Fast degradation of diclofenac by catalytic hydrodechlorination

Julia Nieto-Sandoval[*], Macarena Munoz, Zahara M. de Pedro, Jose A. Casas

Seccion Departamental Ingenieria Quimica, Universidad Autonoma de Madrid, Ctra. Colmenar km 15, 28049 Madrid, Spain

HIGHLIGHTS

- HDC is a fast and environmentally-friendly technology for the removal of diclofenac.
- The commercial Pd/Al_2O_3 catalyst showed a high activity and a reasonable stability.
- A kinetic model based on a consecutive reaction pathway fitted the experimental data.
- Non-toxic effluents were achieved at the end of reaction.
- The versatility of the system was proved in environmentally-relevant water matrices.

GRAPHICAL ABSTRACT
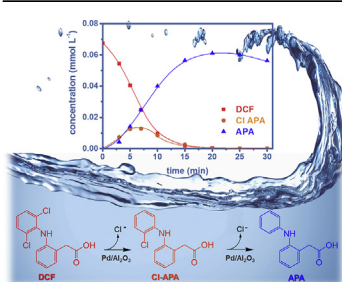
ABSTRACT

Aqueous-phase catalytic hydrodechlorination (HDC) has been scarcely explored in the literature for the removal of chlorinated micropollutants. The aim of this work is to prove the feasibility of this technology for the fast and environmentally-friendly degradation of such kind of compounds. Diclofenac (DCF), a highly consumed anti-inflammatory drug, has been selected as the target pollutant given its toxicity and low biodegradability. The commercial Pd/Al_2O_3 (1% wt.) catalyst has been used due to its prominent role on this field. Complete degradation of DCF was achieved in a short reaction time (20 min) under ambient conditions (25 °C, 1 atm) at $[DCF]_0 = 68\,\mu M$; $[Pd/Al_2O_3]_0 = 0.5\,g\,L^{-1}$ and H_2 flow rate of $50\,N\,mL\,min^{-1}$. Remarkably, the chlorinated intermediate (2-(2-chloroanilino)-phenylacetate (Cl-APA)) generated along reaction was completely removed at the same time, being the chlorine-free compound 2-anilinophenylacetate (APA) the only final product. A reaction scheme based on this consecutive pathway and a pseudo-first-order kinetic model have been proposed. An apparent activation energy of $43\,kJ\,mol^{-1}$ was obtained, a comparable value to those previously reported for conventional organo-chlorinated pollutants. Remarkably, the catalyst exhibited a reasonable stability upon three successive uses, achieving the complete degradation of the drug and obtaining APA as the final product in 30 min. The evolution of ecotoxicity was intimately related to the disappearance of the chlorinated organic compounds and thus, the final HDC effluents were non-toxic. The versatility of the system was finally demonstrated in different environmentally-relevant matrices (wastewater treatment plant effluent and surface water).

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1. Introduction

The wide occurrence of pharmaceutical compounds in the aquatic ecosystems, especially the organochlorinated ones,

* Corresponding author.
  E-mail address: julia.nieto-sandoval@uam.es (J. Nieto-Sandoval).

represents an environmental issue of increasing concern. These compounds, originated from domestic and industrial sources, are not completely removed in conventional wastewater treatment plants (WWTPs), and thus, they are usually present in surface waters, groundwaters and even drinking waters (Gros et al., 2007). Although they appear at trace concentrations (ng L^{-1} − µg L^{-1}), their high toxicity and long-term persistence in the ecosystems make them an important threat to the environment as well as to the public health (Luo et al., 2014).

Among those chlorinated pharmaceuticals, the anti-inflammatory drug diclofenac (DCF) is receiving particular attention and has been recently included in the watch list for micro-pollutants monitoring in the European Union as a potential priority pollutant (Barbosa et al., 2016). This highly consumed pharmaceutical, stands out for its ecotoxicity to terrestrial and aquatic organisms and very low biodegradability (Chong et al., 2017). Due to the high consumption of DCF, it is usually present in urban wastewaters. In fact, it has been quantified in Norway, Switzerland, Finland, and Greece influent wastewater between 0.19 and 1.9 µg L^{-1} (Krzmarzick and Novak, 2014). And thus, it usually appears in WWTP effluents at variable concentrations (14.9 ng L^{-1} − 4.4 µg L^{-1}) (Barbosa et al., 2016). For instance, a recent study carried out in a Luxembourg WWTP, DCF was detected in 100% of the samples taken during three consecutive weeks, at concentrations within the range of 50−125 ng L^{-1} (Majewsky et al., 2013). In average, DCF removal in conventional WWTPs is between 21% and 40% (Chong et al., 2017). Its continuous input in the environment is leading to negative effects in the aquatic living organisms (Acuña et al., 2015; Ebele et al., 2017). DCF has been shown to bio-accumulate in a number of fish and invertebrate species, affecting their growth, reproduction and metabolism (Acuña et al., 2015). Although DCF appears at relatively low concentrations in the aquatic environment, its persistence causes combined toxic effects (Lonappan et al., 2016). As a relevant example, rainbow trout has shown alteration of gills, liver and kidneys due to prolonged exposure to DCF at a concentration of 5 µg L^{-1} (Perez-Estrada et al., 2005). Additionally, the accumulation of different micropollutants in the aquatic environment can cause synergic effects that should be also taken into account. For instance, DCF can act as ligand in such a way that interacts with inorganic groups changing toxic effects (Lonappan et al., 2016).

In order to solve this issue, different advanced water treatment technologies have been tested for DCF removal. Adsorption onto activated carbon and advanced oxidation processes (AOPs) have received major attention so far (Leone et al., 2018; Perez-Estrada et al., 2005). The former has proved to be quite effective in the removal of DCF (Leone et al., 2018; Wu et al., 2015) but it is not selective and it only allows the separation of the pollutant from the water phase, requiring further management of the saturated adsorbent. On the other hand, the latter involves the oxidation of the molecule but it can lead to a wide variety of more toxic by-products (De Corte et al., 2012). Furthermore, DCF is particularly refractory to oxidation, requiring longer reaction times than other pharmaceutical compounds (Hofmann et al., 2007; Manu and Mahamood, 2012). In this context, catalytic hydrodechlorination (HDC) appears as a promising technology for the abatement of chlorinated pharmaceutical compounds (Keane, 2011). In this process, hydrogen reacts with the pollutant to produce the corresponding hydrogenated chlorine-free product and hydrochloric acid. Therefore, HDC is an environmentally-friendly process, which allows to reduce significantly the ecotoxicity of the effluent, and avoid the formation of more harmful intermediates (Munoz et al., 2014). In addition, this treatment can be operated under ambient temperature and pressure (Munoz et al., 2016). Pd is recognized as the most suitable active phase for liquid-phase HDC due to its high activity and strong resistance towards chloride poisoning (Díaz et al., 2008; Munoz et al., 2014). Regarding the support, activated carbon and alumina have received major attention (Díaz et al., 2008). Among them, the latter is particularly interesting due to its higher mechanical resistance as well as to its strong interaction with the supported metal nanoparticles, enhancing their dispersion.

Despite the huge potential of HDC for the removal of chlorinated drugs, it has been scarcely investigated for such goal so far. De Corte et al. (2011, 2012) studied this process using biogenic Pd-catalysts with the aim of reducing its cost. Unfortunately, very long reaction times were required to achieve significant removals of DCF (44% at the most in 24 h) even using relatively high concentrations of catalyst (50 mg$_{Pd}$ L^{-1}). In a recent work, Wu et al. (2015) evaluated the effect of the catalytic support on the HDC of DCF. Pd/CeO$_2$ was selected as the optimum catalyst and, although it allowed the relatively fast removal of DCF (50 min) under ambient conditions, it showed a significant and progressive deactivation upon sequential applications, being its activity reduced by 75% after 5 runs.

The aim of this work is to demonstrate the effectiveness of catalytic hydrodechlorination as a fast and stable process for the removal of the persistent pharmaceutical DCF. The commercially available catalyst Pd/Al$_2$O$_3$ has been used due to its prominent role on this field (Díaz et al., 2008). A complete operating condition study has been carried out and a kinetic model has been accordingly proposed. The stability of the catalyst has been evaluated upon three consecutive runs. To further demonstrate the feasibility of this process, the ecotoxicity of the effluents has been analysed. Finally, the versatility of the system has been proved using different real environmentally-relevant aqueous matrices such as WWTP effluent, surface water and hospital wastewater.

2. Materials and methods

2.1. Materials

Diclofenac sodium salt (analytical standard) and 2-anilinophenylacetic acid (88%) were provided by Sigma-Aldrich. Acetonitrile (99.9%) and acetic acid (99.5%) were supplied by Scharlau and Panreac, respectively. Hydrogen (99.999%) was obtained by Praxair. The catalyst Pd/Al$_2$O$_3$ (1% wt.) was delivered by Alfa Aesar. Briefly, the Pd content was 0.95% wt., the particles show a mean diameter of 24 µm and the specific surface area was 270 m^2 g^{-1}. Regarding the oxidation state of Pd, a Pd^0/Pd^{n+} molar ratio of 1.04 was determined. The characterization procedures are explained in the Supplementary Material whereas additional physicochemical properties of the catalyst can be found in Table S1. All the experiments were carried out using deionized water.

2.2. Experimental procedure

Aqueous phase catalytic hydrodechlorination of DCF was performed batch-wise in a magnetically stirred glass slurry-type reactor (500 mL). H$_2$ was continuously fed to the reactor at 50 N mL min^{-1}. Initial concentration of DCF was established at 20 mg L^{-1} (0.068 mM) whereas the catalyst concentration was evaluated from 0.1 to 2 g L^{-1}. The effect of temperature was investigated within the range of 17−35 °C. The stirring velocity was assessed within the range 600−1000 rpm in preliminary experiments, being 900 rpm the selected for further experiments (see Fig. S1 of the Supplementary Material for experimental data).

2.3. Analytical methods

Liquid samples were periodically withdrawn from the reactor