



May a natural lake behave as an efficient Fenton reactor under dark conditions?

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Abstract

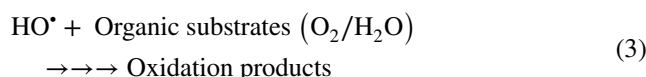
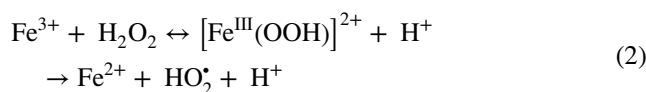
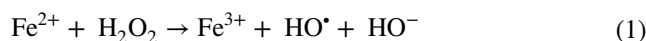
Phenol degradation experiments were performed to study the potential behavior of the acidic Lake Caviahue (LC) as a dark Fenton reactor under natural conditions and upon H₂O₂ addition at doses typically used for technological applications. In both cases, to assess the influence of dissolved organic matter present in the lake, control experiments were carried out under identical initial conditions (pH, concentrations of phenol, iron, and H₂O₂), but in the absence of organic matter. A first set of experiments was performed to test the feasibility of dark Fenton processes under environmental conditions. Lake water samples were used as reaction matrix and catalyst source, whereas phenol and H₂O₂ were added as model pollutant and oxidant, respectively. H₂O₂ concentrations used were similar to those reported for rainwater. Results show that phenol can be degraded under all conditions studied and that the amount of phenol consumed depends on both the H₂O₂ concentration added and the matrix composition LC. A second set of experiments was designed to characterize the lake behavior as a natural Fenton reactor upon the addition of H₂O₂ concentrations typically used for technological applications. Although phenol concentration profiles obtained for LC and the artificial solution show the characteristic behavior of Fenton-like systems, the trends are rather different, since for LC, the lag phase is much longer than that for the artificial matrix. Overall, the results suggest that the Fe(III)-chelating effect of the organic matter present in LC slows down reaction rates, but it does not block phenol degradation through Fenton-like processes.

Keywords Dark Fenton process · Natural lake reactor · Natural organic matter

Introduction

Wastewater treatment by means of advanced oxidation processes (AOPs) is of major interest in modern environmental chemistry. These processes are based on the production of oxidizing species, such as hydroxyl radicals ($\bullet\text{OH}$), which react with most organic compounds due to their high reactivity and low selectivity (von Sonntag 2008). Among AOPs, the Fenton reagent combines ferrous salts (Fe^{2+}) with hydrogen peroxide (H_2O_2), whereas Fenton-like processes

involve a series of dark reactions catalyzed by transition metal salts (frequently ferric salts, hereafter represented as Fe^{3+}), which trigger H_2O_2 decomposition leading to the oxidation of organic substrates. Fenton processes have attracted great interest for technical development due to the relatively low cost of the Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), the absence of iron toxicity, and the environmentally benign character of H_2O_2 . Despite the complexity of the oxidation mechanisms involved, the most relevant reactions for these systems can be represented as (Nichela et al. 2008; Pignatello et al. 2006)



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where the production of HO^\bullet occurs mainly through H_2O_2 decomposition in the presence of ferrous species in an acidic medium [Reaction (1)]. In most Fenton-like processes (where Fe^{3+} is the catalyst), Fe^{2+} regeneration is the rate limiting step in the catalytic iron cycle, and the overall process efficiencies are strongly dependent on the contribution of reduction pathways for Fe^{3+} species other than the reaction between Fe^{3+} and H_2O_2 [Reaction (2)]. It has been reported that, in these systems, aromatic pollutants degradation usually displays an autocatalytic behavior with an initial “slow phase” when the compound concentration slightly decreases, and a subsequent “fast phase” when the process is substantially accelerated (Chen and Pignatello 1997; Nichela et al. 2008, 2010, 2015). In contrast, systems based on the Fenton reagent are characterized by a completely different kinetic behavior, with an initial fast phase governed by Fe^{2+} oxidation usually followed by a much slower oxidation phase (Carlos et al. 2008; Pignatello et al. 2006).

Despite Fenton and Fenton-like systems having been broadly studied as appropriate processes for the elimination of recalcitrant pollutants, their applicability in natural environments is rather limited, since pH values of natural water bodies are usually neutral or slightly alkaline, quite far from the acidic conditions required for achieving efficient Fenton and Fenton-like processes. However, there are some acidic lakes throughout the world (Geller et al. 1998; Gómez-Ortiz et al. 2014; Hao et al. 2017; McCullough 2015; Varekamp 2008) which may be potential basins for the occurrence of natural or technological Fenton and Fenton-like processes. These water bodies are characterized by mineral acidity with $\text{pH} < 4$, high concentrations of sulfate and dissolved metals such as iron, aluminum and manganese, as well as trace elements. Most of acidic water bodies are streams or lakes affected by acid mine drainage (Geller et al. 1998; Nixdorf et al. 2005), but there are some scarce systems acidified by natural processes (Gammons et al. 2008; Nixdorf et al. 2005; Stumm and Morgan 1996).

An example of the latter is Lake Caviahue (LC) (Pedrozo et al. 2001), a natural acidic lake situated at 1600 m a.s.l. in the Copahue–Caviahue Provincial Park, in the Andean north-west of the Province of Neuquén, Argentina. LC acidity ($\text{pH} 2.56$, acidity: $45 \text{ mmol H}^+ \text{ L}^{-1}$) is controlled by the high sulfate content of the Upper River Agrio (one of the two main inflows with $\text{pH} 1.78$ and acidity: 420 mmol.L^{-1}) and is attributed to sulfuric acid generated in the source water from the Copahue Volcano (altitude 2800 m a.s.l.) (Diaz et al. 2007). LC is characterized by high concentrations of Al, Ca, Fe, SO_4^{2-} , total P, total N, N-NO_3^- , and N-NH_4^+ , with mean concentrations of 40 mg.L^{-1} , 28.4 mg.L^{-1} , 20.4 mg.L^{-1} , 478 mg.L^{-1} , 0.51 mg.L^{-1} , 0.2 mg.L^{-1} , 0.035 mg.L^{-1} , and 0.05 mg.L^{-1} , respectively. On the other hand, in LC, there is a settlement with 700 permanent inhabitants, located on the west side of the lake. This town varies

considerably in population throughout the year, attracting tourists to the thermal bath complex in summer and also to the winter sports centre. The town lacks an adequate treatment plant for sewage effluents, which are directly discharged into the lake. There are many physical, chemical, and biological processes which could be used to treat sewage to an acceptable standard for discharge to river, lakes, etc. all with varying degrees of success, technology, and cost. In general, usually, method includes screening to remove large particles, settlements to remove the heavy gritty or inorganic matter, followed by further settlement to remove most of the remaining solid impurities from the liquid portion. The resultant clearer liquid, which contains dissolved and colloidal matter, is then subjected to a biological stage, where most of the remaining organic matter and impurities are oxidized to carbon dioxide and water, or converted into biomass which is removed by final settlement before discharge to the receiving water (Rae 1998). Villa Caviahue does not have an efficient sewage treatment system, because it only has an initial sieving stage to remove the large particulate material and a settling pool, where a part of the organic matter is biologically oxidized. The liquid thus treated is discharged directly to the lake. This methodology has the advantage of being not expensive, but it is an incomplete treatment. On the other hand, the main advantages of Fenton and Fenton-like processes are the characteristic of the reactants (iron is abundant and non-toxic, and H_2O_2 is environmentally friendly and easy to use) and the simple reactor design. The principal limitations are related to the restricted pH range of application and the reagent consumption that leads to a partial mineralization. The possible application as pre treatment or post treatment, make Fenton and Fenton-like processes particularly interesting in the case of the incomplete methodology applied on LC effluents.

The low pH values and the high dissolved iron levels [i.e., $\text{pH} = 2.56$, $[\text{Fe}] = 19.5 \text{ mg.L}^{-1}$] suggest that LC could be a suitable environment for natural progress of Fenton and Fenton-like processes. Noteworthy, despite some authors having investigated the possibility of occurrence of these processes at near neutral pH in typical natural water environments (Qin et al. 2013; Vermilyea and Voelker 2009), to the best of our knowledge, natural Fenton and Fenton-like reactions in acidic lakes have not been assessed before. Therefore, a study of the occurrence of Fenton or Fenton-like processes under optimal natural conditions and the possibility of taking advantage of these environmental conditions in the degradation of pollutants are important to tackle the development of cost-effective treatments of residues in lake acids.

The objectives of the present work were, using phenol as model substrate, (1) to evaluate whether dark Fenton and/or Fenton-like processes are likely to occur in LC under natural conditions and (2) to assess the feasibility of exploiting the particular composition of this natural matrix

for contaminants oxidation upon external addition of H_2O_2 in concentrations typically used for technological applications. Samples were taken in Caviahue Lake (autumn 2017) and experiments were carried out in Bariloche (Río Negro, Argentina) during the year 2017.

Materials and methods

Reagents

Phenol proanalysis (98%, Cicarrelli), $\text{Fe}(\text{ClO}_4)_2 \cdot x \text{H}_2\text{O}$ (< 0.10% chloride, Aldrich), $\text{Fe}(\text{ClO}_4)_2 \cdot x \text{H}_2\text{O}$ (98%, Aldrich), and H_2O_2 (30%, Merck) were used without further purification. H_2SO_4 (95–97%, Merck) was used to adjust the pH, when needed HPLC mobile phase was prepared with H_3PO_4 (85%, AR grade, Anedra), triethylamine (AR grade, Anedra), and acetonitrile (ACN) for liquid chromatography (Isocratic Grade, Lichrosolv). Deionized water (> 18 M Ω cm) was obtained from a Rephile Purist Ultrapure water system.

Analytical techniques

Quantification of the model substrate in the reaction mixtures was performed by HPLC using a Waters Delta 600 instrument equipped with an in-line degasser AF, a Waters 2998 PDA Detector, a 717 plus Autosampler, and a C18 Column (Hyperclone 5 μ ODS 120A, 250 \times 4.6 mm). The mobile phase was a mixture 75/25 (v/v) of ACN and an aqueous buffer at pH 3 (11 mM H_3PO_4 and 6.4 mM triethylamine). The flow rate was 0.8 mL \cdot min $^{-1}$ and the detection wavelength was set to 271 nm. Dissolved organic matter (DOM) was measured as total organic carbon (TOC) using a Shimadzu instrument (5000A TOC analyzer, catalytic oxidation on Pt at 680 °C).

Experimental procedures and setup

Evaluation of the feasibility of natural Fenton processes in Lake Caviahue

To evaluate whether dark Fenton processes are feasible under natural conditions, phenol degradation experiments were performed using the average iron concentration of the lake and H_2O_2 concentrations usually reported for rain water (Olszyna et al. 1988; Gonçalves et al. 2010). All experiments were carried out in triplicate at room temperature (19 °C), in 40-mL batch reactors, under dark conditions and without automatic stirring. The reactors were covered with perforated parafilm to work under aerated conditions and minimize evaporation. The reactors were, daily, manually stirred. Two different solutions were employed as reaction

matrices: natural water samples from LC filtered through 0.45 μm (cellulose acetate membrane filters) and acidic solutions prepared in the laboratory (hereafter, artificial solutions) with the same iron concentrations as those of LC [i.e., $[\text{Fe}^{2+}] \sim 34 \mu\text{M}$ and $[\text{Fe}^{3+}] \sim 300 \mu\text{M}$]. Phenol concentration was 1.54 mM for experiments carried out in artificial water and 1.56 mM for experiments performed in LC matrix. The pH of the artificial solution was adjusted 3.05 (closely similar to the pH = 2.97 measured for LC). The experiments were conducted using two different initial concentrations of H_2O_2 : 20 and 50 μM , for each reaction matrix. Concentrations of phenol before and after (48 h) the addition of H_2O_2 were registered. Phenolic solutions, prepared in both matrices but without H_2O_2 , were preserved as controls. For the control solutions, phenol concentrations remained constant after 48 h. Analysis of variance (ANOVA) was applied to test statistically relevant differences between degradation treatment and the Tukey test to compare pairs of treatments. The confidence level was set at 5%.

Kinetic characterization of Lake Caviahue as Fenton reactor

To assess the kinetic behavior of phenol degradation in LC under dark conditions (i.e., considering only the contribution of non-photochemical processes), oxidation experiments were performed using filtered LC water as reaction matrix and hydrogen peroxide in excess with respect to phenol concentration. For comparison purposes, phenol degradation experiments with equivalent initial conditions [[phenol], $[\text{H}_2\text{O}_2]$, temperature, and pH] were performed using an artificial acidic solution prepared with the same iron concentration as that of LC as reaction matrix. Experiments were conducted in a 250 mL batch reactor, under dark conditions and at room temperature (21.0 °C). Initial concentrations of phenol and H_2O_2 were 5 and 7 mM, respectively. Hydrogen peroxide was added just before the start of each run. All experiments were performed under continuous stirring and without bubbling. The degradation profiles were studied by measuring the time evolution of HPLC peak areas.

Results and discussion

Evaluation of the feasibility of natural Fenton processes in Lake Caviahue

Given the high iron concentration, the acidic pH conditions of LC, and the potential input of H_2O_2 through rain or snow falls, the occurrence of natural dark Fenton Processes could be expected. The presence of H_2O_2 in rainwater samples at different locations around the world has been studied. The H_2O_2 levels reported for locations with environmental conditions similar to those in LC range from 20 to 50 μM

(Gonçalves et al. 2010; Hanson et al. 2001; Olszyna et al. 1988; Qin et al. 2013).

In this context, we have focused on dark processes which properly describe the potential occurrence of Reactions 1 and 2, since this would imply a natural “ability” of LC to efficiently degrade pollutants. The results obtained allow us to ascertain whether or not these processes are feasible in the natural environment, and provide us with a starting point for further study of other potential pathways involved, such as photochemical processes. Hence, the “in situ” formation of H_2O_2 through photochemical processes is out of the scope of the present work. On the other hand, it is important to mention that, given LC chemical composition [i.e., $[NO_3^-] = 2.5 \mu M$ and $[NO_2^-] = 8.2 \mu M$], the contribution of dark reactions driven by the presence of inorganic nitrogen species such as NO_2^- to H_2O_2 consumption may be neglected (Carlos et al. 2010).

Figure 1 shows the phenol concentrations recorded, before and 48 h after H_2O_2 addition, for both reaction matrices at two different oxidant concentrations. The experimental conditions were (a) LC: $[Fe^{2+}] \sim 34 \mu M$, $[Fe^{3+}] \sim 300 \mu M$, $[Phenol] = 1.56 \text{ mM}$, $pH = 2.97$, temperature = $19^\circ C$, and $[DOM] = 1.5 \text{ mg/L}$ and (b) Artificial Matrix: $[Fe^{2+}] = 34 \mu M$, $[Fe^{3+}] = 300 \mu M$, $[Phenol] = 1.54 \text{ mM}$, $pH = 3.05$, temperature = $19^\circ C$, and absence of DOM. Results provide evidence that phenol degradation may occur in both aqueous matrices. Given the relative excess of total iron with respect to H_2O_2 (i.e., Fe/H_2O_2 molar ratios of about 17 and 7), phenol oxidation is expected to be limited by the dose of H_2O_2 .

Statistical analysis showed that decreases in phenol concentrations are significant in all cases ($p < 0.05$) and that, for each H_2O_2 concentration used, phenol conversion degree was lower for the natural water matrix than for the artificial solution ($p < 0.05$). The latter results can be explained by considering that some LC matrix components may have a detrimental effect on the availability of iron species towards

peroxide attack and that the presence of organic matter in LC matrix may exert some scavenging effect on the produced reactive species.

Despite further investigation regarding H_2O_2 presence, concentration, and seasonal fluctuation due to precipitations in LC area would certainly be needed to propose a comprehensive description of the system as a natural reactor; the results presented in this section clearly show the feasibility of natural Fenton processes in LC.

Kinetic characterization of Lake Caviahue as Fenton reactor

Given that the results presented in Fig. 1 show the feasibility of dark Fenton processes under LC environmental conditions, the next stage of our research was focused on assessing the potential use of the natural water matrix as iron source for technological applications. To this end, kinetic experiments were performed using phenol as model substrate using LC and an artificial matrix with the same pH and iron ion concentrations. The temporal evolution of phenol concentrations recorded is depicted in Fig. 2. The experimental conditions were LC Matrix: $[Fe^{2+}] \sim 29 \mu M$, $[Fe^{3+}] \sim 285 \mu M$, $[H_2O_2] = 7 \text{ mM}$, $[Phenol] = 5 \text{ mM}$, $pH = 2.40$, temperature = $21^\circ C$ and $[DOM] = 1.5 \text{ mg/L}$. Artificial Matrix: $[Fe^{2+}] \sim 35 \mu M$, $[Fe^{3+}] \sim 320 \mu M$, $[Phenol] = 5 \text{ mM}$, $pH = 2.68$, temperature = $19^\circ C$ and absence of DOM. Experimental data are represented as circles and triangles solid lines were drawn by fitting the experimental data to an empirical equation capable of describing the decay profiles with inverted S-shape usually found in Fenton-like systems (Nichela et al. 2010).

The results show that, upon addition of H_2O_2 concentrations in the range used for technological applications, phenol concentration substantially decreases, conversion degrees being at least 70% within the first 30 min for both

Fig. 1 Average phenol degradation (\pm SD) at two H_2O_2 concentrations in both reaction matrices. Black bars stand for mean initial concentrations and grey bars stand for mean final concentrations

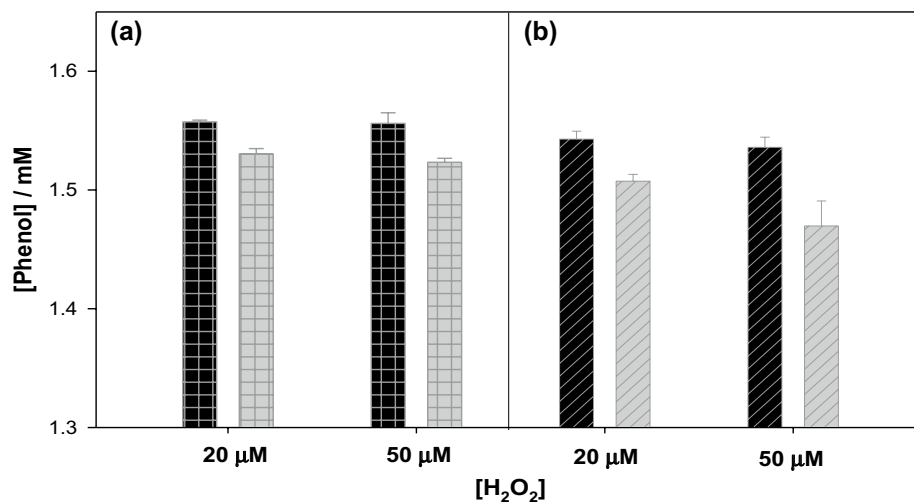
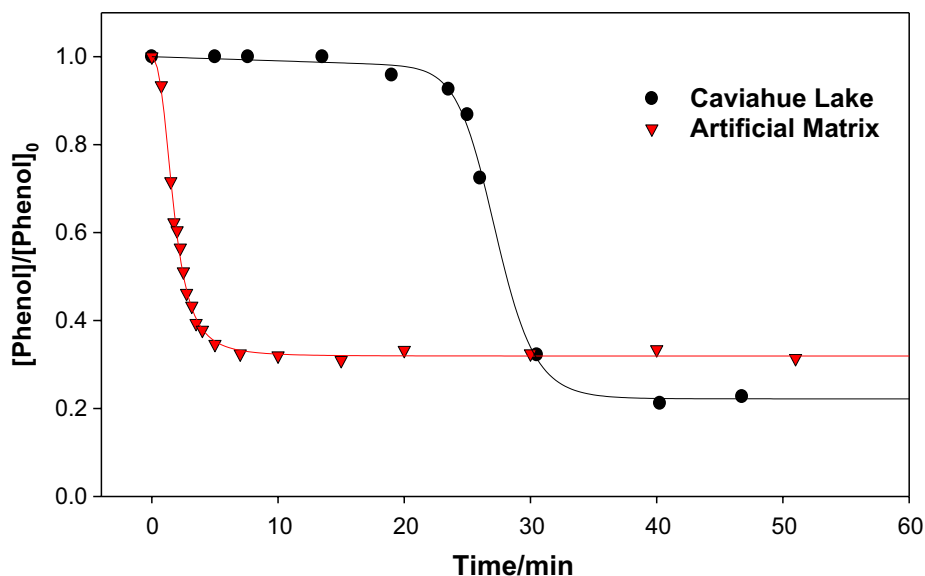


Fig. 2 Normalized concentration profiles obtained during phenol degradation using different water matrices under similar conditions



aqueous matrices. A careful inspection of Fig. 2 shows that, despite the rapid entry into the fast phase recorded for the artificial matrix, both profiles may be considered as Fenton-like systems. Actually, the decay obtained for the artificial matrix may be accurately fitted by an empirical equation that describes Fenton-like S-shaped profiles frequently observed in Fenton-like systems (Nichela et al. 2010). The acceleration in the degradation can be explained considering the increase of Fe^{2+} production associated with intermediate organic compounds (produced from phenol oxidation) capable of reducing Fe^{3+} (Carta and Desogus 2013). In both matrices, phenol is expected to yield dihydroxylated compounds, among which hydroquinone and catechol like are efficient Fe^{3+} reducers (Du et al. 2006).

However, the trends in Fig. 2 are quite different, since for LC, the lag phase (of about 23 min) is much longer than that for the artificial matrix (of about 1 min). The latter difference suggests a much slower reduction of the Fe^{3+} species present in the lake matrix. At this point, it is worth mentioning that the lake matrix is composed of metals, ions (Pedrozo et al. 2001), and dissolved organic matter (DOM) (Cabrera 2016). In natural environments, the presence of organic matter can affect the production and the fate of $\bullet\text{OH}$ radicals (Ohashi et al. 2007; Wang et al. 2017). DOM influence may be ascribed mainly to two different mechanisms: (1) the chelation of ferric species (Nichela et al. 2015) and (2) the scavenging of $\bullet\text{OH}$ radicals which otherwise would attack the target pollutants (Wols and Hofman-Caris 2012).

It is worth noting that the fraction of $\bullet\text{OH}$ that reacts with LC organic matter may be estimated by taking into account the concentrations of both phenol and DOM as well as the reported rate constants for these substrates against $\bullet\text{OH}$ radicals (Bach et al. 2010; Georgi et al. 2007)). A simple calculation shows that the latter fraction is negligible. Moreover,

this result is supported by the fact that the degree of phenol conversion in both matrices is comparable. Hence, the foremost role of DOM in LC matrix is to chelate Fe^{3+} , thus increasing its stability and decreasing its reactivity towards H_2O_2 and reducing intermediates formed in situ. These results are in line with those reported for Fe^{3+} complexes of several ligands bearing carboxylic groups (Nichela et al. 2015; Ohashi et al. 2007; Rahmawati et al. 2005).

Overall, the kinetic results suggest that the main difference between the artificial and the natural matrices is associated with Fe^{3+} availability. In contrast with the artificial matrix, Fe^{3+} is much less available for reduction in the natural water matrix, since its complexation by NOM (Cabrera 2016) increases the stability of ferric oxidation state. Hence, the strong matrix effect exerted by NOM is mainly due to its high complexing ability that suppresses Fe^{3+} reduction. Therefore, for the LC system, although reducing intermediates may be produced, the reduction efficiency for ferric-DOM complexes is expected to be much lower than that observed for the Fe^{3+} aqua complex, thus leading to a much longer lag phase for the natural system (Fig. 2). It is worth mentioning that, although phenol oxidation is retarded in the natural matrix, it is not blocked. Despite different timescales, the pollutant degradation is achieved in both matrices.

Conclusion

In this work, we have studied the behavior of an acidic Lake as a natural Fenton reactor under natural conditions and upon the addition of H_2O_2 concentrations typically used for technological applications. In both cases, the influence of DOM in phenol degradation was evaluated by comparing

results with experiments performed under identical initial conditions, but in the absence of organic matter.

A first set of experiments, carried out with concentrations of H₂O₂ reported for rainwater, clearly showed the feasibility of natural Fenton processes in LC. Noteworthy, for each H₂O₂ concentration tested, phenol conversion degrees for the natural water matrix were lower than those for the artificial solution. Results suggest that some components of the LC matrix exert a detrimental effect on the availability of iron species towards reaction.

A second set of experiments was designed to characterize the lake behavior as a natural Fenton reactor upon addition of H₂O₂ concentrations typically used for technological applications. Although profiles obtained in both matrices show autocatalytic profiles, for the experiment carried out in LC water, the lag phase was much longer than that observed for the artificial matrix. The kinetic results suggest that the main difference between the artificial and the natural matrices is associated with Fe³⁺ availability. Hence, the high complexing ability of NOM present in the LC matrix increases the stability of ferric oxidation state, thus suppressing Fe³⁺ reduction and leading to a much longer lag phase for the natural system.

Overall, the results obtained show that LC is a suitable environment for the occurrence of Fenton-like processes. Despite the retardation effect exerted by the DOM present in the lake matrix, the oxidation is not blocked, but it occurs in a different time scale. Moreover, since the model compound achieves comparable conversion degrees in both matrices, LC gains interest for the development of pollutant degradation techniques profiting from their particular composition. Broadly, this work poses acidic lakes worldwide as interesting environments from an environmental technical viewpoint.

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