Abstract
Membrane fouling is a major drawback of reverse osmosis (RO) membrane filtration as it negatively affects the quantity and quality of the permeate and lifespan of the membrane. Spacer plays a pivotal role in hydrodynamics of the membrane channel thus influencing the membrane fouling. In this study, a series of novel sinusoidal spacers that can form unobstructed sinusoidal membrane channels were built and the performance of various novel sinusoidal spacers and the conventional mesh spacer on mitigating foulant deposition onto membrane surface was evaluated both experimentally on a bench-scale RO system and numerically with a three dimensional computational fluid dynamics (CFD) model. The results of the fouling experiments with humic acid and calcium ions showed that sinusoidal spacers were able to mitigate the membrane fouling and increasing the tortuosity of the sinusoidal wave pattern enhanced the efficiency of fouling mitigation. In addition, the CFD simulation revealed the development of fouling process and the CFD results were compared with the scanned fouled membrane images collected at different stages of fouling process. CFD results matched well with the experimental results and showed that the geometry of sinusoidal spacers could make an impact on membrane fouling development.

Introduction
Membrane fouling, which generally refers to the attachment, accumulation and adsorption on membrane surface or with membrane pores, is a critical issue in membrane filtration [1–6]. Studies on membrane fouling patterns often suggest that spacers play an important role in fouling development. Tran et al. [7] reported that fouling initially started along the feed spacer and then gradually encroached upon the rest of the clean membrane area. Gimmelshitein et al. [8] studied the flow in spacer-filled channels and they found spacer exacerbated the particle deposition on places near the mesh spacer filaments. Vrouwenvelder et al. [2] and Paassen et al. [9] independently studied the correlation between spacers and biofouling. They reported that biofouling was largely initiated on feed spacers and the pressure drop caused by biomass accumulation was much higher when the spacer was present. It is well acknowledged that spacer design is critical in creating a favorable fluid dynamics condition to mitigate membrane fouling. However a great effort has been paid on influent pretreatment and membrane surface modification to make anti-fouling or foulant-resistant membranes[10,11], the benefits of those efforts may be diminished if spacer design is not sufficiently addressed. The goal of this study is to test the sinusoidal spacer’s performance on mitigating membrane fouling as a continuum of our previous work of sinusoidal spacer on concentration polarization reduction[12].

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There are many studies on improving the current prevailing mesh spacer [13–16]. For example, Schwinge, et al. [15] built a three-layer mesh spacer that produced higher flux compared to the traditional two-layer spacer, but it incurred higher pressure drop. Schwinge and Wiley [16] investigated the performance of a zigzag spacer in a spiral-wound module and saw that pressure drop was lower than with a mesh spacer, but the permeate flux was also reduced. To sum up, one drawback of those novel spacers is that the higher flux comes at the expense of higher energy consumption, vice versa[17–22].the mesh spacer has another shortcoming: it creates
deadzones near the side of the filaments that are not facing the flow and it provides extra free surface area which will facilitate the deposition fouling and the growth of the biofilm in the membrane channel.

The key to design a spacer that can provide a favorable hydrodynamic condition is understand the nature and mechanism of membrane fouling. Conventional methods such as flux decline or transmembrane pressure increment measure or the scanning electron microscopy (SEM) are not able to show the distribution of velocity and foulant[23]. The recent methods that use ultrasound and optical technology can determine and help predict the development of fouling layer[24–26]. However they require to have the real system built which can be very costly and time consuming. Computational fluid dynamics (CFD), as a fast and economic tool, has become an important tool in spacer design and testing [15,17,27–32]. CFD models are usually used to study the membrane channel’s velocity, pressure and concentration distribution which cannot be observed directly from experiments. Many researchers used simplified 2D models to investigate the spacer’s geometry’s effect on fluid dynamic. In such studies, spacer’s configurations such as the cavity, submerged, and zigzag are commonly chosen as representative cross sections of spacer filled membrane channel[16,21,22,28,33]. Thanks to the improvement of computer speed and numerical efficiency in CFD codes, 3D models started to emerge and become increasingly popular. By comparing 2D and 3D models, many studies pointed out that 3D models provided more accurate results[34,35]. In addition, 3D models enable researchers to study the spacers from new perspectives such as flow angle, filament angle etc.[18,30,36].

In this study, the performance of sinusoidal spacer’s performance on preventing foulant deposition on membrane surface has been tested via bench-scale experiments and three-dimensional CFD models. Humic acid was used as trace foulant in this study. Humic acid is a natural organic matter (NOM) which can be found in lakes, rivers and reservoirs and it is considered as a major foulant during membrane process [37]. Even though humic acid is often removed by recommendation before entering RO [38], the efficacy of its flux reduction and the membrane surface coloring makes it an ideal option for the purpose of this study. Humic acid can form brownish gel-like chelates with multivalent ions [39,40] on membrane surface. It was reported that calcium-humate combination would cause significant irreversible flux decline [41]. Simulation is also employed in this study to investigate the mechanism and pattern of fouling development. Because humic acid consists of various organic compounds and its exact physical and chemical characteristics is very hard to determine[38] and mathematic model on humic acid adsorption onto membrane surface is not available, necessary assumptions, which will be explained in details in the chapter of materials and methods, have to be made to make sure the model can run.

Materials and Methods

Model Description
The purpose of the modeling was to study the fouling development, velocity distribution and pressure drop which were not available for direct observation via experiments and use these information to predict and prevent membrane fouling. Five models of RO spacer channels were created (Fig. 1). The detailed geometry description is available in our previous paper [12]. Simulations were performed using Comsol Multiphysics 4.2a on the Palmetto Cluster, Clemson University's primary high-performance computing (HPC) resource. Mesh density of each model was evaluated by comparing results from different mesh densities. The desired mesh density was achieved if two mesh schemes that were 10% different in density would produce results (the pressure drop was chosen as the criterion in this study) within 1% difference and the smaller mesh density would be chosen to decrease the computational intensity.

To reduce the simulation time and size, one assumption made was that the fouling did not cause flux decline in the modeling which enabled us to solve the problem by using fluid dynamic data from a static state solver first and coupling it to the chemical reaction process. As a result, only chemical reaction was solved in the burdensome time-dependent solver. Therefore, the model solved the fouling process in two steps. In the first step, a stationary solver was employed to solve the fluid dynamics such as velocity, pressure and shear rate etc.. And they were solved by Equations (1) and (2),

$$\nabla \cdot \mathbf{u} = 0$$

$$\rho \mathbf{u} \nabla \cdot \mathbf{u} = \nabla \cdot [-P + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)]$$

Figure 1 Geometries of sinusoidal channels. The overall length of each channel is 130 mm. The cross-sectional view (bottom) applies to all geometries.
where \( \mathbf{u} \) is fluid velocity, \( \rho \) is density, \( P \) is pressure, \( \mu \) is dynamic viscosity. The inflow velocity is 0.148 m/s and applied pressure is 600 Psi. The solution obtained from this step would be used as the premises of the second step.

In the second step, a time-dependent solver was used to simulate the chemical transport and reaction that resulted in membrane fouling. In the model, the inflow concentration of foulant was 1 mmol/L and the chemical transportation was solve by Equation (3)

\[
\mathbf{u} \nabla \cdot \mathbf{c} = D \nabla^2 c
\]

Where \( c \) is concentration of foulant and \( D \) is the diffusion coefficient. It is important to note that the foulant was considered to be 100% dissolved in the water which was in contrary with the nature of humic acid that also included various size of suspended particles.

The flux through the membrane was solved by Equation (4):

\[
u_m = A \cdot (\Delta p - a_{osm} \cdot c_w)
\]

Where \( c_w \) the fouling concentration at the membrane surface, \( A \) is water permeability of the membrane, \( \Delta p \) is pressure difference between feed side and permeate side and \( a_{osm} \) is osmotic coefficient.

And the fouling formation on membrane was solved by Equation (5):

\[
\frac{dc_s}{dt} = k_1 (c_{s,max} - c_s) c - k_2 c_s \gamma
\]

Where \( c_s \) is the foulant concentration on membrane surface, \( c_{s,max} \) is the maxium surface foulant concentration on membrane, \( k_1 \) is the adsorption coefficient and \( k_2 \) is the desorption coefficient, and \( \gamma \) is the local shear rate. For all models, the simulated time was 10000s.

Since the inflow concentration of the foulant was very small (1 mmol/L), the effect of concentration polarization was also negligible. As a result, the Equation (6) could be simplified as:

\[
u_m = A \cdot (\Delta p)
\]
Experimental setup

Figure 2. Oblique view of a representative sinusoidal spacer built for experiments. This spacer has the $3\sin(\pi/12)$ geometry.

Figure 3. Plan and section views of a representative sinusoidal spacer. As with Fig. 2, this spacer has the $3\sin(\pi/12)$ geometry. Blue arrows indicate the water flow path. Dimensions are in mm.

The experimental setup is the same used in our previous study [12]. The spacers used in the experiments were built by 3D printing techniques with clearvero materials. A 3D rendering of one sinusoidal spacer is shown in Fig. 2 with the detailed drawing with dimensions depicted in Fig. 3 where fluid flow directions are also indicated. One thing worth noting is that within a single channel the cross section was maintained as a 6 mm by 1.5 mm rectangular at any location for all spacers. And the changes in sinusoidal geometry did not alter the active membrane area, which was 78 cm².
The detailed description of the RO unit (Fig.4) is available in our previous paper [12]. The size and shape of each channel in the experiment were the same as in the CFD simulations. For comparison to conventional RO operation, one experimental set was performed using the 65 mil mesh feed spacer that is a standard accessory of the SEPA II membrane cell. (Though 65 mil is the spacer designation, its actual thickness was measured to be 1.5 mm.) Experimental pressure and flow rate were the same as those used in the simulations. The membrane was a SWC5 (Hydranautics) cut from a 4-inch spiral-wound element.

![Figure 4 Bench-scale RO membrane test setup. Square symbols stand for controls (V for needle valve actuator voltage and Qf for the feed flow rate control). Diamond symbols stand for the data acquisition (Cf for feed concentration, Mp for permeate mass, Cp for permeate concentration, and Pf for feed pressure).](image)

Each membrane coupon was operated initially with deionized (DI) water for 60 minutes to stabilize the membrane and obtain the clean-water flux and hydraulic permeability of the membrane. At the end of the first hour, the DI water was replaced by 10 L of fouling solution which consisted of humic acid (catalog number: 198763) (30 mmol/L), calcium chloride (30 mg/L) and sodium bicarbonate (1 mmol/L). The pH value of the fouling solution was 5.95. The fouling experiment was terminated as soon as 5 L of permeate was collected. All experiments were performed in triplicate, meaning that three different membrane coupons were tested for each spacer.

To qualitatively verify the modeling results, another series of fouling experiments were performed. The only difference was the fouling process stopped after 1L of permeate were collected instead of 5L. The membrane coupons after the fouling experiments were saved and scanned to compare the fouled membrane image from simulation. These membrane coupons were chosen because at this stage of fouling, the variation of fouling severity in different locations was clearly visible which made it very useful to study the fouling development.
Results and Discussion

Flux decline

The flux decline ratio was measure as:

\[ \alpha = \frac{J_{DI} - J_f}{J_{DI}} \times 100\% \]

where \( \alpha \) is the flux decline ratio, \( J_{DI} \) is the average flux at the final three minutes of DI water run and \( J_f \) is the average flux at the final three minutes of the fouling experiment. Flux decline ratio was used as the criterion to evaluate the fouling resistance performance of each spacer.

Among the sinusoidal spacers, the value of \( J_{DI} \) were very close but the difference of \( J_f \) among was obvious (Fig. 5). By increasing the amplitude or the frequency of the sinusoidal wave, \( J_f \) was increased. Mesh spacer showed higher \( J_{DI} \) because it had larger active membrane area but it should be noted that the active membrane area for all sinusoidal spacers and straight spacer is the same.

![Figure 5 The averaged DI water flux (blue) and averaged final flux (red) from the experiments.](image)

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Fig. 6 showed the flux decline ratios $\alpha$ from the experiments. Comparing to the straight spacer ($\alpha=44.1\%$), sinusoidal spacers and mesh spacer all exhibited lower flux decline ratios. In addition, the flux decline ratio of sinusoidal spacers $3\sin(\pi/6)$ ($\alpha=22.8\%$) and $6\sin(\pi/6)$ ($\alpha=13.8\%$) were lower than conventional mesh spacer ($\alpha=23.6\%$) which proved an improvement of fouling resistant performance. The velocity distribution (Fig.8) from simulation showed that the flow turbulence inside the sinusoidal channels increased with the tortuosity of the geometry and the turbulence would cause stronger mixing and higher shear rate which was responsible for the fouling reduction [12].
Figure 7 Pressure gradient obtained from simulations for various channels. The mesh spacer data point is highlighted in red for quick comparison to this conventional condition.

**Pressure drop**

The longitudinal pressure drop of the various channels were evaluated by computational simulation (Fig.7). The smallest pressure drop was observed from the straight channel (1 kPa/m) and the largest pressure drop from the channel formed by $6\sin(\pi/6)$ (60.1 kPa/m). The mesh spacer showed the second largest pressure drop ($22.8$ kPa/m) which was more than $3\sin(\pi/6)$ (12 kPa/m). From the aforementioned, $3\sin(\pi/6)$ proved capable of reducing membrane more effectively with less energy consumption compared to mesh spacer. In our previous study regarding sinusoidal spacer’s performance on salt water desalination proved that sinusoidal spacers showed potential of enhancing flux while reducing energy consumption.
Fouling pattern study

The fouling images from simulation and experiments were shown and compared in Fig. 9. Simulation results captured the important details of the fouling pattern on membrane surface. In straight channel, the foulant tended to deposit on membrane surface evenly on the direction perpendicular to the flow and a trend of fouling concentration reduction was observed along the flow direction. In sinusoidal spacers, the fouling concentration exhibited a periodic pattern along the sinusoidal wave: (1) Fouant tended to accumulate in the concave and convex locations where the least shear rate was observed in the sinusoidal period (Fig. 10); (2) the shade contrast was more obvious in channels with higher tortuosity suggesting the hydraulic dynamic played an important role in fouling prevention.
Conclusion

The performance of sinusoidal spacers on reducing deposition fouling was tested and compared with conventional mesh spacer and straight spacer. The results showed that sinusoidal spacers were capable of generating flow turbulence which caused high shear rate to prevent fouling deposition on membrane surface thus maintaining high flux. The flux decline ratio and pressure drop results showed the promising prospect of using sinusoidal spacers to achieve higher flux with less energy consumption under fouling condition. Simulation was used to qualitatively study the fouling process and the fouling images produced by simulation successfully predicted where the foulant tended to accumulate which identified increasing shear rate could reduce membrane fouling.

List of symbols

\( A \)  
Hydraulic permeability of the membrane, m/(s·Pa)

\( a_{\text{osm}} \)  
Osmotic pressure coefficient, Pa·m\(^3\)/mol

\( c \)  
Foulant concentration in the bulk, M

\( c_w \)  
Foulant concentration near the membrane, M
$c_s$  Foulant concentration being adsorbed to the membrane, mol/m$^2$

$c_{s, \text{max}}$  Maximum foulant concentration that can be adsorbed to the membrane, mol/m$^2$

$k_1$  Adsorption coefficient, 1/s

$k_2$  Desorption coefficient

$D$  Diffusivity, m$^2$/s

$n$  Normal direction of boundary

$p$  Pressure in the channel, kPa

$\Delta p$  Pressure difference across the membrane, kPa

$u$  Velocity magnitude, m/s;

$u_m$  Permeate flux, m/s

$J_{DI}$  Averaged flux during the DI water run, LMH

$J_f$  Averaged flux at the end of fouling experiment, LMH

**Greek letters**

$\Delta \pi$  Osmotic pressure, Pa

$\mu$  Viscosity of water, Pa·s

$\rho$  Density of water, kg/m$^3$

$\gamma$  Shear rate, 1/s

$\alpha$  Flux decline ratio

**References**


