



Coupling membrane separation and photocatalytic oxidation processes for the degradation of pharmaceutical pollutants

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ARTICLE INFO

Article history:

Received 6 February 2013

Received in revised form

7 June 2013

Accepted 22 June 2013

Available online 3 July 2013

Keywords:

Pharmaceutical pollutants

Nanofiltration

Reverse osmosis

Photocatalysis

Photo-Fenton

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^{-1} and a rejected flux highly concentrated (in the range of $16\text{--}25 \text{ mg L}^{-1}$ and $18\text{--}32 \text{ mg L}^{-1}$ 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^{-1} of each pharmaceutical). The abatement of concentrated pharmaceuticals of the rejected stream was evaluated by means of heterogeneous photocatalytic oxidation using TiO_2 and $\text{Fe}_2\text{O}_3/\text{SBA-15}$ 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.

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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 (Farre et al., 2008).

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<http://dx.doi.org/10.1016/j.watres.2013.06.045>

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 (Farre 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 litre (Gros et al., 2007; Gómez et al., 2007; Martínez-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; Boussu et al., 2008; López-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 physico-chemical properties of the solute (molecular weight, charge, hydrophobicity, 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 retentate pollutants would be also produced, requiring an additional treatment.

In order to sort out the final removal of pharmaceutical contaminants, the treatment of the retentate 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 as 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 (Pérez-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 (Rodríguez-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 ($\text{Fe}_2\text{O}_3/\text{SBA-15}$) was assessed for the treatment of the resultant retentate 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 ranitidine hydrochloride (RNT, histamine H_2 -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,

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