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Effect of TiO_2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration

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Abstract

Membrane bioreactors (MBRs) have been widely used as advanced wastewater treatment process in recent years. However, MBR system has a membrane fouling problem, which makes the system less competitive. Thus there have been great efforts for fouling mitigation. In this study, two types of TiO_2 immobilized ultrafiltration membranes (TiO_2 entrapped and deposited membranes) were prepared and applied to activated sludge filtration in order to evaluate their fouling mitigation effect.

Membrane performances were changed by addition of TiO_2 nanoparticles to the casting solution. TiO_2 entrapped membrane showed lower flux decline compared to that of neat polymeric membrane. Fouling mitigation effect increased with nanoparticle content, but it reached limit content above which fouling mitigation did not increase. Regardless of polymeric materials, membrane fouling was mitigated by TiO_2 immobilization. TiO_2 deposited membrane showed greater fouling mitigation effect compared to that of TiO_2 entrapped membrane, since larger amount of nanoparticle was located on membrane surface. It can be concluded that TiO_2 immobilized membranes are simple and powerful alternative for fouling mitigation in MBR application.

Keywords: TiO_2; Nanoparticle; Membrane fouling; Membrane bioreactor; Fouling mitigation; Activated sludge

1. Introduction

Conventional wastewater treatment systems have been improved by introduction of membranes as solid/liquid separation devices and these combined systems, which are called membrane bioreactors (MBRs), have been widely used in recent years. However, acceptances of MBR system as wastewater treatment process have been limited by membrane fouling problem. Membrane fouling is derived from depositions of microorganisms and their microbial products on membrane surface [1,2]. Since microorganisms in MBR mixed liquor can create the biofilm and grow attached fashion on membrane surface, membrane fouling can be accelerated. So it is necessary to develop the fouling resistant membranes for MBR application.

It is well known that fouling in MBR system can be influenced by surface property of membrane. Since hydrophobic adsorption of microbial products, such as extra-cellular polymeric substances (EPS), on membrane surface plays a key role in membrane fouling [2,3], hydrophilic modification of polymeric membrane surface can be one of the fouling mitigation methods [2].

There are growing interests on photocatalytic degradation of recalcitrant pollutant in wastewater [4,5]. Various semiconductors can be used for photocatalytic reaction, but TiO_2 have attracted great attention among the semiconductors because of its stability under harsh conditions, commercial availability, and ease of preparation [4,5]. TiO_2 nanoparticles have also been used in water treatment membrane technology in recent years [5–9]. Molinari et al. reported about photocatalytic membrane reactor for toxic organic removal [7–9]. They tried to immobilize TiO_2 nanoparticles on flat polymeric ultrafiltration (UF) membranes in two different ways. One is depo-

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sition of TiO_2 nanoparticles on membrane surface by direct filtration of nanoparticle aqueous suspension. The other is the entrapment of TiO_2 nanoparticles in polymer matrix of membranes by addition of nanoparticles to casting solution [9]. Another researcher studied about TiO_2/polymer thin film composite (TFC) reverse osmosis membrane in order to mitigate biofouling by photobactericidal effect under ultraviolet (UV) radiation [10,11]. However, no studies have been done on TiO_2 immobilized membranes for activated sludge filtration.

In this study, various TiO_2 entrapped membranes were prepared by phase inversion using the same method reported by Molinari et al. Three different polymer, polysulfone (PSf), polyvinylidenefluoride (PVDF) and polyacrylonitrile (PAN), were used as membrane material. TiO_2 deposited membrane was also prepared from dipping and pressurizing method by the authors. Then those membranes were applied to the activated sludge filtration in order to examine the feasibility for MBR application. The purpose of present work was to investigate the fouling mitigation effect of TiO_2 immobilized UF membranes during the activated sludge filtration. This study was mainly focused on (1) the fouling mitigation effect of TiO_2 immobilized membrane compared to neat polymeric membrane, (2) the effect of membrane material and TiO_2 concentration and (3) the comparison between TiO_2 deposited and entrapped membrane.

2. Experimental

2.1. Membrane preparation

TiO_2 entrapped membranes were prepared by phase inversion methods. PSf (Udel-P 3500, Amoco), PVDF (Kynar 760, Atofina) and PAN were used as membrane materials. Casting solutions consisting of polymer, *n*-methyl-2-pyrrolidone (NMP, Aldrich) and TiO_2 nanoparticles (P25, particle size of 20 nm, Degussa) were cast with 200 μm casting knife onto polyester non-woven fabric. The nascent membrane was evaporated at $25 \pm 1\,^{\circ}C$, $65 \pm 5\%$ relative humidity for 30 s and then immersed in $18 \pm 1\,^{\circ}C$ deionized water coagulation bath.

TiO_2 deposited membrane was prepared by dipping and pressurizing method. Neat PSf membrane was dipped into 1% TiO_2 aqueous suspension for 1 min then pressurized at 400 kPa for 2 h using compressed nitrogen gas.

2.2. Membrane characterization

Membrane performance was tested using membrane cells which having 18.1 cm^2 of membrane surface area. Flux was measured at 100 kPa after the flux reached steady state and calculated by the following equation:

$$J_w = \frac{V}{At} \tag{1}$$

where J_w is the pure water flux (l/m^2 h), V the permeate volume (l), A the membrane area (m^2) and t the time (h).

Membrane pore size was characterized by solute passage method using polyethyleneoxide (PEO, MW 100,000) aqueous solution. Rejection was calculated by the following equation:

$$R\,(\%) = \left(1 - \frac{C_{per}}{C_{feed}}\right) \times 100 \tag{2}$$

where C_{per} is the concentration of permeate and C_{feed} the concentration of feed.

The morphologies of membranes, cross-section and surface, were observed with a scanning electron microscope (SEM, JSM 1025, JEOL). Membranes were cryogenically fractured in liquid nitrogen and then coated with gold. The contact angles of membranes were measured with VCA Optima (AST Products Inc., USA). All data were measured 10 times and averaged.

Since new polymeric membrane can be compacted by applied pressure during the filtration, the flux can be declined without membrane fouling. Thus all membranes were previously filtered by pure water until flux reached steady state before the fouling tests in order to eliminate the compaction effect on flux decline.

2.3. Activated sludge

Activated sludge used in this study was cultivated in submerged MBR plant with synthetic substrate for more than 5 months. Glucose, $(NH_4)_2SO_4$, and KH_2PO_4 were used as carbon, nitrogen and phosphorus sources, respectively. Additional nutrients and alkalinity ($NaHCO_3$) were also supplied to the reactor. Mixed liquor suspended solid (MLSS) concentration was about 7000 mg/l. Sludge retention time was about 30 days and organic loading rate was about 0.2 g COD/g MLSS-day. In the MBR mixed liquor, most particles existed in a size range between 10 and 40 μm, and the mean particle size was 24 μm, which was much lower than that of conventional activated sludge (figures are not shown). Thus, the MBR sludge used in this study had a greater fouling potential compared to that of conventional activated sludge.

After the activated sludge mixed liquor was supplied to the crossflow filtration system described in the following section, the membrane fouling tests were performed.

2.4. Experimental system and analysis

Flux decline behavior was measured using membrane cell and surface area was 18.1 cm^2. Schematic diagram of the filtration system used in this study was shown in Fig. 1. Filtration tests were performed under the condition of 100 kPa at $20 \pm 2\,^{\circ}C$. Crossflow velocity was controlled at 1.2 m/s and the flow rate was 2.5 l/min. Each set of experiment was performed simultaneously at the same condition. Feed tank (reactor) was consistently aerated during the filtration test