COUPLING MEMBRANE SEPARATION AND PHOTOCATALYTIC OXIDATION PROCESSES FOR THE DEGRADATION OF PHARMACEUTICAL POLLUTANTS

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Abstract

The coupling of membrane separation and photocatalytic oxidation has been studied for the removal of pharmaceutical pollutants. The retention properties of two different membranes (nanofiltration and reverse osmosis) were assessed. Comparable selectivity on the separation of pharmaceuticals were observed for both membranes, obtaining a permeate stream with concentrations of each pharmaceutical below 0.5 mg/L and a rejected flux highly concentrated (in the range of 16-25 mg/L and 18-32 mg/L of each pharmaceutical for NF-90 and BW-30 membranes, respectively), when an initial stream of six pharmaceuticals was feeding to the membrane system (10 mg/L of each pharmaceutical). The abatement of concentrated pharmaceuticals of the rejected stream was evaluated by means of heterogeneous photocatalytic oxidation using TiO_2 and Fe_2O_3/SBA-15 in presence of hydrogen peroxide as photo-Fenton system. Both photocatalytic treatments showed remarkable removals of pharmaceutical compounds, achieving values between 80 and 100 %. The nicotine was the most refractory pollutant of all the studied pharmaceuticals. Photo-Fenton treatment seems to be more effective than TiO_2 photocatalysis, as high mineralization degree and increased nicotine removal were attested. This work can be considered an interesting approach of coupling membrane separation and heterogeneous photocatalytic technologies for the successful abatement of pharmaceutical compounds in effluents of wastewater treatment plants.

Keywords:

pharmaceutical pollutants, nanofiltration, reverse osmosis, photocatalysis, photo-Fenton

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1. Introduction

Pharmaceuticals constitute a large group of medicinal human and veterinary compounds with a high consumption worldwide. As pharmaceuticals are designed to increase their potency, bioavailability and degradation resistance, they became persistent organic compounds in the environment (Xu et al., 2007). Moreover these chemicals are not currently regulated by water-quality laws, which make them emerging pollutants (Farré et al., 2008).

Although, the presence of these compounds in the environment corresponds to low concentration levels, its continuous input from wastewater treatment plants or direct discharge to natural riverbeds may represent a long-term potential threat for the aquatic and terrestrial ecosystems. Several authors have reported that the health and environmental risks are not only associated with the impact of the bioactive metabolites generated from the metabolic conversion of pharmaceutically active compounds (PhACs), but also with plausible synergetic effects of the mixture of various bioactive metabolites in addition to other micropollutants (Farré et al., 2008). Therefore, the pharmacologically valuable properties of bioavailability and degradation resistance happen to be hazardous as they become unwelcomed exposures of humans and the environment to bioactive anthropogenic compounds.

Several reports have reported a huge variety of PhAcs and bioactive metabolites in influents and effluents of wastewater treatment plants (WWTPs), rivers and drinking waters: antibiotics, analgesics, antiepileptic, anti-rheumatics, beta blockers, chemotherapeutics and steroid hormones (Al-Rifai et al., 2007; Gómez et al., 2007; Santos et al., 2010). Particularly in Spain, several studies on the efficacy of WWTPs for the removal of PhACs have been performed with very sensitive analytical methods, confirming the occurrence of high amounts of a variety of PhACs and subproducts in surface waters in concentrations ranging from nano to micro grams per liter (Gros et al., 2007; Gomez et al., 2007; Martinez-Bueno et al., 2007). The removal rates of PhACs in current WWTPs are, in general, around 40-60% (Clara et al., 2005; Miegé et al., 2009). Therefore, it makes necessary the implementation of efficient technologies in the wastewater treatment plants for the elimination of these refractory pharmaceuticals residues prior to entering into the aquatic environment.

High pressure driven membrane processes as nanofiltration (NF) and reverse osmosis (RO) have appeared as useful options to remove a wide range of organic contaminants in terms of solute rejection (Braeken et al., 2006; Bousse et al., 2008; Lopez-Muñoz et al., 2009). Thus, numerous works have been focused on

the study of the main transport mechanisms of PhACs through commercially available NF/RO membranes (Nghiem et al., 2005; Ozaki et al., 2008; Verliefde et al., 2009; Simon et al., 2009). Rejection of pharmaceuticals by these membranes is really complex as consequence of the large number of variables involved in the separation mechanisms. This parameter is influenced by the physic-chemical properties of the solute (molecular weight, charge, hidrophobicity, dipole moment, and acid-base character), the membrane properties (surface hydrophobicity and charge, pore size and water permeability), the solution chemistry (ionic environment, pH and solute concentration) and the operational conditions (temperature, trans-membrane pressure and cross-flow velocity). The application of NF or RO separation processes can be very useful for the generation of a permeated stream of very high quality, but a secondary stream with a concentrated solution of the retenate pollutants would be also produced, requiring an additional treatment.

In order to sort out the final removal of pharmaceutical contaminants, the treatment of the retenate stream by means of advanced oxidation processes (AOPs) can be taken into account. (Klavarioti et al., 2009). Among them, AOPs based on UV irradiation such as heterogeneous photo-catalysis using TiO_2 or photo-Fenton processes based on iron-containing catalysts in presence of H_2O_2 are considered of great potential. Moreover, benefits in terms of disinfection can be accomplished. The photolysis (alone or combined with an oxidant, such us H_2O_2) and heterogeneous photocatalysis with TiO_2 have been widely used for the treatment of pharmaceuticals in aqueous solutions (Baran et al., 2006; Yang et al., 2008). For the heterogeneous TiO_2 photocatalysis, an important effort has paid attention to the integration of photocatalytic reactors with membrane cells that enable the separation and recirculation of TiO_2 catalysts to the photoreactor. Thus, an increase in the overall performance of the process by the double effect of the photocatalytic oxidation and the effective rejection of non-converted contaminants can be obtained. This strategy has been found in literature for the treatment of different pollutants such as dyes (Grzechulska-Damsz et al., 2009; Mozia et al., 2010) or even some pharmaceuticals (Molinari et al., 2006). In the case of the photo-Fenton process, most of the studies have been focused on the application of the homogeneous Fenton reagent based on the dissolution of iron salts in presence of hydrogen peroxide (Perez-Estrada et al., 2005, Shemer et al., 2006; Klamerth et al., 2010). However, the application of new heterogeneous photo-Fenton catalytic systems based on the immobilization of iron species over a solid silica matrix, have offered promising results, avoiding the recovering of the iron ions from final effluent

and the restricted working pHs (2-3) that are necessary in homogeneous photo-Fenton systems (Rodriguez-Gil et al., 2010; Molina et al., 2012).

The aim of this work is dealing with the application of membrane separation and heterogeneous photocatalytic oxidation processes for the treatment of aqueous solutions containing pharmaceutical pollutants. In this coupled system, two different membranes, one of nanofiltration and another of reverse osmosis, were evaluated as selective barriers for the retention of pharmaceutical compounds. Additionally, the efficiency of heterogeneous photocatalytic methods using the semiconductor Degussa P-25 TiO_2 and hematite iron oxide supported over a mesoporous silica support (Fe_2O_3/SBA-15) was assessed for the treatment of the resultant retenate stream.

2. Materials and methods

2.1. Pharmaceuticals

Six pharmaceuticals representative of different families of drugs were selected as model pollutants for the assessment of separation/oxidation combined processes: sulfamethoxazole (SMX, antibiotic), diclofenac sodium (DCF, anti-inflammatory), hydrochlorothiazide (HCT, diuretic, drug to treat hypertension), 4-acetamidoantipyrine (4AAA, antipyretic), nicotine (NCT, stimulant) and ranitinide hydrochloride (RNT, histamine H2-receptor antagonist that inhibits stomach acid). They have been usually found in the influents and effluents of wastewater treatment plants being hardly affected by the conventional treatment processes (Gros et al., 2010). All of them were provided by Sharlab, with purity higher than 99 %.

Table 1 summarizes some physico-chemical properties of the selected pharmaceutical compounds. As it can be seen, they all have rather similar molecular weights, except nicotine, but their hydrophobicitiy, expressed as logarithm of octanol-water partition coefficient (log K_{ow}) and the ionization balance determined by the acid dissociation constant (pK_a) show a wide range of values. These features related to hydrophobic and ionic interactions are usually of particular influence on the selective rejection of the pollutants over the membrane surface.

Stock solutions of 20 L with 10 mgL^{-1} of each pharmaceutical compound were prepared by simultaneous dissolution of each solute in deionised Milli-Q water. The resultant combined mass concentration of the stock solution was of ca. 60 mgL^{-1} with a pH of ca. 7

Table 1

2.2. Description of the separation/oxidation coupling system

A coupling system of membrane separation and photocatalytic oxidation has been evaluated for the removal of pharmaceuticals in wastewaters. The aqueous solution containing pharmaceuticals is fed to the membrane unit, obtaining a permeate free of pollutants and a rejected flux with high concentration of pharmaceuticals. Subsequently, the rejected stream was treated by photocatalytic systems. Two different photo-catalytic technologies have been studied, one of them using TiO_2 as heterogeneous catalyst and another one using Fe_2O_3/SBA-15 and hydrogen peroxide as the photo-Fenton process. A simplified diagram of the overall process is shown in Fig. 1.

Fig. 1.

2.3. Membrane filtration

NF-90 and BW-30 membranes supplied by Dow/Filmtec were evaluated in this investigation on the basis of their distinct molecular weight cut-offs (MWCO) and zeta-potential values at neutral pH (Lopez-Muñoz et al., 2009). These membranes were received as flat sheet samples. According to the manufacturers, the studied membranes are polyamide thin-film composite with a microporous polysulfone supporting layer. Table 2 summarizes their most relevant features. The reverse osmosis membrane (RO), BW-30, is designed to purify water with high biological or organic fouling potential in systems with well-controlled pretreatment. The nanofiltration membrane (NF), NF-90, is widely used for the removal of divalent salts and organic compounds (Nghiem et al, 2007).

Table 2

Selected membranes were tested as flat sheet membrane specimens in a commercial SEPA II cross-flow filtration test cell (Osmonics, Minnetonka, MN). The experimental set-up has been previously described elsewhere (Arsuaga et al., 2011). The effective membrane area in the test unit is 139 cm^2. Prior to each experiment, membranes were soaked in ultrapure water for a minimum of 24 h. During this period

ultrapure water was replaced every 4-8 h to remove chemicals used for membrane preservation. Additionally, the membranes were pre-compacted for approximately 1 h at 20 bar until constant flux.

In order to explore the separation efficiency of the selected NF/RO membranes, the filtration experiments were carried out in a reconcentration mode, collecting the permeate stream in a external vessel and recirculating the retentate stream to the feed tank up to a volume reduction factor of 10, being defined this factor as the ratio between the initial volume (V_o) and the final retentate volume (V_r). The volume of the initial aqueous solution with the selected pharmaceuticals was 20 L. The first volume pumped from the tank at the beginning of each experiment was left out in order to guarantee the homogeneous content of feed stream (the dead volume of the filtration setup is approximately 1 L). The permeate flux was determined gravimetrically by weighting the mass of permeate stream collected at predetermined time interval (1 min) with an analytical balance. The retention performance of NF-90 and BW-30 membranes was compared in terms of initial and final concentrations of the feed stream at the beginning and the end of the reconcentration experiment. Temperature was controlled at 25 ºC. Trans-membrane pressure was fixed at 5.5 bar and 14.8 bar in NF-90 and BW-30, respectively. To reduce membrane fouling and effects due to concentration polarization, a high cross-flow velocity was selected (1.5 ms^{-1}).

In order to explore the influence of solute sorption on the performance of tested membranes, preliminary permeation experiments were operated in a recycling mode in which both concentrate and permeate streams were flowed back to the feed tank. Experiments were extended until steady flux and retention values were reached. In all cases, the drop of the pharmaceutical concentrations due to solute adsorption was lower than 5 %. These results are in agreement with recent published studies related to adsorption of organic solutes on the membrane surface and the filtration performance of NF-90 and BW-30 membranes (Sotto et al, 2013).

2.4. Experimental set-up of the photocatalytic oxidation systems

Concentrated effluent rejected by the membrane unit was treated by means of two heterogeneous photocatalytic oxidation processes under UV-Visible light irradiation: i) photocatalytic oxidation (UV/TiO_2) and ii) Fe_2O_3/SBA-15 photo-Fenton (UV/Fe_2O_3/H_2O_2). In both cases, the photocatalytic experiments were carried out in a cylindrical Pyrex batch reactor of 1 L as effective solution volume (. This photo-reactor provides an overture located on the top to submerge the lamp and two additional openings for withdrawing samples and air bubbling if necessary (heterogeneous photocatalysis experiments).

The irradiation of the reacting solution was performed with an immersed 150 W medium pressure mercury lamp (Heraeus TQ-150) placed inside a jacket. This jacket was used for the circulation of a copper sulphate solution (0.01 M) as a cooling system to prevent overheating of the reaction mixture and to absorb energetic UV irradiation with wavelengths below 320 nm. The lamp was always switched on for 15 min before being fitted into the reactor, in order to achieve a stabilised radiation emission (Martinez et al., 2005).

Typically, for photo-catalytic oxidation, 1.0 gL^{-1} of catalyst (TiO_2, Degussa P25) was added to the pharmaceutical aqueous solution, and 80 $mLmin^{-1}$ air flow was bubbled in the reacting mixture throughout the overall catalytic experiment. For photo-Fenton oxidation, 0.6 gL^{-1} of Fe_2O_3/SBA-15 catalyst was used and the pH of the reacting mixture was adjusted to ca. 3 with a sulfuric aqueous solution (0.1 M). The photo-Fenton catalyst based on ca. 18 wt% of Fe_2O_3 supported over a mesoporous SBA-15 silica catalyst was prepared according to the procedure reported elsewhere (Martínez et al., 2005). In both catalytic runs (UV/TiO_2 and UV/Fe_2O_3/H_2O_2), the catalysts were maintained in suspension by a magnetic stirrer placed at the bottom of the reactor. In the case of photo-assisted experiments that requires hydrogen peroxide (UV/H_2O_2 and UV/Fe_2O_3/H_2O_2), 0.135 gL^{-1} of the oxidant was set by addition of aqueous hydrogen peroxide solution (33% p/v) in the concentrated pharmaceutical solution just after the stabilization the radiation emission. The efficiency of all the photoassisted catalytic systems was assessed for periods of treatment of 6 hours taking aliquots from the reactor along the time at fixed intervals.

2.5 Characterization of aqueous samples

Prior to characterization, all the samples were filtered through 0.22 μm nylon filters in order to remove the suspended solids. The concentration of pharmaceutical compounds was measured by means of a HPLC chromatograph Varian Prostar apparatus equipped with a Phenomenex Gemini column (150 x 3.0 mm) and an array diode detector. A 150 μL volume loop was filled with sample, from which a total volume of 50 μL was injected into the column. A gradient method with 20mM formic acid and acetonitrile mobile phase, starting with a volume ratio of 10:90 and finishing in 100:0 after 45 minutes was employed (total flow rate 0.2 mL/min). UV absorbance at 275 was used for the determination of all the compounds except nicotine, in which the detector was set to 254 nm. All samples were analysed by

duplicate. Additionally, standard samples of calibration were periodically analyzed every 10 samples in order to verify the repeatability of the measurements. The variation of the standards along an analysis sequence was always lower than 5%. The quantification limit of this method was set to 0.5 mgL^{-1} for all the pharmaceutical compounds in basis of the standard deviation of the measurements of blank samples multiplied by 15.

Total organic carbon (TOC) content of the samples was analyzed using a combustion/non dispersive infrared gas analyzer model Shimadzu TOC-V. Repetitive measurements of both standards and samples of reaction did not exceed 5% difference for the range of the measured TOC concentrations. Hydrogen peroxide concentration in the samples taken off from the photocatalytic runs that the oxidant was measured by iodometric titration, with an error interval confidence of ±15 mgL^{-1}.

3. Results and discussion

3.1 Reconcentration of pharmaceuticals by nanofiltration and reverse osmosis

Fig. 2 shows the retention comparison between NF-90 and BW-30 membranes displayed in terms of initial and final concentrations of experiments in reconcentration mode. As expected, the reverse osmosis BW-30 membrane exhibited systematically, for all solutes, larger retention rates than NF-90 membrane; although the differences are hardly significant. The highest final concentrations were found for 4-AAA and ranitidine in both nanofiltration and reverse osmosis experiments. For the other four solutes (NCT, HCT, SMX and DCF) NF-90 membrane showed a rather similar reconcentration performance, whereas the final reconcentration values were more distinct when the BW-30 membrane was employed.

Fig. 2.

Regarding to the molecular weight of PhACs as descriptor of molecular size, the differences of final concentrations of ranitidine (highest value) and nicotine (lowest value) show that steric hindrance is the main factor determining the retention capacity of both membranes. Hydrophobic interaction and electric repulsion between solute species and the membrane surface seem to be of minor importance. However, the comparatively high rejection of 4-AAA for the tested membranes can be attributed to a cooperative effect of two compound characteristics: size and hydrophilic nature. Since 4-AAA molecules remain

mainly uncharged at pH 7, electrostatic interaction between solute and the negatively charged surface membrane can be neglected (Nghiem et al, 2007). On the other hand, when comparing the physico-chemical parameters of 4-AAA with the values of the other investigated PhACs of similar molecular weight, its hydrophilic nature is remarkable (Table 1). Consequently, hydrophobic interaction between organic solute and membrane surface to promote the solute transfer through the membrane is less favored for 4-AAA.

In order to combine membrane technology with photocatalytic processes processes the NF-90 membrane was selected for the proposal of pharmaceutical reconcentration. The selection of this membrane was based in considerations of time saving (permeability for NF-90 membrane is quite larger) and power saving (BW-30 membrane operates at higher pressure), since the observed differences between them in terms of the retention capacity for the selected compounds were not significant (Fig. 3). For this reason, a more detailed study of the membrane performance was solely carried out for NF-90.

Membrane flux performance was studied by observing the permeate flux evolution at constant pressure as a function of time (Fig.3). Significant flux decline is observed during the fouling run. The flux drops steeply around 20 % at the initial stage of the filtration run (first 12 h). After that, the flux decreases slowly during the next 12 h exhibiting a permeate flux decline of 5%. Finally, the permeate flux of NF-90 membrane decreases rapidly promoting an additional flux reduction of 13 % after 32 hours of experiment. For the whole interval time studied, the flux reaches no apparent stationary state with equilibrium values. At this point, it can be assumed that the deposition/adsorption of pharmaceuticals on the membrane surface could be the main responsible of the observed flux declines (Nghiem et al, 2007; Sotto et al, 2013). Previous studies have suggested that organic deposition onto the membrane surface can destabilize the membrane performance, causing a denser fouling layer with greater hydraulic resistance (Van der Bruggen, 2008). The flux decline observed at the initial stage is probably caused by pore restriction and initial deposition of organics on the membrane surface. The gradual decline exhibited by membrane in the intermediate stage of the filtration process could be associated to the thickening as well as the compaction of the fouling layer. After that, the severe flux drop observed in the membrane performance after 24 h of running could be explained both by pore blocking process or cake layer formation. Pore blocking essentially results in a decrease of the membrane porosity and an increase in membrane resistance to mass transfer. It is caused by bulk phase solutes that are small enough to enter into the membrane pores and

deposit on their surface. The solutes that are retained on the membrane surface either attach to the membrane or contribute to cake layer formation (Sotto et al, 2013).

Fig. 3.

The time-dependence of compound concentrations in the rejected flux during the filtration with the NF-90 membrane at pH 7 are illustrated in Fig. 4. For all compounds the concentration in the rejected flux increases. The simultaneous solute concentration in the permeate stream remains almost invariable. Hence, it is clearly evident that the feed concentration and the corresponding concentration in the rejected stream should increase as result of decreasing of water feed volume in the reconcentration test.

Fig. 4.

Temporal evolution of solute reconcentration displayed in Fig. 4 is in accordance with the values shown in Fig. 2. As previously discussed, steric hindrance is the main physico-chemical effect determining PhAcs rejection, except for 4AAA. Concentration in the rejected stream (concentrate) slowly increases (almost linearly) until an abrupt change is observed. This rapid variation occurs around after 24 h of the filtration run, which is in agreement with the behavior of temporal flux evolution described in the previous Figure 3. For this reason, the concentration increasing at the final stage of operation could be associated to the fouling effect (cake layer formation). On the other hand, during the filtration experiments, the permeate concentration for every pharmaceutical compound was found almost constant for the studied time interval below the detection limit of the analytical procedure (0.5 mgL^{-1}).

3.2 Heterogeneous photocatalytic treatments of concentrated stream from nanofiltration membrane separation

After 32 hours of NF-90 membrane operation under reconcentration mode, the concentrated solution was treated by two UV-heterogeneous oxidation processes: TiO_2 photocatalysis and Fe_2O_3/SBA-15 photo-Fenton.

3.2.1. Performance of TiO_2 photocatalysis

Preliminary blank experiments were performed to evaluate the extent of dark adsorption and photolysis on the degradation of the different pharmaceutical compounds. Fig. 5 shows the degradation profiles of each pharmaceutical at the different experimental conditions. As it can be observed for the dark adsorption test, hydrochlorothiazide showed the highest affinity for the TiO_2 particle surface, achieving a 50% of adsorption after 6 hours. A 30% and ca. 20% of adsorption was measured for diclofenac and ranitidine, respectively, at the end of treatment, whereas no significant adsorption was observed for the other pharmaceutical compounds.

The experiments performed only with UV-Vis irradiation in the absence of catalyst displayed a distinct sensitivity of each pharmaceutical to direct photolysis by UV-Vis irradiation. The concentration of nicotine, hydrochlorothiazide and the 4-AAA, remained almost constant after 6 hours of irradiation. By contrast, diclofenac sodium was degraded around 60% and sulfamethoxazole and ranitidine hydrochloride were 20% degraded after 6 hours. Degradation of the latter pharmaceuticals by direct photolysis has been previously reported in the literature. However, there are some discrepancies in the efficiency of the process that can be justified in terms of the experimental conditions employed in each case, such as the applied intensity and type of UV light and the initial pharmaceutical concentrations. Kim et al. (2009) demonstrated that sulfamethoxazole and diclofenac are photo-sensible to UV irradiation. They found a high removal efficiency (>95%) for both compounds using a low pressure mercury lamp with maximum wavelength at 254 nm. Beltrán et al. (2008) observed a total disapearance of 10^{-4} M sulfamethoxazole at 40 minutes of reaction using a high pressure mercury lamp with bandwidth in the range 238–579 nm. Our results for sulfamethoxazole photolytic degradation (Fig. 5) are in agreement with those obtained under sun-light irradiation, a rapid decay of 40% of the initial concentration of the pharmaceutical (10 mgL^{-1}) during the first 45 minutes of irradiation, followed by a slowdown of the degradation rate for longer reaction times (Trovó et al., 2009). Degradation of diclofenac by photolysis processes has been previously reported to occur by exposition to a Xe lamp (Méndez-Arriaga et al., 2008) and under solar radiation (Perez-Estrada et al., 2005; Balters et al., 2007) and it is attributed to the tailing over 300 nm of its maximum absorption centred at 273 nm.

Fig. 5.

Irradiation of pharmaceutical compounds in the presence of TiO_2 resulted in a remarkable enhancement of the degradation activity as compared to photolysis or adsorption experiments. After 6 hours of reaction, all pharmaceuticals compounds had approximately a 90% of removal (100% in the case of diclofenac sodium), with the exception of nicotine which has demonstrated to be the most refractory compound to the TiO_2 photocatalytic treatment among all pharmaceuticals evaluated. Photocatalytic degradation of diclofenac, ranitidine, sulfamethoxazole and hydrochlorothiazide showed typical first-order kinetics (with initial reaction rates of 1.25, 0.87, 0.63 and 0.57 $mgL^{-1}min^{-1}$, respectively), whereas the kinetics for 4-AAA and nicotine disappearance are closer to zero-order. It is interesting to note that in the two latter compounds the contribution of both adsorption and photolysis on the overall process was negligible. The faster degradation was found for diclofenac sodium for which >99% removal was achieved within 70 min of irradiation. The pH of the solution along the reactions above 7 ensures that the disappearance of diclofenac cannot be attributed to the pollutant precipitation at acidic conditions as it has been reported in literature (Perez-Estrada et al., 2005). On the other side, the slower degradation rate of nicotine could be related to its scarce affinity for adsorption on TiO_2 (Fig. 5) or to the negative influence of the other pharmaceuticals or by-products present in the reaction mixture.

The TOC mineralization was also measured, obtaining ca. 20 % after 6 hours. This result shows that even though the evaluated pharmaceuticals are prone to undergo photocatalytic degradation with TiO_2, they are not easily mineralized. The reaction proceeds through the formation of a variety of by-products which are not completely oxidized to CO_2 and H_2O, at least after 6 hours of operation.

3.2.2. Performance of Fe_2O_3/SBA-15 photoFenton

The heterogeneous photo-Fenton system based on the application of home-made Fe_2O_3/SBA-15 catalyst and H_2O_2 has been also employed. Similar photocatalyic system was also used for the abatement of pharmaceuticals in surface rivers (Rodriguez-Gil et al., 2010). The photo-Fenton reaction involves the addition of a strong oxidant such as the hydrogen peroxide, the acidification of the reaction medium and a heterogeneous catalyst with remarkable photocatalytic properties (Martinez et al., 2005; Rodriguez-Gil et al., 2010). For those reasons, several blank reactions were carried out in order to establish the influence of

those variables in the overall activity of the photo-Fenton system. The results of these experiments have been also included in Fig.6.

Fig. 6.

The photolysis of the pharmaceuticals in presence of hydrogen peroxide was firstly evaluated, in comparison with only UV photolysis presented previously in Fig. 5. The hydrogen peroxide hardly affects the results obtained by only UV-Vis irradiation, achieving similar degradation rates in both cases. Only in the case of ranitidine, a higher degradation was observed (from 20% to 85% after 6 hours of reaction).These results seems to be related to a low hydroxyl radical production from hydrogen peroxide photolysis as consequence of the incident UV-Vis irradiation (higher than 320 nm). Acidification of the solution in absence of UV, H_2O_2 and catalyst produced a significant disappearance of diclofenac sodium. The adjustment of the pH of the solution (close to 3) can be responsible of the pollutant precipitation, although not its degradation, as it has been previously mentioned (Perez-Estrada et al., 2005). Additionally, 4-AAA, hydrochlorothiazide and sulfomethoxazole partially disappeared after acidification (ca. 20% of removal in all cases). This fact may be consequence of changes of speciation by pH-dependence instead of effective oxidation and could have some of influence in the overall degradation obtained by the photo-Fenton system. The combination of the hydrogen peroxide and acid conditions without UV irradiation and catalyst yielded a remarkable removal of ranitidine. It can be attributed to the oxidizing power of hydrogen peroxide even without activation of UV-Vis irradiation, and it makes sense the results previously shown by the experiment carried out with hydrogen peroxide in presence of UV-Vis irradiation. For the rest of pharmaceutical compounds, the effect of acidification and hydrogen peroxide is not of statistic relevance. An additional experiment was carried out with the catalyst in absence of UV and hydrogen peroxide. Ruling out the effect of the pH in the diclofenac sodium removal, the disappearance of hydrochlorthiazide and sulfomethoxazole (60 and 40 %, respectively) clearly evidences a significant contribution of the adsorption phenomena on the photo-Fenton catalyst. However, this result can be explained in two different ways. On one hand, it can be attested that removal of these compounds can be driven by its adsorption over the photo-Fenton catalysts assuming that the photo-oxidation reaction take place over the catalyst surface. On the second hand, it could be considered that pharmaceutical compounds can be adsorbed instead of degraded, particularly in the case of low disappearance degrees.

Regarding the photo-Fenton system, a high efficiency in the degradation of the six pharmaceutical compounds was exhibited, achieving a total degradation of the pharmaceuticals, except for ranitidine and nicotine. Nevertheless, a remarkable degradation of ca. 90% and 85% for ranitidine and nicotine were obtained. The high degradation degree obtaining for the nicotine, the most refractory compound for the TiO_2 heterogeneous catalyst could be related to the influence of the initial pH of the photo-Fenton reaction. As it has been reported in literature, the dominant nicotine specie at the pH of the photo-Fenton experiment (3.0) is diprotonated nicotine, which has shown a higher photodegradation rate with wavelength of 254 nm (Nienow et al., 2009). Nevertheless, an induction period of 100 minutes is observed before starting the degradation process. This period of time is just the necessary to obtain a degradation grade higher than 90 % for the other pharmaceuticals. This result suggests that the induction period for the nicotine can be related to the selective oxidation of the other chemicals rather than the nicotine. It should be pointed out that this fact has been also observed using goethite as heterogeneous Fenton-like catalyst for the treatment of a mixture of different pharmaceutical pollutants (Molina et al., 2012).

The degradation profiles of the pharmaceutical compounds are typical of a first-order kinetic with constants of 0.66, 0.62, 0.69 and 1.09 $mgL^{-1}min^{-1}$ for RNT, 4-AAA, HCT and SMX, respectively. However, a zero-order kinetic was also obtained for nicotine after the induction period. The faster degradation was obtained for the diclonenac sodium, although the decrease of pH until ca. 3 at the beginning of the photo-Fenton experiment can be responsible of the pollutant precipitation, preventing the degradation of the compound, as it has been previously mentioned. It should be pointed out that the maximum degradation of each compound is obtained after 180 min, and the rest of the treatment is necessary only to ensure a remarkable degradation of the nicotine.

The initial hydrogen peroxide dosage is considered a critical variable affecting the effectiveness of the oxidation process. The influence of this variable was studied by different photo-Fenton experiments using other initial hydrogen peroxide concentrations of 0.05, 0.1, 0.2, 0.3 and 0.4 g/L. Results shown that initial oxidant concentration lower than 0.135 g/L (0.05 and 0.1 g/L) yielded a decrease in the overall performance of the photo-Fenton treatment. Concentrations of 0.2 and 0.3 g/L did not show a relevant enhancement and 0.4 g/L even led to the decrease of performance for some of the pharmaceuticals, which is attributed to secondary reactions of scavenging of hydroxyl radicals. Thus, 0.135 g/L of hydrogen peroxide was established as optimum initial oxidant concentration in the range of study.

A remarkable TOC mineralization of the pharmaceuticals (ca. 46%) was achieved by the photo-Fenton system after 6 hours, although the presence of remaining oxygenated by-products of less molecular weight seems is still significant. A common problem of these remaining by-products is related to their plausible toxicity. In a previous work, the application of photo-Fenton process for the abatement of a wide variety of pharmaceuticals detected in surface river waters demonstrated the removal of all these compounds with a remarkable reduction of acute phytotoxicity but a remaining chronic toxicity after treatment (Rodriguez Gil et al., 2010). In this work, a more exhaustive investigation of toxicity was not carried, but further studies based on specific bioassays of acute and chronic toxicities should be done in order to asses the overall performance of the photocatalytic processes.

4. Conclusions

Coupling of membrane separation and heterogeneous photocatalytic oxidation processes is a feasible alternative for the treatment of pharmaceutical contaminated wastewaters. Nanofiltration membrane exhibits better conditions for the integrated system, in terms of time saving and power operation. This membrane allows obtaining a permeate stream free of pharmaceuticals (below 0.5 mgL^{-1}). The resulting concentrate stream was successfully treated by heterogeneous TiO_2 photocatalysis and the Fe_2O_3/SBA-15 photo-Fenton processes. In both systems, remarkable degradation removals of all six pharmaceuticals were obtained. TiO_2 photocatalysis achieved a lower degradation of nicotine and mineralization of the organic compounds in terms of the TOC reduction. Fe_2O_3/SBA-15 photo-Fenton system enhanced the nicotine removal as well as the TOC mineralization degree, although acidification and hydrogen peroxide as extra oxidant were required. This work evidences the potential alternative of coupling membrane/heterogeneous photocatalytic in order to reduce the continuous discharge of non-biodegradable pharmaceutical compounds through the WWTP effluents. This combination would ensure not only the effective separation of pharmaceuticals, but also their degradation by photo-oxidation. Additionally, the used heterogeneous photocatalysts, TiO_2 or Fe_2O_3/SBA-15, prevents the contamination of the effluents by the inclusion of the catalyst in the liquid phase.

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REFERENCES

Al-Rifai, J., Gabelish, C., Schäfer, A., 2007. Occurrence of pharmaceutically active and nonsteroidal estrogenic compounds in three different wastewater recycling schemes in Australia. Chemosphere 69, 803-15.

Arsuaga, J.M., Sotto, A., López-Muñoz, M.J., Braeken, L., 2011. Influence of type and position of functional groups of phenolic compounds on NF/RO performance. Journal of Membrane Science 372 (1-2), 380-386.

Baran, W., Sochacka, J., Wardas, W., 2006. Toxicity and biodegradability of sulfonamides and products of their photocatalytic degradation in aqueous solutions, Chemosphere 65, 1295-1299.

Bartels, P., von Tümpling, Jr.W., 2007. Solar irradiation influence on the decomposition process of diclofenas in surface waters. Science of the Total Environment 374, 143-155.

Beltran, F. J., Aguinaco, A., Garcia-Araya, J. F., Oropesa A., 2008. Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water. Water Research 42, 3799-3808.

Boussu, K., Vandecasteele, C., Van der Bruggen, B., 2008. Relation between membrane characteristics and performance in nanofiltration. Journal of Membrane Science 310 (1-2) 51-65.

Braeken, L., Bettens, B., Boussu, K., Van der Meeren, P., Cocquyt, J., Vermant, J., Van der Bruggen, B., 2006. Transport mechanisms of dissolved organic compounds in aqueous solution during nanofiltration. Journal of Membrane Science 279 (1-2) 311-319.

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Research 39 (19) 4797-4807.

Farre, M., Perez, S., Kantiani, L., Barcelo, D., 2008. Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. TrAC-Trends in Analytical Chemistry 27, 991-1007.

Gómez, M.J., Martínez Bueno, M.J., Lacorte, S., Fernández-Alba, A.R., Agüera, A., 2007. Pilot Surrey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. Chemosphere 66, 993-1002.

Gros, M., Petrovic, M., Barceló, D., 2007. Wastewater treatment plants as a pathway for aquatic contamination by pharmaceuticals in the Ebro river basin (northeast Spain). Environmental Toxicology and Chemistry 26 (8), 1553-1562.

Gros, M., Petrovic, M., Ginebreda, A., Barceló, D., 2010. Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. Environment International 36, 15–26.

Grzechulska-Damszel, J., Tomaszewska, M., Morawski, A.W., 2009. Integration of photocatalysis with membrane processes for purification of water contaminated with organic dyes. Desalination 241, 118-126.

Klamerth, N., Rizzo, L., Malato, S., Maldonado, M. I., Agüera, A., Fernández-Alba, A., 2010. Degradation of fifteen emerging contaminants at mg L^{-1} initial concentrations by mild solar photo-Fenton in MWTP effluents. Water Research 44 545-554.

Klavarioti, M., Mantzavinos, D., Kassinos, D., 2009. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environment International 35 402-417.

López-Muñoz, M.J., Sotto, A., Arsuaga, J.M., Van der Bruggen, B., 2009. Influence of membrane, solute and solution properties on the retention of phenolic compounds in aqueous solution by nanofiltration membranes. Separation and Purification Technology 66 (1) 194-201.

Martínez, F., Calleja, G., Melero, J.A., Molina, R., 2005. Heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst Applied Catalysis B: Environmental 60, 181-190.

Martinez Bueno, M.J., Aguera, A., Gomez, M.J., Hernando, M.D., Garcia-Reyes, J.F., Fernandez-Alba A.R., 2007. Application of liquid chromatography/quadrupole-linear ion trap mass spectrometry and time-of-flight mass spectrometry to the determination of pharmaceuticals and related contaminants in wastewater. Analytical Chemistry 79 (24), 9372-9384.

Méndez-Arriaga, F., Esplugas, S., Giménez, J., 2008. Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO_2 and simulated solar irradiation. Water Research 42, 585-594.

Miège, C., Choubert, J. M., Ribeiro, L., Eusèbe, M., Coquery, M., 2009. Fate of pharmaceuticals and personal care products in wastewater treatment plants. Conception of a database and first results. Environmental Pollution 157 (5) 1721-1726.

Molina, R., Segura, Y., Martinez, F., Melero, J. A., 2012. Immobilization of active and stable goethite coated-films by a dip-coating process and its application for photo-Fenton systems. Chemical Engineering Journal 203, 212-222.

Molinari, R., Pirillo, F., Loddo, V., Palmisano L., 2006. Heterogenous photocatalytic degradation of pharmaceuticals in water using polycrystalline TiO_2 and a nanofiltration membrane reactor. Catalysis Today 118, 205-213.

Mozia S., Morawski A. W., Toyoda M., Tsumura T. Integration of photocatalysis and membrane distillation for removal of mono- and poly-azo dyes from water Desalination 250 (2010) 666–672

Nghiem, L. D., Schäfer, A. I., Elimelech, M., 2005. Pharmaceutical retention mechanism by nanofiltration membranes. Environmental Science and Technology 39 (19) 7698-7705.

Nghiem, L. D., Hawkes, S., 2007. Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size Separation and Purification Technology 57 (1), 176-184.

Nienow, A. M., Hua, I., Poyer, I. C., Bezares-Cruz, J. C., Jafvert, C. T., 2009. Multifacto Statistical Analysis of H2O2-enhanced photodegradation of nicotine and phosphamidon. Industrial and Engineering Chemistry Research, 48, 3955-3963.

Ozaki, H., Ikejima, N., Shimizu, Y., Fukami, K., Taniguchi, S., Takanami, R., Giri, R. R., Matsui, S., 2008. Rejection of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting

chemicals (EDCs) by low pressure reverse osmosis membranes. Water Science and Technology 58 (1) 73-81.

Pérez-Estrada, L., Maldonado, M.I., Gernjak, W., Agüera, A., Fernández-Alba, A.R., Ballesteros, M.M., Malato, S., 2005. Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale. Catalysis Today 101, 219-226.

Rodriguez-Gil, J. L., Catala, M., Gonzalez Alonso, S., Romo Maroto R., Valcarcel, Y., Segura, Y., Molina, R., Melero, J. A., Martinez, F., 2010. Heterogeneous photo-Fenton treatment for the reduction of pharmaceutical contamination in Madrid rivers and ecotoxicological evaluation by a miniaturized fern spores bioassay. Chemosphere 80, 381-388.

Santos, J.L, Aparicio, I, Alonso, E. 2010. Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). Environmental International 33, 596-601.

Shemer, H., Kunukcu, Y. K., Linden, K. G., 2006. Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes. Chemosphere 63, 269–276.

Simon, A., Nghiem, L. D., Le-Clech, P., Khan, S. J., Drewes, J. E., 2009. Effects of membrane degradation on the removal of pharmaceutically active compounds (PhACs) by NF/RO filtration processes. Journal of Membrane Science 340 (1-2) 16-25.

Sotto, A., Arsuaga, J.M., Van der Bruggen, B., 2013. Sorption of phenolic compounds on NF/RO membrane surfaces: Influence on membrane performance. Desalination 309, 64-73.

Trovó, A. G., Nogueira, R.F.P., Agüera, A., Fernández-Alba, A. R., Sirtori, C., Malato, S., 2009. Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation. Water Research 43, 3922-3931.

Van der Bruggen, B., Mänttäri, M., Nyström, M., 2008. Drawbacks of applying nanofiltration and how to avoid them: A review. Separation and Purification Technology 63 (2), 251-263.

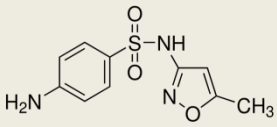
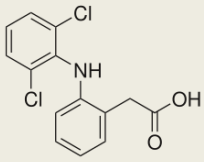
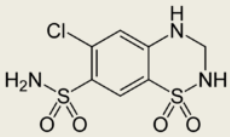
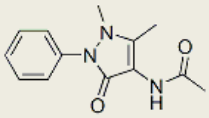
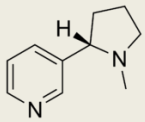
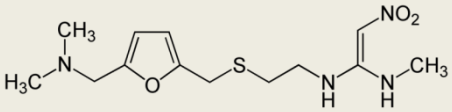
Verliefde, A.R.D., Heijman, S.G.J., Cornelissen, E.R, Amy, G. L., Van der Bruggen, B., Van Dijk, J. C., 2009. Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water. Water Research 41 (15), 3227-3240.

Xu, W., Zhang, G., Li, X., Zou, S., Li, P., Hu, Z., Li, J., 2007. Occurrence and elimination of antibiotics at four sewage treatment plants in the Pearl River Delta (PRD), South China. Water Research 41, 4526-4534.

Yang, L., Yu, L. E., Ray, M. B., 2008. Degradation of paracetamol in aqueous solutions by TiO2 photocatalysis. Water Res 42, 3480-3488.

Tables

Table 1. Intrinsic physicochemical properties of selected pharmaceuticals

Compound	Structure	MW(gmol^{-1})	logK_{ow}	pK_a
Sulfamethoxazole (SMX)		253.3	0.9	5.8
Diclofenac[a] (DCF)		296.2	4.5	4.1
Hydrochlorothiazide (HCT)		297.7	-0.5	7.9
4-Acetamidoantipyrine (4-AAA)		245.3	-0.1	4.6[b]
Nicotine (NCT)		162.2	1.1	3.1[b]
Ranitidine hydrochloride[c] (RNT)		350.9	1.3	8.2[b]

a Reported data corresponds to pure diclofenac (acid form), although the sodium salt was actually used.

b pK_a of the monoprotonated form

c Hydrochloric acid is not displayed in the chemical structure

Table 2. Physicochemical properties of selected membranes

	NF-90	BW-30
Manufacturer	Dow/Filmtec	Dow/Filmtec
Classified as	NF	RO
Active layer material	Polyamide	Polyamide
MWCO	200	N.A.
NaCl rejection (%)	90	99
Test pressure (psi)	70	225
pH range	4-11	2-11
Membrane charge (pH 7)	-26.5	-5.2
Pure water permeability [L / m^2 day kPa] (25°C)	2.49	0.67
Contact angle(^{o})	63.2	62

Figure Captions

Fig. 1. Scheme of the coupling separation/photocatalytic processes.

Fig. 2. Comparative of initial and final concentrations for NF-90(A) and BW-30(B) membranes as result of reconcentration experiments from 20 L of feed solution.

Fig. 3. Temporal evolution of permeate flux for NF-90 membrane during reconcentration experiments.

Fig. 4. Pharmaceutical concentrations of the rejected flux as a function of filtration time for the NF-90 membrane. Concentrate stream was circulated back to the feed tank during experiments.

Fig. 5. Pharmaceutical profiles for the TiO_2 photocatalysis treatment of the rejected flux and blank reactions related. ■ Photo-catalysis with TiO_2, ▲ Adsorption in absence of UV, ● Photolysis in absence of TiO_2.

Fig. 6. Pharmaceutical profiles for Fe2O3/SBA-15 photo-Fenton treatment of the rejected flux and the blank reactions related: ∇ Photo-Fenton reaction, Δ Photolysis with hydrogen peroxide, ◊ Acidification in absence of UV, H_2O_2 and catalyst, ○ Acidification with H_2O_2 in a dark system in absence catalyst, □ Adsorption over the catalyst in absence of UV and H_2O_2.

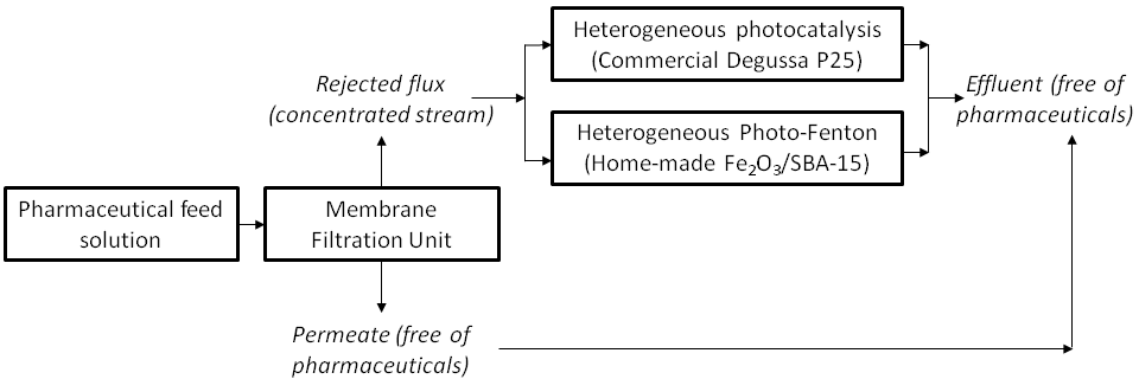

Heterogeneous photocatalysis
(Commercial Degussa P25)
Rejected flux
(concentrated stream)
Effluent (free of
pharmaceuticals)
Heterogeneous Photo-Fenton
(Home-made Fe_2O_3/SBA-15)
Pharmaceutical feed
solution
Membrane
Filtration Unit
Permeate (free of
pharmaceuticals)

Fig 1.

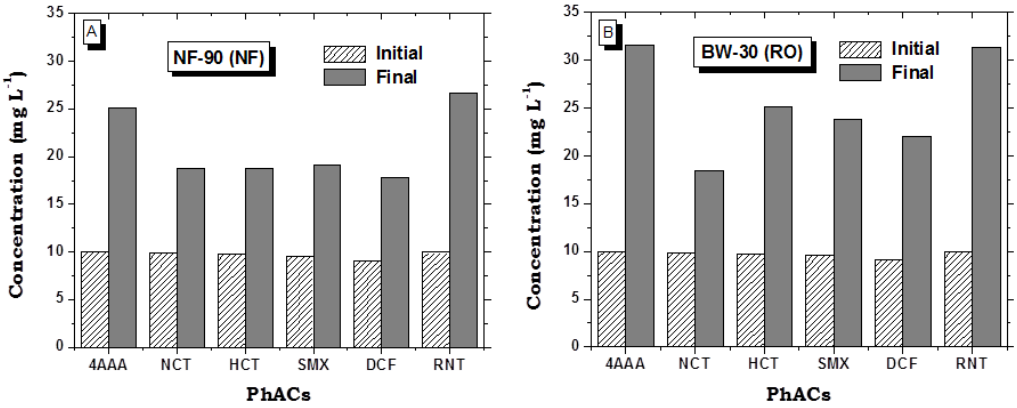

A
NF-90 (NF)
Initial
Final
Concentration (mg L-1)
35
30
25
20
15
10
5
0
4AAA
NCT
HCT
SMX
DCF
RNT
PhACs
B
BW-30 (RO)
Initial
Final
Concentration (mg L-1)
35
30
25
20
15
10
5
0
4AAA
NCT
HCT
SMX
DCF
RNT
PhACs

Fig 2.

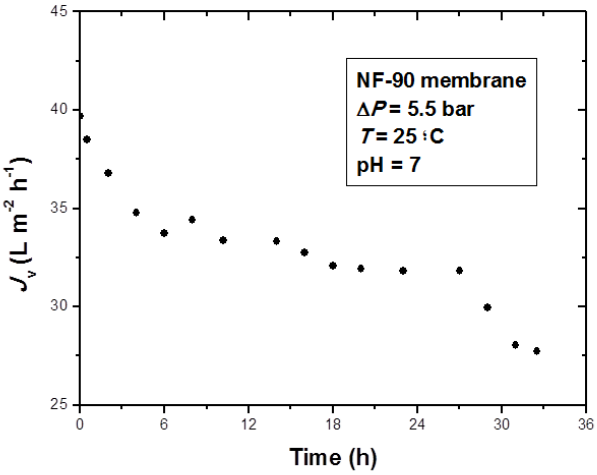

NF-90 membrane
ΔP = 5.5 bar
T = 25 ºC
pH = 7
J_v (L m^{-2} h^{-1})
Time (h)
45
40
35
30
25
0
6
12
18
24
30
36

Fig 3.

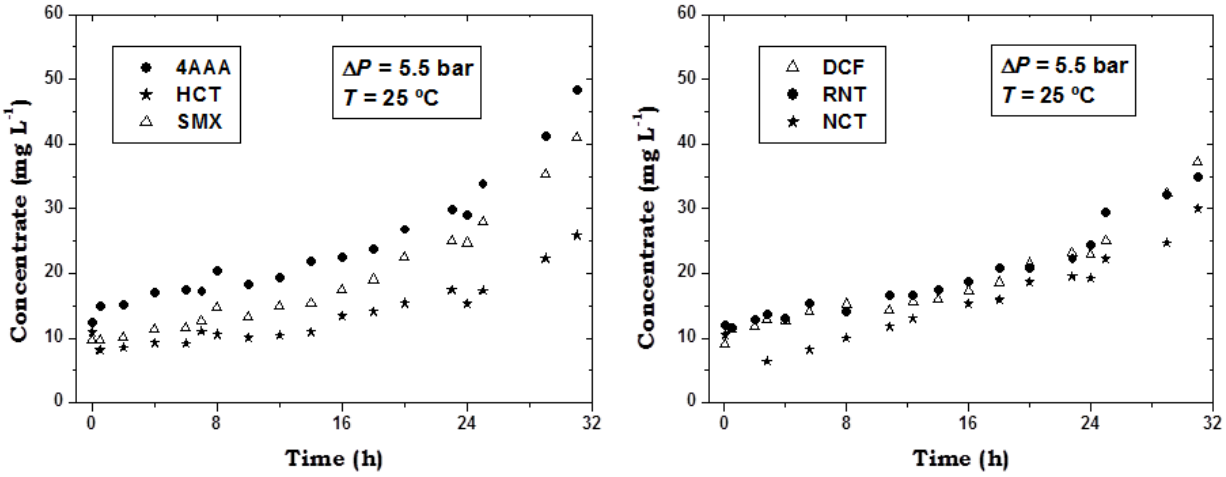

4AAA
HCT
SMX
ΔP = 5.5 bar
T = 25 °C
Concentrate (mg L-1)
Time (h)
DCF
RNT
NCT
ΔP = 5.5 bar
T = 25 °C
Concentrate (mg L-1)
Time (h)

Fig 4.

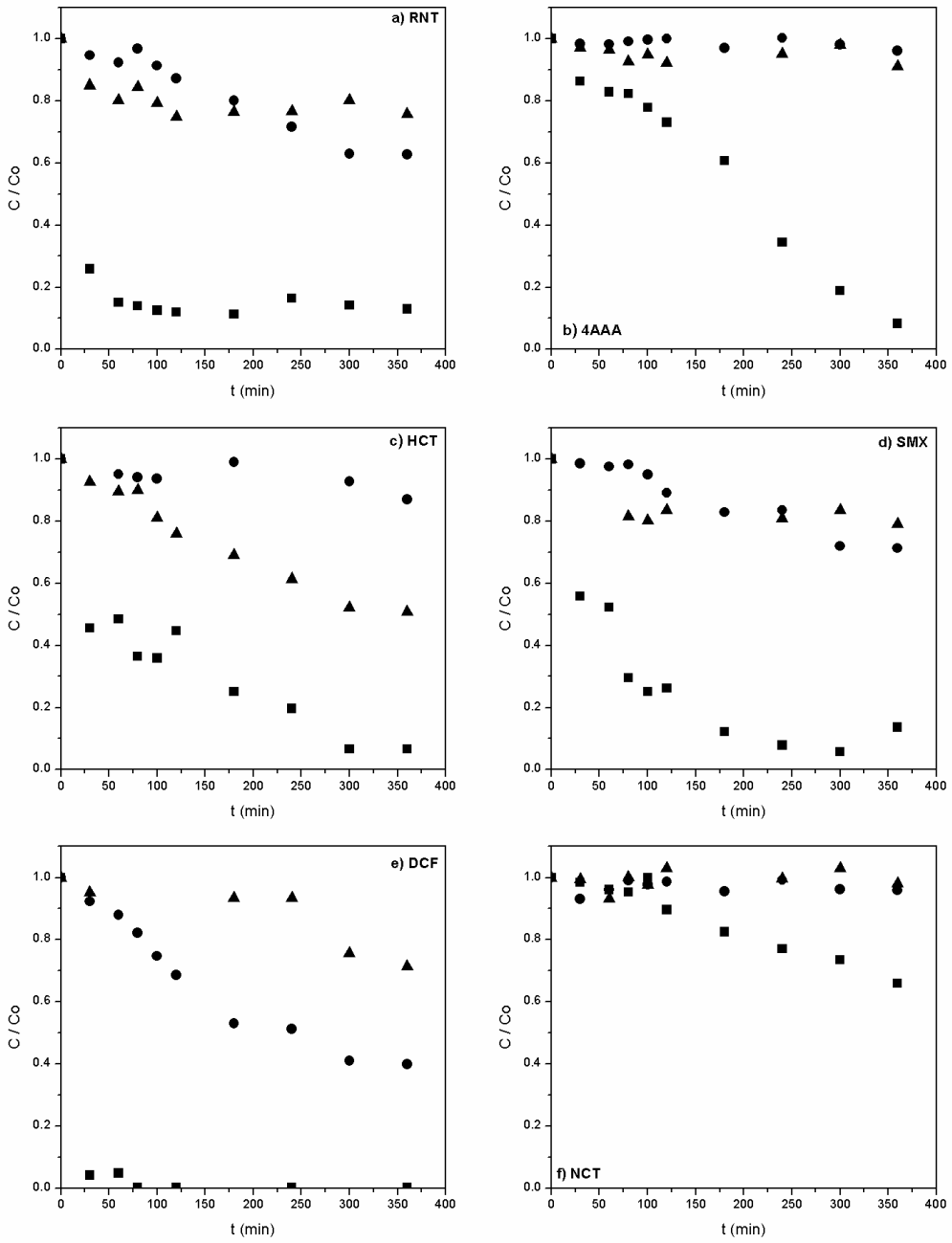


Fig 5.

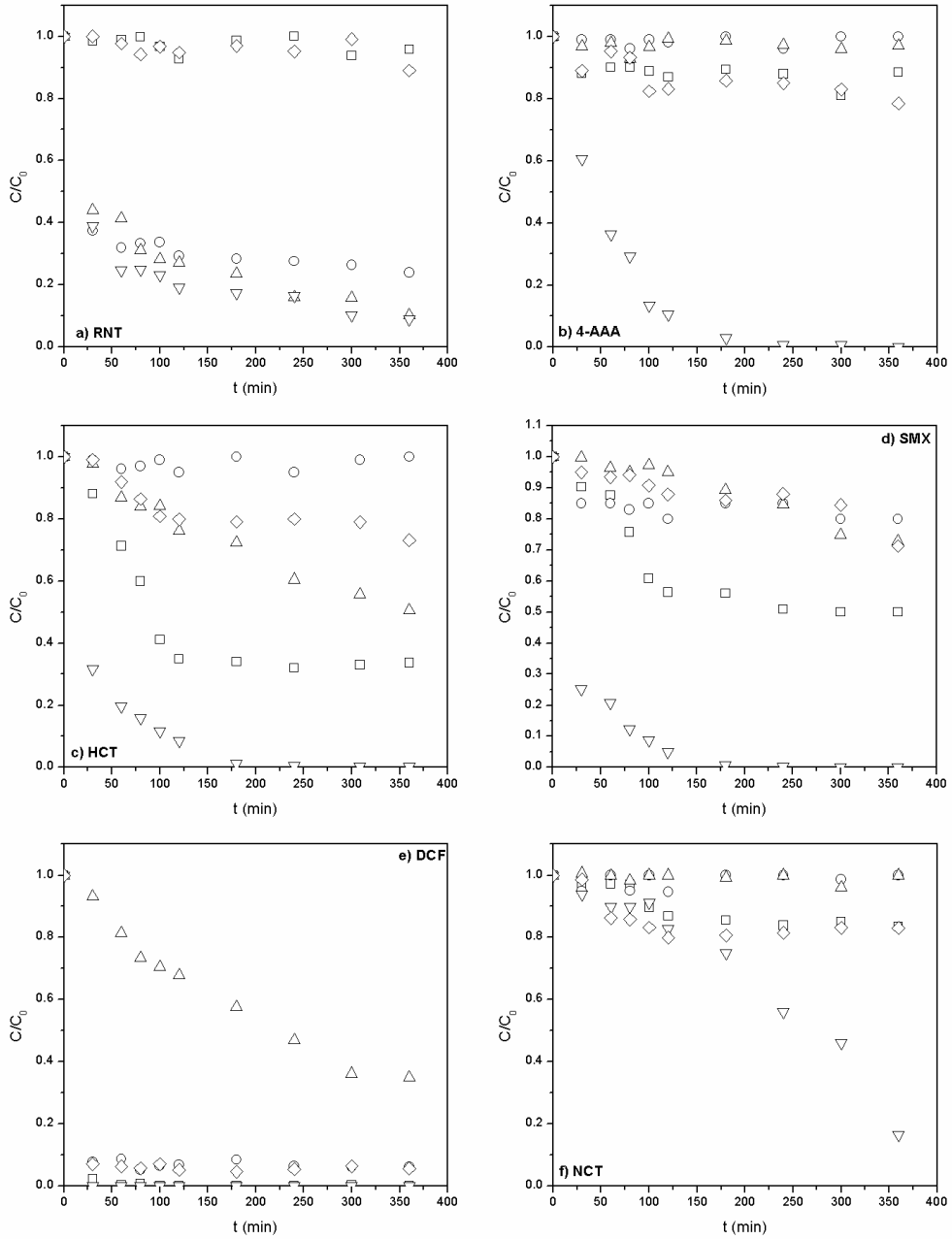


Fig 6.