Automated photochemical reactor based on sequential injection analysis. Application to the study of aqueous diclofenac photoproducts.

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Pharmaceuticals are considered as an emerging environmental problem due to their continuous input and persistence into the aquatic ecosystem. Drugs are excreted through urine or feces from the body, entering in wastewater as biologically active substances. Due to their low elimination efficiency in sewage treatment plants, they can further spread through the water cycle. A typical case is diclofenac (DCF), a popular non-steroidal anti-inflammatory drug (NSAID) used as analgesic, antiarthriitic and anti-rheumatic. DCF is one of the most frequently detected pharmaceuticals in surface waters and urban wastewaters, since its biodegradation and physical elimination (filtration and adsorption process) in wastewater treatment plants is limited. UV irradiation is often employed for disinfection of water, and it has been demonstrated to effectively reduce the concentration of diclofenac [1]. Also, photodegradation by sunlight can be considered other important process responsible of DCF degradation in environmental systems [2]. Several publications have reported the formation of transformation products (TPs) upon exposure of DCF to UV light and natural sunlight [1,2]. Nevertheless, there is still lack of data regarding their ecotoxicological effects, since TPs could be more toxic and dangerous than the DCF itself.

In this way, we propose a new system allowing the study of the degradation kinetics and the extent transformation of chemicals with different irradiation sources and time by an automatic method based on sequential injection analysis (SIA). As an example, DCF was studied, since the results can be compared to the literature. Photolysis experiments were carried out in a reactor with two types of lamps, one UV lamp (8 W), which is widely used for disinfection during water treatment, and one UV/VIS lamp (8 W), which was used to simulate the solar radiation. Preliminary studies were performed to confirm the DCF thermostability. Thus, in UV and UV/VIS conditions, DCF was fully degraded, following pseudo-first order kinetics, with half-lives ($t_{1/2}$) of 2.3 seconds for UV and 17 min for UV/VIS irradiations. Moreover, after the total disappearance of the parent compound, nine photoproducts could be identified by LC-MS and LC-MS/MS analysis with a high resolution Q-TOF instrument. With both lamps the same carbazole derivatives, formed by an initial step of cyclization of DCF and, by dechlorinations, decarboxylations or hydroxylations were generated. Some of these products have already been reported by other authors; however, four of them had not been identified until now. This indicates that the automated system can provide a better understanding of aqueous photoreaction routes. The photodegradation of drug was also evaluated in different water matrixes, being not affected by the dissolved organic matter present in real samples. A preliminary software estimation of the ecotoxicity of the detected TPs was performed with the EPA TEST software, where it can be observed that the toxicity of some TPs is predicted to be higher than DCF.

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