INSIGHTS INTO DICLOFENAC REMOVAL USING A SOLAR PHOTO-FENTON PROCESS MEDIATED BY FERRIOXALATE AT NEAR NEUTRAL PH

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ABSTRACT – This study evaluates the degradation of the drug diclofenac (DCF) in aqueous solutions by a photo-Fenton process using natural and simulated solar radiation. Literature describes that DCF precipitates at acid pH and Fenton's processes are more efficient at pH 2.8. In order to work at near neutral pH and iron concentrations below the discharge limits (2 ppm), a photo-Fenton process mediated by ferrioxalate was used. Different iron/oxalate molar ratios (1:3; 1:6 and 1:9) were tested at different pH values (5.0 and 6.0). At pH 6.0, a 1:9 iron/oxalate molar ratio was necessary to achieve complete degradation of the DCF solution (below the detection limit of the equipment) and 63% mineralization in 90 min. Lower dose of oxalic acid (1:3 iron/oxalate molar ratio) was needed to achieve the same results at pH 5.0. The reaction rate was also evaluated at different temperatures (15-45ºC), radiation intensities (27.8-59.9 W_{UV}/m^2), presence of inorganic ions (0.1 g/L; Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, NH_4^+) and radical scavengers (sodium azide 10 mM and D-mannitol 50 mM).

1. INTRODUCTION

Diclofenac is a nonsteroidal anti-inflammatory drug commonly used as analgesic. It is one of the compounds most found in aquatic environments. In general, it is present in low concentrations, but its continuous release may constitute a potential long-term risk to aquatic ecosystems. Although it is not expected that these compounds present a significant acute toxicity at low concentrations (typically μg/L or ng/L), they are persistent and bioaccumulation phenomena or synergistic toxicity should not be discarded (Bernabeu *et al.*, 2011). Korzeniewska *et al.* (2013) and Michael *et al.* (2013) reported that urban WWTPs are the major hotspots for the release of emerging pollutants to the aquatic ecosystems such as rivers and lakes. Pérez-Estrada *et al.* (2005a) showed that in combination with other pharmaceuticals compounds present in water samples, the toxic effect of DCF can be considerably increased.

Advanced oxidation processes (AOPs) are characterized by the production of reactive oxygen species, such as hydroxyl radicals (•OH), which are very reactive and non-selective. Among the solar AOPs, photo-Fenton process is one of the most studied since it can use radiation up to 580 nm,

representing 35% of the solar radiation spectrum (Trovó and Nogueira, 2011). The photo-Fenton reaction comprises the combination of hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}) and UV-Vis solar radiation resulting in the production of two moles of •OH per mole of H_2O_2.

DCF is a molecule whose ionization occurs in the carboxylic group (pKa = 4.15) (Trovó and Nogueira, 2011). At pH below 2.0, DCF is a neutral molecule (DCF-H). For pH values higher than 6.0, DCF mainly exists in the anionic form as DCF^-, by losing hydrogen at the carboxylic group. The application of a photo-Fenton process to the degradation of DCF at aqueous solutions has a critical limitation in terms of solution pH due to the fact that: i) above pH 3.0-3.5 ferric hydroxides starts to precipitate (Pignatello et al., 2006), ii) low solubility of DCF-H for pH < 4.0 (Pérez-Estrada *et al.*, 2005a), iii) DCF^- specie can form a stable complex with Fe^{3+}, limiting the photoreduction of Fe^{3+}, decreasing the decomposition of H_2O_2 in the Fenton reaction and the overall efficiency of the photo-Fenton process (Kenawi, 2005; Agatonović-Kuštrin et al., 1997). Although DCF precipitates at acid pH, its degradation occurs in the homogeneous phase governed by a precipitation-redissolution-degradation process (Pérez-Estrada *et al.*, 2005b).

In this work, the degradation of diclofenac aqueous solutions was performed using different processes (UV, H_2O_2, H_2O_2/UV, Fe^{3+}/H_2O_2/UV-Vis, Fe^{3+}/H_2O_2/UV-Vis and Fe^{3+}/H_2O_2 mediated by ferrioxalate with different iron/oxalate molar ratios) at lab-scale using a CPC photoreactor under simulated solar radiation. A solar photo-Fenton process mediated by ferrioxalate was applied to prevent the precipitation of iron and facilitate the degradation and mineralization of the drug (20 mg/L) at near neutral pH. The UV-Vis/ferrioxalate/H_2O_2 process is more efficient than the conventional photo-Fenton process, since ferrioxalate has a i) much higher quantum yields than ferric iron-water complexes; ii) can use a higher fraction of the solar radiation spectrum, up to 580 nm; iii) are photodecarboxylated under visible radiation; iv) provide a quicker pathway for Fe^{3+} regeneration accelerating thereby the process (Safarzadeh-Amiri *et al.*, 1997). The effect of different process variables, such as temperature, radiation intensity, presence of radical scavengers (sodium azide and D-mannitol) and some inorganic ions such as Cl^-, SO_4^{-2}, NO_3^-, NH_4^+ and HCO_3^-, were evaluated for the photo-Fenton process mediated by ferrioxalate at pH 5.0.

2. MATERIALS AND METHODS

Diclofenac sodium was purchased from Sigma-Aldrich. Acetonitrile and dried oxalic acid were obtained from Merck. NaCl, Na_2SO_4, $NaNO_3$, $NaHCO_3$, NH_4Cl, NaN_3 and D-mannitol were used in analytical grade. $FeCl_3.6H_2O$ and H_2O_2 50% were used in photo-Fenton experiments. Pharmaceutical solution was prepared by diluting a weighted amount of DCF salt in pure water.

The AOPs experiments were carried out in a lab-scale photoreactor with artificial sunlight comprising: i) a solar radiation simulator (ATLAS, model SUNTEST XLS) with 1100 cm^2 of exposition area, a 1700 Watt air-cooled xenon arc lamp, a daylight filter and quartz filter with IR coating; ii) a compound parabolic collector (CPC) with 0.026 m^2 of illuminated area with anodized aluminium reflectors and Duran tube (cut-off at 280 nm, internal diameter 46.4 mm, length 161 mm and thickness 1.8 mm); iii) one glass vessel (capacity of 1.5 L), covered with aluminium paper, with a cooling jacketed coupled to a refrigerated thermostatic bath (Lab. Companion, model RW-0525G) to

ensure a constant temperature during the experiment; iv) a magnetic stirrer (Velp Scientifica, model ARE) to ensure complete homogenization of the solution inside the glass vessel; v) one peristaltic pump (Ismatec, model Ecoline VC-380 II, with a flow of 0.55 L/min) to promote the water recirculation between the CPC and the glass vessel; vi) pH and temperature meter (VWR symphony - SB90M5). The UVA irradiance was measured by a broadband UV radiometer (Kipp & Zonen B.V., model CUV5), which was placed on the interior of sunlight simulator at the same level than the photoreactor center. The radiometer was plugged into a handheld display unit (Kipp & Zonen B.V., model Meteon) to record the incident irradiance (W_{UV}/m^2), measured in the wavelength range from 280 to 400 nm.

The recirculation glass vessel of the lab-scale prototype was filled with 1.6 L of DCF solution (20 mg/L), which was pumped to the CPC unit and homogenized by recirculation in the closed system during 15 min in the darkness. Afterwards, pH was slightly increased (to prevent DCF precipitation with oxalic acid addition), then oxalic acid was added (iron/oxalate molar ratio of 1:3; 1:6 or 1:9), pH was adjusted and controlled (5.0 or 6.0) with sulfuric acid/sodium hydroxide and ferric chloride was added (2 mg Fe^{3+}/L). The temperature set-point of the refrigerated thermostatic bath was controlled to keep the solution in the intended temperature (25ºC). The suntest was turned on and the radiation intensity was defined at 350, 500 or 700 W/m^2, which is equivalent to 27.8, 41.6 and 59.9 W_{UV}/m^2 measured in the wavelength range from 280 to 400 nm. Afterward, a theoretical stoichiometric amount of H_2O_2 necessary to complete mineralize the 20 mg/L DCF solution ($[DCF_0]/[H_2O_2] = 1:33$ (molar)) was all added at the beginning of the reaction and samples were taken at pre-defined times to evaluate the degradation process.

Solar experiments were carried out in a CPC pilot plant photoreactor installed at the roof of the Chemical Engineering Department of the Faculty of Engineering, University of Porto (FEUP), Portugal. The pilot plant was operated with 0.455 m^2 of CPCs and a working volume of 15 L. The experimental procedure was equal to that described for the lab-scale system. The UV radiation was measured with a UV radiometer global PLS-ACADUS 85, placed in the pilot plant with the same inclination of the reactor. All assays were conducted in batch mode for 90 min with continuous recirculation flow and recycle.

The process efficiency was evaluated in terms of dissolved organic carbon removal, measured in a TC-TOC-TN analyser equipped with ASI-V autosampler (Shimadzu, model TOC-VCSN) and DCF degradation, using a HPLC-VWR Hitachi ELITE LaChrom (Merck–Hitach, Tokyo, Japan) with reverse-phase column (PuroSpher® Star RP-18 endcapped: 125 x 4 mm). The quantification and detections limits for DCF were 0.07 and 0.02 mg/L, respectively. HPLC quantification was performed with isocratic method, 60% acetonitrile and 40% oxalic acid 0.014 M, 1 mL/min during 7 min. During the experiments, H_2O_2 and total dissolved iron concentrations were determined by colorimetric method with ammonium metavanadate and orthophenanthroline, respectively.

The accumulated UVA energy ($Q_{UV,n}$, kJ/L) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt, is calculated using the Equation 1, where t_n is the time corresponding to n-water sample (s), V_t the total reactor volume (L), A_r the illuminated collector surface area (m^2) and $\overline{UV}_{G,n}$ the average solar ultraviolet

radiation (W/m^2) measured during the period Δt_n (s).

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{1000 \times V_t}; \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

2. RESULTS AND DISCUSSION

Firstly, the efficiency of different AOPs was evaluated in the DCF degradation at pH 6.2 ± 0.2 as shown in Figure 1. In the absence of UVA radiation (H$_2$O$_2$ and Fenton reaction), DCF degradation or mineralization is negligible, mainly due to the low oxidant power of H$_2$O$_2$ and ferric iron precipitation. UVA, H$_2$O$_2$/UVA and Fe^{3+}/H$_2$O$_2$/UVA processes results in a low DCF removal, due to three main factors: i) only a small fraction of UVA-Vis solar radiation is absorbed by the DCF molecule; ii) photolysis of H$_2$O$_2$ is not significant due to the fact that radiation below 280 nm is needed for an effective H$_2$O$_2$ cleavage, and borosilicate glass tubes have a cut-off at 280 nm; and iii) ferric iron precipitation (Pignatello et al., 2006). Results reported by several authors (Pérez-Estrada *et al*., 2005a,b) showed the same limitations for DCF removal using AOPs at neutral pH values. On the other hand, the photo-Fenton reaction mediated by ferrioxalate increased substantially the DCF degradation rate, since avoids ferric iron precipitation and enhances the absorption of solar photons until 580 nm. However, the ferrioxalate complexes are rapidly photodecarboxylated under visible radiation, leading to iron precipitation and DCF degradation stops. An iron/oxalate molar ratio of 1:9 was necessary to achieve complete degradation of the DCF solution (below the detection limit) and 63% mineralization in 90 min (3.65 kJ$_{UV}$/L) at pH 6.2 ± 0.2.

Only nearly 0.81 kJ$_{UV}$/L of accumulated UVA energy (20 min) was necessary to achieve DCF removal values of 53%, 74% and 94% using iron-oxalate molar ratios of 1:3, 1:6 and 1:9, respectively. A DCF removal of only 25% after 3.65 kJ$_{UV}$/L (90 min) was achieved for the photo-Fenton process without addition of oxalic acid, due mainly to the precipitation of Fe(OH)$_3$ (Fig. 1), confirming the important role of oxalic acid to keep the iron complexes in solution. Trovó and Nogueira (2011) reported the complete degradation of 33.4 mg/L of DCF and 45% mineralization over 10 min under similar pH conditions (pH = 5.0), with 68 mg/L H$_2$O$_2$ (30%) and 0.2 mM of ammonium iron(III) citrate (above iron discharge limits imposed by the Portuguese law), using artificial solar irradiation in a lab-scale system. However, after the same reaction period, DCF removal values of only 77% and 62% where achieved at pH 6.0 and 7.0.
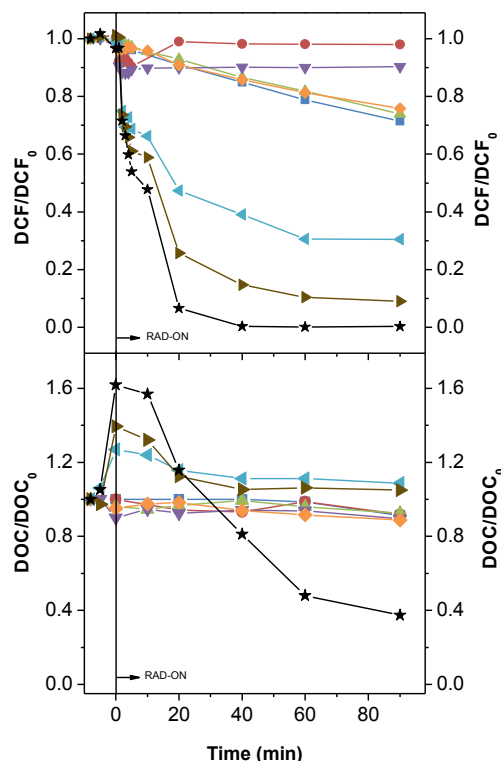
Figure 1. Effects of different AOPs on degradation of DCF ($[DCF]_0$ = 20 mg/L) at pH 6.2 ± 0.2.
(■) – UVA; (●) – H_2O_2; (▲) – H_2O_2/UVA; (▼) – Fe^{3+}/H_2O_2; (◆) – Fe^{3+}/H_2O_2/UVA;
(◄) – Fe^{3+}/H_2O_2/oxalic acid/UVA (1:3 – iron/oxalate molar ratio); (►) – Fe^{3+}/H_2O_2/oxalic acid/UVA
(1:6 – iron/oxalate molar ratio); (★) – Fe^{3+}/H_2O_2/oxalic acid/UVA (1:9 – iron/oxalate molar ratio).
(time = 90 min, $[Fe^{3+}]$ = 2 mg/L, T = 25ºC, I = 41.6 W_{UV}/m^2).

Due to high doses of oxalic acid needed at pH 6.2, the efficiency of the photo-Fenton reaction mediated by ferrioxalate was also evaluated at pH 5.0 ± 0.1 with 2.0 mg Fe^{3+}/L (0.036 mM) and using iron/oxalate molar ratios of 1:3 (with and without addition of H_2O_2) and 1:6. Figure 2 shows a DCF degradation efficiency of 50% for the experiments without addition of H_2O_2, which can be attributed to photodecarboxylation of ferrioxalate complexes leading to the generation of radicals species ($C_2O_4^{\bullet-}$; $CO_2^{\bullet-}$; $O_2^{\bullet-}$; $HO_2^{\bullet}$) and with H_2O_2 addition, which will react with ferrous iron leading to the formation of $^{\bullet}OH$ radicals. A generation of 0.1 mM H_2O_2 was also observed during the reaction with no H_2O_2, confirming the formation of H_2O_2 in intermediate reactions. Figure 2 also shows a complete removal of DCF, below the detection limit of the analytical method, and approximately 55% and 60% mineralization at pH 5.0 using iron/oxalate molar ratios of 1:3 and 1:6, respectively. On the other hand, at pH 6.0, to achieve the same results, it is needed an iron/oxalate molar ration of 1:9, as reported in the previous section. Considering that DCF degradation efficiency, degree of mineralization and H_2O_2 consumption were similar for reactions at pH 5.0 (iron/oxalate molar ratios of 1:3 and 1:6) and pH 6.0 (iron/oxalate molar ratio of 1:9), and low amounts of oxalic acid minimizes the operation costs, further experiments were performed at pH 5.0 with an iron/oxalate molar ratio of 1:3.
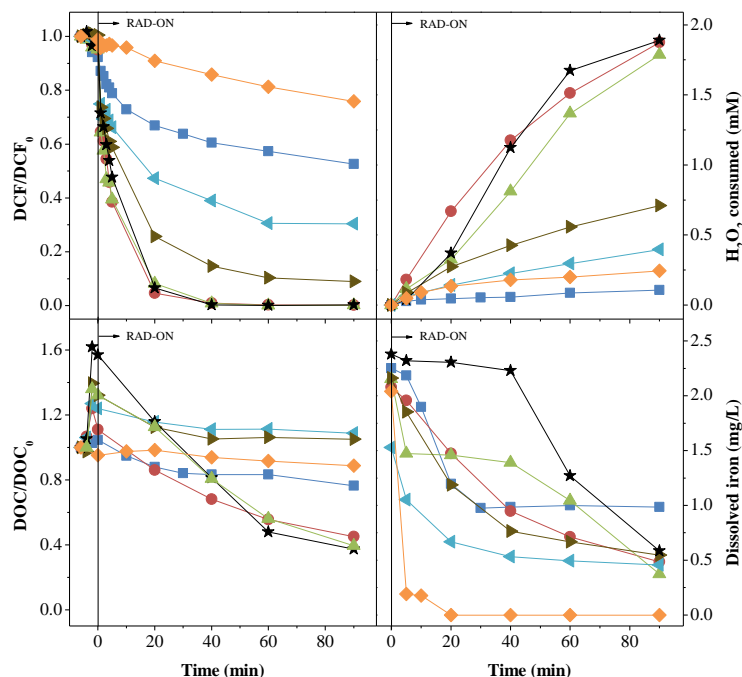
Figure 2. Evaluation of the photo-Fenton efficiency using different iron/oxalate molar ratios at pH 5.0 (■) – 1:3 (no H_2O_2), (●) – 1:3 and (▲) – 1:6, and at pH 6.0 (◄) – 1:3, (▶) – 1:6, (★) – 1:9, and (◆) – no oxalic. ($[DCF]_0$ = 20 mg/L, $[Fe^{3+}]$ = 2 mg/L, T = 25°C, I = 41.6 W_{UV}/m^2).

Although the effect of solution temperature (T), according to the range of temperatures tested (15-45ºC), on the reaction rate was negligible, a slight increment in the H_2O_2 consumption was verified mainly attributed to the thermal Fenton reaction and H_2O_2 decomposition (the rate of decomposition of hydrogen peroxide doubles every time the temperature rises by 10ºC) (Figure 3). For temperatures of 15, 25 and 35°C, DOC profile were similar (47%, 55% and 49%, respectively), and increasing temperature to 45°C, DOC removal increased to 72% after 90 min.

The increase of UVA irradiance (I) from 27.8 to 41.6 W_{UV}/m^2, showed also a negligible influence on the reaction kinetic rate (concerning UVA energy). However, for the irradiance of 59.9 W_{UV}/m^2, the reaction rate decreased slightly, since the amount of light absorbing species present in the solution, mainly iron complexes, considering the UVA-visible radiation, are not enough to absorb all the emitted photons in the optic length of the reactor, and a part of the photons are lost provably (Figure 3). The decrease of H_2O_2 consumption with the increase of the radiation intensity may be attributed to the predominance of the photochemical pathway involving ferric ions regeneration in detriment of thermal Fenton reaction.

Figure 3 also shows that the presence of inorganic ions (0.1 g/L Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, NH_4^+), considering the concentration used, does not interfere in DCF removal reaction rates. In the same way, DOC degradation profile were similar for all inorganic ions, achieving DOC removal of 66%, 59%, 63%, 62% and 63% after 90 min in the presence of Cl^-, SO_4^{2-}, NH_4^+, HCO_3^- and NO_3^-, respectively. Selective scavengers D-mannitol (50 mM) and sodium azide (NaN_3 10 mM) were used

to assess the role of reactive oxygen species, hydroxyl radical ($^{\bullet}OH$) and singlet oxygen ($^{1}O_2$), respectively, on the photocatalytic degradation of DCF. Figure 3 shows that DCF degradation is mainly attributed to the $^{\bullet}OH$ attack, while $^{1}O_2$ plays a negligible role. Degradation mechanism can also be explained by the participation of the radicals species generated during the photodecarboxylation of ferrioxalate complexes. Pilot plant results using natural solar radiation (pH 5; iron/oxalic molar ratio of 1:3; $[Fe^{3+}] = 2$ mg/L) were similar to those obtained at lab-scale, achieving ~ 63% mineralization and complete DCF removal below the detection limit after 90 min (average temperature and UV radiation intensity of 32 ºC and 38.8 W_{UV}/m^2, respectively). The degradation kinetics of DCF at lab and pilot scale were very similar, consuming 1.35 mM H_2O_2 to achieve complete DCF degradation below the detection limit.
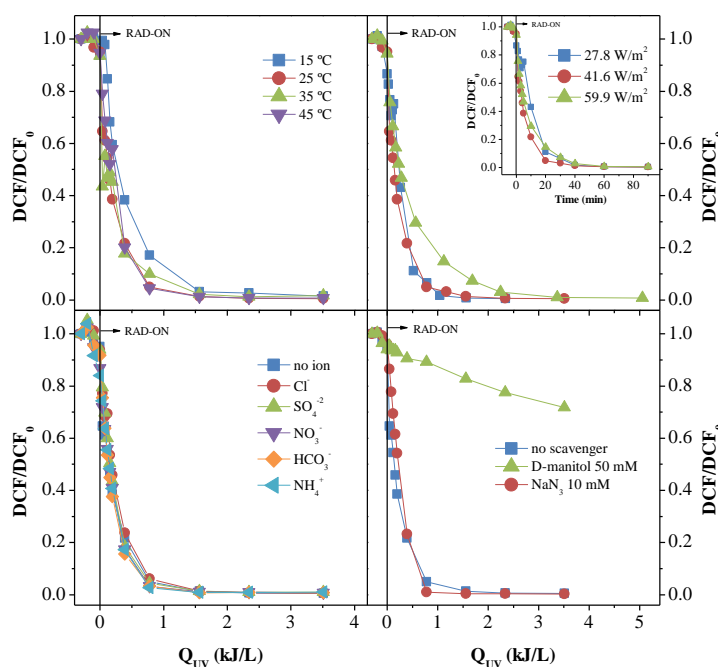

Figure 3. Evaluation of the UVA-Vis/ferrioxalate/H_2O_2 efficiency at different temperatures, radiation intensities, inorganic ions and radicals scavengers ($[DCF]_0 = 20$ mg/L; time = 90 min; pH = 5; $[Fe^{3+}] = 2$ mg/L; iron/oxalate molar ratio of 1:3, $T = 25$ºC, $I = 41.6$ W_{UV}/m^2).

CONCLUSION

Process intensification of a solar photo-Fenton reaction with ferrioxalate complexes showed promising results in the elimination of diclofenac at lab and pilot scale, as a model compound of emergent pollutants, at near neutral pH conditions, and using low iron concentrations ($[Fe^{3+}] = 2$ mg/L). pH and iron/oxalic acid molar ratio play an important role on the ferric species present in solution, which presents different quantum yields for Fe(II) formation, affecting greatly the efficiency of the photo-Fenton reaction. To achieve complete removal of DCF below the detection limits, after 90 min of reaction period ($T = 25$ ºC and $I = 41.6$ W_{UV}/m^2), it was necessary an iron/oxalate molar ratio of 1:3 at pH 5.0 and 1:9 at pH 6.0, resulting in 55% and 63% mineralization, consuming 2.0 and

1.9 mM H_2O_2, respectively. Although the DCF degradation was mainly attributed to hydroxyl radicals, other radicals species formed during the photodecarboxylation of ferrioxalate complexes also can play an important role. The presence of inorganic ions, such as sulphate, chloride, nitrate, ammonium and bicarbonate, with a concentration of 0.1 g/L, temperature (15-45°C) and irradiance (27.8-59.9 W_{UV}/m^2), did not influence significantly the DCF kinetic reactions rates.

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