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Production of ceramic membranes with different pore sizes for virus retention

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ABSTRACT

Porous ceramic capillary membranes made of yttria-stabilised zirconia (YSZ) are presented, which are conditioned for virus filtration by varying the initial YSZ particle size. Compared to polymeric membranes, ceramic membranes offer remarkable advantages for filtration processes as they show excellent chemical, thermal and mechanical stability and can easily be cleaned by backflushing. YSZ powders with different particle sizes (30 nm, 40 nm and 90 nm) are individually and mixed processed by extrusion, dried and finally sintered at 1050 °C for 2 h. The sintered YSZ capillaries are characterised by microstructural analysis including Hg-porosimetry, BET analysis and 3-point bending tests. By increasing the initial YSZ particle size, increased average membrane pore sizes ranging from 24 nm to 146 nm are obtained. Mechanically stable membranes are provided showing high open porosities of ~45% and ~36% for capillaries composed of single and mixed YSZ powders, respectively. By increasing the membrane pore size, reduced virus retention capacities in combination with increased water permeate fluxes are achieved. Capillaries made of YSZ-40 nm ensure both, log reduction values (LRV) ≥ 4 for small model bacteriophages MS2 and PhiX174 and high water permeate fluxes (~30 L/(m^2 hbar)), being suitable for sustainable virus filtration as requested by the World Health Organisation (WHO) and the United States Environmental Protection Agency (USEPA). Due to long-term virus filtration for two weeks, membrane pore plugging is successfully avoided by iterative backflushing and relatively high membrane fluxes in combination with requested LRV 4 level fulfilling the virus filter criterion are achieved.

1. Introduction

Water is essential to life, but today, 783 million people still have an inadequate access to clean drinking water [1]. Especially in developing countries, an access to safe drinking water and sanitation is not ensured, e.g. for 46% of the population in Oceania and 39% of the population in Sub-Sahara Africa [1,2]. According to the World Health Organisation (WHO), 1.8 million people die annually from diseases such as diarrhoea, cholera and dysentery transmitted through polluted water [3,4].

The three main contaminations for water pollution are of chemical (e.g. heavy metals, organic and inorganic species), physical (e.g. colour) and biological (e.g. bacteria and viruses) origin [5]. The biological pollutants are the most frequent and deadly contaminations in the drinking water of developing countries, because waterborne diseases are mainly caused by viruses (e.g. adenovirus, enterovirus, rotaviruses, hepatitis A and E virus) and bacteria (e.g. *Vibrio cholerae*, *Escherichia coli*, *Salmonella enterica*) [2,5,6].

Nowadays, water disinfection methods to inactivate viruses are based on physical or chemical processes. Conventional methods to inactivate viruses in water are heat treatment techniques, chemical treatments using free chlorine or chlorine dioxide, and the application of ozone or UV-irradiation. Especially for heat and chemical treatments, a virus inactivation can be achieved, but high costs and the potential production of toxic disinfection by-products (DBPs) are given at the same time. Ozone treatments and UV-irradiations can induce virus inactivation, but high investment costs and trained personal are required [7–11].

A promising alternative for water disinfection is the filtration which is based on removing suspended solids from a fluid by passing it through a permeable fabric (e.g. membranes). Filtration is based on size exclusion effects and therefore, contaminants which are larger than the membrane pore size can be effectively retained [12,13]. A virus removal using ceramic filters made of raw materials (e.g. diatomaceous earth) or chemically synthesised ceramics (e.g. zirconia) is possible as shown by several authors [14–16]. To ensure a high virus removal even for pore sizes larger than the viruses a pretreatment by coagulation/flocculation was performed by other authors [17–20]. Beside size exclusion methods particularly functionalised ceramic particles (e.g. amino-silanised)

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and ceramic components (e.g. MgO-doped, colloidal zirconia) are applied for virus adsorption to enhance the virus titre reduction. [21–23]

Today, polymeric membranes possess high water permeate fluxes combined with required high virus retention levels [24,25]. Compared to polymeric membranes, ceramic membranes show excellent chemical, thermal and mechanical stability. The importance of porous ceramic membranes is increasing in water purification, because monomodal and narrow pore size distributions in the meso- and macroporous range can be tailored depending on applied processing parameters (e.g. initial ceramic particle size, shaping technique, drying and sintering conditions). Because of their high mechanical strength ceramic membranes can withstand high pressure loads and therefore, they are able to endure high water permeate flux rates. Another advantage of ceramic membranes is that they can easily be cleaned by backflushing, thermal, acidic or basic treatment without affecting the pore morphology [26]. In addition, ceramic membranes do not show any swelling behaviour during water filtration maintaining their structural compactness. In contrast to polymeric membranes, the production costs of ceramic membranes are 3 up to 5 times higher, but this can be compensated by their longer lifetime of up to ten years instead of one year for polymeric membranes [27]. Further disadvantages of ceramic membranes are their brittle behaviour and higher material weight compared to polymeric membranes [28].

For a highly efficient virus filtration it is necessary that a reliable pore size of the membrane of less than or equal to virus size is provided to act as a mechanical filter based on size exclusion principle. Viruses are the smallest pathogens and have diameters between 20 and 300 nm [6]. Therefore, virus removal can be attained by ultrafiltration showing pore sizes in the range between 2 and 100 nm, that is, mesoporous and lower macroporous range [29]. To ensure high virus removal capacities, pore sizes less than the virus are preferred leading to low water permeate fluxes [15,30,31]. Based on the guidelines from WHO and United States Environmental Protection Agency (USEPA) a log-reduction value of 4 (i.e. at least 99.99 percent (4-log) removal) is required to fulfil the virus filter criterion providing safe and clean drinking water. The generation of tubular ceramic membranes offering both, a reliable cut-off for virus retention in combination with high open porosities and water permeate fluxes, is challenging and requires in-depth knowledge of the whole processing route.

The aim of this work is to extrude yttria-stabilised zirconia (YSZ) capillaries for virus filtration that feature ideally pore sizes and porosities for realising high virus retention capacities of LRV $\geq$4 in combination with high water permeate fluxes. YSZ was chosen because of its high fracture toughness and strength compared to other ceramic oxide materials (e.g. alumina). The effect of initial YSZ powders showing different particle sizes on the membrane microstructure (pore size, open porosity, specific surface area), mechanical stability (bending strength) and water permeate flux were analysed in detail. Virus retention capacities of the extruded and finally sintered capillary membranes were determined by virus filtration tests in dead-end mode using two small bacteriophages, MS2 and PhiX174, which served as surrogates for human pathogenic viruses. Finally, long-term virus filtration tests for two weeks were performed applying iterative backflushing to control the membrane fouling.

2. Materials and methods

2.1. Materials

The yttria-stabilised zirconia (YSZ) powders and reagents were purchased from commercial sources and used as received. Three different YSZ powders were used: VP Zirkonoxid 3-YSZ (YSZ-30 nm, Lot. 3157061469, specific surface area = 40 ± 15 m^2/g, particle size < 30 nm) was purchased from Evonik Industries, Germany, TZ-3Y-E (YSZ-40 nm, Lot. Z302131P, specific surface area = 16 ± 3 m^2/g, particle size = 40 nm) and TZ-3YS-E (YSZ-90 nm, Lot. S300886P, specific surface area = 7 ± 2 m^2/g, particle size = 90 nm) were obtained from Krahn Chemie GmbH, Germany.

3-Aminopropyltriethoxysilane (APTES, 99%, product number 440140, Lot. SHBC8357V), magnesium chloride hexahydrate ($MgCl_2$, product number M2670, Lot. BCBJ3659V), polyvinyl alcohol (PVA, fully hydrolysed, product number P1763, Lot. SLBC9027V), sodium chloride (NaCl, product number S7653, Lot. SZBC2560V), tryptic soy agar (TSA, product number 22091, Lot. BCBG4777V) and culture media tryptic soy broth (TSB, product number T8907, Lot. 109K0165) were obtained from Sigma–Aldrich Chemie GmbH, Germany.

For virus retention tests we used the bacteriophage MS2 (DSM Cat. No. 13767) and its host bacteria *E. coli* (DSM Cat. No. 5210) as well as the bacteriophage PhiX174 (DSM Cat. No. 4497) and its host bacteria *E. coli* (DSM Cat. No. 13127) from German Collection of Microorganisms and Cell Cultures (DSMZ), Germany.

All experiments were carried out using double-deionised water with an electrical resistance of 18 MΩ, which was obtained from a Synergy® apparatus (Millipore, Germany).

2.2. Characterisation of YSZ powders

The particle properties of three different YSZ powders, namely VP Zirkonoxid 3-YSZ (YSZ-30 nm), TZ-3Y-E (YSZ-40 nm) and TZ-3YS-E (YSZ-90 nm), were characterised determining the particle size distribution, density, specific surface area and zeta-potential. Particle size distributions and average particle sizes (d_{50}-values) were determined by acoustic spectroscopy (DT 1200, Dispersion Technology) using ceramic suspensions containing 1 vol.% particles. An ultrasonic treatment was applied for 10 min at 240 W with a pulse rate of 0.5 s (ultrasonic finger, Branson Sonifier 450, Heinemann, Germany) to deagglomerate the YSZ powders before the measurement. The acoustic spectroscopy was taken out at pH 3 to ensure a particle rejection, because YSZ has an isoelectric point (IEP) in the neutral to low basic pH range (IEP_{YSZ} = ∼7–9) [32].

Additionally, transmission electron microscopy (TEM, FEI Titan 80/300) was performed to estimate the particle size and morphology. The density of the three different YSZ powders was analysed by helium pycnometry (Pyconmatic ATC, Porotec). The specific surface area was obtained by nitrogen adsorption according to BET method (BELSORP-Mini, BEL Japan Inc.) after degassing the YSZ powders using argon for at least 3 h at 120 °C followed by flushing with dry argon. Zeta-potential measurements (DT 1200, Dispersion Technology) with suspensions containing 1 vol.% particles were performed to determine the IEPs of the YSZ powders. The pH titration was carried out with an integrated titration unit using 1 M HCl or 1 M KOH.

2.3. Fabrication of YSZ capillaries by extrusion

Fig. 1 shows the processing route for the fabrication of YSZ capillaries by extrusion. The fabrication is divided into four main parts involving slurry preparation, shaping by extrusion process, drying of the extruded capillaries and finally, sintering of the obtained green capillaries.

2.3.1. Slurry preparation

As shown in Fig. 1, four components were used to prepare the ceramic slurry: YSZ powder as ceramic material, APTES as dispersant, PVA as binder and double-deionised water as solvent. As already described by Qui et al., PVA was used because of the low