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Investigation on the conditions mitigating membrane fouling caused by TiO_2 deposition in a membrane photocatalytic reactor (MPR) used for dye wastewater treatment

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ABSTRACT

In this study, the effects of MPR's operating conditions such as permeate flux, solution pH, and membrane hydrophobicity on separation characteristics and membrane fouling caused by TiO_2 deposition were investigated. The extent of fouling was measured in terms of TMP and tank turbidity variation. The results showed that, at mildly acidic conditions (pH ~ 5), the turbidity within the tank decreased and the extent of turbidity drop increased with increasing flux for all the membranes. On the other hand, at pH ≥ 7, the turbidity remained constant at all flux and for all membranes tested. The fouling variation at different pH was closely linked with the surface charge (zeta potential) and hydrophilicity of both membrane and particles. It was observed that the charge differences between the particles and membranes accelerate the intensity of fouling and binding of TiO_2 particles on the membrane surface under different pH conditions. The presence of a very thin layer of TiO_2 can alter the hydrophilicity of the membranes and can slightly decrease the TMP (filtration resistance) of the fouled membranes. Besides, the resistance offered by the dense TiO_2 cake layer would dominate this hydrophilic effect of TiO_2 particles, and it may not alter the filtration resistance of the fouled membranes.

1. Introduction

Heterogeneous photocatalysis (UV/TiO_2 system) has been extensively researched and commercialized in the last two decades for its environmental applications. In this process, the pollutants are oxidized by the action of hydroxyl radical's generated by the photocatalyst (titanium dioxide, TiO_2) and ultraviolet (UV) photons. The hydroxyl radical is able to mineralize the majority of hazardous organic compounds to innocuous end-products [1–5]. The key advantage of this process is that photo-oxidation can be carried out under ambient conditions (atmospheric oxygen is used as the oxidant) and may lead to complete mineralization of organic carbon into CO_2 and H_2O. Moreover, the photocatalyst, TiO_2, is easily available, inexpensive, non-toxic and shows relatively high chemical stability [5–9].

The photoreactors described in the literature can be divided into two main groups, *viz*., slurry photoreactor (in which TiO_2 suspended in the reaction mixture), and immobilized photoreactor (in which TiO_2 is fixed or supported on a carrier material). The slurry type photoreactor offers several advantages that include: high surface area for adsorption and reaction, high degradation rate, no mass transfer limitation, and simple reactor configuration. On the other hand, the photocatalyst immobilized on a support, within the photoreactor, usually shows lower degradation rates due to loss of photo-activity with operational time. However, application of suspended photocatalytic system is rather limited by the time consuming step of the photocatalyst separation from the treated water after detoxification. This process can be made ecologically and economically feasible by means of confining or recycling the photocatalyst within the treatment unit [10–13].

Recently, application of membrane separation technique has shown to solve the important issue of catalyst separation in a slurry type photocatalytic reactor [13]. The separation characteristic of membrane also allows maintaining, constantly, the desired levels of TiO_2 suspension within the photoreactor. Among the different MPR configurations available, catalyst in suspension confined by means of a submerged membrane configuration (a hollow fiber or flat sheet) appears to be more feasible for industrial/practical applications [14–16]. Recent studies have proved that low-pressure membranes can effectively be used for separation of TiO_2 in submerged MPR system owing to its inherent advantages, such as low fabrication, maintenance and operating costs [16–19]. In MPR, both photocatalytic degradation reactions and TiO_2 separation are achieved simultaneously. Thus, the different operating conditions

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Table 1
Characteristics of the membrane used in this study.

Item	PAN	PVDF	PTFE
Manufacturer	C.M.T.	C.M.T.	C.M.T.
Material	Polyacrylonitrile	Polyvinylidene fluoride	Polytetrafluoro-ethylene
Pore size (μm)	0.035	0.38	0.22
Contact angle (°)	54.6 ± 1.6	78.3 ± 3.4	120 ± 3.5

of MPR will simultaneously affect the photocatalytic degradation efficiency, as well as the separation (filtration) efficiency of the membrane. It was also reported that the operation of MPR was severely affected by fouling, caused by the accumulation of TiO_2 particles on the membrane surface during continuous filtration [14,20–22]. An analysis of fouling resistance on the membrane filtration process showed that a cake layer formation on the membrane surface was the main mechanism responsible for fouling [23,24]. The effect of different operating conditions of MPR on degradation efficiency was extensively studied and reported by many researchers [3,4,13,19,25,26], however, so far its effect on separation efficiency and fouling of the membrane was not reported in detail.

The efficiency of the photocatalytic degradation process is affected by several operating parameters such as: pH of the solution to be degraded, initial concentration of the target compound, UV light (source, intensity and exposure/depth of penetration), temperature, reactor configuration, aeration (intensity, bubble size, dissolve oxygen, and mixing/circulation rate), catalyst characteristics (type, size, and surface area) and loading, among others [4,6,13,25,26]. The selection of proper polymeric membranes is an important challenge in the UV/TiO_2 photocatalytic-membrane process. Chin et al. [27] studied the stability of different membrane materials, and the results from their study showed that polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) membranes possess the greatest stability and resistivity in comparison to other membrane types studied. The TiO_2 powders are very small (average particle size of Degussa P25 is about 21 nm). However, in aqueous media, the TiO_2 particle forms an aggregate within the micron range. Therefore, microfiltration (MF) process range (0.1–5 μm) easily meets such a size requirement of the TiO_2 particle separation process [21,28]. For a suspension system, zeta potential is an important index which reflects the intensity of attractive/repulsive force among particles and the stability of dispersion. The point of zero potential charge (zpc) of Degussa P25 TiO_2 particles is around pH_{zpc} 6.3. Hence, the TiO_2 surface is positively charged under acidic medium (pH < 6.3) and negatively charge under basic medium conditions (pH > 6.3). Thus, TiO_2 particles form agglomerates when dissolved in water and its size depends on several factors, such as the chemical composition of the particle surfaces, the composition of the surrounding solvent, the environmental pH value and ions in the suspension [29]. The TiO_2 particle size distribution, its charge and membrane's surface charge in the aqueous medium are affected simultaneously by the solution pH and this may also affect the interaction between particle and membrane surface.

According to Huisman et al. [30], both, the amount of fouling and the reversibility of fouling are dependent on the zeta-potential of the feed suspension particles and the membrane surface. From this point of view, the membrane surface can either have a positive or a negative effect on the filtering process [31]. Therefore, the membrane's surface properties (such as hydrophobicity, pore size and charge), its operating flux and TiO_2 properties (such as particle size distribution and surface charge) at different pH of solution will greatly affect the membrane fouling caused by TiO_2 deposition. In this study, the effects of MPR operating conditions such as permeate flux, solution pH and membrane type (hydrophobicity) on separation characteristics and membrane fouling caused by TiO_2 deposition were investigated.

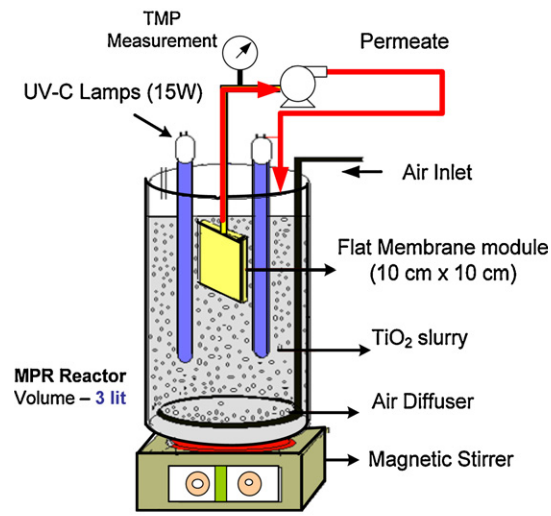

Fig. 1. Schematic of the membrane photocatalytic reactor (MPR) setup.

2. Materials and methods

2.1. Materials

Three kinds of flat sheet membranes such as PVDF, PAN and PTFE (provided by the R&D Center for Membrane Technology (CMT) of Chung Yuan Christian University, Taiwan) were tested in the MPR unit. PTFE and PVDF were relatively hydrophobic, while PAN was hydrophilic (Table 1). A highly dispersed and hydrophilic titanium dioxide powder (AEROXIDE® TiO_2 Degussa P 25) used in this experiment was supplied by Evonik *Degussa* Taiwan Ltd. The reactive black-5 (RB5, $C_{26}H_{21}N_5Na_4O_{19}S_6$; Mol Wt 991) dye was used as a model pollutant for this study.

2.2. Membrane photocatalytic reactor setup

The lab-scale MPR setup (Fig. 1) was fabricated using cylindrical glass (V 3 L) consisting of two UV-C lamps (15 W, 254 nm). One flat sheet membrane module (size 10 cm × 10 cm, with effective filtration area 0.01515 m^2) was placed at the middle and center of a tank, and surrounded by UV lamps. The solution was mixed using a magnetic stirrer. Aeration (flow rate 1.5 L/min) was provided through an air diffuser placed at the bottom of the tank in order to maintain the desired dissolved oxygen concentration and for mixing. Initially, few batch experiments were performed (in a same reactor without membranes), at different TiO_2 concentrations (0–1 g/L) and UV light exposures (continuous, semi-continuous) in order to envisage the optimum catalyst dose UV exposure required for the different experiments. RB5 removal (at pH 6.7, C_{dye} 100 mg/L) was monitored by measuring the absorbance at 595 nm and true color (ADMI) removal was measured using a spectrophotometer, as per the standard procedure provided by Taiwan EPA Standard Methods.