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Bacterial inactivation and degradation of organic molecules by titanium dioxide supported on porous stainless steel photocatalytic membranes

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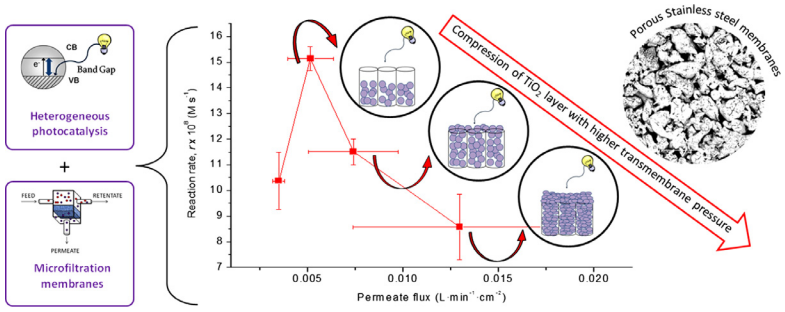
HIGHLIGHTS

- Photocatalysis/microfiltration hybrid system with TiO_2–PSS membranes.
- Average pore size of membrane plays a significant role on photocatalytic efficiency.
- Optimal TiO_2 loading is a compromise of light absorption, pressure and surface area.
- Photocatalytic membranes show a significant inactivation of the retained bacteria.
- The feasibility of the hybrid process for biofouling control has been confirmed.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel integrated photocatalysis/microfiltration hybrid system based on the use of TiO_2 immobilized by filtration on porous stainless steel supports has been demonstrated to provide a good efficiency in the removal of bacteria for water disinfection applications. A synergistic effect derived of the physical removal of microorganisms coupled to its photocatalytic inactivation was proved to be achieved. The membrane pore size and the TiO_2 loading were found to play a significant role on the efficiency of the process and the value of the transmembrane pressure. An optimal value of 8.5 $g \cdot m^{-2}$ TiO_2 supported over the membranes provides good photocatalytic activity keeping the transmembrane pressures in the range of 1.5–2 bar. Moreover the photocatalytic activity of the membrane was proved to have as an additional advantage the possibility of the simultaneous oxidation of the chemical pollutants present in the feed water. Continuous operation of the photocatalytic membrane reactor in dead-end configuration confirms the accumulation of bacteria on the membrane leading to an increase in the transmembrane pressure, whereas the photocatalytic functionality demonstrated a significant inactivation of the retained cells, confirming the feasibility of the hybrid process for biofouling control.

1. Introduction

Membranes play an important role in the separation technologies and represent promising alternatives to conventional water and wastewater treatment processes [1–3], with well-known advantages: small footprint, small size (compact modules), lower energy consumption, admission of fluctuations in feed quality and its excellent separation efficiencies. This technology provides many advantages over conventional treatments, as demonstrated by the rapidly increase in their industrial use in potable water production in the past decade [4,5]. In general, filtration uses the difference of pressure between the feed and permeate side as the driving force to transport the solvent through the membrane. In this way, the particles and dissolved components are retained

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based on the membrane properties such as pore size, shape, and surface charge [6]. The most general and known classification of membranes is based on the pore size. This classification distinguishes microfiltration (50–500 nm), ultrafiltration (2–50 nm), nanofiltration (⩽2 nm), and reverse osmosis (0.3–0.6 nm) [6]. Depending on the application and the required pore size the base materials of the membranes are different [1]. Polymeric membranes (i.e., polysulfone (PS), polyethersulfone (PES), polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), cellulose acetate (CA) and Nafion membranes are commonly used for ultrafiltration, nanofiltration and reverse osmosis. For microfiltration applications organic, metallic or ceramic membranes are usually employed [7–9], being the ceramic materials supports more frequently used than polymers or metals due to their higher resistance to oxidation [8–10].

The microfiltration process is commonly used to remove big particles and also works as a disinfection barrier to assist in the removal of pathogenic microorganisms [1,6,11] that may cause problems in further treatment steps, moreover, microfiltration is also a common pretreatment step of other membrane processes. Nevertheless, this technology has the main problem of the membrane fouling (deposition of retained particles at the membrane surface or inside the pores) which causes several adverse effects on membrane systems as gradual reduction in the permeate flux, increase in transmembrane pressure (TMP), biodegradation of membrane materials and poor permeability [2,12], which can lead as well to operational problems as rising energy demand, increase of the cost in chemical cleaning agents and finally system failure [1,13]. To control biofouling the most common method is periodic cleaning of the membranes by acid or basic chemical solutions and backflushing with water that raises the cost of the process [12].

The combination of filtration processes with Advanced Oxidation Technologies (AOTs) has received a growing interest in the last years [14]. Among the different AOTs, titanium dioxide photocatalysis constitutes one of the most promising and studied processes for the generation of reactive oxidant species upon illumination of a semiconductor material. The high efficiency of TiO_2 to generate hydroxyl radicals when it is irradiated with UV light, together with its environmentally friendly properties and low cost, make this material the most popular and studied photocatalyst. Therefore, the incorporation of TiO_2 to the membranes enables the coupling of both processes by the simultaneous action of pollutant rejection and photocatalytic degradation of contaminants.

Titania has been previously reported to have antibacterial and antiadhesion properties for microorganisms due to the photogenerated reactive oxidant species, as hydroxyl radicals and superoxide that can completely degrade most of organic pollutants, bacteria, fungus and even viruses from water [15,16]. The possibility of reducing membrane fouling by the incorporation of a photocatalyst makes extensible the useful lifetime of the membranes. These hybrid photocatalysis/membrane processes are conducted in photocatalytic membrane reactors (PMR) where the catalyst can be immobilized in a membrane (fixed bed reactors) [14,17] or suspended in a feed tank (slurry reactors) and the membrane might act as a barrier not only for the degraded by-products but also for the catalysts particles [18–20]. In the case of fixed bed reactors the surface of the membrane constitutes the catalyst support and must be illuminated with UV light. The TiO_2 nanoparticles can be either deposited over the membrane surface or trapped in the polymeric membrane [7,10,21], being the first option more commonly used in microfiltration membranes. The photocatalytic process occurs in the TiO_2 layer providing the features of biofouling control and disinfection of the permeate stream. This PMR configuration, however, reduces the photocatalytic active surface areas as a consequence of catalysts immobilization which usually results in a loss of activity [2].

Despite the extensive work on photocatalytic membranes for removal of organic contaminants [10,22] and anti-bacterial and anti-fouling effects [21,23,24], to the best of our knowledge there are no reports on the application of photocatalytic membranes based on TiO_2 supported on porous stainless steel (PSS) membranes for the disinfection of water and simultaneous removal or organic pollutants. PSS membranes present significant advantages due to their mechanical stability, chemical resistance and possibility of fine tuning of their properties during the preparation step. Ames et al. [25] investigated the characterization of stainless steel membranes for aqueous waste separation processes. Li et al. [26] reported the preparation of TiO_2 films incorporated onto 316L PSS pieces of 1 μm pore size by dip coating to study the synthesis conditions of the films, whereas Potter et al. [17] studied tubular TiO_2–PSS membranes with a nominal pore size of 0.2 μm for the filtration of anionic dyes in tap and deionized water solutions. However, there is a lack of investigations on the photocatalytic applications of metallic membranes. The novelty of this work is focused in the further investigation of the PSS membranes and its behavior in a hybrid photocatalytic/microfiltration TiO_2–PSS membrane system. The preparation and photocatalytic performance of TiO_2–PSS microfiltration membranes for water disinfection applications, including not only the removal and inactivation of microorganisms, but also the possibility of simultaneous oxidation of chemicals is described in this work. The influence of parameters such as TiO_2 loading and transmembrane pressure on the process efficiency is also addressed, together with the analysis of the process both in batch and continuous operation mode using deionized water (DW) and a simulated wastewater treatment plant effluent (SWTPE).

2. Materials and methods

2.1. Microfiltration system and photocatalytic membrane reactor

Microfiltration and photocatalytic experiments were carried out in the experimental setup schematized in Fig. 1. The system consist of a 4 L feed tank, a positive displacement pump couple to a pulsation damper and two pressure and flow gauges located before and after the photocatalytic membrane reactor. The liquid flow rate provided by the pump can be regulated by a variable-frequency drive and a piston displacement system. By default, experiments were carried out using a flow rate of 1.1 $L{\cdot}min^{-1}$. The photocatalytic membrane reactor consists of an annular reactor of 15 cm long, with a 3 cm in diameter glass inner tube and 6 cm in diameter poly-methylmethacrylate outer tube, being the membrane (5 cm in outer diameter) located concentrically between both walls (Fig. 1b and c). Illumination of the TiO_2 layer in the inner surface of the membrane is provided by a black light lamp (Philips TL 6 W with an emission maximum at 365 nm) located in the axis of the annular reactor.

Both concentrate and permeate outlet streams of the reactor, can be driven to an external storage tank (in continuous operation mode) or recycle to the feed tank (in batch operation mode). A valve in the outlet of the concentrate stream allows operation of the system under cross flow or dead end filtration modes.

2.2. Preparation of photocatalytic membranes

The 316 L porous stainless steel (PSS) membranes were supplied by Shijiazhuang Beot Inorganic Membrane Separation Equipment Co. Ltd with nominal average pore sizes of 0.20 and 0.50 μm and will be reference as PSS-0.2 and PSS-0.5, respectively. They were fabricated by synterization of stainless steel microparticles conforming a final tubular shape geometry (15 cm length, 5 cm