Degradation of Amitriptyline Hydrochloride, Methyl Salicylate and 2-Phenoxyethanol in Water Systems by the Combination UV/Cl$_2$

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Abstract—Three emerging contaminants (amitriptyline hydrochloride, methyl salicylate and 2-phenoxyethanol) frequently found in waste-waters were selected to be individually degraded in ultra-pure water by the combined advanced oxidation process constituted by UV radiation and chlorine. The influence of pH, initial chlorine concentration and nature of the contaminants was firstly explored. The trend for the reactivity of the selected compounds was deduced: amitriptyline hydrochloride > methyl salicylate > 2-phenoxyethanol. A later kinetic study was carried out and focused on the specific evaluation of the first-order rate constants and the determination of the partial contribution to the global reaction of the direct photochemical pathway and the radical pathway. A comparison between the rate constant values among photochemical experiments without and with the presence of Cl$_2$ reveals a clear increase in the oxidation efficiency of the combined process with respect to the photochemical reaction alone. In a second stage, the simultaneous oxidation of mixtures of the selected contaminants in several types of water (ultrapure water, surface water from a reservoir, and two secondary effluents) was also performed by the same combination UV/Cl$_2$ under more realistic operating conditions. The efficiency of this combined system UV/Cl$_2$ was compared to other oxidants such as the UV/S$_2$O$_8^{2-}$ and UV/H$_2$O$_2$ AOPs. Results confirmed that the UV/Cl$_2$ system provides higher elimination efficiencies among the AOPs tested.

Keywords—Emerging contaminants, amitriptyline, methyl salicylate, 2-phenoxyethanol, chlorination, photolysis, rate constants, UV/chlorine advanced oxidation process.

I. INTRODUCTION

WITHIN the denomination of emerging contaminants (ECs), several families of compounds are included, such as nanomaterials, pesticides, pharmaceuticals and personal care products (PPCPs), hormones, dyes, fragrances water treatment by-products, flame retardants and surfactants, etc. [1]. Nowadays, they constitute a new group of hazard pollutants that are frequently present in water systems. New technologies have recently been assayed with the aim of achieving higher levels of elimination of ECs. Among others, chemical oxidation treatments have demonstrated to be effective in degrading organic constituents in waters, including persistent organic pollutants such as the ECs [2]. A new oxidation technology recently tested with promising results is that constituted by the photolysis of free chlorine. Several works have reported that the potential of the UV/Cl$_2$

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combined system in the degradation of ECs is really high [3]. The present work was designed for the study of the degradation of three selected ECs (amitriptyline hydrochloride (AH), methyl salicylate (MS), and 2-phenoxyethanol (PE)), taken as model compounds, by the UV/Cl$_2$ AOP in order to explore its application in water and wastewater treatments. The specific objectives were: 1) to evaluate the effectiveness of the UV/Cl$_2$ AOP for the degradation of selected ECs in both, UP and real waters (surface water and municipal wastewater) and to investigate the influence of operating conditions; 2) to compare the efficiency of ECs removal by UV/Cl$_2$, by single UV photolysis or chlorine, and by other UV-based AOPs such as UV/H$_2$O$_2$ and UV/S$_2$O$_8^{2-}$) to determine the degradation kinetics (first-order rate constants) of selected ECs under different conditions.

II. EXPERIMENTAL SECTION

In this work, chlorine was fed as hypochlorous acid. For that, previous chlorine stock solutions were prepared by diluting a commercial solution of sodium hypochlorite (Panreac, nominally 10% w/w chlorine) and were standardized iodometrically [4].

The ECs degradation experiments were carried out in a 500 cm3 thermostated cylindrical glass reactor, that was equipped with a low pressure mercury vapor lamp (TNN 15/32 nominal electrical power 15 W; Heraeus, Spain) which emitted a monochromatic radiation at 254 nm.

In the first group of experiments, individual ECs dissolved in ultrapure (UP) water were degraded by chlorine, UV irradiation and the UV/Cl2 AOP. For this purpose, a solution of 350 mL of the corresponding EC (1 μM in all cases) at the designed pH (3, 5, 7 and 9) by means of phosphoric acid/phosphate buffer (0.01 M) was fed into the reactor. The reactor was located in a thermostatic bath at the desired temperature (20±0.2 ºC). Each run was initiated by injecting into the reactor aliquots of the chlorine stock solution to achieve the desired initial chlorine concentration (from 5x10-6 to 15x10-6 M). At regular reaction times, 2 mL samples were retired and rapidly transferred with a syringe into a HPLC vial containing 10 μL of thiosulfate (0.1 M) to stop the reaction. At the same time, a second sample was withdrawn from the reactor to immediately analyze the residual chlorine concentration according to the ABTS method.

In a second step, experiments for the degradation of selected ECs in surface water and municipal wastewater were

performed with the aim to study the degradation process under more realistic conditions. In these experiments, the three ECs were spiked to the real water samples at concentrations of 1 μM for each one. These experiments were performed at the natural pH of the water (pH 7-8) and 20 ºC, following the procedures described above for the individual degradation of the ECs in UP water, and with an initial concentration of chlorine of 10×10^{-6} M. Finally, several experiments of ECs degradation in these real waters by the $UV/S_2O_8^{2-}$ and UV/H_2O_2 AOPs were performed with similar oxidant concentration (10×10^{-6} M of $S_2O_8^{2-}$ or H_2O_2) for comparison purposes

The water matrices used in the present study for the degradation of the selected ECs were: ultrapure water (UP) obtained from a Milipore Milli-Q system; a surface water collected from the public reservoir "Peña del Aguila" (PA), located in the Extremadura Community (southwest Spain); and two secondary effluents from municipal wastewater treatment plants, located in Badajoz (BA) and La Albuera (LA). All these effluents were collected, filtered through a 0.45 μm cellulose nitrate filter within the first 24 hours and stored at 4 ºC until used.

The three selected ECs were analysed by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column (5 μm 150x3.9 mm). The detection was performed at 238 nm for AH and MS; and 220 nm for PE. The mobile phase was a mixture of methanol and 0.01 M aqueous phosphoric acid solution in different proportions, depending on the mixture analysed. The elution flow rate was 1 mL min⁻¹ and the injection volume was 100 μL in all samples. Chlorine concentration was determined spectrophotometrically according to the ABTS (2,2-azino-bis (3-ethyl benzothiazoline)-6-sulfonicaciddiammoniumsalt) method.

III. Results and Discussion

The individual degradation of the three selected ECs in UP water by the UV/Cl_2 AOP was investigated in experiments carried out at 20 ºC with initial concentration of free chlorine varied between 5×10^{-6} and 15×10^{-6} M, and the pH from 3 to 9. In addition, degradation of individual ECs by single UV photolysis or chlorine (10×10^{-6} M) was also investigated at pH 7 for comparative purposes. Table I summarizes the operating conditions for this group of experiments, as well as the percentage of EC degradation obtained after 7 min of reaction (X_7), which is enough to reach a significant removal in all cases.

This parameter X_7 indicates, in a first approach, the efficiency of this process for the removal of selected ECs in the experimental conditions applied.

Fig. 1 shows the time-dependent degradation of AH, taken as example, by single UV photolysis, single chlorination and by the UV/Cl_2 AOP. Similar results were obtained for MS and PE. From the degradation curves for AH shown in Fig. 1 and the results of X_7 summarized in Table I for the three ECs, it can be deduced that the UV/Cl_2 AOP provided significant

higher removals than the single degradation processes (UV radiation or chlorine alone). While the removal of PE and MS with chlorine alone was not appreciable, the removal of AH was lower that 50% after 10 min of chlorination. In a similar way, single UV irradiation was able to partially remove AH, while the degradations of PE and MS were much lower. Moreover, slightly higher degradation of ECs was obtained with single UV photolysis than with 10x10-6 M of chlorine alone at pH 7. On the other hand, the increase in the degradation rates in the UV/Cl2 AOP is due to the generation of very reactive radicals, such as HO· and Cl·. In effect, the radical pathway promotes an important contribution to the overall degradation process in addition to the contribution of single UV photolysis and chlorine.

TABLE I
DEGRADATION OF INDIVIDUAL ECS IN UP WATER BY THE UV/CL₂ AOP:
PSEUDO-FIRST-ORDER RATE CONSTANTS

Expt.	pH	$[Cl_2]_0 \times 10^{-6}$, M	X_7, %	k_T, min⁻¹	k_{UV}, min⁻¹	k_R, min⁻¹
PE-1	3	10	95.1	0.42	0.069	0.36
PE-2	5	10	95.3	0.39	0.071	0.32
PE-3	7	5	87.8	0.30	0.091	0.21
PE-4	7	10	90.5	0.35	0.091	0.26
PE-5	7	15	93.2	0.41	0.091	0.32
PE-6	9	10	83.8	0.21	0.120	0.09
PE-7	7	0	32.4	0.091	0.091	-
PE-8*	7	10	5.0	0.002	-	-
MS-1	3	10	100	0.60	0.058	0.54
MS-2	5	10	100	0.59	0.054	0.53
MS-3	7	5	86.4	0.28	0.052	0.23
MS-4	7	10	96.5	0.44	0.052	0.39
MS-5	7	15	99.9	0.52	0.052	0.47
MS-6	9	10	92.6	0.42	0.055	0.37
MS-7	7	0	15.5	0.052	0.052	-
MS-8*	7	10	8.9	0.008	-	-
AH-1	3	10	100	0.82	0.11	0.72
AH-2	5	10	95.5	0.68	0.12	0.56
AH-3	7	5	82.4	0.47	0.13	0.33
AH-4	7	10	94.1	0.56	0.13	0.43
AH-5	7	15	100	1.27	0.13	1.13
AH-6	9	10	90.5	0.46	0.21	0.25
AH-7	7	0	56.0	0.13	0.13	-
AH-8*	7	10	41.5	0.076	-	-

* Experiments PE-8, MS-8 and AH-8 were carried out with chlorine alone (absence of UV radiation).

Finally, the comparison of the X7 values for the three selected ECs allows establishing that the level of degradation at the same operating conditions is: AH > MS > PE.

The shape of the decreasing concentration of ECs as a function of reaction time shown in Fig. 1 suggests a pseudo-first order reaction with respect to the EC concentration. Similarly, the degradation of selected ECs by single UV photolysis and chlorine alone also follows pseudo-first-order kinetics [5]. According to this model, the rate constant values were deduced for every experiment conducted, being the obtained results summarized Table I. From the values of k_T, it can firstly be deduced that much higher values were obtained in the combined process in comparison to the single

photochemical process or the single chlorination. Secondly, the rate constants in the combined UV/Cl$_2$ system at the same operating conditions again confirm the trend observed in the degradation percentage already mentioned previously: AH > MS > PE.
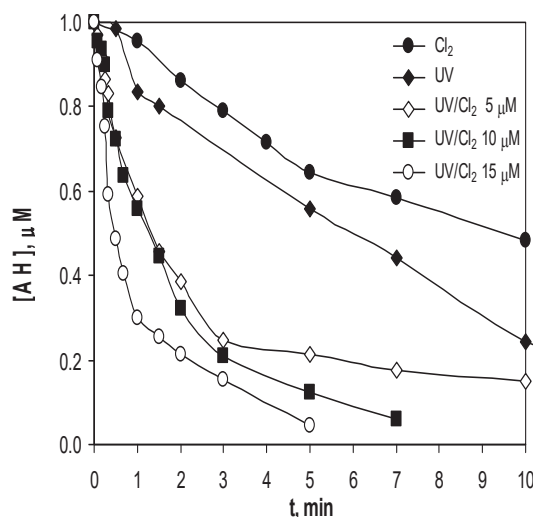

Fig. 1 Evolution of AH (C) concentration with reaction time in experiments performed with UV radiation alone, chlorine alone and the combination UV/Cl$_2$ at different initial concentration of chlorine. Experimental conditions: [ECs]$_0$=1 μM, T=20 ºC, pH=7

As commented before, an additional contribution to the single photoreaction or single chlorination is promoted by the radical pathway that takes place in the UV/Cl$_2$ AOP. This radical contribution can be evaluated for each EC. Thus, the overall reaction rate (r$_T$) for the combined process can be assumed to be the addition of the rate corresponding to the direct photochemical reaction (r$_{UV}$) plus the rate corresponding to the radical reaction (r$_R$):

$$-r_T = -\frac{[dEC]}{dt} = -\left(r_{UV} + r_R\right) = \left(k_{UV} + k_R\right)[EC] = k_T[EC]$$

In accordance to this equation, the rate constants for the radical reaction k$_R$ are easily deduced by subtracting from k$_T$ values those k$_{UV}$ values obtained for the experiments performed with UV radiation alone (Expts. PE-7, MS-7 and AH-7 for PE, MS and AH, respectively). Table I summarizes the k$_{UV}$ values, as well as the values of k$_R$ with the combined system UV/Cl$_2$. The comparison of k$_R$ values obtained for the three compounds tested in the UV/Cl$_2$ AOP with the values of k$_{UV}$ for single photolysis confirms that the radical reaction has a greater contribution to the overall reaction than the direct photolysis, especially at higher chlorine concentrations. As also observed, the values of k$_R$ decreased with pH for the three selected ECs, which indicate that the contribution of the radical pathway to the overall degradation of EC decreases at higher pH. These results are consistent with the lower

production and higher consumption of HO· and Cl· at high pH.

In a next stage, the simultaneous degradation of mixtures of selected ECs (initial concentration of 1 μM for each compound) dissolved in different types of waters (ultra-pure water (UP), reservoir water (PA), and two secondary effluents from municipal WWTPs (LA and BA)) was carried out by the combined UV/Cl$_2$ system. For comparison purposes, similar experiments were performed by applying single photolysis and the UV/H$_2$O$_2$ and UV/S$_2$O$_8$$^{2-}$ AOPs, using an oxidant (H$_2$O$_2$ or S$_2$O$_8$$^{2-}$) concentration of 10x10^{-6} M. Table II summarizes the experiments performed and the main results obtained.

TABLE II
DEGRADATION OF ECS IN REAL WATERS BY DIFFERENT AOPS: PSEUDO-FIRST-ORDER RATE CONSTANTS FOR EC REMOVAL

WM*	T*	ICO* (μM)	k$_{PE}$ (min^{-1})	k$_{MS}$ (min^{-1})	k$_{AH}$ (min^{-1})
UP	UV-Cl$_2$	10	0.14	0.25	0.38
	UV	0	0.029	0.020	0.086
	UV-H$_2$O$_2$	10	0.0566	0.074	0.13
	UV-S$_2$O$_8$$^{2-}$	10	0.11	0.13	0.26
PA	UV-Cl$_2$	10	0.075	0.13	0.30
	UV	0	0.017	0.016	0.046
	UV-H$_2$O$_2$	10	0.018	0.018	0.08
	UV-S$_2$O$_8$$^{2-}$	10	0.048	0.056	0.14
LA	UV-Cl$_2$	10	0.074	0.15	0.19
	UV	0	0.013	0.066	0.088
	UV-H$_2$O$_2$	10	0.014	0.078	0.12
	UV-S$_2$O$_8$$^{2-}$	10	0.045	0.093	0.15
BA	UV-Cl$_2$	10	0.051	0.063	0.10
	UV	0	0.0067	0.010	0.068
	UV-H$_2$O$_2$	10	0.009	0.014	0.07
	UV-S$_2$O$_8$$^{2-}$	10	0.036	0.054	0.09

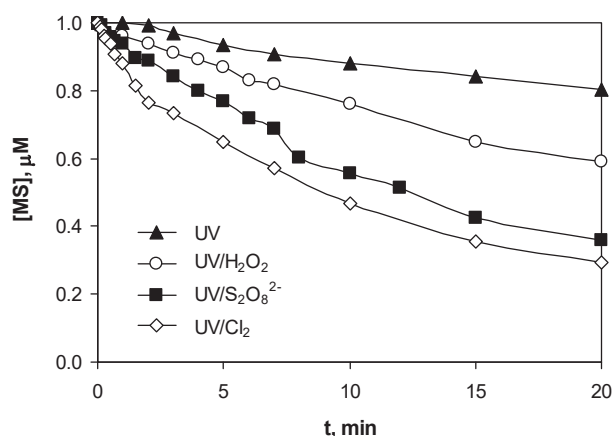WM*=Water matrix. T*=Treatment. ICO*=Initial concentration of oxidant

Fig. 2 Degradation of methyl salicylate by different oxidation systems in BA water. Experimental conditions: [MS]$_0$=1 μM, [oxidant]$_0$=10 μM, T=20 ºC

Firstly, the efficiency of the UV/Cl$_2$ system for the degradation of selected ECs was compared to other oxidants or combinations of oxidants. Thus, Fig. 2 shows, as an example, the decrease of MS concentration with reaction time

in experiments carried out with those different oxidation systems in BA water. Similar trends were obtained for the rest of compounds and water matrices. It is clearly observed that the combined UV/Cl_2 system provided the best degradation rates; intermediate rates were obtained with the $UV/S_2O_8^{2-}$ and UV/H_2O_2 AOPs, and the lowest rates corresponded to the single photodegradation. Similarly, Fig. 3 shows the degradation curves for the three selected compounds by UV/Cl_2 in PA water, taken as example. It can be observed that 2-phenoxyethanol presented the lowest elimination rate, intermediate for methyl salicylate, while amitriptyline hydrochloride reached the highest elimination rate. Similar results were obtained in the remaining water systems. Then, this disappearance rate sequence completely agrees with the sequence of rate constants r_T for AH, MS, and PE during the individual degradation of these ECs in UP water by the UV/Cl_2 system. These results are confirmed with the evaluation of the pseudo-first-order rate constants (k_{PE}, k_{MS}, and k_{AH} for PE, MS, and AH, respectively) for the disappearance rates of the selected ECs, whose values are also compiled in Table II: it can be observed that the commented sequence of degradation rates was fulfilled in the four water matrices tested.
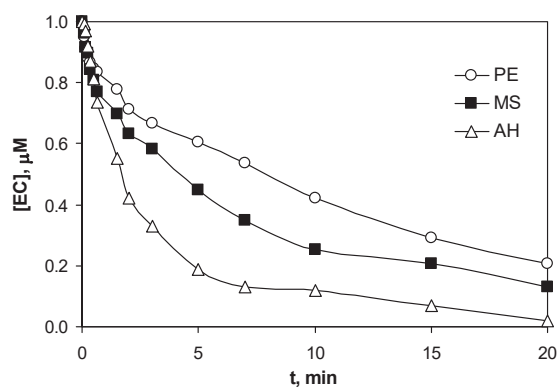

Fig. 3 Degradation the three selected compounds by the UV/Cl_2 AOP in PA water. Experimental conditions: $[ECs]_0=1$ μM, $[Cl_2]_0=10$ μM, T=20 ºC

Finally, the effect of the water matrix nature on the ECs decomposition is shown in Fig. 4, where the concentration curves of methyl salicylate, taken as example, are plotted *vs* reaction time in experiments performed with the UV/Cl_2 system. It can be observed that the fastest degradation was obtained in UP water (higher pseudo-first-order rate constants in Table II), followed by PA and LA waters with intermediate degradation rates, and much lower eliminations in BA water. Similar results were obtained for amitriptyline hydrochloride and 2-phenoxyethanol, as can be deduced from the values of k_{AH} and k_{PE} summarized in Table II.

The highest rates of ECs removal in UP water can be expected in advance: in effect, in this water there is an almost total absence of organic and inorganic matter that could consume direct UV radiation and radicals; and consequently, all the oxidant load is consumed in the degradation of the ECs.

On the contrary, in PA, LA, and BA waters, the presence of some organic compounds and bicarbonate ion promotes the absorption of UV radiation and the consumption of radicals; and consequently, the effective radical concentration available to react with the ECs decreases. In other words, there is a competition between ECs and the organic and inorganic matter present in the water for the absorption of UV radiation and the consumption of radical species.
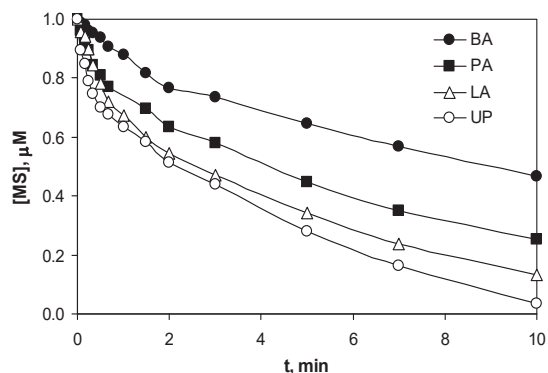

Fig. 4 Effect of the water matrix on the degradation of methyl salicylate by the combination UV/Cl_2. Experimental conditions: $[MS]_0=1$ μM, $[Cl_2]_0=10$ μM, T=20 ºC

IV. CONCLUSIONS

Three emerging contaminants were selected to be oxidized in different water matrices by the combined oxidation process constituted by UV radiation plus chlorine, and the following conclusions were established:

- Amitriptyline hydrochloride was the most reactive compound towards this AOP; methyl salicylate showed intermediate reactivity, while 2-phenoxyethanol was found to be the least reactive.
- While the degradation of selected ECs was improved with increasing the initial concentration of chlorine, the pH exerted a negative influence on ECs removal.
- Pseudo-first-order rate constants were determined, and the values obtained confirmed the reactivity sequence.
- Simultaneous oxidation experiments of the selected ECs performed in four water matrices by the combined UV/Cl_2 system confirmed the trend previously stated about the reactivity of the compounds: amitriptyline hydrochloride > methyl salicylate > 2-phenoxyethanol.
- A direct effect between the ECs reactivity in every water tested and the organic and inorganic content of each water (measured as absorbance at 254 nm, TOC and bicarbonate) could be also established.

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