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Enhancement of membrane filtration ability by pretreatment of secondary effluent using a new photocatalytic oxidation system

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ABSTRACT

Secondary effluent including different kinds of foulants, e.g. extracellar polymeric substances (EPS), soluble microbial products (SMP), and humic acids was considered as a major barrier for wastewater reuse and reclamation when a membrane was applied to obtain high quality treated water. A new hybrid system of photocatalytic oxidation and non-woven membrane separation was studied for treating secondary effluent. Initially, the foulant properties, such as polysaccharide, protein, and biopolymer, etc., were examined in a batch test. The experimental results revealed that foulants in secondary effluent could be photodegraded. Then, a continuous experiment with this new hybrid system, three applied fluxes of 16.6, 33.3, and 50.0 L/m^2/h (LMH), was applied to investigate the photodegradation ability and the filtration behavior. The results revealed that the concentration of foulants in permeate increased with increasing applied flux, due to the reduction of hydraulic retention time (HRT). In comparison with the system using microfiltration (MF) or ultrafiltration (UF) membrane, larger specific flux was obtained in our non-woven membrane system. In addition, a batch-stirred cell test using UF membrane was performed to compare filtration performance before and after photodegradation in secondary effluent. Such results proved that this new hybrid system was an effective treatment process for foulant removal in secondary effluent.

Keywords: Secondary effluent; Photocatalytic oxidation; EPS; Biopolymer; Non-woven membrane

1. Introduction

Secondary effluent contains colloids and infracolloids [1] or extracellar polymeric substance (EPS) [2] which have been identified as playing an important role in fouling microfiltration (MF) and ultrafiltration (UF) membranes [3]. Secondary effluent components are quite complex and are of interest when microporous membranes are applied as a pretreatment process before reverse osmosis (RO). The fractions of chemical oxygen demand (COD) separated by molecular weight cut-off (MWCO) have revealed that solute is major contributor for membrane fouling [1]. Furthermore, there is a relationship

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Table 1
Characteristics of secondary effluent in Ruhleben WWTWs

pH	Turbidity (NTU)	DO* (mg/L)	DOC* (mg/L)	UV_{254}* (cm^{-1})	SUVA* (Lm^{-1} mg^{-1})	Protein (mg/L)	Polysaccharide (mg/L)
7.2	1.7	4.9	11.7	0.27	2.3	10.9	4.6

*DO, dissolved oxygen; DOC, dissolved organic carbon; UV_{254}, ultraviolet light (specifically at a wavelength of 254 nm); SUVA, specific ultraviolet absorbance.

between the apparent molecular weight distribution (AMWD) and membrane resistance in secondary effluent using UF membrane [4].

Coagulation, adsorption or both have been used to pre-treat secondary effluent before membrane filtration in order to reduce fouling causing materials and enhance membrane permeability [1,2]. However, coagulants added resulted in increasing running and sludge disposal costs. Exhausted activated carbon regeneration costs after adsorption also need to be considered. Consequently, an advanced oxidation process (AOP) has also been proposed for oxidizing foulants in secondary effluent. Preozonation can break foulants down into small fractions, but this process cannot completely oxidize the pollutants in secondary effluent, which may result in different fouling characteristics [4]. By contrast, heterogeneous photocatalysis has been considered as one of the more promising AOPs for treating persistent organic pollutants [5] and humic acids [6] in water and wastewater treatment.

A suspended photocatalyst has more effective photocatalytic activity than a fixed one because more active surface area is available. However, the effective separation of suspended photocatalysts in an aqueous solution is still an issue. In recent years, the separation of photocatalyst particles from an aqueous solution has been tried by using MF [7], UF [8], or even nanofiltration (NF) [9] membrane. However, problems such as low flux, high operational pressure, and membrane fouling were still not overcome.

It is well known that non-woven fabric with a random structure is cheap and has been extensively applied as a filtration material for water treatment [10]. In our laboratory, we have successfully developed submerged non-woven fabric membrane bioreactor technology for industrial wastewater treatment [11] and wasted sludge reduction [12]. Afterward, we also developed a side stream non-woven membrane reactor to separate photocatalysts and degrade methylene blue [13]. In previous study, we used the hybrid system combining a photocatalytic oxidation with titanium dioxide particles separated by submerged non-woven membrane to simplify a process [14]. The aims of this study were to photodegrade foulants in secondary effluent in a batch test to investigate the photodegradation ability with different react time. Sequentially, we examined the filtration performance of the hybrid system in a continuous mode with various operating conditions to compare their filtration behavior. Finally, we also tested the secondary effluent before and after photodegradation to determine whether there was any improvement in filtration performance of UF membrane in a batch-stirred cell test.

2. Methods and materials

2.1. Characteristics of secondary effluent

The secondary effluent conducted in this study was emitted from the Ruhleben wastewater treatment works (Berlin, Germany). The effluent was prefiltrated with a 100 μm filter before the photocatalytic experiments. The characteristics of the secondary effluent are listed in Table 1 [15].

3. Experimental conditions

3.1. Description of batch test

A batch reactor having a working volume of 8 L (22 cm (diameter (φ))×21 cm (height (*H*))) without installing a submerged non-woven membrane was used. Degussa P25 TiO_2 powder with a primary particle size of 20–30 nm was selected as photocatalyst. The concentration of the photocatalyst was set at 1000 mg/L in all batch tests. A set of four black lamps (F4T5BLB, Sankyo Denki, Japan) each with 4 W power and a wavelength of 365 nm was used for UV radiation. The light intensity of each lamp was 6 mW/cm^2. Each lamp (15 mm (φ) × 134 mm (length (*L*)) was submerged into the reactor using lamp holder (40 mm (φ) × 300 mm (*L*)) which was made of Pyrex glass and located at the middle of radius. A mixer with 150 rpm was installed at center of batch reactor to maintain suspending photocatalysts during experimental periods. pH value of secondary effluent was adjusted from 7.5 to 5.5 to obtain the highest photocatalytic oxidation efficiency for all foulants (data were not available here) before experiments.

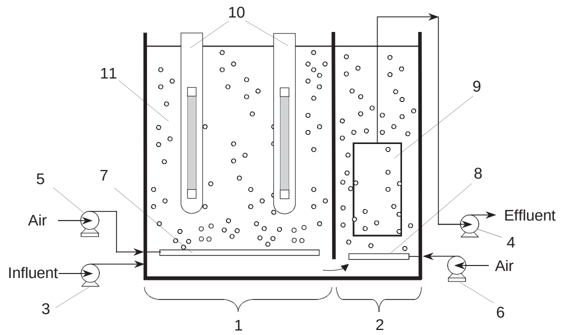

Fig. 1. Schematic diagram of the hybrid system coupling photocatalytic oxidation with a non-woven membrane reactor.

The samples with photocatalysts were taken from bulk solution in reactor and settled 10 min. Then, the supernatant was filtrated by a 0.45 μm acetate nitrate filter (Sartorius, Goettingen, Germany) before analysis and precipitated photocatalysts were returned to reactor. All experiments were carried out at room temperature.

3.2. Description of continuous test

The hybrid system of photocatalytic oxidation and non-woven membrane separation was used for a consecutive test, as shown in Fig. 1. The reactor was made of Pyrex glass with a working volume of 22.4 L. The reactor was divided into two sections by a UV light blocking baffle: a photocatalytic reaction region with volume of 16 L (20 cm (*L*) × 20 cm (width (*W*)) × 40 cm (*H*)), and a membrane separation region with volume of 6.4 L (8 cm (*L*) × 20 cm (*W*) × 40 cm (*H*)). A non-woven membrane cell with pore size of 2.0 μm manufactured by KNH Co. Ltd., Taiwan, was submerged into the filtration region of reactor. The optimum pore size of non-woven membrane used in hybrid system was determined in previous study [16]. The aeration units were installed at the bottom part of the reactor to maintain suspending particles in reactor, and also induce a cross flow along the membrane surface. The photocatalysts and UV lamps used in continuous mode were same as in batch test. The permeate was drawn by a suction pump. A vacuum pressure gauge and flow meter were installed and connected to a computer to monitor trans-membrane pressure (TMP) and record flow rate during the entire experiment. The samples were taken from permeate of non-woven membrane using a 0.45 μm acetate nitrate filter before analysis except the measurement of residual turbidity. All experiments were carried out at room temperature.

3.3. Analysis

Foulants (polysaccharide and protein) were measured by photometric methods [17], based on Dubois and Lowry method, respectively. Photometric signals of samples for polysaccharide, protein, and UV_{254} were conducted with a Perkin Elmer UV/Vis Spectrometer Lambda 12 (Perkin-Elmer GmbH, Berlin, Germany) at different wavelengths.

DOC concentration of analyzed samples was measured by High Total Organic Carbon (TOC) meter (Elementar Analysensysteme) after being filtrated by a 0.45 μm acetate nitrate filter.

Liquid Chromatography–Organic Carbon Detection–Organic Nitrogen Detection (LC-OCD-OND) (manufacturer DOC-LABOR Dr. Huber, Karlsruhe, Germany) was used to analyze a biopolymer and humic acids with a dissolved organic carbon detector used non-dispersive infrared absorption (Ultramar 6 from Siemens, Munich, Germany), a UV254 detector (K-200-UV254) and a size exclusion column HW55S (GROM Analytik + HPLC GmbH, Herrenberg, Germany). The LC unit separates organic compounds according to their molecular size through the size exclusion column.

3.3.1. UF membrane filtration performance by a batch-stirred cell test [18]

The filtration performances of UF membrane with samples taken from batch and continuous experiments before and after photodegradation were determined as normalized flux declined over specific cumulative permeate volume, using a batch-stirred cell test (Amicon 8200, Millipore, USA) and a hydrophilized polyether sulfone (PES) UF membrane with MWCO 150 kDa (NADIR @ UP150, Germany).Used filtration area for test was 28.7 cm^2. A stirrer was set 150 rpm to control a cake layer on the surface of UF membrane. All measured samples were prefiltrated with a 0.45 μm acetate nitrate filter. All membrane filtration experiments were performed at 1 bar TMP and at room temperature.

4. Results and discussion

4.1. Batch study

4.1.1. Foulant reduction as a function of reaction time

Suspended photocatalytic oxidation of foulants in terms of DOC, protein, polysaccharide, SUVA, and UV_{254} in secondary effluent was studied at pH 5.5 and TiO_2 concentration of 1000 mg/L. The concentration of foulants versus different UV irradiation times is presented in Fig. 2. There were no obvious changes in any

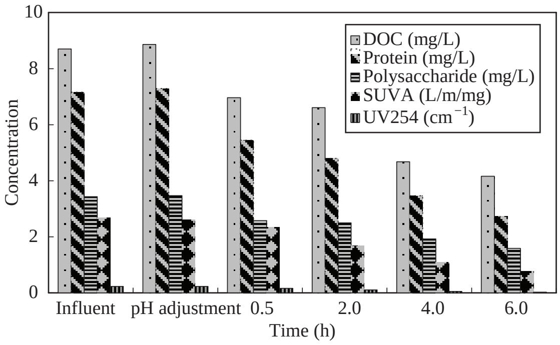

Fig. 2. The concentration of DOC, protein, polysaccharide, SUVA, and UV_{254} (TiO_2 = 1000 mg/L, light source = 4 W × 4 lamps, mixing rate = 150 rpm, irradiation time = 0, 0.5, 2, 4, 6 h).

of the constituents when a sample was taken immediately after a pH adjustment from 7.2 to 5.5. Then followed by 30 min adsorption by photocatalysts without UV radiation, we observed that all constituents were adsorbed onto the photocatalysts reducing their concentration (Fig. 2) after adsorption. This was a positive result for a heterogeneous photocatalytic system which is dominated by surface reactions. After radiation by UV light, the concentration of the foulants in the secondary effluent was progressively photodegraded with time, as shown also in Fig. 2.

4.1.2. Effect of photocatalytic time on filtration performance of UF membrane

We carried out a batch-stirred cell test with UF membrane to examine the degree of membrane fouling in secondary effluent under different photocatalytic oxidation times. Basically, lower fouling potential wastewater indicated higher filtration ability, which resulted in less normalized flux decline for the same permeate volume [15]. Fig. 3 shows the normalized flux decline as a function of specific cumulative permeate volume (Specific cumulative permeate volume is cumulative permeate volume divided by membrane area.). The normalized flux reduction of secondary effluent without photocatalysts was around 70%. A similar trend of the normalized flux reduction was observed after pH adjustment. After 30 min, adsorption without radiation the normalized flux reduction was about 30%. After 2 h, photocatalytic oxidation, the normalized flux reduction was less than 10%. Thereafter only a slight normalized flux reduction was observed after 4 and 6 h reaction time, as shown Fig. 3. The experimental results confirmed that foulants in secondary effluent could be photodegraded and which would dramatically improve the filtration performance of UF membrane in a batch-stirred cell test.

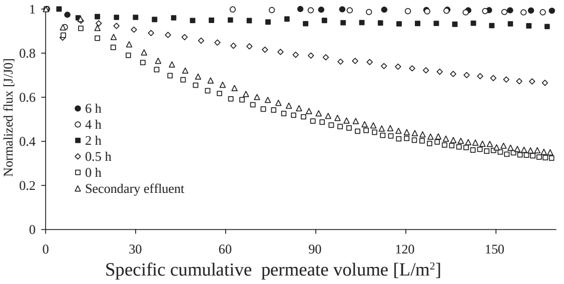

Fig. 3. Normalized permeate flux versus specific cumulative permeate volume (membrane = PES membrane UP 150, mixing rate = 150 rpm, filtered volume = 500 mL): effect of adsorption (0.5 h) and irradiation time.

4.1.3. LC-OCD profile at different reaction times

The DOC composition of the secondary effluent was characterized by using size exclusion chromatography with continuous UV_{254} and organic carbon detectors. An LC-OCD chromatogram is typically composed of four principal fractions, biopolymers (including EPS), humic substances, low molecular weight acids, and low molecular weight neutrals, which are eluted from the column with decreasing molecular weight with increasing elution time [2]. Biopolymers were identified as a more sensitive and precise indicator for membrane fouling [2,16]. In this study, we focused on how the concentration of biopolymers varied with different reaction times. Fig. 4 shows the LC-OCD chromatogram profile of secondary effluent at different photocatalytic oxidation times. The first peak, at an elution time of about 40 min, represents biopolymers. The six lines represent biopolymer values of secondary effluent, immediately after pH reduction, after 1/2 h of adsorption, and at 2, 4, and 6 h of photocatalytic oxidation, respectively. The biopolymer profile after photocatalysis is shown close to the base line, as depicted in Fig. 4. This means that biopolymer

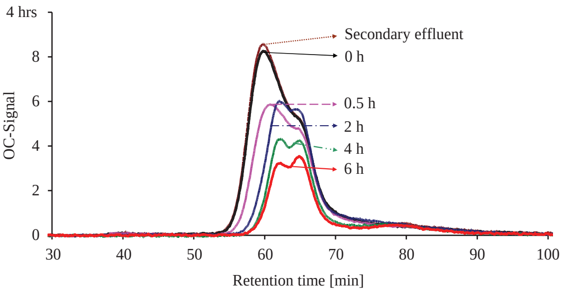

Fig. 4. The LC-OCD profile with different reaction times.

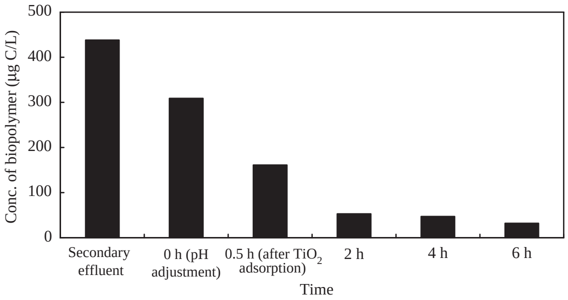

Fig. 5. The concentration of biopolymer versus different reaction times.

could be removed by photodegradation. Moreover, the second peak, shown in Fig. 4, represents humic acids after an elution time of around 65 min. This peak was also reduced with increasing reaction time. These results confirmed that biopolymer and humic acids can be removed by photocatalytic oxidation. The shift to the right hand side of the humic acids peak (Fig. 4) also shows that the molecular weight of the humic acids was reduced by photocatalysis resulting in lower fouling potential of UF membrane in a batch-stirred cell test. The quantified biopolymer is shown in Fig. 5. A concentration of biopolymer in secondary effluent of around 438 μg C/L decreased with increasing reaction times, and was dramatically reduced to range from 32 to 53 μg C/L after photodegradation. More than 87% of the biopolymer was removed from secondary effluent treated by photocatalysis. Most of it was oxidized by photocatalysis which led to dramatically improved filtration performance when tested with a batch-stirred cell test.

4.2. Continuous test

4.2.1. Foulants reduction with different applied fluxes

Non-woven membrane instead of microporous membrane, e.g. MF or UF was incorporated into system to separate the suspended TiO_2 particles in continuous test. Non-woven membrane with a pore size larger than either MF or UF has been showed to obtain lower TMP and stable applied flux in a hybrid photocatalytic system [16]. Three fluxes, i.e. 16.6, 33.3, and 50.0 LMH were applied continuously for 24 h each. The quality of the treated water for protein, polysaccharide, biopolymer, DOC, SUVA, and UV_{254} at different applied fluxes is shown in Fig. 6. The concentration of pollutants in the treated water increased with increasing applied flux due to the reduction of hydraulic retention time (HRT). Treated secondary effluent was then subjected to a batch-stirred cell test. Fig. 7 shows that normalized flux reduction in influent was around 60%. The trends of normalized flux reduction for the three applied fluxes were similar and less than 10%. Although the concentration of the pollutants in treated water was different with applied fluxes, filtration performance was improved because the major foulants were photodegraded (Fig. 6).

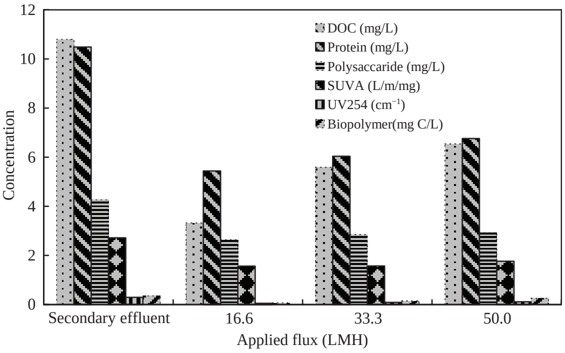

Fig. 6. The effect of flux on variation of wastewater quality (TiO_2 = 1000 mg/L, pH 7.2, light intensity = 4 W × 4 lamps).

4.2.2. Effect of different applied fluxes on filtration performance in a hybrid system

TMP, specific flux, and residual turbidity for each applied flux experiment are summarized in Table 2. A little accumulated TMP increased with increasing applied flux because a more dense cake layer was formed on the surface of the non-woven membrane. This phenomenon also explained why residual turbidity (shown in Table 2) decreased with increasing applied flux. Finally, specific flux, defined as applied flux divided by TMP, was calculated to compare our results with other photocatalytic oxidation plus membrane systems using MF or UF membrane. Specific flux was reduced from 128.5 to 3.1 LMH/kPa when applied flux was increased from16.6 to 50.0 LMH and TMP was increased from 0.1 to 16.0 kPa. Therefore, specific flux

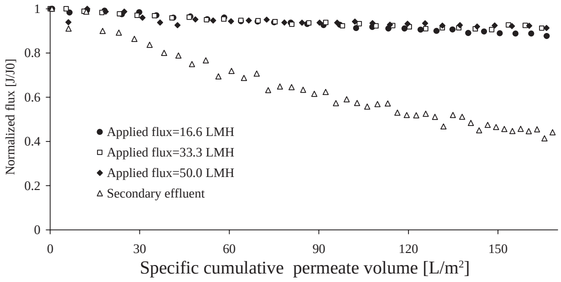

Fig. 7. Normalized permeate flux versus specific cumulative permeate volume (membrane = PES membrane UP 150, mixing rate = 150 rpm, filtered volume = 500 mL): effect of different applied fluxes.

Table 2
Summary of filtration behavior in continuous test

Applied flux (LMH)	TMP (kPa)	Residual turbidity (NTU)	Specific flux (LMH/kPa)
16.6	0.1	1.0	128.5
33.3	2.7	0.8	12.5
50.0	16.0	0.7	3.1

was usually several times higher than in systems using MF or UF membrane [19], when an appropriate flux, i.e. equal to or less than 33.3 LMH was applied in this hybrid system.

5. Conclusions

A new hybrid system coupling photocatalytic oxidation with non-woven membrane separation was found to be an effective treatment process for removing foulants in secondary effluent. The experimental results demonstrated that the foulants could be photocatalytic oxidation in our batch and continuous tests. In batch experiment, the photocatalytic efficiency in terms of biopolymer removal was more than 87% after 2 h photodegradation. However, the photocatalytic efficiency decreased with increasing applied flux in continuous test. The appropriate applied flux was equal to or less than 33.3 LMH to obtain an excellent filtration performance in terms of lower TMP and higher specific flux. In batch-stirred cell test, the remarkable enhancement of filtration performance to below level of fouling potential on UF membrane was also obtained.

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