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Investigation of diclofenac degradation in a continuous photo-catalytic membrane reactor. Influence of operating parameters

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HIGHLIGHTS

- Successful application of submerged-type PMR system for diclofenac degradation.
- Steady state operation with more than 96% diclofenac degradation.
- Highest TOC removal with near optimum operating parameters pH ~ 6, TiO_2 0.5 g/L.
- Significant effect of feed water composition on diclofenac mineralization.
- Negligible membrane fouling in long-term continuous operation of the PMR system.

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ABSTRACT

A laboratory pilot photocatalytic membrane reactor (PMR), employing a hybrid TiO_2/UV-A catalysis–ultrafiltration process, is evaluated for degradation of diclofenac (DCF), a typical micro-pollutant frequently encountered in source waters. The combination of membrane ultrafiltration with photocatalysis allows TiO_2 separation and reuse whereas the automatic periodic membrane backwashing, combined with moderate permeate flux, effectively control membrane fouling, thus permitting stable continuous operation with no wastewater stream. The operation under steady state conditions permitted the assessment of the PMR system performance (for DCF degradation), in terms of water pH and catalyst dosage, in relatively long-term tests. The results demonstrate excellent system performance. Experiments with groundwater, at UV-A radiant power per unit volume 6.57 W/L, show an optimum DCF removal at pH ~ 6 and TiO_2 loading near 0.5 g/L with maxima of DCF molecular degradation and mineralization ~99.5% and ~69%, respectively. Significant differences of photo-catalytic oxidation performance are identified with different water matrices (i.e. ultrapure water, tap water, groundwater), confirming the important role of feed-water characteristics (i.e. presence of organic and inorganic scavengers) on process effectiveness. The new results highlight, among other factors, the need for good knowledge of feed water properties, to successfully design a PMR treatment process for effectively removing organic micropollutant.

1. Introduction

Over the past three decades a wide variety of pharmaceutically active compounds (PhAC) have been reported as environmental contaminants, including commonly used drug groups with antibiotic, analgesic, antiseptic, anti-inflammatory action, and many others [1]. One of the most frequently detected PhAC in sewage water, sludge, surface water, groundwater and even drinking water is diclofenac (DCF) (2-[(2,6-dichlorophenyl)amino] benzeneacetic acid), a frequently prescribed non-steroidal anti-inflammatory drug [2]. DCF is considered to be pseudo-persistent as there is a rather permanent background concentration in the environment due to the constant load of this pharmaceutical in water, primarily from municipal sewage treatment plant effluents at concentrations usually ranging from pg L^{-1} to ng L^{-1} [3]. The DCF persistence and potential adverse effects on the aquatic environment [4–6] have led the European Commission to propose diclofenac for inclusion in the existing list of 33 priority substances (Annex X) of the Water Framework Directive (WFD).

The potentially adverse effects of DCF and of other toxic organic micropollutants on the aquatic environment and the need for their essentially complete removal from potable water has increased the interest in advanced technologies including isolation/separation methods based on physicochemical processes; e.g. membrane separation processes (nanofiltration, ultra-low pressure reverse osmosis) [7–9], as well as destruction technologies based on chemical and microbiological/enzymatic methods [10]. Significant R&D

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efforts have been devoted to Advanced Oxidation Processes (AOP) as promising alternative methods to efficiently remove recalcitrant, toxic, and non-biodegradable organic micropollutants from water [11]. These processes are capable of degrading organic pollutants through the formation *in situ* of highly reactive oxygen species (e.g. hydroxyl radicals – $^{\bullet}OH$) which exhibit faster rates of oxidation reactions compared to conventional oxidants (chlorine, $KMnO_4$, H_2O_2).

Among AOP, heterogeneous photocatalysis employing UV-A irradiation and semiconductor catalyst particles – commonly TiO_2 – has exhibited high efficiency for degrading a broad range of organic substances, mainly at experimental scale [12,13]. The process operates at ambient conditions and is capable of mineralizing organic pollutants using only atmospheric oxygen dissolved in water [13]. Development of two process types is pursued, with the catalyst/TiO_2 either dispersed in the reaction mixture (*suspended type*) or embedded in a carrier material such as a membrane (*fixed type*) [13,14]. Both process types have advantages and disadvantages in different applications [14]; the conditions under which the former process type can be successfully employed are discussed in this paper. In the fixed type process, the nanostructured TiO_2 composite membranes exhibit enhanced photocatalytic activity and can also effectively decompose organic pollutants in water (e.g. [15,16]); however, there is concern about possible drawbacks of this process type including mass transfer limitations, low catalyst surface area-to-volume ratio and the implications of catalyst deactivation [14]. Nevertheless, a number of studies have shown the potential of pharmaceuticals' photocatalytic degradation over simple or modified TiO_2 under UV [17–19] or sunlight irradiation [20–23]. Studies related to the TiO_2-mediated photocatalytic oxidation of DCF have shown rather high degradation rates for relatively short irradiation times, although the process efficiency was strongly influenced by the particular type of the catalyst used, its dosage, and the feed water composition [24–27].

Despite the large number of experimental studies showing that the suspended – TiO_2 photocatalysis process holds significant advantages, successful application of this mode of photocatalytic water treatment is constrained by some technical challenges; an important one is the effective recovery and reuse of the catalyst particles to allow continuous water treatment [13]. A promising approach for separation and reuse of suspended TiO_2 is the photocatalytic membrane reactor (PMR) concept, involving the coupling of a photocatalysis reactor with catalyst separation by a membrane module [14,28,29]. Such a hybrid system, properly designed, combines the attributes of the suspended catalyst photoreactor (large catalyst surface area accessible to the UV irradiation) with the efficiency and operating stability of modern membranes types.

A number of PMR configurations have been tested in the last decade for the removal of various organic pollutants, with the majority of studies focused on degrading natural organic matter (humic and fulvic acids) from source waters [30–33] and dyes from wastewaters [34–36]. Satisfactory results have been also reported for pharmaceuticals, using TiO_2 and different types of commercial microfiltration (MF) [37], nanofiltration (NF) [38–40] and custom-made ceramic membranes [37,41]. However, most of these studies dealt with short-time experiments in batch mode and PMR configurations in which the catalyst is recirculated in the pressurized side of flat-sheet membranes [39,40]. Very few studies tested the long-term stability of TiO_2 photocatalytic activity in continuous application, with satisfactory catalyst recovery through ceramic tubular membrane filtration [37,41]. In these studies high cross-flow velocity was required as well as frequent membrane backwashing to cope with fouling due to catalyst particle deposition on the membrane surfaces.

In previous papers [33,42] the successful application of a specially designed PMR system was reported, for degradation of typical natural organic compounds (sodium alginate, humic acids), involving the coupling of a suspended TiO_2 particle photocatalysis operation with submerged ultrafiltration membrane separation; i.e. a submerged-type PMR. The role of the membrane in PMR systems is twofold; it mainly acts as a barrier for the complete retention of catalyst particles in the PMR tank, and can retain to a significant extent dissolved organic compounds as well as degradation by-products adsorbed on the photocatalyst surface, thereby enhancing the overall pollutants rejection performance of the hybrid PMR-UF system [33,42]. This PMR configuration allowed a continuous, once-through flow operation, with no reject stream, and efficient control of membrane fouling, through aeration and automatic periodic backwashing, capable of dislodging foulants accumulating on the membrane surface. The absence of a reject stream is very important as it eliminates the subsequent treatment of waste streams generated in similar conventional treatment processes as well as in cross-flow membrane filtration. The aforementioned excellent performance of the PMR system and the possibility of effectively removing synthetic organic micropollutants, with no addition of oxidants, motivated the present study.

This work aims at the assessment of PMR performance for DCF degradation, in terms of pollutant molecular degradation and mineralization, by investigating the effects of feed water pH, TiO_2 loading and initial DCF bulk concentration. The influence of the water matrix on the photocatalysis process is also assessed by using three different water types. In the following section, a novel experimental set-up, materials and methods are described, including a suitable experimental protocol developed for the long-term performance evaluation of both the photocatalysis and filtration operations.

2. Experimental

2.1. Material and reagents

Titanium dioxide (Aeroxide® P25, Degussa-Evonik, Germany) was used as photocatalyst without any pre-treatment. According to manufacturer, this product is a mixture of 75% anatase and 25% rutile with BET surface area 50 m^2/g, average primary particle size 21 nm and energy band gap 3.18 eV. In aqueous dispersions, TiO_2 particles tend to aggregate and form fairly large agglomerates of size depending on various parameters [43]. To prepare a catalyst suspension, TiO_2 powder was dispersed in water and vigorously stirred for 3 h; three different concentrations of TiO_2, 0.3, 0.5 and 0.75 g/L were employed in this investigation. Diclofenac sodium salt was of analytical grade (98.6% purity), purchased from Sigma–Aldrich and used as received. Feed solutions with concentration of approx. 2 mg/L DCF were prepared to feed the PMR system. Information on the chemical structure and the physico-chemical properties of DCF are included in Table S1. DCF is considered as hydrophilic ionic compound, with an acid dissociation constant (pK_a) 4.15; the latter, considering the pH range of the present tests, indicates a neutral to positively charged molecule at pH 4 and a negatively charged one at pH values 6.2 and 7.5. All chemicals (Sigma–Aldrich) used for the analysis of DCF were reagent grade or better.

Three different water types, *Ultrapure Water* (UW), *Tap Water* (TW) and *Ground Water* (GW) were employed in this study. Water quality parameters of these feed water types are included in Table 1. UW was Milli-Q water (Millipore, Milford, MA, USA) with 2 mM analytical grade anhydrous sodium sulfate (Na_2SO_4) added in order to slightly increase UW conductivity, above approx. 100 μS/cm, which is required for the operation of the conductivity-based level control system. Sodium sulfate was selected for the modification of solution conductivity due to the reduced