

# Glyphosate and AMPA removal from water by solar induced processes using low Fe(III) or Fe(II) concentrations

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A solar photo-Fenton-like (SPF-like) process is explored for the removal of 1 mg L<sup>-1</sup> glyphosate and its main degradation by-product, aminomethylphosphonic acid (AMPA), from Milli-Q water by means of low Fe(III) concentrations (0.6–2 mg L<sup>-1</sup>) at pH = 2.8 and variable H<sub>2</sub>O<sub>2</sub> concentrations at the laboratory scale. The research is focused on glyphosate and AMPA oxidation, which present similar toxicity patterns. A 1 mg L<sup>-1</sup> glyphosate solution requires 5–6 h of the SPF-like process to be degraded when a minute Fe(III) concentration (0.6 mg L<sup>-1</sup>) is used in acidic water. Glyphosate abatement time is diminished to 2 h when the Fe(III) concentration is increased to 2 mg L<sup>-1</sup>. At pH levels above 2.8, the herbicide is partially adsorbed onto the colloids of iron oxy(hydroxide) compounds. AMPA requires a higher oxidative power than glyphosate to be degraded, and more than 6 h of solar treatment are needed, using 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> and 2 mg L<sup>-1</sup> Fe(III) at acidic pH. Solar photo-Fenton (SPF), using 4 mg L<sup>-1</sup> Fe(II) and 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at pH = 2.8, must be applied to achieve practically total AMPA removal in 6 h of irradiation. SPF-like and SPF treatments led to 70% and 80% mineralization, respectively, under the best operational conditions. This work demonstrates that SPF-like and SPF at low Fe(III) or Fe(II) concentrations are effective treatments for the removal of glyphosate from water at acidic pH. Continuous addition of H<sub>2</sub>O<sub>2</sub> is required for AMPA abatement.

## Water impact

Glyphosate, an herbicide frequently used worldwide, can be rapidly eliminated when Fe(III) is naturally present in the polluted water under solar irradiation. However, glyphosate is degraded into AMPA, which has a similar toxicity pattern to its precursor and needs a higher oxidative potential to be removed. SPF-like and SPF are technically feasible treatments to remove both pollutants from water.

## 1. Introduction

The global agricultural productivity has increased by 100% in the last decades (1990–2016),<sup>1</sup> concomitant with the use of pesticides with a worldwide consumption of 4 million tons in 2016.<sup>2</sup> Genetically modified soybean, corn, and cotton crops, among others, often demand high amounts of glyphosate (*N*-

(phosphonomethyl)glycine), a highly soluble organophosphate compound, as a main herbicide.<sup>3</sup> Consumption in the United States, the largest producer of soybean, rose from 635 tons in 1974 to 125 384 tons in 2014,<sup>4</sup> and 55 300 tons of glyphosate were commercialized during 2016 in Argentina, the third largest soybean producer worldwide.<sup>5</sup>

There is concern over the contamination of surface water or groundwater by a significant fraction of the applied pesticides through agricultural runoff, threatening the environment and human health. Several studies have reported the presence of glyphosate or its primary degradation by-product, aminomethylphosphonic acid (AMPA), in river water samples and sediments.<sup>6–9</sup> The half-life of glyphosate is estimated to be between 2 and 174 days, while AMPA's half-life is 199–958 days,<sup>10</sup> depending on soil type and microbial activity among other environmental factors. However, the presence of both

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glyphosate and AMPA in surface waters has been reported months after their application.<sup>11,12</sup>

The International Agency for Research on Cancer (IARC) classified glyphosate as a probable carcinogen to humans (Group 2A),<sup>13</sup> and as such, is regulated for drinking water, although the allowed levels vary significantly. The maximum contaminant level in the U.S. is  $700 \mu\text{g L}^{-1}$ ,<sup>14</sup> but it is much lower in Argentina at  $300 \mu\text{g L}^{-1}$  glyphosate isopropylamine salt ( $222 \mu\text{g L}^{-1}$  glyphosate);<sup>15</sup> the maximum total concentration of pesticides permissible in drinking water in the European Union is only  $0.5 \mu\text{g L}^{-1}$ .<sup>16</sup> Although AMPA is not currently regulated, the two compounds have similar toxicological profiles.<sup>17</sup> Therefore, technical and economically feasible processes are needed to remove not only glyphosate from water but also AMPA, since their presence in water is highly extended, especially in rural areas. Advanced oxidation processes (AOPs), which have, as the main feature, the *in situ* production of strongly oxidative reactive oxygen species (ROS) such as the hydroxyl radical ( $\cdot\text{OH}$ ), are often used to degrade persistent and/or toxic organic compounds.<sup>18</sup> Among the AOPs, the photo-Fenton process seems to be a promising technology to mineralize the waterborne pollutants, especially when solar light is used as a radiation source due to low operational costs.

Historically, the photo-Fenton process has been applied using relatively high amounts of the reagents ferrous ions and hydrogen peroxide, but glyphosate degradation by photo-Fenton at acidic (2.8–3.0) and circumneutral pH has not been extensively studied in the literature using minute amounts of reagents. For example, Huston and Pignatello<sup>19</sup> reported the degradation of several pesticides including  $34 \text{ mg L}^{-1}$  glyphosate, using  $2.8 \text{ mg L}^{-1} \text{Fe(III)}$  and  $340 \text{ mg L}^{-1} \text{H}_2\text{O}_2$  at pH 2.8 upon fluorescent blacklight UV irradiation; de Souza *et al.*<sup>20</sup> reported glyphosate abatement by the photo-Fenton process claiming the use of  $15\text{--}100 \text{ mg L}^{-1} \text{Fe(III)}$  and/or  $\text{Fe(II)}$  and  $350 \text{ mg L}^{-1} \text{H}_2\text{O}_2$  at pH 2.8, under artificial light irradiation (high pressure mercury vapor lamp). Additionally, the photo-Fenton with artificial UV light using  $5\text{--}73 \text{ mg L}^{-1}$  ferric pyruvate and ferric citrate at acidic–circumneutral pH has also been reported to degrade 1.0 to  $5.0 \text{ mg L}^{-1}$  glyphosate.<sup>21,22</sup> Results showed that at acidic and circumneutral pH (5.0), glyphosate was efficiently degraded. These studies were performed using relatively high concentrations of iron (ferric or ferrous) and  $\text{H}_2\text{O}_2$ , which leads to the undesirable formation of iron sludge and the presence of high amounts of  $\text{H}_2\text{O}_2$  after the treatment.<sup>23</sup> On the other hand, experiments at circumneutral pH were performed using ferric complexes (pyruvate and citrate) which are highly stable and photochemically active under those conditions.<sup>21,22</sup> Although adding complexing agents seems to be a promising strategy to extend the pH range of photo-Fenton process, it presents additional drawbacks such as the extra cost of chelator addition, increase of the total organic carbon content and most importantly, concerns about the ecotoxicity and biodegradability of chelators and by-products formed after the photochemical event.<sup>24</sup> None of these studies considered the formation of AMPA.

Manassero *et al.*<sup>25</sup> studied the degradation of 27–91  $\text{mg L}^{-1}$  glyphosate by a  $\text{H}_2\text{O}_2/\text{UV-C}$  process at several initial pH values (3.5, 7 and 10), but the pesticide was not totally degraded after 5 h of treatment and AMPA was not detected as a by-product. Trinelli *et al.*<sup>26</sup> investigated the photodegradation of glyphosate (50, 250 and  $500 \text{ mg L}^{-1}$ ) using 5 UV-C lamps ( $\lambda_{\text{max}} = 254 \text{ nm}$ ); more than 60 h were needed to completely degrade the herbicide.

Ozonation and chlorination were reported as effective processes for the removal of glyphosate and AMPA (>95%).<sup>27</sup> However, toxic chlorinated byproducts may be produced when chlorine is used as an oxidant. On the other hand, the cost of ozone treatment is not negligible, and therefore, there is enormous potential for the photo-Fenton process as the appropriate technology to be applied for the removal of these organic compounds.

Some authors have argued that photo-Fenton processes may occur in natural water since dissolved or colloidal iron (naturally present) at concentrations ranging from  $0.05\text{--}2 \text{ mg L}^{-1}$  and hydrogen peroxide coming from bacterial activity could participate in the reactions induced by natural sunlight irradiation.<sup>28,29</sup> Sciacca *et al.*<sup>30</sup> found that the simple addition of  $10 \text{ mg L}^{-1} \text{H}_2\text{O}_2$  to Sahelian surface waters, naturally occurring at pH 7 with  $0.3 \text{ mg L}^{-1}$  total iron, enhanced solar disinfection probably due to sunlight photoinduced events such as photo-Fenton and other photochemical reactions. Serra-Clusellas *et al.*<sup>31</sup> investigated the removal of another water-soluble herbicide, 2,4-D, at acidic pH using minute ferric ion concentrations ( $0.3\text{--}0.6 \text{ mg L}^{-1}$ ) and low  $\text{H}_2\text{O}_2$  concentrations ( $3\text{--}20 \text{ mg L}^{-1}$ ), obtaining very encouraging results. These results suggest the feasibility of organic pollutant removal by photo-Fenton processes using iron concentrations as those frequently found in natural waters and by the simple addition of hydrogen peroxide.

Herein, the degradation of glyphosate ( $1 \text{ mg L}^{-1}$ ) and AMPA was studied through a solar photo-Fenton-like (SPF-like) process at acidic pH (2.8) using low amounts of  $\text{Fe(III)}$  ( $0.6$  and  $2 \text{ mg L}^{-1}$ ) and  $10 \text{ mg L}^{-1} \text{h}^{-1} \text{H}_2\text{O}_2$ . The levels of  $\text{Fe(III)}$  considered are representative of those found in Argentinean rivers, *i.e.* La Plata river,  $0.6 \text{ mg L}^{-1}$ ,<sup>32</sup> or in some mineral waters.<sup>33</sup> The abatement of glyphosate and AMPA under solar light when  $\text{Fe(III)}$  is naturally present in the water was also evaluated and compared to that in the presence of  $\text{Fe(II)}$ .

## 2. Methods

### 2.1. Chemicals

Glyphosate and AMPA were purchased from Sigma Aldrich® (St Louis, MO), analytical HPLC grade standards with a purity >96%.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , both from ANEDRA® (Buenos Aires, Argentina), were used as a source of  $\text{Fe(III)}$  and  $\text{Fe(II)}$ , respectively. Reagent grade 30%  $\text{H}_2\text{O}_2$  was also supplied by ANEDRA® (Buenos Aires, Argentina).

Solutions were prepared with high-purity water from a Classic UVMK2 Purelab Ultra (Elga-Veolia) system (resistivity > 18 MΩ cm, at 25 °C).

Analytical grade 98% H<sub>2</sub>SO<sub>4</sub> and NaOH pellets from ANEDRA® were used for the preparation of diluted solutions used for pH adjustment.

98% *p*-toluenesulphonyl chloride from Sigma Aldrich®, analytical grade 99% dipotassium hydrogen phosphate and 99% sodium phosphate tribasic (anhydrous) from Biopack® (Buenos Aires, Argentina) were used for the glyphosate and AMPA derivatization.

Isocratic grade acetonitrile from Merck Millipore's LiChrosolv®, analytical grade 85.5% H<sub>3</sub>PO<sub>4</sub> from Anedra® and sodium dihydrogen phosphate salt from Biopack® were used in the preparation of the mobile phase for high-performance liquid chromatography (HPLC).

To determine the H<sub>2</sub>O<sub>2</sub> concentration, a 1000 mg L<sup>-1</sup> Ti standard solution ((NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub>) from Merck® and analytical grade 98% H<sub>2</sub>SO<sub>4</sub> were used.

## 2.2. Instruments and analytical procedures

Determination of glyphosate and AMPA was performed by reverse-phase HPLC after derivatization with *p*-toluenesulphonyl chloride, modifying the method proposed by Kawai and Uno.<sup>34</sup> 2.00 mL of samples with glyphosate and AMPA, previously filtered with 0.45 μm PVdF (polyvinylidene fluoride) membranes, were basified (pH 11) with 0.25 mL of 0.4 M phosphate buffer and derivatized with 0.20 mL of a *p*-toluenesulfonyl chloride solution (1 mg TsCl per mL acetonitrile) for 5 min at 50 °C. Afterwards, the derivatized solutions were filtered (0.45 μm PVdF) and 20 μL aliquots were injected into an HP 1100 Series chromatograph fitted with a ZORBAX Eclipse XDB-C18 column (4.6 × 250 mm, 5 μm) at 25 °C coupled to an Agilent Technologies 1200 UV-vis detector, working at λ = 240 nm. A mobile phase consisting of 0.2 M phosphate buffer (pH 2.30):acetonitrile (85:15, v/v) at a flow rate of 0.8 mL min<sup>-1</sup> was used. Limit of quantification (LoQ) (glyphosate) = 0.03 mg L<sup>-1</sup>; LoQ (AMPA) = 0.02 mg L<sup>-1</sup>.

Dissolved organic carbon (DOC) was monitored using a Shimadzu TOC-V<sub>CPH</sub> analyzer. Reproducible DOC values, within ±2% accuracy, were obtained by injecting 50 μL aliquots previously filtered with 0.45 μm PVdF membranes.

A Shimadzu UV/vis UV-1650 PC spectrophotometer was used to determine H<sub>2</sub>O<sub>2</sub> concentrations from absorption of the Ti-H<sub>2</sub>O<sub>2</sub> colored complex at λ = 410 nm,<sup>35</sup> by previously filtering 2 mL of samples with 0.45 μm PVdF filters. LoQ (H<sub>2</sub>O<sub>2</sub>) = 0.6 mg L<sup>-1</sup>.

Total iron concentrations were measured at the beginning and at the end of assays by flame atomic absorption spectroscopy (AAS) using a Thermo Scientific iCE 3000 Series spectrometer at λ = 248.3 ± 0.2 nm (LoQ = 0.03 mg L<sup>-1</sup>). Aliquots were acidified and directly measured by AAS in order to determine the total (dissolved and suspended) iron in the solutions.

PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> concentrations were determined by ion chromatography with conductometric detection (IC-CD) at Leitao Technological Center facilities (Terrassa, Spain). Samples were properly diluted with Milli-Q water to be analyzed by IC-CD. The chromatograph was fitted with an IonPac anion exchange column AS11HC and a precolumn AG11HC. In this technique, 25 μL samples were injected; the mobile phase was 10% NaOH (100 mM):90% Milli-Q water during the first 10 min, increasing the NaOH ratio up to 50% from 10–35 min, at 1 mL min<sup>-1</sup> (PO<sub>4</sub><sup>3-</sup>: LoQ = 0.1 mg L<sup>-1</sup>, *t<sub>r</sub>* = 32.2 min; NO<sub>3</sub><sup>-</sup>: LoQ = 0.1 mg L<sup>-1</sup>, *t<sub>r</sub>* = 17.8 min).

## 2.3. Experimental setup and operational conditions

500 mL samples of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) were treated by the solar photo-Fenton like (SPF-like, using initially Fe(III)) or solar photo-Fenton (SPF, using initially Fe(II)) process at pH 2.8 in a recirculating set-up.

Trials were performed for 6 h (10 a.m to 4 p.m) in sunny and clear days during the months of January–April 2017 (austral summer) at the university building roof top (Buenos Aires, Argentina, longitude: 58° 22' W, latitude: 34° 36' S). Target solutions were pumped (Masterflex® peristaltic pump) from a 500 mL Pyrex® reactor thermostated at 25 °C (located in the darkness) to a 250 mL cylindrical Pyrex® reactor located on a reflective surface adapted from “SolarMate” (a device similar to 1 liter metal insulated bottles that allows heating of water inside with solar energy, Universidad Nacional de San Martín, Argentina) exposed to solar radiation at an angle of 34°, changing its inclination during the day to maximize the capture of light. The solution was continuously recirculated at 12 L h<sup>-1</sup>. The UV-B + UV-A radiation was monitored throughout the treatment time by means of a Lutron YK-35UV UV light meter in order to calculate the normalized irradiated time (*t*<sub>30W,n</sub>). This parameter was defined to standardize the solar irradiation, considering that the average solar UV flux on a perfect sunny day is around 3 mW cm<sup>-2</sup>,<sup>36</sup> as defined in the following equation:

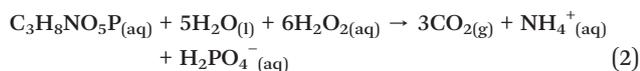
$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T} \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where *t<sub>n</sub>* is the experimental time for each sample; *t*<sub>30W</sub> is considered to be the “normalized illumination time” considering a constant solar UV power of 30 W m<sup>-2</sup>, which represents the typical value on a perfect sunny day at noon; UV is the average solar UV radiation (W m<sup>-2</sup>) measured during Δ*t*; *V<sub>i</sub>* is the irradiated volume; *V<sub>T</sub>* is the total water volume (irradiated and non-irradiated).

Aliquots were collected at the following treatment times: 0, 10, 30, 60, 120, 180, 240, 300, and 360 min.

Preliminary experiments were done with a minute Fe(III) concentration (0.6 mg L<sup>-1</sup>), simulating iron concentrations that could be found in superficial water,<sup>32</sup> and the addition of H<sub>2</sub>O<sub>2</sub> in excess at the beginning of the experiment: 20 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (corresponding to 16 times the H<sub>2</sub>O<sub>2</sub> stoichiometric

concentration to completely oxidise 1 mg L<sup>-1</sup> glyphosate mainly to CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>4</sub><sup>+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (eqn (2)) or 40 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>.



The next trials were performed using 2 mg L<sup>-1</sup> Fe(III). In these experiments, H<sub>2</sub>O<sub>2</sub> was added continuously throughout the treatment, and variable concentrations (5, 10 and 20 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>) were tested.

Control dark experiments (Fenton and peroxidation) and control light trials (glyphosate photolysis, photo-peroxidation, and assisted Fe(III)-photolysis) were also performed under the best operational conditions in order to evaluate separately the contribution of each process to the global SPF-like treatment.

The SPF process using Fe(II) was also tested to compare the efficiency of the treatment when Fe(II) or Fe(III) is used as the catalyst.

## 3. Results and discussion

### 3.1. Preliminary tests with minute Fe(III) concentrations

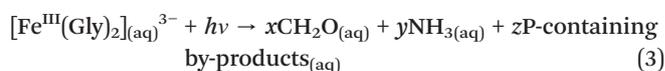
Fig. 1a shows the glyphosate degradation by the SPF-like process using a minute ferric ion concentration (0.6 mg L<sup>-1</sup>) and initial H<sub>2</sub>O<sub>2</sub> concentrations of 20 mg L<sup>-1</sup> (a) and 40 mg L<sup>-1</sup> (b) at pH 2.8. An additional experiment was performed with a second addition of 20 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at 90 min (*t*<sub>3mW,n</sub>). The differences in the H<sub>2</sub>O<sub>2</sub> concentrations tested did not play an important role in the glyphosate or AMPA degradation. Glyphosate was successfully removed after 360 min (*t*<sub>3mW,n</sub>) in all cases. However, the AMPA concentration increased during the first 90 min (*t*<sub>3mW,n</sub>) (Fig. 1b) and then underwent a slow decrease down to 0.25 mg L<sup>-1</sup>. The

photochemical process was unable to efficiently remove AMPA to 0.15 mg L<sup>-1</sup>, which would be the theoretical limit of AMPA calculated by the authors considering its toxicity equivalence with glyphosate and taking as a reference the limit 0.22 mg L<sup>-1</sup> glyphosate.<sup>33</sup> No significant DOC removal was observed under these conditions.

### 3.2. Effect of Fe(III) and H<sub>2</sub>O<sub>2</sub> concentrations

Glyphosate is a weak acid with four acidity constants, 2 for the phosphonic group (pK<sub>a1</sub> = 0.78 and pK<sub>a3</sub> = 5.96), one for the carboxylic group (pK<sub>a2</sub> = 2.29) and one for the amino group (pK<sub>a4</sub> = 10.98). It is known that glyphosate, depending on the pH and symmetry of the central atom, can coordinate as a mono-, bi-, or tridentate ligand forming complexes with different cations through its phosphonate group.<sup>37-41</sup>

Makanova *et al.*<sup>42</sup> identified the complex [Fe<sup>III</sup>(Gly)<sub>2</sub>]<sup>3-</sup> in aqueous media, with an absorption spectrum consisting of two shoulders, one located at 250 nm (ε = 7800 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) and the other at 310 nm (ε = 4400 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). They also found that under irradiation of this complex with a medium pressure Hg-lamp, the coordinated glyphosate was degraded yielding mainly ammonia, formaldehyde and phosphorus containing by-products (eqn (3)).



Barja and Dos Santos Alfonso<sup>39</sup> suggested that although the carboxylic group would be deprotonated at pH values ranging from 2 to 5, the phosphonate group could be the molecular site complexing with ferric ions. In a later study, Barja *et al.*<sup>40</sup> proposed that Fe(III) was coordinated with glyphosate (FeOH<sup>-</sup>(OOC-CH<sub>2</sub>-NH<sup>2+</sup>-CH<sub>2</sub>-PO<sub>3</sub><sup>2-</sup>)) and AMPA ([FeO<sub>2</sub>-POCH<sub>2</sub>NH<sub>3</sub>]<sup>2+</sup>) with a molar relationship of 1 : 1 at acidic pH.

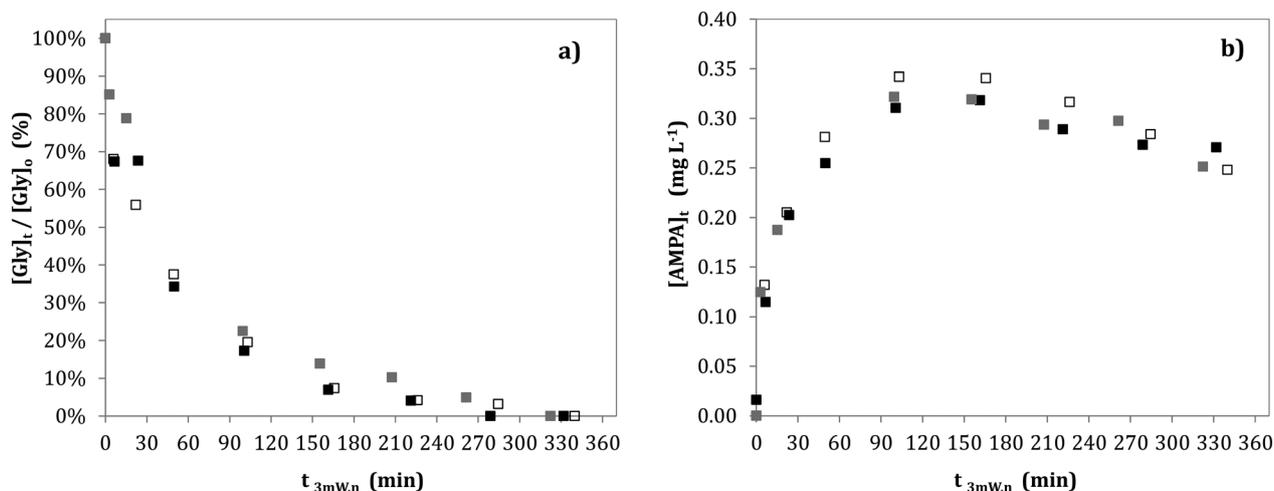


Fig. 1 Glyphosate (a) and AMPA (b) time courses of 500 mL of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) during the SPF-like process with a minute Fe(III) concentration (0.6 mg L<sup>-1</sup>) at pH = 2.8, under the following H<sub>2</sub>O<sub>2</sub> concentration conditions: (■) 20 mg L<sup>-1</sup>, added at the beginning of the experiment; (□) 40 mg L<sup>-1</sup>, added at the beginning of the experiment; (▣) 20 mg L<sup>-1</sup>, added at the beginning of the experiment +20 mg L<sup>-1</sup>, added at 90 min (*t*<sub>3mW,n</sub>).

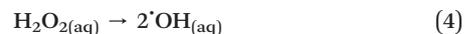
Thus, at pH 2.8, the coordinated fraction of Fe(III) in the above mentioned experiments accounted for more than 50% of the initial concentration ( $0.3 \text{ mg L}^{-1} \text{ Fe(III)}$ ) and resulted in less Fe(III) available to directly participate in the photo-Fenton treatment. Therefore, the Fe(III) concentration was raised to  $2 \text{ mg L}^{-1}$  (iron permissible limit of mineral water)<sup>33</sup> in order to accelerate the kinetics of the herbicide degradation. The quantity of  $\text{H}_2\text{O}_2$  added to the system was also increased, testing the following concentrations: a)  $20 \text{ mg L}^{-1}$  added every 2 h; b)  $10 \text{ mg L}^{-1}$  added every hour; c)  $5 \text{ mg L}^{-1}$  added every hour. The increase in Fe(III) concentration showed a faster glyphosate and AMPA degradation kinetics compared with a dose of  $0.6 \text{ mg L}^{-1} \text{ Fe(III)}$  (Fig. 2). Glyphosate was practically degraded after  $t_{3\text{mW},n} = 90 \text{ min}$ , whereas the AMPA concentration was decreased to below  $0.10 \text{ mg L}^{-1}$  at the end of the treatment. Although no significant differences for glyphosate and AMPA degradation were observed by modifying the addition rate and concentration of  $\text{H}_2\text{O}_2$ , the DOC removal was around 60% when  $5 \text{ mg L}^{-1} \text{ h}^{-1} \text{ H}_2\text{O}_2$  was added and escalated to 70% at higher  $\text{H}_2\text{O}_2$  concentrations. Thus a concentration of  $10 \text{ mg L}^{-1} \text{ h}^{-1} \text{ H}_2\text{O}_2$  was selected for further experiments.

Fig. 3 depicts the control experiments for glyphosate and AMPA degradation. The SPF-like process was compared with the following individual processes: a) controls without solar light (Fenton-like and peroxidation processes); b) controls with solar irradiation (glyphosate direct photolysis, glyphosate photolysis with Fe(III), and photo-peroxidation).

Glyphosate practically did not degrade directly with sunlight at pH = 2.8 (less than 10% removal at the end of the trial) in the absence of the other reactants/compounds. Its photolysis produced a very low concentration of AMPA.

Glyphosate aqueous solutions in the absence of Fe(III) but with the addition of  $10 \text{ mg L}^{-1} \text{ h}^{-1} \text{ H}_2\text{O}_2$  under sunlight irradiation, showed around 70% of herbicide degradation. Manassero *et al.*<sup>25</sup> and Mariani *et al.*<sup>43</sup> reported the degradation of glyphosate ( $15\text{--}50 \text{ mg L}^{-1}$ ) using initial

amounts of  $\text{H}_2\text{O}_2$  between  $75\text{--}800 \text{ mg L}^{-1}$  with UV-C irradiation. It is well known that  $\text{H}_2\text{O}_2$  ( $\epsilon_{254 \text{ nm}} = 19.6 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) undergoes homolytic photolysis under UV-C irradiation yielding  $\cdot\text{OH}$ .<sup>44,45</sup>



This reaction also occurs upon solar light irradiation, although the extinction coefficient of hydrogen peroxide is quite low at UV-B and UV-A wavelengths.<sup>46</sup> Serra-Clusellas *et al.*<sup>31</sup> found similar results in the degradation of herbicide 2,4-D, where it was suggested that solar and UV-B light irradiation could induce  $\text{H}_2\text{O}_2$  photolysis leading to the formation of  $\cdot\text{OH}$  radicals. Nevertheless, in our investigation, with  $1 \text{ mg L}^{-1}$  glyphosate and AMPA generated, had similar degradation kinetics when  $\text{H}_2\text{O}_2$  was added alone to the polluted water, with or without the use of solar light at pH = 2.8. This fact would indicate that hydrogen peroxide is mainly responsible for glyphosate oxidation.

During the peroxidation process, the total consumption of  $\text{H}_2\text{O}_2$  was around  $3.5 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ , approximately three times higher than the theoretical one ( $1.2 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ ) for the amount of glyphosate removed. The photo-peroxidation process led to similar results compared to peroxidation in terms of glyphosate elimination and  $\text{H}_2\text{O}_2$  consumption.

The dark processes, applying only  $10 \text{ mg L}^{-1} \text{ h}^{-1} \text{ H}_2\text{O}_2$  (peroxidation) or the simultaneous addition of  $2 \text{ mg L}^{-1} \text{ Fe(III)}$  and  $10 \text{ mg L}^{-1} \text{ h}^{-1} \text{ H}_2\text{O}_2$  (Fenton), showed a slightly higher degradation kinetics when the Fenton process was carried out, indicating that under dark conditions, oxidation occurred mainly through  $\cdot\text{OH}$  and  $\text{H}_2\text{O}_2$  contributions.

Peroxidation, photo-peroxidation or Fenton led to the continuous formation of AMPA without further depletion; between  $0.15\text{--}0.20 \text{ mg L}^{-1}$  AMPA was detected at the end of the trials.

Surprisingly,  $1 \text{ mg L}^{-1}$  glyphosate in the presence of  $2 \text{ mg L}^{-1} \text{ Fe(III)}$  at pH 2.8, irradiated by solar light but without  $\text{H}_2\text{O}_2$

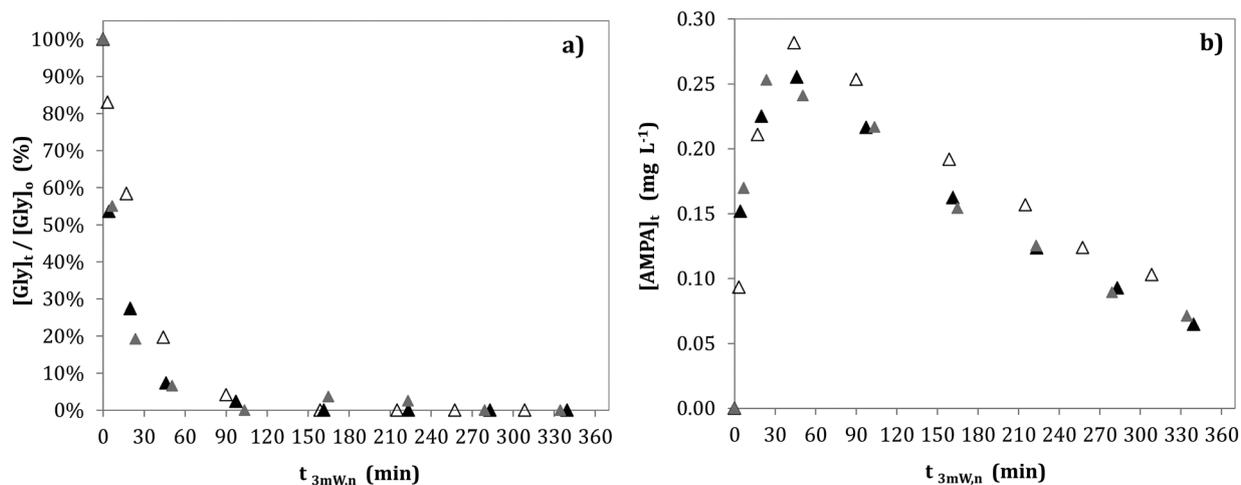


Fig. 2 Glyphosate (a) and AMPA (b) time courses of 500 mL of  $1 \text{ mg L}^{-1}$  glyphosate (Milli-Q water) during the SPF-like process with  $2.0 \text{ mg L}^{-1} \text{ Fe(III)}$  at pH = 2.8, under the following  $\text{H}_2\text{O}_2$  concentration conditions: ( $\Delta$ )  $20 \text{ mg L}^{-1}$ , every 2 h; ( $\blacktriangle$ )  $10 \text{ mg L}^{-1} \text{ h}^{-1}$ ; ( $\blacktriangle$ )  $5 \text{ mg L}^{-1} \text{ h}^{-1}$ .

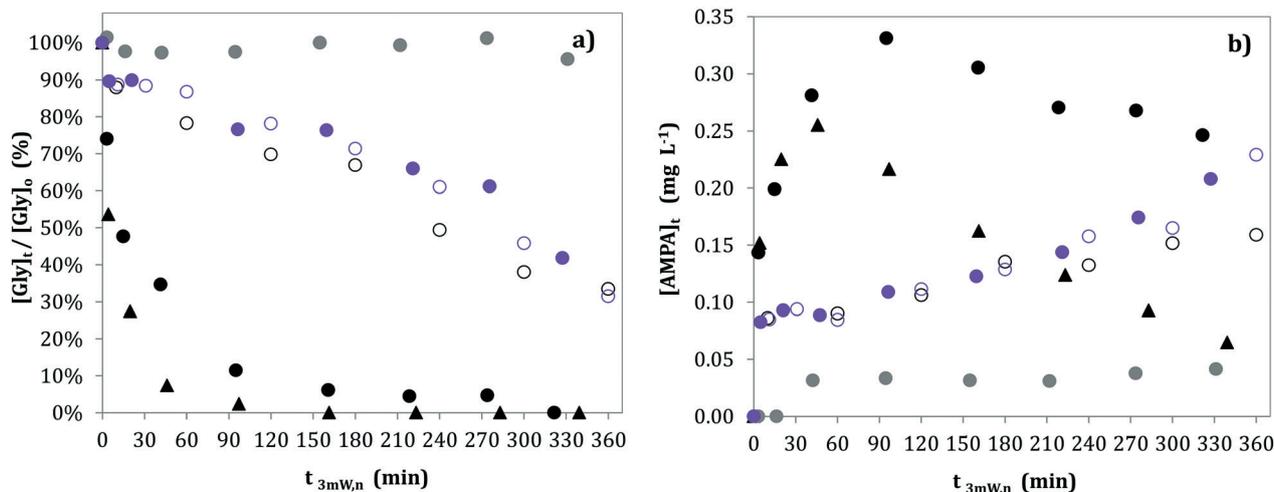


Fig. 3 Control experiments. Glyphosate (a) and AMPA (b) time courses of 500 mL of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) at pH = 2.8 under the following conditions: (▲) SPF-like process (10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 2 mg L<sup>-1</sup> Fe(III)); (●) solar photolysis of glyphosate with 2 mg L<sup>-1</sup> Fe(III) (without the H<sub>2</sub>O<sub>2</sub> addition); (○) Fenton-like process (10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 2 mg L<sup>-1</sup> Fe(III)); (●) solar photolysis of glyphosate (without the presence of Fe(III) and H<sub>2</sub>O<sub>2</sub>); (●) photo-peroxidation process (10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>; without Fe(III)); (○) peroxidation process (10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>; without Fe(III) and without solar light).

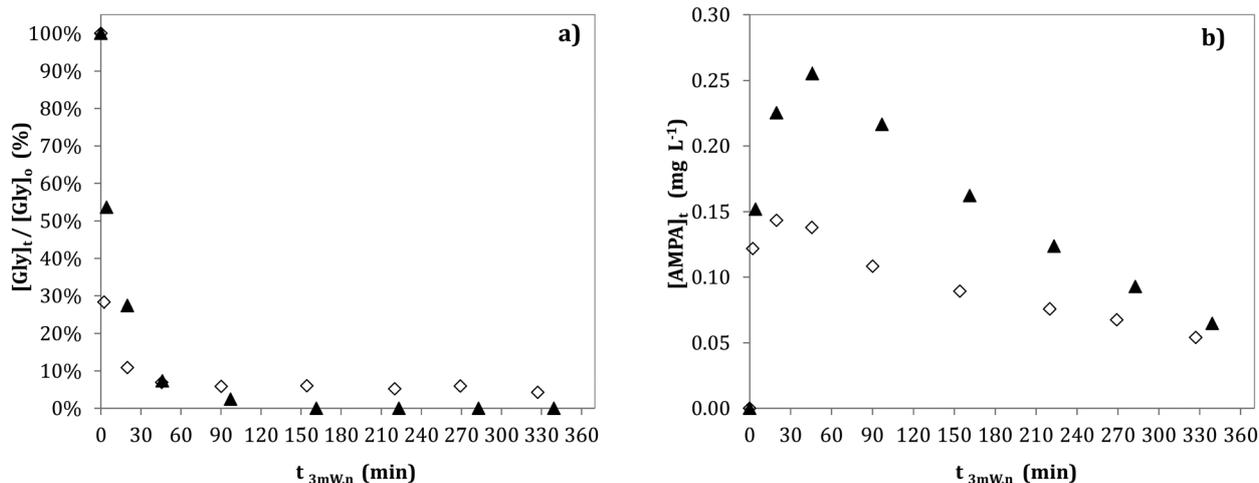
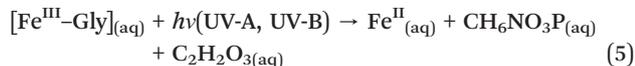


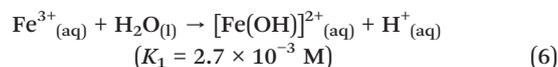
Fig. 4 Glyphosate (a) and AMPA (b) time courses of 500 mL of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) treated by the SPF-like process with 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> and 2 mg L<sup>-1</sup> Fe(III), at the following pH values: (▲) pH = 2.8; (◇) pH = 3.6.

addition, exhibited total glyphosate degradation after 240 min ( $t_{3mW,n}$ ). In this case, AMPA was produced in the first 90 min ( $t_{3mW,n}$ ) of sunlight irradiation, followed by slight depletion.

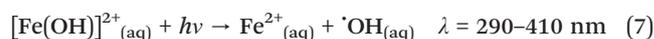
The results of this control experiment (1 mg L<sup>-1</sup> glyphosate + 2 mg L<sup>-1</sup> Fe(III) at pH = 2.8) evidenced that the complex between Fe(III) and glyphosate is photolysed under solar light yielding AMPA as the main by-product and ferrous iron through a very well-known mechanism already reported for the photo-Fenton process, where the photo-active ferric complex induces the oxidation of the ligand and the reduction of ferric ions to ferrous ions (eqn (5)) (metal-to-ligand charge transfer).



Besides,  $\text{Fe}(\text{OH})^{2+}$  is the main ferric-hydroxy complex in aqueous solutions at pH = 2.8,<sup>47</sup> as described by eqn (6).



This highly photo-active complex has two important light absorption maxima at 297 nm ( $\epsilon = 2030 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 205 nm ( $\epsilon = 4640 \text{ M}^{-1} \text{ cm}^{-1}$ ),<sup>48</sup> and enables the photo-production of hydroxyl radicals by UV-B, UV-A and visible light absorption (eqn (7)). The hydroxyl radicals can simultaneously oxidize several dissolved organic compounds in water.



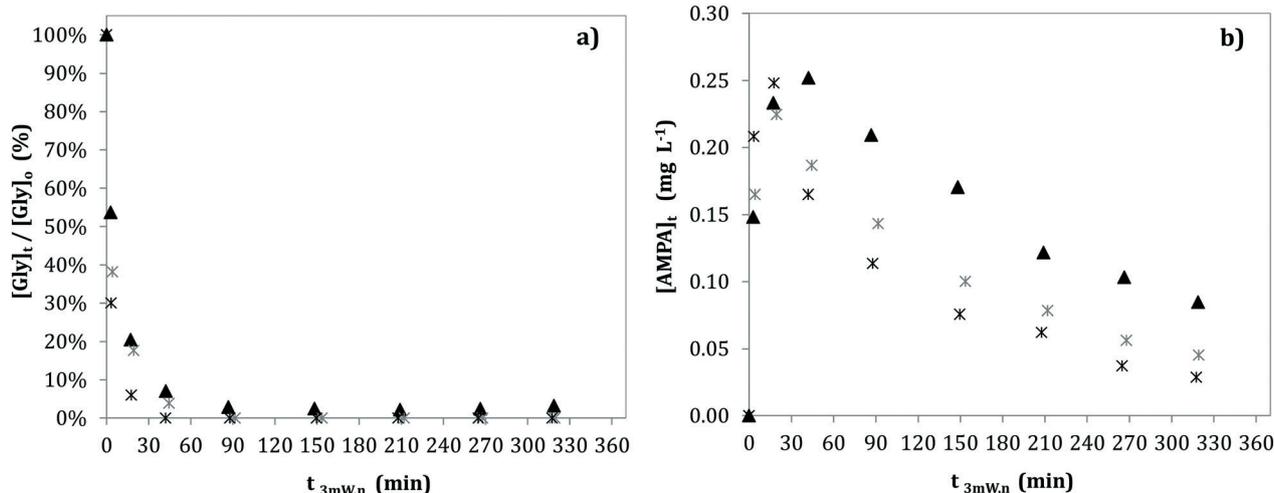


Fig. 5 Glyphosate (a) and AMPA (b) time courses of 500 mL of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) treated by the SPF-like process with 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>; pH = 2.8 at (▲) 2 mg L<sup>-1</sup> Fe(III) (SFP-like), (✱) 2 mg L<sup>-1</sup> Fe(II) (SPF) and (✱) 4 mg L<sup>-1</sup> Fe(II) (SPF).

Finally, as stated before, the SPF-like process resulted in the complete degradation of glyphosate after 90 min ( $t_{3mW,n}$ ) of sunlight irradiation and an enhanced AMPA removal compared to Fe(III)-assisted photolysis (only 0.06 mg L<sup>-1</sup> AMPA remaining at the end of the treatment). H<sub>2</sub>O<sub>2</sub> was also practically consumed after each addition (10 mg L<sup>-1</sup> every hour). In the SPF-like process, H<sub>2</sub>O<sub>2</sub> reacts with Fe(III) cations and the regenerated Fe(II) participates in the classic Fenton reaction forming  $\cdot$ OH (eqn (8)). The hydroxyl radical, together with H<sub>2</sub>O<sub>2</sub> and other ROS, are responsible for the glyphosate and AMPA mineralization into CO<sub>2</sub>, and phosphate and ammonium ions in the last steps of the treatment.

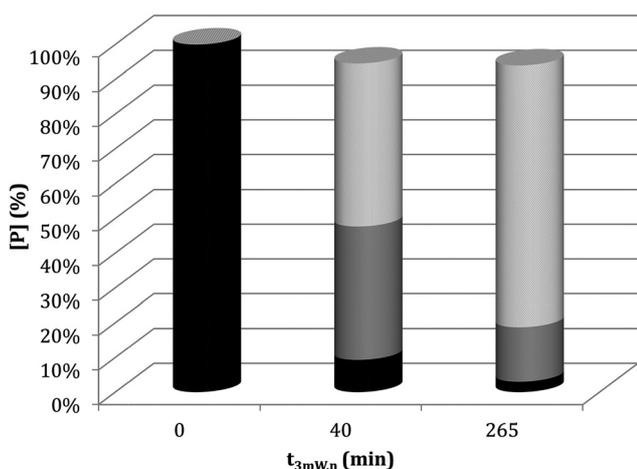
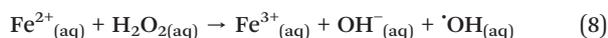


Fig. 6 Phosphorous time courses of 500 mL of 1 mg L<sup>-1</sup> glyphosate (Milli-Q water) at pH = 2.8 during the SPF-like process (10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 2 mg L<sup>-1</sup> Fe(III)) for the following species: (■) glyphosate; (■) AMPA; (□) PO<sub>4</sub><sup>3-</sup>.

Thus, the simultaneous degradation of glyphosate and AMPA at pH 2.8 was only observed when Fe(III), H<sub>2</sub>O<sub>2</sub> and sunlight were applied simultaneously to the polluted water.

### 3.3. Effect of pH

In order to investigate the effect of pH, experiments were performed at pH 3.6 (Fig. 4), using 2 mg L<sup>-1</sup> Fe(III) and 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>. This pH level was selected, following previous studies,<sup>41</sup> since it proved to be the most suitable for 2,4-D removal. However, in this case, an important initial loss of glyphosate (30%) was observed at pH 3.6 even before irradiation, probably due to its adsorption onto colloidal iron. Nevertheless, complete degradation of non-adsorbed glyphosate was observed with a concentration in water below 0.05 mg L<sup>-1</sup> after 90 min ( $t_{3mW,n}$ ) of sunlight irradiation. AMPA formation and further abatement revealed also a similar pattern to that at pH 2.8, where an important concentration increase was detected during the first 90 min ( $t_{3mW,n}$ ) of solar light irradiation followed by depletion; the low AMPA production at pH 3.6 could also be related to the low free glyphosate concentration initially present in the solution. At the end of the treatment, 60% DOC removal and 90% H<sub>2</sub>O<sub>2</sub> consumption after each hour of addition was detected. However, this removal could not only be the result of pollutant oxidation but also of adsorption on the iron oxy(hydroxide) colloids.

Oxidation experiments at pH 7 were not performed since around 50% glyphosate was adsorbed on the suspended iron. Therefore, the contribution of the adsorption phenomena would be significant to the whole process.

### 3.4. Nature and concentration of iron

Experiments using 2 mg L<sup>-1</sup> Fe(III) (SPF-like) or Fe(II) (SPF process), 1 mg L<sup>-1</sup> glyphosate (Milli-Q water), and 10 mg L<sup>-1</sup> h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at pH 2.8 were carried out to investigate the effect of Fe(III)/Fe(II) on the treatment efficiency (Fig. 5). As

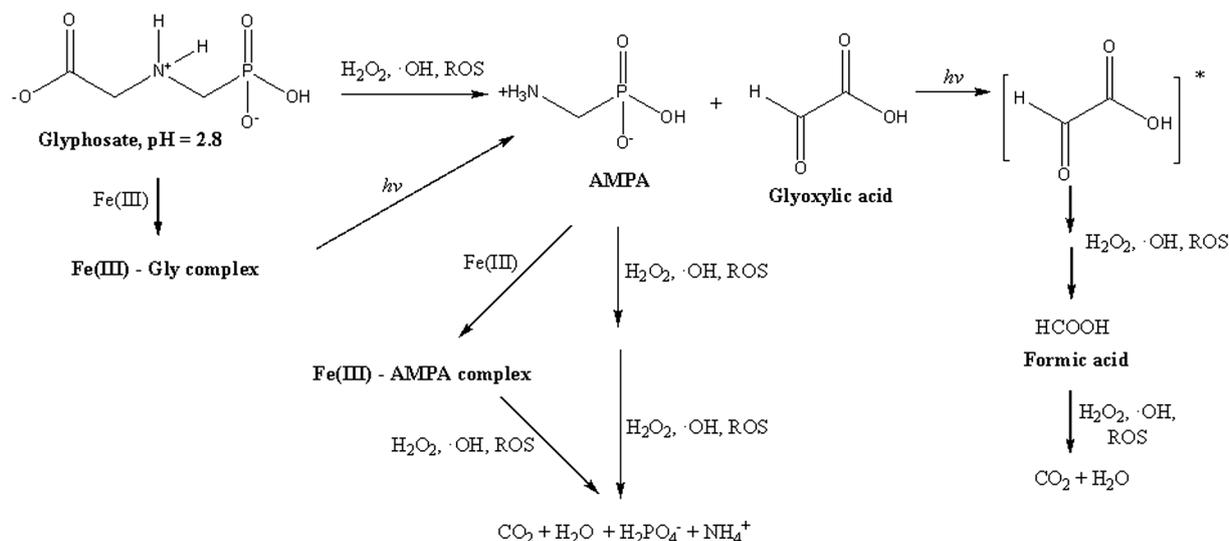


Fig. 7 Proposed mineralization pathway for the removal of  $1 \text{ mg L}^{-1}$  glyphosate (Milli-Q water) by the SPF-like process.

demonstrated largely by numerous studies, the SPF process shows faster degradation of organic matter than the SPF-like treatment. Results showed that the addition of Fe(II) caused higher levels of glyphosate degradation during the first minutes of the treatment than when Fe(III) was used; this fact was especially evident from the AMPA generation/depletion curves (Fig. 5b). In the presence of Fe(II), AMPA formed rapidly after 20 min ( $t_{3\text{mW},n}$ ) of irradiation and leveled off at around  $0.05 \text{ mg L}^{-1}$  at the end of the treatment whereas when Fe(III) was used, the AMPA concentration reached its maximum after 40 min ( $t_{3\text{mW},n}$ ).

The behavior of the system at higher Fe(II) concentrations was also investigated, and the SPF process at 2 and  $4 \text{ mg L}^{-1}$  Fe(II) were compared (Fig. 5), in an effort to identify the conditions of enhanced AMPA degradation. A dose of  $4 \text{ mg L}^{-1}$  Fe(II) resulted in slightly higher glyphosate degradation than  $2 \text{ mg L}^{-1}$  Fe(II), reaching the former case's total glyphosate degradation after 40 min ( $t_{3\text{mW},n}$ ) of sunlight irradiation. The final AMPA concentration at the higher Fe(II) concentration was  $0.03 \text{ mg L}^{-1}$ , close to the LoQ. DOC removal values by the SPF experiments were around 80%. As expected, the  $\text{H}_2\text{O}_2$  consumption rate for the SPF process with  $4 \text{ mg L}^{-1}$  Fe(II) was higher than those for the other treatments, in particular, during the first hour of the treatment.

### 3.5. Proposed glyphosate degradation pathway

It is well known that the C–P bond in the glyphosate molecule is highly stable. Jaisi *et al.*<sup>49</sup> stated that this molecule has two well established degradation pathways. The first one involves the formation of sarcosine and phosphate ions (sarcosine pathway), and the second one leads to the AMPA and glyoxylic acid formation (AMPA pathway).<sup>49</sup> Neither sarcosine nor glycine was detected in our experiments, whereas glyphosate is to a large degree converted to AMPA and phosphate ions. Moreover, high

mineralization (70% of DOC removal) was obtained, which could be due to further oxidation of the other by-products such as glyoxylic acid by ROS generated during the treatment.

The inorganic anions (nitrate and phosphate) formed during the SPF-like process at  $10 \text{ mg L}^{-1} \text{ h}^{-1}$   $\text{H}_2\text{O}_2$ ,  $2 \text{ mg L}^{-1}$  Fe(III) and pH = 2.8 were also monitored.

Fig. 6 displays the phosphorous mass balance differentiating the forms present: glyphosate, AMPA and phosphate ions. The decrease in the concentration of glyphosate and AMPA was observed concurrently with the increase of free phosphate.

The concentration of nitrate ions at the end of the experiment was below their LoQ ( $0.1 \text{ mg L}^{-1}$ ). Thus it would be expected that after the mineralization process, nitrogen was mainly transformed into  $\text{NH}_4^+$ .

These results suggest that glyphosate was degraded mainly through the AMPA pathway by the photo-Fenton like process using solar light irradiation (SPF-like). So, during the SPF-like process, metal-to-ligand charge transfer in the Fe(III)–Gly complex was induced by solar light absorption, yielding AMPA, phosphate ions and glyoxylic acid.<sup>49</sup> ROS generated during the treatment slowly mineralized the AMPA into ammonia, water and  $\text{CO}_2$ . During our experiments, the Fe(III)–AMPA complex seemed to exhibit poor photolysis and its degradation could be associated mostly with the attack by oxidant species.

According to Jaisi *et al.*,<sup>49</sup> glyoxylic acid was also generated during the glyphosate oxidation through the AMPA pathway. The aqueous photochemistry of glyoxylic acid was studied by Eugene *et al.*,<sup>50</sup> who showed that this compound can photogenerate reactive species under solar irradiation. During irradiation, excited state glyoxylic acid can undergo  $\alpha$ -cleavage or participate in hydrogen abstraction, and glyoxal is the main intermediate produced during direct photolysis. This compound can undergo degradation into other carboxylic acids such as oxalic or formic acids.

Therefore, based on the above discussed literature and the experimental results of this study, a degradation pathway of glyphosate by SPF-like process under our experimental conditions is suggested and schematized in Fig. 7.

## 4. Conclusions

This investigation demonstrated that glyphosate can be rapidly removed from water under solar light irradiation when Fe(III) or Fe(II) is dissolved at pH = 2.8. At higher pH, glyphosate was partially adsorbed onto iron oxy(hydroxide) colloids suspended in water. The results evidenced that, also under natural conditions, glyphosate can be efficiently eliminated by exposing the polluted water to solar radiation in the presence of Fe(III)/Fe(II) salts. However, glyphosate can partially degrade into AMPA under water natural conditions. This is particularly concerning since AMPA's toxicity is similar to that of glyphosate, but the metabolite is more persistent and thus requires more powerful oxidative conditions for its removal.

Our results suggest that glyphosate was degraded mainly through the AMPA pathway by metal-to-ligand charge transfer in the Fe(m)-Gly complex promoted by solar light absorption, yielding AMPA, phosphate ions and glyoxylic acid. ROS generated during the treatment slowly mineralized the AMPA into ammonia, water and CO<sub>2</sub>.

In conclusion, solar photo-Fenton-like and solar photo-Fenton processes using low amounts of Fe(III) (2 mg L<sup>-1</sup>) or Fe(II) (2–4 mg L<sup>-1</sup>) and 10 mg L<sup>-1</sup> h<sup>-1</sup> at pH = 2.8 are proposed as technically viable treatments for the abatement of glyphosate and AMPA from water, achieving over 70% mineralization after 6 h exposure to solar light.

## Conflicts of interest

The authors declare that they have no conflict of interests that may influence the work reported in this article.

## Acknowledgements

The authors would like to acknowledge CONICET (Resolución 3646/14), ITBA, UNLP and Banco Santander Río (ITBACyT “Glyphosate removal by solar photo electro-Fenton process”) for their financial support, Pablo Covicchioni, ITBA, for technical support during the experimental stage, and the Analytical Department of Leitat Technological Center (Terrassa, Spain), for the analysis of anions in water samples. Dr. Serra-Clusellas thanks CONICET for her postdoctoral fellowship.

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