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3D printed feed spacers based on triply periodic minimal surfaces for flux enhancement and biofouling mitigation in RO and UF

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ABSTRACT

In this proof of concept study, 3D printed feed spacers with complex geometries based on triply periodic minimal surfaces (TPMS) were designed and tested in reverse osmosis (RO) and ultrafiltration (UF) processes. The spacers showed flux enhancement of 15.5% and 38% in brackish water RO and UF tests with sodium alginate solution, respectively, in comparison to a commercial feed spacer. Moreover, lower feed channel pressure drop was also observed for the TPMS spacers. Biofouling tests were performed and the membranes were characterized using total organic carbon (TOC) and fluorescence microscopy. The TPMS spacers yielded a reduction in biofouling when compared to commercial feed spacers. Fouling patterns on the membranes were visualized for the different spacers using crystal violet stain, which also revealed a significantly reduced biofilm deposition using the TPMS spacers. The TPMS-based feed spacers have shown great promise in enhancing both RO and UF membrane processes, both in terms of flux enhancement and fouling reduction.

1. Introduction

Almost all membrane-based systems, such as microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO), are susceptible to fouling [1]. Feed spacers are an essential part of spiral wound modules (SWM) where they separate the membrane leaves and provide a flow channel for the feed. Spacers also increase the turbulence of the flow along the surface of the membrane, which reduces the concentration polarization effect and enhances the mass transfer. However, commonly used commercial feed spacers create dead zones, such as at the intersection of the spacer's nodes of strand, where the flow is reduced and particle deposition begins. Such dead zones are the prime locations for the origination of biofouling since they provide an ideal location for the attachment and growth of microbes. Hence, feed spacers design plays a significant role in both the enhancement of mass transfer through the membrane as well as fouling control in the feed channel.

The effect of commercial feed spacer design and its various characteristics on mass transfer and pressure drop was studied by Da Costa et al. in the early 90s, providing correlations between spacer design and performance [2,3]. In 1995, it was reported that most of the initial deposition of biofouling was along the feed spacer. Subsequently, biofouling encroached onto the entire membrane surface, though it remained concentrated in the area adjacent to the feed spacer [4]. In a series of studies conducted by Vrouwenvelder et al., it was suggested that biofouling is a feed spacer, not a membrane, problem as it was observed that the feed spacer has a great effect on the consequences of biofouling such as feed channel pressure drop [1,5–9]. Consequently, various spacer geometries have been suggested as a potential method to improve the different aspects of membrane module performance, from mass transfer [10] to fouling prevention [5]. However, optimized spacer design has largely been limited by conventional spacer manufacturing methods that struggle to manufacture complex geometry.

In recent years, various types of additive manufacturing (3D printing) technologies have been gaining attention in membrane applications. The potential application of 3D printing technologies in different aspects of membrane systems has been discussed [11,12]. 3D printing was used to fabricate conventional feed spacers by Siddiqui et al. and it was demonstrated that the performance was similar to a commercially manufactured spacer of the same design [13]. Tan et al. printed commercial net type spacers using the selective laser sintering (SLS) technology and optimized the printing process parameters [14]. Recently, a comparison study was done by Tan et al. to evaluate the effects of different printing technologies on the performance of feed spacers [15]. The major advantage of 3D printing is that it allows the freedom of fabricating spacers with the novel, complex geometries. Researchers have reported a gamut of spacer geometries and shapes

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using 3D printing, including ladders, herringbones and helices [16], helically micro-structured [17], twisted tapes, modified filaments and multi-layer [18] spacers. Liu et al. fabricated static mixing spacers using stereolithography that enable the mixing of fluids from the center of the flow channel to the membrane surface [19].

In this study, novel feed spacers were fabricated using 3D printing, based on triply periodic minimal surface (TPMS) mathematical architectures. These shapes have many topological properties that were proven beneficial to spacer design in this study. The first reference to a TPMS was made by Schwarz in the 19th century, who introduced the Primitive and Diamond surfaces [20]. In nature, minimal surfaces topologies usually exist as interfaces separating two sub-volumes, as can be observed in soap films. Such geometries can be found in block copolymers [21], cell membranes [22] and butterfly wings [23], among others. The association of the geometrical characteristics of TPMS with physical properties holds great promise in the multi-functional design of metamaterials and structural systems. Several researchers have employed TPMS in a range of applications [24–31] to enhance functionalities through their topology-property relationship. TPMS are surfaces created mathematically such that they have no self-intersecting or enfolded surfaces. "Triply periodic" means that the structure can be patterned in the 3D space and "minimal surface" means that it locally minimizes surface area for a given boundary such that the mean curvature at each point on the surface is zero [20]. The complex and intertwined minimal surface divides the space into two or more entangled convoluted domains, such that each domain is a single connected and infinite component. TPMS were suggested as architectures for membrane surface design and predictions were made regarding the enhancement of mass transfer through these structures [32]. However, to the best of our knowledge, TPMS shapes have never been applied to feed spacer designs.

In this study, TPMS architectures are designed and printed for use as feed spacers in RO and UF systems. Based on the enhanced performance shown by these shapes in heat exchange units [32] with an analogous nature of heat and mass transport, as well as in gas transport [33], it stands to reason that these shapes should provide enhanced turbulence in membrane systems as well. The feed spacers based on TPMS architectures were tested in RO and UF to demonstrate their efficacy in pressure-driven membrane processes which suffer from similar undesirable phenomena such as concentration polarization and biofouling. In these processes, the enhanced turbulence can disturb the boundary layer and reduce concentration polarization for UF and RO, as well as reduce bacterial attachment on the membrane surface, thereby mitigating biofouling. The perfectly curved minimal surfaces of the spacers should reduce feed channel pressure drop compared to commercial feed spacer designs, hence minimizing the turbulence-pressure trade-off that is expected with feed spacer designs. Therefore, the objectives for this study are: i) Determine the printability of these complex structures at the scale needed for feed spacers (Section 3.1), ii) assess the impact of TPMS spacer structure on flux in RO and UF (Section 3.2), iii) evaluate the pressure drop experienced with TPMS spacers (Section 3.2), and iv) evaluate the efficacy of TPMS spacers in alleviating or mitigating biofouling (Section 3.3).

2. Materials and methods

2.1. Materials

Dow Filmtec XLE polyamide flat sheet membranes and Synder ultrafiltration polyethersulfone flat-sheet membranes with a 30 kDa molecular weight cut-off (MWCO) were purchased from Sterlitech (Kent, WA, USA). All membranes were soaked in deionized water and rinsed thoroughly prior to use. The reference spacer used for all the tests, in comparison with the 3D printed TPMS feed spacers, is a commercial polypropylene feed spacer (Naltex N08006, provided by Delstar, USA). It has a thickness of 80 mils (2.032 mm), angle of intersection 60° and strand count of 6 per inch. This particular spacer was selected for two reasons: i) it is one of the most commonly applied spacer architectures in RO's SWM and ii) it has the same thickness as the feed channel depth of the RO and UF test cell used (see Section 2.3).

An *Escherichia coli* (*E. coli*) strain DH5α (New England BioLabs, MA, USA) was used in all biofouling experiments. A 2 mL Luria broth (LB) culture was started from single colonies growth on LB agar plates. A total of 500 μL of this culture was added to 200 mL 0.5 × LB media flask and cultured in a shaking incubator at 37 °C for 24 h. The culture was then diluted in deionized water with nutrients (sodium acetate, sodium nitrate and sodium dihydrogen phosphate at C:N:P ratio of 100:20:10) to an OD of 0.5 [34,35]. All sets of biofouling experiments were performed using cultures from the same inoculum at this cell concentration. SYTO9 green fluorescent nucleic acid stain (Molecular Probes, Invitrogen) was purchased from Thermo Fisher.

2.2. 3D printing of feed spacers

2.2.1. TPMS design

For feed spacers, the smooth-curved TPMS is expected to help in reducing topology-induced fouling. Additionally, the intertwined geometry can enhance the turbulence of the flow passing through the feed spacer. The smoother flow could also minimize feed channel pressure drop. As such, these geometrical aspects result in enhanced mixing and increased interaction between the flow and the membrane, which can lead eventually to increased process efficiency.

TPMS can be described mathematically using level-set approximation technique [36]. There are numerous TPMS shapes available. However, in this work, we employed three promising TPMS structures to create the spacers, namely; the Schwarz primitive (referred to as P-skeletal), the Schoen Gyroid and the Schwarz crossed layers of parallel (CLP), which are described using the following level-set approximation equations [32,37].:

Schwarz P surface:

$$\cos x + \cos y + \cos z = C \tag{1}$$

Schoen Gyroid:

$$\sin x \cos y + \sin y \cos z + \sin z \cos y = C \tag{2}$$

Schwarz CLP:

$$\sin z \sin y - 0.4 \sin(1.2x) \cos z \cos y = C \tag{3}$$

where x, y and z are the Cartesian coordinate system, and C is a constant controlling the porosity of the spacer. Using the level-set equations, two different strategies were followed to employ TPMS topologies to create cellular structures [31], as highlighted in Fig. 1. In the first strategy, the minimal surface was thickened to create a solid structure known as the "sheet TPMS", where in the second strategy, the volume separated by the TPMS was solidified to create the solid structure known as the "skeletal TPMS".

For this study, the first strategy was employed to create the CLP sheet TPMS (henceforth referred to as CLP-sh) while the second strategy was employed for the Gyroid and Primitive surfaces (henceforth referred to as Gyroid-sk and Schwarz P-sk) to create skeletal TPMS. This was done to minimize the area of contact between the spacer and the membrane. Increased contact area between the membrane and the spacer reduces the area for the permeation through the membrane through the so-called "the shadow effect" [11] and increases the chances of biofouling, which develops at the area of contact between the spacer and the membrane [38]. Thicker spacers will lead to an increased feed channel pressure drop which needs to be avoided.

2.2.2. Printing technique

The feed spacers were designed based on the TPMS geometries described above and fabricated by 3D printing. Fig. 2a shows the unit cell for each type of the tested TPMS-based spacers. The mathematically