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MEMBRANE REACTORS IN PHOTOCATALYTIC PROCESSES

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Photocatalytic membrane reactors are integrated systems where the photocatalytic process and separation by a membrane occur simultaneously. This simultaneous arrangement has been found to be more effective than traditional methods. In this mini review, the membrane techniques applied as well as their features, behavior and operation in addition to some of the applications of PMRs are presented.

Keywords: membrane separation, pollutants, oxidation, membrane techniques

1. Introduction

Membrane reactors are special setups where a chemical reaction step and a separation step take place simultaneously [1]-[3], moreover, the two steps are connected. In general, they are used in equilibrium reactions where catalysts are present and the insertion of a (in-situ or in-line) separator may enhance the effectiveness of the reaction. Membrane reactors can be applied in, for example, the petrochemical industry for dehydrogenation and hydrogenation processes [3]-[4].

The reaction takes place in a membrane bioreactor if *biocatalysts* are used instead of catalysts, where bioprocesses and membrane techniques are coupled [5]. These systems have been studied extensively in our research group and various membrane techniques inserted into enzymatic or fermentation processes [6]-[8].

Photocatalysis is a process where special semiconductor materials are used to facilitate redox reactions, i.e. oxidation, when they are irradiated with light of a suitable energy [9]-[11]. Photocatalytic oxidation, which is characterized as an "advanced oxidation process" (AOP), has recently been comprehensively studied and found to break down some organic pollutants in wastewater. Titanium dioxide is widely used as a photocatalyst due to its high chemical stability, relatively low cost, optical and electronic properties as well as its non-toxicity. A semiconductor catalyst – mainly related to TiO_2 – is mostly applied as a powder suspended in a liquid, hence is referred to as heterogeneous photocatalysis. Therefore, it is necessary to insert a separation step into the technology to recover it. This can be realized by membranes, which are able to prevent the catalyst from being washed out, moreover, some membrane techniques are capable of controlling the amount of products or by-products in the photooxidation process [12]-[13]. These membrane processes have become more and more attractive due to their beneficial features, namely chemical additives are not necessary and little energy is required.

When photocatalytic oxidation is integrated with membrane separation, photocatalytic membrane reactors (PMRs) can be assembled. When the catalyst is in a suspended form in the photoreactor, the system is often called a suspension photocatalytic membrane reactor (SPMR).

PMRs boast numerous advantages [13]-[14] when compared to conventional photocatalytic processes, e.g.:

- the photocatalyst remains in the reaction thanks to a membrane;
- the process can be continuous, moreover, the photocatalysts can be recovered and the products separated simultaneously;
- the treated water does not contain any biocatalysts;
- the process can be controlled better, moreover, is more stable and efficient;
- no additional operations are necessary, e.g. coagulation, flocculation, sedimentation, etc., moreover, their installation occupies less space and consumes less energy.

2. Membrane techniques

Various membrane separation processes can be coupled to a photocatalytic reactor [1, 12-14], which are listed in *Table 1*. Among the pressure-driven methods, microfiltration, ultrafiltration and nanofiltration may be

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Table 1: Membrane processes applied in photocatalytic processes

Membrane process	Reference
ultrafiltration microfiltration nanofiltration	Molinari (2002) [13]
pervaporation	Camera-Roda (2007) [18]
membrane distillation	Mozia (2008) [19]
membrane contactor	Loddo (2011) [12]
dialysis	Azrague (2007) [20]

applied. The driving force in these techniques is the transmembrane pressure and are often called "membrane *filtration* methods" since the separation is based on the pore size of the membrane. Membrane filtration processes were the first membrane techniques applied in photocatalysis in water treatment technologies during the 1960s.

Pervaporation is a process where the liquid feed flows into the primary side of the non-porous membrane film and the permeate is obtained in vapor phase under a vacuum (which can be condensed to convert the permeate into a liquid).

In *membrane distillation*, the volatile compounds of the feed are evaporated and passed through the pores of the hydrophobic membrane before being condensed into the permeate. The driving force is the difference in vapor pressure on either side of the membrane.

In the case of *membrane contactors*, the membrane not only separates the phases but also functions as a contact site between them, facilitating the transportation of certain components. Membrane contactors can be classified as gas–liquid, liquid–liquid and liquid–gas membrane contactors. Although the main driving force is the difference in concentration, in some cases, solubility may play a role, e.g. when an organic solvent is applied in the secondary phase, extraction occurs whereby distribution coefficients are the determining factors. This kind of contactors are called pertractors (derived from the words 'permeation' and 'extraction').

Dialysis is driven by the difference in concentration on either side of the membrane and the transport mechanism is diffusion.

Regarding the membrane module, a flat sheet as well as hollow fiber modules are used in SPMRs in addition to ceramic tubular modules.

3. Photocatalytic membrane reactors

Membrane filtration techniques have been applied in PMRs to separate and recover the photocatalytic particles [13, 15-16]. In this way, the loss of photocatalysts can be minimized, rendering the operation more reliable and cost-effective. Using PMRs, several types of dyes (Congo red, methylene blue, rhodamine B, Eosin Y), pharmaceuticals (ibuprofen, diclofenac, carbamazepine, tetracycline), pesticides (diuron, chlorfenvinphos) and other pollutants (phenol, humic acids) were degraded before being removed.

Sedimentation of the suspended photocatalysts can be controlled by applying fine bubble aeration and intermittent membrane filtration as reported by Huang et al. (2007) [17].

A *pervaporation* unit was integrated into the photocatalytic process to remove 4-chlorophenol (4-CP) [18]. In this hybrid system, the solution contained the pollutant which passed through the photocatalytic reactor into the pervaporation module by means of a pump before the permeate was obtained as a vapor. The retentate was recycled in the photoreactor. It was found that the removal of 4-CP was greatly enhanced by this integrated system, indicating a synergistic effect between photocatalysis and the pervaporation process.

Photocatalysis was coupled with *membrane distillation* [19] to remove 3 azo dyes from the water. 0.0014 m^2 polypropylene (PP) hollow fiber membranes were used. A 3 dm^3 photoreactor containing the dyes and the photocatalyst Aeroxide TiO_2 P25 was positioned in front of the membrane module for the photocatalytic reaction. When the system was operated in batch mode, the photoreactor also acted as the feed tank. When the system was operated in continuous flow mode, an additional feed tank was applied to continuously supply fresh feedwater to the photoreactor. A UVA lamp was positioned above the photoreactor as the light source. The fresh feedwater was heated to 333 K by a heater at the start of the experiment. The retentate was reintroduced into the feed tank and the permeate collected in the distillate tank.

Another type of separation which can be coupled with photocatalysis uses *membrane contactors* [12]. The main driving force of the separation is the distribution coefficient of the transported species. Photocatalytic membrane contactors have several advantages compared to other configurations of reactors, e.g. it is possible to selectively separate the product(s) of interest during the photosynthetic process, preventing undesirable secondary reactions from occurring.

Dialysis was used in the SPMR system where a model pollutant, namely 2,4-dihydroxybenzoic acid (2,4-DHBA), was mineralized from turbid waters by photocatalysis [20]. The membrane retained the TiO_2 catalyst in the photoreactor compartment, so filtration was unnecessary. Meanwhile, the organic compounds were allowed to pass through the membrane without transmembrane pressure.

4. Special considerations

When applying microfiltration or ultrafiltration, two different SPMRs can be described [13] regarding the operation as presented in *Figures 1* and *2*. In one of them, the catalyst is suspended in a recirculation reactor (tank), while the membrane module – as an external unit – is connected to the reactor. The permeate is forced to pass through the membrane by pressurizing the primary side of the membrane surface. This kind of operation often causes severe fouling which should be controlled by, for example, backwash or backflush [21].

To overcome fouling, another type of PMR was developed [22], where the membrane module is immersed in the reactor. The catalyst is suspended in the reactor and the permeate withdrawn by a vacuum pump. It can be referred to as an internal (or depressurized) system. As an example, the decomposition of reactive Orange 29 (RO29) was carried out in this kind of submerged PMR.

Although external (pressurized) and internal (depressurized, submerged) membrane reactors are also well-known when treating wastewater, *microorganisms* are used during the degradation process, therefore, are considered as *membrane bioreactors* [23]-[24]. The two systems with the photocatalysts and biocatalysts, however, are analogous configurations of the membrane reactors, moreover, their operations are similar in several ways.

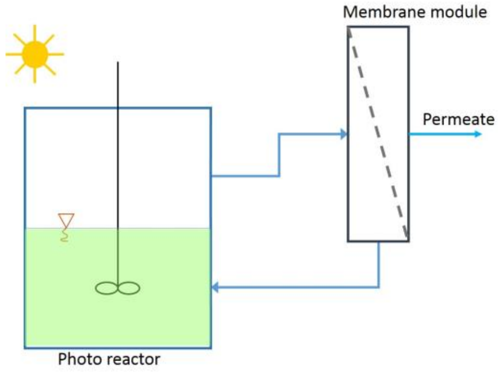

Figure 1: Scheme of an external photocatalytic membrane reactor

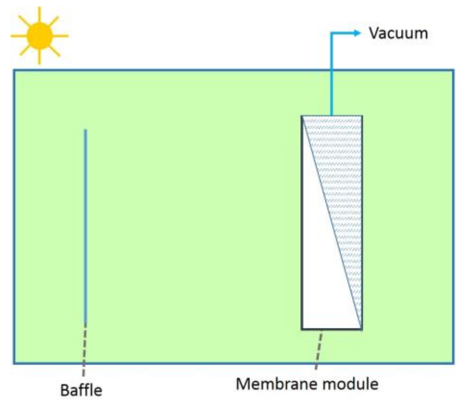

Figure 2: ~~-~~Schematic diagram of an internal photocatalytic membrane reactor

5. Immobilized photocatalysts

More recently, in addition to suspension photocatalytic membrane reactors ~~(SPMR)~~, another configuration of membrane reactor known as an *immobilized photocatalytic membrane reactor (IPMR*) was studied, where the catalyst is immobilized on the membrane surface [16]. Thus, the membrane has two functions namely to support photocatalysts and separate. Photocatalysts can be fixed on the membrane by various methods, e.g.:

- Physical deposition
- Dip coating
- Phase inversion
- Hydrothermal synthesis—filtration
- Electrospinning and hydrothermal reactions
- Atomic layer deposition

In these systems, the most important factor is the stability of the membrane since severe photodegradation might occur during the process.

6. Outlook

Since PMRs were originally successfully developed for water treatment and environmental processes, their success was a motivation to expand the application areas [16]. Recently, several novel usages of PMRs have been reported, e.g.:

- photocatalytic conversion of CO_2;
- photocatalytic water splitting for hydrogen production;
- other oxidative chemical processes like the conversion of ferulic acid into vanillin or the direct oxidation of benzene into phenol;
- disinfection of water.

These new applications are making PMRs more and more known worldwide in industrial and environmental engineering areas, moreover, novel, innovative applications may arise.

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