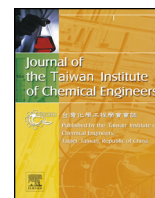




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## Dye degradation and antifouling properties of polyvinylidene fluoride/titanium oxide membrane prepared by sol–gel method

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### ABSTRACT

The modified polyvinylidene fluoride (PVDF) membranes were fabricated by grafting acrylic acid on the membrane and coating it with titanium dioxide sol. TiO<sub>2</sub> sols were prepared using varying precursor volume and solution pH. The TiO<sub>2</sub> coated membranes were tested for its photocatalytic property using Reactive Black 5 (RB5) dye and antifouling and self-cleaning properties using 1%BSA solution. FT-IR spectroscopy and contact angles confirmed the presence of polyacrylic acid (PAA) and TiO<sub>2</sub> on the membrane surface. The performance of the membranes, evaluated via crossflow filtration experiment, significantly improved as evident in the increase in flux and permeability of modified membranes. The rate of RB5 dye color removal due to immobilized TiO<sub>2</sub> follows a pseudo-first-order kinetics. PVDF/PAA/TiO<sub>2</sub>/pH1.25 exhibited superior photocatalytic property, removing 98.77% of the color in a span of 5 h. The resistance study showed that modified membranes have lower total filtration resistance ( $R_T$ ) with PVDF/PAA/TiO<sub>2</sub>/PH1.25 having the lowest. The performance of fouled membranes flux and transmembrane pressure (TMP) was recovered through UV irradiation, and the highest recovery was demonstrated by PVDF/PAA/TiO<sub>2</sub>/pH1.25.

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### 1. Introduction

The use of membrane bioreactors (MBRs) in wastewater treatment has increased significantly due to its favorable qualities over traditional wastewater treatment technology. Its advantages include reduced footprint and reactor requirements, excellent and consistent effluent quality, good disinfection potential, high volumetric loading capacity, and ease of operation due to greater process control [1–4]. MBRs can operate at high mixed liquor suspended solid concentration, and thus produce lower sludge concentration. It can achieve high removal efficiency for biological and chemical oxygen demand [2], and can withstand wide range of influent quality. The generated effluent can be readily used for non-potable purposes due to its high purity [5].

Membrane fouling is considered as a hindrance for MBR commercialization. Fouling refers to the unwanted settling and accumulation of “foulants” such as microorganisms, colloids, and solutes onto the surface of the membrane or within the membrane structure [2] caused by interactions between fluid and membrane

[6], resulting to a decrease in permeate flux and increase in transmembrane pressure (TMP) [1].

Polyvinylidene fluoride (PVDF) is one of the most used organic polymers in filtration processes. It has outstanding anti-oxidation activity, excellent thermal and hydrolytic stability, strong chemical resistance against aggressive reagents, and exceptional mechanical and membrane-forming properties [7–9]. However, due to its hydrophobic nature, PVDF is vulnerable to protein and impurity contamination from the influent, resulting to severe fouling and decline in water flux [8–10]. To solve this problem, PVDF membranes are modified to increase their affinity toward water molecules.

The use of titanium dioxide (TiO<sub>2</sub>) has acquired popularity in the hydrophilic modification of membranes because of it is superb stability, inexpensiveness, and accessibility. Moreover, it displays photocatalytic, antibacterial, self-cleaning, and ultra-hydrophilic properties upon UV irradiation [11]. One way to synthesize TiO<sub>2</sub> is via sol–gel method, which is a wet-chemical technique that produces materials in the form of monosized powders, thin films, and fibers [12,13]. Its advantage over other techniques can be attributed to pure product generation, solution homogeneity, controllability of concentration, nucleation and growth of colloidal particles (shape, size and size distribution), low-temperature operation, and ease of preparation [14]. Generally, sol–gel synthesis starts with a solution containing an oxide source such

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as metal alkoxides (precursor), an alcohol (solvent), water (hydrolysis agent), and an acid/base (catalyst). The metal compounds will go through hydrolysis, followed by condensation that will result to a sol of well-dispersed particles or polymers. Further reaction links the particles together causing the sol to solidify into a wet gel. Vaporizing the water and solvents in the wet gel will yield a dry gel as a final product, while heating gels at higher temperatures gives a dense oxide material [15]. For the sol-gel synthesis of  $\text{TiO}_2$ , one precursor commonly used is titanium tetraisopropoxide (TTIP). TTIP is known to be more susceptible to hydrolysis [12]. If reactions proceed to completion, TTIP will be completely hydrolyzed with maximal O–Ti–O formation [16,17].

In this study, PVDF membranes were modified through  $\text{Ar}/\text{O}_2$  plasma treatment, grafting of acrylic acid, and coating of the membranes with  $\text{TiO}_2$  sols. The membranes were characterized by contact angle (CA) and Fourier-transform infrared spectroscopy (FT-IR). Its photocatalytic property was evaluated through the photodegradation of Reactive Black-5 (RB5) dye, and antifouling and self-cleaning properties through fouling with 1% BSA solution. The performance of  $\text{TiO}_2$  coated PVDF membrane was compared with neat PVDF membrane to assess its fouling mitigation capacity under UV light after modification.

## 2. Materials and methods

### 2.1. Preparation of PVDF/PAA/ $\text{TiO}_2$ membranes

The PVDF/PAA/ $\text{TiO}_2$  membranes were prepared through plasma treatment using  $\text{Ar}/\text{O}_2$ , liquid grafting of AA, and coated with  $\text{TiO}_2$  sol.

#### 2.1.1. Plasma treatment

The plasma treatment for the PVDF membrane (0.45  $\mu\text{m}$  Durapore<sup>TM</sup>, Millipore) used a set-up similar to Pawde and Deshmukh [18]. The plasma treatment applies argon and oxygen to introduce carboxylic group in the system that will aid the coating  $\text{TiO}_2$  on the membranes.

The Plasma Processing Unit (PPU) for treating the membranes, as illustrated in Fig. 1, used a typical glass bell jar type plasma reactor, made from Pyrex heat resistant glass with a height of 34 cm and a diameter of 15 cm. Two electrodes, each 3 cm wide and spaced 5 cm apart, are coupled to a radio frequency source. Various ports are fitted for Ar and  $\text{O}_2$  gases alongside with mass flow control (MFC) and pressure sensors to control and monitor parameters. The reaction gas enters through the tubes in the

bottom of the jar. The virgin PVDF membranes samples, having a dimension of 5 cm  $\times$  5 cm, are placed at center of the electrode.

Argon gas was introduced to the system at a flow rate of 20  $\text{cm}^3(\text{STP})/\text{min}$  (sscm) with the reactor pressure set to 0.3 Torr and the plasma created at 100 W. After 2 min, Ar flow was stopped and the pressure was allowed to decrease. Subsequently, oxygen was supplied in the system at a flow rate of 60 sscm for 420 s. These operating parameters were adapted from the work of You et al. [19].

#### 2.1.2. Liquid grafting of AA

The plasma treated membranes were soaked in AA solution to prevent surface restructuring and to reduce fouling through the hydrophilic polyacrylic acid (PAA) layer formed on the surface [20]. The functional groups formed in plasma treatment undergo decomposition and initiate grafting of AA to create brushes on the polymer surface. See Fig. 2 for the grafting mechanism of PAA.

The pre-treated membranes were immersed in 70% AA solution. The grafting reaction was carried out by placing the reagent bottles in a water bath (60  $^\circ\text{C}$ ) for 2 h. The membranes were washed in DDW to remove any PAA that did not covalently bound to the PVDF surface.

#### 2.1.3. Coating of $\text{TiO}_2$ on PVDF/PAA membranes via sol-gel method

The preparation of  $\text{TiO}_2$  sol and its coating on PVDF membranes were based on the method presented by Kim et al. [21]. Different amounts (1, 1.5, 2, 3, and 4 mL) of TTIP (98%, Merck) were mixed in 25 mL of ethanol (95%, TTL) then added drop wise to 250 mL DDW at 4  $^\circ\text{C}$  and at a specific pH [1.1, 2.5, 1.5 adjusted using 1 M HCl (Nacalai Tesque)] under vigorous stirring. The mixture was stirred for 24 h to get a clear colloidal solution of the  $\text{TiO}_2$  that can be stored in a cold room (4  $^\circ\text{C}$ ) for a year without coagulation [22].

The plasma treated membranes were coated with  $\text{TiO}_2$  by dipping it in the sol for 60 min then in DDW for 30 min.

### 2.2. $\text{TiO}_2$ sol density

Density was measured by weighing the  $\text{TiO}_2$  solid in a representative sample of the sol. 5-mL for each sol were transferred into empty pre-weighed aluminum dishes. These dishes were put in an oven at 100  $^\circ\text{C}$  for 24 h to maximize liquid evaporation then weighed in an analytical balance (Shimadzu AU220, Japan). To minimize experimental error, the weight of a dish was the average of three representative samples of each sol. The density was computed by subtracting the weight of the oven dried weighing dish to the weight of the empty dish per 5 mL of  $\text{TiO}_2$  sol.

### 2.3. Determination of the characteristics and performance of the PVDF membranes

The performance and characteristic of the PVDF/PAA/ $\text{TiO}_2$  samples were studied through crossflow filtration, FT-IR, and CA measurement.

The set-up used for the crossflow experiment (Fig. 3) was adapted from Mansourpanah et al. [23]. Here, pressure was maintained at 1  $\text{kg}/\text{cm}^2$  with DDW inflow at a range of 0.18–0.22 m/s. A 4 cm  $\times$  1 cm membrane was sandwiched between two parts of the alloy cell. The two pressure gauges indicate the pressures before and after the cell. The water outflow was collected in a beaker, weighed and recorded every 10 s for 1 h and the water flux was computed using Eq. (1).

$$\text{flux} = \frac{\text{permeate volume}}{\text{membrane effective area} \times \text{time}} = (\text{L}/(\text{m}^2 \text{ h})) \quad (1)$$

FT-IR spectrometer (Perkin-Elmer Spectrum One, USA), was used to determine the molecular fingerprint of the membranes. The

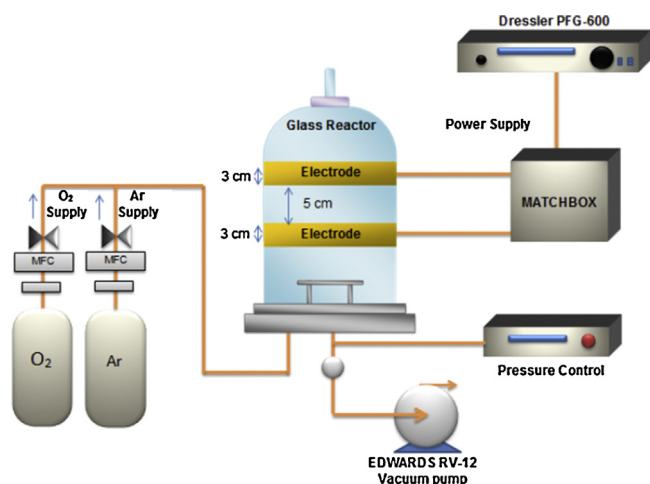


Fig. 1. Schematic representation of the PPU.

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