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Fast oxidation of the neonicotinoid pesticides listed in the EU Decision 2018/840 from aqueous solutions

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Abstract

Neonicotinoid pesticides family is nowadays identified as the most important type of insecticides in the world. Their consequent widespread occurrence in the environment represents not only a well-known risk for bees but also a significant negative impact in aquatic ecosystems. In this work, the capability of catalytic wet peroxide oxidation (CWPO) ($\text{Fe}_3\text{O}_4\text{-R400}/\text{H}_2\text{O}_2$) as a low-cost and environmentally-friendly system for the treatment of the neonicotinoid pesticides listed in the EU Watch List (Decision 2018/840) (acetamiprid (ACT), clothianidin (CLT), imidacloprid (IMD), thiacloprid (THC) and thiamethoxam (THM)) has been investigated. Remarkably, complete elimination of the pollutants ($1000\text{ }\mu\text{g L}^{-1}$) and the aromatic by-products was reached in 20 min reaction time operating at $25\text{ }^\circ\text{C}$, 1 atm, and $\text{pH}_0 = 5$, with the stoichiometric H_2O_2 amount ($\sim 4 - 5\text{ mg L}^{-1}$) and 1 g L^{-1} catalyst load. The reactivity order of the insecticides decreased as follows: $\text{THC} > \text{IMD} > \text{THM} > \text{CLT} > \text{ACT}$, being the pseudo-first order rate constant values within the range of $0.26 - 0.61\text{ min}^{-1}$. Notably, high mineralization yields were obtained ($>50\%$), being the final effluents non-toxic. As example, the oxidation pathway of ACT was proposed. Finally, the catalytic system was tested in real surface water.

46 1. Introduction

47 Pesticides are used worldwide to improve crop yields, protect the human health and increase
48 the esthetic value of recreational areas like parks or ponds. Nevertheless, their extensive application
49 has led to a degradation of environmental ecosystems, as these substances are characterized by a huge
50 persistence, strong bioaccumulation and high toxicity [1-3]. In the nineties, neonicotinoid pesticides
51 emerged as a novel environmentally-friendly class of chemical insecticides, as they present a low
52 toxicity to mammals, birds and fish [4-6]. Neonicotinoids are much more selective for insects
53 compared to mammals than the earlier classes of organic insecticides *i.e.* organophosphates,
54 methylcarbamates and organochlorines [4]. These favorable properties promoted an extremely fast
55 growth of this pesticide family, being nowadays identified as the most used type of insecticides [7].
56 Accordingly, neonicotinoid pesticides are commonly employed in more than 120 countries, being
57 their annual sales around €1.5 billion, which accounts for 24% of the total insecticide market [7].

58 Neonicotinoid pesticides are derived from the natural toxin nicotine and are known to affect the
59 insects nervous system, leading to the blockage of receptors, and thus, stopping nerve impulse
60 transmission and finally causing the death [8-10]. Up to seven neonicotinoid insecticides are
61 nowadays available: three cyclic compounds, two five-membered ring neonicotinoids (thiacloprid
62 (THC) and imidacloprid (IMD)) and the six-membered pesticide thiamethoxam (THM), and four
63 non-cyclic compounds (acetamiprid (ACT), clothianidin (CLT), nitenpyram (NTP) and dinotefuran
64 (DNF)) [7]. Despite their outstanding insecticide properties, the marketing success of these pesticides
65 has been stained in the last few years due to their association with honey bee failures [8,11]. This fact
66 represents a high risk given the essential role as pollinators of bees [12]. This environmental issue
67 has had a big impact in the press, with hundreds of news in the media related to the repercussions of
68 neonicotinoids on bees. Consequently, different countries such as Slovenia, Germany and France
69 banned the use of seeds treated with neonicotinoids [13,14]. The European Union (EU) has also
70 recently banned the use of THM, CLT and IMD (EU Regulations 2018/783-784-785) [15-17]. Apart
71 from the unacceptable risk for bees, the negative impact of these pesticides in aquatic ecosystems has

72 been demonstrated in recent times [14]. The initial consideration of neonicotinoids as harmless
73 pollutants promoted reduced the monitoring efforts, leading to a widespread contamination of the
74 aquatic environment with these pollutants [14], given their strong photo-stability, high water
75 solubility and polarity, and high persistence in soil and water [18]. Main effect is the decline of
76 invertebrate population such as mollusks, copepods or cladocerans, which strongly affects the aquatic
77 ecosystems [14, 19, 20]. For instance, in the Netherlands, correlations between IMD traces and the
78 decline of some arthropods and crustaceans have been found [21]. In this context, the European Union
79 (EU) has recently included five neonicotinoid pesticides (ACT, CLT, IMD, THC and THM) in the
80 Watch List (Decision 2018/840) [22] as potential priority pollutants with the aim of monitoring their
81 concentration in EU water basins and assessing their associated environmental risks.

82 Advanced oxidation processes (AOPs), which are based on the oxidation promoted by hydroxyl
83 radicals under ambient conditions, represent the most promising system for the removal of
84 neonicotinoids from water. In particular, photo-Fenton [23-26], photocatalysis [13], electro-Fenton
85 [27, 28] and ozonation [29] have received wide attention. Segura et al. (2008) [23] achieved the
86 complete removal of IMD (100 mg L^{-1}) in 25 min but at the expense of the use of UV light ($I = 5 \times 10^{-6}$
87 Einstein s^{-1}) and a high Fe^{2+} dose (35 mg L^{-1}) at acidic pH ($\text{pH}_0 = 2.8$). It must be also noted that the
88 final effluents were toxic to *Daphnia magna*, which was associated to the presence of harmful by-
89 products. In the same line, Banic et al. (2011) [24] reached the complete conversion of THC (80 mg
90 L^{-1}) in 25 min reaction time using a heterogeneous photo-Fenton system based on the photocatalyst
91 Fe/TiO_2 (1.67 g L^{-1}), but operating under acidic pH ($\text{pH}_0 = 2.8$) and using an extremely high dose of
92 H_2O_2 (1500 mg L^{-1}). Quite similar findings have been recently evidenced by Fasnabi et al. (2016)
93 [26] in the removal of ACT (50 mg L^{-1}) by homogeneous photo-Fenton. On the other hand, longer
94 reaction times (2 h) have been reported for the removal of IMD (100 mg L^{-1}) by electro-Fenton using
95 iron alginate gel spheres (1.3 mM) at acidic pH ($\text{pH}_0 = 2.0$) [27]. Better results were obtained by the
96 homogeneous electro-Fenton reaction in the treatment of THM (60 mg L^{-1}), where the total
97 degradation of the pesticide was achieved after 10 min under the optimal conditions (300 mA, 11 mg

L⁻¹ Fe²⁺, pH₀ = 2.8) [28]. The application of ozonation allowed to operate under a wider pH range (pH₀ = 5 – 11), as demonstrated in the degradation of THM (200 mg L⁻¹) but a long reaction time (90 min) was required to achieve its complete removal using an O₃ concentration of 21 mg L⁻¹ [29]. In general, AOP studies have been focused on the treatment of a single neonicotinoid, using high initial pesticide concentrations (mg L⁻¹) and unaffordable doses of oxidants/catalysts. Furthermore, the formation of aromatic by-products along the processes remains unclear.

In this work, the capability of dark heterogeneous Fenton oxidation, also known as catalytic wet peroxide oxidation (CWPO), for the elimination of the neonicotinoid pesticides listed in the EU Decision 2018/840 (ACT, CLT, IMD, THC and THM) has been investigated using the low-cost and environmentally-friendly system Fe₃O₄-R400/H₂O₂ [30]. The kinetics of the reactions has been studied at 25 °C, 1 atm and pH₀ = 5, using a representative concentration of the pesticides (1000 µg L⁻¹), a catalyst load of 1 g L⁻¹ and the stoichiometric H₂O₂ concentration for the total oxidation of the target pollutants (~4 – 5 mg L⁻¹). Apart from considering the elimination of the pesticides, the evolution of the aromatic by-products has been also followed. As example, the reaction pathway for the ACT oxidation has been proposed. In the same line, the ecotoxicity of initial pesticides and final oxidation effluents has been also evaluated, including the detailed evolution of ecotoxicity upon ACT removal. Finally, the system has been also tested using a representative range of natural organic matter amount (1 – 10 mg L⁻¹) and also a real surface water matrix.

2. Materials and methods

2.1. Materials

The five neonicotinoid pesticides were provided by Sigma-Aldrich (analytical grade quality). Their molecular weights and structural formulas are summarized in Table 1. Acetic acid (>99%), nitric acid (65%), formic acid (>98%), methanol (HPLC grade), humic acid (Ref: 53680; CAS: 1415-93-6) (>98%) and hydrogen peroxide solution (30% w/v), were also obtained from Sigma-Aldrich, and acetonitrile (analytical grade) was given by Fluka. Magnetite (Fe₃O₄) (ref: 50121500) was

purchased from Marphil S.L. (Spain). Deionized water was used as matrix in all CWPO experiments unless otherwise indicated (surface water).

2.2. Preparation and characterization of Fe₃O₄-R400

The procedure followed for the modification of magnetite to obtain Fe₃O₄-R400 can be found in a previous work [30]. Pure magnetite was submitted to a thermal treatment under 250 N mL min⁻¹ H₂ flow at 400 °C for 3 h. The characterization of the resulting catalyst has been reported in detail elsewhere [30]. Briefly, the amount of iron was 73% wt., the surface area 7 m² g⁻¹ and the particles exhibited a mean diameter of 0.2 µm. It must be also mentioned that crystalline magnetite was the only phase of the solid, which, as expected, presented strong magnetic properties (81.5 emu g⁻¹).

2.3. Typical procedure for CWPO experiments

Oxidation experiments were carried out at atmospheric pressure and 25°C using a glass batch reactor (500 mL) under temperature control and stirring (750 rpm). The operating conditions were selected taking into account a previous work [31]. The initial pH was adjusted to 5 while the starting concentration of the target pollutants was established at 1000 µg L⁻¹. This pesticides concentration was selected to facilitate their quantification as well as the following of the aromatic intermediates with the available analytical techniques in the laboratory, although it must be noted that it is higher than the representative amounts of these pollutants in surface waters (0.13-0.63 µg L⁻¹) [32]. The concentration of catalyst was fixed at 1 g L⁻¹ and the stoichiometric amount of H₂O₂ for the complete oxidation of each pesticide was used (Table 1).

In order to elucidate the reaction pathway of ACT from the compounds identified along reaction, a new experiment was carried out using a higher initial concentration (20 mg L⁻¹) of this pesticide. The load of catalyst was fixed at 2 g L⁻¹ and the stoichiometric dose of H₂O₂ for its complete oxidation (106 mg L⁻¹) was used.

The impact of water matrix composition on the CWPO performance was also evaluated using a common component of fresh waters: natural organic matter (NOM) within the representative range of 1 – 10 mg L⁻¹. A real surface water was used to evaluate the efficiency of the catalytic system.

Control runs were previously performed in the absence of H₂O₂ under similar operating conditions and the effect of catalyst adsorption was discarded (pesticide disappearance below 5%). In the same line, experiments carried out in the absence of catalyst demonstrated the key role of Fe₃O₄-R400 in the system as pesticides conversion was below 5%. All reactions were accomplished in triplicate (standard deviation <5%).

2.4. Analytical methods

Liquid samples were withdrawn from the reactor to follow the evolution of the reaction. After catalyst separation using a magnet, the samples were immediately analyzed. A high performance liquid chromatograph with UV detector (diode array, SPD-M30A) mod. Prominence-i, LC-2030C LT was used to quantify the neonicotinoid pesticides and also to follow the oxidation intermediates. The analyses were realized at 270 nm using an Eclipse Plus C18 column supplied by Agilent (150 mm length, 5 µm 4.6 mm diameter, particle size) and, as mobile phase, a 22/78% mixture of acetic acid aqueous solution (75 mM) and acetonitrile (ACN).

The tentative identification of the aromatic by-products formed along ACT reaction at high starting concentration (20 mg L⁻¹) was performed with HPLC-MS11000, 6120 Q (Agilent). In this case, the column Phenomenex Gemini 5µm C18 column (4.6 mm diameter and 15 cm length) was used. As mobile phase a 25/75% mixture of ACN and water (0.1% formic acid) was employed. The acquisition and processing of the data was performed with the LC/MSD ChemStation software package.

An ion chromatograph Metrohm 790 IC was used to analyze short-chain organic acids. A Shimadzu TOC VSCH analyzer was used to determine total organic carbon (TOC) and colorimetric

methods were employed to measure the concentrations of H₂O₂ (titanium oxysulfate) [33] and dissolved iron (*o*-phenantroline) [34] with the spectrophotometer Shimadzu UV/Vis 1603.

2.5. Ecotoxicity test

The ecotoxicity of the neonicotinoid pesticides and the final oxidation effluents was analyzed by the toxicity test Microtox® (1998, ISO 11348-3) with the M500 Microtox Analyzer. Prior sample analysis, the osmotic pressure was adjusted using a 2% NaCl solution and the pH was fixed within the range of 6 – 8. The tests were performed at 15 °C. The effective concentration (EC₅₀), which corresponds to the amount of a compound (mg L⁻¹) that reduces the light emission intensity of the marine bacterium *Vibrio fischeri* by 50% after 15 min, was calculated for each pesticide. For oxidation effluents, the toxicity units (TU) were obtained. TU values are calculated as the reciprocal of the half-maximal inhibitory concentration, IC₅₀ value (%), *i.e.* sample dilution ratio that yields 50% light decrease.

3. Results and discussion

3.1. Removal of neonicotinoid pesticides by CWPO

The degradation of the isolated neonicotinoid pesticides upon CWPO at 25 °C is shown in Fig. 1. As observed, the process was quite fast, reaching the complete removal of all pollutants in 20 min reaction time. The experimental results were properly described by a pseudo-first order kinetic equation. The apparent rate constants are given in Table 2. Although the process was versatile for the removal of all neonicotinoids, it is clear that the different structure of the molecules (Table 1) determined somehow their oxidation rate. The reactivity order decreased as follows: THC>IMD>THM>CLT>ACT. As a general trend, the cyclic compounds, two five-membered ring (THC and IMD) and six-membered ring (THM) pesticides, showed higher apparent rate constants

than the non-cyclic compounds (CLT and ACT). The structures of THC and IMD are quite similar, being the only difference the presence of a CN- or a NO₂- group as substituents as well as the presence of sulfur or nitrogen in the five-membered cyclic ring, which explains that their apparent rate constants are comparable. On the other hand, THM did not show double bonds in the six-membered ring, which explains its significantly lower reactivity towards hydroxyl radical oxidation [35]. Finally, CLT and ACT showed the longest aliphatic chains, which are well-known to be less prone to be oxidized by HO· [35].

Scarce works can be found in the literature dealing with the removal of various neonicotinoid pesticides. Banic et al. (2011) [24] investigated the application of photocatalysis using the system UV/Fe-TiO₂/H₂O₂ for the removal of several neonicotinoids (ACT, IMD, THC and THM) and also found that THC and IMD were the most reactive compounds. In the same line, Zabar et al. (2012) [13] also observed that IMD oxidation was remarkably faster than those of THM and CLT, which showed very similar apparent rate constants, upon photocatalysis with immobilized TiO₂ on glass slides. In general, the results obtained in the current work improve those previously achieved by other AOPs, where significantly longer reaction times have been commonly reported. For instance, in the abovementioned works focused on photocatalysis, 2 – 3 h were necessary to achieve the total degradation of the pesticides under optimized conditions [13, 24]. Although the application of photo-Fenton has proved to be a remarkably faster alternative [23, 25, 26], with similar reaction times as those required in the current work, it shows important limitations like the strong acidic pH as well as the use of H₂O₂ doses higher than the stoichiometric ones and significant amounts of leached iron. It must be noted that in the application of the catalytic system Fe₃O₄-R400/H₂O₂, the pH was adjusted to 5 and the dose of H₂O₂ was fixed at the stoichiometric amount required for the complete oxidation of the pollutants. Furthermore, the catalyst concentration, whose easy separation is warranted given its magnetic properties, was 1 g L⁻¹ and the leaching of iron was practically negligible (0.8% wt. of the initial iron load in the catalyst), being the dissolved iron concentration at the end of the reactions below 0.6 mg L⁻¹. Furthermore, the catalyst showed a remarkable stability upon three sequential runs

in the CWPO of ACT (see Fig. S1 of the Supplementary Material for experimental data). Consistent with our prior work [30], a slight deactivation of the solid occurred due to the partial oxidation of the catalytic surface upon consecutive uses. Nevertheless, the complete conversion of the pesticide was reached in less than 20 min in all cases.

To further demonstrate the effectiveness of $\text{Fe}_3\text{O}_4\text{-R400}/\text{H}_2\text{O}_2$ for the degradation of the neonicotinoid pesticides, it is crucial to follow not only the target pollutants but also the aromatic by-products formed as well as the ecotoxicity of the resulting effluents. In fact, the formation of even more harmful by-products along reaction is one of the main disadvantages of AOPs [23, 26]. In this sense, the formation of the aromatic by-products was monitored by HPLC-UV (see Fig. S2-S6 of the Supplementary Material for experimental data). Remarkably, the complete disappearance of such species was achieved in all cases once the target pollutant had disappeared (20 min). As representative example, the evolution of the aromatic by-products generated in the oxidation of a cyclic (IMD) and a non-cyclic (CLT) pesticides is depicted in Fig. 2 (the results obtained with the rest of neonicotinoids can be found in Fig. S7 of the Supplementary Material). Consistent with the complete removal of both target pollutants and aromatic by-products, 50 – 60% mineralization yields were achieved together with H_2O_2 consumption above 60% at the end of the process (1 h). Notably, the residual organic carbon of those effluents corresponded to short chain organic acids (oxalic, formic and acetic acids), being the carbon balance closed above 90% (see Table S1 of the Supplementary Material for experimental data). Accordingly, the reaction medium pH value was decreased to a small extent (final pH \sim 4.0).

To learn about the abatement of ecotoxicity upon CWPO, both the initial neonicotinoid pesticides and the reaction effluents were measured by the Microtox[®] ecotoxicity test. In first place, the EC_{50} values of each pesticide was calculated (Table 3). The obtained results showed a slightly higher toxicity values for ACT and THC but in the same order of magnitude as those previously reported in the literature [36-39]. In this sense, the ecotoxicity of the neonicotinoid pesticides decreased in the order $\text{ACT} > \text{THC} > \text{IMD} > \text{CLT} > \text{THM}$. It is clear that, with the exception of ACT

and THC, the ecotoxicity of the pesticide solutions can be practically neglected at the initial concentration of the pollutants tested in this work ($1000 \mu\text{g L}^{-1}$) taking into account that their EC_{50} values were well above 100 mg L^{-1} . All in all, the CWPO effluents were also analyzed by the ecotoxicity test and, as expected, the ecotoxicity values were negligible ($<0.1 \text{ TU}$).

3.2. Intermediates and ecotoxicity study

Once confirmed the ability of CWPO for the removal of the neonicotinoid pesticides family, further experiments were focused on the degradation of ACT. It must be noted the use of THM, CLT and IMD has been recently banned by the EU (EU Regulations 2018/783-784-785) [15-17]. In the same line, THC has been stated as a candidate for substitution based on its endocrine disrupting properties (EU Regulation 1107/2009) [40]. Nevertheless, the approval for the application of ACT for plant protection has been recently renewed (UE Regulation 2018/113) [41] and it will expire in 2033, probably due to its lower toxicity to bees compared to its neonicotinoid counterparts [42]. Therefore, it is expected that ACT would appear in freshwaters of the UE water basins. Furthermore, this pesticide showed the slowest oxidation rate upon CWPO (Table 2) and, according to the ecotoxicity study, it is the most toxic among the group of pesticides tested in this work (Table 3).

To get better insights about the evolution of ecotoxicity along the treatment as well as the nature of the aromatic by-products generated, a new experiment was performed with a remarkably higher concentration of the target pollutant (20 mg L^{-1}). This run was carried out with the stoichiometric amount of H_2O_2 (106 mg L^{-1}) for the mineralization of ACT and 2 g L^{-1} catalyst concentration. Fig. 3a depicts the time-course of the neonicotinoid concentration and ecotoxicity along reaction. The initial ecotoxicity of ACT solution was 2.5 TU considering its starting concentration (20 mg L^{-1}). As can be seen, that ecotoxicity value significantly increased in the course of the reaction up to almost 12 TU after 1.5 h reaction time. Afterwards, it was progressively reduced, being the effluent non-toxic ($<0.1 \text{ TU}$) once ACT was completely eliminated (500 min). This is in agreement with the fact that more than 50% of the initial carbon content was then mineralized, being the oxalic, acetic and

formic acids the final products. These results clearly demonstrate that the intermediates generated along the oxidation reaction are much more toxic than the parent compound. In fact, as shown in Fig. 3b, the evolution of the aromatic by-products (followed by HPLC-UV) was almost parallel to the ecotoxicity data trend. The increase of ecotoxicity upon organic pollutants removal by AOPs has been widely reported in the literature, being recognized as one of the most serious disadvantages for the application this technology [29, 43-45].

The samples from the experiment carried out with a high initial concentration (20 mg L⁻¹) of ACT were also analyzed by HPLC-MS with the aim of tentatively identifying the aromatic by-products followed by HPLC-UV (Fig. 3b). The reaction proceeded mainly through hydroxylation of the parent molecule leading to the higher molecular weight intermediates (MW = 238, Intermediates 1a and 1b). According to previous works [36, 46], the oxidation mainly takes place at the methyl group (Intermediate 1b) although in the current work other isomer was detected, which was assigned to the hydroxylation of the aromatic ring. Also N-demethylation by HO• attack at the aliphatic chain took place (MW = 208, Intermediate 2). The ability of hydroxyl radicals for N-demethylation has been reported in prior studies [25, 46, 47]. It must be noted that, in fact, this intermediate appeared at high abundance compared to the other ones identified in the current work, during the whole treatment (Fig. 3b), which is in good agreement with the findings of Carra et al. [25]. The loss of the cyanide substituent was also observed (MW = 197, Intermediate 3) (see Fig. S8-S11 of the Supplementary Material for mass spectrum of the intermediates). The hydrolysis of the aliphatic chain was demonstrated as well by the identification of Intermediate 4 (MW = 97), which could not be followed by HPLC-UV as it does not absorb in the UV light range since it does not present an aromatic ring. The intermediates identified in the current work are consistent with those previously reported in the removal of ACT by UV/H₂O₂ [36] and also by Fenton [46] and photo-Fenton [25]. Further hydroxyl radicals attack led to aromatic ring opening, giving rise to short-chain organic acids and to a relevant mineralization of the effluent (~50%). The reaction effluent analysis by ionic chromatography allowed confirming the presence of oxalic, acetic and formic acids as reaction products. Based on

these results, the reaction scheme for the CWPO of ACT is proposed (Fig. 4). The formation of Intermediate 5, which corresponds to 6-chloronicotinic acid, is suggested as it is generally identified in the literature as a typical intermediate in the oxidation of neonicotinoid pesticides [25, 27, 36, 46]. It has not been detected in this work due to its high reactivity compared to the other intermediates. In fact, Carra et al. [25] observed that this intermediate was degraded during the first 20 min of reaction while the other ones, like Intermediates 1 and 2, required up to 240 min, in the photo-Fenton treatment of ACT.

3.3. Operation in complex water matrices

The catalytic system was finally used in complex water matrices. The impact of a common component of fresh waters *i.e.* NOM was firstly investigated within the relevant range of 1 – 10 mg L⁻¹ [48, 49]. As can be seen in Fig. 5, the presence of NOM somehow inhibited the oxidation reaction, especially in the case of 10 mg L⁻¹ NOM, where the conversion of ACT was around 60% after 2 h reaction time while only 20 min were necessary to achieve its complete removal in deionized water. Accordingly, the apparent rate constant decreased with increasing NOM concentration (0.26, 0.14 and 0.009 min⁻¹ were obtained for deionized water, 1 mg L⁻¹ NOM and 10 mg L⁻¹ NOM matrices, respectively). These results can be explained by the ability of NOM (humic acids) for HO· scavenging as well as the coating of magnetite particles by these compounds, which is consistent with previous works in both homogeneous and heterogeneous Fenton oxidation [48, 50]. At pH 5, humic acids are negatively charged (average pKa ~ 4.0 [51]) and thus, electrostatically attracted to the positively catalyst surface (pH_{PZC} ~ 7.5).

In second place, a real surface water (TOC = 2.7 mg L⁻¹, IC = 14.9 mg L⁻¹, Cl⁻ = 14.1 mg L⁻¹, SO₄²⁻ = 11.2 mg L⁻¹, conductivity = 200 µS cm⁻¹) fortified with ACT (1000 µg L⁻¹) was employed as reaction matrix. In this case, ACT complete degradation was reached in 2 h reaction time, with an apparent rate constant value of 0.04 min⁻¹. This value is almost three times lower than the obtained with 1 mg L⁻¹ NOM in deionized water, which is consistent with the presence of almost 3 mg L⁻¹ of organic carbon in the real matrix. The same behavior was also observed with the other neonicotinoid

pesticides (CLT, IMD, THC and THM). Their apparent rate constant values were decreased up to 80% when they were treated in the real water matrix (see Fig. S12 of the Supplementary Material for experimental results). This fact indicates that the presence of organic matter is a relevant aspect to consider in the application of the proposed catalytic system in real surface matrices to remove neonicotinoid pesticides, being the presence of salts of significantly lower importance. Although bicarbonate anions are potent HO \cdot scavengers, and sulfate and chloride anions can also present an important effect on the kinetics of Fenton-like processes, their influence on the oxidation performance was of negligible importance in the current work given the low amounts present in the real surface water sample. In fact, the effect of inorganic ions on the Fenton oxidation kinetics has been investigated using significantly higher concentrations than the commonly present in fresh waters [52].

4. Conclusions

The development of environmentally-friendly and cost-effective technologies for the removal of micropollutants is crucial to optimize current wastewater and drinking water treatment plants. In this work, the inexpensive Fe₃O₄-R400/H₂O₂ system has proved to be efficient for the treatment of all neonicotinoid pesticides recently included in the EU Watch List due to their significant risk for the environment. Notably, the insecticides were quickly removed along reaction under ambient conditions and slightly acidic pH (pH₀ = 5) regardless of their nature. In this sense, although their reactivity was found to decrease in the order: THC>IMD>THM>CLT>ACT, the pseudo-first order rate constants were comparable (0.26 – 0.61 min⁻¹). Apart from warranting the total removal of the target pollutants, the aromatic by-products formed along reaction were also completely eliminated. Accordingly, a high extent mineralization (>50%) was achieved, being the reaction effluents non-toxic (<0.1 TU). Finally, the process was also tested using relevant concentrations of the major component of fresh waters *viz.* NOM and a real surface water. The presence of organic matter somehow inhibited the reaction due to HO \cdot scavenging while the occurrence of inorganic salts did not significantly influence the kinetics of the process. These results prove the potential of the Fe₃O₄-

R400/H₂O₂ catalytic system for the fast and effective removal of neonicotinoid pesticides from water, which in practice could be used similar to an adsorption process.

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Table and Figure captions

Table 1. Neonicotinoid pesticides investigated and theoretical stoichiometry for their complete oxidation.

Table 2. Values of the pseudo-first order rate constants for the CWPO of the neonicotinoid pesticides at 25°C.

Table 3. EC₅₀ of the neonicotinoid pesticides.

Fig. 1. Time-course of ACT, CLT, IMD, THC and THM upon CWPO individually treated at 25°C ([Pesticide]₀ = 1000 µg L⁻¹; [Fe₃O₄-R400] = 1.0 g L⁻¹; [H₂O₂]₀ = stoichiometric concentration; pH₀ = 5). Symbols (experimental data) and solid lines (model fit).

Fig. 2. Evolution of the aromatic by-products generated upon CWPO of CLT (a) and IMD (b) at 25 °C ([Pesticide]₀ = 1000 µg L⁻¹; [Fe₃O₄-R400] = 1.0 g L⁻¹; [H₂O₂]₀ = stoichiometric concentration; pH₀ = 5).

Fig. 3. Evolution of ACT and ecotoxicity (a) as well as aromatic intermediates (b) upon CWPO ([ACT]₀ = 20 mg L⁻¹; [Fe₃O₄-R400] = 2.0 g L⁻¹; [H₂O₂]₀ = 106 mg L⁻¹; pH₀ = 5).

Fig. 4. Proposed reaction pathway for ACT degradation upon CWPO.

Fig. 5. Time-course of ACT along CWPO in different water matrices (deionized water, deionized water with 1 and 10 mg L⁻¹ NOM and surface water) ([Pesticide]₀ = 1000 µg L⁻¹; [Fe₃O₄-R400] = 1.0 g L⁻¹; [H₂O₂]₀ = 5.3 mg L⁻¹; pH₀ = 5). Symbols (experimental data) and solid lines (model fit).

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580 **Supplementary Material**
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582 **Fast oxidation of the neonicotinoid pesticides listed in the**
583 **EU Decision 2018/840 from aqueous solutions**
584

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Table S1. Concentration of short-chain organic acids, TOC and carbon balance closure at the end of the CWPO reactions (1 h) of all the pesticides (individually treated) ($[\text{Pesticide}]_0 = 1000 \mu\text{g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric amount}$; $[\text{Fe}_3\text{O}_4\text{-R400}] = 1 \text{ g L}^{-1}$; $\text{pH}_0 = 5$).

| Pesticide | Acetic acid (mg L^{-1}) | Formic acid (mg L^{-1}) | Oxalic acid (mg L^{-1}) | TOC (mg L^{-1}) | Carbon balance closure (%) |
|-----------|---------------------------------------|---------------------------------------|---------------------------------------|-------------------------------|-------------------------------------|
| ACT | 0.55 | 0.15 | 0.20 | 0.29 | >99 |
| CLT | 0.38 | 0.14 | 0.18 | 0.23 | >99 |
| IMD | 0.33 | 0.10 | 0.37 | 0.29 | 93 |
| THC | 0.11 | 0.12 | 0.32 | 0.18 | 91 |
| THM | 0.25 | 0.10 | 0.12 | 0.14 | >99 |

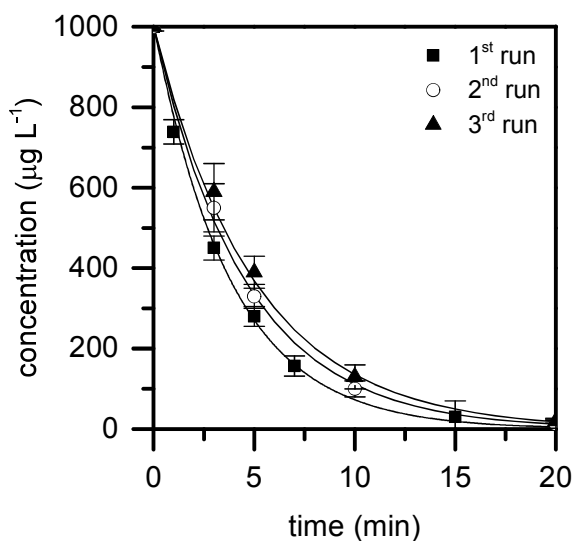
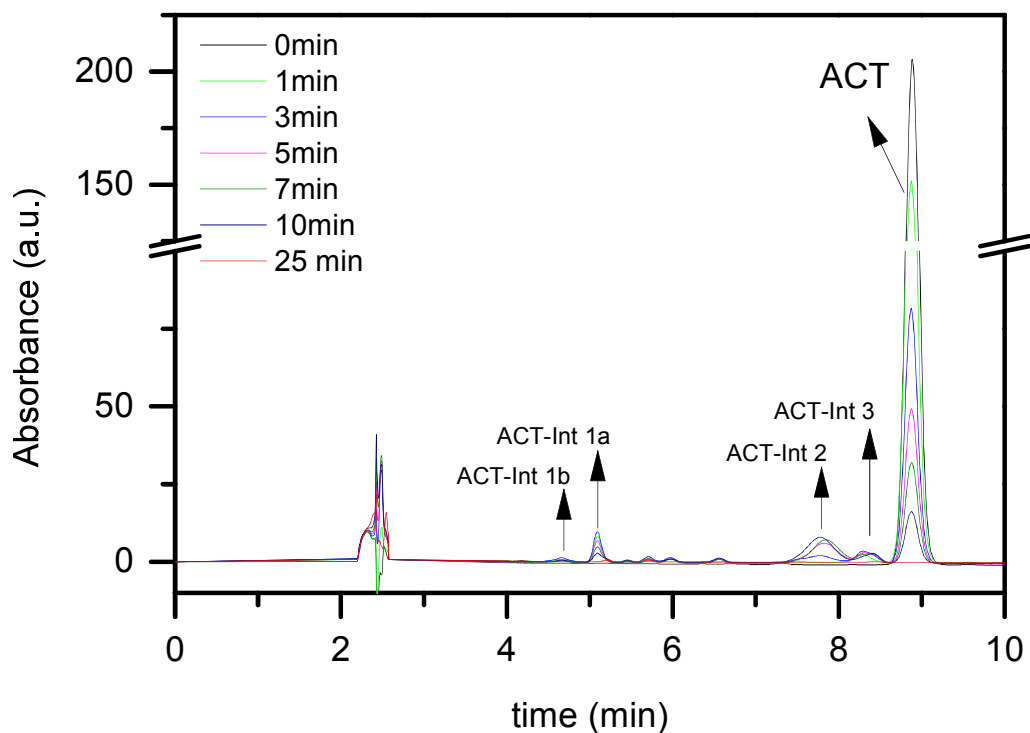
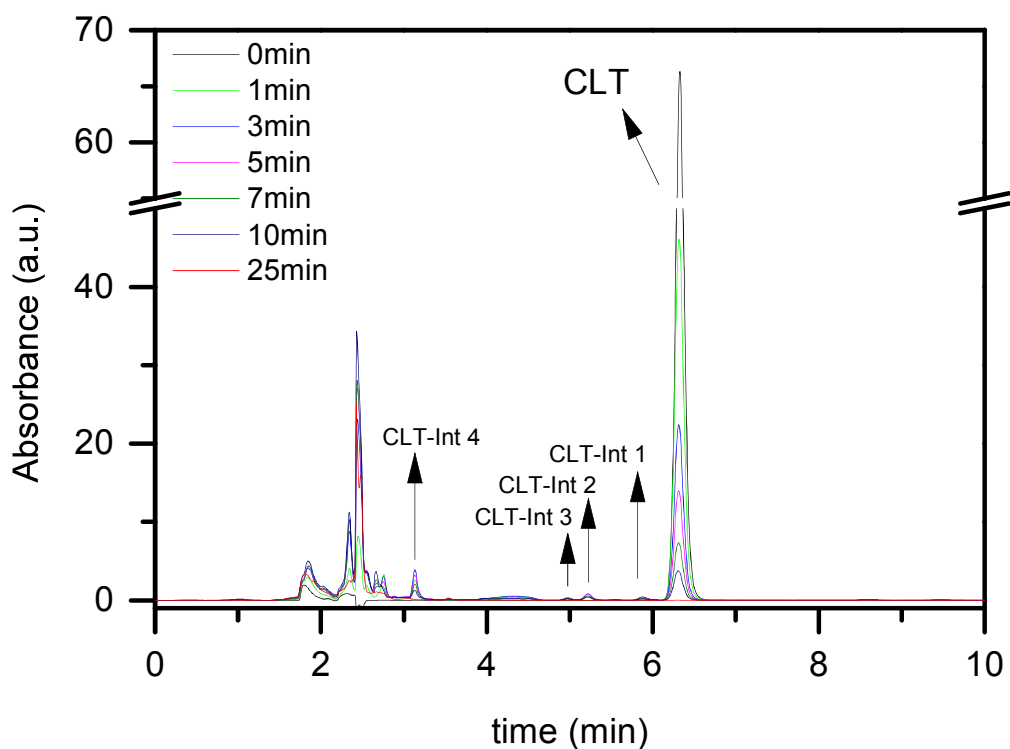


Fig S1. Stability of $\text{Fe}_3\text{O}_4\text{-R400}$ upon ACT oxidation in three sequential runs (individually treated) ($[\text{Pesticide}]_0 = 1000 \mu\text{g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric amount}$; $[\text{Fe}_3\text{O}_4\text{-R400}] = 1 \text{ g L}^{-1}$; $\text{pH}_0 = 5$).



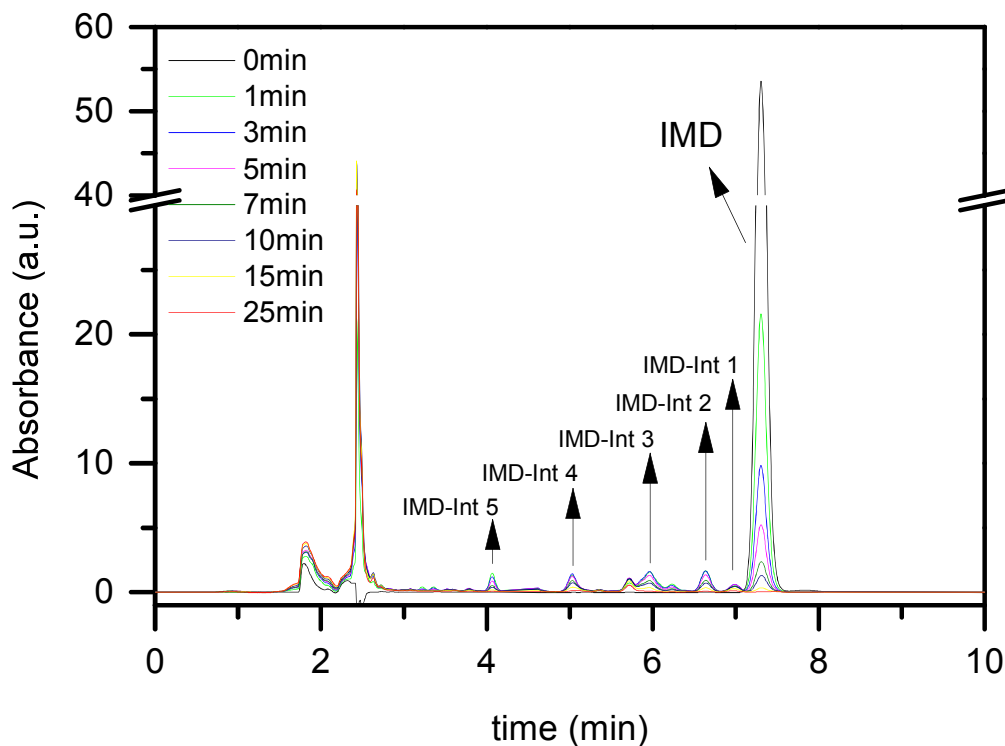
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Fig S2. HPLC/UV chromatograms obtained along the CWPO of ACT (individually treated) ($[\text{Pesticide}]_0 = 1000 \mu\text{g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric amount}$; $[\text{Fe}_3\text{O}_4\text{-R400}] = 1 \text{ g L}^{-1}$; $\text{pH}_0 = 5$).



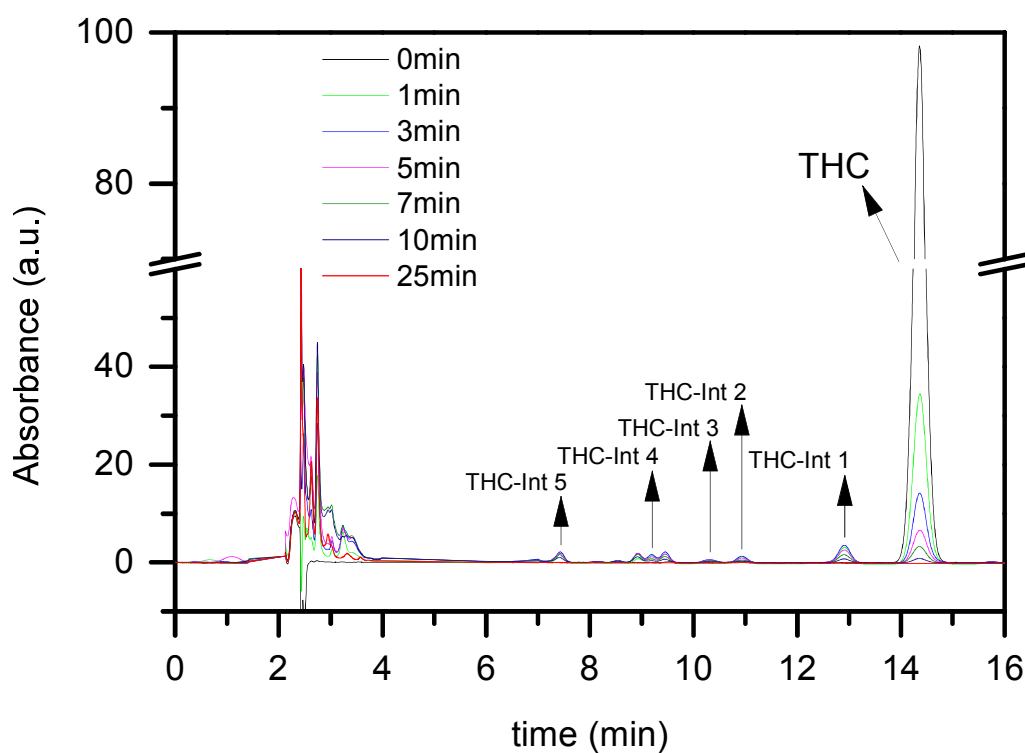
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Fig S3. HPLC/UV chromatograms obtained along the CWPO of CLT (individually treated) ($[\text{Pesticide}]_0 = 1000 \mu\text{g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric amount}$; $[\text{Fe}_3\text{O}_4\text{-R400}] = 1 \text{ g L}^{-1}$; $\text{pH}_0 = 5$).



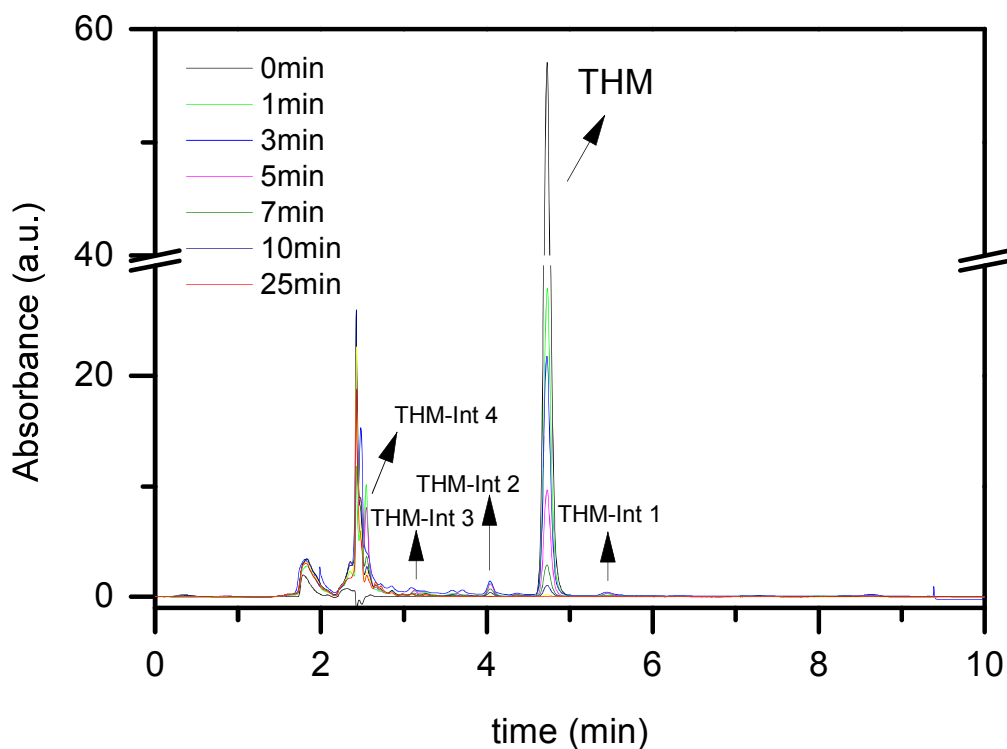
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Fig S4. HPLC/UV chromatograms obtained along the CWPO of IMD (individually treated) ([Pesticide]₀ = 1000 μg L⁻¹; [H₂O₂]₀ = stoichiometric amount; [Fe₃O₄-R400] = 1 g L⁻¹; pH₀ = 5).



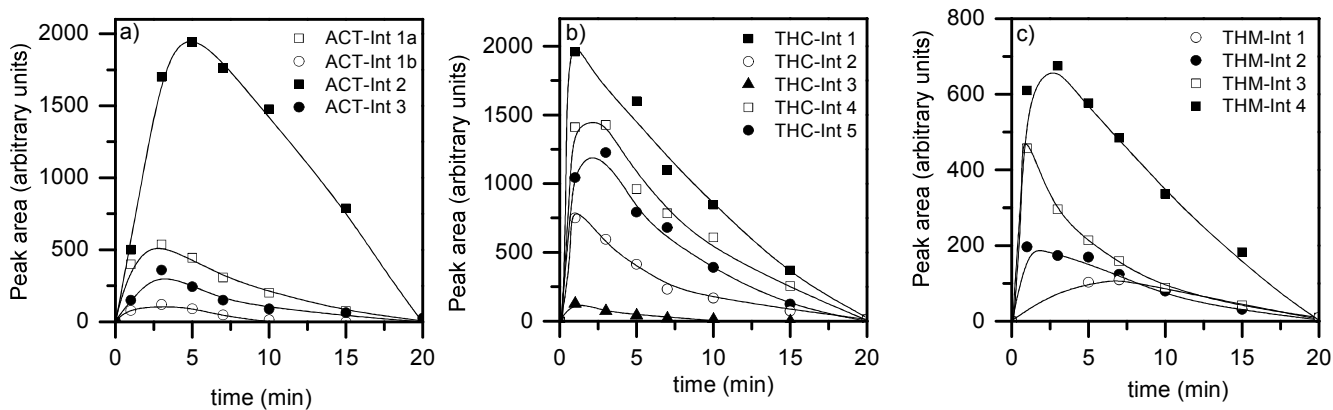
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Fig S5. HPLC/UV chromatograms obtained along the CWPO of THC (individually treated) ([Pesticide]₀ = 1000 μg L⁻¹; [H₂O₂]₀ = stoichiometric amount; [Fe₃O₄-R400] = 1 g L⁻¹; pH₀ = 5).



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Fig. S6. HPLC/UV chromatograms obtained along the CWPO of THM (individually treated) ($[Pesticide]_0 = 1000 \mu g L^{-1}$; $[H_2O_2]_0 =$ stoichiometric amount; $[Fe_3O_4-R400] = 1 g L^{-1}$; $pH_0 = 5$).



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Fig. S7. Evolution of the reaction intermediates formed upon CWPO of ACT (a), THC (b) and THM (c).

($[Pesticide]_0 = 1000 \mu g L^{-1}$; $[H_2O_2]_0 =$ stoichiometric amount; $[Fe_3O_4-R400] = 1.0 g L^{-1}$; $pH_0 = 5$).

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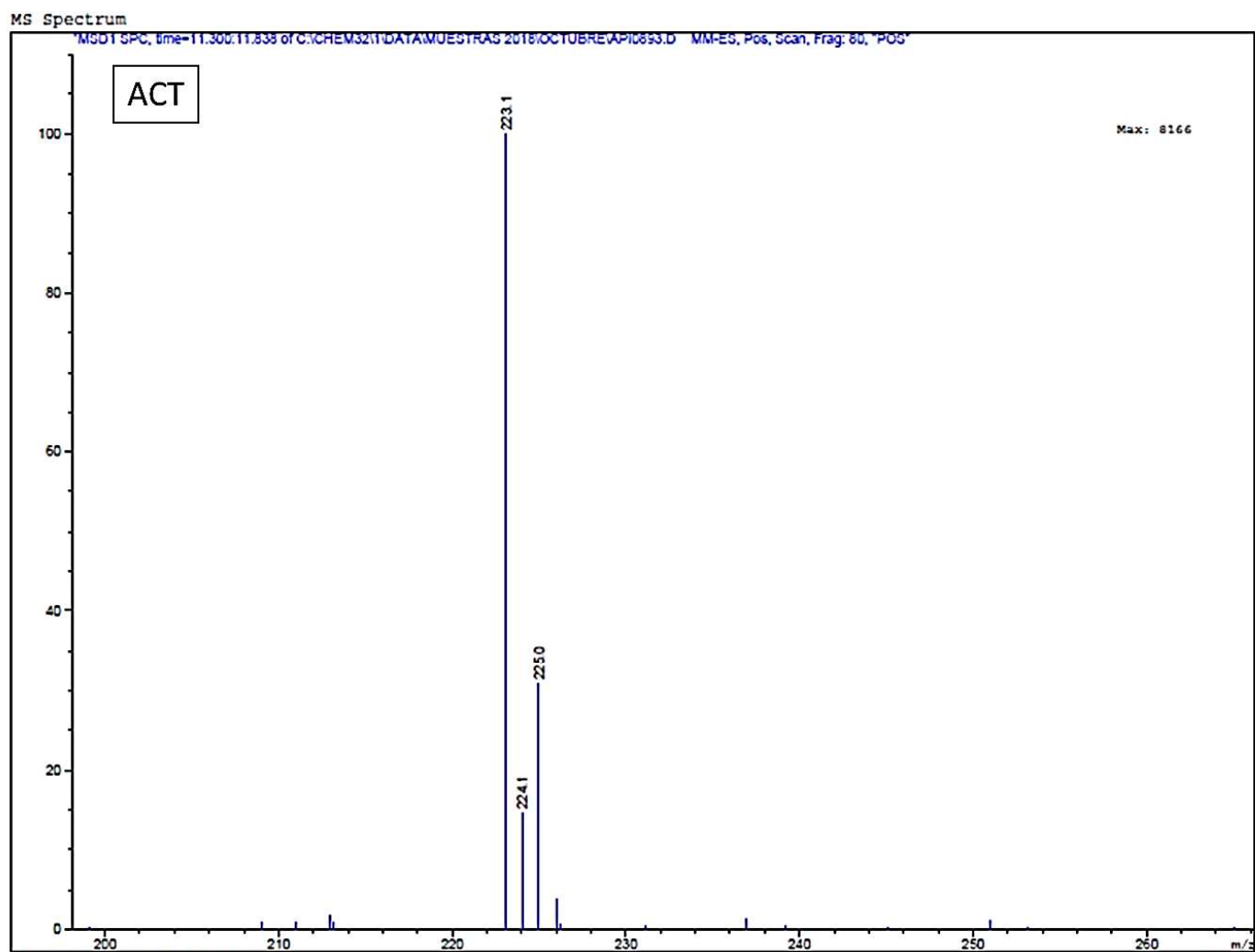


Fig. S8. Mass spectrum (ESI+) of ACT.

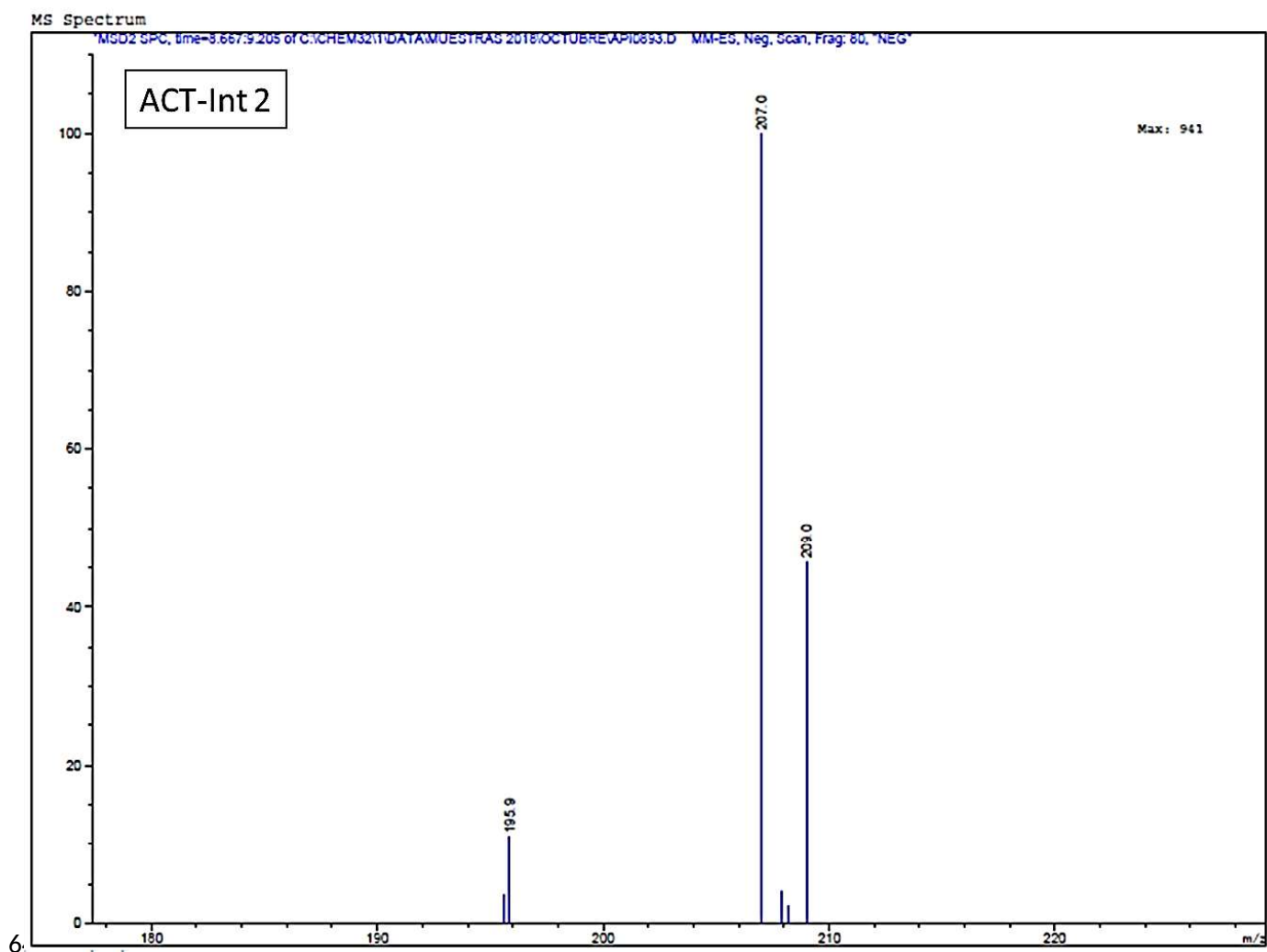


Fig. S10. Mass spectrum (ESI-) of ACT-Int 2.

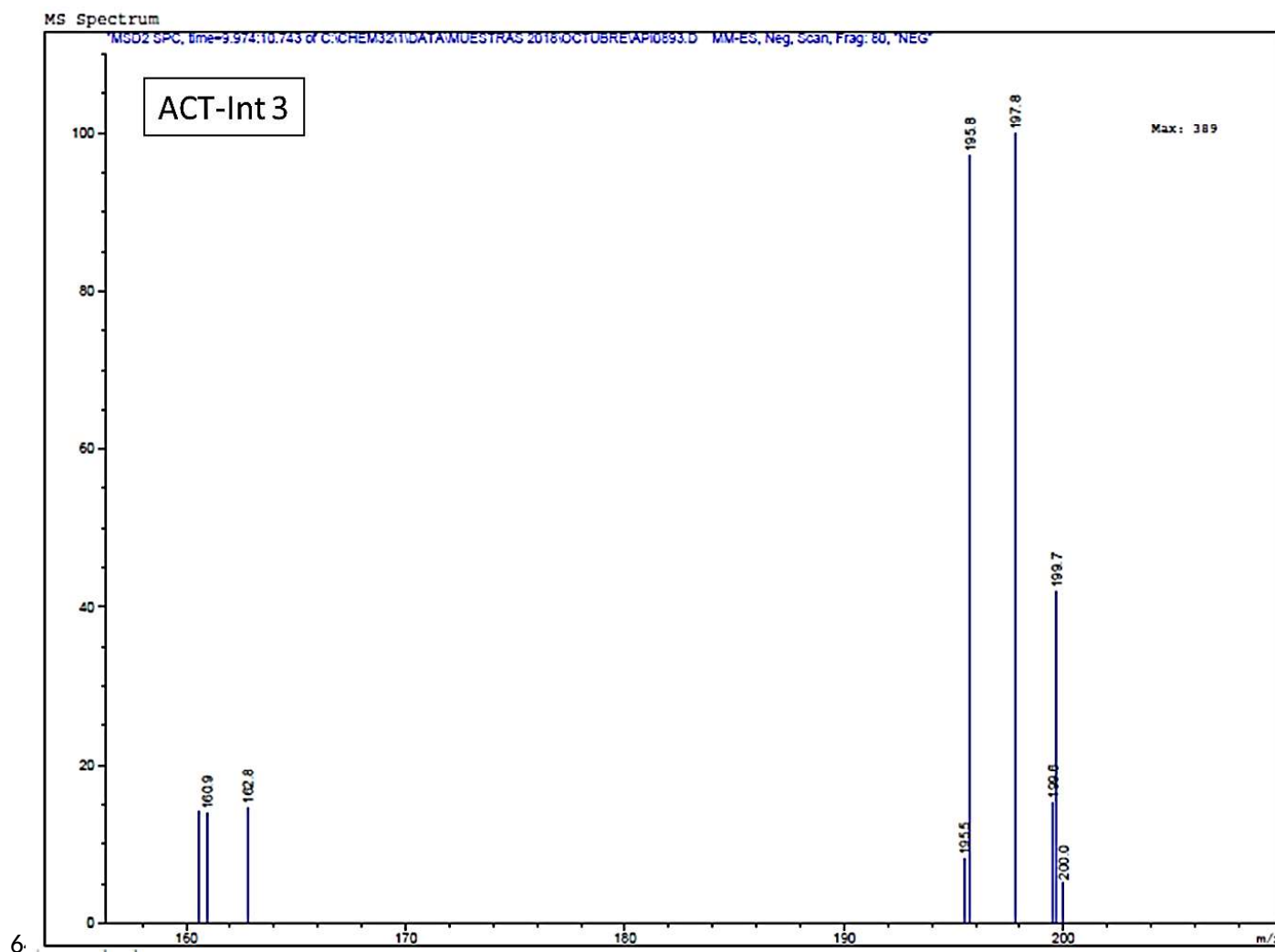


Fig. S11. Mass spectrum (ESI-) of ACT-Int 3.

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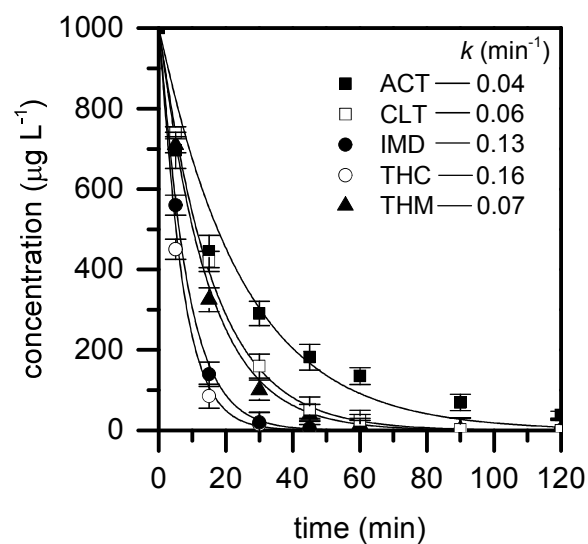


Fig. S12. Time-course of ACT, CLT, IMD, THC and THM upon CWPO individually treated in surface water at 25°C ($[\text{Pesticide}]_0 = 1000 \mu\text{g L}^{-1}$; $[\text{Fe}_3\text{O}_4\text{-R400}] = 1.0 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = \text{stoichiometric concentration}$; $\text{pH}_0 = 5$). Symbols (experimental data) and solid lines (model fit).

Figure 1

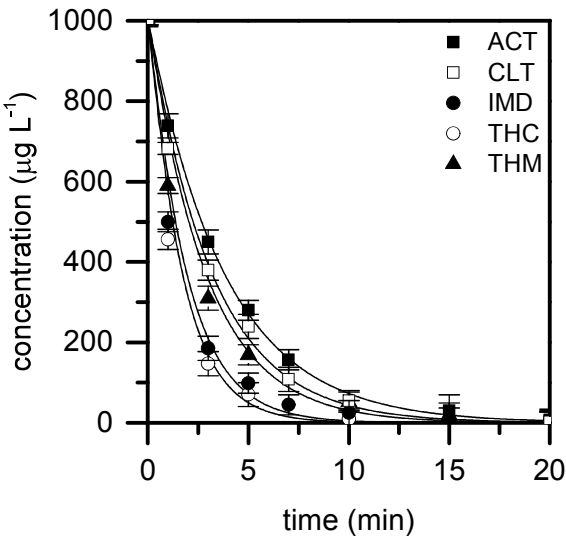


Figure 2 revised

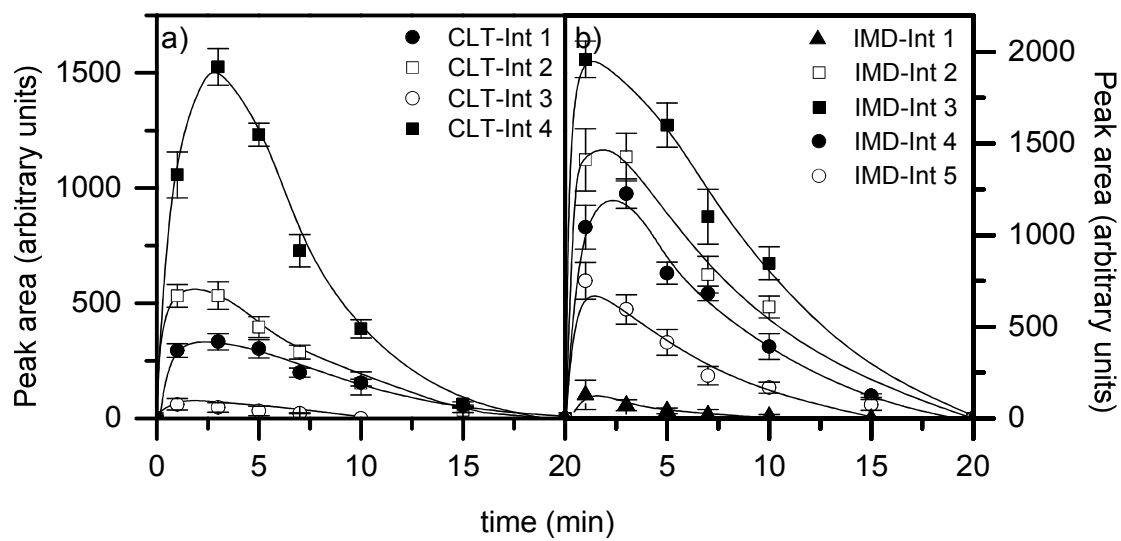


Figure 3 Revised

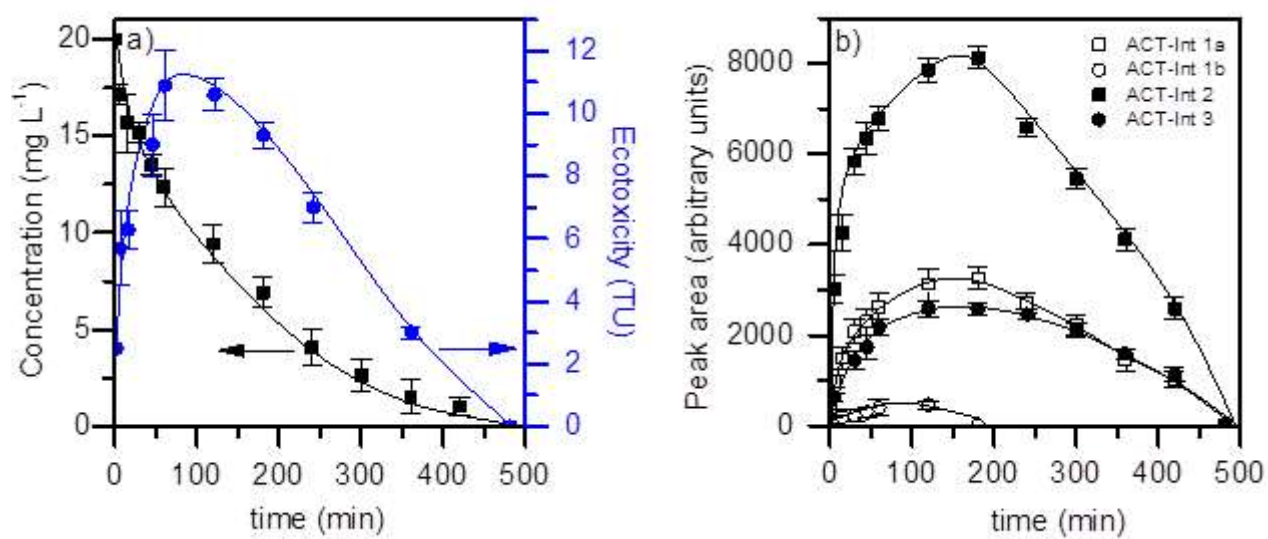


Figure 4

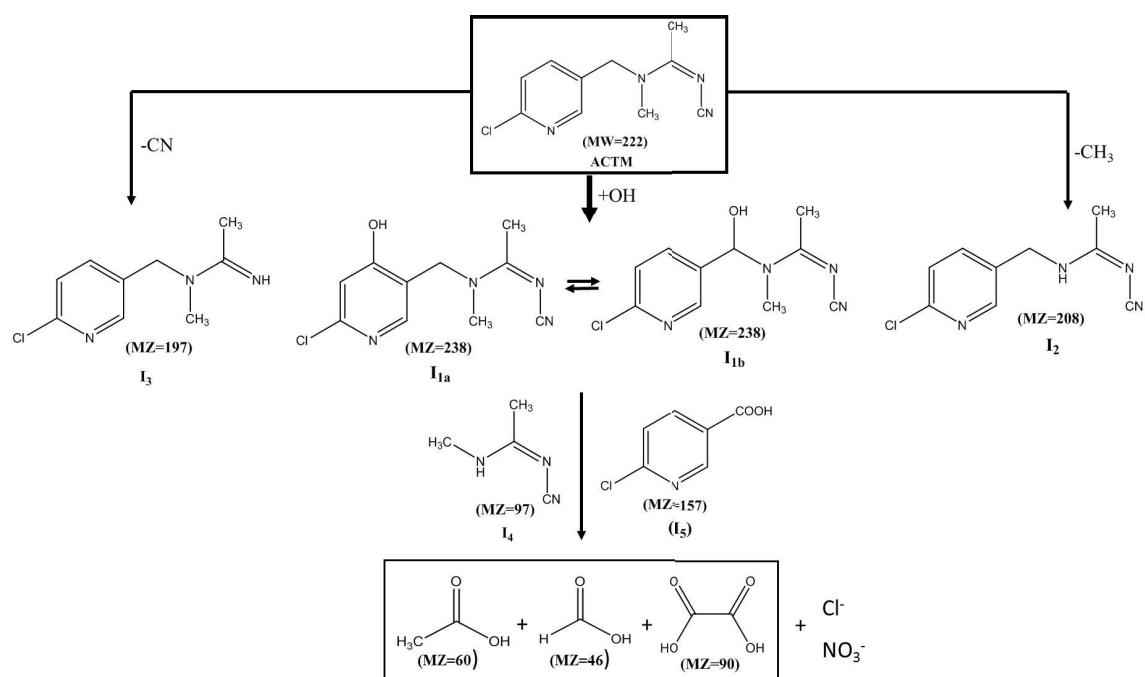


Figure 5

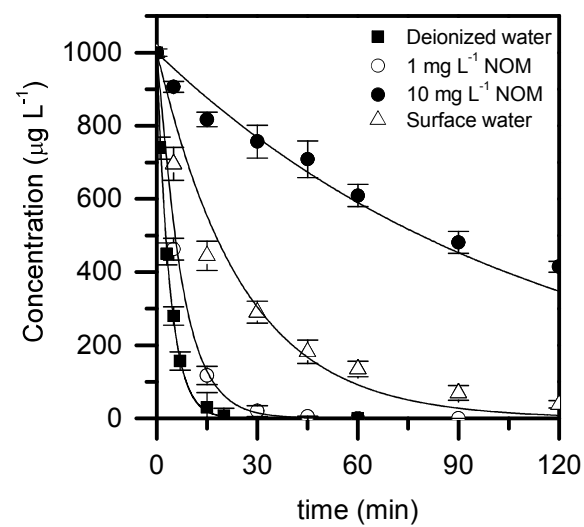
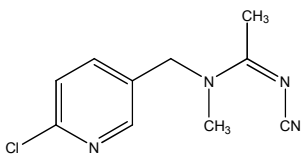
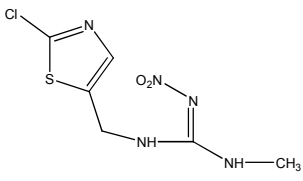
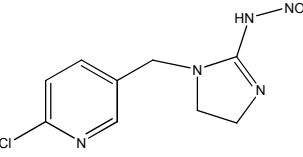
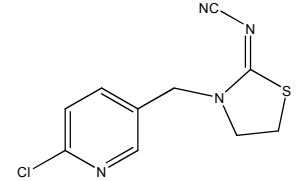
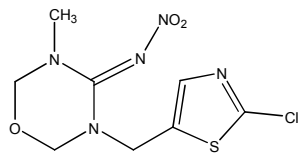


Table 1

| Compound | Structural formula | Reaction | H ₂ O ₂ (mg L ⁻¹)* |
|---|---|---|---|
| Acetamiprid (ACT) (222.7 g mol ⁻¹) |  | $\text{C}_{10}\text{H}_{11}\text{ClN}_4 + 35\text{H}_2\text{O}_2 \rightarrow 10\text{CO}_2 + \text{HCl} + 4\text{HNO}_3 + 38\text{H}_2\text{O}$ | 5.3 |
| Clothianidin (CLT) (249.7 g mol ⁻¹) |  | $\text{C}_6\text{H}_8\text{ClN}_5\text{O}_2\text{S} + 29\text{H}_2\text{O}_2 \rightarrow 6\text{CO}_2 + \text{HCl} + 5\text{HNO}_3 + \text{H}_2\text{SO}_4 + 29\text{H}_2\text{O}$ | 4.0 |
| Imidacloprid (IMD) (255.7 g mol ⁻¹) |  | $\text{C}_9\text{H}_{10}\text{ClN}_5\text{O}_2 + 33\text{H}_2\text{O}_2 \rightarrow 9\text{CO}_2 + \text{HCl} + 5\text{HNO}_3 + 35\text{H}_2\text{O}$ | 4.4 |
| Thiacloprid (THC) (252.7 g mol ⁻¹) |  | $\text{C}_{10}\text{H}_9\text{ClN}_4\text{S} + 37\text{H}_2\text{O}_2 \rightarrow 10\text{CO}_2 + \text{HCl} + 4\text{HNO}_3 + \text{H}_2\text{SO}_4 + 38\text{H}_2\text{O}$ | 5.0 |
| Thiamethoxam (THM) (291.7 g mol ⁻¹) |  | $\text{C}_8\text{H}_{10}\text{ClN}_5\text{O}_3\text{S} + 33\text{H}_2\text{O}_2 \rightarrow 8\text{CO}_2 + \text{HCl} + 5\text{HNO}_3 + \text{H}_2\text{SO}_4 + 34\text{H}_2\text{O}$ | 3.9 |

* Theoretical stoichiometric amount of H₂O₂ referred to an initial target pollutant concentration of 1000 µg L⁻¹.

Table 2

| Neonicotinoid pesticide | k (min⁻¹) | r^2 |
|------------------------------------|--|-------------------------|
| ACT | 0.26 | 0.99 |
| CLT | 0.32 | 0.99 |
| IMD | 0.54 | 0.99 |
| THC | 0.61 | 0.98 |
| THM | 0.35 | 0.97 |

Table 3

| Sample | EC₅₀ (mg L⁻¹) |
|---------------|--|
| ACT | 8 |
| THC | 18 |
| THM | 260 |
| IMD | 122 |
| CLT | 192 |