



Removal of paraquat pesticide with Fenton reaction in a pilot scale water system

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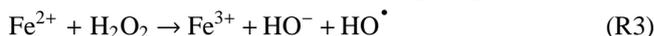
Abstract. Advanced oxidation processes, such as the Fenton's reagent, are powerful methods for decontamination of different environments from recalcitrant organics. In this work, the degradation of paraquat (PQ) pesticide was assessed (employing the commercial product gramoxone) directly inside the pipes of a pilot scale loop system; the effect of corroded cast iron pipe and loose deposits for catalysing the process was also evaluated. Results showed that complete degradation of paraquat ($[PQ]_0 = 3.9 \times 10^{-4}$ M, $T = 20\text{--}30$ °C, $pH_0 = 3$, $[H_2O_2]_0 = 1.5 \times 10^{-2}$ M and $[Fe(II)] = 5.0 \times 10^{-4}$ M,) was achieved within 8 h, either in lab scale or in the pilot loop. Complete PQ degradation was obtained at pH 3 whereas only 30 % of PQ was degraded at pH 5 during 24 h. The installation of old cast iron segments with length from 0.5 to 14 m into PVC pipe loop system had a significant positive effect on degradation rate of PQ, even without addition of iron salt; the longer the iron pipes section, the faster was the pesticide degradation. Addition of loose deposits (mostly corrosion products composed of goethite, magnetite and a hydrated phase of FeO) also catalysed the Fenton reaction due to presence of iron in the deposits. Moreover, gradual addition of hydrogen peroxide improved gramoxone degradation and mineralization. This study showed for the first time that is possible to achieve complete degradation of pesticides in situ pipe water system and that deposits and corroded pipes catalyse oxidation of pesticides.

1 Introduction

Contamination of raw waters with pesticides is recognised as a problem in many countries. Even in trace amounts, pesticides may pass water treatment plants and over long periods accumulate in water distribution pipes (Klamerth et al., 2010; Kralj et al., 2007; Sanches et al., 2010). Moreover, during an accident or deliberate contamination large concentrations may enter the system. Due to sorption in biofilm or on the surfaces of the pipes their removal by network flushing is not efficient. Advanced oxidation processes (AOP) are well-known for generating highly reactive and non-selective hydroxyl radical species, which are used to degrade (and mineralize into water, carbon dioxide and mineral salts) most of organics present in water and wastewater – cf. Reactions (R1)

and (R2) (Bautitz and Nogueira, 2007; Hassan et al., 2012; Homem and Santos, 2011; Klamerth et al., 2009; Walling, 1975).

Fenton's reaction is one type of AOP which generates the hydroxyl radicals ($\cdot OH$) but in this case through the reaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) according to Reaction (R3) (Andreozzi et al., 1999; Neyens and Baeyens, 2003; Pérez et al., 2002; Ramirez et al., 2007; Venny et al., 2012; Walling, 1975).



Numerous studies have been reported about removal of organic contaminants through Fenton's reaction. Among them, it is worth mentioning the decontamination of wastewaters from dyes (Kuo, 1992; Duarte et al., 2009), chlorophenols (Pera-Titus et al., 2004), or pharmaceuticals (De la Cruz et al., 2012). Decontamination of pesticides like chlorfenvinphos, paraquat, carbofuran, among others by the Fenton's process has also been addressed, this AOP showing to be a very efficient technology (e.g., complete elimination of paraquat was reached after 200 min (Santos et al., 2011), and 90 % of carbofuran elimination after only 5 min of reaction, Ma et al., 2010).

Apart from the classic Fenton to eliminate paraquat from waters, there are other AOPs that present also good efficiencies. Among them are the photocatalytic degradation, using TiO_2 as catalyst (complete degradation after 120 min has been reached) or the direct photolysis (60 % of paraquat was destroyed in less than 3 h) (Moctezuma et al., 1999); the catalytic wet peroxidation (based on heterogeneous oxidation) has also been tested recently – with 92 % of chemical oxygen demand removal after 12 h (Dhaouadi and Adhoum, 2010). Removal of paraquat from water was also the focus of recent work by adsorption over deposits from water networks (Santos et al., 2013); however, in this case there is no degradation of the pesticide, rather simple transfer to another phase (the adsorbent).

Because the Fenton's process requires dissolved iron (homogeneous oxidation), corrosion process in cast iron networks should not be detrimental for the Fenton reaction. Moreover, as an alternative to the homogeneous oxidation, heterogeneous catalysis can be applied by using a solid matrix to support the iron species (Duarte et al., 2009; Herney-Ramirez et al., 2010; Navalon et al., 2010). So, pipe material or corrosion product present in old networks can potentially be used as catalysts of this reaction. Recently it was found that pipe deposits can also act as catalysts in this AOP (Oliveira et al., 2012). This way, such deposits can be reused (upon cleaning/maintenance operations in water networks), or used as catalysts for in situ water treatment, in case of a contamination event.

The objective of this study was (i) to test whether with Fenton reaction it is possible to degrade pesticides (gramoxone) directly in a water distribution system and (ii) to assess the influence of length of cast iron pipe sections and amount of loose deposits on the catalytic process. The study was carried out in a pilot loop to simulate a real water supply system.

Up to the author's knowledge, this is the first report dealing with the use of the Fenton reaction at pilot scale, in a loop reactor, for in situ decontamination of water.

Table 1. Composition of the tap water used along this study.

Tap water properties	Value/concentration
Al, mg L^{-1}	0.07
Ammonium, mg L^{-1}	0.045
Fe, mg L^{-1}	0.022
Electrical conductivity, $\mu\text{S cm}^{-1}$	325 ± 45
Chlorides, mg L^{-1}	9
Mn, mg L^{-1}	0.02
Na, mg L^{-1}	5.5
pH	6.8 ± 0.1
Sulphates, mg L^{-1}	71 ± 7

2 Materials and methods

2.1 Reagents

Commercial Paraquat – Gramoxone (GMX) – 32.5 % (w/w) in paraquat dichloride was supplied by Syngenta. Gramoxone was used instead of analytical standard paraquat due to economical reasons. In addition, in case of a deliberate contamination event of a drinking water distribution system, it is more likely that such available commercial products are used instead of expensive analytical ones, even if other organics are also introduced in the network. Two loose deposits samples, one obtained from a local water distribution system (deposit A), and another taken from the tower of a water distribution system (deposit B), both from the city of Riga, were tested as catalysts of the Fenton-like reaction. H_2O_2 solution (30 % v/v), FeSO_4 heptahydrate (99.5 %) and anhydrous Na_2SO_3 were purchased from Merck (Darmstadt, Germany). H_2SO_4 (96 %) was from José M. Vaz Pereira, Lda (Lisbon, Portugal), while NaOH (98.7 %) was from José Manuel Gomes dos Santos, Lda (Odivelas, Portugal). Heptafluorobutyric acid (HFBA) was from Sigma Aldrich, and acetonitrile (HPLC grade) from Prolabo.

2.2 Standards preparation

Experiments were conducted with paraquat (PQ) solutions of 100 mg L^{-1} , which were prepared diluting the appropriate amount of gramoxone (GMX) in current tap water (composition data presented in Table 1). This high concentration was chosen to simulate a deliberate contamination of a drinking water system. All gramoxone solutions were stored at 4°C in polypropylene containers, in which adsorption does not occur. These solutions are stable when exposed to the used conditions (room temperature and while stored at 4°C or frozen).

2.3 Experimental setup

2.3.1 Stirred batch reactor (Lab scale)

Oxidation reactions done in lab scale were carried out in a stirred batch reactor with 250 mL of capacity. The temperature and the pH of the reaction mixture were respectively measured by a thermocouple and a pH electrode (WTW, SenTix 41 model), connected to a pH-meter from WTW (model Inolab pH Level 2). The temperature was kept constant in the desired value by a Huber thermostatic bath (Polystat CCI unit) that ensured water recirculation through the jacket of the reactor. No temperature variations higher than ± 1 °C were observed. After temperature stabilisation, the pH of the gramoxone solution was adjusted to the desired value by adding small amounts of 2 M H_2SO_4 or NaOH aqueous solutions. The start of the oxidation process was remarked by the addition of the catalyst (solid deposit or iron salt, the later for homogenous experiments) and the oxidant agent (hydrogen peroxide). During the reaction, samples were withdrawn, filtered with a 0.2 μm pore size PTFE syringe filter, and analysed as described in Sect. 2.4. To stop the homogenous reaction in the vial samples an excess of Na_2SO_3 was used to instantaneously consume the remaining hydrogen peroxide.

2.3.2 Recirculation tubular reactor (Pilot loop)

The pilot loop used in these experiments (Fig. 1) is made of polyvinyl chloride (PVC) pipes; however, some sections were replaced (see Table 2), if necessary, by iron pipes. The total length of the pilot loop is 28 m (l) and internal diameter is 75 mm (d_i). Iron pipes were obtained from inner heat supply system. However these pipes were made accordingly to the same standard as drinking water system pipes. The reagents (GMX, H_2SO_4 , H_2O_2 and ferrous iron) were introduced into the pilot loop using the manual pump coupled to the system.

The pilot loop was filled with tap water that passed through the filter before the experiments (composed of a water softening with manganese dioxide being the colloidal and dissolved iron removed by ion exchange resins). Water was recycled in the loop for 1 h to reach equilibrium conditions. Afterwards gramoxone was introduced into the system to reach the final concentration in paraquat of 100 mg L^{-1} ($3.9 \times 10^{-4} \text{ M}$), followed by the addition of the necessary amount of concentrated H_2SO_4 to achieve the desired initial pH.

After the addition of these reagents, the solution was recycled in the system for around one hour to assure the homogeneous mixing. Afterwards, the ferrous iron (or loose deposits – see Table 2) was added to the loop followed by the addition of the H_2O_2 to reach the final concentration of $1.5 \times 10^{-2} \text{ M}$; this corresponds to time zero of the reaction. Samples were taken along the reaction time and filtrated with a 0.2 μm pore size PTFE syringe filters, for further analysis, as described in the following section. All the experiments were carried out at room temperature (20 ± 2 °C).

Experiments performed are described in Table 2.

2.4 Analytical methodology

The paraquat degradation was followed by HPLC-DAD (High Performance Liquid Chromatography with Diode Array Detection), as described previously (Santos et al., 2011). The HPLC-DAD is a Hitachi Elite LaChrom that consists in an L-2130 pump, an L-2200 auto sampler and an L-2455 diode array detector (DAD). Chromatographic analysis of paraquat was performed by direct injection of 99 μL of sample. The chromatographic separation was achieved by a RP C18 Purospher® STAR column (240 mm \times 4 mm, 5 μm) reversed phase, supplied by VWR, using a mobile phase of 95 % (v/v) of 10 mM HFBA in water and 5 % (v/v) of acetonitrile, at isocratic conditions, with a flow rate of 1 mL min^{-1} . The spectra acquisition was recorded from 220 to 400 nm and paraquat was quantified at 259 nm, characterized by a retention time of 3 min. The calibration curve for paraquat in water was performed by direct injection of 9 standards, from 0.1 to 100 mg L^{-1} of paraquat. The coefficient of determination obtained was 0.9999 and the tests revealed an excellent linearity. A detection limit of 0.05 mg L^{-1} was reached.

Dissolved organic carbon (DOC) measurements were performed in a TOC-5000A Analyzer with an auto sampler ASI-5000 (Shimadzu Corporation, Kyoto, Japan). The methodology is based on a standard method (LVS EN 1484, 2000). Each sample was tested in duplicate and the mean values were calculated ($\text{CV} \leq 2\%$). The blank and control solutions were analysed with each series of samples in order to verify the accuracy of the results obtained by the method. The minimal detection limit (MDL) was $380 \mu\text{g L}^{-1}$.

The metals (namely iron) in the solution were determined using a UNICAM 939/959 flame atomic absorption spectrophotometer.

2.5 Solids characterization

Chemical composition of the loose deposit samples was determined by wavelength dispersive X-ray fluorescence (WDXRF) in a Bruker S8 TIGER spectrometer. Samples were analysed in helium atmosphere without previous treatment. The analyses were performed in Full Analysis mode. Results of measurements are expressed in oxide formula units. Mathematical data processing was carried out with integrated Spectra plus software.

To obtain the XRD (X-ray diffraction) diffractograms, a PANalytical model X'Pert PRO with a X'Celerator detector was used. The energy used to produce de X-rays was of 40 kV and 30 mA. Data acquisition was based in the geometry Bragg-Brentano, between $15^\circ \leq 2\Theta \leq 70^\circ$.

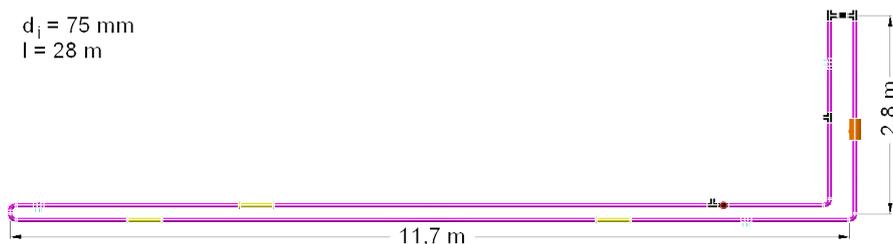


Figure 1. Illustration of the pilot loop used.

3 Results and discussion

3.1 Homogeneous process of PQ degradation

3.1.1 Batch scale vs. pilot loop

A previous parametric study in a stirred batch reactor was done to establish the best conditions for mineralization of PQ in water. The work is described elsewhere (Santos et al., 2011) but briefly the best conditions were: $T = 30\text{ }^{\circ}\text{C}$, $\text{pH}_0 = 3$, $[\text{H}_2\text{O}_2]_0 = 1.5 \times 10^{-2}\text{ M}$ and $[\text{Fe}(\text{II})] = 5.0 \times 10^{-4}\text{ M}$, for $[\text{PQ}]_0 = 3.9 \times 10^{-4}\text{ M}$ (100 mg L^{-1}). This study was performed using the same conditions, but not the temperature because it is not controllable neither in the pilot loop nor in a real situation. The operating conditions used for each experiment in the pilot loop are presented in Table 2, where parameters changed in each run are highlighted in bold.

The first step of this study was to find out if the degradation process in the pilot loop would be similar to the one in the lab scale, so that it could be easily scaled up to the size of a real water network. This possibility would represent a main novelty and step forward as a decontamination in-situ. The same operational conditions were then applied in both lab and pilot scale, and compared in terms of paraquat degradation and gramoxone mineralization.

Figure 2a presents the changes of paraquat concentration in both reactors, i.e., the evolution of the pesticide concentration along reaction time, while Fig. 2b refers to the dissolved organic carbon data. It can be seen that the performance of the process, for both degradation and mineralization, was very similar in both reactors, although their dimensions and mode of operation are considerably different, as well as initial DOC (because in the pilot loop reactor commercial GMX was used, as described above). Besides, it is shown that the decrease of temperature ($20\text{ }^{\circ}\text{C}$ in the loop instead of $30\text{ }^{\circ}\text{C}$) does not influence significantly the process, representing an important advancement in water decontamination in-situ, avoiding the concerns about high temperatures. It should be noted that after 8 h, in the pilot loop, paraquat was completely degraded, even using lower temperatures than in the lab scale; it can thus be concluded that the process can be easily scaled up, keeping the good performance.

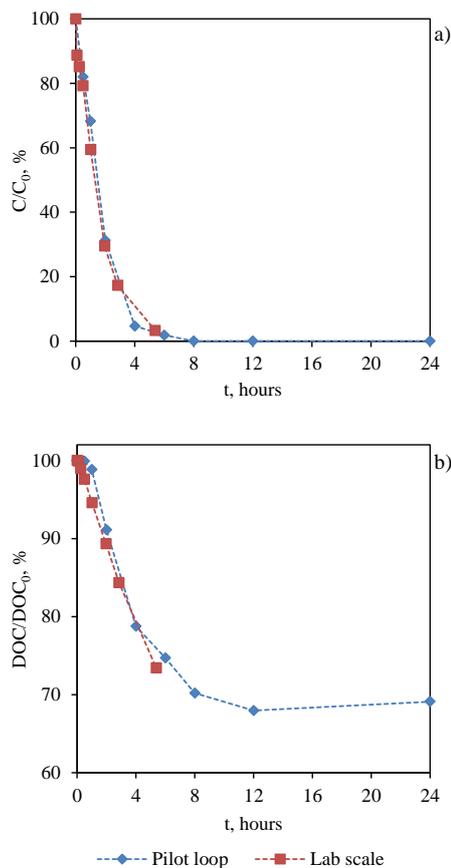


Figure 2. Comparison of PQ degradation (a) and GMX mineralization (b) between experiments in lab scale ($T = 30\text{ }^{\circ}\text{C}$) and in the pilot loop ($T = 20\text{ }^{\circ}\text{C}$, for the other conditions refer to Table 2, Run #1).

3.1.2 Effect of the initial pH

As it is relatively hard to control the pH in the real water distribution system, the effect of the initial pH in the performance of paraquat degradation was evaluated. Experiments were performed with the initial pH of 3 (Run #1) and the initial pH of 5 (Run #2) – see Table 2 – which is closer to the pH of tap water, and would allow decreasing acid consumption.

From Fig. 3a and b it can be seen that the initial pH has a significant impact in the catalytic process. Indeed, at the

Table 2. Operating conditions for each experiment.

	Run #1	Run #2	Run #3	Run #4	Run #5	Run #6	Run #7	Run #8
[H ₂ O ₂] ₀ , M	1.5 × 10 ⁻²	1.5 × 10 ⁻²	1.5 × 10 ⁻²	1.5 × 10 ⁻²	1.5 × 10 ⁻²	1.5 × 10 ⁻²	1.5 × 10 ⁻² ^a	1.5 × 10 ⁻² ^b
[FeSO ₄ · 7H ₂ O] ₀ , M	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	–	–	–	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴
[Fe] _{salt} , mg L ⁻¹	139	139	139	–	–	–	139	139
[deposit], mg L ⁻¹	–	–	–	–	128	744	–	–
[Fe] _{deposit} , mg L ⁻¹	–	–	–	–	94	606	–	–
[PQ] ₀ , M	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴	3.9 × 10 ⁻⁴
pH ₀	3.0	5.0	3.0	3.0	3.0	3.0	3.0	3.0
T _{average} , °C	≈ 20	≈ 20	≈ 20	≈ 20	≈ 20	≈ 20	≈ 20	≈ 20
Pipes types	PVC	PVC	PVC + iron, 0.5 m	PVC + iron, 13.6 m	PVC	PVC	PVC	PVC
Iron source	Iron (II) salt	Iron (II) salt	Iron (II) salt + iron pipe	Iron pipe	Loose deposit A	Loose deposit B	Iron (II) salt	Iron (II) salt

^a Gradual addition of H₂O₂ (32 mL × 5).

^b Gradual addition of H₂O₂ [(15 mL × 2) + (30 mL × 2) + 70 mL].

initial pH of 5 no mineralization was achieved and only 30 % of the pesticide degradation was reached in 24 h, while for the initial pH of 3 the degradation was complete after 8 h of reaction, and after 12 h the mineralization reached a plateau of 30 %.

The evolution of pH in these runs is presented in Fig. 3c. In both cases there is a pH decrease for short reaction times, which is typical when oxidation occurs with formation of organic acids. The increase of pH for long reaction times can be due to presence of small and unknown particles present along the pipes that are released to the liquid phase and can also be related with the release of the dissolved CO₂ present in the water. It should be noted that in case of initial pH of 5 even after pH dropped to 3.5 within first 1 h of the reaction it did not promote GMX mineralization.

Figure 3d and e shows, respectively, the evolution of soluble and total iron concentration along reaction time, for both experiments. These experiments have the same source of iron – iron (II) salt – and also the same initial load (Table 2); thus, the evolution of total iron concentration is similar for both experiments; however, there are important differences in the soluble iron concentration (Fig. 3d), once the initial pH is quite different and it affects the solubility of the iron species. In fact, it can be seen that much less soluble iron is present in the reaction using an initial pH of 5 (RUN #2) because at high pH values part of the iron present is converted into Fe³⁺, which precipitates, becoming not available to react with the oxidant and catalyze the process. Therefore, degradation of gramoxone is much worse in such conditions (Fig. 3a and b).

3.2 Heterogeneous Fenton reaction

3.2.1 Iron pipe as catalyst – influence of the length

To evaluate the ability of distribution system water pipes in catalysing the Fenton's reaction, some sections of the PVC from the pilot loop were replaced by used iron pipes (see Table 2). The installed iron pipe sections represented approximately 2 and 50 % of the total length of the loop (RUN #3 and RUN #4, respectively).

It should be highlighted that previous experiments without iron and H₂O₂ (either in PVC or PVC + iron pipes) were per-

formed to assess the possibility of occurring sorption of the pesticide in the pipes. Any significant variation of the pesticide concentration was found. Results presented in Fig. 4a show that the paraquat degradation rate, in the experiment where no iron pipes were installed, was slower than the experiment where 2 % iron pipes were installed (0.5 m long iron pipe), in the presence of FeSO₄. This shows that the presence of the iron pipe can promote a faster production of hydroxyl radicals and thus increase the rate of paraquat degradation. As it could be predicted, the greater part of the iron pipes, the faster is the pesticide degradation; this can be confirmed by the analysis of the data from Fig. 4a, from the experiment where 50 % of PVC pipes were replaced by iron pipes (and no iron salt was used), which shows that the degradation rate is the fastest among tested. This can be considered as a great advantage in case of a decontamination demand, once it allows operating in-situ and avoiding the use of some chemicals once the pipes can promote the catalysis.

It should be noted that the fastest and highest mineralization was also achieved in the experiment where 50 % of the loop consisted of iron pipes (Fig. 4b). According to the data shown in Fig. 4a and b, these conditions provided a more effective degradation, with complete pesticide degradation and a remarkable mineralization of 50 % (such mineralization is due not only to the carbon present in the pesticide paraquat but also to that in other organics present, as the pesticide employed is not analytical grade but rather commercial gramoxone – cf. Sect. 2.1). Thus it can be stated that the heterogeneous reaction is quite effective for PQ degradation and mineralization of organics.

It should be noted that, after some time the pH of water started to increase (Fig. 4c), being however more noticeable in the runs with longer pipe sections, in accordance with the explanations given before. One should take into account that mineralization is the highest in RUN #4, so more organics got oxidized and more CO₂ was formed.

From the analysis of Fig. 4d, it can be seen that the iron concentration in solution is the lowest for the experiment using the longer iron pipe length; on the other hand, for the same experiment, the total iron is the highest (Fig. 4e), which means that the iron that acts as catalyst is released from the

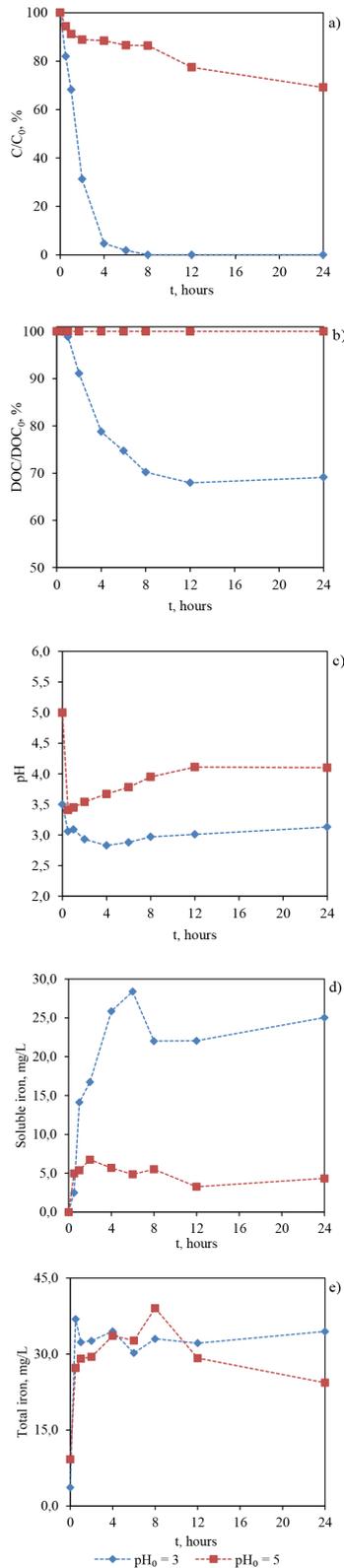


Figure 3. Effect of the initial pH in the PQ degradation (a), GMX mineralization (b), pH evolution (c), soluble iron concentration (d) and total iron concentration (e) along the time of reaction (Runs #1 and #2).

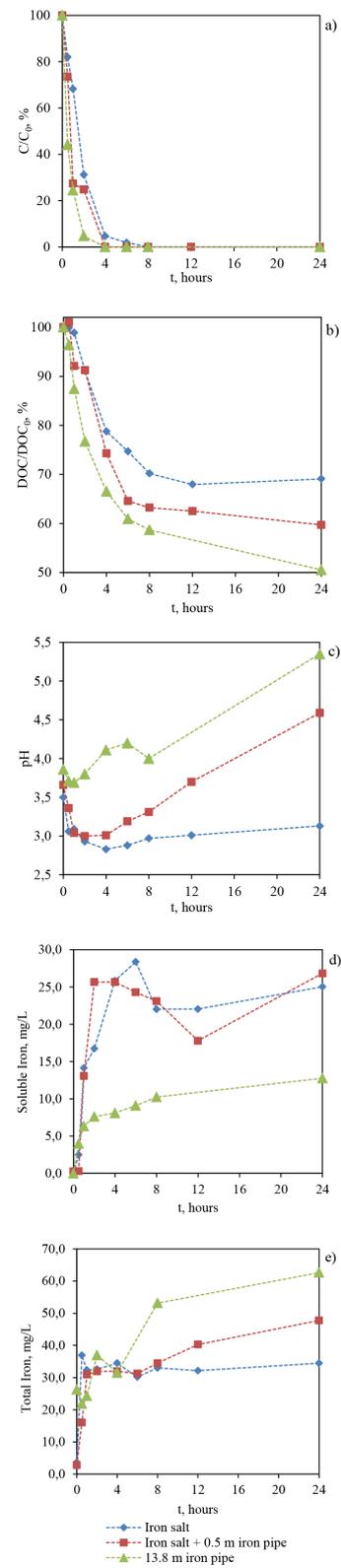


Figure 4. Effect of the use of iron pipes in the PQ degradation (a), GMX mineralization (b), pH evolution (c), soluble iron concentration (d) and total iron concentration (e) along the time of reaction (Runs #1, #3 and #4).

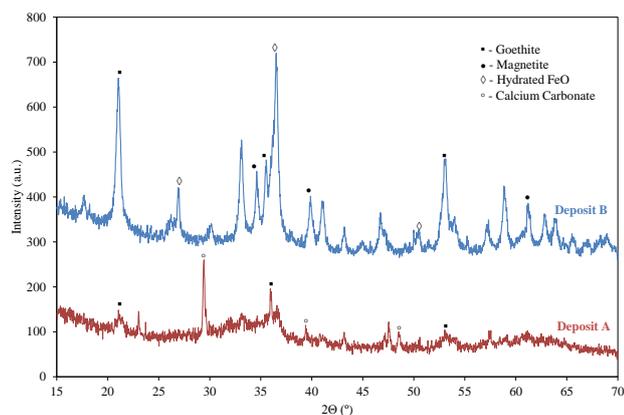


Figure 5. XRD patterns obtained for each deposit.

pipes and remains in suspension in the solution, part of it being solubilized. In the case of the other two runs, dissolved iron is at a higher level, because FeSO_4 was added (Table 2).

Figure 4e shows that the longer is the iron pipes section more iron will be detected in solution as a consequence of the leaching phenomenon. The thickness of the iron pipe used in RUN #3 (2% of pipes made of iron) was checked before and after the experiment. This measurement was done using ultrasound. The results showed that pipe wall thickness decreased 10 542 nm during the 48 h of reaction, meaning that pipe wall thickness decrease rate is approximately 1.92 mm yr^{-1} . In normal conditions, for the iron pipe, the thickness reduction along time would be around 160 nm day^{-1} . Using more aggressive conditions against pipes permanently, i.e. like the ones employed here for in situ decontamination ($\text{pH} = 3$ and $[\text{H}_2\text{O}_2] = 1.5 \times 10^{-2} \text{ M}$), one can conclude that this pipe should be replaced only after 3–4 yr of use.

3.2.2 Loose deposits as catalysts

Two loose deposit samples (one obtained from a real drinking water distribution system – deposit A – and another obtained from the tower of the water distribution system – deposit B) were tested for their ability to catalyse the Fenton's reaction. These deposits were analysed by XRD and their characterization can be found in Table 3 and Fig. 5. Both deposits are mainly a mixture of iron oxyhydroxides; in the case of the deposit B, it has mostly goethite, magnetite and a hydrated phase of FeO ; the sample named deposit A has in its composition mostly CaCO_3 and goethite.

The main minerals present in the samples were also determined by WDXRF. The results can be found in Table 3. It can be seen that both solids are quite complex, with numerous oxides in their composition, being however the iron-species the predominant, in agreement with the XRD data; for instance, for deposit A, it amounts to 73.35 wt. %, expressed as Fe_2O_3 .

Table 3. Composition of the inorganic deposit samples used (determined by WDXRF).

Compounds	Deposit A	Deposit B
	Composition (wt. %)	
Fe_2O_3	73.35	81.51
SiO_2	3.23	2.71
CaO	5.65	0.73
SO_3	0.24	0.68
MnO	0.17	0.15
TiO_2	0.04	0.05
P_2O_5	2.15	–
Al_2O_3	–	0.44
Cr_2O_3	0.01	–
ZrO_2	–	0.01
ZnO	–	0.15
CuO	–	0.05
K_2O	–	0.02
NiO	–	0.01
BaO	0.24	–
MgO	0.14	–
SrO	0.05	–
ZnO	0.03	–
Cl	–	0.11
Water	14.70	13.38

RUN #1 shows the degradation process in the presence of iron salt, while RUN #5 and RUN #6 present, respectively, the oxidation in the presence of the deposit A and the deposit B. The iron content was 73.4% in deposit A and 81.5% in deposit B (Table 3), which means that the iron concentration used was, respectively, 94 mg Fe L^{-1} and 606 mg Fe L^{-1} – Table 2. In the RUN #1, an iron concentration of $5.0 \times 10^{-4} \text{ M}$ (139 mg Fe L^{-1}) was provided by the addition of the FeSO_4 .

Analysing Fig. 6a and b it can be said that the process is more effective when using FeSO_4 ; the experiment with deposit A yielded no paraquat degradation after 24 h, while the deposit B shows oxidation performance, being able to almost completely degrade paraquat. Significant difference in performances between deposits cannot be explained by the different doses used, but rather by their natures and composition. This evidences the possibility of using some pipe deposits as catalysts of the Fenton's process, which performance depends on the deposit used, in agreement with the results obtained previously and detailed below. However, this was now proved in a pilot-scale reactor.

It is of big interest to understand the evolution of the pH along time (Fig. 6c); as said before, the increase in the medium pH affects the availability of the Fe^{2+} to react with H_2O_2 . Once the Fe^{2+} precipitates as Fe^{3+} , no more iron is available to react with the peroxide and thus no radicals are generated. Besides, upon increasing the medium pH, the peroxide is decomposed into oxygen and water. All these issues

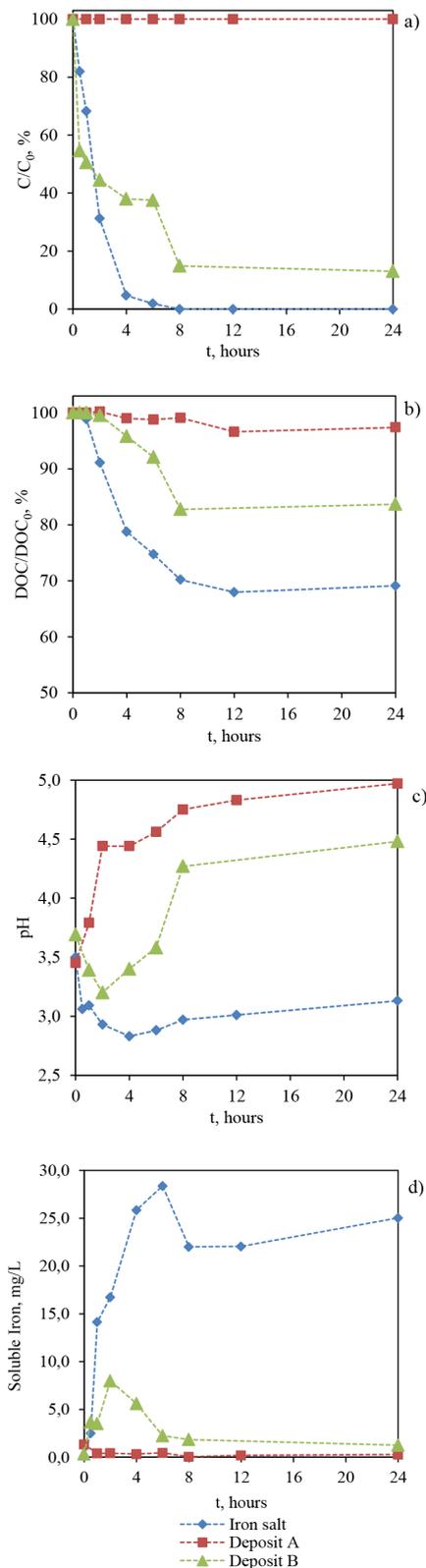


Figure 6. Effect of the loose deposits in the PQ degradation (a), GMX mineralization (b), pH evolution (c) and soluble iron concentration (d) along the time of reaction (Runs #1, #5 and #6).

Table 4. Way of H_2O_2 addition.

Time, h	Volume of H_2O_2 , mL		
	Run #1	Run #7	Run #8
0	~ 160	32	15
2	–	32	15
4	–	32	30
6	–	32	30
8	–	32	70

are responsible for the decrease in the reaction performance. The increase in the pH along the reaction can be related also with the pH_{pzc} of each deposit, as reported previously (Oliveira et al., 2012). Loose deposits as sample A, rich in calcium carbonate, have higher pH_{pzc} values and thus are responsible for the higher pH in the medium and lower catalytic performance.

The above results are also in line with the dissolved iron (Fig. 6d), which is much lower for the experiment with the deposit A, where the final pH is higher.

The absence of catalytic activity of deposit A can be due to the fact of being mostly composed by $CaCO_3$ and goethite, which, according to Matta et al. (2007) and Oliveira et al. (2012), has a very low catalytic activity when compared with other iron minerals. Also the pH during experiment with deposit A (Fig. 6c) increased fast from the very beginning. It should be noted that in experiment with deposit B after pH raised to approximately 4.2 the degradation of the GMX and the mineralization also stopped.

3.3 Effect of the gradual addition of hydrogen peroxide in the oxidation process

The gradual addition of H_2O_2 was also tested because it is known to be a more effective way of oxidant use (Santos et al., 2011). Three experiments were performed: in the first one (RUN #1 – Table 2), 160 mL of oxidant were added at initial instant ($t = 0$ h); in the second the same amount of oxidant was used – RUN #7 – but divided in 5 doses: 32 mL of oxidant were added at 0, 2, 4, 6 and 8 h of reaction; in the third experiment (RUN #8), 15 mL were added at 0 and 2 h, and 30 mL were added after 4, 6 and 8 h of reaction (method described in Table 4). The experiments are compared in Fig. 7. All other experimental conditions were kept (cf. Table 2).

As can be seen in Fig. 7a and b, in the case of progressive addition of the oxidant (RUN #7 and RUN #8) the performance is similar to the one of RUN #1. However, after 24 h of reaction (Fig. 7b) much better mineralization degree was achieved as consequence of the decreased parallel and undesired reactions that are favoured by a higher H_2O_2 concentration – e.g., scavenging of radicals as shown in Reaction (4) (Laat and Le, 2006; Ramirez et al., 2007; Rodrigues et al., 2009). One should note also that for RUN #8 the final

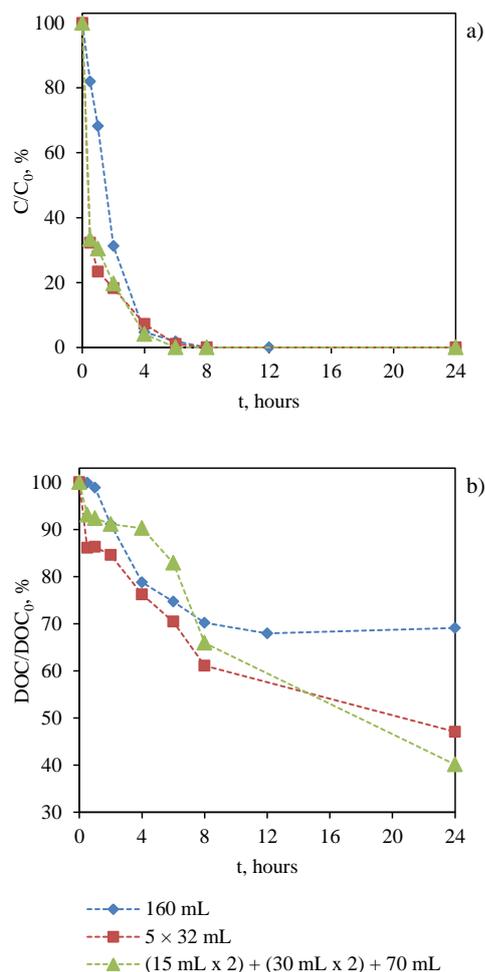


Figure 7. Effect of the gradual addition of H₂O₂ in the performance of PQ degradation (a) and mineralization (b) along the time of reaction (Runs #1, #7 and #8).

mineralization degree is even bigger than for the RUN #7, once the gradual addition in RUN #8 was made with increasing amounts of peroxide; a remarkable DOC reduction of 60% (which is the best result among all the experiments) was reached in these conditions, which could probably be increased for higher reaction times.



From these experiments it can be concluded that the best paraquat degradation performance is achieved when gradual addition of H₂O₂ is used.

In spite of the promising results obtained in this study, some limitations were found. In fact, to be more representative of a real water network, the length of the loop should be increased, and the permanent circulation of fresh water should be included (flow-through situation, in opposition to a recirculation system). Other types of pipes with iron and/or other transition metals in their composition should also be

tested. This also applies to the loose deposits; deposits from different places and natures should be tested, considering the iron content and the content of other metals that can work as catalyst (iron, cobalt, nickel, copper, etc.).

It should be also remarked that the costs for the Fenton treatment are low, especially when compared with final disposal costs, being the more relevant those associated with the hydrogen peroxide consumption (Bigda, 1996). In addition, the operating costs are also reduced, once the process runs under moderate conditions of temperature and pressure. In the particular application studied in this work, the costs are further reduced because neither temperature control, neither the use of iron salt as catalyst is required. Other authors also claim that the Fenton's process is very cheap when compared to other AOP's such as photo-Fenton (Audebert et al., 2011), ozonation or photocatalysis (e.g. photocatalytic oxidation with TiO₂ – Béltran, 2004); on the other hand, results of previous studies proved that the costs associated to AOP treatments are similar to the costs associated to well-established technologies of contaminants removal (Andreozzi et al., 1999). Of course, in an emergency situation like in the event of contamination of a water distribution system this aspect (cost) should not be the limiting issue.

4 Conclusions

It was found that Paraquat degradation can be done in the pilot loop, achieving similar results to those obtained in a lab scale reactor, i.e., homogeneous Fenton's reaction is an effective process in both scales for the pesticide degradation. Initial pH was proven to be a very important factor for Fenton reaction. Results showed complete paraquat degradation (nearly 100% within 8 h) if initial pH was 3 and little degradation rate (30% within 24 h) if initial pH was 5.

It was for the first time shown that distribution system pipes can work as a catalyst for Fenton reaction providing also complete paraquat degradation – the size of metallic pipes has a big influence in the oxidation process; the larger the pipe, the bigger is the contribution of the heterogeneous process. Once iron pipes work as catalysts, water decontamination can be done in-situ, using the appropriate operating conditions. Loose deposits can be used as catalysts, but special care must be taken to their composition.

The gradual addition of H₂O₂ showed to be the best option in the oxidation process, allowing reaching higher mineralization degrees, up to 60% in only 24 h.

Summarizing, this work illustrated that it is possible to decontaminate water in a real water network by advanced Fenton oxidation. Besides, it is also possible to run the process efficiently using either the iron pipes or the loose deposits as the catalyst iron source.

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