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Membrane fouling in a fermentative hydrogen producing membrane bioreactor at different organic loading rates

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ABSTRACT

In a lab-scale continuously running fermentative hydrogen producing membrane bioreactor (HPMBR), the properties of biomass, extracellular polymeric substances (EPS) and colloidal material in the mixed liquor along with their influence on the performance of submerged hollow-fiber membrane modules were investigated. Five experimental runs were conducted at organic loading rates (OLRs) of 4.0, 6.0, 13, 22 and 30 g COD L^{-1} d^{-1}. As OLR increased, the biomass content, colloidal hydrophobicity and mean particle diameter increased. Additionally, the membrane fouled more rapidly as OLR increased. The bound and soluble EPS content of biomass in the HPMBR were higher than that found in a hydrogen producing system in CSTR mode and in an aerobic activated sludge system. At a constant permeate flux rate of 11.1 L min^{-1} m^{-2} and N_2 sparging intensity of 4.26 L min^{-1} m^{-2}, membrane fouling was characterized by two distinct stages: an initial stage characterized by a relatively faster fouling rate and a second stage where the fouling rate was slower. Both fouling rates increased with increased biomass concentration and colloidal zeta potential. Increases in pore clogging resistance R_{coll} correlated to increased concentrations of colloidal proteins and polysaccharides. The observed relationships between the membrane fouling properties and the properties of biomass and colloids (including soluble EPS), accompanied by scanning electron and confocal microscopy examination of the fouled membrane surfaces suggest that colloid adhesion and biomass deposition were the two dominant membrane fouling mechanisms in the HPMBR system.

1. Introduction

Hydrogen gas is an ideal alternative fuel to replace oil and natural gas because it has a high energy content and is a clean fuel [1,2]. Biological hydrogen production by fermentative processes is less energy intensive when compared to physical/chemical processes, has a higher rate of hydrogen evolution and is able to utilize a wide range of substrates and waste streams when compared to biological photosynthetic processes [3].

Fermentative hydrogen production in a continuously stirred tank reactor (CSTR) has substrate utilization and hydrogen production rates that are limited by the amount of biomass retained in the system because the solids retention time (SRT) is equal to the hydraulic retention time (HRT). In contrast, fermentative hydrogen production in a membrane bioreactor (MBR) effectively uncouples SRT from HRT. This facilitates increased biomass concentrations and potentially higher hydrogen production rates and more effective substrate utilization, particularly at high organic loading rates (OLRs) [4,5].

When membrane technology is employed in biological wastewater treatment, membrane fouling becomes a key process limitation and remains one of the most challenging issues in future MBR development [6]. Fouling leads to a decline in membrane flux or an increase in transmembrane pressure (TMP) to achieve a target flux. Frequent membrane cleaning and replacement are needed to mitigate fouling [7], consequently reducing the process economics. A full understanding of fouling mechanisms may lead to better membrane design, better membrane modules, and better membrane cleaning strategies [8,9].

To date, most membrane fouling studies have focused on aerobic MBRs. Fewer studies have examined anaerobic MBRs (AnMBRs), and most of those have examined methanogenic systems. Membrane fouling is attributed to biomass (volatile suspended solids) with bound extracellular polymeric substances (EPS) [10] and sol-

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uble EPS and colloidal particles [11,12]. Gas scouring, backwashing and backpulsing are effective control strategies to mitigate cake resistance due to biomass deposition on the membrane. In contrast, the colloidal particles (≤1 μm in diameter) found to be the major foulants in methanogenic AnMBRs [13] exhibit complex interactions with the membrane pore surface, resulting in pore clogging and pore sealing which cannot easily be managed by physical cleaning processes [11,12,14,15]. Moreover, some of the clogged pores cannot be recovered even by chemical cleaning, thus reducing the membrane lifetime.

Hydrogen producing MBRs (HPMBRs) are distinctive in relation to methanogenic AnMBRs. Differences in the microbial community composition, physicochemical and operational conditions of the bioreactors (e.g. pH) may lead to different properties of the foulants and different fouling mechanisms. In a limited number of studies on the HPMBRs [4,5,16], only Oh et al. [5] specifically examined membrane fouling. They demonstrated that in a lab-scale HPMBR system coupled with flat sheet membranes, membrane resistance was associated with a combination of reversible cake formation and irreversible fouling. Nevertheless, membrane fouling mechanisms and an understanding of how mixed liquor properties and operational conditions affect membrane fouling in HPMBRs are still largely unknown. The objectives of this work, then, were to examine the effect of organic loading rate (OLR) on the properties of the mixed liquor and on membrane fouling in a lab-scale HPMBR, and to predict the underlying fouling mechanisms associated with HPMBRs.

2. Materials and methods

2.1. Experimental setup and operating

The continuous HPMBR system consisted of a 7-L reactor (4-L liquid volume) with a submersible hollow-fiber ultrafiltration membrane module (ZW-1, GE Water & Process Technologies, Oakville, ON, Canada) as described by Shen et al. [16]. ZeeWeed membrane systems are proprietary technologies. The hollow-fibre membrane is composed of polyvinylidene fluoride characterized by a nominal pore size of 0.04 μm and a surface chemistry which is considered to be negatively charged (communication with the manufacturer) and hydrophilic. These membranes have been widely applied and used in numerous research studies. After an extended filtration period, these surface parameters are expected to play only a minor role in membrane fouling. Once conditioned, the membrane's surface characteristics are considered secondary to those of the foulant or constituents derived from the mixed liquor material covering the membrane surface. The ZW-1 membrane module has an effective surface area of 0.047 m^2. The seed sludge was taken from the anaerobic digester at the North Toronto Treatment plant (Toronto, ON, Canada). The reactor was fed a synthetic, glucose-based wastewater previously described by Kraemer and Bagley [17].

The reactor was operated at 23.0 ± 0.1 °C (constant room temperature) and at a pH of 5.5 ± 0.1. The HRT was 8 h and the SRT was 24 h. Feed and waste pumps maintained the influent flow rate at 12 L d^{-1} and the waste flow rate at 4 L d^{-1}, respectively. The permeate pump was automatically controlled to maintain a 5 min permeate with a permeate flow rate of 13.3 L d^{-1} and 1 min backwashing with a backwashing flow rate of 5.3 L d^{-1}. Nitrogen gas (99.999% pure, Praxair, Mississauga, ON, Canada) was sparged directly into the membrane module for gas scouring of the membrane surface with a sparging flow rate of 0.2 L min^{-1} and sparging intensity of 4.26 L min^{-1} m^{-2}. A pressure transducer (PX209-30V15GI, Omegadyne, Toronto, ON, Canada) and process indicator (DP41-E-S2, Omegadyne Inc., Toronto, ON, Canada) were placed before the permeate pump to monitor TMP changes. The TMP reading was automatically recorded using data collection software (Collect XL™ V6.0, Labtronics Inc., Guelph, ON, Canada).

Five experimental runs were conducted examining OLRs from 4.0 to 30 g COD L^{-1} d^{-1} (equivalent to influent glucose concentrations of 1.3–10 g COD L^{-1}, respectively). The actual run sequence proceeded as follows: OLR = 4.0, 13, 6.0, 22 and finally 30 g COD L^{-1} d^{-1}. Each run lasted a minimum of 7 days. Samples were collected beginning from the 3rd day in each run when the system performed stably with no statistically significant difference (95% confidence) in the daily measured concentrations of produced gaseous hydrogen, soluble metabolites and biomass in the reactor. Before each experimental run, the bioreactor was operated continuously without the membrane (in CSTR mode) for 7 days to acclimate microorganisms to a new OLR and ensure the system was at a steady state. During experimental runs, when the TMP exceeded 6 psi (41 kPa), the working membrane module was removed for cleaning and another clean membrane module was installed to maintain the MBR mode.

2.2. Membrane cleaning

A recovery cleaning procedure was utilized to treat fouled membranes. First, a physical cleaning step was applied to mainly remove the visible biomass cake deposited on the membrane surface. The membrane module was submerged in 2 L distilled water and shaken vigorously by hand for at least 2 min. This step was repeated twice until the visible biomass cake was removed. Then the module was transferred to a 200 ppm sodium hypochlorite solution (5 L) and soaked for 24 h to mainly remove colloids and soluble EPS which were not removed by physical cleaning as described above. Finally, the module was rinsed and soaked in distilled water until it was re-employed in the HPMBR.

2.3. Analytical measurements

2.3.1. Standard measurements of wastewater parameters

Headspace gases were measured by gas chromatography with a thermal conductivity detector following the method of Shen et al. [16]. Total suspended solids (TSS) and volatile suspended solids (VSS) in the reactor were measured using methods modified from those in *Standard Methods* [18]. A GF/B type (Whatman Inc., Piscataway, NJ, USA) glass fibre filter was used with a nominal pore size of 1.0 μm instead of 934-AH type filter with a nominal pore size of 1.5 μm. Chemical oxygen demand (COD) in the influent, the reactor and the permeate was measured according to *Standard Methods*. Residual glucose in the reactor was analyzed enzymatically following the method of Kraemer and Bagley [17].

2.3.2. Microbial community analysis

A 16S rDNA clone library was prepared from the HPMBR mixed liquor. DNA was extracted from the mixed liquor using MoBio's Ultraclean Soil DNA Kit. 50 ng of genomic DNA was amplified using eubacteria specific primers EUB27f and EUB1492r [19] and a BioRad MyCycler Personal Thermal Cycler. The 50 μL reaction contained 200 μM dNTP, 1 mM $MgCl_2$, 0.5 μM of each primer, and 0.5 units of DNA polymerase. The thermal cycler program consisted of an initial denaturation step of 94 °C for 10 min followed by 27 cycles of 94 °C for 1 min, 55 °C for 2 min, and 72 °C for 2 min. The obtained PCR products were purified using the GenElute PCR Cleanup Kit (Sigma–Aldrich, Oakville, ON, Canada) before ligating them into PCR2.1 Vector (Invitrogen, Carlsbad, CA, USA) and transforming into One-Shot TOP10 Chemically Competent *E. coli* cells. Transformants were selected by growing cells overnight on Luria–Bertani (LB) agar plates containing 50 ng mL^{-1} ampicillin at 37 °C. Isolated colonies were then grown overnight in LB broth containing 50 ng mL^{-1}