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Effect of a macromolecular- or bio-fouling layer on membrane distillation

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ABSTRACT

Membrane distillation (MD) is a continuous process whereby a hot aqueous feed provides the latent heat to vaporize water that diffuses through a hydrophobic microporous membrane and condenses. MD is attractive for saline and wastewater treatment as well as concentrating heat-sensitive solutions such as fruit juices and biological fluids since it operates at moderate temperatures and atmospheric pressure, rejects particulates and nonvolatile solutes, uses non-selective membranes, and has low capital costs. However, MD and MD bioreactor (MDBR) performance is compromised by fouling. The effect of fouling layers with reasonably large pores (>50 nm) is reasonably well-understood and has been incorporated into MD models. However, the effect of fouling layers with very small pores or free volume (<50 nm) owing to macromolecular- and bio-fouling (MMBF) is not well-understood. While MMBF introduces an additional resistance to heat transfer, it can also reduce the vapor-pressure driving force. This latter effect is unique to MD fouled by MMBF. In this analysis the vapor pressure reduction has been incorporated into a model that indicates the large flux declines observed in prior studies can be explained by the vapor-pressure reduction associated with pore diameters ranging from 3.9 to 8.5 nm, which agree well with evapoporometry characterization of MMBF sludges. The predicted flux decline and temperature polarization coefficient indicate that the vapor-pressure reduction increases markedly for effective pore diameters less than 10 nm, but can be mitigated by increasing the thermal resistance of the membrane and by fabricating a dual-layer membrane for which the feed side is hydrophilic with relatively large pores.

1. Introduction

Membrane distillation (MD) is a technology for removing non-volatile solutes and impurities in order to produce high purity water or to concentrate aqueous solutions. MD was first described in 1963 in a patent by Bodell [1]. Lawson and Lloyd [2] reviewed the development of MD up to the late 90s. Recent reviews have been done by Alklaibi and Lior [3], El-Bourawi et al. [4], Gryta et al. [5], Alkhudhiri et al. [6], and Camacho et al. [7]. MD employs a hydrophobic microporous membrane to separate the hot aqueous feed side from the cold distillate side. The pores in the hydrophobic membrane are sufficiently small to prevent penetration of liquid water through the membrane, but are reasonably large to minimize the resistance to diffusion of water vapor. The hot feed provides the heat-of-vaporization needed to evaporate water at the liquid–vapor interface at the mouth of the pores in the hydrophobic membrane. The water vapor diffuses through the microporous membrane owing to a vapor-pressure gradient and is condensed or swept away on the cold distillate side. MD offers several advantages: nearly complete rejection of nonvolatile solutes and particulates; low operating temperature (typically 30–90 °C) and pressure (typically atmospheric); use of non-selective membranes (i.e., separation is done by vaporization); low capital cost relative to RO; ability to concentrate heat-sensitive aqueous solutions such as fruit juices or biological fluids; and the ability to remove dissolved gases or trace volatile organics from water [2]. However, MD has limitations: low water fluxes relative to processes such as RO; flux decline owing to fouling; and adsorption of organics that cause wetting and wicking of water through the hydrophobic membrane [2].

The wetting and wicking caused by the presence of inorganic and organic solutes had precluded wastewater treatment via MD. This limitation has been addressed by the development of the MD bioreactor (MDBR) that consists of an MD module submerged in

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an aerobic–thermophilic bioreactor [8,9]. The bacteria in the MDBR break down and consume the inorganic and organic solutes, thereby maintaining the functionality of the MD membrane module. However, due to the biomass, bio-fouling is a problem in the MDBR as it is in conventional membrane bioreactors (MBRs). This paper shows that bio-fouling plays an additional role in the MDBR.

It is claimed that fouling is less in MD relative to other membrane separation processes owing to the relatively large pores in the hydrophobic microfiltration (MF) membranes [2]. However, fouling due to the deposition of inorganic and organic solutes has been observed to cause a significant flux decrease in the use of MD for industrial waste-water treatment and seawater desalination [10,11]. Whereas the fouling caused by inorganic and organic solutes can be mitigated in an MDBR, the latter is necessarily subject to significant bio-fouling. In contrast to the porous fouling layers formed by inorganic salts and cake-forming humic materials, macromolecular deposition and bio-fouling involve fouling layers with very small pores or free volume, typically less than 50 nm. Fouling layers are thought to add a resistance to heat transfer from the hot feed to the evaporating liquid. However, the flux reduction associated with fouling layers having very small pores or free volume cannot be explained just by an added heat-transfer resistance since these layers are typically very thin ($<100\ \mu m$) [11,12]. Gryta [11] speculated that the thin layers associated with protein fouling offer an additional resistance to mass transfer, although this hypothesis has not been tested. Goh et al. [13] showed via direct measurements that water-saturated bio-fouling layers display a reduced evaporation rate relative to a free-standing water layer. Since the apparent reduction in vapor pressure is larger than can be explained by the presence of solutes in the water-saturated bio-fouling layers, they attributed the reduced evaporation rate to the Kelvin effect associated with very small pores. They contend that the presence of bio-fouling in an MDBR causes liquid water to be drawn by capillary action to the interface between the hydrophilic bio-fouling layer and the hydrophobic membrane. Since the interface between the liquid water and vapor phase is within the hydrophilic bio-fouling layer and is concave, it causes a vapor-pressure depression and thereby a direct reduction in the driving force for water-vapor diffusion through the hydrophobic MF membrane. However, Goh et al. made no attempt to incorporate the Kelvin effect into a model for MD or to develop any experimental protocol for assessing whether this mechanism is operative in an MD or MDBR process.

Hence, the focus of this paper is to develop an MD model that incorporates the effect of a fouling layer having very small pores or free volume that is characteristic of macromolecular- or bio-fouling, henceforth to be referred to as MMBF.

2. Prior relevant studies

Fouling is a major problem in MD that can take the form of inorganic scaling, particulate or colloidal fouling, natural organic matter (NOM) fouling, and bio-fouling [2,11]. Scaling owing to the precipitation of inorganic solutes is a problem in MD only for nearly saturated feed solutions [14,15] such as in the continuous MD crystallization (CMDC) process [16]. Particulates, colloids and NOM in the form of humic acids can result in a relatively thick ($>100\ \mu m$) loosely packed fouling layer that can affect both the liquid water transport to the membrane and the resistance to heat transfer from the hot feed to the evaporating liquid. Srisurichan et al. [17] adapted the MD model of Schofield et al. [18] to show that the principal effect of humic acid fouling in MD was to add a resistance to the heat conduction. Fouling by particulates, colloids and NOM in the form of humic acids results in a layer with pores typically larger than 50 nm. However, fouling owing to NOM in the form of proteins, aminosugars, polysaccharides and polyhydroxyaromatics can result a gel layer with very small pores or free volume [11,19]. Fouling layers with very small pores or free volume can offer a resistance to both heat and mass transfer in MD and possibly can have other effects as well [11,20,21]. Bio-fouling caused by the growth of bacteria on a membrane also results in a gel-like layer. Bio-fouling in conventional MD can be mitigated by UV or chemical treatment of the feed [2]. However, bio-fouling is a major problem in the MDBR [9,10,12,13] since the feed must sustain the thermophilic bacteria. Whereas the effects of fouling layers with large pores have been incorporated into MD models that corroborate well with experiment, models have not been able to account for the anomalously large flux decline that occurs for fouling layers with small pores or free volume [9,11–13].

It is appropriate to review experimental and modeling studies of fouling in MD caused by gel layers. Gryta [11] studied the concentration of saline wastewater containing proteins and polysaccharides via MD and reported a 70% decline in the flux over 55 hours. FTIR characterization of the fouled membranes indicated protein deposits. SEM characterization of the dry fouling layer indicated a thickness of 10 μm. Gryta estimated a wet fouling layer thickness of 90 μm assuming the hydrated proteins contain 90% water. His MD model incorporating a heat-transfer resistance owing to a 90 μm fouling layer predicted only a 20% flux decline. He speculated that the additional flux decline might be caused by a hydraulic resistance to water permeation resulting from the protein fouling layer. However, no attempt was made to incorporate this effect into an MD model.

Phattaranawik et al. [9] used an MDBR with submerged flat sheet PVDF and PTFE membranes to treat a synthetic wastewater. They observed flux declines of 85% over 7 days for the PVDF and 82% over 5 days for the PTFE membrane. Mass analysis of the fouling layer on the PVDF membrane indicated 12.5% proteins, 37.5% polysaccharides, and 50% EPS (extracellular polymeric substances). Mass analysis for the PTFE membrane indicated 21.4% proteins, 28.6% polysaccharides, and 50% EPS. They concluded that the flux decline could not be explained by an added resistance to heat transfer from the hot feed to the evaporating water. They speculated that a bio-fouling layer in an MDBR might contribute a hydraulic resistance to water permeation. However, no attempt was made to incorporate this effect into an MD model.

Goh et al. [12] used an MDBR with submerged flat sheet PVDF membranes to treat synthetic wastewater. They observed a flux decline of 5.9% over 3 days and 51% over 23 days. Confocal microscopy indicated a bio-fouling layer thickness of 2–8 μm after 7 days and 20 μm after 22 days. SEM imaging indicated pore diameters of smaller than 50 nm. They concluded that the thin bio-fouling layer did not offer any significant resistance to heat transfer, but might result in a resistance to mass transfer owing to very small pores. No attempt was made to incorporate this into an MD model.

Goh et al. [13] studied bio-fouling in cross-flow MD where they isolated two sludges having different hydrophilicity. They observed a flux decline for both sludges of 60% relative to using a Milli-Q water feed in cross-flow MD over 180 h. Confocal microscopy indicated a thickness of the bio-fouling layer after 180 h of 7.4–15.1 μm for the more hydrophilic and 8.1–14.4 μm for the less hydrophilic sludge. Gravimetric experiments indicated that water evaporated from the less hydrophilic sludge more than twice as fast as from the more hydrophilic. This was attributed to a vapor-pressure depression arising from the small pores in the bio-fouling layers that is described by the Kelvin equations [22,23]. The average pore diameters determined from the evaporation rates were 4.7 nm and 9.4 nm for the more and less hydrophilic sludges, respectively. Goh et al. [13] also used evapoporometry to