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Study of biofilms on PVDF membranes after chemical cleaning by sodium hypochlorite

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ABSTRACT

Sodium hypochlorite (NaOCl) is widely used to remove biofouling in membrane bioreactors (MBRs) to recover the membrane performance. In this study, the effect of membrane cleaning with different NaOCl concentrations (0.01%, 0.1%, 1% and 10% of a stock solution containing 39.92 g/L of free chlorine) on biofouling was investigated in a molasses based lab-scale MBR. Study of the bacterial biofilm community re-growth after six consecutive cleanings revealed that a minimal concentration of 0.1% NaOCl diminishes the bacterial richness and cell density on the membranes. ATR-FTIR analysis of the layer on the membrane surface revealed the presence of peaks associated with proteins and carbohydrates present in the biofouling layer and their intensity decreased after treatment with NaOCl. Analysis of the membrane performance by chemical oxygen demand (COD) measurement of the permeate and retentate showed that the rejection of the membranes after NaOCl chemical treatment was still high. The data showed that since NaOCl removes the bacterial biofilm and at the same time does not affect the membrane treatment performance, NaOCl can be recommended as a cleaning agent to remove biofouling in a lab-scale molasses based MBR.

1. Introduction

Membrane bioreactors (MBRs) are a promising technology for wastewater treatment [1], but their widespread application is hindered by the inability to control effectively membrane fouling. Fouling is the process where solutes or particles deposit onto a membrane or into the membrane pores causing membrane obstruction and decrease of MBR performance. Fouling limits the achievable permeate flux, reduces the sustainability of operation, increases the cleaning frequency, reduces the lifetime of the membrane, etc. Membrane fouling can be classified as colloidal (clays, floc), organic (oils, humics), inorganic (mineral participates) or biofouling (caused by bacteria or fungi) [2]. Biofouling is driven by bacteria, present in the activated sludge, that adhere to the membrane surface and start to produce a biofilm by excreting extracellular polymeric substances (EPS) [3]. EPS are a complex mixture of mainly proteins and carbohydrates, but also acid polysaccharides, DNA and lipids, that form a matrix that surrounds cells in flocs and biofilms [4,5]. The initial phase of biofilm formation also promotes the aggregation of other activated sludge components, such as metal ions, resulting in a dense structure present on the membrane surface. Biofouling increases the transmembrane pressure (TMP) that is required over the membrane to maintain a constant flux operation. Therefore, when a critical threshold pressure is reached, the membrane requires chemical cleaning or even replacement [6].

Various strategies are used to control membrane biofouling and include physical cleaning, such as, back-washing [7], back-pulsing [8] and air sparging [9]. Another promising effort to alleviate biofouling is membrane modifications [10–14]. Yet other methods involve the application of biological based cleaning by using EPS degrading enzymes, such as proteases, polysaccharases and DNAses [15–17], by adding bacteriophages [18] or by inhibiting quorum sensing signals [19,20]. However, all these methods are still in their developmental phase and have not been translated into effective strategies for industrial MBRs. Therefore, in many full-scale MBRs, membrane chemical cleaning is still an essential step to maintain performance on the longer term. In most full-scale MBR installations, the most popular cleaning agent remains sodium

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hypochlorite (NaOCl) [21], often combined with citric acid [6]. Up to date, studies on NaOCl mainly focussed on its direct impact on MBR performance, investigating the effect of NaOCl cleaning with respect to water flux recovery [22] and membrane permeability recovery [23]. Also, a number of studies have investigated the effects of chemical cleaning using sodium hypochlorite on polyvinylidene fluoride (PVDF) membranes [24,25] or other membranes such as polysulfone (PSf), polyether-sulfone (PES) and cellulose acetate based ones [26–30]. Only two studies refer to microbial community characterization after chemical cleaning. In both of them, the cleaning was performed inside the MBR (chemically enhanced backwashing), thus these studies focused on microorganism activities in activated sludge as a function of NaOCl doses supplied via backwashing [31,32].

However, the initial biofilm formation with respect to microbial communities re-growing after multiple cleanings and under different regimes has not yet been examined. Fundamental information such as bacterial richness and density is essential for optimising anti-biofouling strategies. In practice, it is also important to determine optimal NaOCl concentrations that eliminate most of the attached organic material and bacteria with limited damage to the membrane. To gain insight into these aspects, a series of cleaning experiments was performed in a lab-scale MBR treating molasses wastewater and using NaOCl as a cleaning agent. The objectives of this study were to analyze the effect of the chemical cleaning with four different NaOCl concentrations on (i) bacterial communities attached to the membrane in terms of bacterial richness and cell density, (ii) chemical functional groups of initially formed biofilms, and (iii) PVDF membrane functionality.

2. Materials and methods

2.1. Experimental set-up

2.1.1. MBR system and operating conditions

A lab-scale MBR (High-Throughput Membrane Systems, Leuven, Belgium) (30 L) was equipped with a holder for 20 membrane modules (Fig. 1). The pressure difference created by the pump (transmembrane pressure, TMP) was monitored by a pressure gauge (accuracy ±2%), which was installed for each module individually. The operational flux was 20 L/m^2 h. Each membrane had a maximum effective filtration area of 165 cm^2 and a pore size of approximately 0.138 μm. The air source with constant pressure of 2 bar, was directly linked to the bottom of each module position. The MBR was operated in a fed-batch mode using sludge that was fed with a 2.2 mL/L molasses-based synthetic wastewater. The sludge seed was obtained from a pilot-scale MBR treating molasses wastewater (Waterleau, Wespelaar, Belgium). The characteristics of the wastewater and operational parameters are presented in Table 1. The MBR was run for one year for a different experiment prior to this study and therefore can be considered as fully stabilized.

2.1.2. PVDF Membrane preparation

The lab-made polyvinylidene fluoride (PVDF) membranes were prepared via the phase inversion technique. Membranes were lab-prepared to ensure full control over the membrane chemistry and morphology.

Polyvinylidene fluoride (PVDF) membranes were prepared by dissolving 12 wt% of polymer ($M_W \sim 534$ kDa, Aldrich, Germany) into N,N-dimethylformamide (DMF, supplied by Acros Organic). The solution was cast to form a 250 μm wet-thickness film onto a polypropylene support (Novatexx 2471, supplied by Freudenberg, Germany) at a casting speed of 2.25 cm/s and then coagulated into a demineralised water bath, acting as the non-solvent. After complete coagulation, all membranes were washed with water, dried and stored in open air.

2.1.3. Methods of PVDF membrane characterization

The surface and cross-section images of the membranes were obtained using scanning electron microscopy (SEM) (Philips SEM-XL30 FREG with EDX dx-4i system) and further analyzed for pore size and surface porosity with Image J (http://rsbweb.nih.gov/ij/). Before SEM analysis, the membranes were dried by immersing

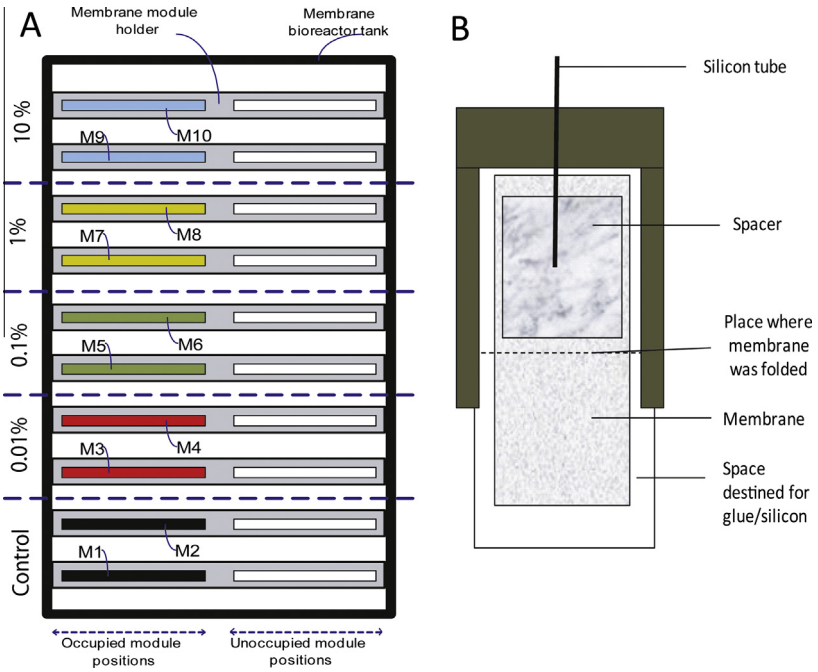

Fig. 1. (A) Scheme of the membrane module arrangement and cleaning strategy. Membranes (M1 to M10) were cleaned *ex situ* using different NaOCl concentrations (0.01–10%) or Milli-Q (control) during 24 h and placed back in the same position after water rinsing and one hour of water filtration to remove the residual NaOCl, (B) A scheme of single membrane module.