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Micro-structured alumina hollow fibre membranes – Potential applications in wastewater treatment

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ABSTRACT

In this study, three types of micro-structured alumina hollow fibre membranes, i.e. Membranes I, II, and III, have been developed and characterised for potential use in wastewater treatments. They consist of two basic structures: finger-like micro-channels for reduced transmembrane resistance, and sponge-like layer(s) for micro-filtration (MF). They have been fabricated via a combined phase-inversion and sintering technique, whereby the viscous fingering phenomenon that takes place concurrent to phase inversion leads to the formation of a plurality of finger-like voids or micro-channels within the membranes. The three internal coagulants used were hexane, DMSO and tap water with air gaps of 0 or 30 cm. Mechanical strength and water permeation flux were found to be sensitive to changes in membrane morphology, while pore size distribution of the separation layer(s) were less affected and were all in the microfiltration range. Membrane II, with just one very thin separation layer, exhibited the highest water permeation flux of 1874 L/(m^2 h) at 0.1 MPa. Effects of sintering temperature on pore size distribution, mechanical property and water permeation of the three membranes, in particular Membrane II, were systematically investigated. Sintering temperatures between 1300 °C and 1350 °C are suggested for Membrane II, taking into consideration of the reduced water permeation at higher sintering temperatures and the lowered mechanical strength at lower sintering temperatures.

1. Introduction

Human population has more than doubled since the 1960s, along with an increased rate of global water consumption [1]. The high water demands are mainly contributed by the agricultural, industrial and domestic sectors, placing considerable strain on the clean water sources. Increasing awareness on water pollution, stricter legislations and the inflating fresh water price have led to the discouragement of water wastage. For many industries, recycling water can assist to reduce operating costs significantly. Advanced wastewater treatment methods that are effective, economical and environmentally friendly are desired in order to reach an ideal 'zero-discharge' state. A promising advanced treatment method is membrane separation processes.

The development of suitable and economical membranes for waste water treatments has become increasingly attractive since the 1960s and are now extensively used for a wide range of purposes, such as for the removal of suspended solids, bacteria and viruses, heavy metals, oil and water separation, etc. [2,3]. Microfiltration and ultrafiltration are relatively less energy intensive processes with membrane pore sizes ranging from micrometres to nanometres. They require mild operating conditions and may be operated so that components in the wastewater are separated but not physically or chemically altered. They can be used as standalone processes or combined with other technologies to form hybrid systems.

A hybrid system that has been experiencing increasing attention and development from the early 1990s is the membrane bioreactor (MBR, Kubota system from Japan) [3,4]. MBRs used for treating municipal and domestic sewage hold the largest market value and the largest treatment capacity [5]. Anticipated stricter environmental regulations are driving sales of MBRs to industry and municipalities. Currently, fouling and replacement costs of the polymeric membranes that dominate the water treatment industry are the important limiting factors for the broadening of MBRs' applications [6].

Ceramic membranes may be an alternative material to use in MBR systems. Their renowned superior chemical, thermal and mechanical properties mean that they can be backwashed, cleaned with harsh cleaning agents and sterilised at high temperatures, extending their lifetime considerably, cutting down on replacement costs.

The scarcity of ceramic membranes in wastewater treatments has historically been due to their high fabrication costs and intrinsic brittleness, as well as sealing difficulties and lower packing densities. The most common ceramic membrane configurations employed in

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water treatment are the tubular, monolith and honey-comb architectures, produced by extrusion techniques [7]. However, when compared with the hollow fibre configuration, (surface area to volume up to 9000 m^2 m^{-3}) [8], the much lower membrane area provided by the common ceramic membranes can make them less competitive.

Although extrusion techniques are not inherently energy intensive and expensive, they can only be used to achieve symmetric membranes. However, asymmetric membranes with a thin selective layer on top of thicker and more porous sub-layers made of larger particles are desired for MF and UF applications in order to reduce the resistance to permeate flow. Conventionally, asymmetric membranes are achieved by coating a membrane substrate with multiple layers of ceramic particles of different sizes, which are sintered after each layer coating in order to form a membrane with a gradated pore structure. These additional steps increase the time and costs of the overall fabrication process considerably.

The combined phase inversion and sintering technique is a new method for producing asymmetric ceramic hollow fibre membranes with significantly reduced steps. A suspension of ceramic particles in solvent with a polymer binder is first prepared and then through the phase inversion of the polymer binder (via exchange with a non-solvent) during casting or spinning, the ceramic particles are immobilised. This method can form membrane precursors with specific morphologies and surface properties that can be tailored. Then calcination and sintering is required to remove all the organics from the membrane precursor and to consolidate the membrane structure and mechanical strength, respectively. Asymmetric membranes have been fabricated from a wide range of ceramics as well as metals via this method [9–14].

So far two basic sub-structures have been achieved via this method: sponge-like denser structures, and finger-like structures that can be either isolated voids or micro-channels. The dimensions of the different sub-structures can be tailored by changing fabrication process parameters. Kingsbury et al. studied the effect of various spinning parameters on the morphology of the membrane precursors and final membranes [15,16]. By changing the spinning conditions such as air gap, bore fluid choice and bore fluid flow rate etc., different proportions of the two sub-structures could be achieved during the continuous precursor fabrication process.

By using combinations of the different sub-structures, various applications of ceramic hollow fibre membranes have been generated, such as hollow fibre membrane micro-reactors, solid-oxide fuel cells, membrane contactors, gas separation, etc. [16–20]. In this study, three distinct membrane morphologies with one layer of finger-like voids and sponge-like separation layer(s) were designed and delivered by manipulating the spinning conditions, in particular the bore fluid choice and air gap. The three types of membranes were characterised and the effects of different ceramic membrane morphologies on properties such as pore size, pore size distribution, mechanical strength and pure water permeation flux were systematically investigated to probe the potentiality in wastewater treatment. The membrane morphology most promising for potential applications in aqueous microfiltration was further characterised looking at the effects of sintering temperature on membrane properties.

2. Experimental

2.1. Materials

Aluminium oxide powders of 1 μm (alpha, 99.9% metals basis, surface area 6–8 m^2/g) were purchased from Alfa Aesar (a Johnson Matthey company) and used as supplied. Polyethersulfone (PESf, Radal A300, Ameco Performance, USA), dimethyl sulphoxide (HPLC grade, Rathbone) and Arlacel P135 (polyethyleneglycol 30-dipolyhydroxystearate, Uniqema) were used as binder, solvent and additive, respectively. Tap water was used as the external coagulant and hexane (HPLC grade, VWR International), dimethyl sulphoxide and deionized water were used as the internal coagulants of Membranes I, II and III respectively.

2.2. Preparation of alumina hollow fibre membranes

First Arlacel P135 at a concentration of 1.3 wt% was weighed and dissolved in 28.3 wt% DMSO solvent. Then 64.0 wt% aluminium oxide powder of 1 μm particle size was added to the solvent. This mixture was then rolled/milled with 20 mm agate grinding balls with an approximate Al_2O_3/agate weight ratio of 2 for 48 h. PESf at 6.4 wt % was then added and the suspension was milled for a further 48 h. The continuous suspension was transferred to a gas tight reservoir and degassed under vacuum until bubbles were no longer visible. Once the suspensions have been degassed, they were transferred to 200 ml Harvard Stainless steel syringes. The suspension was then extruded through a tube-in-orifice spinneret with an O.D. of 3.0 mm and I.D. of 1.2 mm. The suspension was extruded into a coagulation bath that contained tap water. The extrusion rate and bore fluid flow rates of the spinning suspension and bore fluid were controlled and monitored by two Harvard PHD 22/2000 Hpsi syringe pumps. Spinning parameters can be found in Table 1 and more details of the inorganic hollow fibres spinning process can be found in previous studies [15,16].

The hollow fibre membrane precursors were left in the external coagulation bath overnight for phase inversion to complete. To remove traces of the DMSO, the membrane precursors were immersed in an excess of DI water, replaced every 48 h. Then, the membrane precursors were calcined and sintered in air (CARBOLITE furnace) to form the final hollow fibre membranes. The temperature was increased from room temperature to 600 °C at a rate of 2 °C/min and held for 2 h, and then to the target temperature (1200–1600 °C) at a rate of 5 °C/min and held for 4 h. The temperature was then reduced to room temperature at a rate of 5 °C/min.

2.3. Characterisation

SEM characterisation was conducted for the sintered membranes which were flexed at ambient temperature until a fracture occurred prior to being mounted on an SEM slide. Samples were coated with gold under vacuum for 3 min at 20 mA (EMITECH Model K550) and SEM images at varying magnifications were collected (JEOL JSM-5610 LV).

For pore size determination mercury intrusion data was collected at absolute pressures of between 1.38×10^3 and 2.28×10^8 Pa (Micromeritics Autopore IV) with an equilibration time of 10 s and assuming a mercury contact angle of 130°. The hollow fibre membranes were broken into sections of approximately 4 mm in length prior to mercury intrusion analysis. Pore size determination was also carried out using a gas–liquid displacement technique and was undertaken according to an established method [21,22].

Mechanical strengths were obtained by performing diametrical compression tests on the hollow fibres (Instron Model 5544 with a

Table1
Spinning parameters used for the alumina hollow fibre membranes.

Membrane	Bore fluid	External coagulant	Air gap (cm)
I	Hexane	Water	0
II	Dimethyl sulphoxide	Water	0
III	Water	Water	30