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Study on a photocatalytic membrane reactor for water purification

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Abstract

Some results obtained in a photocatalytic membrane reactor, to be used for degradation of toxic organic species dissolved in water, are reported. The catalyst, TiO_2 P25 Degussa, was immobilised by means of a flat sheet polymeric membrane and 4-Nitrophenol (4-NP) was used as a model molecule to evaluate the reactor performance. A preliminary investigation of the stability, under UV irradiation, of some eligible polymeric membranes was carried out by using scanning electron microscopy (SEM), optical microscopy (OM), determinations of water permeation flux (WPF) and total organic carbon (TOC). These tests showed that commercial membranes made of fluoride + PP (FS 50 PP-Dow), polysulphone + PP (GR 51 PP-TechSep) and polyacrylonitrile (PAN-TechSep) seemed to be quite stable to UV light over a 24 h period of irradiation. Immobilisation of TiO_2 onto membranes by ultrafiltrating TiO_2 suspensions showed an optimal layer density slightly >2.04 mg TiO_2 per square cm of membrane surface area. Results obtained from membrane reactor studies indicated that the observed initial rate constants for the degradation of 4-NP were almost independent on the amount of TiO_2 employed over the range 0.76–4.08 mg/cm^2. A 50% weight degradation of 4-NP after 5 h of irradiation in the presence of air was obtained. Instead, an almost complete degradation of 4-NP was observed in the presence of TiO_2 suspended in the solution and pure oxygen. The permeate deriving from the membrane photoreactor was clear and 4-NP concentration was approximately equal to that found in the retentate. The possibility of the continuous reuse of the photocatalyst and the continuous separation of products from the reaction medium give some advantages over traditional approaches. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Membrane photoreactor; TiO_2 photocatalyst; 4-Nitrophenol photodegradation

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1. Introduction

Before water is admitted in public aqueducts or it is reused in industrial processes or it is discharged in surface water courses it is necessary to degrade the dissolved toxic organic species. This is today one of the more relevant problems and imposes the use of sophisticated cleaning up methodologies.

New emerging technologies permit both the reduction of the global environmental impact and the use of chemicals in treatment processes. The coupling of a photocatalytic reaction with a membrane separation process could take advantage of the synergy of both technologies resulting in a very powerful system, with the membrane having the simultaneous task of supporting the photocatalyst as well as acting as a selective barrier for the species to be degraded.

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Photocatalytic reactions, both in liquid–solid and in gas–solid regimes, are today receiving a growing interest because of their potential applications [1]. An example of their industrial importance is the utilization of the UV radiation coupled with chemical oxidants in the area of pollutant degradation. In this way the oxidising power can be enhanced and the elimination of dangerous chemical pollutants from potable, industrial and waste waters can be efficiently actuated [2]. The photocatalysts more suitable to be used are some polycrystalline semiconductors such as TiO_2, ZnO, $SrTiO_3$, RuO_2 and CdS [3–5]. In particular, TiO_2 in the crystalline form anatase, has been widely used due to its low cost and photostability.

Despite the potential applications of photocatalytic methods, up-to-date studies reported in literature concern only the scientific aspects of this process and principally refer to batch discontinuous systems where the catalyst is simply suspended in water or in continuous fluidized-bed reactors. In the case of these later systems there is no need to recover the suspended solids, although the problem of separating microparticles can not be neglected.

On the other hand, the technology of membrane separation has long been demonstrated to be competitive with respect to other separation processes with respect to energy costs, materials recovery, reduction of the environmental impact and realise of integrated processes [6–8]. Consolidated applications of this technology such as tangential flow microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and gas separation, are receiving today further attention to perform new processes based on integrated reactors/separators. One of the problems encountered when photocatalysts are immobilised on supports is the detachment of the microparticles from the support for high flow rates of the liquid effluent. To reduce this problem some authors immobilise the semiconductor on various types of supports such as polycarbonate, Pyrex [9], cellulose microporous membranes [10] or aerogels [11]. Membranes have been used in all of these approaches, but their main role, that is to separate given molecules and/or ions from a solution with permeability and selectivity dependent on the type of membrane employed, has not been well studied. The possibility of a continuous process with simultaneous product(s) separation from the reaction environment can be cited among the advantages of such a membrane photoreactor.

In particular, it is expected that some problems present when a photocatalyst is used in traditional reactors, i.e. its reuse and separation from the reaction mixture and its stability in immobilised form, may be minimized using a hybrid photoreactor.

In this work, some results obtained by using a photocatalytic membrane reactor with TiO_2 physically immobilised on the membrane or retained in suspension by means of the membrane are reported. A preliminary investigation on the stability, under UV irradiation, of some polymeric membranes, eligible to be used in the photoreactor was performed. The behaviour of the membrane photoreactor using the two different confination techniques of TiO_2 was studied. 4-NP was chosen as a model molecule because its photodegradation in aqueous TiO_2 suspensions, irradiated with UV–VIS light, was already studied [12–14].

2. Experimental

Eleven polymeric membranes (Table 1) eligible to be used in the photoreactor for the photodegradation experiments, described in the following, were chosen. Some preliminary UV absorbance studies on the membranes, as a screening technique, were carried out. In these stability tests the membranes were irradiated with UV–VIS light provided by a 500 W medium pressure mercury lamp, Helios Italquartz, Milan.

Table 1
Types of commercial membranes used in UV–VIS irradiation tests

Types of membrane	Manufacturer	Type of polymer	Cut-off/ Pore size
MPPS 0000 u002	Separem	polysulphone	15 kDa
MPPS 0000 u006	Separem	polysulphone	40 kDa
MPCU 0000 u20	Separem	polyamide	2.5 kDa
MPCU 0000 u25	Separem	polyamide	2.0 kDa
P-12-10	Our lab	PEEK	–
FS 50 PP[a]	Dow	fluoride + PP	50 kDa
PES	TechSep	polyethersulphone	40 kDa
PVDF	TechSep	polyvinylidenefluoride	0.1 μm
GR 51 PP	TechSep	polysulphone + PP	50 kDa
PAN	TechSep	polyacrylonitrile	40 kDa
CA 600 PP	Dow	cellulose acetate + PP	20 kDa

[a] Polypropylene.

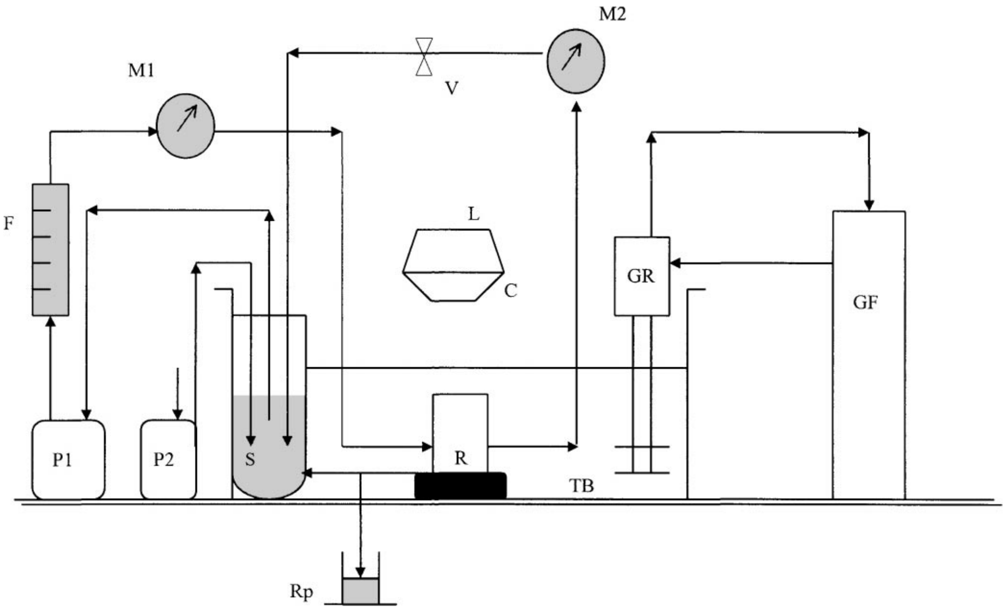

Fig. 1. Scheme of the set-up for the photoreactivity experiments carried out with immobilized TiO_2.(F, flowmeter; M1 and M2, pressure gauges; P1, peristaltic pump; P2, air pump or oxygen cylinder; S, recirculation tank; Rp, permeate reservoir; R, flat sheet membrane photoreactor; L, UV lamp; C, rays concentration cone; V, pressure control valve; GR, thermostatic group; TB, thermostatic water bath; GF, refrigerator group).

To this aim, the membranes were immersed in a Petri dish filled with distilled water and irradiated by a lamp placed at a distance of 10 cm emitting an average value of light intensity (365 nm) equal to 6.4 mW cm^{-2} impinging on the free liquid surface. A radiometer UVX-36 (Helios Italquartz, Milan) was used to measure the light intensity.

The stability of the membranes was evaluated by means of TOC and WPF determinations and SEM observations. TOC analyses of the solution where the membranes were immersed during the irradiation were carried out by using a Total Carbon Analyser 480 (Carlo–Erba Instrument) in order to verify the presence of released organic species. The determination of WPF, that means the flux of water permeated through the membrane, was carried out by placing the membranes, before and after irradiation, in a laboratory ultrafiltration plant (Separem, Biella) equipped with five cells in parallel and measuring the permeate flux. Distilled water at variable pressures of 1 and 2 bar and axial flow rates in the range 0.10–0.15 m^3/h were used at the temperature of 25°C. A SEM instrument (Philips 505) was used to observe the membrane surface morphology before and after the irradiation, while the TiO_2 layers deposited as described in the following on the membranes surface were observed by means of an optical transmission microscope.

For the photodegradation tests 4-NP was used as a probe substrate at an initial concentration of 10 or 40 mg/l in water. The photocatalyst was TiO_2 P25 from Degussa (ca. 80% anatase, 20% rutile) and its BET specific surface area was ca. 55 $m^2 g^{-1}$. 4-NP and other chemicals were used as received and were provided by Fluka. The 4-NP concentration was determined by using a Shimadzu UV/VIS 160A spectrophotometer operating at $\lambda = 315$ nm.

In Fig. 1 the set-up for the photoreactivity runs is reported. The membrane photoreactor consisted of a closed loop containing a recirculation reservoir and a membrane cell, made in the upper part of Pyrex glass, that was irradiated by UV–VIS light emitted by the lamp placed at a distance of 30 cm (light intensity ca. 8 mW/cm^2 using an aluminum cone to concentrate the emitted light); the permeate was collected in another reservoir. The useful membrane surface area was 19.63 cm^2 and during all the photodegradation tests the reactor was thermostated by a water bath at 30°C.

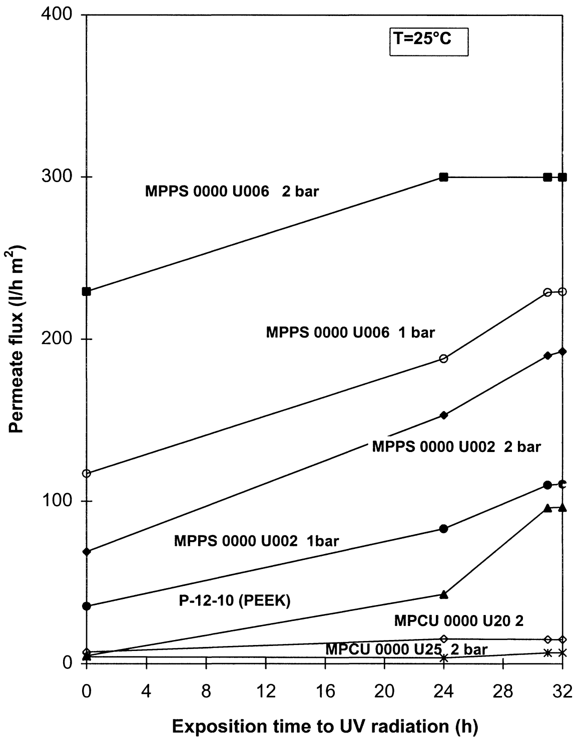

Fig. 2. Behaviour of the permeate flux through some membranes (1st group) as a function of the exposition time.

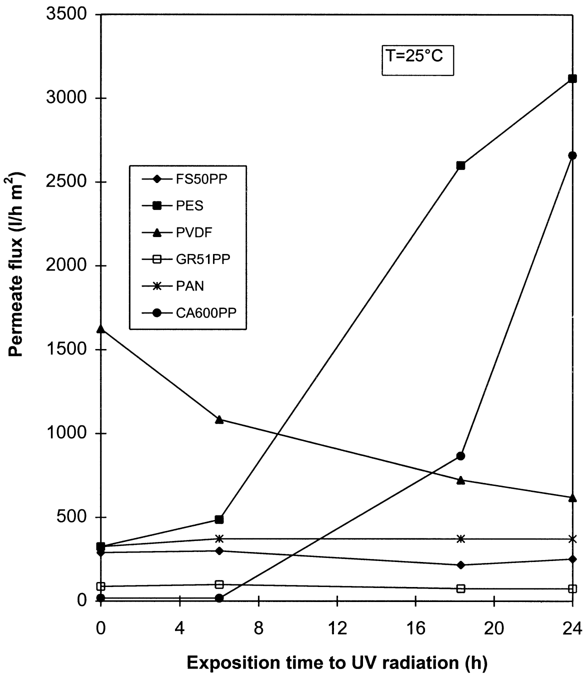

Fig. 3. Behaviour of the permeate flux through some membranes (2nd group) as a function of the exposition time ($P = 1$bar).

Physical immobilisation of TiO_2 on the membrane was realised by ultrafiltrating suspensions containing various amounts of TiO_2 in water. The UF cell was connected in the set-up of Fig. 1 and it was runned at a pressure of 1.8 bar until an almost complete permeation of water was reached. The amounts of TiO_2 deposited were in the range 0.76–6.12 mg TiO_2/cm^2 of membrane. In the other reactor configuration the confining of the TiO_2 slurry, in the set-up of Fig. 1, was obtained by means the membrane. Amounts of 0.2 and 0.5 g/l were used.

3. Results and discussion

The subject of membrane reactors in the photocatalytic field is quite new. For this reason a preliminary study was carried out to screen the type of polymeric material to use and the techniques for confining the photocatalyst.

Polymeric membranes could interact with UV–VIS light changing their characteristics. The behaviour of the WPF versus the exposition time to the radiation was chosen as a parameter that can be roughly related to the photostability of the membrane. In Figs. 2 and 3 the WPFs of the 11 membranes (devided in two groups) were determined before irradiation and after various irradiation times. It should be noticed that the damage can be considered as higher as larger the WPF values found after the illumination. The results indicate that the WPF increases rapidly with the exposition time for the less stable membranes. The most stable membranes were PAN (WPF at 1 bar 300 l/h m^2), FS 50 PP (WPF at 1 bar 195 l/h m^2) and GR51PP (WPF at 1 bar 88 l/h m^2). These results were also confirmed by TOC analyses (see Table 2) of the soaking water in which the membranes were immersed and irradiated for 6 h. The release of the organic carbon was not much significant for the three membranes above mentioned which appeared to be very stable if we consider the very small distance from the lamp.

In Fig. 4 two micrographs showing the FS 50 PP membrane before and after UV irradiation are reported. The surface presents a weft of interlaced sticks of cylindrical shape with the interstices covered

Table 2
Results of TOC measurements on soaking water of some membranes after 6 h of UV–VIS exposition

Membrane type	TOC (mg/l)
CA 600 PP	67
FS 50 PP	2.7
PES	4.2
GR 51 PP	5
PVDF	3.6
PAN	3.7

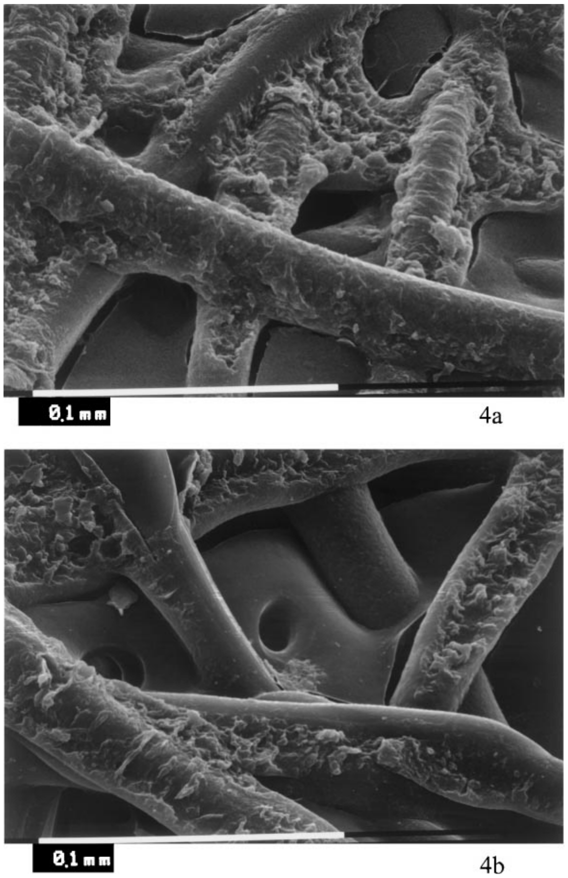

Fig. 4. Micrographs of the porous surface of the FS50PP membrane: (a) before UV irradiation; (b) after UV irradiation; magnification 6.25×10^2; 25 kV.

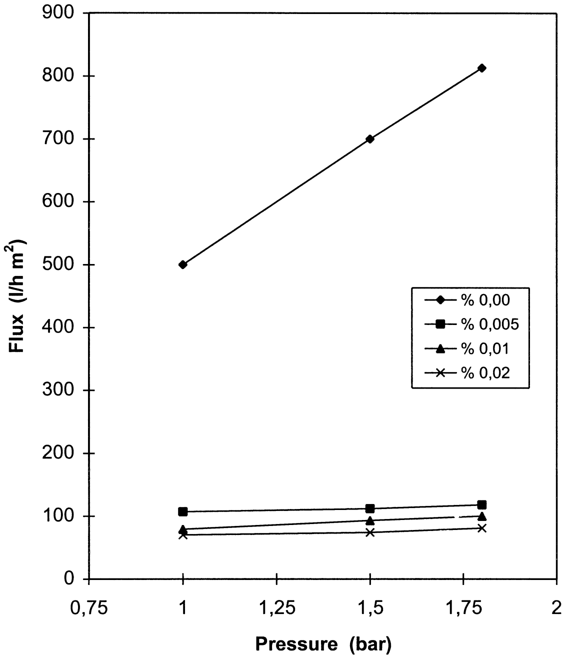

Fig. 5. Behaviour of the permeate flux through the PAN + TiO_2 membrane versus the pressure at various TiO_2% w/w in the initial solution.

by precipitated polymer. No significant variations were observed while similar micrographs of the PAN membrane revealed some damage after irradiation. Despite this and some slight degradation (see Table 2), this latter membrane was chosen to carry out the photoreactivity experiments in order to investigate the performance of the photocatalytic reactor. Indeed PAN membrane showed the highest permeate flux, which was constant in the time. Furthermore, it was expected a lower degradation during the photoreactivity runs on respect to the photostability tests, due to the formation of a catalyst layer on the membrane and to the bigger distance to which the lamp was placed.

The photocatalyst was immobilised on the flat sheet PAN membrane by ultrafiltrating TiO_2 suspensions in water (600 ml) at 0.05, 0.1, 0.2 and 0.3 g/l using the lab plant of Fig. 1. The amounts of immobilised TiO_2 were 0.76, 2.04, 4.08 and 6.12 mg/cm^2 of membrane. By measuring the turbidity of the recirculating suspension in the time the maximum amount of gelled TiO_2 was found by using a pressure of 1.8 bar. The water permeate flux (Fig. 5) through the membrane with immobilised TiO_2 was less than five times that observed with the bare membrane; the WPF showed a linear trend which increased very slightly with the pressure in the range 1–1.8 bar and decreased slightly by increasing the amount of TiO_2. This behaviour is characteristic of a cake layer formation on the membrane surface. The cake was observed by using an

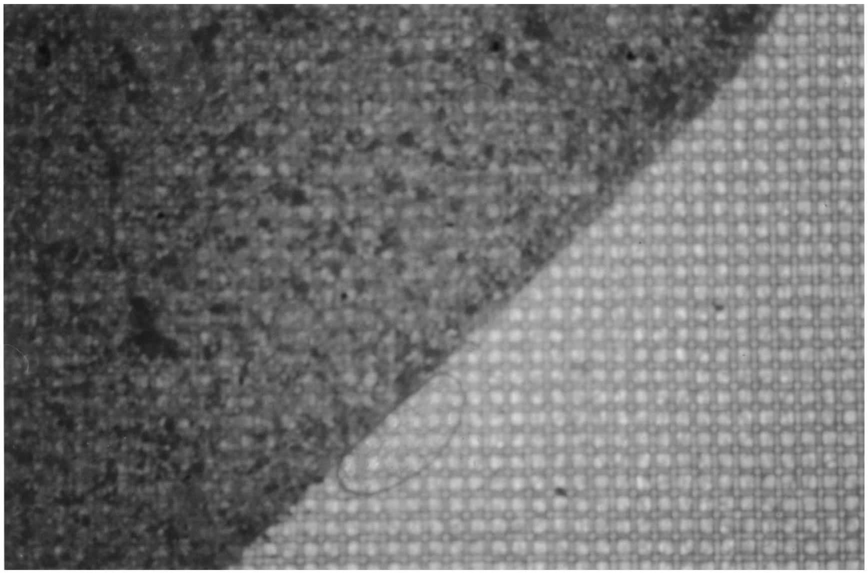

Fig. 6. Optical microscope observation of the deposited layer with 4.08 mg/cm^2 on the PAN membrane; magnification 25×.

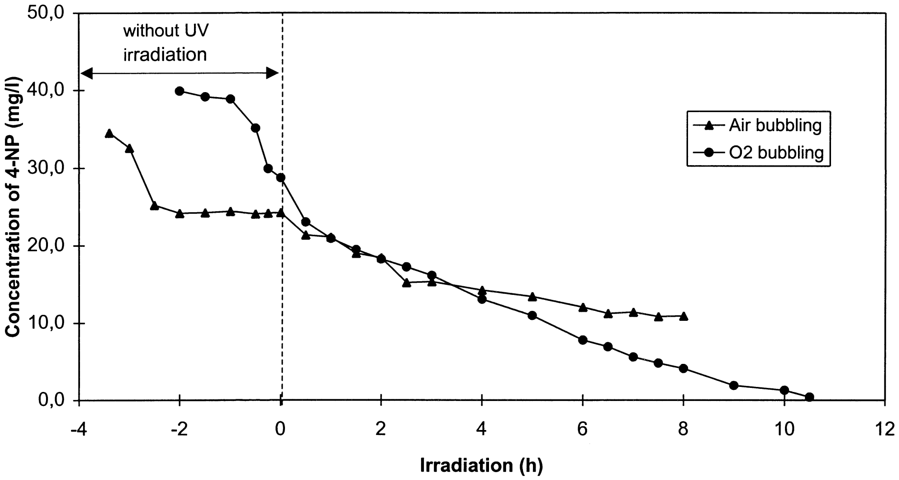

Fig. 7. Concentration of 4-NP versus irradiation time: comparison by using air or oxygen bubbling in a batch reactor (TiO_2 amount = 1 g/l; Temperature = 30°C).

optical transmission microscope confirming a gel-like structure. It should be mentioned that a cake density of 0.76 mg/cm^2 was insufficient to cover completely the membrane surface showing, in addition, a poor mechanical resistance. On the contrary, a density of 6.12 mg/cm^2 was too high and did not form a uniform surface as it was observed by peaks of accumulated particles. Fig. 6 shows a selected optical micrograph showing a PAN membrane onto which a layer of deposited TiO_2 (4.08 mg/cm^2) covers uniformly all the surface.

As the photoreactivity results are concerned, it can be noticed a better performance using suspended catalyst rather than deposited catalyst. In the first reactor 80% w/w 4-NP degradation was obtained in ca. 5 h of operation using 0.5 g/l of suspended TiO_2 while in

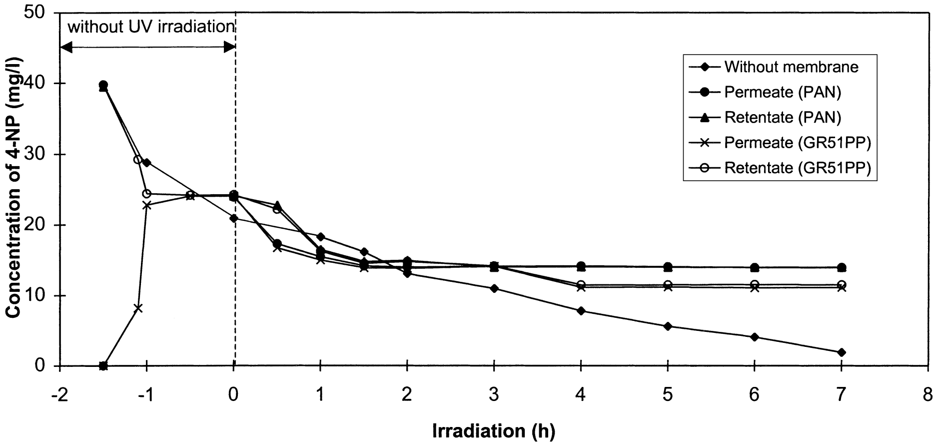

Fig. 8. Concentration of 4-NP versus irradiation time: comparison by using two reactors with or without membranes (TiO_2 amount = 1 g/l, oxygen bubbling, Temperature = 30°C, Pressure = 1.6 bar).

the second one the degradation, independent on the amount of TiO_2 on the membrane, was ca. 51% w/w in the same time.

Both the reaction rate and the total amount of 4-NP photodegraded increased by using pure oxygen as bubbling gas instead of air and some selected results are shown in Fig. 7. Consequently, in order to test the membrane reactor performance, two of the polymeric membranes, i.e. PAN and GR51PP, showing a good stability under UV irradiation, were tested by using oxygen as bubbling gas and the suspended photocatalyst. A significant different transmembrane flux was determined for them: 540 and 150–190 l/h m^2, for PAN and GR51PP, respectively. Fig. 8 shows that the concentration of 4-NP versus irradiation time follows the same trend for both membranes. Moreover, it must be emphasised that the 4-NP concentrations in the permeate and in the retentate were found the same, indicating that the concentration of the pollutant outside and inside the photoreacting ambient was not different. Consequently an optimisation of the experimental conditions in the reacting ambient would be reflected in the permeate. This indicates a big advantage of this system, in addition to the possibility to retain the catalyst confined, avoiding any final filtration as happens in traditional reactors. Furthermore, the degraded amount of 4-NP was slightly higher for less permeable membranes, due to longer contact time of 4-NP/catalyst/UV light and this result is consistent with the behaviour observed in enzymatic membrane reactors [15]. Finally, as shown in Fig. 8 a higher performance of the photoreactor in the absence of membrane was observed for longer times.

Work is in progress to understand this behaviour and to improve the performance of the membrane photoreactor in order to take advantage of the benefits of both the photocatalytic and membrane technology for pollutants degradation.

4. Conclusions

Polymeric membranes can be used for photocatalytic reactions, but it is necessary to carry out preliminary tests to choose suitable polymers stable under UV–VIS illumination.

Commercial membranes made of fluoride + PP (FS 50 PP-Dow), polysulphone + PP (GR 51 PP-TechSep) and polyacrylonitrile (PAN-TechSep) resulted quite stable to UV light.

Immobilisation of TiO_2 on the membranes by ultrafiltration of its suspensions in water was a very simple technique. The optimal layer density was found to be slightly higher than 2.04 mg TiO_2/cm^2: indeed, for lower values, the cake layer showed a poor mechanical stability while the catalyst detached very easily from the membrane and presented peaks of accumulated particles for higher values. Degradation of 4-NP in this membrane reactor was almost independent on the amount of TiO_2 in the range 0.76–4.08 mg/cm^2

and presented 51% reduction of the initial concentration versus 80% of the suspended catalyst reactor. When PAN and GR51PP membranes were used in the presence of suspended catalyst and pure oxygen, the degraded percentage of 4-NP was comparable to that of the suspended catalyst reactor without membrane. Work is in progress in order to better characterise the performance of the reactor and its kinetic behaviour.

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