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Photocatalytic membrane reactors for degradation of organic pollutants in water

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Abstract

Different flowsheets (batch and continuous) of photocatalytic membrane reactors, to be used for degradation of organic pollutants present in water, together to some experimental results, are reported. 4-Nitrophenol (4NP) was used as a probe polluting agent and titanium dioxide in suspension was the catalyst. The photodegradation tests in the batch system were carried out without membrane changing the characteristic variables of the process (light intensity, TiO_2 concentration, 4NP concentration, O_2 concentration, pH) to find their optimum values. The batch system consisted of a water jacket thermostatted and stirred beaker irradiated from above with a UV–Vis lamp (light intensity on the surface of the liquid 4.4 mW/cm^2). An empirical predictive equation was obtained describing the reaction rate as a function of the reported variables.

Photodegradation tests in the membrane reactors (total volume from 400 to 700 ml) were carried out coupling the batch to a re-circulation cell containing various types of flat sheet membranes which were able to retain the suspended catalyst and partially selective to the pollutant. The membranes were: NTR7410 and NTR7450 (Nitto Denko); N30F and NF-PES-010 (Hoechst); MPCB0000R98 (SEPAREM). The measured permeate flux was in the range 5–30 l/h m^2 at 4 bar and all membranes showed both a rejection and a capacity to adsorb the pollutant with a transitory phase varying from 80 to 400 min at 4 bar. This behaviour could be a benefit for the process because oscillations in the pollutant concentration are not transmitted in the permeate. Three factors: rejection, photocatalytic degradation and adsorption were able to maintain the 4NP concentration in the permeate at very low values. For the continuous system, the lowest 4NP concentration in the permeate was 6–7% (w/w) of the initial 4NP concentration (40 mg/l) after a transient period of 300 min. Further improvements of this process are under investigation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2 photocatalysis; Membrane photoreactor; Water purification; 4-Nitrophenol photodegradation

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1. Introduction

Today water pollution, caused by hazardous organic chemicals used in industry and agriculture, is a very serious problem; moreover, environmental laws are very severe and they are becoming more and more restrictive in the next years.

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Classical methods (e.g. adsorption on active carbon, chemical oxidation, aerobic biological treatments [1,2]) to clean-up waters, before sending them to rivers or in municipal supplies as drinking water, usually transfer pollutants from a phase to another.

New methods, such as photocatalytic reactions, allow in many cases a complete degradation of organic pollutants in very small and not noxious species, without using chemicals, avoiding sludge production and its disposal. This process is based on the electronic excitation of a molecule or solid caused by light absorption (usually UV light) that drastically alters its ability to lose or gain electrons. The electronic excited state is both a better oxidising and reducing agent than its ground-state counterpart, so the electron transfer process involving the excited state and the conducting medium (e.g. water) can generate highly reactive species like hydroxide $^{\bullet}OH$ and super-oxide $O_2^{\bullet -}$ radicals that promote decomposition of pollutants to harmless by-products [3].

The most suitable photocatalysts appeared to be some polycrystalline semiconductor solids such as TiO_2, ZnO, $SrTiO_3$, RuO_2 and CdS [4,5]. In particular, TiO_2 in the crystalline form of anatase has been widely used due to its low cost, its photostability and to the fact that it is not a noxious chemical. The photocatalyst is usually employed in suspension, so its recovery and recycle is a major problem. To this aim, coupling the photocatalytic and membrane techniques should result a very powerful process with a great innovation in water polishing. In fact technology of membrane separation processes, thanks to selective property of membranes, has already shown to be competitive with respect to other separation processes for what concerns energy costs, material recovery, reduction of the environmental impact and achievement of integrated processes with selective removal of some components [6–8].

Among the advantages of a membrane photoreactor there is the possibility of a continuous process with simultaneous product(s) separation from the reaction environment. The membrane principally allows two functions: confining of the photocatalyst and selective separation at molecular level maintaining the pollutants in the reaction environment.

Nowadays a very few plants utilise the cleaning up photocatalytic technique whereas photocatalytic membrane applications are rare yet [9,10]. Preliminary, very recent promising results were reported on a photocatalytic membrane process with TiO_2 physically immobilised on the membrane or retained in suspension by means of the membrane [11].

In this paper, some experimental results on a batch photocatalytic reactor without membrane to find the influence of the characteristic variables of the process and a kinetic equation for degradation rate using a semi-empirical approach are reported. Moreover, some results on membranes characterisation, e.g. their ability to retain the pollutant, followed by their use in photodegradation tests in recycle and continuous membrane reactors, using 4-nitrophenol (4NP) as a probe polluting molecule, are described.

2. Experimental

In the photodegradation tests without membrane the plant flowsheet shown in Fig. 1 was used. It consisted of a beaker where the catalyst was maintained in suspension by means of a magnetic bar that made uniform concentration of the pollutant to be degraded and also the temperature in the bulk of the solution. The beaker was thermostatted by means of a water jacket at the operative temperature of 30 ± 2°C. The external beaker surface was covered with aluminium for foods whose reflecting surface was directed in the inner side. The interposition of an aluminium cone

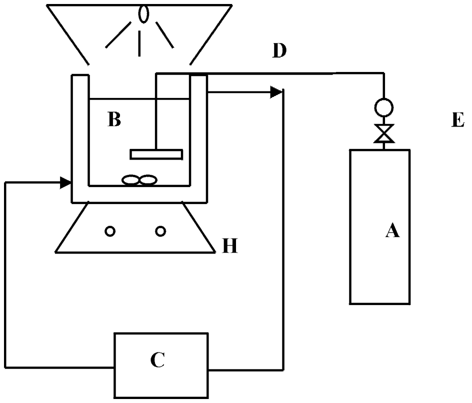

Fig. 1. Scheme of the photoreactor utilised in the tests with catalyst in suspension (A: oxygen cylinder; B: jacketed beaker stirred magnetically; C: thermostat; D: UV lamp; E: manometer; H: magnetic stirrer).

between the lamp and the solution was very important because it conveyed on the beaker the part of radiation which otherwise would have been missed due to the non-coincidence of the rectangular lamp surface (with a side longer than the beaker diameter) with that one of the beaker (circular). The diameter of the beaker was 7.5 cm and the volume of solution was 400 ml. Oxygen was bubbled into the solution by means of two capillary macroporous polypropylene membranes ($\Phi_{\mathrm{int.}} =$ 0.5 cm, length = 3 cm, average pore diameter = 0.2 μm), at a pressure of 0.3 bar, which was necessary to achieve saturation and promote photodegradation reaction. In fact, they were able to maximise exchange surface in order to achieve an optimal oxygen dissolution into solution by means of microbubbles formation. A medium pressure mercury lamp (500 W), made by Helios Italquarz (Milan) emitting radiation in the 300–400 nm range was used to irradiate the batch reactor where the suspension was contained. The lamp was placed upper the reactor and the distance between its bulb and the surface of the liquid was 17 cm; the measured light intensity (radiometer UVX-36, by Helios Italquartz, Milan) at this distance was 4.4 mW/cm^2.

The catalyst used was TiO_2 Degussa P25 (20% rutile, 80% anatase, surface area about 50 m^2/g, band-gap of 3.0 eV, average wet particles diameter 8 μm). 4NP (Carlo Erba, 99.9%) was used as the polluting agent; the pH was adjusted to a value of 3 by using H_2SO_4 after mixing catalyst and pollutant. The determination of 4NP concentration was obtained by spectrophotometric measurements (UV–Vis 160A by Shimadzu) at 315 nm which corresponds to the maximum absorbance wavelength.

Concerning membrane photoreactors various flowsheet configurations were tested; the most interesting one was the continuous system presented in Fig. 2, where the catalyst is suspended in the aqueous solution and the irradiation is done on the recirculation reservoir. The other flowsheets studied were: irradiation of the membrane cell with deposited photocatalyst [11]; irradiation of the membrane cell with suspended photocatalyst [11]; irradiation of recirculation reservoir containing the suspended photocatalyst in a permeate recycle mode (batch membrane system). Photodegradation tests in the continuous and batch membrane reactors were carried out by coupling the irradiated batch to a pressurized cell with a volume of 96 cm^3, containing various types of nanofiltration membranes. They were: NTR7410 (Nitto Denko, Tokyo; rejection 10% with 0.2% NaCl at 4.9 bar, 25°C, pH 6.5) composite synthetic polymer; NTR7450 (Nitto Denko, Tokyo; rejection 50% with 0.2% NaCl at 4.9 bar, 25°C, pH 6.5) composite synthetic polymer; N30F (Hoechst, Celgard, Germany; rejection 25–35% with 0.2% NaCl and 85–95% with 0.5% Na_2SO_4, water flux of 40–70 l/h m^2 at 40 bar, 20°C) modified polysulphone able to operate in all the pH range up to an operating temperature of 80–85°C; NF-PES-010 (Hoechst, Celgard, Germany; rejection 10–20% with 0.5% NaCl, 40–70% with 0.5% Na_2SO_4, water flux of 200–400 l/h m^2 at 40 bar, 20°C) polyethersulphone; MPCB0000R98 (Separem, Italy) polyamide of reverse osmosis type (NaCl rejection 98%). The TiO_2 suspension was continuously recirculated through the membrane cell (useful membrane surface area 19 cm^2) and the fresh solution was fed to the batch.

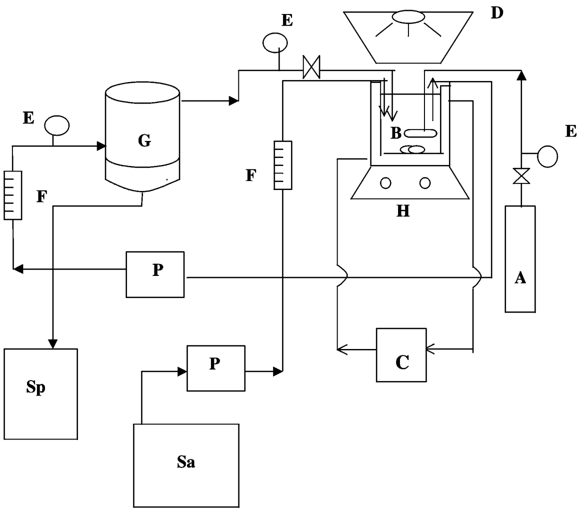

Fig. 2. Scheme of a continuous membrane photoreactor system with suspended catalyst (A: oxygen reservoir; B: recirculation reservoir (reactor); C: thermostatting water; D: UV lamp; E: manometer; F: flowmeter; G: membrane cell; H: magnetic stirrer; P: peristaltic pump; Sa: feed reservoir; Sp: permeate reservoir).

3. Results and discussion

Before using the membrane photoreactor, some tests were performed to find the optimum values of operating parameters which influence reaction rate (e.g. oxygen, catalyst and 4NP concentrations, pH, irradiation intensity (*I*)). As far as the diffusive gas–liquid resistance for oxygen adsorption in solution is concerned, it could be neglected because a great exchange surface area was available in the experimental conditions investigated, i.e. using polypropylene membranes that work as diffusers to create microbubbles. Furthermore, the solution was well agitated, oxygen was blown in pressure and liquid–solid mass transfer resistance could also be neglected because micrometer powdered catalyst particles were used [12]. By taking into account the above considerations, the only controlling step for the process derived from the reaction occurring on the particles surface.

Temperature and pH were not considered because they were fixed at 30°C and 3, respectively. Different curves showing 4NP concentration versus time were obtained from photodegradation tests maintaining constant to the other parameters at their optimum values. Reactions were run for about 1 h, till to obtain 70–90% degradation, and the plotted data were well correlated. After 1 h, other factors, such as competition between intermediates, can change the time course of the reaction.

By knowing the kinetic constant dependence from each single variable, the product of those functions was chosen to determine the global kinetic constant as a function of the four variables (oxygen, catalyst and 4NP concentrations and irradiation intensity). A model with five parameters (constants) was obtained. Minimising the square deviation (distance between experimental points and curve given by the model) with Newton–Raphson method, the global kinetic expression for the reaction rate ($-r_{4NP}$), in the well-mixed batch reactor, which correlates the four considered variables, was obtained [13]:

$$\begin{aligned}-r_{4NP} &= -\frac{dC_{4NP}}{dt}\\ &= 1.54\frac{[TiO_2][O_2]I}{(9.138+[TiO_2])(0.646+[O_2])}\\ &\quad\times\left[1.36\times10^{-3}+\frac{14.842}{[4NP]_o^2}\right]C_{4NP}\end{aligned}$$

From the upper equation it can be seen that dependence of kinetic constant (all the terms before C_{4NP}) by the product of four variables significantly influences the reaction rate, e.g. if a couple of variables are simultaneously changed, significant variation of reaction rate is obtained. This equation is useful to understand the experimental data and can be used to model the membrane photoreactor.

Membranes to be used in the photoreactors were previously characterised: (i) at various pressures measuring the water permeate flux (wpf) by using distilled water; (ii) rejection tests, using 4NP; (iii) comparison of 4NP concentration in the permeate for the various membranes tested; (iv) adsorption behaviour. In Fig. 3, the comparison among wpf at steady state, at various transmembrane pressures, for the five tested membranes is reported; all of them have a wpf in the range 5–38 l/h m^2 at 4 bar. The wpf values during the

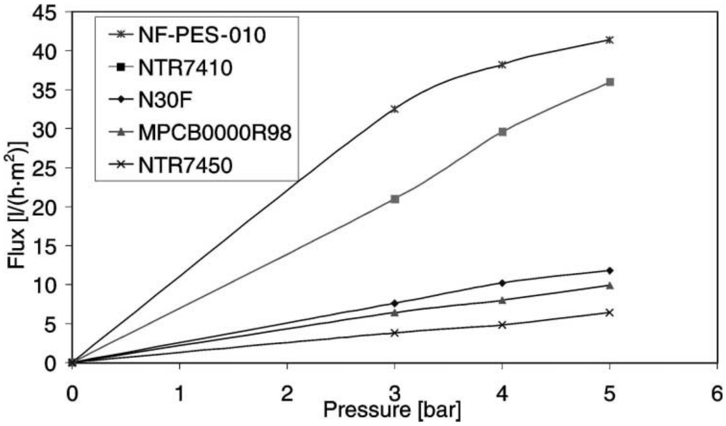

Fig. 3. Comparison between wpf varying the pressure for different membranes ($T = 30°C$, tangential flow rate = 500 ml/min).

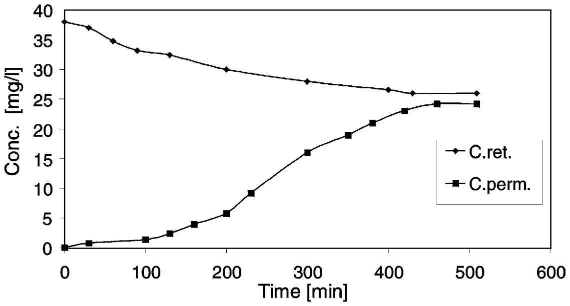

Fig. 4. 4NP concentration versus time using an N30F membrane ($T = 30°C$, $P = 4$ bar, steady-state flux = 10.2-l/h m^2).

run-time were quite constant for all the membranes showing no compaction phenomena at these pressures. However, the curves in Fig. 3 are not straight lines by increasing the pressure; indeed, a more significant number of pores become permeable and, consequently, wpf values increased; but, for high values of pressure all the pores flooded and the wpf trend versus the pressure become flat. No high variations of the flows were observed, with respect to values reported in Fig. 3, when a 4NP solution was used; the slightly lower flux observed was attributed to the resistance opposed by 4NP adsorbed in/on the membrane.

In rejection tests, carried out by using 40 mg/l 4NP solutions and a pressure of 4 bar, time needed to reach a steady-state condition, for the concentration of permeate and retentate, was variable depending on the membrane used (Fig. 4). This insight can be related to the fact that membranes consisted of different kind of polymers with various pore sizes and distribution, different thickness and consequently various permeate flow. Rejection values, at steady-state conditions, were very low for all of the membranes (ca. 10–15%) but, in the transient state, they were higher. Values higher than 30% were obtained for times below 100 min and, for instance, 99.9% rejection could be observed for N30F membrane (see Fig. 4). The different increase versus time of 4NP concentration in the permeate are shown in Fig. 5 for all the membrane tested. This behaviour can be attributed also to different adsorption capability in addition to the previous parameters above-mentioned. Indeed, the decrease of 4NP concentration in the retentate, to reach a constant value, can be explained by considering the possibility of some extend of adsorption on the membranes or on the inox stainless tubes used for the plant connections. Previous tests carried out by circulating the 4NP for 4 h, in the absence of membranes, indicated no decrease of the 4NP concentration. From Fig. 5 it can be observed that, although the steady-state flux through the N30F membrane is higher than that through NTR7450 one (the double), the rate of 4NP concentration increase in the permeate is lower; the same behaviour can be observed for the NF-PES-010 and NTR7410 membranes. These results were confirmed by adsorption tests by immersing each membrane for 48 h in a 200 ml solution of 40 mg/l 4NP. The adsorption was very slow and it occurred only by diffusion and not also by convection as it occurs when the flow rate in membrane pores is obtained under pressure. To verify that equilibrium was reached the 4NP

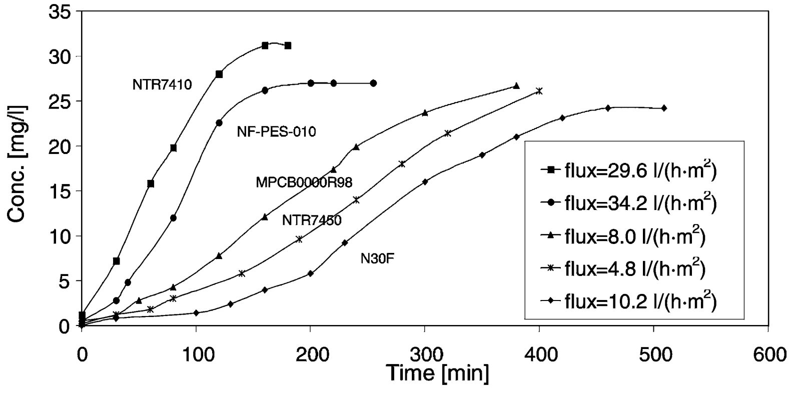

Fig. 5. 4NP concentration in the permeate through different membranes versus time ($T = 30°C$, $P = 4$ bar).

Table 1
Tests of 4NP adsorption on various membranes

Membrane	Initial 4NP amount in the bath (mg)	Final 4NP amount in the bath (mg)	Amount of 4NP adsorbed by membrane (mg)	Percentage of 4NP adsorbed by membrane (%)
NTR7410	8.0	6.4	1.6	20.0
NF-PES-010	8.0	5.5	2.5	31.3
MPCB0000R98	8.0	6.0	2.0	25.0
NTR7450	8.0	6.2	1.8	22.5
N30F	8.0	4.8	3.2	40.0

concentration in the bath was measured after 24 and 48 h. No difference was found between the values at these two times. In Table 1 the results are reported; it shows the following order of decreasing adsorption capability: N30F > NF-PES-010 > MPCB0000R98 > NTR7450 > NTR7410. The adsorbing behaviour of the membrane has been used in the following to develop a very efficient membrane photoreactor.

For the tests on 4NP photodegradation, two different plant flowsheets with the catalyst in suspension were compared. In the first one, the permeate was continuously recycled (batch membrane system), while in the second one (Fig. 2) a 4NP solution was continuously fed to the irradiated beaker and the permeate continuously removed (open system). It must be evidenced that the suspended catalyst permits a more efficient use of its porous surface because of light scattering inside the solution; indeed, when the catalyst is immobilized, the irradiated area is also the real geometrical superficial area that means only a part of the total available catalytic surface area is utilized.

A more permeable (NF-PES-010) and a less permeable (N30F) membrane were tested. Permeate flux through membranes, in the presence of suspended catalyst, was a little lower than that in the absence of the catalyst (only water) and the deposition of the catalyst on the membrane was avoided by using a cell geometry that guaranteed turbulence and presence of vortexes in the cell.

In Fig. 6, the trends of 4NP concentration in the retentate and permeate versus time for recirculating and continuous system configurations are reported. The maximum 4NP concentration in the permeate is 4 mg/l (10% with respect to the initial one) in the first case, and 7 mg/l (17% with respect to the initial one), in the second case. In both cases, the curves of permeate concentration (Fig. 6) are of bell shape type owing to three factors: rejection, photocatalytic degradation and adsorption that were able to maintain the 4NP concentration in the permeate at very low values. From the observations of Fig. 6, it can be noticed that although 4NP concentration in the retentate for the continuous configuration decreased less quickly than for the recycle one, the continuous system seems more promising for its possible potential industrial application. The lowest 4NP concentration, in fact, in the permeate was 6–7% (w/w) of the initial 4NP (40 mg/l) for the continuous system after a transient period of 5 h. In this last system, the optimum choice of the ratio between the irradiated volume and the total volume (V_i/V_t) was important. When total suspension volume was increased from 400 to 700 ml (Fig. 7), the ratio V_i/V_t increased owing to a constant recycle volume and, consequently, the 4NP abatement was higher due to the increased percentage of irradiated with respect to recycled suspension.

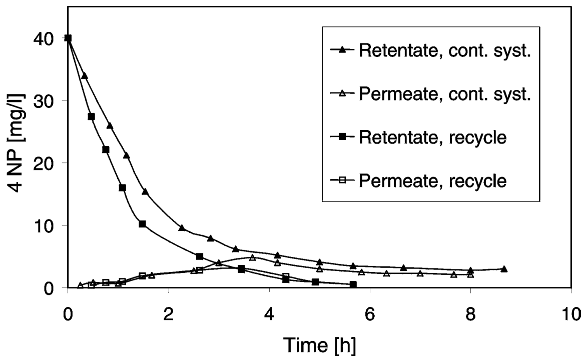

Fig. 6. 4NP concentration in the retentate and permeate versus time for continuous and recycle system configurations ($T = 30°\text{C}$, $P = 3.5\,\text{bar}$, $[\text{TiO}_2] = 1\,\text{g/l}$, $[\text{O}_2] = 22\,\text{ppm}$, $I = 3.6\,\text{mW/cm}^2$, tangential flowrate $= 500\,\text{ml/min}$, permeate flux $= 10\,\text{l/h m}^2$).

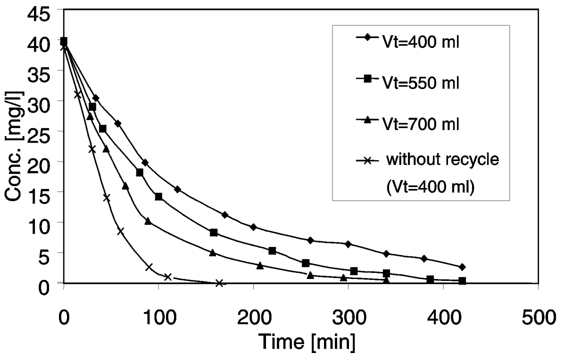

Fig. 7. 4NP concentration in the retentate versus time varying the total volume of the recycle system in comparison to the system without recycle. ($T = 30°C$, $P = 3.5$ bar, $[TiO_2] = 1$ g/l, $[O_2] = 22$ ppm, $I = 3.6$ mW/cm^2, tangential flowrate = 500 ml/min).

4. Conclusions

The configuration of continuous membrane photoreactor that combines both the advantages of classical photoreactors (catalyst in suspension) and membrane processes (separation at molecular level) seems very interesting. Photocatalytic degradation was carried out in reasonable times due to the high available irradiated surface area of the suspended particles in the batch.

The empirical predictive equation, describing the reaction rate, as a function of the main variables, allowed to draw a mathematical model for the membrane photoreactors studied. The selected membranes showed both the capability to retain the catalyst and to reject partially organic species controlling the residence time in the reacting system. Three factors: rejection, photocatalytic degradation and adsorption were able to maintain the steady-state 4NP concentration in the permeate at very low values (<2.5 mg/l). This adsorption phenomenon (transient phase varying from 80 to 400 min at 4 bar) is particularly important when oscillating concentrations of pollutant are fed to the membrane photoreactor resulting in a negligible variation of concentration in the permeate.

These results suggest the use of the hybrid continuous membrane photoreactor as a new scheme for some industrial applications of the photocatalytic technique. Further improvements of this process are under study.

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