Photocatalytic mineralization of secondary effluent organic matter with mitigating fouling propensity in a submerged membrane photoreactor

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HIGHLIGHTS

- A membrane photoreactor had the potential to remove secondary effluent organics.
- TiO$_2$ attachment as well as colloids and air bubbles interfered with photocatalysis.
- Bubble-free backpulsing enhanced the photocatalytic performance.
- The synergy of adsorption and catalysis enabled TiO$_2$ particles' self-regeneration.

GRAPHICAL ABSTRACT
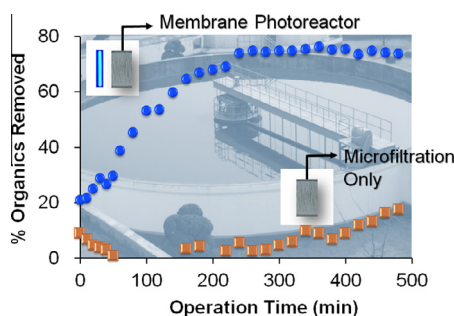
ABSTRACT

Secondary effluent organic matter (SEOM) is an unwanted constituent that impairs the reuse of wastewater effluent. The potential of a membrane photoreactor (MPR) involving TiO$_2$ photocatalysts and submerged microfiltration (MF) membranes was investigated with regard to SEOM degradation and fouling control. Colloidal particles interfered with the photocatalysis of the SEOM when accumulated inside the reactor. Air bubbles, which were continuously supplied to disturb the cake formation at the membrane surface, also hindered the photocatalytic performance due to light scattering. Intermittent bubble-free backpulsing was attempted and found to help improve membrane permeability, with considerably reduced energy requirements, while detaching photocatalysts from the membrane. Bubbleless backpulsing for short periods (30 s every 1 h) at low pressures (0.5 bar) was effective in reversing the fouling layers. MPR treatments removed >60% of the SEOM at a hydraulic residence time of 140 min, degrading a wide range of SEOM molecules. The synergistic reactions of adsorption and photocatalysis of the SEOM at the TiO$_2$ surfaces induced their self-sustaining capability after rapid organics sequestration.

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1. Introduction

Advanced treatments of municipal and industrial wastewater are becoming increasingly important to supply growing water demands for domestic and industrial use, as well as to sustain natural ecosystems [1–5]. The residual organic matter present in secondary effluents, such as natural organic matter, soluble microbial products, and micropollutants, should be further removed to meet stringent water quality regulations [6–9]. Various processes have been considered to do so, such as activated carbon adsorption [10–12], ion exchange [13–15], advanced oxidation [16–18], and membrane filtration [14,18–21]. In particular, membrane technology is an attractive option because of its compact design, small footprint, lower chemical consumption, and ease of automation and maintenance [22,23]. However, low-pressure membrane processes alone, such as microfiltration (MF) and ultrafiltration (UF), are limited in removing the secondary effluent organic matter

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(SEOM) and have a secondary problem due to membrane fouling [24–26].

Coagulants (Fe^{3+} or Al^{3+}) in combination with membranes can sequester organics from the secondary effluent, but generate chemical sludge that requires disposal [26,27]. Adsorbents (e.g., activated carbons, carbon nanotubes, and mineral oxides) can also remove the SEOM as well as micropollutants, but again, the spent sorbents require regeneration or disposal [11,28,29]. In addition, the interaction between SEOM and micropollutants (e.g., perfluorinated compounds and bisphenol A) affected the sorption capability of micropollutants onto carbon [12,30]. Advanced oxidation processes (AOPs), which are associated with the use of strong oxidants (e.g., ozone and hydrogen peroxide) and/or UV radiation, can destroy SEOM and micropollutants [6,31–33]. A large dose of oxidants (e.g., O_3 and Cl_2) may generate unwanted, toxic by-products (e.g., nitrosamines and halogenated compounds) and should be quenched before they come into contact with polymeric membranes to avoid damage to the membranes [34,35].

Heterogeneous TiO_2-mediated photocatalysis has received much attention because it has demonstrated superior degradation of hazardous and refractory organic compounds in wastewater to other AOPs [36–38]. In addition, photocatalysis has the potential to directly utilize sunlight (solar energy) instead of fossil fuel energy [39,40]. Membrane photoreactors (MPRs), which are a hybridized system consisting of photocatalysis and membrane filtration, have been developed and tested for the degradation of humic acids [24,41,42], natural organic matter [43], dyes [44,45], wastewater effluents [46,47], and toxic chemicals [44,48]. These organic pollutants were degraded well by the MPR, although the extent of the mineralization of organic matter in a salt solution (e.g., seawater) was marginal due to the scavenging of hydroxyl radicals by chloride ions in seawater [49]. Addition of iron oxide to the MPR, or use of an iron oxide-coated membrane, helped improve the adsorptive removal of natural organics that were otherwise desorbed by the photocatalysis reactor [42,43]. In addition, membrane fouling was mitigated as long as the organics were degraded by photocatalysis [42]. In recent years, photocatalytically active membranes have been fabricated for the degradation of organic contaminants, with the simultaneous prevention of membrane fouling [50,51]. However, ensuring adequate light irradiation of the membrane surface is the main problem that has not yet been answered. In this context, the use of a MPR with photocatalytic slurries seems more feasible for real applications. Despite the merits of the MPR system, little information is available on its use for the treatment of real wastewater streams containing colloidal particles and refractory organics.

The present study focused on the MPR treatment of the secondary effluent (whose character is different from natural water) obtained from a real municipal wastewater treatment plant, with regard to the organics removal and fouling control. The effects of secondary effluent colloids, aeration bubbles, and backpulses (BP) were investigated during continuous flow MPR operations. A newly devised physical cleaning method (i.e., bubble-free backpulsing) was evaluated and compared with normal aeration in terms of fouling control. The synergy of adsorption and photocatalysis on TiO_2 particles was discussed, with particular regard to organics degradation and fouling control.

2. Materials and methods

2.1. Secondary effluent

The secondary effluent used in this study was taken from the Shincheon Municipal Wastewater Treatment Plant in Daegu, Korea. The secondary effluent samples that were collected were shipped to the laboratory and then stored at 4 °C before use. The key characteristics of the secondary effluent samples are given in Table 1. To remove the particulate matter present in the secondary effluent, it was pretreated using filters (Millipore, USA) with different pore sizes ranging from 0.45 μm to 100 μm.

2.2. Photocatalyst and membrane

The TiO_2 particles (P25, Degussa, Germany) used as photocatalysts had a surface area of 50 m^2/g and an average grain diameter of 3 μm when suspended in water [48]. The hollow fiber MF membrane (Econity, Korea) used in the MPR was made of hydrophilized polyethylene, with a nominal pore size of 0.4 μm in diameter and a surface area of 60 cm^2.

2.3. Membrane photoreactor operations

The MPR comprised a blacklight blue UV lamp (TL8W/08, Philips, Holland) and a submerged MF membrane and had a working volume of 700 mL (Fig. 1). The UV lamp with a measured power consumption of 6.5 W had a photon flux of 40 mW/cm^2 at a maximum wavelength of 365 nm. TiO_2 particles were dosed into the reactor, initially at 1.0 g/L, and the reactor was continuously mixed at 300 rpm using a magnetic stirrer. The TiO_2 dosage (1.0 g/L) was selected based on our preliminary tests on the effects of TiO_2 doses on organics degradation (Fig. S1). Peristaltic pumps (Cole Parmer, USA) were used for continuous feeding and suction at a flow rate of 5 mL/min, while aeration (2 L/min, corresponding to a G value of 479 1/s) was provided to maintain the liquid phase TiO_2 concentration by using an air diffuser underneath the membrane. The air flow rate was measured using a flow meter (32457-40, Cole Parmer, USA).

In particular, periodic backpulsing (instead of aeration) was devised and performed using a compressed gas (N_2) at 0.5–1.0 bar, which is below the bubble point (~1.5 bar) of the membrane; thus, no bubbles were generated during backpulsing. Backpulse frequencies (every 30 min or 1 h) and durations (from 30 s to 105 s) were changed to investigate their effects. Backpulsing required no permeate while achieving ~100% water recovery. A two-stage soap bubble flow meter (Perkin-Elmer, USA) was used to measure the gas flow rate during backpulsing.

During continuous MPR testing, the reactor volume was maintained at 700 mL using a level sensor, which controlled the pump, adding the sample from the feed tank when required. The MPR was operated under a constant flux of 50 L/m^2/h. The hydraulic residence time of the MPR was 140 min and each continuous experiment ran for 8 h. During the experiments, the variation of the transmembrane pressure (TMP) was monitored using a digital pressure transducer (ZSE40F model, SMC Corporation, Japan), together with a digital multimeter (M-3850D, METEX, Korea), and a personal computer.

Table 1
Ranges of key characteristics of the secondary effluent samples.

Parameter	Value
pH	7.0–7.7
UV$_{254}$ (1/cm)	0.064–0.077
TOC (mg/L)	2.1–3.7
SUVA (L/mg-m)	2.0–2.9
Conductivity (μS/cm)	748–789
Turbidity (NTU)	1.18–1.72
Alkalinity (mg/L as CaCO$_3$)	87–90
Hardness (mg/L as CaCO$_3$)	146–176
Total suspended solids (mg/L)	3–6