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Photodegradation of diclofenac in wastewaters

Pasquale Iovino[a], Simeone Chianese[b], Silvana Canzano[a], Marina Prisciandaro[c,*], Dino Musmarra[b]

[a]*Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli Studi di Napoli, Via Vivaldi 43, 81100 Caserta, Italy.*
[b]*Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Real Casa dell'Annunziata, Via Roma 29, 81031 Aversa (CE), Italy.*
[c]*Dipartimento di Ingegneria Industriale e dell'Informazione e di Economia, Università dell'Aquila, viale Giovanni Gronchi 18, 67100 L'Aquila, Italy, Tel. +39 0862 434241, Fax +39 0862 434203, email: marina.prisciandaro@univaq.it*

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ABSTRACT

A major environmental concern has recently developed due to emerging pollutants (EC) that are nowadays being detected in the effluents of municipal and industrial wastewater treatment plants (WWTP) at very low concentrations, thanks to improved analytical techniques. Pharmaceutical compounds (PhACs) are some of the most hazardous EC. These compounds can be retained into the water cycle (from users to WWTP, and then to water sources by discharge) virtually endlessly. Thus innovative solutions are required, such as the advanced oxidation processes (AOP). Among them, combined treatments based on UV light appear to be eco-friendly, giving very interesting removal efficiencies if opportunely devised. In this paper, the removal of diclofenac, a widely used non-steroidal anti-inflammatory drug (NSAID), from synthetic water streams was explored by using a lab-scale experimental device, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at fixed wavelength and intensity (254 nm; 400 mJ m^{-2}). The experimental tests have been carried out to evaluate the effect of treatment time and to verify the possibility of further degrading the obtained compound. The preliminary results confirm what has been recently and unexpectedly found in literature, that is the formation of a dimer during the first minutes of photolysis, carbazole, a very stable coloured intermediate.

Keywords: Diclofenac; Photo degradation; Carbazole; Advanced oxidation processes; Modelling; Wastewaters

1.Introduction

Despite their widespread use, the fate of many of pharmaceutical compounds (PhACs) is still mostly unknown because of the lack of chemical measurement techniques that till now have been unable to detect contaminants at low concentrations in the environment. Moreover, the presence of trace pharmaceuticals and other xenobiotic compounds in drinking and superficial waters is a major public health concern, since little is known about the potential chronic effect on human health associated with the long term ingestion of mixtures of these substances [1–4]. The problem is felt even more in the case of water reuse, since PhACs are persistent, toxic, bio-accumulative and bio-refractory.

Non-steroidal anti-inflammatory drugs (NSAIDs) are among the most frequently detected pharmaceuticals in environmental samples and among the most widespread drugs in the world [5,6]. Diclofenac (2-(2,6-dichloranilino) phenylacetic acid, hereinafter DCF, chemical formula $C_{14}H_{11}Cl_2NO_2$), belongs to this family of medicines. DCF

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*Corresponding author.

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concentration in the environment is reported to be 250 ng L^{-1} at the inlet of wastewater treatment plants and 215 ng L^{-1} at the outlet of the plants, thus confirming that conventional treatments remove only a small percentage of this compound, max 14% [7]. In order to improve the removal efficiency of this compound for water source prevention and reclamation, the development of innovative technologies is therefore mandatory. Among the technologies aimed at the oxidization of organic pollutants, advanced oxidation processes (AOPs) are based on the generation of extremely reactive species, the OH radicals. Over the past two decades the AOP treatments have been studied from both the experimental and the theoretical point of view [8–12]. Despite their great potential in the field of WWT and the recent advances of scientific knowledge, AOPs are still scarcely employed on pilot and industrial scales. Moreover, they present several disadvantages of being energy- and material-intensive, and they often need further treatment to remove their residuals [13].

On the other hand, combined treatments based on UV light appear to be more eco-friendly, also with very interesting removal efficiencies if opportunely devised. Many of the common pharmaceutical compounds can be degraded by UV at disinfection doses [14–17]. Photodegradation of DCF has been scarcely investigated so far. Among the few results on DCF photolysis are those obtained by Shu et al. [13], whose investigations showed that diclofenac UV direct photolysis is very effective to remove DCF that reacts rapidly with hydroxyl radicals which was also confirmed by Packer et al. [18] who showed hydroxyl radical rate constant values approaching to diffusion-control limits. Giri et al. [19] reported that DCF is degraded very efficiently within short reaction periods regardless of the AOP employed. Fatta-Kassinos et al. [1] reports that 13 photoproducts have been identified, showing that the photolysis of DCF occurs by two main routes: one is the consequence of the initial photocyclisation of diclofenac into carbazole derivatives, while the other goes through the initial decarboxilation of diclofenac and further oxidation of the alkyl-chain, which are typical photolytic process reactions. As for the conventional removal of DCF, the work by Rivera-Utrilla et al. [7] shows that at least five by-products are formed in diclofenac chlorination, although none of them is a chloramine [20], and the degree of mineralization achieved is not acceptable. In addition, Lekkerkerker-Teunissen et al. [21] studied the degradation of a possible degradation product of diclofenac, carbazole, showing that it was not appreciably removed by UV or UV/H_2O_2 treatment. In the recent work by Keen et al. [22] the formation of a dimer was observed during the ultraviolet (UV) photolysis of diclofenac, confirmed by mass spectrometry, NMR and fluorescence analysis. The dimers were combinations of the two parent molecules or of the parent and the product of photolysis, and had visible colour.

This paper deals with a preliminary investigation concerning DCF removal by direct photodegradation. In particular, the effect of the irradiation time was investigated and the preliminary detection of DCF photolysis reaction by-products was carried out. Moreover the effect of photodegradation on carbazole, a dimer detected as the main by-product, was preliminary studied. Finally, a possible DCF degradation pathway by photolysis was proposed.

2. Materials and methods

2.1. Chemicals

A diclofenac sodium salt (Na-DCF) purchased by Sigma-Aldrich (UK) (CAS Number 15307-79-6), without any further purification, was used. Solution was made by using MilliQ water (20 mL, containing 20 mg L^{-1} DCF). Samples were directly analyzed after irradiation.

2.2. Experimental set-up

A lab-scale experimental device, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at fixed wavelength and intensity (254 nm; 400 mJ m^{-2}) was used to explore diclofenac removal from synthetic water streams. The results confirm the unexpected formation of the dimer carbazole, a very stable coloured intermediate, during the first minutes of photolysis, in agreement with literature findings. The experimental apparatus is shown in Fig. 1.

The irradiation of the aqueous samples was carried out in plastic Petri dishes of 90 mm diameter. The sample pH was adjusted by addition of NaOH or HCl. For the irradiation a Vilber-Lourmat BLX-254 with Ultraviolet wavelength of 254 nm was used. The temperature was measured and kept constant at 20°C in all the experiments.

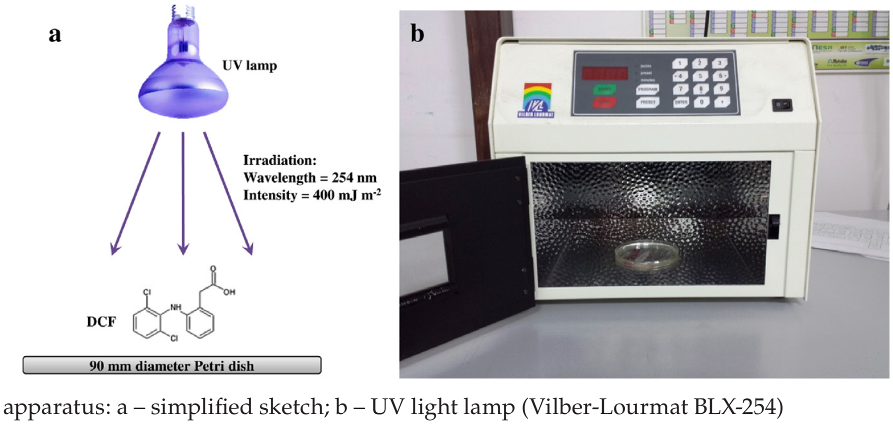

Fig. 1. Experimental apparatus: a – simplified sketch; b – UV light lamp (Vilber-Lourmat BLX-254)

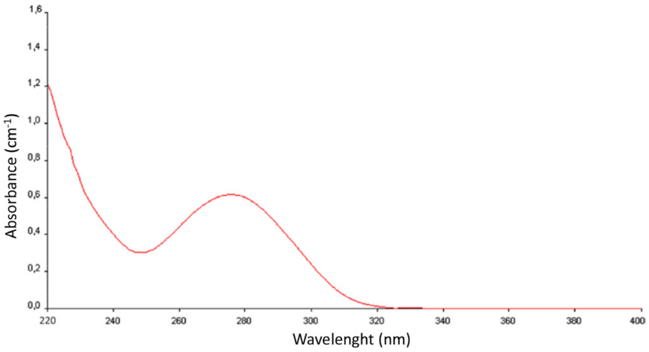

Fig. 2. Diclofenac absorbance spectrum

2.3. *Analysis*

An UV-V is field spectrophotometric analysis (Perkin Elmer LAMBDA 40) was carried out to assess by-product formation by DCF photodegradation. The absorbance spectrum of diclofenac is shown in Fig. 2. As illustrated, a typical peak in the wavelength range of 270–290 nm can be observed. The colour formed by the oxidation by products was measured at 400 nm.

Quantitative analyses have been carried out using a reverse phase high performance liquid chromatography (RP-HPLC system, Shimadzu) performed with a Shimadzu DAD detector (SPD-M20A), equipped with Shimadzu LC-20AD. The column used was a Discovery C18 (250 × 4.6 mm; 5 µm; Supelco, Bellefonte, PA), operated at 25°C.

The analytical measurement of the chloride ions in irradiated solution was performed by an ionchromatography (DIONEX DX-120) with conductivity detector. An Ion-Pac AS14A anion column (4 × 250 mm, Dionex) was used to perform separation.

3.Results and discussion

3.1 *Effect of irradiation time on DCF removal*

DCF removal was studied as a function of the irradiation time in the range 0–50 min. A solution volume of 20 mL, an initial solution pH of 6.6 and DCF concentration of 20 mg L^{-1} were used. Photodegradation experiments were carried out by using an UV-light with an irradiation wavelength of 254 nm and an intensity of 400 mJ m^{-2}. Experimental results are sketched in Fig. 3. Investigations were performed in triplicate; however, the average values are reported.

As shown, diclofenac removal rapidly increased with exposure time since a treatment time of 1 minute was sufficient to achieve a DCF degradation close to 60%, while after an irradiation time of 5 min diclofenac was almost completely treated and a DCF removal higher than 98% was obtained. In the range 5–50 min, no significant increase of DCF removal was found. Investigations highlight the extreme high degradation rate of diclofenac, in agreement with literature findings [22].

These results (Fig. 3) are supported by the UV-V is absorbance spectra of the irradiated solution monitored overt the exposure time in the range 0–5 min, as reported in Fig. 4. The colour formation was apparent after 5 min of oxidation as seen in Fig. 3.

3.2. *Formation of by-products*

As shown in Fig. 4, the characteristic absorbance spectrum of diclofenac (i.e. t = 0 min) was not more detected since by products were formed were found (i.e. t = 1–5 min). The results confirm the unexpected formation of the dimer carbazole, a very stable coloured intermediate, during the first minutes of photolysis, in agreement with findings by Keen et al. [20]. They observed dimer formation by irradiating sample solutions with UV fluence of 100 mJ cm^{-2}. Experiments were carried out by using both low (10 µg L^{-1}) and high (100 mg L^{-1}) diclofenac concentrations.

As shown in Fig. 4, samples at different exposure times produce the same spectrum, characterized by multiple peaks, in the wavelength ranges of 230–250 nm and 330–350 nm. This observation underlines the formation of the same by-product by diclofenac photodegradation. The trend of the spectra observed coincides with the typical spectrum of a dimer, the carbazole-1-acetic acid that is sketched in the box in Fig. 4. In agreement with several investigations [6,22–25] Carbazole was identified as the main by-product of the DCF photolysis.

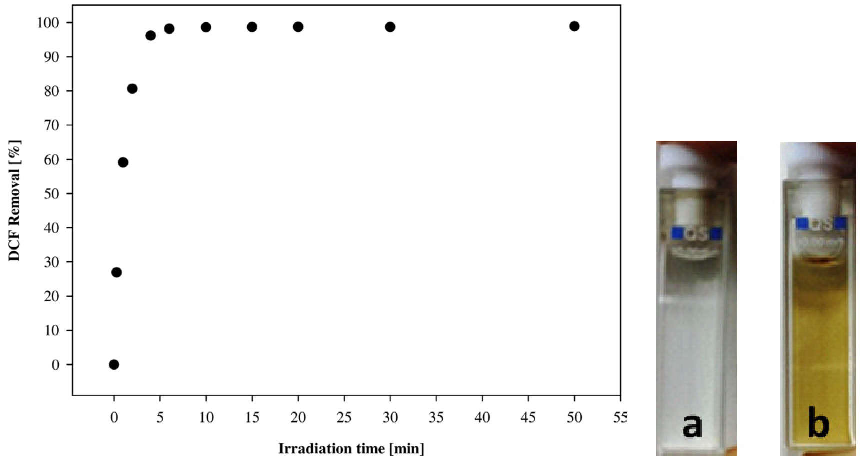

Fig. 3. Diclofenac removal as a function of the irradiation time. Colour of the investigated diclofenac solution is shown in a – before the UV light irradiation; b – after an irradiation time of 5 min.

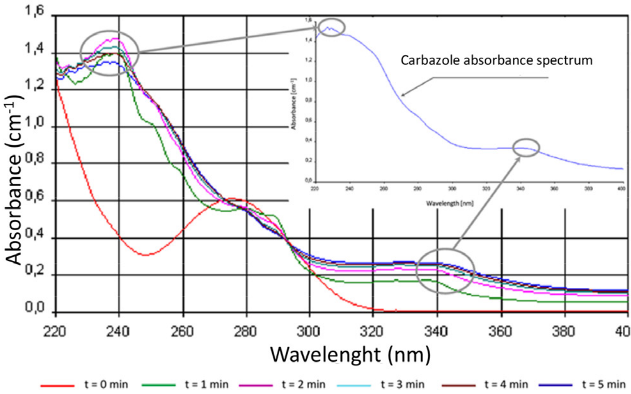

Fig. 4. By-product absorbance spectra of the diclofenac photodegradation (total irradiation time = 5 min)

The photolysis results were not used to quantify by-products, however a concentration of the dimer of about 8 mg L^{-1} was estimated with a treatment time of 5 min. Since no significant variation of DCF degradation was found, the concentration of the dimer can be supposed to be constant during the exposure time. In order to support this finding, UV-V is absorbance spectra of the irradiated solution monitored overt the exposure time in the range 10–30 min are reported in Fig. 5. As shown, no relevant changes may be observed in the width of absorbance spectra, in agreement with the results shown in Fig. 3. Moreover the persistence of the carbazole-1-acetic acid to the direct photolysis was highlighted, as reported by Lekkerkerker-Teunissen et al. [21] and Kanakaraju et al. [24].

A possible dimer formation pathway from the DCF degradation by photolysis is sketched in Fig. 6. As shown, carbazole-1-acetic acid formation can occurs starting from an epoxide production by the inclusion of dissolved oxygen, followed by the loss of both chlorine atoms [22,26]. The formation of the carbazole-1-acetic acid may be supported by the pH decrease that was observed during the investigations, from the initial value of 6.6 to the final value of 4.1, in agreement with literature results [22].

An ion chromatographic technique was used to carry out the analytical measurement of the ions in the treated solution. As shown by the ion chromatograph reported in Fig. 7, chloride ions were found in the irradiated solution and a concentration of about 15 mg L^{-1} was calculated. The detection of chloride ions may support the hypothesized pathway degradation based on the loss of chloride atoms from the diclofenac under an UV-light exposure treatment, in agreement with literature findings [27]. Calza et al. [27] investigated diclofenac photolysis over aqueous titania suspensions, detailing photodegradation by product formation and presenting fragmentation pathways. They observed a fragment at m/z 215 due to the loss of chlorine radicals, which are released as chlorine ions, in agreement with derivatives produced by diclofenac photodegradation, since chlorinated and dichlorinated intermediates disappeared after an hour of treatment [27].

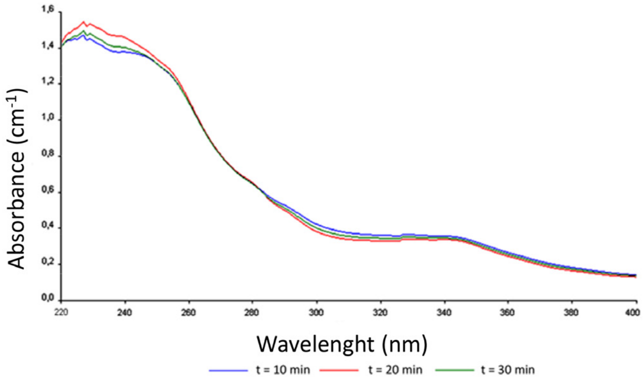

Fig. 5. By-product absorbance spectra of the diclofenac photodegradation (total irradiation time = 30 min)

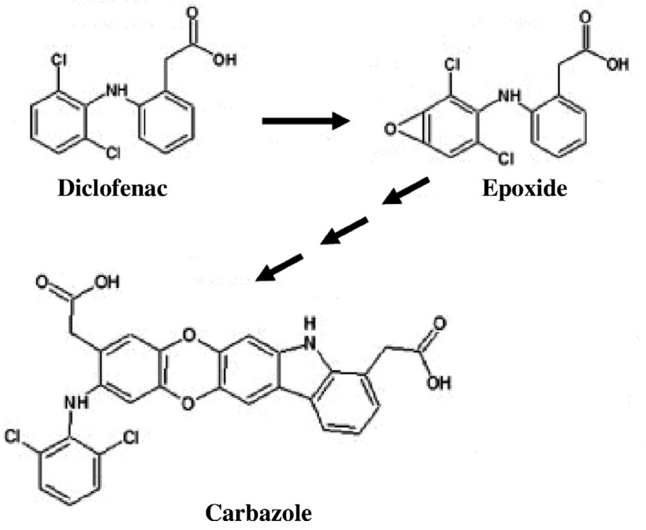

Fig. 6. Possible DCF photolysis degradation pathway.

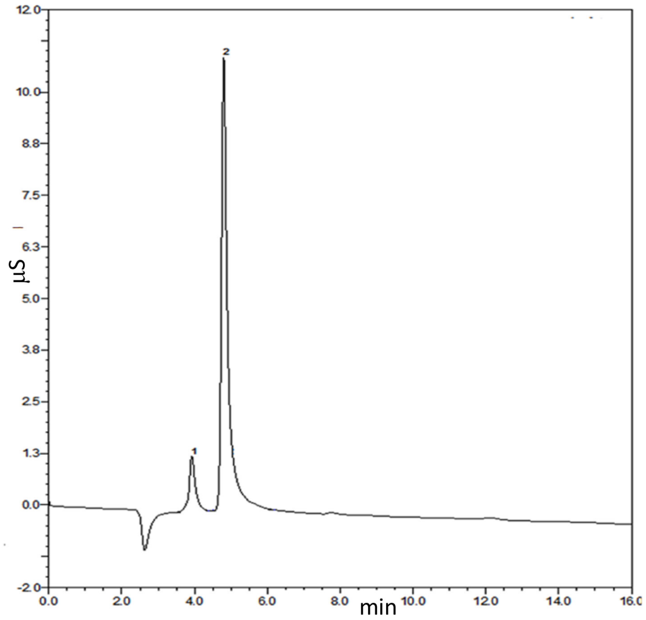

Fig. 7. Ion chromatograph of the irradiated solution (1 – Acetate ion; 2 – Chloride ion)

4. Conclusions

A preliminary investigation concerning the degradation of diclofenac from simulated water streams via direct UV-light irradiation was carried out; a lab-scale batch reactor, equipped with a lamp emitting monochromatic UV-light at a wavelength of 254 nm and an intensity of 400 mJ m^{-2}, was used. In particular, the effect of the irradiation time was investigated and the dimer carbazole was detected as the main by-product of the DCF photolysis reaction. Furthermore the effect of photodegradation on carbazole was studied.

The experimental tests have been carried out to evaluate the effect of treatment time on the diclofenac removal: the results show that after few treatment minutes the diclofenac has been almost completely degraded and a dimer, the carbazole, a very stable, persistent and coloured by-product, has formed. Moreover, the possibility of further degrading the obtained compound has been investigated, however an appreciable removal of the dimer has not been found. Finally, a possible dimer formation pathway from the DCF degradation by photolysis has been proposed.

The formation of the carbazole during the first minutes of photolysis, observed in the preliminary investigations, agrees with the recent and unexpected findings in literature.

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