequently doped with Ag_{nano}. Using zirconia as the membrane material and Ag_{nano} as the bactericidal coating, we combine a promising filtration material exhibiting high fracture toughness and bending strength with a highly effective antibacterial agent. Pore sizes of the capillary membrane of less than 0.2 μm and high open porosities of 51% enable the retention of bacterial cells during filtration [30]. Generated by direct reduction of silver nitrate on the membrane surface, immobilized Ag_{nano} display a bactericidal surface that kills filtrated bacteria directly on the membrane surface. Filtration experiments were performed by applying intracapillary feeding with bacterial suspensions and bacterial retention after different filtration times was determined using microbiological methods. The viability of retained bacteria was analyzed to evaluate the bactericidal action of immobilized Ag_{nano} and silver leaching during filtration was determined to consider eco-toxicological requirements.

2. Materials and methods

2.1. Preparation of Ag_{nano}-doped zirconia capillaries

Zirconia capillary membranes were fabricated by extrusion and sintered at 1050 °C for 2 h as described in our previous study [30]. As shown in Fig. 1, Ag_{nano} were immobilized on the membrane surface by a two-step immersion procedure according to the Creighton method [31] by direct reduction of silver ions on the surface of the capillaries. Capillaries featured an outer diameter (D_O) of 1.48 ± 0.01 mm, an inner diameter (D_I) of 0.90 ± 0.01 mm and an average wall thickness of 0.29 mm ± 0.01 mm. For all further tests, capillary pieces of 25 mm length were used which is in accordance with a weight of 82.9 ± 0.7 mg and a geometric surface area of 189 mm^2, except for the filtration experiment where 100 mm capillaries were applied (geometric surface area of 750 mm^2).

For the immobilization of Ag_{nano} one sintered capillary with a length of 25 mm was immersed in 2 mL silver nitrate ($AgNO_3$) solution (Sigma Aldrich, Germany, product number 209139) with varying concentrations from 2.5 to 10 mM at 25 °C and shaken at 1000 rpm for 5 min (pH was not adjusted). For the reduction of the immobilized silver ions, capillaries were subsequently immersed in 2 mL sodium borohydrate ($NaBH_4$) (Sigma Aldrich, Germany, product number 209139) for further 5 min. The reduction of the pre-immobilized silver ions was performed using a constant concentration of 2 mM $NaBH_4$. Prior to use, the $NaBH_4$ solution was stirred for 30 min at 25 °C followed by a cooling step to 4 °C without adjusting the pH. The number of immersion steps was varied between 1, 3, 5 and 10. Afterwards, the capillaries were washed twice in 15 mL of ddH_2O under shaking at 1000 rpm

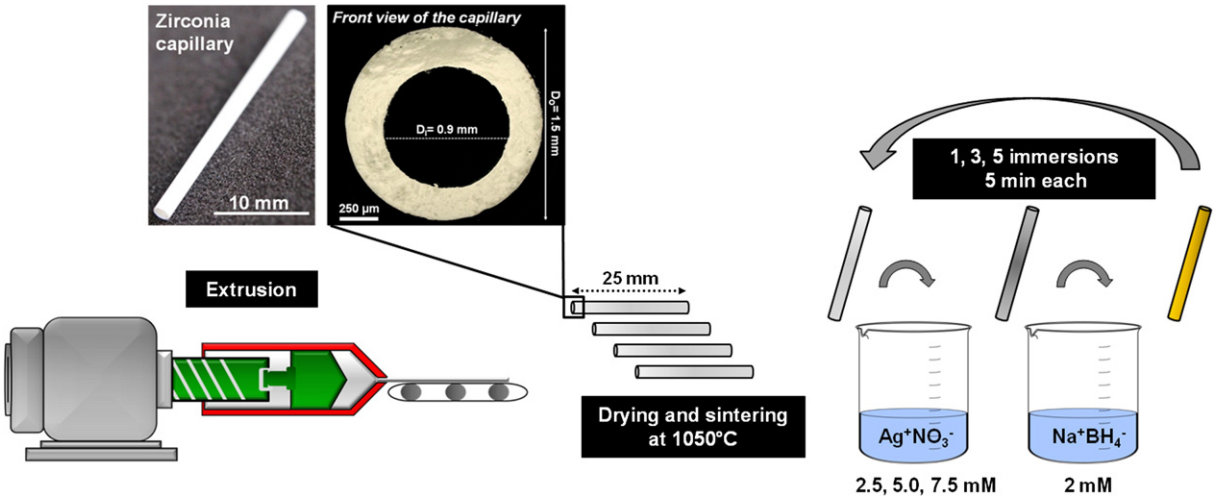

Fig. 1. Synthesis of zirconia capillaries by extrusion and immobilization of Ag_{nano} by reduction of $AgNO_3$ using $NaBH_4$. Zirconia capillaries with an outer diameter (D_O) of 1.48 ± 0.01 mm, an inner diameter (D_I) of 0.90 ± 0.01 mm and an average wall thickness of 0.29 mm ± 0.01 mm were fabricated by extrusion. The extruded capillaries were dried at room temperature for 2 days and the obtained green parts were sintered at 1050 °C for 2 h. Silver ions were directly reduced on the surface of the capillary membranes by immersion in $AgNO_3$ solution with varied concentrations and subsequently reduced in $NaBH_4$ at a constant concentration of 2 mM. This two-step immersion procedure was repeated 1–5 times to obtain adequate silver loading capacities.