Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 118 (2006) 205–213
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO_2 and a nanofiltration membrane reactor

R. Molinari [a,*], F. Pirillo [a], V. Loddo [b], L. Palmisano [b]

[a] *Dipartimento di Ingegneria Chimica e dei Materiali, Università della Calabria, Via Pietro Bucci, CUBO 45 A, 87030 Rende, Cosenza, Italy*
[b] *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

Available online 14 July 2006

Abstract

A study of the photodegradation of different pharmaceuticals [furosemide, ranitidine (hydrochloride), ofloxacine, phenazone, naproxen, carbamazepine and clofibric acid] in aqueous medium at various pHs by using a batch photoreactor and a photocatalytic membrane reactor working in recirculation regime was carried out. Polycrystalline TiO_2 was used as the photocatalyst, and different membranes (NTR 7410, PAN GKSS HV3/T, N 30 F, NF PES 10) were tested. A different adsorption of the substrates onto the catalyst surface was observed owing to the hydrophilic/hydrophobic character of the catalyst, depending on the pH. The photodegradation of the seven molecules in the batch reactor was successfully carried out and the behaviour was in accordance with pseudo-first order kinetics. Furosemide and ranitidine were selected to carry out the study of rejection and photodegradation in the hybrid membrane system. The permeate flux of the treated water was in the 31.5–60.0 L/(h m^2) range for NTR 7410 membrane, whereas rejection values in the range 10–60% for furosemide and 5–30% for ranitidine in the dark (without photoreaction) were found. The degradation in the hybrid membrane photoreactor showed that the photocatalyst was retained by the membrane in the reaction ambient, while the membrane rejection towards the pollutants was not very satisfactory. A net decrease of the rejection down to 0 was observed in the contemporary presence of light, photocatalyst and oxygen.
© 2006 Elsevier B.V. All rights reserved.

Keywords: TiO_2 photocatalysis; Pharmaceuticals photodegradation; Nanofiltration membrane reactor; Water purification

1. Introduction

A large amount of drugs is consumed in each part of the world. For example it is estimated that in Germany in 1995, more than 100 t of drugs [1] were prescribed by doctors to their patients. Recent estimations indicate that in Europe, which holds about 26% of the international pharmaceutical market, more than 2000 different pharmaceutical products are used [1] while annual consumption of antibiotic type substances is similar in quantity to that of some pesticides [2]. The drugs assumed and not metabolized by the organism, are excreted through urine and faeces [3]. The present tendency to synthesize drugs resistant to common biotransformation mechanisms to protract their persistence in organisms, results in obtaining very stable molecules. This means resistance to chemical and biological degradation with a consequent increase of these products in the environment and especially in surface waters. Traditional treatment processes may prove ineffective for the removal of these substances [1], thus pharmaceuticals and hormones such as antimicrobial agents and steroids [4] and antibiotics [2] have been detected in concentrations of some μg/L in the waters deriving from municipal treatment plants in Germany. Great part of the antibiotics reported in Ref. [2] have also been discovered in Brazil in the effluents of treatment plants as well as in various rivers in concentrations from 0.1 to 1 μg/L [4]. The presence of some pharmaceutical substances even in natural waters in concentrations of about 1 μg/L has been allowed [5–7]. Zuccato et al. [8] carried out an extensive investigation on the presence of drugs in drinking and surface waters also in the Lombardy region of Italy. Transformation of antibiotics [7,9–11] has been widely studied. At present only for few pharmaceutical substances (aspirin, caffeine, clofibrate, ciclofosphamide, oestrogens, ibuprofen, naproxen) literature

* Corresponding author. Tel.: +39 0984 496 699; fax: +39 0984 496 655.
E-mail addresses: r.molinari@unical.it (R. Molinari), palmisano@dicpm.unipa.it (L. Palmisano).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.091

information on the biodegradability are available [7,12–15]. Moreover, most studies refer to the toxicity for living organisms of antibiotic type substances [13–19] showing effects in the endocrine system of fish [20] even at levels of some ng/L. The results so far reported suggest considering the presence of pharmaceutical substances in the environment a risk for human health and for living species, even at very low concentration levels [21]. For example, clofibric acid, used as a regulator of lipids in the blood, shows an ‘‘estimated persistence in the environment of 21 years and is still detected in lakes and rivers after it was withdrawn from the market’’ [22].

Various researches [23–26] report that in the natural aquatic environment direct or indirect type of photodegradation processes can occur. Indirect type processes are due to the interaction of sunlight with photosensible species such as nitrates, humic acids and metal ions capable of producing highly reactive chemical species, which activates the degradation of the pollutants.

In this context it is useful to apply various technologies to purify aqueous civil and industrial effluents containing pharmaceutical substances. Among them, advanced oxidation processes (AOP) have been the subject of major interest in recent years. These processes are characterized by the formation of OH radicals, which ensure high reactivity and low selectivity, as they are required for the degradation of different pollutants. Heterogeneous photocatalysis represents an example of AOP capable of achieving a complete oxidation of organic and inorganic species, including also pharmaceutical substances. It takes advantage of some semiconductor solids, which can be used as photocatalysts suspended in the water effluent to be treated, or immobilised on various types of supports. Among the various solids, polycrystalline anatase TiO_2 is largely used because of its low cost and its (photo)stability [27,28].

Unfortunately, from an economic point of view the treatment of polluted waters with the photocatalytic process can be competitive, with respect to conventional processes, only under particularly favourable circumstances.

The use of membrane technology processes, instead, has already been demonstrated to be competitive with respect to the other separation processes, owing to low energy cost and environment impact [29–31]. To couple photocatalytic and membrane processes introduces a synergy for both technologies: in particular the presence of the membrane ensures the confining of the photocatalyst and/or the separation at molecular level, maintaining the pollutant species in the reacting ambient. Satisfactory results were recently obtained by using photocatalytic membrane reactors with immobilised TiO_2 and the advantage of the separation at molecular scale was demonstrated owing to the presence of the membrane [32–34]. In addition, the membrane photoreactors allow operation in continuous systems without the need to separate the catalyst from the reaction ambient, the system to be easily scaled up and high surface/volume ratios to be obtained.

Seven pharmaceuticals have been studied in this work. They can be present in water at different concentrations depending on their use and on their solubility: furosemide, ranitidine (hydrochloride), ofloxacine, phenazone and clofibric acid have high solubility, while carbamazepine and naproxen have low solubility. They are used for health benefit purposes, but they can also exert deleterious effects at certain concentrations. Indeed, furosemide has a diuretic effect and it has been found not only to have a toxic effect at certain concentrations, but also it is suspected to be carcinogenic. Ranitidine is used for ulcer disease because it is an antagonist of H_2 gastric receptors and it reduces the secretion of chloridric acid. Ofloxacine is an antibiotic inhibitor of girase (a DNA enzyme): both these pharmaceuticals at certain concentrations are toxic for humans. Clofibric acid is an ipolidemic agent used as anticolesteric; its pharmacological principle can produce a toxic effect on liver inducing biliary calculi. Carbamazepine is an antiepileptic agent used as sedative; by a toxicological point of view it can produce serious toxic effects on liver and on the emopoietic system. Phenazone is an antiphlogistic agent, but it could give rise even to death when it is overdosed. Naproxen is an antiphlogistic agent that can induce toxic effects on the lung system.

The main aim of this study is to prove the feasibility of photodegradation of the above drugs by using polycrystalline TiO_2 and different types of commercial nanofiltration (NF) membranes operating at different conditions (pH, initial concentration of pollutant, pressure, permeate flowrate) in a membrane photoreactor working in total recirculation regime.

2. Experimental

Solutions of different commercial pharmaceuticals [furosemide, ranitidine (hydrochloride), ofloxacine, phenazone, naproxen, carbamazepine and clofibric acid] provided from Sigma–Aldrich, dissolved in ultrapure water (ELIX 5, Millipore) were used. Their structures together with the raw formula and molar weight are reported in Fig. 1.

TiO_2 P25 Degussa (BET specific surface area: ca. 50 $m^2\ g^{-1}$; size of the primary particles: 30–50 nm) was used as the photocatalyst for all of the photoreactivity experiments. Commercial membranes, mainly of the nanofiltration type (Table 1), were tested in rejection and photocatalytic degradation experiments. The membranes after each run were regenerated by immersing them for 15 h in 200 mL of an aqueous solution containing 0.5% (w/w) of an enzymatic detergent (Ultrasil 50 by Henkel).

The Pyrex annular photoreactor had a volume of 500 mL. In order to sample and to bubble the gas, it was provided of ports in the upper section. A 125 W medium pressure Hg lamp (Helios Italquartz, Milan), equipped with a Pyrex cylindrical cooling jacket, was axially positioned inside the reactor, which was filled with the aqueous dispersion containing the pollutant. The photocatalyst was maintained in suspension by means of a magnetic stirrer. Oxygen was continuously bubbled by using a horizontal microfiltration polypropylene tubular membrane (internal diameter 0.5 cm, length 3 cm, mean pore size 0.2 μm) in the reservoir. The cell containing the membrane was connected to the annular photoreactor in a recirculation loop (Fig. 2). This scheme was used in discontinuous mode but it can

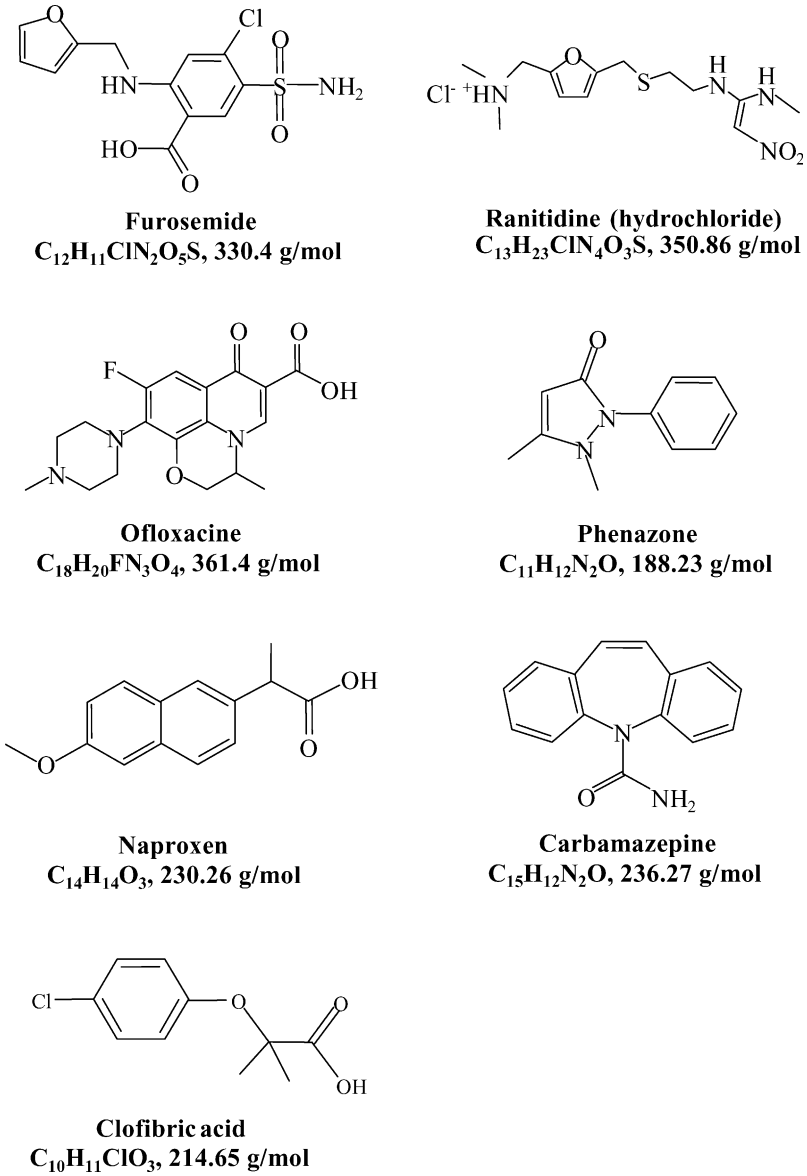

Fig. 1. Structure, formula and molar weights of the substrates used.

be also used for continuous operations. The membrane (19 cm^2 surface area) was placed in the bottom of the cell (95 mL volume) on a porous disk of sintered stainless steel and it was maintained under pressure by means of a diaphragm pump (Cole–Palmer: Q = 360 L h^{-1}; P_{max} = 14 bar) equipped with an AISI 316 stainless steel head and a pulse dumping. The pressure in the cell was regulated by means of a valve in the retentate line. The suspension entered tangentially the cell downward generating a turbulence, which minimised catalyst sedimentation onto the surface of the membrane and left the cell from the

Table 1
Main characteristics of the membranes employed

Membranes	Manufacturer	Characteristics	Material
NTR 7410	Nitto Denko, Tokyo	Rejection 10% with 0.2% NaCl at 4.9 bar, 25 °C and pH 6.5	Sulphonated polysulphone
PAN GKSS HV3/T	GKSS, Germany	Cut-off = 30 kDa; water flux 423.1 L/(h m^2) at 2 bar and 846.2 L/(h m^2) at 4 bar	Polyacrylonitrile
N 30 F	Hoechst, Celgard, Germany	Rejection 25–35% with 0.2% NaCl and 85–95% with 0.5% of Na_2SO_4; water flux 40–70 L/(h m^2) at 40 bar and 20 °C	Modified polysulphone
NF PES 10	Hoechst, Celgard, Germany	Rejection 10–20% with 0.5% NaCl and 40–70% with 0.5% of Na_2SO_4; water flux 200–400 L/(h m^2) at 40 bar and 20 °C	Polyetersulphone

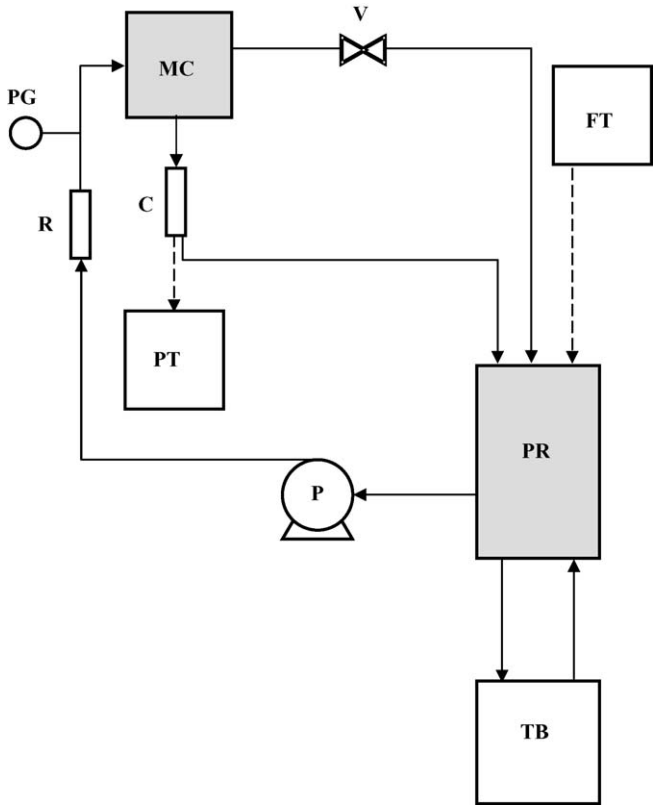

Fig. 2. Scheme of the systems used with membrane and suspended catalyst: PR, photoreactor system; MC, membrane cell; TB, thermostatic bath with cooling water; P, pump; R, rotameter; C, graduate cylinder for permeate sampling; PG, pressure gauge; V, valve; FT, feed tank (continuous regime); PT, product tank (continuous regime). The dotted lines, FT and PT are used in continuous regime.

top. All the tubing used was stainless steel to avoid the adsorption of the organic species.

The oxygen concentration, the catalyst amount and the temperature were 20 mg L^{-1}, 1 g L^{-1} and 30 °C, respectively, for all the tests. After 30 min of mixing in the dark (to allow the saturation of the dispersion with oxygen and the achievement of steady state conditions for the adsorption phenomena) the lamp was switched on and samples were withdrawn at fixed intervals of time.

The photodegradation and rejection experiments by using the various pharmaceuticals were carried out in the system shown in Fig. 2, in which a membrane cell is coupled to the photocatalytic reactor. The rejection tests for the various membranes (characteristics shown in Table 1) with the different pharmaceuticals were carried out before starting the photoreactivity runs by using 500 mL of an aqueous solution containing 5 or 10 mg/L of drug under pressures of 4, 6 and 8 bar. Membrane rejection ($R\%$) was calculated as $R\% = (1-(C_p/C_r)) \times 100$ where C_p and C_r are the concentrations of the drugs present in the permeate and in the retentate, respectively. They were periodically analyzed and the catalyst was added to the system and the oxygen was bubbled only when steady state conditions were reached.

The experiments for the adsorption study of the pharmaceuticals on the TiO_2 surface at different initial pHs were carried out by using suspensions of 200 mL volume with a concentration of 10 mg/L of drug and an amount of 1 g/L of TiO_2. The blank for each drug was considered the corresponding solution in the absence of TiO_2. The pH of the suspension or of the solution was adjusted in the range 2–12 with 1 M $H_2SO_{4(aq)}$ or $NaOH_{(aq)}$. The concentrations of the pharmaceuticals were determined by measuring the absorbance by means of a Shimadzu UV-1601 spectrophotometer. The readings were performed at the following absorbance maxima: 231 nm for furosemide; 229 nm for ranitidine; 288 nm for ofloxacine; 227 nm for clofibric acid; 210 nm for carbamazepine; 240 nm for phenazone and 230 nm for naproxen. Three milliliters of samples were filtered by means of a membrane with a mean pore size of 0.22 μm in order to separate the TiO_2 particles before carrying out the analyses. The pH measurements were carried out by means of a INOLAB-TERMINAL LEVEL 3 pH-meter by WTW (Germany).

3. Results and discussion

In order to analyze the results of the photodegradation experiments in the membrane reactor, some tests were carried out at various pHs to study separately the main factors involved in the overall performance of the photoreactor, i.e. (i) adsorption of the drugs on the TiO_2 particles; (ii) degradation of the drugs in the absence of the membrane; (iii) membrane rejection on respect to the drugs by changing the operating pressures; (iv) synergic effects of the above factors in the membrane photoreactor. The tested compounds were almost completely soluble at the various pHs in the range of investigated concentrations (5–10 mg/L).

3.1. Adsorption tests of the drugs on the catalyst at various pHs

All the pharmaceuticals were tested in the pH range 2–12 at an initial concentration of 10 mg/L to observe their adsorption behaviour on the titanium dioxide particles (1 g/L). A different adsorption of the substrates onto the catalyst surface was observed. Indeed, the hydrophilic/hydrophobic character of the catalyst changed with the pH (point of zero charge, PZC, TiO_2 in the pH range 4.5–6.2 [35]) and, consequently, the adsorption changed by considering the acid–base properties of the seven molecules, although a straightforward correlation of the extent of adsorption and the acidity/basicity of the molecules is not easy, owing to the complexity of their structure. In Table 2 some selected values of adsorption percentages are reported. Specifically, for furosemide a sigmoid decreasing adsorption trend from pH 1.9 to 4.7 was observed; for phenazone a negligible adsorption was observed, while for clofibric acid the adsorption increased by decreasing the pH; for naproxen a slight adsorption was observed at pH 11 while it increased by decreasing the pH. As an example, in Fig. 3 the adsorption behaviour of ofloxacine is reported. It can be deduced a higher adsorption percentage at pH around the PZC TiO_2. This finding can be explained by taking into account that both acidic and basic sites exist on TiO_2 surface at this pH value and consequently the molecule can interact more significantly.

Table 2
Values of adsorption percentages of the seven pharmaceuticals vs. pH

Substrate	pH	Adsorption (%)
Furosemide	1.9	90
	1.9–4.7	Sigmoid decreasing trend
	≥4.7	0
Ranitidine	2 < pH < 11	25.5
	>11	0
Phenazone	2 < pH < 12	Negligible
Clofibric Acid	3	≈100
	11	80
Ofloxacine	3	33
	6	54
	12	9
Carbamazepine	3	30
	11	8
Naproxen	3	95
	11	3

V = 200 mL, T = 30 °C; C_o = 10 mg/L, C_{TiO_2} = 1 g/L.

The adsorption percentage can be also related to the drug solubility in water: for phenazone and clofibric acid a complete solubility in all the pH range was observed; for carbamazepine it was complete at pHs around 3 and 11; for naproxen the solubility was complete at pH 11 while it decreased by decreasing the pH. As a general trend, a high solubility of the drug in water corresponds to a low adsorption percentage on TiO_2 particles.

3.2. Photodegradation tests in a batch photoreactor in the absence of membrane

The photodegradation behaviour for furosemide, carbamazepine and naproxen at acidic and alkaline pHs (3 and 11) was studied starting from the initial concentration of 5 mg/L, while the concentration of 10 mg/L was chosen for the other molecules by taking into account the different solubility in water (see in Table 3 the values of the logarithm of octanol/water partition coefficients, log K_{ow}, indicative of the solubility in water). The used batch photoreactor is part of the scheme in Fig. 2 without the membrane cell. The drugs concentration versus irradiation time, for runs carried out at pHs equal to 3 and 11, are reported in Figs. 4 and 5, respectively. It can be noticed that the concentration of the substrates decreases by increasing the irradiation time and the behaviour is in accordance with pseudo-first order kinetics with a good exponential fitting of the data. The values of the observed rate constants are reported in Table 3 together with pK_a and log K_{ow}.

Table 3
Values of pseudo-first order rate constants, pK_a and log K_{ow} for the different substrates

	k_{obs} (min^{-1})		pK_{a1}	pK_{a2}	log K_{ow}
	pH 3	pH 11			
Furosemide	3.21×10^{-2}	1.13×10^{-1}	3.9	9.93	2.03
Clofibric acid	3.28×10^{-2}	5.93×10^{-2}	–	–	–
Naproxen	7.86×10^{-2}	4.91×10^{-1}	4.2	–	3.18
Carbamazepine	1.52×10^{-1}	1.54×10^{-1}	13.9	–	2.45
Ranitidine	9.74×10^{-2}	5.35×10^{-2}	2.7	8.2	0.27
Ofloxacine	2.94×10^{-1}	7.27×10^{-2}	5.97	–	–
Phenazone	1.74×10^{-1}	1.60×10^{-1}	1.4	–	1.14

The differences in photoactivity of the various substrates at the different pHs used probably are mainly attributable to the fact that different equilibrium species are present in solution by changing the initial pH. It is not easy to straightforward correlate the photoreactivity with the physico-chemical properties of the molecules, due to their complexity and to the fact that some of them show both acid and basic groups and/or atoms.

Anyway, an attempt can be made by taking into account their pK_a values. It is worth noting that the photodegradation observed

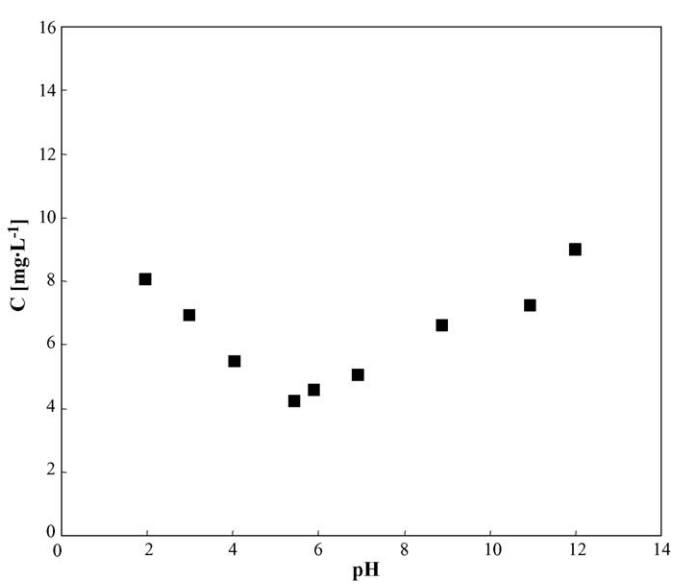

Fig. 3. Ofloxacine concentrations vs. pH in the presence of TiO_2 (V = 200 mL, T = 30 °C, C_o = 10 mg/L, C_{TiO_2} = 1 g/L).

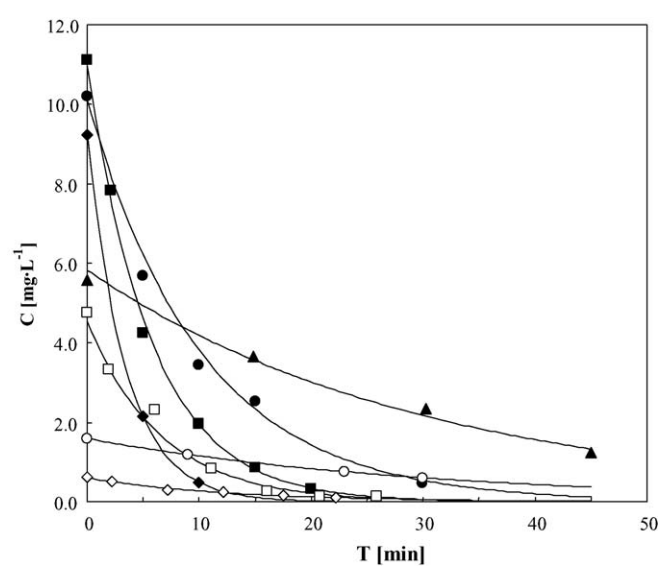

Fig. 4. Substrate concentration vs. irradiation time for runs carried out at initial pH 3 (C_{TiO_2} = 1 g/L; C_{O_2} = 22 ppm; immersed lamp 125 W). Furosemide (○); ranitidine (●); phenazone (■); clofibric acid (▲); ofloxacine (◆); carbamazepine (□); naproxen (◇).

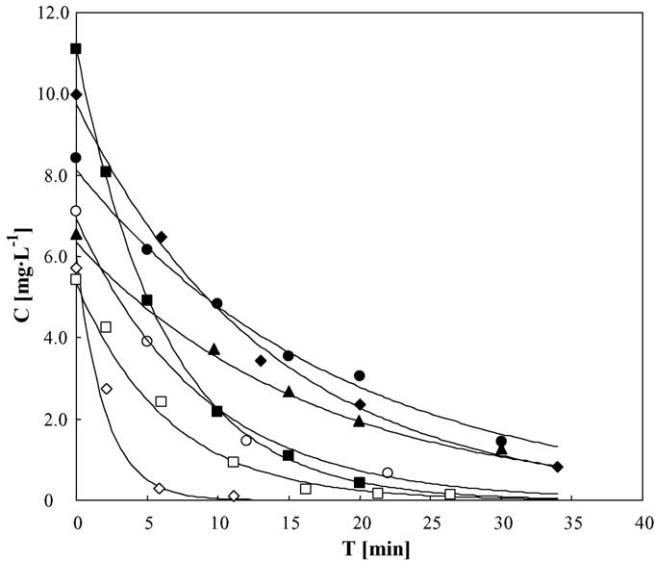

Fig. 5. Substrate concentration vs. irradiation time for runs carried out at initial pH 11 ($C_{TiO_2} = 1$ g/L; $C_{O_2} = 22$ ppm; immersed lamp 125 W). Furosemide (○); ranitidine (●); phenazone (■); clofibric acid (▲); ofloxacine (◆); carbamazepine (□); naproxen (◇).

rate constants of carbamazepine and phenazone at pH 3 and 11 do not differ significantly each other, while the other molecules show higher or lower values at the two investigated pHs.

In the first case the constancy of the values could be explained by considering that only one main species for each drug probably exists at the different pHs, owing to the values of the pK_as, although the molecules are very different from a chemical point of view (for carbamazepine p$K_{a1} > 7$, for phenazone p$K_{a1} < 7$). Consequently for each drug, the values of k_{obs} at the different pHs are representative only of one principal species present, both at pH 3 and at pH 11.

The situation is different for the other molecules as the k_{obs} values are different: i.e. they are an order of magnitude lower (ofloxacine) or higher (furosemide and naproxen) at alkaline pH. This suggests a dependence of the activity changes on the relative abundance of an acidic or a basic form of the drugs.

Moreover, by changing the pH from 3 to 11 an excess of negative charges are generated on the photocatalytic surface and this phenomenon can influence the photodegradation rate.

The obtained activity data are not related with the results of the adsorption tests of the different drugs performed at different initial pHs in the dark. This finding indicates that both the adsorption equilibria and the active sites on semiconductor surface dramatically change under irradiation, influencing the interaction between the photocatalyst and the substrates.

As a general consideration the reported results suggest that not only the (photo)adsorbed species but also the species present in various acid–base forms in the solid–liquid interface, i.e. just close to the surface but still dissolved in water, play an essential role in the photoreactivity steps.

In order to correctly compare the data presented in Figs. 4 and 5, the direct photolysis (homogeneous phase) under the same experimental conditions used for the heterogeneous system should be taken into account. For phenazone, carbamazepine and clofibric acid it was observed a same percentage of photodegraded drug by irradiating the homogeneous system six times longer for phenazone and clofibric acid and 2.5 longer for carbamazepine. Thus, the photodegradation by direct photolysis can be neglected.

3.3. Influence of pH and operative pressure on the membrane rejection (R)

Among the tested drugs, furosemide and ranitidine were selected to carry out the study of rejection and photodegradation by using the hybrid membrane system. As can be deduced from the definition given before, a rejection of 100% means that the molecule is completely retained by the membrane. The influence of pH (acidic, neutral, basic) and operative pressure on the rejection was studied by using the four membranes reported in Table 1. Preliminary measurements of the fluxes with ultrapure water at three different pressures were carried out and their values are reported in Fig. 6. It can be observed that the four membranes cover a wide range of permeate flux. The rejection percentages are reported in Tables 4 and 5 for furosemide and ranitidine, respectively. From the analysis of the data it is possible to notice the following general indications: (i) *R%* generally increases with the pressure for a same pH. This phenomenon means that the permeate flux of water increases with the pressure more than that of the drugs and consequently the concentration of the drugs in the permeate decreases; (ii) a variable polarized drug layer is probably formed on the membrane surface of the retentate zone causing a variable resistance to the passage of molecules of the two drugs through the membrane pores. Indeed the linear structure of the ranitidine molecule can explain the lower rejection observed with respect to furosemide; (iii) the behaviour of *R%* toward furosemide and ranitidine at a fixed pressure could depend on the chemical properties of the substrates and of the materials constituting the different membranes. At acidic and alkaline

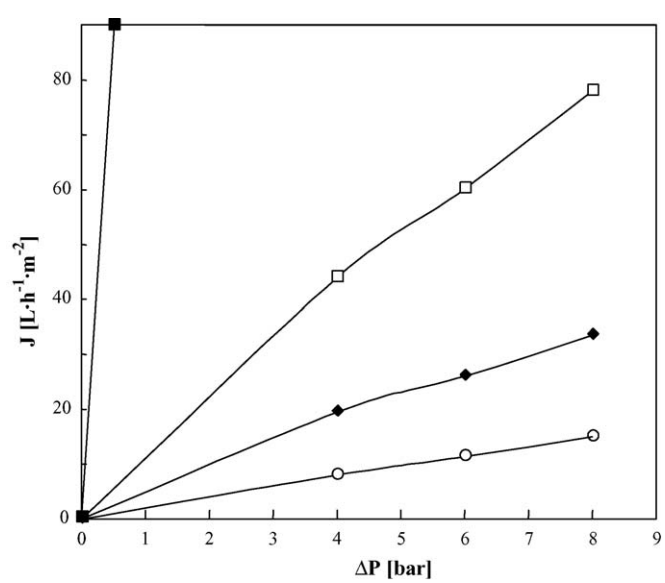

Fig. 6. Fluxes of ultrapure water vs. pressure. NTR 7410 (◆); N 30 F (○); GKSSHV3/T (■); NF PES 10 (□).

Table 4
Rejection percentages for furosemide

Membranes	Pressure								
	4 bar			6 bar			8 bar		
	Acidic pH (2.5–3.0)	Neutral pH (6.5–7.1)	Basic pH (11.0–11.3)	Acid pH (2.5–3.0)	Neutral pH (6.5–7.1)	Basic pH (11.0–11.3)	Acid pH (2.5–3.0)	Neutral pH (6.5–7.1)	Basic pH (11.0–11.3)
NTR 7410	9.8	52.9	54.0	21.8	54.0	57.5	34.5	56.3	62.1
PAN GKSS HV3/T	2.3	5.1	11.5	2.7	5.1	12.0	3.3	5.1	13.2
N 30 F	40.0	48.5	20.0	44.5	61.6	28.8	50.0	75.3	36.7
NF PES 10	0.0	27.3	81.4	4.4	40.0	81.4	8.8	51.8	81.4

Table 5
Rejection percentages for ranitidine

Membranes	Pressure								
	4 bar			6 bar			8 bar		
	Acidic pH (2.5–3.0)	Neutral pH (6.2–7.0)	Basic (11.0–11.1)	Acidic pH (2.5–3.0)	Neutral pH (6.2–7.0)	Basic pH (11.0–11.1)	Acidic pH (2.5–3.0)	Neutral pH (6.2–7.0)	Basic pH (11.0–11.1)
NTR 7410	20.0	13.2	16.2	19.5	13.2	15.3	19.4	16.7	18.8
PAN GKSS HV3/T	–	–	–	–	–	–	–	–	–
N 30 F	−32.9	−27.4	−44.6	−26.6	−3.9	−9.7	−19.9	20.0	26.6
NF PES 10	6.9	2.5	5.5	18.1	2.6	17.5	31.1	2.6	28.4

pHs some membranes may be electrically charged by an ionic exchange with the solution: then repulsive or attractive interactions between the substrate molecules and the membrane surface may occur if the charges are of the same or of different sign, respectively. Repulsive interactions increase rejection values whereas attractive ones decrease them.

Table 5 shows some negative rejection values of the N 30 F membrane toward ranitidine by changing pH and pressure values. Indeed, only at $\Delta P = 8$ bar and neutral and alkaline pHs the rejection values are positive (20 and 26.6%, respectively). The negative values of rejection can be explained by considering strong adsorption phenomena of ranitidine onto N 30 F membrane. Indeed, the results of an experimental run showed that after ca. 22 h the average mass of ranitidine adsorbed by the N 30 F membrane immersed in 200 mL of a 40 mg/L aqueous solution of ranitidine (8 mg) was 1.07 mg, corresponding to 13.4% of the ranitidine present initially in solution.

The results of these rejection runs indicate that for furosemide, the membranes which show the best performances in terms of rejection percentages seem to be NF PES 10 at alkaline pH followed by NTR 7410 at neutral and alkaline pHs and by N 30 F at acidic pH, operating at pressures in the 4–8 bar range. As far as ranitidine is concerned, NTR 7410 membrane seems to be the best in all the pH range although its rejection at $P = 8$ bar is slightly lower than that found for NF PES 10. The advantage should be noticed, then, of operating with NTR 7410 at pressures lower than the highest one.

3.4. Photodegradation tests in the membrane photoreactor

In order to check the possible synergic effect when heterogeneous photocatalysis and membrane technology are coupled, rejection and photodegradation tests were carried out simultaneously. One of the main advantage when a membrane photoreactor is used instead of a ‘‘traditional’’ photoreactor, can be found in the possibility of confining photocatalyst, pollutants and intermediates in the reaction ambient, while the treated water is obtained as permeate. Consequently the performance of a suitable membrane should have a high membrane water flux and a high rejection towards the pollutants and the intermediates. The use of nanofiltration membranes can allow these goals to be achieved if the interaction between membrane and pollutants represents the main mechanism regulating the rejection. For example, in some cases, thanks to Donnan effect [36], it is possible to retain in the reaction ambient molecules that otherwise can pass the membrane by simply modifying the pH [37].

In this work the membrane NTR 7410 which is a good compromise for the different drugs both at acidic and alkaline pHs (see Table 4) was selected. The molecular weight cut-off of this membrane is 600–800 g/mol, but charged molecules of lower size can be also retained.

Among the seven pharmaceuticals the three ones with the highest molecular weights (furosemide, ranitidine and ofloxacine) were chosen to carry out the simultaneous rejection and photodegradation tests.

Figs. 7 and 8 show the results of representative experimental runs for furosemide and ranitidine carried out at acidic and alkaline pHs, respectively. The concentrations of retentate and permeate decrease during the photodegradation steps ($60 < t < 200$ min). It can be noticed (Fig. 7) that some figures of permeate concentrations under irradiation for both substrates are higher than those of retentate. This insight is due probably to the Donnan effect, a phenomenon of electrical

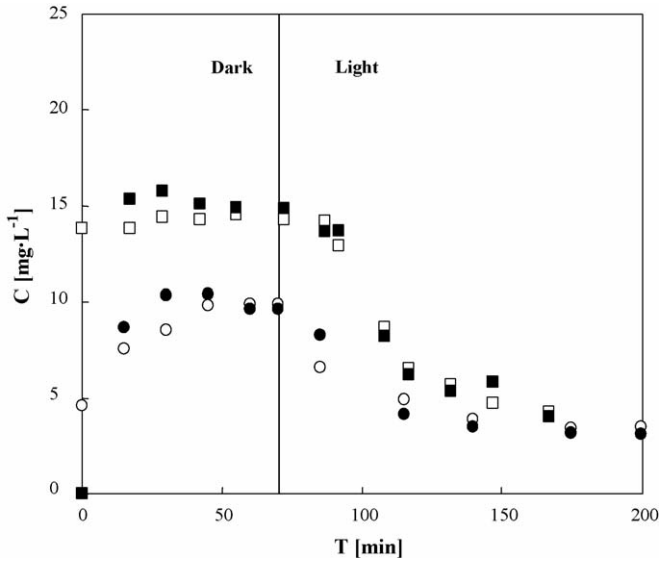

Fig. 7. Substrate concentrations vs. time for runs carried out by using the hybrid system with the NTR 7410 membrane at initial pH 3 ($C_{TiO_2} = 1\,g/L$; $C_{O_2} = 22\,ppm$; immersed lamp 125 W). Furosemide: (○) retentate; (●) permeate. Ranitidine: (□) retentate; (■) permeate.

nature. During the run carried out with furosemide, the pH decreased from 10.9 to 9.1 and the permeate flux was in the range 43.4–44.9 L/(h m^2) at acidic and alkaline pHs. As far as ranitidine is concerned, the concentration of permeate and retentate during the photodegradation step decreased of ca. 67% and 73% for acidic and alkaline conditions, respectively. The pH changed from 3 to 5.2 during the irradiation time for the run carried out at acidic pH whereas it changed from 10.9 to 8.8 for runs carried out at alkaline pH; the permeate flux was in the range 43.4–49.0 L/(h m^2) both at acidic and alkaline pHs.

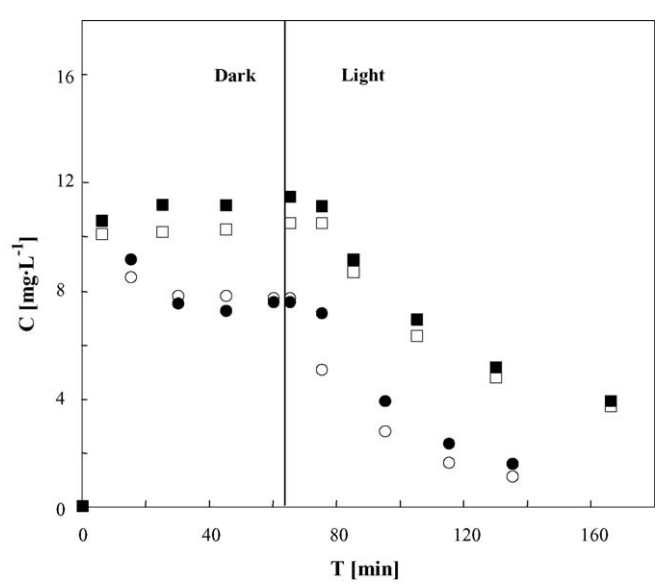

Fig. 8. Substrate concentrations vs. time for runs carried out by using the hybrid system with the NTR 7410 membrane at initial pH 11 ($C_{TiO_2} = 1\,g/L$; $C_{O_2} = 22\,ppm$; immersed lamp 125 W). Furosemide: (○) retentate; (●) permeate. Ranitidine: (□) retentate; (■) permeate.

The trend observed in Figs. 7 and 8 was the same also for ofloxacine. It can be observed that rejection measured in the presence of photocatalyst and oxygen, both in the dark and under irradiation conditions, was almost 0, so that the membrane in this case was beneficial only because it allowed the confinement of the photocatalyst. This was not a useless result because the costly separation of the catalyst from the treated water can be avoided.

Nevertheless the maximum benefit when a photocatalytic membrane reactor is used consists in retaining also the pollutant in the reaction ambient as it was observed for humic acids and some dyes [37]. Consequently further work is required to look for other types of membranes, as for instance higher rejection NF-type or low rejection reverse osmosis-type membranes, by taking into account the relatively low molecular weight of the drugs studied.

It is worth noting that most of the ions present in water could pass through the membrane because the main aim of this application would be only the removal of pharmaceutical molecules contained as pollutants in aqueous effluent.

4. Conclusions

The photocatalytic degradation of pharmaceuticals such as furosemide, ranitidine (hydrochloride), ofloxacine, phenazone, naproxen, carbamazepine and clofibric acid in a batch photoreactor was carried out successfully. For furosemide, ranitidine and ofloxacine a hybrid membrane photoreactor was also used. While the photocatalyst was retained by the membrane in the reaction ambient, the pollutant was not satisfactory retained by the membrane. The flux through the membrane NTR 7410 had an average value of 45 L/(h m^2) at both acidic and alkaline pHs. Rejection values were in the range 10–60% for furosemide and 5–30% for ranitidine in the dark (without photoreaction), but a net decrease down to 0 was observed in the contemporary presence of light, photocatalyst and oxygen. Further investigation is in progress to extend the benefit in the use of membrane photoreactors not only to the catalyst confinement but also to the confinement of drugs and their intermediates in the reaction ambient.

Acknowledgement

The authors thank the MIUR within the PRIN 2002 programme for the financial support.

References

[1] T. Ternes, Water Res. 32 (1998) 3245.
[2] R. Hirsch, T. Ternes, K. Haberer, K. Kratz, Sci. Tot. Environ. 225 (1/2) (1999) 110.
[3] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Environ. Sci. Technol. 36 (2002) 1202.
[4] M. Stumpf, T.A. Ternes, R.D. Wilken, S.V. Rodriques, W. Baumann, Sci. Tot. Environ. 225 (1999) 135.
[5] A. Waggott, W.J. Cooper (Ed.), Chem. Water Reuse, Ann. Arbor. Sci., Milan, 1981, pp. 55–99.

[6] C. Watts, M. Crathorne, M. Fielding, C.P. Steel, G. Angeletti (Eds.), Analysis of Organic Micropollutants in Water, Reidel Publ. Corp., Dordrecht, 1983, pp. 120–131.
[7] M.L. Richardson, J.M. Bowron, J. Pharm. Pharmacol. 37 (1985) 1.
[8] E. Zuccato, D. Calamari, M. Natangelo, R. Fanelli, Lancet 355 (9217) (2000) 1789.
[9] B. Halling-Sorensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lutzhoft, S. Jorgensen, Rev. Chemosp. 36 (2) (1998) 357.
[10] T.J. Gilbertson, R.E. Hornish, P.S. Jaglan, K.T. Koshy, J.L. Nappier, G.L. Stahl, A.R. Cazers, J.M. Nappier, M.F. Kubicek, G.A. Hoffman, P.J. Hamlow, J. Agric. Food Chem. 38 (3) (1990) 890.
[11] H. Oka, Y. Ikai, N. Kawamura, M. Yamada, K. Harada, S. Ito, M. Suzuky, Aquaculture 112 (1989) 113.
[12] T. Steger-Hartmann, K. Kummerer, J. Schecker, J. Chromatogr A 726 (1/2) (1996) 179.
[13] L. Shore, Y. Kapulnik, B. Ben-Dov, Y. Fridam, S. Wininger, M. Shemesh, Physiol. Plant. 84 (1992) 217.
[14] L. Shore, M. Gurevitz, M. Shemesh, Bull. Environ. Contam. Toxicol. 51 (1993) 361.
[15] A. Sanyal, D. Roy, B. Chowdhury, A.B. Banerjee, Lett. Appl. Microbiol. 17 (1993) 109.
[16] K. Elvers, S.J.L. Wright, Lett. Appl. Microbiol. 20 (1995) 82.
[17] Knoll, BASF, Pharma safety data sheet ibuprofen. Issue/revision date 6/4/1995. Knoll, Pharmaceuticals, Notthingam, NG2 3AA, England.
[18] M.C. Calleja, G. Persone, P. Geladi, Alternat. Lab. Anim. 21 (1993) 330.
[19] H. Lilius, T. Hastbacka, B. Isomaa, Environ. Toxicol. Chem. 14 (1995) 2085.
[20] D. Larsson, M. Adolfsson-Erici, J. Parkkonen, M. Pettersson, A. Berg, P. Olsson, L. Förlin, Aquat. Toxicol. 45 (1999) 91.
[21] T. Colburn, C. Clement, Adv. Modern Environ. Toxicol. 21 (1992) 129.
[22] H.R. Buser, M.D. Muller, Environ. Sci. Technol. 32 (1998) 188.
[23] O.C.J. Zafiriou, M.B. True, Mar. Chem. 8 (1979) 9.
[24] R. Zepp, G.L. Baughman, P.F. Scholtzhauer, Chemosphere 10 (1981) 109.
[25] R. Zepp, P. Scholtzhauer, R. Sink, Environ. Sci. Technol. 19 (1985) 74.
[26] F.E. Scully, J. Hoigné, Chemosphere 16 (1987) 681.
[27] M. Schiavello (Ed.), Photocatalysis and Environment. Trends and Applications, Kluwer Academic Publishers, Dordrecht, 1988.
[28] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis Fundamentals and Applications, John Wiley & Sons, New York, 1989.
[29] E. Drioli (Ed.), Proceedings of the International Symposium Membrane and Membrane ProcessesHangzhou, China, April 5–10, 1994.
[30] A.J. Howell, A.J. Noworyta (Eds.), Towards Hybryd Membrane and Biotechnology Solutions for Polish Environmental Problems, Wroclaw Technical University Press, Wroclaw, 1995.
[31] A. Caetano, M.N. De Pinho, E. Drioli, H. Muntau (Eds.), Membrane Technology: Applications to Industrial Wastewater Treatment, Kluwer Academic Publishers, Dordrecht, 1995.
[32] R. Molinari, M. Mungari, E. Drioli, A. Di Paola, V. Loddo, L. Palmisano, M. Schiavello, Catal. Today 55 (2001) 71.
[33] R. Molinari, C. Grande, E. Drioli, L. Palmisano, M. Schiavello, Catal. Today 67 (2001) 273.
[34] R. Molinari, L. Giorno, E. Drioli, L. Palmisano, M. Schiavello, Photocatalytic nanofiltration reactors, in: A.I. Schäfer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration Principles and Applications, Elsevier Advanced Technology, Oxford, 2005, , pp. 435–458, Chapter 18.
[35] K.J. Buechler, T.M. Zawistowski, R.D. Noble, C.A. Koval, I&EC Res. 40 (2001) 1097.
[36] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academy Publishers, Dordrecht, Holland, 1991.
[37] R. Molinari, M. Borgese, E. Drioli, L. Palmisano, M. Schiavello, Catal. Today 75 (2002) 77.