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## Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review

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### ABSTRACT

Hybrid processes combining membrane separation and heterogeneous photocatalysis represent an exciting technology because each technique complements the advantages and overcomes the challenges of the other. This combination gives plants set-up named Photocatalytic Membrane Reactors (PMRs). PMRs can be designed in two configurations: reactors in which the catalyst is suspended in the reaction mixture and reactors that utilize the photocatalyst immobilized/deposited on membrane surface, giving a photocatalytic membrane. PMRs allow to perform a variety of chemical reactions (e.g. degradation or synthesis of organic compounds) and separation in one step thus minimizing environmental and economic impacts in agreement with the Green Chemistry principles.

Different PMR configurations (pressurized, submerged, with photocatalytic membrane, photocatalytic reactors with membrane distillation, with membrane dialysis, with a pervaporation membrane) have been applied in water treatment for degradation of different organic pollutants (such as dyes, pharmaceuticals and other pollutants) and in the synthesis of organic compounds (such as phenol, vanillin and phenylethanol). The main experimental results of the different applications will be described and critically examined in this review.

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### 1. Introduction

Heterogeneous photocatalysis is an advanced oxidation process (AOP) based on the use of light and a semiconductor (the photocatalyst) to generate the oxidizing/reducing species. It has been extensively studied since about four decades, when Fujishima and Honda [1] discovered the photocatalytic splitting of water on TiO<sub>2</sub> electrodes.

It has been object of a large amount of studies related to environment recovery by the total degradation to innocuous substances of organic and inorganic pollutants [2,3], the removal of toxic metals, and for synthesis of organic compounds [4]. It is a discipline that includes a large variety of reactions [5]: partial or total oxidations, metal deposition, water detoxification, gaseous pollutant removal, bactericidal action [6–8], and, recently, dehydrogenation and hydrogenation (e.g. hydrogen transfer) [5].

The main difference of photocatalysis compared to conventional catalysis is the photonic activation mode of the catalyst, which replace the thermal activation [6]. The electronic structure of a semiconductor is characterized by a conduction band (CB) and a

valence band (VB) separated by a band gap of energy (E<sub>g</sub>). When semiconductors are excited by photons with energy (hν) equal to or higher than their band gap energy level (E<sub>g</sub>), valence electrons (e<sup>-</sup>) are promoted from VB to CB, thus leaving a positive hole (h<sup>+</sup>) in the VB.

For a generic semiconductor (SC), this step can be expressed as:

$$SC + h\nu \rightarrow SC(e^- + h^+) \quad (1)$$

In the absence of suitable electron and/or hole scavengers, the photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the adsorbed substrate.

The overall photocatalytic process can be summarized in four steps: (i) absorption of light followed by the separation of the electron–hole couple; (ii) adsorption of the reagents; (iii) redox (reduction and oxidation) reaction; (iv) desorption of the products.

Thanks to the favorable energetic level of its band structure, making it suitable to catalyze a wide range of oxidation/reduction reaction, relatively high quantum yield, stability under irradiation, low cost and availability, TiO<sub>2</sub> represents the archetypical photocatalyst, virtual synonym for photocatalysis. Nevertheless, this material does not present photo-response under visible light

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**Nomenclature***List of symbols*

AOP	Advanced oxidation process
APR	Annular photocatalytic reactor
AR1	Acid red 1
AR18	Acid red 18
AROMA	Advanced recovery and oxidation method for aldehydes
AY36	Acid yellow 36
BET	Brunauer–Emmett–Teller
BSA	Bovine serum albumin
CB	Conduction band
CMD	Cimetidine
4-CP	4-Chlorophenol
CR	Congo red
CVD	Chemical vapor deposition
DCF	Diclofenac
DCMD	Direct contact membrane distillation
DG99	Direct green 99
2,4-DHBA	2,4-Dihydroxybenzoic acid
DPH	Diphenhydramine
DW	Distilled water
Eg	Band gap energy level
GEM	Gemfibrozil
GO	Graphene oxide
GO-TiO <sub>2</sub>	Graphene oxide doped TiO <sub>2</sub>
GW	Groundwater
HA	Humic acids
HFM	Hollow fiber membrane
IBU	Ibuprofen
K <sub>D</sub>	Partition coefficient
LIN	Lincomycin
MB	Methylene blue
MC	Membrane contactor
MD	Membrane distillation
MO	Methyl orange
NaA	Sodium alginate
NAP	Naproxen
NF	Nanofiltration
NOM	Natural organic matter
N-TiO <sub>2</sub>	Nitrogen doped TiO <sub>2</sub>
PhACs	Pharmaceutically active compounds
PB	Patent blue
PC	Photocatalysis
Pd/TiO <sub>2</sub>	Palladium doped TiO <sub>2</sub>
PE	Primary effluent
PEBA	Polyether-block-amide
PES	Polyethersulfone
POMS	Polyoctylmethylsiloxane
PM	Photocatalytic membrane
PMC	Photocatalytic membrane contactor
PMR	Photocatalytic membrane reactor
PR	Photoreactor
PV	Pervaporation
PVDF	Polyvinylidene fluoride
PVDF-NFs	Polyvinylidene fluoride nanofibers
PVPR	Pervaporation photocatalytic reactor
SBW	Simulated brackish water
SC	Semiconductor
SE	Secondary effluent
SEM	Scanning electron microscopy
SPMR	Submerged photocatalytic membrane reactor
SSF	Stainless steel filter

SW	Seawater
TAM	Tamoxifene
TCEP	Tris(2-chloroethyl) phosphate
TiO <sub>2</sub> -NFs	TiO <sub>2</sub> nanofibers
TMP	Transmembrane pressure
TOC	Total organic carbon
TrOCs	Trace organic contaminants
TTIP	Titanium tetraisopropoxide
TW	Tap water
UV	Ultraviolet radiation
UW	Ultrapure water
UF	Ultrafiltration
VA	Vanillin
Vis	Visible radiation
VB	Valence band
XRD	X-ray powder diffraction

illumination because of its wide band gap, taking advantage of only less than about 5% of the solar energy. Thus its potential as a green technology cannot be entirely fulfilled. Considering that usually the quantum yield of photocatalytic processes decreases when the intensity of the radiation increases [9,10], the preparation of visible active photocatalysts results convenient only in the case that the quantum yield remains relatively high, which means a wide use of photons from visible light. In the last years a great number of new photocatalysts have been synthesized and tested as possible alternatives to TiO<sub>2</sub> [11,12] in view of solar application. For example, the use of graphene quantum dots/TiO<sub>2</sub> nanotubes composite permitted, very recently, to obtain a significantly enhanced photocatalytic activity in the degradation of methyl orange (MO) compared with that of pure TiO<sub>2</sub> nanotubes [13].

Because of the highly unselective reactions involved in the photocatalytic processes, these ones have been widely studied in remediation processes, in which organic and inorganic pollutants in liquid and gas phases are totally degraded to innocuous substances. However, in last decade some studies have been carried out on the application of photocatalysis for synthesis such as selective reduction and oxidation. These studies demonstrated that high selectivity could be obtained in photo-oxidation and photo-reduction processes in comparison to conventional methods by appropriately selecting or modifying some photocatalytic parameters, as the semiconductor surface or the excitation wavelength. In this framework, the photocatalytic oxidation of organic compounds has been largely studied because the most common semiconductors have VB edges more positive than oxidation potentials of most organic functional groups [14]. Instead, photocatalytic reductions are less frequently found, because the reducing power of a CB electron is significantly lower than the oxidizing power of a VB hole [2,15].

Important characteristics of photocatalysis, making it in agreement with the Green Chemistry principles, consist in the mild operating conditions (ambient temperature and pressure, very few auxiliary additives and short reaction times) and in the possibility to abate refractory, very toxic and non biodegradable molecules [16,17]. Besides, photocatalysis: (i) avoids the use of environmentally and unhealthy dangerous heavy metal catalysts by using safer photocatalysts (mainly TiO<sub>2</sub>); (ii) avoids the use of strong oxidants/reducing agents; (iii) permits the real destruction of the contaminants with the formation of innocuous by-products; (iv) can be applied to a wide range of substrates in aqueous, solid and gaseous phase; (v) is applicable to solutions at low concentrations; (v) offers a good alternative to the energy-intensive conventional treatment methods; (vi) permits to use renewable solar energy;

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