On photocatalytic membrane reactors in water and wastewater treatment and organic synthesis

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Abstract

A brief overview of hybrid photocatalysis-membrane processes and their possible applications in water/wastewater treatment and organic synthesis is presented. Moreover, a short introduction to photocatalysis is shown. The paper summarizes the main advantages and disadvantages of photocatalytic membrane reactors (PMRs) with photocatalytic membranes or a photocatalyst in suspension. Furthermore, the influence of photocatalysis on membranes performance in terms of fouling and efficiency of removal of organic contaminants during treatment of water and wastewater is discussed. In the second part of the review the examples showing the possibilities of application of PMRs in recovery of valuable compounds (benzaldehyde, vanillin) or photocatalytic partial oxidation of benzene to phenol are presented. It was concluded that PMRs exhibit numerous advantages over the conventional photoreactors, however, further investigations are still needed in order to improve the hybrid processes performance.

Keywords: photocatalytic membrane reactor, photocatalysis, membrane, hybrid process, water treatment, organic synthesis

1. Introduction to photocatalytic membrane reactors

In recent years a significant attention has been directed to the photocatalytic membrane reactors (PMRs) being hybrid systems coupling photocatalysis and membrane separation. Photocatalysis is one of Advanced Oxidation Processes (AOPs), i.e. processes based on the generation of very reactive oxidizing species such as hydroxyl radicals (OH$^{\bullet}$). According to IUPAC recommendations [1] photocatalysis is defined as a "*change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance - the photocatalyst - that absorbs light and is involved in the chemical transformation of the reaction partners*". Further, a photocatalyst is a "*substance able to produce, by absorption of ultraviolet, visible, or infrared radiation, chemical transformations of the reaction partners, repeatedly coming with them into intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions*" [1]. In case of heterogeneous photocatalysis such photocatalysts are solid semiconductors amongst which TiO$_2$, due to its high photoactivity and stability is the most commonly used.

A simplified idea of photocatalysis is presented schematically in Fig. 1
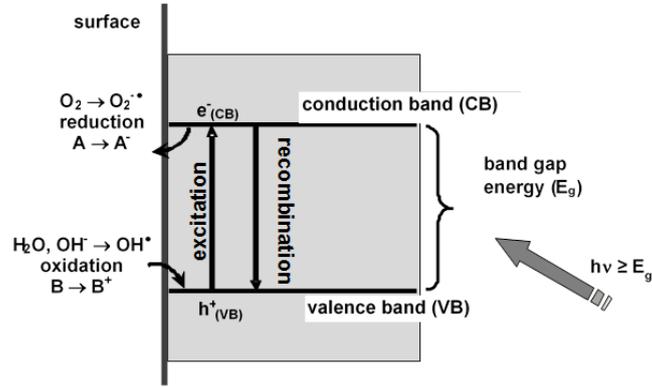
Fig. 1. Idea of photocatalysis: A, electron acceptor; B, electron donor [2].

The photoinduced reactions are activated by absorption of a photon (hv) with sufficient energy, i.e. equal or higher than the band gap energy (E_g) of the photocatalyst [2]. In case of anatase phase TiO_2 the Eg amounts to 3.23 eV which corresponds to the wavelength of 384 nm. This means that UV irradiation is necessary to realize the photocatalytic process with application of TiO_2.

After the absorption of a photon (Fig. 1) an electron (e^-) may be promoted from the valence band (VB) to the conduction band (CB) thus generating an electron vacancy – "hole" (h^+):

$$TiO_2 + hv \rightarrow TiO_2(e_{CB}^- + h_{VB}^+) \tag{1}$$
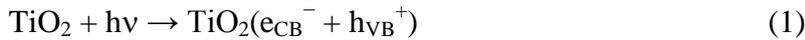
The electron and the hole can migrate to the surface of the photocatalyst and participate in redox reactions:

$$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \tag{2}$$

$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet \tag{3}$$

$$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO2 + O2^{\bullet-} \tag{4}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{5}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{6}$$

$$TiO_2(e_{CB}^-) + H_2O_2 \rightarrow OH^\bullet + OH^- \tag{7}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + OH^- + _{O2} \tag{8}$$

$$H_2O_2 + hv \rightarrow 2OH^\bullet \tag{9}$$
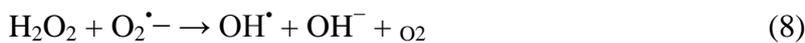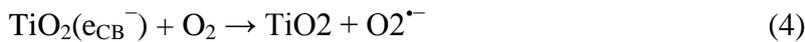
The hydroxyl radicals ($OH^\bullet$) are supposed to be the primary oxidizing species in the photocatalytic oxidation processes [2].

The role of photocatalysis in PMRs is degradation of organic substances while the membrane might act as a simple barrier for the photocatalyst and as a selective barrier for the degraded molecules and products/by-products of their decomposition [2].

There are various configurations of PMRs [2, 3]. Based on the way in which the photocatalyst is introduced to the system the PMRs can be divided into (I) reactors with

photocatalyst suspended in feed solution and (II) reactors with photocatalyst supported in/on the membrane. In case (I) three main configurations can be distinguished, dependent on which element of the installation works as a photoreactor: (a) PMRs with the irradiation source above/in the feed tank, (b) PMRs with the irradiation source above the membrane module and (c) PMRs with the irradiation source above/in an additional reservoir (photoreactor) positioned between the feed tank and the membrane module. In case of PMRs with photocatalytic membranes, the light source must be located in the vicinity of the membrane since the photoreaction takes place on the membrane surface and within its pores. There are also configurations in which the light sources are located above both membrane module and feed tank (or inside them, when immersed UV lamps are used). The PMRs design is affected by numerous factors. They include process mode (dead end or cross-flow, batch or continuous flow, etc.), type of the membrane technique applied (e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), membrane distillation (MD), pervaporation (PV), dialysis), construction of the membrane modules (flat sheet, tubular, submerged, etc.) and the type of the irradiation source.

The main directions of application of PMRs are water and wastewater treatment, however, the possibilities of utilization of these systems in chemical synthesis are also considered.

2. PMRs in water and wastewater treatment

Both PMRs with photocatalytic membranes and PMRs with a photocatalyst in suspension were proposed to treat water and wastewater. PMRs with photocatalytic membranes have been applied for removal of different organic compounds such as sodium dodecylbenzene sulfonate, dyes (methylene blue, direct black, methyl orange, congo red, etc), herbicides, phenols, chlorophenols, 4-nitrophenol, humic acids and others as well as for disinfection purpose [2, 4]. It was also proved that TiO_2-coated membranes exhibited self-cleaning properties under the action of UV irradiation [5].

There are two main types of photocatalytic membranes: (a) with a photoactive layer, which fulfils also the function of a separation layer, and (b) with a non-photoactive separation layer deposited on a photoactive support. Depending on the membrane type, the irradiation source is positioned either on the feed side or on the permeate side. The main advantage of configuration (a) is that membrane fouling could be reduced and permeate flux increased. This is due to the decomposition of organic compounds responsible for the formation of the gel layer and filtration cake (e.g. humic and fulvic acids). It was also reported that modification of the membranes with TiO_2 resulted in an increase in their hydrophilicity, which also contributed to fouling mitigation [3]. The configuration (b) is less common. The main disadvantage of the membranes with the photoactive support and a non-photoactive skin layer is that the purified stream is permeate only, whereas the concentrate contains contaminants which were rejected by the membrane. However, in this system it is possible to obtain permeate of much higher quality than in the configuration (a) [2, 3].

Taking into account that in case of the photocatalytic membranes the light source must be located in the vicinity of the membrane and that the photocatalytic reactions occur on the membrane surface or within its pores, the membrane should exhibit high resistance to UV irradiation and oxidation by hydroxyl radicals or other reactive oxygen species. Therefore, inorganic membranes (ceramic or metallic) are more promising for the application in PMRs than the polymeric ones.

A brief summary of advantages and disadvantages of PMRs with photocatalytic membranes is presented in Table 1.

Table 1. Advantages and disadvantages of PMRs with photocatalytic membranes [2, 3].

Advantages	Disadvantages
No need to separate and recycle a photocatalyst – the membrane can be used as long as the activity of the photocatalyst remains high	In case of aqueous phase reactions the effectiveness of degradation lower than in case of photocatalyst in suspension
Possibility of fouling mitigation due to decomposition of organic contaminants forming the gel layer or filtration cake	Adjustment of photocatalyst loading to the composition of the treated solution is impossible (fixed amount of the photocatalyst immobilized in/on the membrane)
Possibility of fouling mitigation due to enhanced hydrophilicity of the TiO_2-modified membrane	Risk of damage of polymeric membranes by UV light or hydroxyl radicals
No membrane fouling due to presence of TiO_2 particles	Necessity of the membrane exchange when the photocatalyst loses its activity
Contaminants could be decomposed either in feed or in permeate	Complicated construction of membrane modules – the radiation must reach the membrane surface

In most configurations of PMRs with a suspended photocatalyst the pressure driven membrane techniques such as microfiltration (MF) and ultrafiltration (UF) are applied. There are also other types PMRs in which photocatalysis is combined with nanofiltration (NF), dialysis, pervaporation (PV) or direct contact membrane distillation (DCMD, MD) [2, 3]. The main role of a membrane in these systems is separation of photocatalyst particles from the treated solution. Moreover, depending on the membrane type and membrane process applied, the membrane might also act as a barrier for the degraded molecules and products of their decomposition.

PMRs coupling photocatalysis with pressure driven membrane techniques have been applied for the removal of various pollutants, including pharmaceuticals, humic and fulvic acids, trichloroethylene, bisphenol A, chlorophenol, 4-nitrophenol, dyes, as well as for treatment of real dyeing wastewater, synthetic wastewater, grey water, primary and secondary effluents from municipal wastewater treatment plants and surface waters [3, 6]. Both pressurized and depressurized (i.e. with submerged membranes) systems were applied. It is usually reported that the main drawback of the pressurized PMRs is membrane fouling caused by TiO_2 particles leading to the permeate flux deterioration. However, operation below the critical flux value can prevent from deposition of the TiO_2 cake layer on the membrane surface [7]. In general it is reported that the PMRs with submerged membranes are less prone to fouling by TiO_2 than the pressurized systems. This does not mean, however, that fouling does not occur in these systems at all. The investigations on the treatment of river water in a PMR utilizing submerged MF membranes revealed [8] that although photocatalysis had a beneficial influence on the permeate flux, a chemical cleaning after about one month of operation was necessary.

It must be remembered that membrane fouling by TiO_2 is a complex issue and there are numerous factors affecting this phenomenon. They include feed composition and pH, hydraulic conditions (cross flow velocity, transmembrane pressure), operating mode (pressurized, depressurized), operating conditions in membrane module (aeration, intermittent permeation, gas backflushing), etc. [2, 3]. Analyzing the reports on the hybrid photocatalysis

– membrane systems published in recent years it can be concluded that the influence of TiO_2 on permeate flux in PMRs is dual [6]. From one side, in the presence of TiO_2 a deterioration of the flux resulting from the formation of a cake layer on a membrane surface can take place, as was mentioned above. From the other hand, when the feed contains contaminants such as natural organic matter (NOM), especially humic and fulvic acids, the coupling of a membrane process with photocatalysis can lead to the improvement of the flux due to decomposition of organic molecules. A positive influence of photocatalysis on the permeate flux during treatment of primary (PE) and secondary (SE) effluents from a municipal wastewater treatment plant in a pressurized PMR utilizing UF was also reported [6].

Table 2. Advantages and disadvantages of PMRs with suspended photocatalyst utilizing pressure driven membrane techniques [2, 3].

Advantages	Disadvantages
The effectiveness of degradation higher than in case of photocatalyst immobilized in/on the membrane	Membrane fouling due to the presence of TiO_2 particles, especially in case of pressurized systems
The exhausted photocatalyst might be exchanged without membrane replacement	Low quality of permeate – initial compounds and products/by-products of their degradation pass through the membranes, especially in case of MF and UF
Easy adjustment of photocatalyst loading to the composition of the treated solution	
Effective separation of photocatalyst particles	
Possibility of enhancement of permeate flux due to decomposition of NOM forming a gel layer	
Possibility of enhancement of permeate flux by application of depressurized (submerged) systems instead of pressurized ones	
No risk of damage of polymer membranes by the UV light or hydroxyl radicals – the light source can be positioned anywhere in the hybrid system	

The efficiency of removal of organic contaminants in PMRs utilizing MF or UF depends on the effectiveness of both the membrane process and photocatalysis. In general, MF and UF membranes are not able to reject low molecular organic compounds, including initial contaminants and by-products of their decomposition. Therefore, in case of these substances the overall treatment efficiency depends on the effectiveness of photocatalysis. On the other hand, since the mineralization of large molecules proceeds slowly, the overall treatment efficiency in case of such contaminants depends on the effectiveness of a membrane separation.

A brief summary of advantages and disadvantages of PMRs with suspended photocatalyst is presented in Table 2.

3. PMRs in organic synthesis

A majority of literature reports on PMRs refers to their possible application in water and wastewater treatment. The aim of application of photocatalysis in these systems is mineralization of organic contaminants to nontoxic compounds such as CO_2, H_2O and

inorganic salts (chlorides, nitrates, sulfates, etc.). Recently, however, some papers describing possibilities of utilization of PMRs in organic synthesis have also been published. In this approach a partial oxidation of organic compounds aimed at production of useful substances is mainly considered [9]. The proposed solutions include (i) recovery of valuable intermediate compounds (benzaldehyde and 4-methoxybenzaldehyde) produced from the corresponding alcohols (benzyl alcohol and 4-methoxybenzyl alcohol) in an integrated photocatalysis - pervaporation system; (ii) recovery of vanillin produced by trans-ferulic acid oxidation using an integrated photocatalysis - pervaporation system; (iii) photocatalytic partial oxidation of benzene to phenol in a photocatalytic membrane reactor with application of benzene as both substrate and extracting agent [9]. It was reported [10] that the coupling of pervaporation with the photocatalytic partial oxidation of a primary aromatic alcohol to produce the corresponding aldehyde enhanced the rate and the yield of the process. The observed improvement resulted from a continuous recovery of the aldehyde from the reaction environment before its further oxidation. Similarly, the utilization of a highly selective membrane prepared from PEBAX® 2533 (polyether block amide by Arkema) allowed the continuous recovery of vanillin from the reaction environment by means of pervaporation, so that its oxidative degradation was minimized and the yield was substantially enhanced [11]. Nonetheless, the idea of application of PMRs in organic synthesis is still in its early stages and much work should be done before a possible utilization of this technology on the industrial scale.

3. Summary

PMRs exhibit numerous advantages over the conventional photoreactors in case of both water and wastewater treatment as well as organic synthesis. However, further investigations are still needed in order to improve the hybrid photocatalysis – membrane processes performance, especially in terms of permeate flux and membrane fouling as well as product (permeate) quality.

Moreover, it is very important to investigate the real systems, which focus on the treatment of natural waters and real wastewaters. The number of reports concerning this subject is still limited, since most of the experiments have been conducted using model solutions.

Especially extensive investigations are necessary in the area of application of PMRs in organic synthesis. Since the idea is still in its early stages, much work should be done before a potential utilization of this technology on the industrial scale.
Nonetheless, the main obstacles in full scale application of PMRs are:
- the light source: development of photoreactors and photocatalysts efficiently utilizing solar light would be beneficial from the economic point of view;
- the membranes: development of membranes resistant to the severe conditions prevailing in PMRs, especially in terms of resistance to oxidation by hydroxyl radicals and other oxidative species as well as abrasion by photocatalyst particles is necessary.

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