Configurations and Membranes of Photocatalytic Membrane Reactors for Water and Wastewater Treatment

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Abstract. The new photocatalytic membrane reactor composed of photocatalysis and membrane separation not only has the advantages of combination, but also can effectively solve the separation problem of harsh system and recover the catalyst particles in wastewater treatment. Especially, the coupling system greatly improves the efficiency of treatment of high concentration organic wastewater. In this paper, the structure and operation mode of different types of photocatalytic membrane reactors are studied and prospected.

1. Introduction
Membrane separation has the advantages of simplicity, high speed, and high efficiency, and has received extensive attention around the world. It is well known that membrane materials and membrane processes are two of the key factors affecting separation process. The selection of suitable membrane materials is of great significance for good processing results. Many new materials, for example, metal organic frameworks (MOFs), have attracted great interests due to their unique structures [1, 2], which are widely explored in different fields of membrane technology [3, 4]. In addition to a single new material, combination of membrane and other chemical unit also play an important role in recent years. The combination of simple membrane separation and some other processes like catalysis and advanced oxidation has been developed with wide interests [5-7]. As a coupling process between photocatalytic technology and membrane separation technology, photocatalytic membrane reactor (PMR) not only maintains the advantages of photocatalysis technology for degrading high concentration of refractory organic wastewater, but also has the profit of non-selectivity, fast reaction speed and thorough degradation. The interception and phase-free separation characteristics can effectively recover the nano-scale catalyst in the reaction liquid system, maintaining the constant catalyst and catalytic characteristics in the reactor, so that the entire reaction system can be stably operated [8].

2. Configurations
In the PMR studies of the past few years, depending on the form of the catalysts, the PMR can be divided into two types: SPMR (catalyst suspended in solution) and IPMR (catalyst immobilized on the membrane).

2.1. Configurations of SPMR
The suspension photocatalytic membrane reactor (SPMR) separates and recovers the particulate photocatalysts by utilizing the excellent separation ability of the separation membrane, and the
separation effect is complete. The loss of photocatalysts is strictly controlled, the operation is simple, the cost is low and the process model is easy to be realized [9].

2.1.1. Integrative SPMR. In integrative SPMR system, the membrane module is immersed in a photocatalytic reactor, the catalyst does not flow out of the reactor, maintaining a constant catalyst concentration in the reactor, and is more stable than other reactors. At the same time, the reactor is compact, which can shorten the pipeline, reduce system resistance loss, reduce the cost of investment and maintenance [10]. A typical SPMR structure is shown in Figure 1(a). However, this structure has an obvious disadvantage in that when the membrane is exposed to the catalyst for a long time, the ultraviolet light irradiated for a long time might destroy the membrane. In order to avoid such defects, as shown in Figure 1(b), a baffle are used to isolate membrane and ultraviolet lamp [11-13]. As depicted, nanometer titanium dioxides (TiO$_2$) are prepared, and then the wastewater is degraded in a slurry photocatalytic membrane reactor using photocatalyst TiO$_2$ and ultraviolet light as a light source. The reactor comprises a double-layer cylindrical photocatalytic reaction zone and a flat frame membrane [14-16].

**Fig.1** Typical integrative SPMR structure

2.1.2. Independent SPMR. In this SPMR system, the membrane module and the photocatalytic reactor are completely separated. The typical structure is shown in Fig.2, the external type has the advantages of clear structure, easy assembly and low maintenance [17]. However, because the TiO$_2$ particles must be transported from the pipeline to the membrane module for separation, there is a certain pressure loss, and the catalysts are easy to deposit in the corner of the pipeline. Therefore, the concentration of TiO$_2$ in the reactor is difficult to maintain and stabilize, which might affect the efficiency of the catalytic reaction [18-20].

**Fig.2** Independent suspended photocatalytic membrane reactor
2.2. Configurations of IPMR.
The fixed photocatalytic membrane reactor mainly arranges the catalysts on a certain carrier so that they do not discharge with the water flow to cause secondary pollution, which can facilitate the reuse of the catalysts. There are two kinds of fixed forms, one is to fix the photocatalyst on the surface of the carrier medium. The carriers reported in the literature include glass [21], natural zeolite [22], stainless steel [23], quartz [24] and etc. The other kind is directly combined with a photocatalyst and a membrane having a separation function. The photocatalyst is fixed on a surface thereof or incorporated into a membrane forming liquid during the membrane forming process, and at the same time exerts both advantages. The structure and configuration of this PMR is similar to that of SPMR, but the position of the UV light is changed [25, 26]. As shown in Figure 3, the external illumination lamp is applied by a heat-resistant glass to the closed catalyst system, and the nano-catalysts are not easily agglomerated.

![Immobilized photocatalytic membrane reactor](image)

Fig.3 Immobilized photocatalytic membrane reactor

3. Membranes of PMR

| Membrane material | Hollow fiber membrane | Flat sheet membrane | Tubular membrane |
|-------------------|-----------------------|---------------------|-----------------|
| Stability         | Medium                | Medium              | Good            |
| Price             | Less expensive        | Less expensive      | Expensive       |
| Combination mode  | Internal, External    | Internal, External  | Internal, External |
| Module processing | Very easy             | Easy                | Hard            |

At present, the membrane materials used by researchers in membrane modules mainly include ceramic membranes and polymer organic membranes. The photocatalytic reaction has less chemical damage to inorganic ceramic membranes and can better meet the experimental stability requirements [27]. Wu et al. prepared MWCNTs/Ag3PO4/polyacrylonitrile (PAN) ternary composite fiber membranes (TCFM) with good photocatalytic properties by electrospinning combined with in-situ Ag3PO4 formation. The prepared MWCNTs/Ag3PO4/PAN TCFMs showed enhanced photocatalytic activity and stability in the degradation of rhodamine B (RhB) in a batch treatment system [28]. Azrague et al. used a flat membrane and a hollow fiber membrane to construct the photocatalytic membrane reactor which conducted a
comparative experiment on the turbid water. The results showed that the surface contamination of the flat membrane was less, and the obvious pollutants occurred inside the hollow fiber membrane [29]. In terms of structure, as shown in Fig.4, the membrane pore size selected for the photocatalytic reactor is determined by the size of TiO$_2$.

![Fig.4 Schematic diagram of TiO$_2$-based photocatalytic membrane.](image)

### 4. Current & future development

The photocatalytic membrane reactor provides a new method for the safe and effective treatment of water and wastewater. The progresses on modified catalysts with visible light response will make the cost lower and the efficiency higher. These sorts of wastewater treatment modes with diversified configurations and membranes are effective ways to solve major environmental problems. Therefore, with the development of photocatalysis and membrane science, photocatalytic membrane reactors have an unparalleled attractive prospect in the field of water and wastewater treatment.

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