

PROCESS INTENSIFICATION AT NEAR NEUTRAL pH OF A HOMOGENOUS PHOTO-FENTON REACTION USING FERRICARBOXYLATE COMPLEXES: APPLICATION TO OXYTETRACYCLINE DEGRADATION

J.H.O.S. PEREIRA^{1,2}, D.B. QUEIRÓS^{3,4}, A.C. REIS^{1,5}, O.C. NUNES^{1,5}, M.T. BORGES^{3,4},
R.A.R. BOAVENTURA^{1,2}, V.J.P. VILAR^{1,2*}

¹University of Porto, Faculty of Engineering, Chemical Engineering Department

²LSRE - Laboratory of Separation and Reaction Engineering,

³University of Porto, Faculty of Sciences, Biology Department

⁴CIMAR - Centre for Marine and Environmental Research

⁵LEPABE – Laboratory of Process Engineering, Environment, Biotechnology and Energy

*Corresponding author: vilar@fe.up.pt

Abstract – This work demonstrates the application at near neutral pH of the photo-Fenton process mediated by ferricarboxylates on the treatment of aqueous solutions containing the antibiotic Oxytetracycline (OTC) under solar irradiation. The formation of a Fe:OTC complex after Fe²⁺ oxidation to Fe³⁺, in the presence of H₂O₂, showed the inconvenience of using the conventional Fe²⁺/H₂O₂/UV-Vis process at near neutral pH levels, as the Fe:OTC complex is retained in the filter. To overcome this, a Fe³⁺/Oxalate process was proposed. Process efficiency was evaluated for variables such as Fe³⁺ concentration and pH, using a compound parabolic collector (CPC) photoreactor at lab-scale under simulated solar radiation. The effect of the matrix was also tested by spiking OTC into two different real wastewaters.

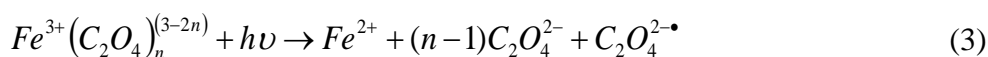
1. INTRODUCTION

Antibiotics are a special group of pharmaceuticals used to control infection diseases in human and veterinary medicine. Residual concentration have been detected in various environmental compartments worldwide due to the fact that a large percentage of the consumed antibiotics are not completely metabolized (and thus are excreted as active substances) and that conventional wastewater treatment methods fail to completely remove them from solution (Kümmerer, 2009).

Advanced oxidation processes (AOPs), a class of treatments involving different ways of generating the highly reactive and non-selective hydroxyl radical ([•]OH) and other reactive oxygen species (Gogate and Pandit, 2004), have been considered for the removal of these substances, especially those involving catalysis and solar irradiation such as the photo-Fenton process (Homem and Santos, 2011). Photo-Fenton comprises the combination of ferrous iron (Fe²⁺) with hydrogen peroxide (H₂O₂) and (solar) UV-Vis radiation resulting in the production of two moles of [•]OH per mole of hydrogen peroxide (Eq. 1 and 2), as simplified by Gogate and Pandit (2004):



Pertinent to this process is the formation of stable complexes between antibiotics such as Oxytetracycline (OTC) and Fe (II) and Fe (III) (Figuerola and Mackay, 2005). It not only decreases degradation efficiencies (due to a lower iron availability to react with hydrogen peroxide), but it may also lead to mistaken readings in analytical equipments. However, this can be overcome by recurring to complexation of Fe (III) with carboxylate ions, which also improves the photo-Fenton process by extending the solubility of iron to higher and more practical pH values, by presenting stronger radiation absorption at wavelengths until 580 nm and by increasing the quantum yield of Fe^{2+} production according to Eq. 3 (Pignatello et al., 2006).



In this context, the aim of this work was the process intensification at near neutral pH conditions of a homogeneous solar photo-Fenton reaction through the use of ferrioxalate complexes applied to the removal of Oxytetracycline in aqueous solutions. Experiments at lab-scale using a CPC photoreactor under simulated solar radiation were performed to i) compare the conventional $Fe^{2+}/H_2O_2/UV-Vis$ with the $Fe^{3+}/Oxalate\ H_2O_2/UV-Vis$ system, ii) choose the optimum dissolved Fe (III) concentration (iron/oxalate molar ratio of 1:3) and also iii) the initial working pH level. Matrix effects were studied by spiking OTC in two different media, a WWTP effluent after secondary treatment and a real troutfarm effluent.

2. EXPERIMENTAL

The experiments were carried out in a lab-scale photoreactor provided with a sunlight simulator. A schematic representation and a detailed description can be consulted elsewhere (Soares et al., 2013). A stirred tank was filled with 20 mg L⁻¹ OTC solution (total volume (V_t) = 1.2 L). This solution was continuously pumped with a peristaltic pump to a Duran reactor equipped with a CPC collector (illuminated volume (V_i) = 270 mL; collector area (A_{CPC}) = 0.023 m²) placed inside an ATLAS SUNTEST CPS+, and recirculated to the tank at a flow rate of 0.65 L min⁻¹. The thermostatic bath was set to keep the solution temperature at 25°C. After 15 min, a sample was taken to confirm initial OTC and Dissolved Organic Carbon (DOC) concentrations. In the $Fe^{2+}/H_2O_2/UV-Vis$ experiments, the initial pH was adjusted to 3.0, 4.0 or 5.0 with sulfuric acid and another sample was taken after 15 min. Iron (II) sulfate was added in order to achieve a concentration of 2 mg L⁻¹ Fe (II). The solution was left to homogenize for 15 min, after which another sample was taken, and the initial iron concentration was also confirmed. Immediately after irradiation began, an initial 30 mg L⁻¹ H₂O₂ dose was added (it kept between 10 and 30 mg L⁻¹, with a total addition around 2 mM), while the pH of the solution was left uncontrolled. The same procedure was followed in the $Fe^{3+}/Oxalate/H_2O_2/UV-Vis$ experiments, except for the addition of a 1:3 iron/oxalate molar ratio dose, before the pH adjustment and iron (III) chloride addition steps. The solution was left to homogenize for 15 min, after which another sample was taken, and the initial iron concentration was also confirmed. The light source was a vapour Xenon lamp (300 nm < λ

< 800 nm) and UV irradiance was set at $I_{300-400\text{ nm}} = 44\text{ W m}^{-2}$. Equation 4 was used to calculate the accumulated UV energy ($Q_{UV,n}$, kJ L^{-1}) received on any surface in the same position regarding the lamp, per unit of volume of water inside the reactor, in time interval Δt :

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{1000 \times V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (4)$$

where t_n is the experimental time of each 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).

Matrix effects were studied by spiking OTC in two different effluents (main characteristics in Table 1), and compared to the analogous results obtained using deionized water (DW). Wastewater effluent (WW) was collected after secondary treatment in a urban WWTP (Northern Portugal), while trout farm effluent (TF) was collected in the outlet of a trout farm operated in open circuit regime (Northern Portugal), after final decantation.

Table 1 - Main characteristics of the tested effluents, before the OTC-spike step.

Effluent	pH	DOC / IC (mg L^{-1})	Average anion concentrations (mg L^{-1})		
			[PO_4^{3-}]	[Cl]	[SO_4^{2-}]
WW	6.46	5.5 / 5.1	13.5	61.5	42.9
TF	6.70	3.9 / 1.8	0.95		

Antibiotic degradation was followed by HPLC-DAD, its mineralization by DOC removal, H_2O_2 and total dissolved iron concentrations were determined colorimetrically using the vanadate and 1,10-phenantroline methods, respectively. A pseudo-first-order mathematical model was used to describe the experimental kinetic data using a non-linear regression method.

3. RESULTS AND DISCUSSION

3.1 Conventional $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ Reaction

The results of the conventional $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-Vis}$ degradation of OTC under different initial pH values (3.0, 4.0 and 5.0) are shown in Figure 1. The concentration of Fe (II) was 2 mg L^{-1} , which is the total iron discharge limit into any water body, according to the Portuguese legislation (D-L 236/98). In the three experiments, after the first addition of H_2O_2 , the concentration of OTC approached LOQ levels approximately after 4 min of illumination ($0.22\text{ kJ}_{\text{UV}}\text{ L}^{-1}$). The DOC levels slowly decreased down to near 30% of their initial values by the end of the photo-treatment period (45 min, $2.7\text{ kJ}_{\text{UV}}\text{ L}^{-1}$), while an average of 1.5 mM of H_2O_2 was consumed.

Taking into consideration Eq. 1, after the Fe (II) oxidation step to Fe (III), the rapid decay of the antibiotic may be explained by the formation of stable complexes between OTC and Fe (III), which strongly interferes with HPLC measurements (Figuerola and Mackay, 2005) and may thus induce in erroneous kinetic calculations. Overall stability constants of the Fe (II)-OTC and Fe (III)-OTC complexes of 10.4 and 22.0, respectively (Albert, 1953), support this conclusion. We have attempted to model the complex formation between OTC and Fe (III) using the equilibrium computer program MINEQL+ (Schecher and McAvoy, 2003). As it can

be seen in Fig. 1b (left), a large fraction of Fe (III) is expected to form complexes with the antibiotic. Bench-scale tests confirmed that by increasing the pH from 3.0 towards 5.0 of solutions containing only 2 mg L⁻¹ Fe (III) and 20 mg L⁻¹ of OTC, the original concentration of OTC not only gradually decreases but it also differs from filtered and non-filtered samples (data not shown). The same phenomenon occurs with DOC. As such, the complete removal of OTC from solution by the conventional photo-Fenton reaction with increasing initial pH values could not be directly attributed.

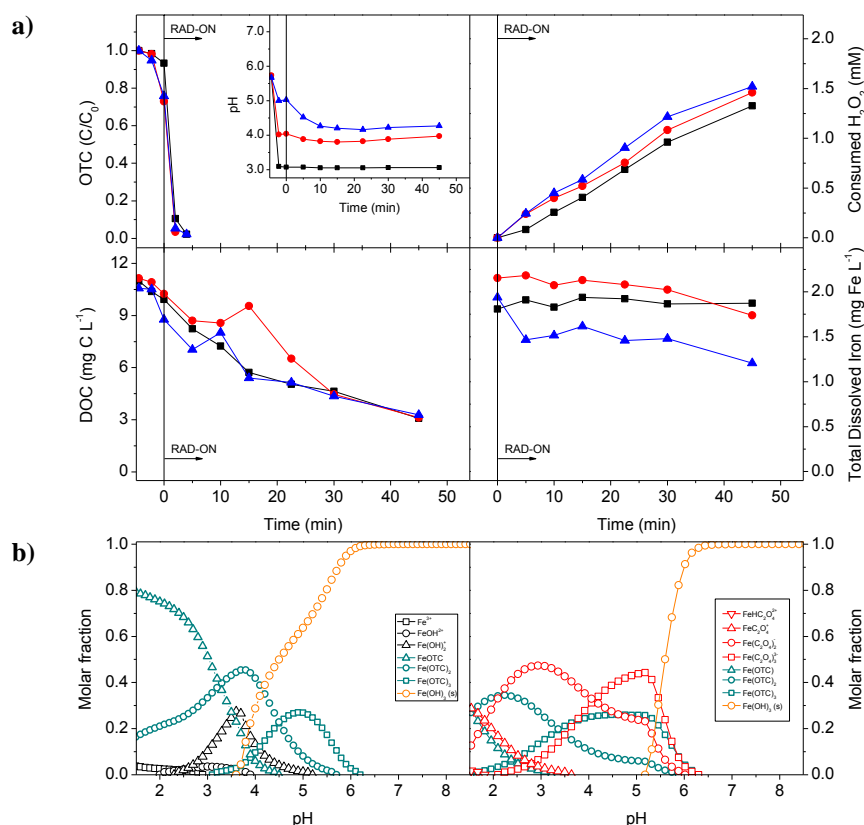


Figure 1 - a) Effect of initial pH (■ - pH = 3.0; ● - pH = 4.0; ▲ - pH = 5.0) on the degradation of OTC, DOC removal, H₂O₂ consumption, total dissolved iron and pH using the conventional solar photo-Fenton process mediated by 2 mg L⁻¹ Fe (II); **b)** Speciation diagrams for iron (III) as a function of pH in a solution containing 20 mg L⁻¹ of OTC and 3.58 × 10⁻² mM (2 mg L⁻¹) of Fe (III) without accounting (left) or accounting (right) for 1.07 × 10⁻¹ mM (9.5 mg L⁻¹) oxalic acid. Ionic strength = 4 mM.

Silva et al. (2010) have demonstrated how the addition of organic ligands such as oxalate displace the herbicide tebuthiuron (TBH) from the non-photoactive Fe (III)-TBH complex, improving the degradation process of TBH via the photo-Fenton reaction. In this way, we have introduced the oxalate and iron-oxalate equilibrium reactions in MINEQL+ in order to calculate the formation of complexes between the same amount of Fe (III), OTC, and 9.5 mg L⁻¹ oxalate (1:3 iron/oxalate ratio) present in solution. Fig. 1b (right) shows that the added oxalate clearly competes with OTC for the available Fe (III) in the pH range of interest. The concentration of OTC can thus be properly followed by HPLC-DAD, which allows for a proper kinetic study. Taking this and the objective of operating this process at neutral pH values into consideration, the ability of oxalate to improve the photo-Fenton process was henceforth studied.

3.2. Fe³⁺/Oxalate/H₂O₂/UV-Vis OTC degradation reactions

Influence of iron concentration: Fig. 2 presents the OTC degradation efficiency by the photo-Fenton reaction using low iron concentrations in the threshold of the iron discharge limit (1.0, 2.0 and 5.0 mg L⁻¹), with an iron/oxalate molar ratio of 1:3, without initial pH adjustment.

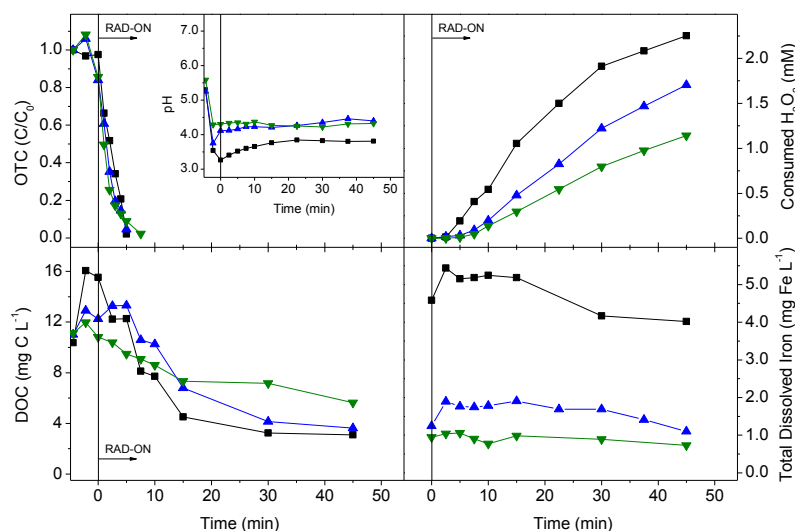


Figure 2 - Effect of Fe (III) concentration (∇ – 1.0 mg L⁻¹; \blacktriangle – 2.0 mg L⁻¹; \blacksquare – 5.0 mg L⁻¹) on OTC degradation, DOC removal, H₂O₂ consumption, total dissolved iron and pH using the Fe³⁺/Oxalate/H₂O₂/UV-Vis system.

The degradation profiles were very similar for all tested Fe (III) concentrations. Even with the lowest tested concentration, OTC was no longer detected (LOD = 0.10 mg L⁻¹) after 10 min of reaction (~0.6 kJ_{UV} L⁻¹). By the end of the photo-treatment period (45 min, 2.75 kJ_{UV} L⁻¹), 80% mineralization was achieved with both 2 and 5 mg L⁻¹ of Fe (III), although a higher H₂O₂ consumption occurred with the highest Fe (III) concentration. In contrast, for 1 mg L⁻¹ of Fe (III) only ~50% mineralization was achieved, with less H₂O₂ consumed than for the other Fe (III) concentrations. A direct relationship between the increases in \cdot OH formation and the Fe dosage is expected according to Eq. 1. The avoidance of the need of an iron removal step at the end of the treatment, associated with a satisfying mineralization degree, has shown 2 mg L⁻¹ to be the concentration that represented the working option for photo-Fenton treatment with Fe (III)-oxalate complex. The pseudo-first order kinetic rate constant of the 2 mg L⁻¹ experiment, 8.6 ± 0.5 L kJ⁻¹, was the double of the rate constant reported in our previous work regarding the solar photocatalytic degradation of OTC in the presence of 0.5 g L⁻¹ TiO₂ at a neutral pH, carried out with the same experimental installation, 4.3 ± 0.4 L kJ⁻¹ (Pereira et al., 2013).

Influence of initial solution pH: The effect of the initial solution pH value was then studied in order to find the highest possible working pH without compromising reaction efficiency. The results, presented in Fig. 3, show that with unadjusted initial pH (~4.1), pH = 5.0 and pH = 6.0, OTC was no longer detected after 5, 10 and 15 min of illumination time (0.3, 0.6 and 0.9 kJ L⁻¹ of Q_{UV} , respectively). By the same order, DOC concentration was reduced by 75, 51 and 37% of its initial value after 45 min of reaction (2.78 kJ_{UV} L⁻¹). The decreasing reaction rates at pH ~ 4.1, pH = 5.0 and pH = 6.0 experiments, 8.6 ± 0.5 , 6.3 ± 0.2 and 2.3 ± 0.1 L⁻¹ kJ, respectively, appear to reflect the relationship between the molar fractions

of the referred iron-oxalate complexes and their respective quantum yields (at 436 nm, 1.40 for $\text{Fe}(\text{C}_2\text{O}_4)_2^-$ and 1.00 for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ (Weller et al., 2013). Cumulatively, $\text{Fe}(\text{C}_2\text{O}_4)_2^-$ and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ are the main iron species in the studied pH range, albeit with changing proportions over pH (Fig. 1b, right). At pH = 6.0, total iron precipitation would be expected. However, this precipitation occurs slowly, and Fe (III) may not be in equilibrium with the solid phase (Balmer and Sulzberger, 1999), so some oxalate is still expected to be found in solution. The working pH of 5.0 was thus chosen for the subsequent experiments, since no extra dosage of oxalic acid was needed to obtain a satisfactory 49% mineralization of the initial DOC content, OTC was no longer detected after 10 min of illumination time ($Q_{\text{UV}} = 0.6 \text{ kJ L}^{-1}$), and the final pH value of the solution approached the legal lower discharge pH value of 6.0 (D-L 236/98).

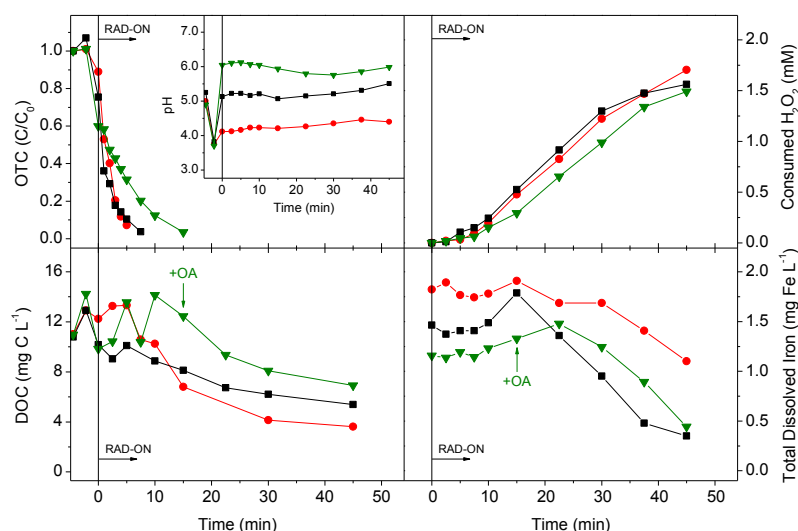


Figure 3 - Effect of initial pH (● - $\text{pH}_0 \sim 4.0$; ■ - $\text{pH}_0 = 5.0$; ▼ - $\text{pH}_0 = 6.0$) on OTC degradation, DOC removal, H_2O_2 consumption, total dissolved iron and pH using Fe^{3+} /Oxalate/ H_2O_2 /UV-Vis system.

Influence of the matrix: Even though $\text{pH}_0 = 5.0$ was set beforehand, experiments were also performed with $\text{pH}_0 = 4.0$ in each media. This was due to the fact that after the oxalate and iron (III) addition steps, the pH of the TF effluent lowered to the same unadjusted pH of the DW solution, around 4.0. In Figure 4a, it can be seen that with $\text{pH}_0 = 4.0$, OTC was no longer detected after 10 min of illumination in WW ($Q_{\text{UV}} = 0.7 \text{ kJ L}^{-1}$), and after 6 min in TF ($Q_{\text{UV}} = 0.4 \text{ kJ L}^{-1}$). Required illumination times were higher in $\text{pH}_0 = 5.0$: 20 min in WW ($Q_{\text{UV}} = 1.4 \text{ kJ L}^{-1}$), and 10 min in TF ($Q_{\text{UV}} = 0.7 \text{ kJ L}^{-1}$). Distribution of the iron (III) species in both media (Fig. 4b) seems to explain the similar kinetic degradation rates achieved with TF ($\text{pH}_0 = 4.0$: 9.59 ± 0.04 ; $\text{pH}_0 = 5.0$: $5.6 \pm 0.4 \text{ L kJ}^{-1}$), and the worse with WW ($\text{pH}_0 = 4.0$: 3.7 ± 0.3 ; $\text{pH}_0 = 5.0$: $1.5 \pm 0.2 \text{ L kJ}^{-1}$). At $\text{pH}_0 = 4.0$, some fraction of iron (III) in the form of the mineral Strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (s)) is already expected to be found in WW, while in TF medium results, there is a relatively higher proportion of the more photo-active $\text{Fe}(\text{C}_2\text{O}_4)_2^-$ complex compared to that in DW (Fig. 4b). The proportion of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (s) at $\text{pH}_0 = 5.0$ in both effluents clearly reflects the lower OTC kinetic degradation rates, especially in the case of WW effluent. Also to be considered is the effect of the additional DOC content of both effluents in the overall process efficiency. Compared to the DW experiments, for instance, less H_2O_2 was consumed by the end of the photo-treatment period (Fig. 4a), which may also reflect the lesser reduction in DOC content comparing with DW experiments at both tested pH values.

Accounting for each effluent's initial DOC values, DOC reduction in WW was of 39 and 31% for $\text{pH}_0 = 4.0$ and 5.0 , respectively, whereas in TF it was 56 and 49%, in the same order.

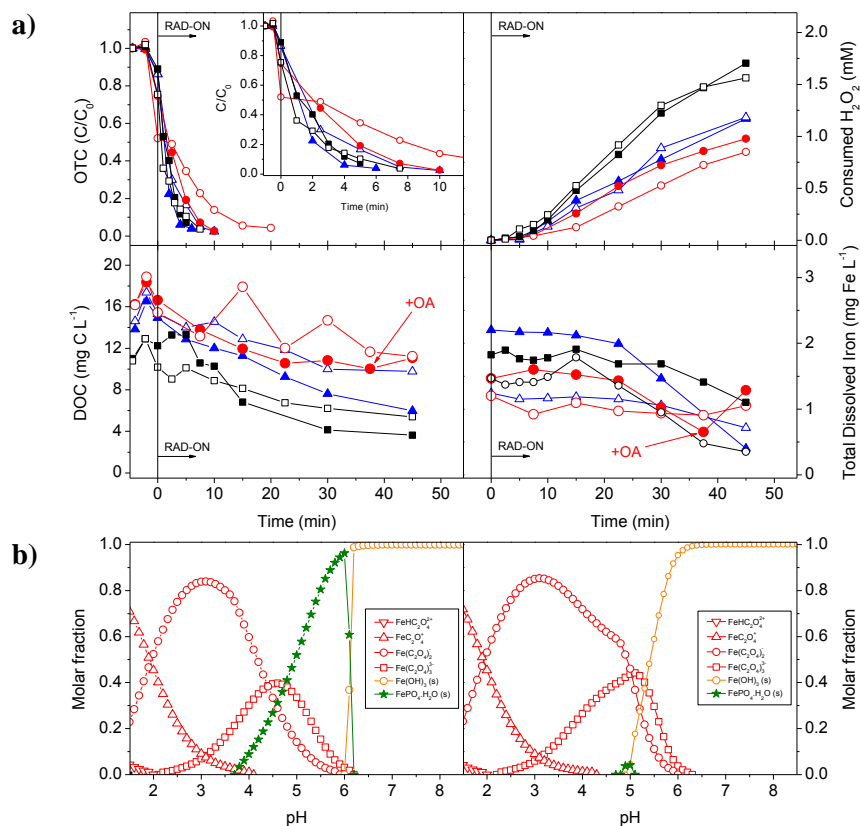


Figure 4 - a) Effect of the matrix on OTC degradation, DOC removal, H₂O₂ consumption and total dissolved iron using the Fe³⁺/Oxalate/H₂O₂/UV-Vis system, performed at $\text{pH}_0 = 4.0$ (closed symbols) and $\text{pH}_0 = 5.0$ (open symbols). Matrices: DW (■, □), TF (▲, △) WW (●, ○); **b)** Speciation diagram for iron (III) as a function of pH in WW (left) and TF (right) effluents, containing 1.07×10^{-1} mM (9.5 mg L⁻¹) oxalic acid and 3.58×10^{-2} mM (2 mg L⁻¹) of Fe (III). Ionic strength = 3 mM.

4. CONCLUSIONS

In this work, it was shown how the highly photo-active ferricarboxylate complexes successfully promotes the photo-Fenton reaction in a lab-scale apparatus simulating solar radiation, equipped with a CPC photo-reactor, to remove the antibiotic Oxytetracycline from aqueous solution at near-neutral pH values.

The oxalic acid in a 1:3 iron/oxalate molar ratio with the aim of forming iron/oxalate complexes showed to deter the inconvenient formation of Fe:OTC complexes, which undermine OTC analytical detection and hamper the regeneration of Fe (III) into Fe (II). Good antibiotic and DOC removals were achieved using the maximum allowed iron concentration in treated effluents (2 mg L⁻¹ of Fe (III)), oxalic acid in a 1:3 iron/oxalate molar ratio, and the initial pH of 5.0, requiring overall low accumulated UV energy per liter of solution. Experiments performed in a domestic WWTP effluent showed slower OTC removal kinetics and lower DOC reduction mainly due to the precipitation of FePO₄. However, in a less complex

effluent from the outlet of a trout farm it was shown that without the pH adjustment step, similar results were achieved, compared with deionized water experiments.

5. ACKNOWLEDGMENTS

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