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Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water[☆]

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Abstract

Tests of degradation in a photocatalytic membrane system with the lamp immersed in the suspension inside the photoreactor have been carried out by using polycrystalline TiO_2 (Degussa P25) as catalyst and humic acids, organic dyes, 4-nitrophenol as pollutants. The influence of the type of nanofiltration membrane, initial concentration of pollutant and pH on the photodegradation rate was investigated in discontinuous and continuous configurations.

Two membranes were tested, i.e. NF-PES-010 (Celgard, Germany) of polyethersulphone and NTR-7410 (Nitto-Denko, Japan) of sulphonated polyethersulphone. The last one was chosen for all of the photoreactivity experiments because permeability and rejection tests indicated that it was able to hold both catalyst and small molecules carrying the same membrane charge (negative), thanks to the Donnan Exclusion.

Despite the fluxes ranged between 20 and 40 l/(h m^2) in operating conditions at 6 bar and these values are interesting for application purposes, the rejections of NTR-7410 nanofiltration membrane, obtained during operation of the membrane photoreactor in the degradation of humic acids, patent blue dye and 4-nitrophenol, were significantly lower than those obtained in the absence of photodegradation probably because of the small molecular size of by-products and intermediate species generated during the photodegradation process. This means that in order to select a suitable membrane, rejection should be determined during operation of the photoreactor. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Potable, industrial and waste waters are, in many cases, polluted by toxic organic species. 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 to municipal supplies as drinking water, usually transfer pollutants from a phase to another one.

Photocatalytic reactions allow in many cases a complete degradation of organic pollutants in very

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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 and promote decomposition of pollutants to harmless by-products [3].

When a semiconductor is illuminated by light of suitable energy, i.e. greater than its bandgap, electrons are promoted from the valence (VB) to the conduction band (CB) (they acquire the reducing power of the CB energy) and positive holes are created in the VB (they acquire the oxidation power of the VB energy). This photoproduced pairs can give rise to recombination with emission of thermal energy and/or luminescence or to redox reactions involving electron acceptor or donor species adsorbed on the surface of the catalyst particles. Consequently, the recombination rate of the photoproduced electron–hole pairs should be as low as possible in order to favour their availability on the surface of the catalyst particle.

The photoreactivity [4,5] depends not only upon the intrinsic electronic characteristic of the photocatalysts, but also upon their structural, textural and surface physico-chemical features. Among them we can cite the VB and CB energies, the bandgap value, the lifetime of the photogenerated electron–hole pairs, the crystallinity, the allotropic phase, the particles size, the presence of defects and of dopants, the specific surface area, the porosity, the surface hydroxylation, the surface acidity and basicity. The relative weight of their importance for the studied reaction determines the final level of the photoreactivity. For this reason it is not always possible to explain and discuss the observed photoreactivity trends by considering only one or few properties of the photocatalysts.

Purification processes, using methodologies that combine photocatalytic reactions with membrane separation processes, taking advantage of the synergy of both the technologies, have been found very interesting. Indeed, the membrane [6,7] would play both the role of simple barrier for the photocatalyst [8–10] and of selective barrier for the molecules to be degraded, thus realising a very powerful system combined to the degradation action of the ultraviolet radiation.

With respect to “traditional” photoreactors, another advantage of membrane photoreactors is the possibility to make a continuous process with simultaneous product(s) separation from the reaction environment. In previous works the interesting perspectives of photocatalytic membrane reactors were described by using immobilised and confined titanium dioxide [11] by means of an ultrafiltration polyacrylonitrile (PAN) membrane and 4-nitrophenol as a model molecule. Different flowsheets (batch and continuous) of photocatalytic membrane reactors and the role of the membrane (rejection and adsorbing ability) were also studied [12]. Moreover the influence of the UV radiation mode and the initial concentration of some pollutants on the photodegradation rate were investigated in discontinuous and continuous photocatalytic processes using nanofiltration membranes [13].

In this work, the rejection of two nanofiltration membranes towards various pollutants was tested and the influence of various operative parameters on the photodegradation rate, such as pH and high initial concentration of some pollutants was investigated in a membrane photoreactor where irradiation was carried out by a lamp located immersed in the suspension inside the photoreactor. A singular continuous operating mode of the system was used when the photodegradation rate was low due to a high initial concentration of pollutant.

2. Experimental

Both membrane rejection and photodegradation tests were carried out in a continuous configuration (feed feeding and permeate withdrawing), containing a pressure resistant cell with a volume of 96 cm^3, which flowsheet was previously described [12]. A pressurisation pump continuously recirculated the suspension between the photoreactor and the membrane separation cell containing one of the two nanofiltration membranes tested: NF-PES-010 (Celgard, Germany) of polyethersulphone and NTR-7410 (Nitto-Denko, Japan) of sulphonated polyethersulphone.

The photoreactor used for the photodegradation runs consisted of a cylindrical Pyrex glass batch reactor with a 125 W immersed medium pressure Hg lamp (Helios Italquartz). The volume of the reactor was 0.5 l and the continuous recirculation maintained uniform the concentration of the catalyst and the temperature. The circulation of distilled water in the Pyrex glass jacket surrounding the immersed lamp allowed it to be cooled and the reactor to be maintained at a temperature of 303 ± 2 K. The pH of the reacting mixture was adjusted to the values indicated throughout the work and in the figures by adding sulphuric acid (2 M) or sodium hydroxide (2 M). Oxygen was bubbled into the reacting mixture to maintain a constant concentration of 22 ppm, i.e. the saturation value under the used experimental conditions as it was determined by means of a dissolved oxygen meter (Mod. HI 9143, Hanna Instruments) with a membrane selective electrode. The photocatalyst was TiO_2 (Degussa P25 with specific surface area ca. 50 m^2/g) at an amount of 1 g/l; 4-nitrophenol (Acros Organics), phenol (Fluka Chemika), benzoic acid (Fluka Chemika), humic acids mixture (Acros Organics), organic dyes (Aldrich) and olive mill wastewater were used as model pollutants in the photodegradation experiments. Pollutant concentrations were measured by a UV–Vis spectrophotometer (Shimadzu UV–Vis 160A) reading at wavelengths of 315 nm for 4-nitrophenol, 210 nm for phenol, 227 nm for benzoic acid, 254 nm for humic acids, 498 nm for congo red, 639 nm for patent blue, 267 nm for neutral red, 280 nm for olive oil wastewater. In order to determine quantitatively the pollutant mineralisation, several samples were subjected to TOC analysis (Lasa 100, Dr. Lange instrument); the analytical procedure allowed to obtain, as intermediate results, also the total carbon (TC) and the total inorganic carbon (TIC).

3. Results and discussion

Before using the two nanofiltration membranes coupled with the photocatalytic system, preliminary permeability and rejection tests were carried out. It was found that membranes hold both catalyst and pollutants, but the NTR-7410 membrane at 8 bar gave a higher water permeate flux (105 l/(h m^2)) than the NF-PES-010 one (30 l/(h m^2)). The NTR-7410 membrane was able to hold also small molecules carrying the same membrane charge (negative), thanks to the Donnan Exclusion (as it will be described in the following) and it was used for many tests carried out at 6 bar giving a flux ranging between 20 and 40 l/(h m^2) in operating conditions. Before its reuse the membrane was immersed for a night in an aqueous bath of an enzymatic detergent (Ultrasil 50, 0.5% (w/v)) and then washed with distilled water. The electrostatic properties, the higher permeate flux and the easy cleaning after a repeated use of the NTR-7410 membrane determined its choice for all the other rejection tests and all of the photoreactivity experiments.

Among the various pollutants tested (humic acids, phenol, benzoic acid, organic dyes, olive mill wastewater), only the rejection tests and the photodegradation results of humic acids, patent blue dye (Acid Blue 1, C.I. 42045) and 4-nitrophenol are reported because they covered all the rejection interval (0–100%).

The membrane provided 100% retention of humic acids (Fig. 1) because this substance is formed

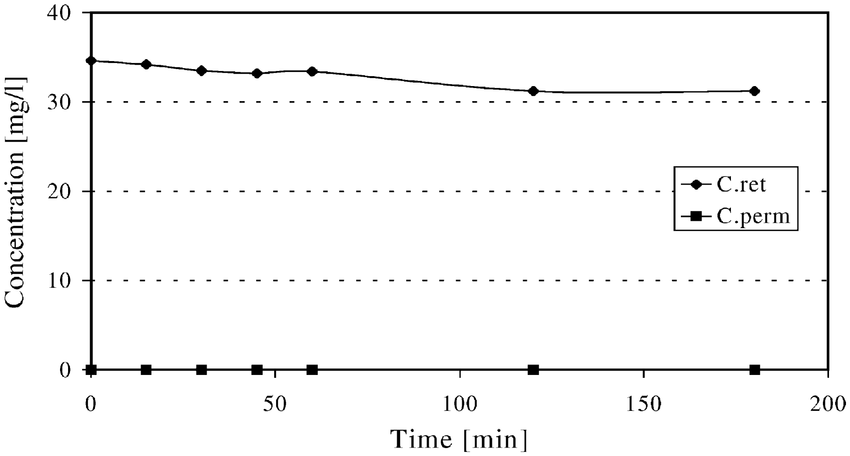

Fig. 1. Concentration of humic acids in the retentate and permeate vs. time by using the NTR-7410 membrane ($T = 30\,^{\circ}C$; $P = 6$ bar; pH = 7.60; tangential flow rate = 650 ml/min; regime permeate flux = 27.7 l/(h m^2)).

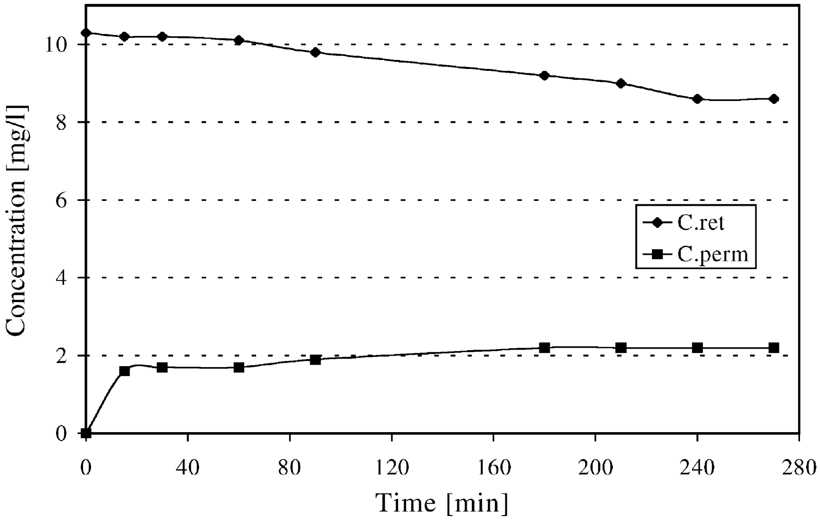

Fig. 2. Concentration of patent blue in the retentate and permeate vs. time by using the NTR-7410 membrane ($T = 30\,^{\circ}\mathrm{C}$; $P = 6\,\mathrm{bar}$; pH = 5.69; tangential flow rate = 650 ml/min; regime permeate flux = 16.5 l/(h m^2)).

by various oligomers with molecular sizes greater than the membrane cut-off (600–800 g/mol). With reference to patent blue (molar weight = 567 g/mol) membrane rejection was about 78.6% (Fig. 2); the steady-state concentration in the retentate achieved after 240 min indicates a saturation by ca. 20% by weight adsorption on the membrane. Concerning 4-nitrophenol (4NP), two rejection tests were done; as it can be noticed by the observation of Fig. 3, 0% rejection can be assumed in the first one at typical pH of the solution (ca. 6.75) because the high extent of adsorption observed (concentration continuously decreasing in the time) caused a slightly higher permeate concentration in respect to that of the retentate;

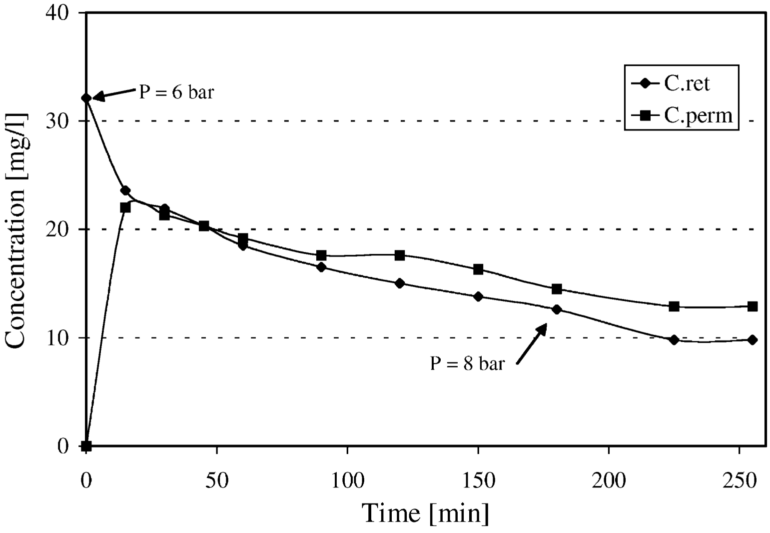

Fig. 3. Concentration of 4NP in the retentate and permeate at pH = 6.75 vs. time by using the NTR-7410 membrane ($T = 30\,^{\circ}\mathrm{C}$; tangential flow rate = 500/650 ml/min; regime permeate flux = 25.4/29.2 l/(h m^2)).

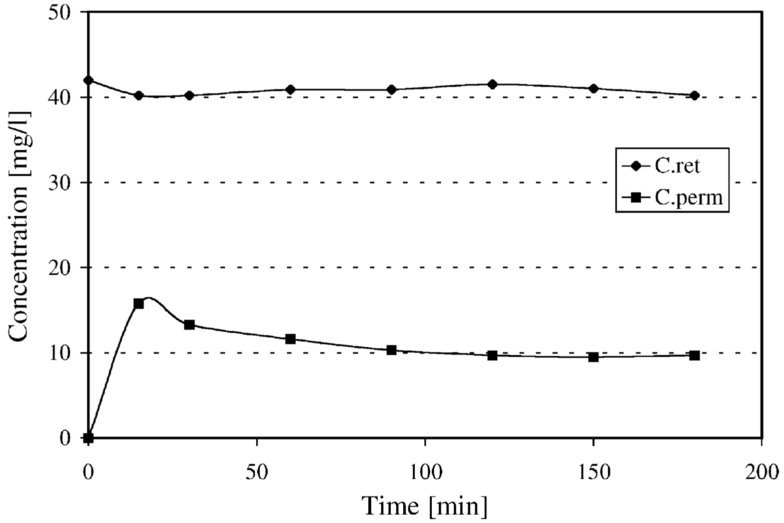

Fig. 4. Concentration of 4NP in the retentate and permeate at pH = 11.0 vs. time by using the NTR-7410 membrane ($T = 30\,^\circ C$; $P = 6$ bar; tangential flow rate = 650 ml/min; regime permeate flux = 18.0 l/(h m^2)).

in the second one (Fig. 4) about 76.9% rejection was measured at pH = 11 and a negligible adsorption was observed. In this last case, according to the following reactions:

$$C_6H_4NO_2OH + H_2O \leftrightarrows C_6H_4NO_2O^- + H_3O^+,$$

$$R\text{–}SO_3{}^-H^+ + H_2O \leftrightarrows RSO_3{}^- + H_3O^+$$

the negative charge of the ionised 4NP ($C_6H_4NO_2O^-$) interacted with the negative charge of the nanofiltration membrane ($RSO_3{}^-$) generating an electrostatic repulsion (Donnan Exclusion [14,15]) between pollutant and membrane.

As far as the photoreactivity experiments are concerned, in preliminary discontinuous tests carried out by using only the batch photoreactor, the effect of the variation of some parameters on the photodegradation rate (e.g. TiO_2 suspension turbidity, initial concentration of pollutant, UV irradiation mode) was studied in order to optimise them and to obtain knowledge for the application of the process to real cases. The rate of pollutant photodegradation was strongly affected by the UV irradiation mode. It was observed that the immersed lamp was three times more efficient than an external lamp previously used [13], although this last was mores powerful (500 W). Indeed, 99% (w/w) 4NP degradation was achieved after about 1 h in the first case,whereas about 3 h were needed in the second case. For this reason all the photodegradation experiments described have been carried out with the immersed lamp.

The dark colour of the solution, turbidity and concentration are other variables influencing the degradation in the time. By using humic acids at two different concentrations and pH = 5, a darker and more turbid solution/suspension was obtained at 200 mg/l with respect to 40 mg/l. It was observed a lower initial degradation rate in the case of 200 mg/l concentration, but decolorisation occurred for both the reacting mixtures after only 1 h. These results indicate that the photocatalytic process is efficient to degrade aggregated molecules. Probably this occurs not only because the big aggregated molecules are transformed in smaller ones after the first oxidant attacks, but also because an equilibrium between them and the single molecules adsorbed on the catalyst surface does exist.

The observed low reaction rate for high initial concentrations of pollutant (especially if it is intensely coloured) is a drawback of heterogeneous photocatalysis due to the difficulty for the photons to penetrate and impinge the catalyst particles. A set of photodegradation tests were carried out in the photoreactor operating in batch without membrane: substrate concentration, TIC and total organic carbon

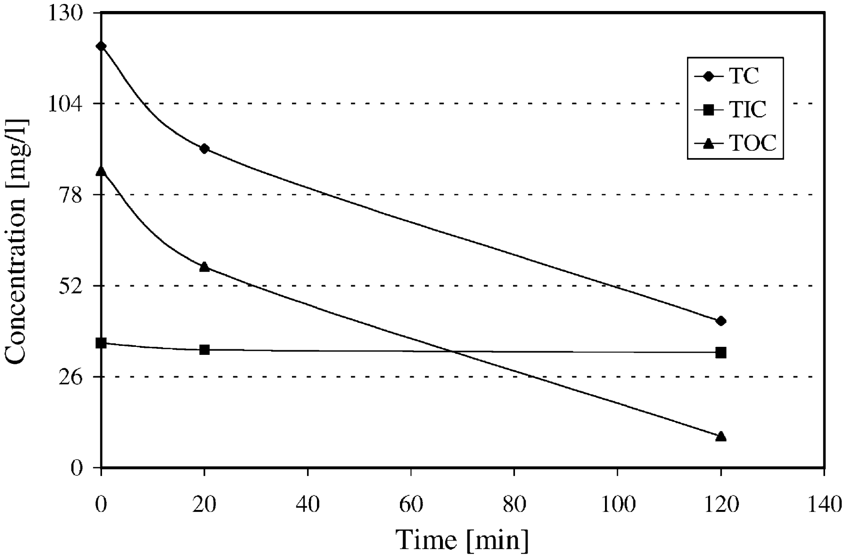

Fig. 5. TC, TIC and TOC vs. irradiation time in the photodegradation of humic acids (initial concentration by UV 200 mg/l; batch system without membrane; lamp: 125 W medium pressure Hg lamp immersed inside the photoreactor; initial pH: 7.15).

(TOC) vs. irradiation time were determined. Fig. 5 shows that for humic acids TOC decreased down to a very low value after ca. 2 h, while UV analyses showed a maximum degradation after 1 h. This is due not only to the different sensibility of the two methods, but mainly to the presence of organic intermediates containing carbon and revealed by TOC analyses. The trend of TIC in Fig. 5 suggests the presence of carbonate and hydrogencarbonate ions that can deactivate $^{\bullet}$OH radicals responsible for oxidant attach [16]. The photodegradation results obtained by using patent blue were similar to that observed with humic acids. A photodegradation rate almost independent of pH (3 or 11) was observed for 4NP when the experiments started soon after the adjustment of pH, while a net decrease of the photodegradation rate occurred at pH $= 11$ when the runs started 15 h later. This was probably because OH^- ions, present in the reaction mixture, were adsorbed on catalyst particle surface producing an electrostatically stabilised mixture. This result could generate a decrease in catalyst performance and/or a reduction of sedimentation when catalyst is used for a long time at high pH.

The last problem and the detrimental effect due to a high pollutant concentration could be minimised by taking advantage of the membrane ability to retain both the catalyst and the pollutant. To this aim the photocatalytic system was tested in a continuous process with an initial concentration of pollutant in the photoreactor equal to zero (only distilled water). A concentrated solution was continuously fed with a flow rate equal to that of the removed permeate. This solution was immediately diluted in the reactor, so photodegradation was effective at low pollutant concentration, although it was continuously fed at high concentration. The membrane process allowed to control the residence time of the pollutant in the reactor obtaining a very low concentration in the permeate.

This approach was tested by performing humic acids photodegradation with an initial concentration in the photoreactor equal to zero and feeding a 200 mg/l solution. The system was able to maintain at steady-state conditions pollutant concentrations lower than 5 and 2 mg/l in the retentate and in the permeate, respectively. A not negligible humic acids rejection was observed although it is worth noting that 100% rejection was obtained in the preliminary tests without irradiation (see Fig. 1). The lower size of the oligomers produced during the photodegradation process probably accounts for this difference.

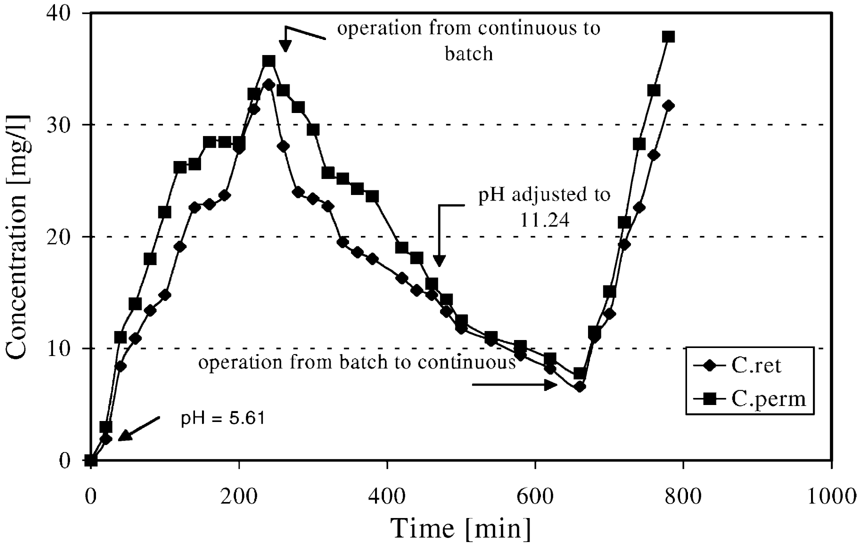

Fig. 6. Concentrations of patent blue dye in retentate and permeate vs. irradiation time in a photodegradation run by using NTR-7410 membrane (feed concentration 500 mg/l; $T = 30\,^{\circ}$C; $P = 6$ bar; tangential flow rate = 450 ml/min; regime permeate flux: 39.0 l/(h m^2) at pH = 5.61 during continuous operation, 38.0 l/(h m^2) at pH = 5.61 during discontinuous operation, 22.0 l/(h m^2) at pH = 11.24 during discontinuous operation, 22.5 l/(h m^2) at pH = 11.24 during continuous operation; lamp: 125 W medium pressure Hg lamp immersed inside the photoreactor; pH as reported in figure).

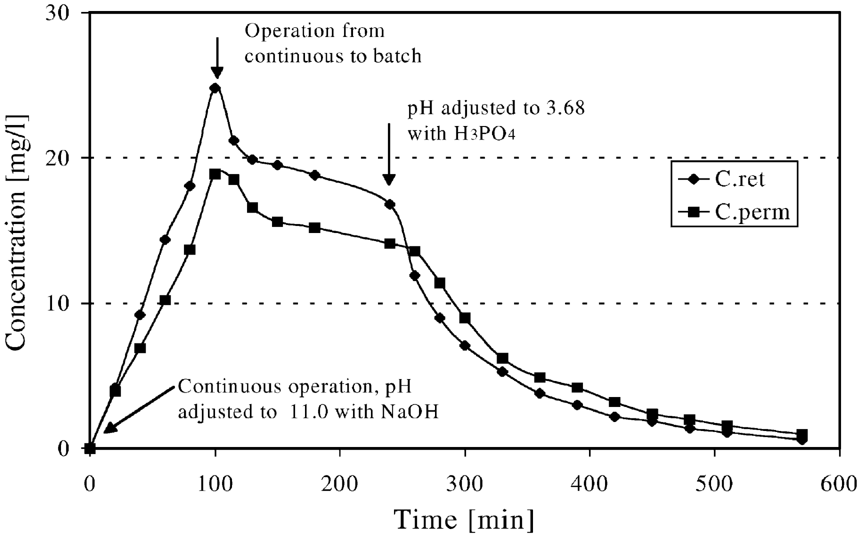

Fig. 7. Concentrations of 4NP in retentate and permeate vs. irradiation time in a photodegradation run by using NTR-7410 membrane (feed concentration 500 mg/l; $T = 30\,^{\circ}$C; $P = 6$ bar; tangential flow rate = 450 ml/min; regime permeate flux = 25.0 l/(h m^2); lamp: 125 W medium pressure Hg lamp immersed inside the photoreactor; pH as reported in figure).

The continuous process was carried out also in the case of patent blue dye and 4NP feeding with high concentration (500 mg/l). The photodegradation rate (the initial slope of the curves) of patent blue in Fig. 6 was lower than that obtained for other pollutants; this probably depends on the occurrence of some adsorption of the acid dye on the amphoteric catalytic surface which prevents UV light absorption. Indeed, at the end of the run the catalyst presented a dark blue colour. The operation was switched from continuous to batch (recirculation of permeate without feeding) after 240 min and a concentration decrease was observed indicating that part of the catalyst was still active or that a photolytic process took place as reported below. Furthermore, concentration increased sharply when the continuous configuration was restablished. The rejection of the membrane was negligible throughout the run despite the interesting value previously obtained (see Fig. 2). This behaviour can be ascribed to the catalytic action of TiO_2 that breaks the dye in small species passing through the membrane. Indeed, when only the homogeneous photolytic process was tested, some rejection was observed but the degradation rate was lower.

In Fig. 7, it can be noticed that initial 4NP photodegradation (first 100 min) is very similar to that observed in Fig. 6. Membrane retention was higher operating at $pH = 11$ while the photodegradation rate was faster operating at ca. $pH = 4$: these contrasting aspects can generate in some cases a difficulty to couple photocatalysis and membrane technologies. In addition to the use of suitable membranes and fluid dynamic parameters (e.g. pressure in the membrane cell and recirculation flow rate) for each type of application, another possibility could be to use a more active TiO_2, e.g. more active at basic pH solution, or to subject the photocatalyst to appropriate physicochemical modifications to optimise its performance.

4. Conclusions

Rejections of NTR-7410 nanofiltration membrane, obtained during operation of the membrane photoreactor in the degradation of humic acids, patent blue dye and 4NP, were significantly lower than those obtained in the absence of photodegradation probably because of the small molecular size of by-products and intermediate species generated during the photodegradation process. This means that in order to select a suitable membrane, rejection should be determined during operation of the photoreactor.

The pressure in the membrane cell, the pH of the polluted water, the molecular size of the pollutants and mainly the photogenerated by-products and intermediate species can influence the permeate flux of the membrane and consequently its choice.

High initial concentrations of the pollutants lowered the photodegradation rate; however this problem can be solved by diluting the feed in the reactor and by controlling the residence time of the pollutant by means of the membrane.

The experimental results indicate that the choice of a suitable membrane is essential for applying the photocatalytic membrane process to the treatment of real effluents. Furthermore, the possibility to use sunlight makes this hybrid process promising in industrial and environmental fields.

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