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# **Coupling Fenton and biological oxidation for the removal of nitrochlorinated herbicides from water**

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## **Abstract**

The combination of Fenton and biological oxidation for the removal of the nitrochlorinated herbicides alachlor, atrazine and diuron in aqueous solution has been studied. The H<sub>2</sub>O<sub>2</sub> dose was varied from 20 to 100% of the stoichiometric amount related to the initial chemical oxygen demand (COD). The effluents from Fenton oxidation were analyzed for ecotoxicity, biodegradability, total organic carbon (TOC), COD and intermediate byproducts. The chemical step resulted in a significant improvement of the biodegradability in spite of its negligible or even slightly negative effect on the ecotoxicity. Working at 60% of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose allowed obtaining highly biodegradable effluents in the cases of alachlor and atrazine. That dose was even lower (40% of the stoichiometric) for diuron. The subsequent biological treatment was carried out in a sequencing batch reactor (SBR) and the combined Fenton-biological treatment allowed up to around 80% of COD reduction.

## **Keywords**

Biodegradability; ecotoxicity; Fenton oxidation; herbicides; sequencing batch reactor

## **1. Introduction**

Herbicides have been used for plague control in intense agriculture from the fifties and their use has yearly increased in the last decades (Sreenivasulu and Aparna 2001, Zapata et al. 2010). Different studies in UE countries have reported the presence of herbicides in surface water, from irrigation ditches and streams (Liess and Von der Ohe 2005) up to rivers and lakes (Environmental Agency 2007). Part from the larger-scale contamination is known to proceed from non-agricultural uses of herbicides (Skark et al. 2004), including containers washing and effluents from agricultural industries (10-100 mg L<sup>-1</sup>) and manufacture plants (1-1000 mg L<sup>-1</sup>) (Ballesteros Martin et al. 2009a). The use of agrochemicals has contributed to improve the agricultural productivity but

the presence of herbicides in soil and water represents an important risk for the environment and human health due to their toxicity and persistence (Barron et al. 2003, DeLorenzo et al. 2001, Otto et al. 2007). Some herbicides like alachlor, atrazine and diuron have been included in the UE list of priority substances in the field of water policy (Decision 2455/2001/EU).

To prevent the environmental hazard and human risks of these herbicides, it is necessary to develop methods allowing their effective breakdown. Biological treatments have shown limited success due to the low biodegradability of these compounds (Sanchis et al., 2013a). Chemical oxidation processes like catalytic and non-catalytic wet air oxidation (Suarez-Ojeda et al. 2007) and advanced oxidation processes (AOPs), including photochemical ( $O_3/UV$  and  $H_2O_2/UV$ ) and photocatalytical processes ( $TiO_2/UV$ ) (Andreozzi et al. 2003, Chelme-Ayala et al. 2010), Fenton and photo-Fenton (Fallmann et al. 1999, Kitsiou et al. 2009, Legrini et al. 1993), ozonation and catalytic ozonation (Ikehata and El-Din 2005, Tahmasseb et al. 2002), ultrasonic oxidation (David et al. 1998, Yano et al. 2005) and electrochemical oxidation (Balci et al. 2009, Brillas et al. 2003) have shown successful results dealing with this kind of recalcitrant compounds. The Fenton process, based on the catalytic decomposition of  $H_2O_2$  into hydroxyl radicals by means of  $Fe^{2+}$  at acid pH, is recognized as one of the most cost-effective AOPs for industrial wastewater treatment (Andreozzi et al. 1999, Azbar et al. 2004, Bautista et al. 2008, Perez et al. 2002). However, chemical oxidation treatments usually present certain limitations, whether economical or due to the recalcitrant behavior of the reaction byproducts (Martin-Hernandez et al. 2012). In this context, the combination of Fenton-like and biological processes for the removal of herbicides has received increasing attention in the last years (Ballesteros Martin et al. 2009b, Farre et al. 2006, Lapertot et al. 2007, Zapata et al. 2010). Among the existing biological systems, SBRs have been widely used in the last decades for industrial wastewaters (Singh and Srivastava 2011, Wilderer et al. 2001) due to their low area and energy requirements, easy control and the possibility of nutrients removal by combining anoxic and aerobic stages in the same reactor (Monsalvo et al. 2012, Zanetti et al. 2012). In addition, SBRs allow changes in the operational and control strategies, so that they work efficiently under variable organic loads (Monsalvo et al. 2009).

The aim of this work is to analyze the combination of Fenton and biological oxidation for the removal of three nitrochlorinated herbicides, alachlor, atrazine and diuron. The

former herbicide acts as a long-chain fatty acid inhibitor whereas the others are photosystem II inhibitors. Since  $\text{H}_2\text{O}_2$  consumption is the critical issue in the economy of Fenton oxidation, the evolution of reaction byproducts, as well as the ecotoxicity and biodegradability of the effluents from this step at different  $\text{H}_2\text{O}_2$  doses have been analyzed. This information is needed in order to determine the optimal reagent dose conducting to a biodegradable effluent which could be treated in a biological system, using a SBR for this purpose.

## **2. Materials and methods**

### **2.1. Fenton oxidation**

The experiments were carried out in a 3 L glass reactor at controlled temperature (30 °C) and stirred at 200 rpm for 3 h. The initial pH was adjusted around 3, which is within the optimal range for Fenton oxidation (Bautista et al. 2007). The starting concentrations of the herbicides (180 mg L<sup>-1</sup> for alachlor and 27 mg L<sup>-1</sup> for atrazine and diuron) were fixed taking into account their restricted solubility limits, since these herbicides can appear at those concentrations in point sources of pollution, such as wastewaters from pesticide containers cleaning. The dose of hydrogen peroxide was varied from the theoretical stoichiometric amount for complete mineralization (2.125 g  $\text{H}_2\text{O}_2$  g<sup>-1</sup> COD) to a 20% of that value, maintaining a  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio of 1/10 (M/M). The samples were neutralized with NaOH 6 N and filtered (Albet FV-C) before their analysis. The evolution of the concentration of the starting herbicide, TOC and  $\text{H}_2\text{O}_2$  upon reaction time was followed at every  $\text{H}_2\text{O}_2$  dose tested. Final samples were also analyzed for COD, BOD<sub>5</sub> and reaction byproducts, as well as ecotoxicity (Microtox®). Respirometric tests for biodegradability assessment were also performed.

### **2.2. Biological treatment**

The biological treatment of the effluents from Fenton oxidation was performed in a 3 L SBR. It was equipped with pH and dissolved oxygen probes to evaluate the biomass activity by respirometry. Air was introduced through a ceramic diffuser at a flow rate of 9 NL min<sup>-1</sup> to avoid oxygen limitations. Peristaltic pumps were used to feed and discharge the bioreactor, as well as for the addition of the sodium hydroxide solution for pH control.

The experiments were conducted at 30 °C, 200 rpm and pH 7 in sequences of 8 h as follows: anoxic filling (1 h), aerated reaction (5.5 h), settling (1 h) and draw (0.5 h),

using a hydraulic retention time of 12 h. Biomass concentration was varied in order to maintain the organic load rate between 0.2 and 0.3 kg COD kg<sup>-1</sup> VSS d<sup>-1</sup> using the selected effluents from Fenton oxidation as the sole carbon source. A cell retention time of 30 d was always used. Ammonium sulfate and phosphoric acid were added as nitrogen and phosphorous sources, respectively, and mineral salts (CaCl<sub>2</sub>, KCl and MgSO<sub>4</sub>) as micronutrients supply at COD:N:P:micronutrients ratio of 100:5:1:0.05 (w/w). Samples were withdrawn along the biological process for measuring TOC, COD, organic byproducts and inorganic nitrogen species. Specific oxygen uptake rate (SOUR) profiles were also recorded during the aerobic stage.

The inoculum used in the bioreactor was collected from the activated sludge sewage treatment plant of Alcala de Henares (Madrid). The biological sludge was maintained with sodium acetate (150 mg COD L<sup>-1</sup>) and glucose (150 mg COD L<sup>-1</sup>) as carbon sources in a SBR operated at 25 °C. It was also used as inoculum in the BOD<sub>5</sub> and biodegradability tests.

### 2.3. Biodegradability assays

The biodegradability of the effluents from Fenton oxidation was assessed by respirometry in a LSS respirometer (Chica et al. 2007) following the fast biodegradability test developed by Polo et al. (2011). The sample (1 L) was mixed with the biomass (350 mg VSS L<sup>-1</sup>) and aerated for 24 h. The biomass concentration was selected after preliminary tests in order to ensure that the oxygen consumption can be detected at the lowest respiration rate and to avoid a maximum oxygen uptake rate higher than the oxygen transfer rate during the aeration stage (Polo et al., 2011). SOUR and TOC were measured along the experiment. The stoppered reaction vessels were placed in a thermostatic bath and continuously stirred by magnetic bars.

### 2.4. Ecotoxicity tests

The ecotoxicity of the effluents from Fenton oxidation was evaluated by the Microtox<sup>®</sup> Acute Toxicity Test (ISO 11348-3 1998), using a Microtox<sup>®</sup> M-500 analyzer from SDI. The toxic effect is calculated from the decay of the luminescence of the bacteria *Vibrio fischeri*, after 15 minutes of incubation at 15°C. Toxicity is evaluated as IC<sub>50</sub>, defined as the percent dilution of the initial solution causing 50% reduction of the luminescence. Results were expressed in toxicity units (TU), calculated from IC<sub>50</sub> values (TU = 100/IC<sub>50</sub>).

## 2.5. Analytical methods

Total organic carbon and total nitrogen (TN) were measured using a TOC-V<sub>CPN</sub> apparatus from Shimadzu. COD and biomass concentration were analyzed following the APHA procedures 5220A and 2540E (APHA 1992), respectively. BOD<sub>5</sub> measurements were carried out in a Velp Scientifica equipment, following the standard procedure 5210 (APHA 1992). Residual hydrogen peroxide concentration was determined by colorimetric titration through the titanium sulfate method (Eisenberg 1943) using a Shimadzu UV-1603 spectrophotometer.

The starting herbicides and the byproducts from Fenton oxidation of atrazine were quantified by HPLC (Varian Prostar 325) with a UV detector and a Teknokroma Mediterranea Sea-18 column (25 cm length, 4.6 mm i.d.) as the stationary phase. Alachlor, atrazine and diuron were determined at 280 nm using a mixture of acetonitrile/H<sub>2</sub>O (80/20% – 65/35% (0 – 15 min) and 65/35% – 25/75% (15 – 30 min)) as the mobile phase, with a constant flow of 0.60 ml min<sup>-1</sup>. The byproducts from atrazine oxidation were analyzed at 220 nm using a mixture of acetonitrile/acetic acid 5 mM (5/95% – 95/5% (0-20 min)) as the mobile phase, with a constant flow of 0.80 ml min<sup>-1</sup>.

Chlorophenols and anilines were analyzed by means of a gas chromatograph (Varian GC-3900) with flame ionizing detector equipped with a capillary column CP WAX-52CB (5 m length, 2 mm i.d.). The rest of the reaction byproducts were identified by using a gas chromatograph (Varian GC-3900) coupled to a mass spectrometer (Varian Saturn 2100T). The analyzer was equipped with a solid-phase microextraction unit (Carbowax/Divinylbenzene, Yellow-Green) and a capillary column Varian FactorFour VF-5ms (30 m length, 0.25 mm i.d.). The identification of the detected compounds was carried out using the NIST 05 library.

Short-chain organic acids, nitrate, nitrite and chloride were analyzed by means of an ion chromatograph with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5-250 column (25 cm length, 4 mm i.d) was used as the stationary phase and 0.7 mL min<sup>-1</sup> of an aqueous solution of 3.2 mM Na<sub>2</sub>CO<sub>3</sub> and 1 mM NaHCO<sub>3</sub> as the mobile phase. The determination of ammonia was carried out by means of Nessler's reagent using an Orbeco-Hellige 975 MP colorimeter.

A residual solid was observed upon Fenton oxidation of atrazine. It was characterized by elemental analysis (Perkin-Elmer analyzer, model 210 CHN) and inductively coupled plasma mass spectroscopy (ICP/MS) by means of a Perkin-Elmer analyzer (model Elan 6000 Sciex).

## **2.6. Data analysis**

The results reported were the average values from at least duplicate runs. In all the cases, the standard errors were lower than 10%.

## **3. Results and discussion**

### **3.1. Fenton oxidation**

Figure 1 shows the time-evolution of  $\text{H}_2\text{O}_2$ , TOC and conversion of alachlor, atrazine and diuron upon Fenton oxidation at 30 °C using the stoichiometric dose of hydrogen peroxide and a  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio of 1/10 (M/M). In the case of atrazine, the available catalyst concentration suddenly decreased at the early stages impeding the  $\text{H}_2\text{O}_2$  decomposition into hydroxyl radicals due to the formation of  $\text{Fe}^{2+}$  complexes. Therefore, a  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio of 1/2 (M/M) was needed in this case in order to have a similar available catalyst concentration as for the two other herbicides. Complete  $\text{H}_2\text{O}_2$  decomposition and herbicide conversion were achieved in all the cases. The TOC reached a constant value after a given reaction time depending on the herbicide tested indicating the refractory character of some reaction byproducts which represented around 50% of the initial TOC in the three cases.

Table 1 shows the conversion of herbicide and the reduction of COD and TOC achieved after 3 h reaction time at different  $\text{H}_2\text{O}_2$  doses. Complete conversion of diuron and alachlor was achieved under frankly substoichiometric conditions and this was also almost the case for atrazine. Nevertheless, the COD and TOC reduction barely reached 60-65% and 50-55%, respectively at the most, confirming the refractory character of a significant fraction of the reaction byproducts. This refractory TOC fraction could not be removed using more oxidizing conditions (Kassinis et al. 2009, Oturan et al. 2011) whereas the application of solar UV (photo-Fenton) has proved to be an efficient method of improving mineralization of alachlor (Ballesteros Martin et al. 2008).

### **3.2. Oxidation byproducts**

The analysis of the effluents from Fenton oxidation of alachlor revealed the presence of aniline (1.2 to 2.7 mg L<sup>-1</sup>, increasing with the reagent dose) and 2,6-diethylaniline (0.54 mg L<sup>-1</sup>) at 20% of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose. Both 2,6-diethylaniline and aniline have also been observed in the oxidation of alachlor by photocatalytic ozonation (Farre et al. 2005). To learn more, an additional experiment was performed with one-half that H<sub>2</sub>O<sub>2</sub> dose. Catechol, 2-chloro-2,6-diethylphenyl-N-(methyl)acetamide (CDEFMA) and N-(methoxymethyl)-N-(2,6-diethylphenyl)-2-hydroxiacetamide (MMDEFHA) were identified as reaction byproducts. These two acetamide derivatives have been also detected as intermediate byproducts in the photo-Fenton oxidation of alachlor (Katsumata et al. 2006).

Three main byproducts were detected for atrazine: desethyldeisopropyl atrazine (DEIA) (C<sub>3</sub>H<sub>4</sub>ClN<sub>5</sub>), desethyl-2-hydroxyatrazine (DEHA) (C<sub>6</sub>H<sub>11</sub>N<sub>5</sub>O) and desethyldeisopropyl-2-hydroxyatrazine (DEIHA) (C<sub>3</sub>H<sub>5</sub>N<sub>5</sub>O). DEIA and DEHA concentration decreased as the H<sub>2</sub>O<sub>2</sub> dose was increased. The former occurred preferentially at low doses whereas the second prevailed at intermediate ones. Above 40% of the stoichiometric dose both compounds were converted into DEIHA. These three byproducts have been observed upon atrazine oxidation by electro-catalytically generated hydroxyl radicals (Balci et al. 2009) and photo-Fenton (Chan and Chu 2006). Oxidation of the amine groups of DEIA by hydroxyl radicals can lead to the formation of cyanuric acid (Chan et al. 2004), which was not detected in the current work.

In the case of diuron, benzenetriol was identified in the experiments carried out with 20-60% of the stoichiometric H<sub>2</sub>O<sub>2</sub> and aniline was detected at any of the doses tested. At 10% of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose, 3,4-dichloroaniline, 3,4-dichlorobenzene, 3,4-dichlorophenol, phenol and hydroquinone were analyzed. The former along with 3,4-dichlorophenyl isocyanate have been identified as the main byproducts from photo-Fenton oxidation (Farre et al. 2007a) and chemical hydrolysis of diuron in aqueous phase (Salvestrini et al. 2002).

Figure 2 shows the concentration of short-chain organic acids in the effluents obtained after 3 h reaction time with different H<sub>2</sub>O<sub>2</sub> doses. In the cases of alachlor (Figure 2.a) and diuron (Figure 2.c), acetic and formic acids were the main byproducts at low H<sub>2</sub>O<sub>2</sub> doses and decayed as the dose was increased whereas for malonic and oxalic acids the opposite trend was observed. The last has been recognized as resistant to conventional



Fenton oxidation (Munoz et al. 2011, Zazo et al. 2005). For atrazine oxidation (Figure 2.b), formic was the main acid at  $\text{H}_2\text{O}_2$  doses up to 60% of the stoichiometric and then decayed whereas the concentration of acetic acid increased with the  $\text{H}_2\text{O}_2$  dose. This was also the case of oxalic, but with final values significantly lower than the observed for the other two herbicides.

From the analysis of oxidation byproducts, the reaction schemes of Figure 3 are proposed.

An orange residual solid was observed in the effluents from Fenton oxidation of atrazine in concentrations of 27 to  $155 \text{ mg L}^{-1}$ , increasing with the  $\text{H}_2\text{O}_2$  dose. This solid was mainly formed by iron (52% w/w), being the main cause of the aforementioned loss of iron from solution.

Measured and calculated TOC and TN from the identified compounds as well as the chlorine balance closure are shown in Figure 4. Around 10-25% of the nitrogen initially present in each herbicide was removed as  $\text{N}_2$ . The concordance between the measured and calculated TOC and TN as well as the closure of the Cl balance increased with the dose of  $\text{H}_2\text{O}_2$  although in the case of alachlor significant differences and around 20% of chlorine deficit were still remaining at the stoichiometric dose. That was also the case with diuron regarding TN. The differences observed correspond to unidentified byproducts. Some authors have reported the formation of dioxins upon Fenton oxidation of chlorophenols (Munoz et al. 2011) and Fenton and electrochemical oxidation of landfill leachates (Vallejo et al. 2013). In the case of atrazine, the TOC and TN calculated from the identified species matched completely the measured values and the Cl balance was almost closed even at the lowest  $\text{H}_2\text{O}_2$  dose tested.

### 3.3. Ecotoxicity and biodegradability of Fenton effluents

Figure 5 shows the ecotoxicity (expressed as TU), the  $\text{BOD}_5/\text{COD}$  ratio (biodegradability index) and the composition in TOC fractions of short-chain organic acids, chlorinated and nitrogenated compounds and unidentified byproducts of the effluents from Fenton oxidation of the three herbicides at different  $\text{H}_2\text{O}_2$  doses after 3 h reaction time. The oxidation process increased (or barely affected in the case of diuron) the ecotoxicity, which has been previously observed upon the Fenton oxidation of chlorinated herbicides (Sanchis et al. 2013b). Looking at the identified byproducts, high ecotoxicity values have been reported for aniline derivatives with  $\text{EC}_{50}$  values of 5.53

mg L<sup>-1</sup> (Aruoja et al. 2011) and 0.61 mg L<sup>-1</sup> (Bonnet et al. 2007) for 2,6-diethylaniline and 3,4-dichloroaniline, respectively. In the case of atrazine (Figure 5.b), the ecotoxicity increased with the H<sub>2</sub>O<sub>2</sub> dose consistently with the increasing concentration of DEIHA (Chan et al. 2004). The increase of toxicity upon UV irradiation or photocatalytic oxidation of these herbicides has been previously reported in the literature (Bonnemoy et al. 2004, Farre et al. 2007b, Farre et al. 2005, Muneer et al. 1999).

In spite of this negative evolution of ecotoxicity, Fenton oxidation gave rise to more biodegradable effluents than the starting herbicide solutions. In the case of alachlor and atrazine, increasing the H<sub>2</sub>O<sub>2</sub> dose above 60% of the stoichiometric did not provide significant changes in the BOD<sub>5</sub>/COD ratio, since the composition in TOC fractions of the effluents remained fairly similar. In both cases, the effluents obtained at H<sub>2</sub>O<sub>2</sub> doses within 20-40% of the stoichiometric showed poor biodegradability, which could be due to the inhibition of the biomass by nitrochlorinated byproducts (DEIA and DEHA in the case of atrazine, and 2,4-diethylaniline in the case of alachlor). Effluents from Fenton oxidation of diuron showed higher biodegradability at intermediate H<sub>2</sub>O<sub>2</sub> doses, where higher concentrations of acetic and maleic acids were found, both more biodegradable than oxalic (Molina et al. 2010).

The biodegradability of the effluents from Fenton oxidation was further measured by the fast biodegradability respirometric test (Polo et al. 2011). The time-evolution of SOUR and TOC/TOC<sub>0</sub> for the effluents obtained at 40-100% of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose are shown in Figure 6. The respirometric profiles were consistent with the TOC decay, showing an important initial biomass activity and, in the case of alachlor, a slight increase at the end of the experiments as a consequence of the acclimation of the biomass. H<sub>2</sub>O<sub>2</sub> doses of 60% of the stoichiometric were selected for the combined treatment in the case of alachlor and atrazine, since the respirometric tests yielded the best efficiency in terms of TOC removal. In both cases, the effluents from Fenton oxidation at 40% of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose included significant amounts of inhibitory compounds, whereas the obtained at the stoichiometric H<sub>2</sub>O<sub>2</sub> dose contained hardly biodegradable compounds (oxalic acid in the case of alachlor and nitrochlorinated species for atrazine). In the case of diuron, the highest TOC removal was observed for the effluent obtained at 40% of the stoichiometric H<sub>2</sub>O<sub>2</sub>, since higher doses led to effluents with more oxalic acid.

### 3.4. Biological treatment of Fenton effluents

The effluents from Fenton oxidation at  $\text{H}_2\text{O}_2$  doses of 40% of the stoichiometric for diuron and 60% for alachlor and atrazine were subjected to biological treatment in SBR. The system was operated for several cycles in order to ensure steady performance. Figure 7 shows the COD and TOC values of the SBR effluents along the cycles, as well as the overall removal percentages achieved upon the combined treatment. The TOC removal remained steadily above 80% in the case of alachlor and between 60 and 70% for atrazine and diuron.

The biodegradation along the last cycle of SBR was evaluated through the evolution of SOUR, COD, TOC, short-chain organic acids and inorganic nitrogen species. As can be seen in Figure 8, a significant decrease of COD and TOC took place during the first hour of the cycle, corresponding to the anoxic filling, as a consequence of the biodegradation of part of the main short-chain organic acids present in the effluents, especially acetic acid and also maleic in the case of diuron. At the same time, it can be observed a remarkable reduction of nitrate. Therefore, the removal of organic matter in absence of oxygen can be attributed to heterotrophic denitrification, where organic compounds are used as external electron donors for nitrate reduction (Carini et al. 2003, Monsalvo et al. 2009). Acetic and maleic acids were completely removed along the first hours of aerobic reaction, leading to an important biomass activity. Formic and oxalic acids were preferentially degraded once acetic and maleic acids had been almost completely removed. The biomass showed an increasing acclimation along the SBR cycles since the aromatic intermediates DEIA and aniline were partially removed.

### 4. Conclusions

Fenton oxidation of alachlor, atrazine and diuron generated effluents integrated mainly by short-chain organic acids. Nevertheless, the presence of aromatic intermediates, like 2,4-diethylaniline (alachlor), DEIHA (atrazine) and 3,4-dichloroaniline (diuron), as well as other non identified byproducts, increased the ecotoxicity. In spite of this, the effluents showed higher biodegradability. Working at 40-60% of the stoichiometric  $\text{H}_2\text{O}_2$  dose in the Fenton step was the best option for the combined treatment, since below that significant concentrations of inhibitory compounds were remaining while higher doses generated more oxalic acid instead of the more biodegradable maleic and acetic. The SBR treatment of the effluents from Fenton oxidation allowed high COD and TOC reduction with partial removal of aromatic byproducts, like aniline and DEIA.

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Table 1. Herbicide conversion, COD and TOC reduction (%) upon Fenton oxidation at 30 °C with different H<sub>2</sub>O<sub>2</sub> doses after 3 h reaction time.

<b>H<sub>2</sub>O<sub>2</sub></b> <b>(% stoic.)</b>	<b>Alachlor</b>			<b>Atrazine</b>			<b>Diuron</b>		
	<b>Herb.</b>	<b>COD</b>	<b>TOC</b>	<b>Herb.</b>	<b>COD</b>	<b>TOC</b>	<b>Herb.</b>	<b>COD</b>	<b>TOC</b>
<b>20</b>	98	23	19	87	44	31	100	32	31
<b>40</b>	100	49	43	95	51	31	100	47	51
<b>60</b>	100	62	51	98	58	40	100	57	52
<b>80</b>	100	62	52	99	61	44	100	60	54
<b>100</b>	100	62	52	100	65	48	100	62	54

Figure 1

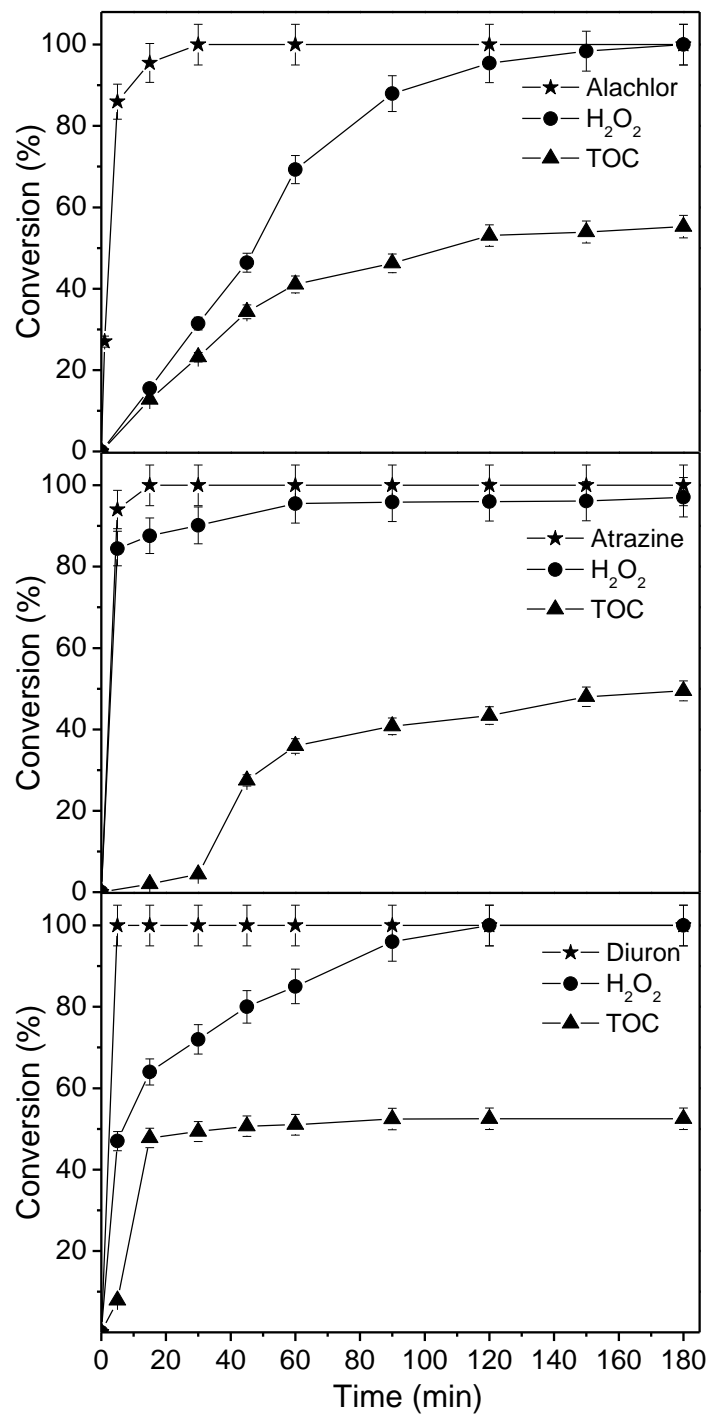


Fig. 1. Time-evolution of H<sub>2</sub>O<sub>2</sub>, TOC and herbicide conversion upon Fenton oxidation at 30 °C with the stoichiometric dose of H<sub>2</sub>O<sub>2</sub>.

Figure 2

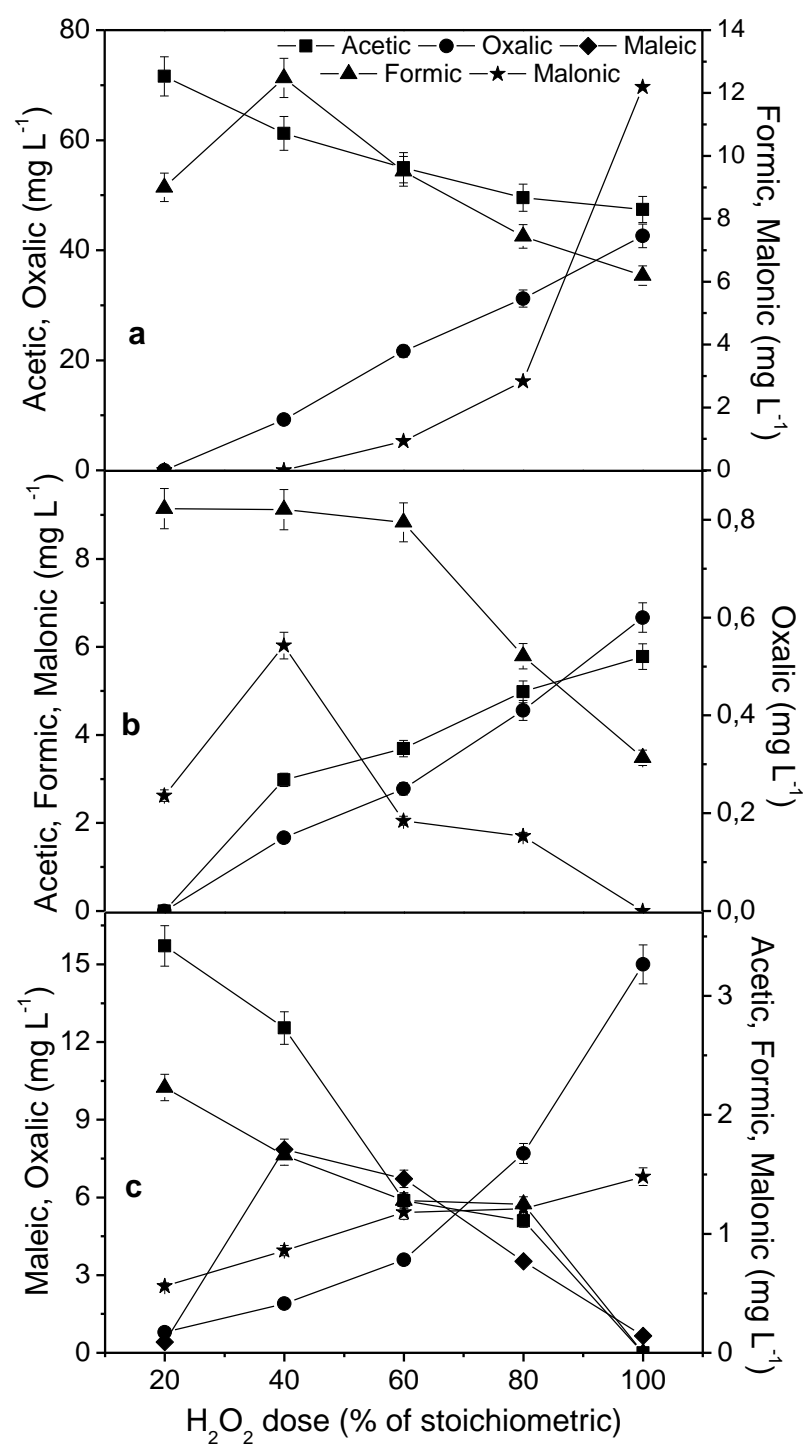


Fig. 2. Short-chain organic acids in the effluents from Fenton oxidation at 30 °C of alachlor (a), atrazine (b) and diuron (c) at different H<sub>2</sub>O<sub>2</sub> doses after 3 h reaction time.

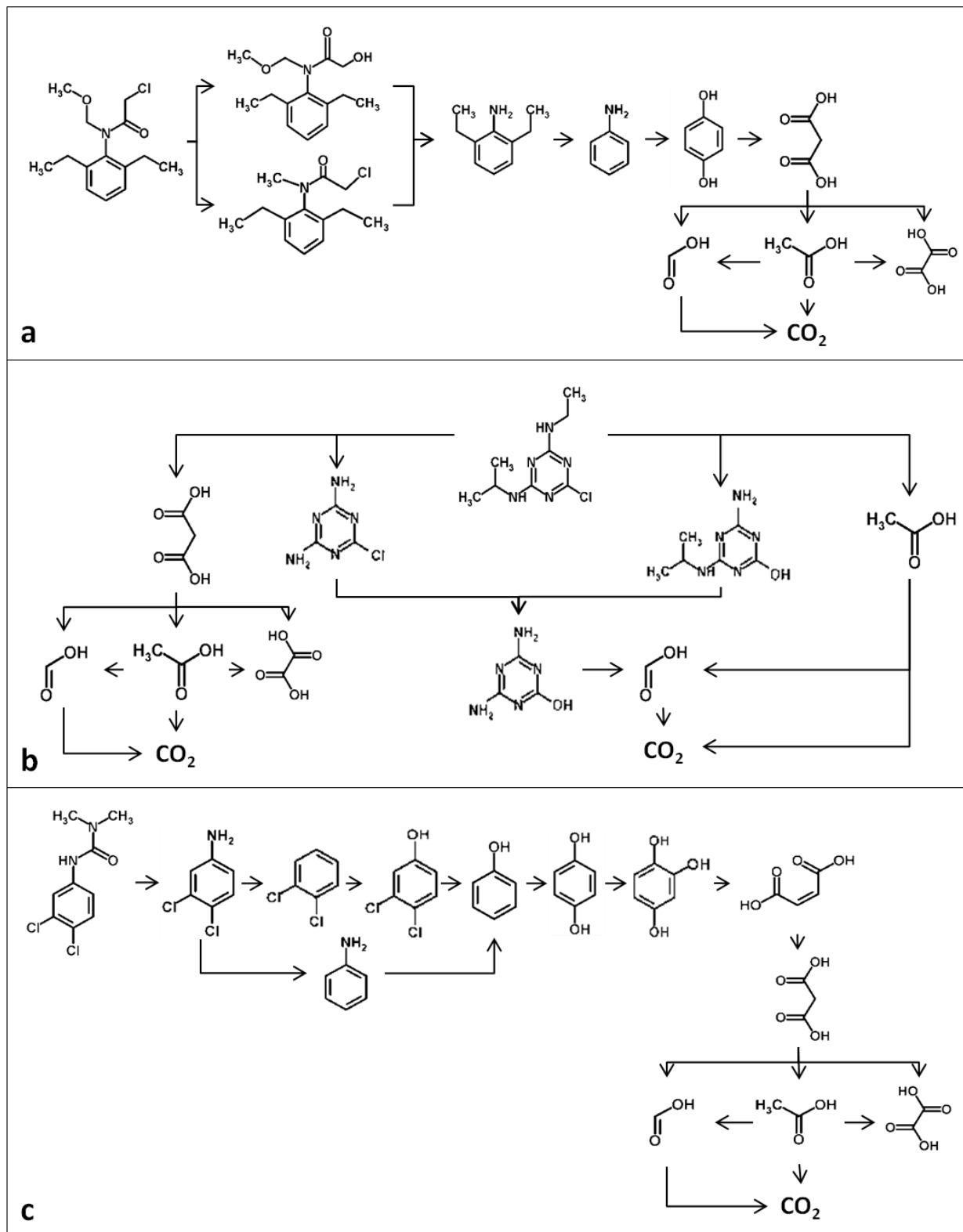


Figure 4

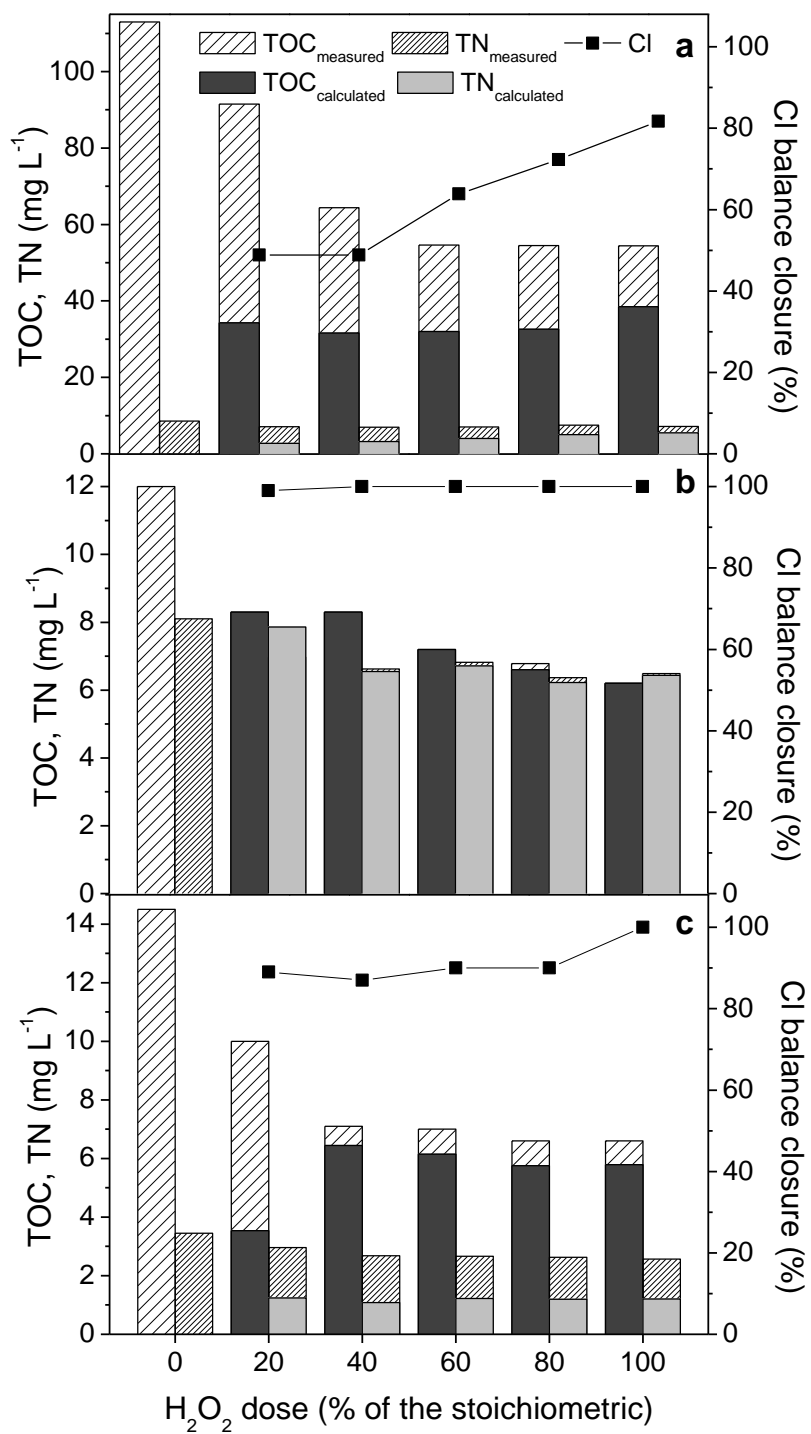


Fig. 4. Measured and calculated TOC and TN, and CI balance closure from Fenton oxidation at 30 °C of alachlor (a), atrazine (b) and diuron (c) at different H<sub>2</sub>O<sub>2</sub> doses after 3 h reaction time.

Figure 5

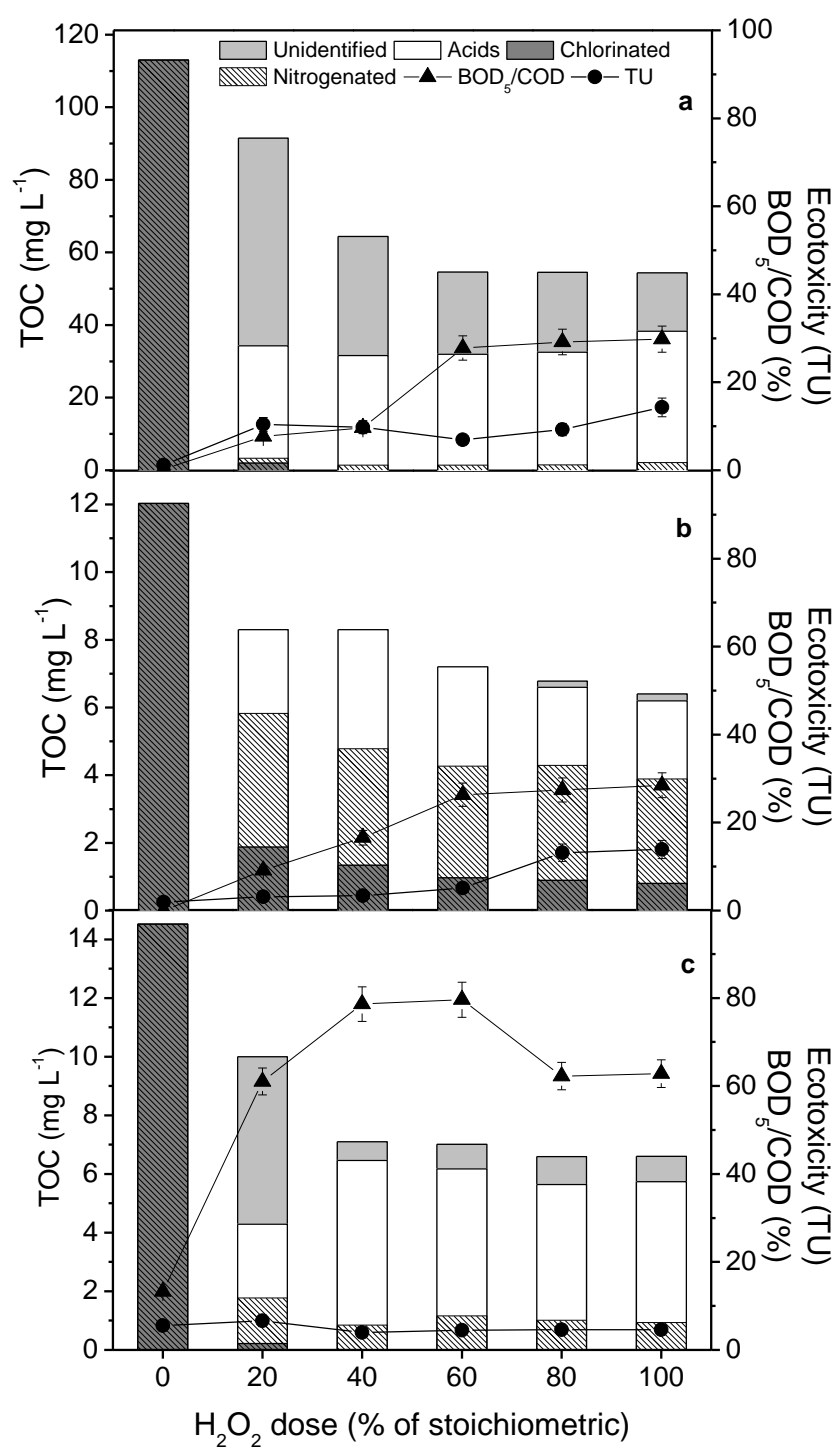


Fig. 5. Ecotoxicity, BOD<sub>5</sub>/COD ratio and composition in TOC fractions of the effluents from Fenton oxidation at 30 °C of alachlor (a), atrazine (b) and diuron (c) at different H<sub>2</sub>O<sub>2</sub> doses after 3 h reaction time.

Figure 6

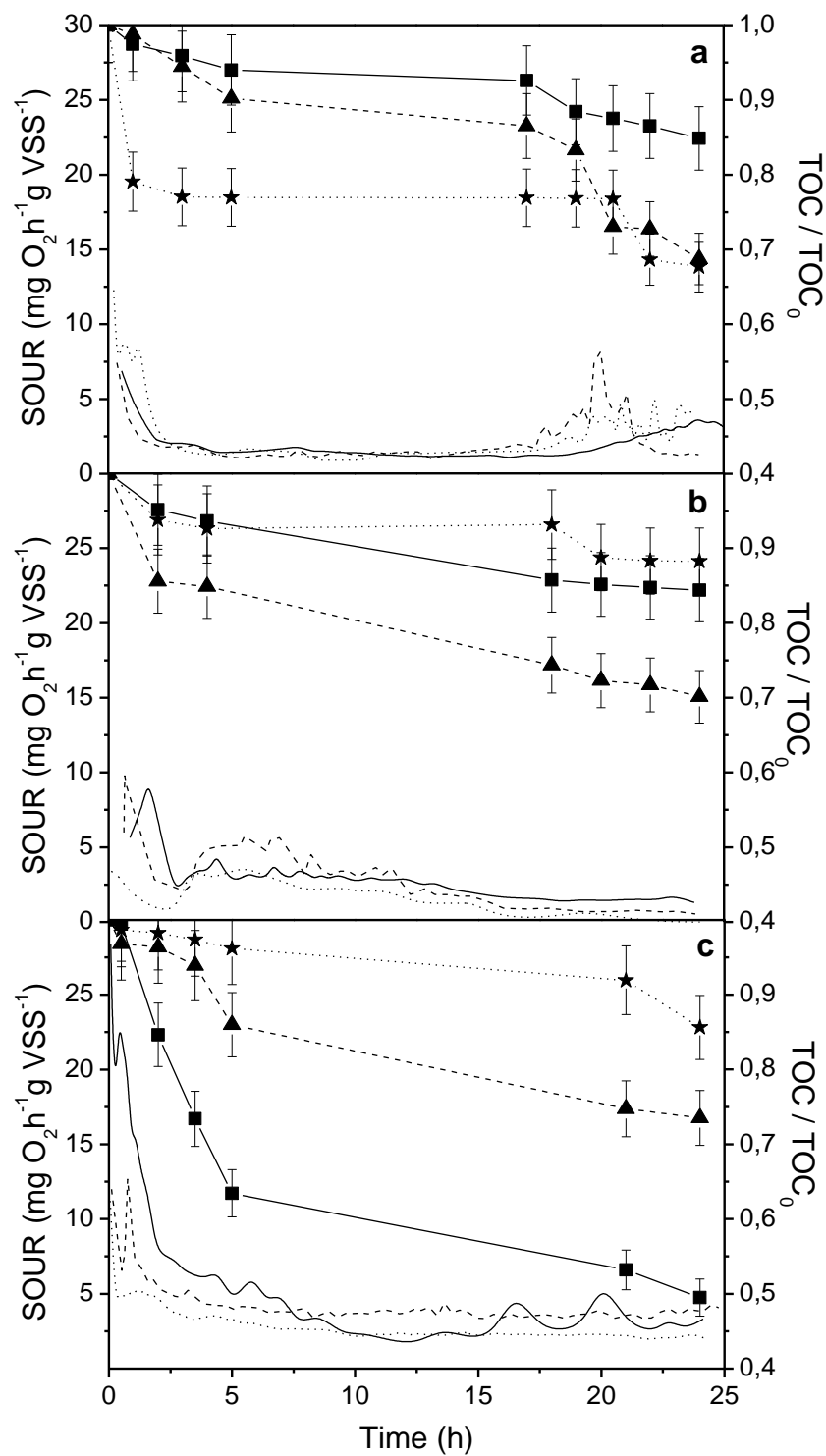


Fig. 6. SOUR (lines) and TOC (line-symbols) evolution during the respirometric tests of the effluents from Fenton oxidation (3 h reaction time, 30 °C) of alachlor (a), atrazine (b) and diuron (c) at 40% (■, solid line), 60% (▲, dash line) and 100% (★, dot line) of the stoichiometric H<sub>2</sub>O<sub>2</sub> dose.



Figure 7

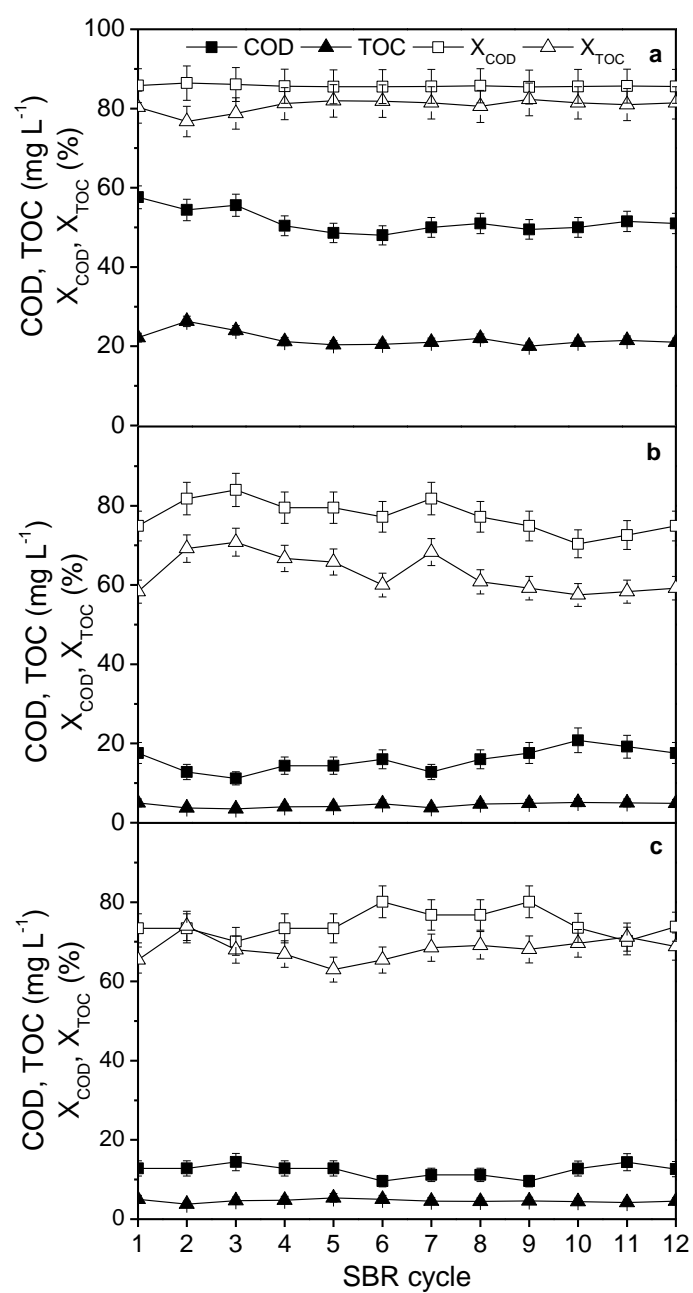


Fig. 7. COD and TOC removal and residual values after Fenton and biological combined treatment of alachlor (a), atrazine (b) and diuron (c).

Figure 8

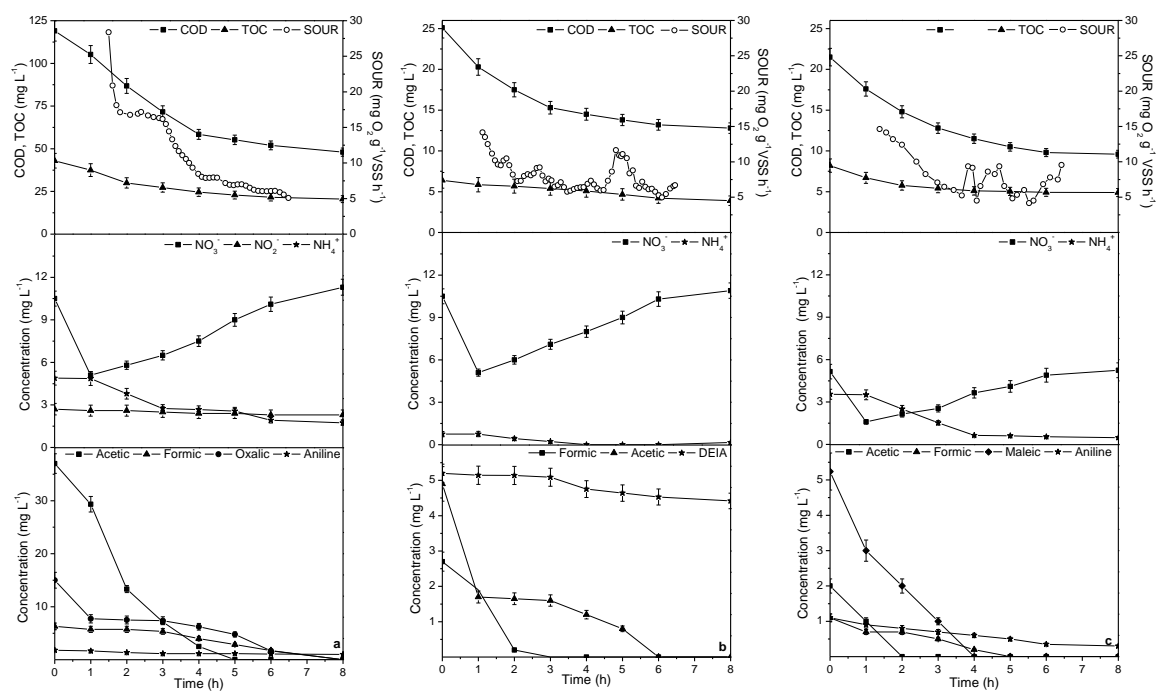


Fig. 8. Time-evolution of SOUR, COD, TOC, nitrogen inorganic species and short-chain organic acids along the last SBR cycle with the effluents from Fenton oxidation of alachlor (a), atrazine (b) and diuron (c).

Graphical abstract

