# Applied Research in Photocatalytic Membrane Reactor (PMR) Systems in Water and Wastewater Treatment

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## Abstract

**The photocatalytic membrane reactor (PMR) systems have been increasingly used in water treatment in recent years. The scope of the current paper was to briefly review literature on different configurations of PMRs. It will be conducive to further application of PMR in the future.**

## Keywords

**Photocatalytic Membrane Reactor (PMR), Photocatalytic Oxidation, Membrane Filtration, $Tio_2$, Potocatalysis Oxidation, Membrane Fouling, Water Treatment.**

## 1. The Photocatalytic Membrane Reactor (PMR) Systems

The photocatalytic membrane reactor (PMR) systems, a new water treatment process coupling with the technologies of membrane separation and photocatalytic oxidation, has gained more and more attentions and resultant investigations in many wastewater treatment and reclamation in recent years [1-5]. PMR can be grouped into two types according to configurations and designs: reactors with catalyst suspended in feed solution and reactors with catalyst immobilized in/on the membrane.

## 2. PMR with Catalyst Suspended in Feed Solution

Zhang *et al*. [6-8] investigated the suspended photocatalytic nanofiltration membrane reactor, combining slurry Cu-doped photocatalyst TiO2 particles and organic nanofiltration membrane separation process and determined the photocatalytic degradation mechanisms and kinetics of the employed model pollutant under the optimum operation conditions. The most problely predominant reasons, to the relatively higher photocatalytic degradation and mineralization efficiencies of the innovative suspended photocatalytic nanofiltration membrane reactor compared to the traditional photorector during the beginning period, were that the coupled nanofiltration membrane played an absolute barrier of the slurry photocatalyst particles and a selective barrier of the substrate, degradation intermediates and final products on the molecular weight basis, which promised a dramatic and significant change in the newly membrane photoreactor, compared to the traditional photoreactor. While during the fmal period of the degradation process,the relatively lower photocatalytic degradation and mineralization efficiencies of the newly nanofiltration membrane photoreactor were possibly due to the exterior circulation of the H-acid aqueous solution in the cell. The basic and dramatic changes in the degradation kinetics should be exclusively dedicated to the significant differences in the substrate concentration in the coupled photocatalytic degradation reactor and the surface concentration of substrate H-acid on the employed photocatalyst in the suspended photocatalytic nanofiltration membrane reactor under the single-component and multi-component conditions respectively.

In the researches of Fu *et* al. [9-10], two kinds of reactors coupling membrane technology and nano-structured $TiO_2$ photoeatalytic oxidation was designed and verified by experiment for degradation of fulvic acid, that is recirculated membrane photoeatalytic reactor (RMPR) and submerged membrane photocataiytic reactor (SMPR). These reactors had the characteristics of the perfect mixing flow reactor. In the reactors, nano-structored $TiO_2$ could be easily separated, recovered and reused by membrane separation process. Comparing the settle velocity, photocatalytic activities and permeate flux rate of P25 powder and nano-stractured $TiO_2$, it was found that the nano-structured $TiO_2$ photocatalyst could be automatically settled while maintained its high activities. The permeate flux rate of microfiltrati could be improved and thus the membrane fouling phenomenon was reduced with the addition of nano-structured TiO2 catalyst. With regard to SMPR, photocatalyst concentration at 0.5g/L and aeration amount at 18.75 m3/m3 ћ were the optimal condition for the removal of fulvic acid.

Xie *et al.* [11] investigated the performance of the integrative reactor by photocatalytic degrading acid red B wastewater with $TiO_2$. Membrane fouling rate can be controlled greatly with bubbling under membrane module and bellow reactor, because of cross-flow rate on face of the membrane and turbulence is enhanced. Membrane fouling rate can be decreased in the conditions of acidic and alkaline. The main factor which caused membrane fouling is $TiO_2$, and membrane fouling becomes serious with $TiO_2$ concentration increasing. The reactor can run in a long and stable way in the condition of backwash online. Alkaline-backwash after face-wash followed by alkaline rising can make the membrane flux recover to 99％.

Zou *et al.* [12] designed a new type of three-phase fluidized bed reactor of solar photocatalysis-organic membrane separation coupling with the technology of solar photocatalysis and organic membrane separation. The reactor includes photocatalytic reaction zone and the membrane separation zone, and they are connected by connected tube and cycling tube, respectively. The photocatalytic reaction zone contains upper tank, bottom tank and tube reactor, while the membrane separation zone contains the membrane separator and the hollow fiber membranes in it. By the experiments of $TiO_2$ suspension performance, degradation of simulated acid red B wastewater and low biodegradability medicine wastewater, and membrane fouling experiments, the basic performance of the reactor is researched. The results show that $TiO_2$ suspension concentration increase with the $TiO_2$ dosage and aeration flux of the photocatalysis alga until its maximum equilibrium suspension concentration, but $TiO_2$deposits phenomenon becomes serious at the same time. Air rinsing in recycle pipe makes $TiO_2$ suspension concentration invariable and the best time and intervals of the air rinsing are 10s and 40 min respectively. $TiO_2$ suspension concentration in the membrane separation reactor is always higher when the connection pipe valve is full open compared with half open. However, the concen Ⅱ ation in the tube reactor before air rising is lower under the condition of full open. $TiO_2$ suspension performance is hardly influenced by the membrane effluent.

## 3. PMR with Catalyst Immobilized IN/ON the Membrane

In order to prevent the membrane fouling and the loss of the nano-sized $TiO_2$, Yan *et al.* [13] prepared the silica-gel supported TiO2 by the sol-gel method as the photocatalyst. The thesis mainly studied on the membrane fouling characters of the photocatalysis-membrane integrated process, the mechanism of photocatalysis degradation of humic acid (HA), and the deactivation mechanism and the reactivation methods of the photocatalysts $TiO_2$. The static experimental results indicate that the HA and the by-products with small molecular weight cannot foul the membrane after 60min degradation. The running results of the photocatalysis-membrane integrated process illustrate that the photocatalysis technology as the pretreatment for the membrane filtration can control the membrane fouling effectively. The structure of the fouling layer on the membrane surface in the integrated process is relative loose and rough, which is benefit for the decreasing of membrane resistance. Low initial concentration of HA, low membrane flux and the intermittent running method is helpful for membrane fouling control.

In order to reduce bicrobial biofouling in reverse osmosis operation, Kim *et al.* [14] devised the hybrid thin-film-composite (TFC) membrane consisted of self-assembly of $TiO_2$ nanoparticles with photocatalytic destructive capability on microorganisms, which offered a strong potential for possible use as a new type of anti-biofouling TFC membrane.

In the study of Li *et al.* [15], PVDF microfiltration membrane was enhanced by spaying nanometer $TiO_2$ one membrane bioreactor (MBR) system was set in this kind of membrane, and another MBR was set in membrane which was not enhanced. In the first step of the stable period, the conclusion was that the flux water quantity of the enhanced MBR was larger than the not-enhanced one, under the condition of the same flux water quality. The clean water trans-membrane resistance of the enhanced MBR was 1/2 less than that of the not-enhanced one. At the same time, the flux water quantity of the enhanced MBR is 67.5％ larger than that of the not-enhanced one.

Molinari *et al.* [16] carried out an investigation of membrane stability under UV irradiation to study the catalyst deposited on the membrane in the photocatalytic membrane reactors. Controlling the size of the reactors and employing the best research results for both the "photocatalytic system" and the "membrane system" could help obtain high irradiation efficiency and high membrane filtration efficiency, which showed interesting perspectives and synergy for coupling photocatalysis and membranes.

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## References

[1] ZHANG Xi-wang, PAN Jia-hong, DU Alan Jiahong, FU Wei-jiong, SUN D. Darren and LECKIE O. James. Combination of one-dimensional TiO2 nanowire photocatalytic oxidation with microfiltration for water treatment [J]. WATER RESEARCH, 2009, 43(5): 1179-1186.

[2] HUANG Xian-huai, LEAL Marlen and LI Qi-lin. Degradation of natural organic matter by TiO 2 photocatalytic oxidation and its effect on fouling of low-pressure membranes[J]. WATER RESEARCH, 2008, 42(4): 1142-1150.

[3] MALEK F., HARRIS J. L. and RODDICK F. A. Interrelationship of photooxidation and microfiltration in drinking water treatment [J]. JOURNAL OF MEMBRANE SCIENCE, 2006, 281(1): 541-547.

[4] FISCHER Kristina, GRIMM Martin, MEYERS Jonathan, DIETRICH Corinna, GLÄSER Roger and SCHULZE Agnes. Photoactive microfiltration membranes via directed synthesis of $TiO_2$ nanoparticles on the polymer surface for removal of drugs from water [J]. JOURNAL OF MEMBRANE SCIENCE, 2015, 478: 49-57.

[5] MOZIA Sylwia, SZYMAŃSKI Kacper, MICHALKIEWICZ Beata, TRYBA Beata, TOYODA Masahiro and MORAWSKI W. Antoni. Effect of process parameters on fouling and stability of MF/UF $TiO_2$ membranes in a photocatalytic membrane reactor [J]. SEPARATION AND PURIFICATION TECHNOLOGY, 2015, 142: 137-148.

[6] ZHANG Ai-yong, XIAO Yu-tang, LV Xiao-long, GAO Guan-dao and ZHANG Meng. Study on influence of coupled separation membrane on synergetic property of suspended photocatalytic nanofiltration membrane reactor [J]. MODERN CHEMICAL INDUSTRY, 2007, 27(8): 38-41, 44. (in Chinese)

[7] ZHANG Ai-yong, REN Yu-hui, XIAO Yu-tang, GAO Guan-dao, LV Xiao-long and ZHANG Meng. Kinetics and efficiency study on degradation process of suspended photocatalytic nanofiltration membrane reactor with cu-modified $TiO_2$ for atrazine aqueous solution [J]. ENVIRONMENTAL CHEMISTRY, 2007, 26(6): 735-740. (in Chinese)

[8] ZHANG Ai-yong, XIAO Yu-tang, LV Xiao-long, GAO Guan-dao and ZHANG Meng. Systematic investigation on photocatalytic degradation efficiency and kinetics of H-acid aqueous solution treated by suspended photocatalytic nanofiltration membrane reactor [J]. CHEMICAL INDUSTRY AND ENGINEERING PROGRESS, 2007, 26(11): 1610-1615. (in Chinese)

[9] FU Jian-feng, Ji Min, WANG Zhen, JIN Luo-nan and AN Ding-nian. A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst[J]. JOURNAL OF HAZARDOUS MATERIALS, 2006, 131(1): 238-242.

[10] FU Jian-feng, JI Min, ZHAO Ya-qian and WANG Li-zhang. Kinetics of aqueous photocatalytic oxidation of fulvic acids in a photocatalysis–ultrafiltration reactor (PUR) [J]. SEPARATION & PURIFICATION TECHNOLOGY, 2006, (1):107-113.

[11] XIE Li-ping, WANG Neng-liang and HUANG Wei. Study on the performance of integrative reactor coupling with photocatalysis oxidation and organic membrane separation [J]. CHINESE JOURNAL OF ENVIRONMENTAL ENGINEERING, 2007, 1(9): 20-24. (in Chinese)

[12] ZOU Chen-xi, WANG Jun, XIE Li-ping, FEI Xue-ning, YANG Ming-qin and YUE Jun-nan. $TiO_2$ suspension performance of three-phase fluidized bed reactor coupling with solar photocatalysis oxidation and organic membrane separation [J]. JOURNAL OF CHEMICAL ENGINEERING OF CHINESE UNIVERSITIES, 2014, (4): 764-770. (in Chinese)

[13] YAN Xiao-ju, YU Shui-li, YANG Xu, SHI Wen-xin and LI Li-zheng. Research on the membrane fouling characters changing of humic acid during the photocatalysis degradation process [J]. JOURNAL OF HEILONGJIANG UNIVERSITY, 2009, 26(6): 804-808.

[14] KIM Sung Ho, KWAK Seung-Yeop, SOHN Byeong-Hyeok and PARK Tai Hyun. Design of $TiO_2$ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem [J]. JOURNAL OF MEMBRANE SCIENCE, 2003, 211(1): 157-165.

[15] LI Zhao-jing, ZHANG Yu-xian, FAN Jian-wei, XIA Mai-lv and XU Qin-mei. Study on MBR modified by nanometer $TiO_2$ for wastewater treatment [J]. CHINA WATER & WASTEWATER, 2008, 24(3): 75-78. (in Chinese)

[16] MOLINARI Raffaele, PALMISANO Leonardo, DRIOLI Enrico and SCHIAVELLO Mario. Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification [J]. JOURNAL OF MEMBRANE SCIENCE, 2002, 206(2): 399-415.