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Alleviation of membrane fouling in a submerged membrane bioreactor with electrochemical oxidation mediated by *in-situ* free chlorine generation

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ABSTRACT

The control of membrane fouling is still the biggest challenge that membrane bioreactor (MBR) for wastewater treatment faces with. In this report, we evince that an *in-situ* electrochemical free chlorine generation is effective for membrane fouling mitigation. An electrochemical oxidation (EO) apparatus with perforated Ti/IrO_2 anodes and Ti/Pt cathodes was integrated into a conventional MBR with microfiltration module (EO-MBR). The membrane fouling characteristics of EO-MBR fed with synthetic wastewater were monitored for about 2 months in comparison to control MBRs. In the EO-MBR at a direct current density of 0.4 mA/cm^2, the frequency of membrane fouling when the trans-membrane pressure (TMP) reached 30 kPa was effectively reduced by 40% under a physical membrane cleaning regime. The evolution patterns of TMP together with hydraulic resistance analysis based on resistance-in-series model indicated that the electrochemically generated active chlorine alleviated the physically irremovable membrane fouling. Further analysis on extracellular polymeric substances (EPS) of sludge cake layer (SCL) revealed significant reductions of protein contents in soluble EPS and fluorescence emission intensities from humic acids and other fluorophores in bound EPS, which in-turn would decrease the hydrophobic accumulation of organic foulants on membrane pores. The chlorine dosage from the EO apparatus was estimated to be 4.7 mg Cl_2/g MLVSS/day and the overall physicochemical properties (bio-solids concentration, floc diameter, zeta-potential) as well as the microbial activity in terms of specific oxygen utilization rate and removal efficiency of dissolved organic carbon (>97%) were not affected significantly. A T-RFLP (terminal restriction fragment length polymorphism) analysis suggested noticeable shifts in microbial community both in mixed liquor and sludge cake layer. Consequently, our electrochemical chlorination would be an efficient fouling control strategy in membrane-based water treatment processes where additional electricity consumption and cathodic scale deposition are not of serious concerns.

1. Introduction

Membrane bioreactors (MBRs) may prove to be an efficient way of wastewater treatment and reclamation in recent years owing to the benefits in effluent quality, process control, and compatibility to various types of wastewater. The demands for MBRs are still expected to increase with more than double-digit growth rate annually over the next decade (Zheng et al., 2010; Santos et al., 2011). Nevertheless, membrane fouling remains the most critical limiting factor of commercialization causing an increased maintenance costs. The membrane fouling is a highly complex process with the deposition and interaction of various foulants, including organic/inorganic compounds and microorganisms on and inside the membrane (Le-Clech et al., 2006; Drews, 2010). Thus far, numerous strategies in attempts to overcome the membrane fouling have been reported; modification of membrane surface (Zhou et al., 2010), improvement of module design (Hai et al., 2006), operation below the critical flux (Cho and Fane, 2002), scrubbing membrane via aerating bubbles in air scour (Drews et al., 2010), relaxation and/or backwashing (Wu et al., 2008), and

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addition of chemicals (Koseoglu et al., 2008).

A considerable body of literature has been reported to employ various methods in advanced oxidation processes (AOPs) as means of fouling control for MBRs. For example, ozonation might be a feasible approach via reducing extractable extra-cellular polymeric substances (EPS) content in MBRs (Huang and Wu, 2008; Wu and Huang, 2010). An ultrasonic treatment could partially remove the organic matters from the membrane surface, primarily owing to cavitation and acoustic streaming (Chen et al., 2006). More recently, an intermittent exposure to minute electric field improved the performances of membrane filtration (Chen et al., 2007; Akamatsu et al., 2010; Liu et al., 2012), where negatively charged colloidal particles are electrophoretically attracted to anodes rather than being accumulated on the membrane surface. These methods commonly seek towards simple equipment adjunctive to the membrane module, in order to reduce the frequency of membrane maintenances (with interruption of effluent flux) and to avoid potential membrane damage by concentrated chemicals.

To our knowledge, this work is the first report that an electrochemical oxidation (EO) is a viable method to alleviate the membrane fouling in MBRs, by *in-situ* generation of free chlorine species. Electrochemical methods, as an effective AOP for transformation of aqueous pollutants, offer many advantages including simple instrumentation, versatility, compatibility to other unit processes, and operational flexibility (Comninellis, 1994; Chen, 2004; Anglada et al., 2009; Panizza and Cerisola, 2009). Oxidative degradations of pollutants are usually mediated by reactive oxygen species (ROS) and reactive chlorine species (RCS), depending on the type of electro-catalytic anodes. In particular, free chlorine species have often been recognized as more effective oxidant than the ROS (*e.g.*, •OH) whose primary reliance on heterogeneous reactions would be limited by mass transport. Owing to their relatively long lifetime, the active chlorines are able to diffuse into the bulk solution for further homogeneous reactions with wide array of electron donating compounds. The generation of active chlorines from heterogeneous oxidation of chloride ions on metal oxide electrodes, represented by dimensionally stable anodes (DSAs) based either on IrO_2 or RuO_2 (Malpass et al., 2006; Costa et al., 2008), have been thoroughly investigated over the past decades (Comninellis, 1994). The extensive use of active chlorines in EO is further justified by the ubiquitous presence of chloride ion in wastewaters. To this end, we envisaged that organic foulants accumulating on surface or inside pores of membrane could be effectively reduced via electrochemically generated free chlorine species. This work addresses the alleviated fouling behavior of an MBR equipped with EO module, also with focuses on the effects of electrochemically generated active chlorines on the sludge cake layer (SCL) and bioreactor.

2. Materials and methods

2.1. Description of the MBR set-ups

As a control MBR, 0.4 μm hollow fiber membrane module (effective filtration area = 0.05 m^2, Mitsubishi Rayon Co. Ltd., Japan) made of polyvinylidene fluoride (PVDF) was immersed in a bioreactor with a working volume of 5.5 L. The permeate from the MBR was collected at a constant flow rate by a peristaltic pump (Masterflex 7518–10, Cole-Parmer Instrument Co. Ltd., USA) with recording the trans-membrane pressure (TMP) by a digital pressure gauge (GC 61, Nagano Keiki Co. Ltd., Japan). The collection of effluent was controlled by a timer to rest for 1 min after every 7 min, while a water level sensor inside the bioreactor actuated the influent pump (hydraulic retention time ~ 8.7 h). A periodic backflush, common practice to reduce membrane fouling (Wu et al., 2008), was excluded in our relaxation scheme so as to monitor the fouling behaviors more quickly. A porous air diffuser under the membrane module provided continuous aeration to maintain the dissolved oxygen (DO) concentration greater than 5 mg/L.

For the EO-MBR (Fig. 1), commercial electrodes (Permelec electrode Ltd., Japan) were inserted into the MBR, where perforated Ti/IrO_2 anodes (100 × 5 mm^2, 6 total) and Ti/Pt cathodes (100 × 30 mm^2, 2 total) were located 5 cm apart from the membrane in between. Direct currents for the electrochemical free chlorine generation were supplied by a galvanostat (Model 2273 A, Princeton Applied Research, USA). A separate EO-MBR set-up was operated in parallel without an applied current (w/o current) in order to assess potential effects of the electrodes assembly on the hydrodynamics of the scrubbing aeration bubbles across the membrane module (*e.g.*, creation of a dead zone or aeration inhomogeneity).

In order to find a current density level not to affect the microbial activities, the rate of free chlorine generation was measured by batch electrolysis. The amounts of active chlorines were monitored in a vessel for the EO-MBR filled with 10 mM NaCl solutions under galvanostatic conditions (10 min) at current densities varying from 0.1 to 5 mA/cm^2. The current efficiencies of free chlorine generation were assessed based on the following equation.

$$CE_{FC} = \frac{nFC_{FC,t}V}{It} \tag{1}$$

where, CE_{FC} is the current efficiency of free chlorine generation, I is the current (A), V is the vessel volume (L), $C_{FC,t}$ is the concentration (M) of free chlorine measured by DPD reagent (Hach, USA) at time t (sec), n is the number of electron required for free chlorine generation (2), and F is the Faraday's constant (96,485.3 C/mol).

2.2. Operation and monitoring of the MBR set-ups

The inoculum sludge was collected from a pilot-scale MBR facility in Japan treating municipal wastewater. The sludge was acclimatized in a fill-and-draw reactor for 30 days prior to the MBR experiments. Each bioreactor set was fed continuously with synthetic wastewater (Table 1) at a COD:N:P ratio of 100:10:2. The influent concentration of chloride was 455 mg/L, which was much greater than typical values (30–100 mg/L) in domestic wastewaters (Tchobanoglous et al., 1991), but often observed in a high salinity industrial wastewater. The pH in the bioreactors was observed to be between 6.5 and 7.5 owing to the buffering capacity of the influent.

At a constant effluent flux of 0.35 m^3/m^2 d (14.6 L/m^2 h), the fouling behavior of each MBR was monitored in terms of the evolution of TMP. Because temporal increase in TMP should be primarily due to fouling at a constant flow rate, membrane cleaning was performed when the TMP reached approximately 30 kPa. The fouled membranes were taken out of the bioreactors and polished physically without exposure to chemicals, in order to assess the effects of EO more clearly (*vide infra*). Wasting of activated sludge was minimized except for analytical purposes described below; *i.e.*, the sludge retention time (SRT) was close to the whole operation duration (60 days). After the operation was finished, microscopic observations were performed on the fouled membrane (after polishing) and cathodes using a JSM-6300 scanning electron microscope (SEM; JEOL, Japan) equipped with an energy dispersive X-ray spectrometer (EDX; KEVEN, USA).

2.3. Analytical methods

2.3.1. Hydraulic resistance of the membrane

A resistance-in-series model was employed to estimate the