

Dye wastewater treatment and membrane fouling in a moving bed-UV-photocatalytic
modified membrane bioreactor

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S2. Materials and methods

S2.1 Membrane characterization

To test the hydrophilicity of the membrane, the water contact angles on the membrane surfaces were measured for five times using a contact angle goniometer (OCA20, Germany). Porosity of membranes was determined by true density and porosity analyzer (BSD-TD, BeiShiDe, China) for 6 times.

To verify the hydrophobicity of the membrane surface, the water contact angle (WCA) was measured. With increasing PVDF/TiO₂ assembly layers, the average WCA value of the MM decreased (Fig.S1). The WCA of the original membrane was 94.96°, and a substantial decrease (to 32.44°) was observed after a surface modification of (PVDF/TiO₂)₉.

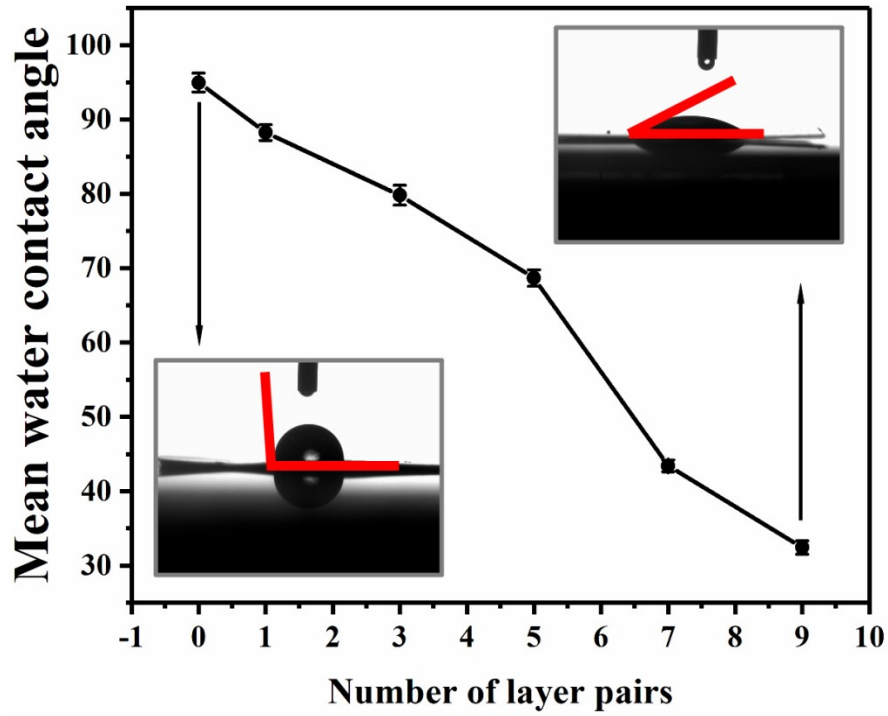


Fig.S1. Water contact angle of the original membrane and modified membranes.

The pore size and porosity was measured. It can be observed that the pore size and porosity decreased of the modified membranes, which might due to the coverage of deposited TiO_2 on membrane surface and pores. The change in membrane pore size and porosity affected the water flux and separation performance of the membrane .

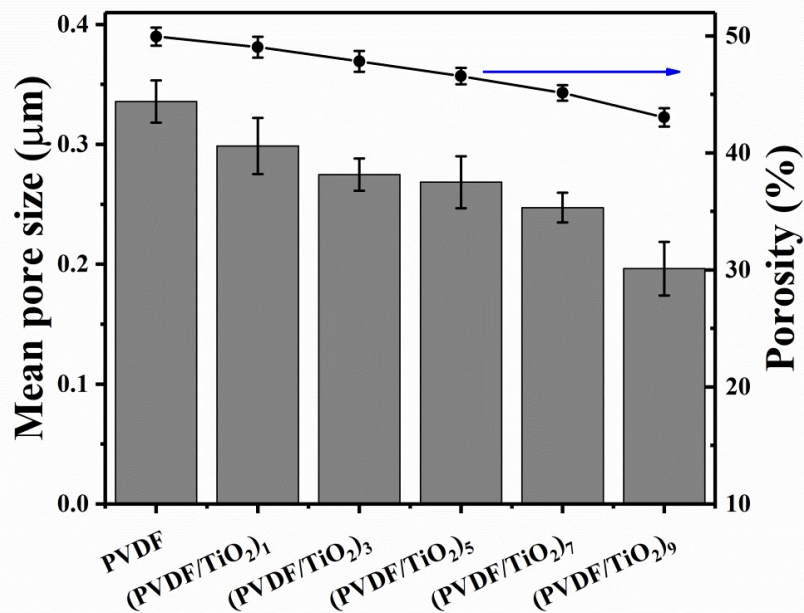


Fig.S2. Mean pore size and porosity of PVDF membrane and modified membranes

S2.3 Analytical procedures

The treatment performance of two systems in terms of influent and effluent were evaluated by total organic carbon (TOC), $\text{NH}_4^+\text{-N}$ and total phosphorus (TP). TOC was obtained by analyzing solutions with a TOC-V analyzer (Analytikjena, Germany). $\text{NH}_4^+\text{-N}$ and TP were obtained by analyzing the influent and effluent with DR890 colorimeter (HACH, USA).

The morphology of external foulants on the membrane surface was investigated by digital camera and scanning electron microscopy (SEM, FEI Inspect F50, USA). FTIR (Nexus 670, Nicolet, USA) was employed to elucidate the chemical composition of the fresh membrane and the fouled membrane. To test the hydrophilicity of the membrane, the water contact angles on membrane surfaces were measured using a contact angle goniometer (OCA20, Germany).

S2.2 Membrane foulants characterization

In order to analyze the dominant contributor of the membrane fouling in each operation stages, composition of cake layer and soluble microbial produce were analyzed. The extracellular polymeric substances (EPS) in the cake layer were measured by heating extraction method. Generally, the total EPS (EPS_T) and the soluble microbial products (SMPs) are composed of proteins and carbohydrates, according to the following equation:

$$\text{EPS}_T = \text{EPS}_P + \text{EPS}_C \quad (1-1)$$

$$\text{SMP} = \text{SMP}_P + \text{SMP}_C \quad (1-2)$$

where the subscripts “P” and “C” indicated proteins and carbohydrates, respectively.

Composition of extracellular polymeric substances (EPS) in the cake layer and soluble microbial produce (SMP) were analyzed in order to analyze the dominant contributor of the membrane fouling in each operation system. The extracellular polymeric substances (EPS) in the cake layer were measured as heating extraction method described [1]. Generally, proteins and carbohydrates are the main components of the EPS and the SMP. Thus, we used the proteins and carbohydrates to characterize the total EPS and the total SMP content in this research. Standard analytical methods were used to measure the concentration of proteins and carbohydrates [2].

TOC, $\text{NH}_4^+\text{-N}$ and TP total removal efficiencies (R_t) were determined by using the following equation [3]:

$$R_t(\%) = \left(1 - \frac{c_e}{c_0}\right) \times 100 \quad (2-1)$$

where c_e and c_0 are TOC, $\text{NH}_4^+\text{-N}$ and TP of effluent and influent, respectively.

TOC, $\text{NH}_4^+\text{-N}$ and TP biodegradation efficiencies (R_e , %) were determined by using the following equation:

$$R_e(\%) = \left(1 - \frac{c_s}{c_e}\right) \times 100 \quad (2-2)$$

where c_s is TOC, $\text{NH}_4^+\text{-N}$ and TP of supernatant.

TOC, $\text{NH}_4^+\text{-N}$ and TP membrane separations efficiencies (R_s , %) were calculated from:

$$R_s(\%) = \left(1 - \frac{c_e}{c_s}\right) \times 100 \quad (2-3)$$

S2.3 Membrane filtration resistance distribution

The distribution of membrane resistance during filtration can be determined using the resistance-in-series model based on Darcy's law, as represented by Eqs.

$$J = \frac{V}{At} \quad (3-1)$$

where J is the permeate flux ($\text{m}^3 \cdot \text{m}^{-2} \text{ s}^{-1}$), V is filtrate volume (m^3), A is membrane effective surface area (m^2), t is filtration time (s).

Membrane fouling resistance can be expressed as total resistance (R_t), which is composed of cake layer resistances (R_c), pore blockage resistance (R_p) and membrane resistance (R_m).

$$R_m = \frac{\Delta P}{\mu J} \quad (3-2)$$

$$R_t = R_m + R_p + R_c \quad (3-3)$$

where ΔP is the applied transmembrane pressure (Pa), μ is filtrate viscosity ($\text{Pa} \cdot \text{s}$), R_t is the total resistance (m^{-1}), R_c is the cake layer resistances (m^{-1}), R_p is pore blockage resistance (m^{-1}), R_m is the intrinsic membrane resistance (m^{-1}).

[1] S. Comte, G. Guibaud, M. Baudu, Relations between extraction protocols for activated sludge extracellular polymeric substances (EPS) and complexation properties of Pb and Cd with EPS: Part II. Consequences of EPS extraction methods on Pb²⁺ and Cd²⁺ complexation, *Enzyme and Microbial Technology*, 38 (2006) 246-252.

[2] M. Yao, K. Zhang, L. Cui, Characterization of protein-polysaccharide ratios on membrane fouling, *Desalination*, 259 (2010) 11-16.

[3] Z.D. Zhang, D.L. Li, X. Zhang, Enzymatic decolorization of melanoidins from molasses wastewater by immobilized keratinase, *Bioresource Technology*, 280 (2019) 165-172.