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Natural iron ligands promote a metal-based oxidation mechanism for the Fenton reaction in water environments

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Natural Iron Ligands Promote a Metal-Based Oxidation Mechanism for the Fenton Reaction in Water Environments

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Abstract

The Fenton reaction is an effective advanced oxidation process occurring in nature and applied in engineering processes toward the degradation of harmful substances, including contaminants of emerging concern. The traditional Fenton application can be remarkably improved by using iron complexes with organic ligands, which allow for the degradation of contaminants at near-neutral pH and for the reduction of sludge production. This work discusses the mechanisms involved both in the classic Fenton process and in the presence of ligands that coordinate iron. Cyclohexane was selected as mechanistic probe, by following the formation of the relevant products, namely, cyclohexanol (A) and cyclohexanone (K). As expected, the classic Fenton process was associated with an A/K ratio of approximately 1, evidence of a dominant free radical behavior. Significantly, the presence of widely common natural and synthetic carboxyl ligands selectively produced mostly the alcoholic species in the first oxidation step. A ferryl-based mechanism was thus preferred when iron complexes were formed. Common iron ligands are here proven to direct the reaction pathway towards a selective metal-based catalysis. Such a system may be more easily engineered than a free radical-based one to safely remove hazardous contaminants from water and minimize the production of harmful intermediates.

Highlights

- Systematic work investigating the Fenton mechanism in the presence of ligands

- The presence of ligands promotes metal-based catalysis

- The oxidation mechanism depends on the concentration of the iron ligand

- Different Fenton mechanisms occur by varying the pH

- A ferryl species is reasonably involved in the oxidation pathway with ligands

1. INTRODUCTION

The Fenton reaction has been known since over a century (Fenton 1894; Giannakis 2019) and represents an effective advanced oxidation process to remove many recalcitrant pollutants (Barbeni et al. 1987; Lipczynskakochany 1991; Maillard et al. 1992; Zhang et al. 2006; Liu et al. 2018; Ricceri et al. 2019). Nevertheless, this process has some major drawbacks when applied to contaminated waters, including the need to operate under acidic conditions, the formation of slurries of precipitated iron in the final basification step, and the competition of pollutants with other aqueous species, e.g., carbonate and dissolved organic matter, in the reaction with non-selective free radicals (Pignatello et al. 1999; Vione et al. 2014). A possible solution to tackle these limitations is the use of iron ligands, in analogy with the biological oxidations catalyzed by iron complexes, e.g., Cytochrome P450 (Cyt P450) or Taurine Dioxygenase (TauD) (Hohenberger et al. 2012). The use of similar iron(II) complexes as engineered catalysts is a promising variation of the traditional Fenton process, because it permits the degradation of persistent contaminants at near-neutral pH, while reducing the sludge production by keeping iron in solution (dos Santos et al. 2011; Song et al. 2015; Giannakis et al. 2016; Clarizia et al. 2017; Messele et al. 2019; Das et al. 2020; Pan et al. 2020). Moreover, the use of an iron ligand can promote a more selective oxidative action, which increases the efficiency of the treatment and allows control over by-product formation.

Such improvements in the selectivity of the reaction depend on the reaction mechanism, more specifically on the active species, but little is known regarding the reaction pathway in these systems. The reaction mechanism is widely debated both for the classic Fenton process and for the modified Fenton process involving the chelation of iron (Barbusinski 2009; Zhang and Zhou 2019). In this work, we evaluate and discuss the application of a simple method to investigate the reaction pathway when iron ligands are present in water.

74   The classic description of the traditional Fenton process is based on the first reaction of the

75   Haber-Weiss mechanism proposal (eq. 1) (Haber and Weiss 1932):

76    $Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$ (1)

77   More recent investigations also proposed a mechanism that includes the formation of a

78   transient species where iron has a formal redox state of IV (Goldstein et al. 1993; Bossmann

79   et al. 1998). The presence of other superoxidized iron species (not only $Fe^{IV}_{(aq)}$, but also

80    $Fe^{V}_{(aq)}$ and $Fe^{VI}_{(aq)}$) has been additionally proven (Wink et al. 1994). However, the reactivity,

81   role, and the stability of such species is only partially known. Essential contributions were

82   provided in the works by Bossmann et al. (1998) and Pignatello et al. (1999), who

83   highlighted the different reactivity of ferryl and hydroxyl radicals and provided evidence of

84   the concurrent presence of different reactive species. More recently, Minero and co-workers

85   corroborated that ${}^{\bullet}OH$ (60% yield) and other species (e.g., FeO^{2+}) (40% yield) are formed

86   simultaneously (Minero et al. 2013). As mentioned above, the oxidation mechanism is amply

87   debated also when the system comprises iron complexes, e.g., in the presence of iron ligands.

88   Rush and Koppenol investigated a variety of chelated iron complexes, concluding that a

89   metal-oxo species was generated in neutral solutions, while ${}^{\bullet}OH$ species dominated the

90   process in acidic solutions of non-chelated iron (Rush and Koppenol 1988). Sutton et al.

91   (1987) reached a different conclusion, proposing that free iron generates a metal-oxo species

92   as the primary oxidant while ${}^{\bullet}OH$ is dominant when chelated iron is present. A reasonable

93   rationalization of this apparent discrepancy is that metal-oxo species and ${}^{\bullet}OH$ can both be

94   generated concurrently in Fenton systems. Indeed, Yamazaki and Piette (1990) suggested that

95   more than one type of oxidizing intermediate is present, and that the stoichiometry

96    ${}^{\bullet}OH:Fe(II)$ is also a function of the nature of the prevailing iron chelators. Different chelating

97   agents for Fe(II) have been reported to promote the formation of oxoiron (ferryl) species in

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98   addition to, or instead of, $^\bullet$OH, thus accelerating (e.g., with fulvic acid (Southworth and

99   Voelker 2003), oxalate (Park et al. 1997), and EDTA (Rush and Koppenol 1986)) or

100   suppressing (e.g., with phosphates) the Fenton reaction (Iwahashi et al. 1990).

101   Because the direct experimental observation of the key intermediates involved in the

102   oxidation pathways is challenging, indirect probes were developed (Klopstra et al. 2004;

103   England et al. 2008; Oloo and Que 2013; Dong et al. 2018). Cyclohexane (Cy) was used in

104   previous studies as an advantageous tool to discriminate between the different pathways of

105   the Fenton reaction in organic solvents, by following the selective production of two

106   products, namely cyclohexanol and cyclohexanone in different ratios (Oloo and Que 2013).

107   Reactions initiated by hydroxyl radicals produce long-lived alkyl radical intermediates. These

108   intermediates may react with dissolved molecular oxygen at diffusion-controlled rates to

109   produce alkylperoxyl radicals, whose subsequent reaction is a Russell-type termination that

110   gives equimolar quantities of alcohol (A) and ketone (K) (**Scheme 1a**) (Russell 1957;

111   Meslennikov et al. 1979). Therefore, A/K ~ 1 suggests the occurrence of hydroxyl radical-

112   based reaction pathways. In contrast, an A/K ratio different than 1 is indicative of a non-free

113   radical mechanism of oxidation, i.e., the presence of metal-based oxidant species (**Scheme**

114   **1b**). However, to our knowledge, Cy oxidation has never been used as a probe to clarify in a

115   systematic way the mechanism of the Fenton reactions in water.
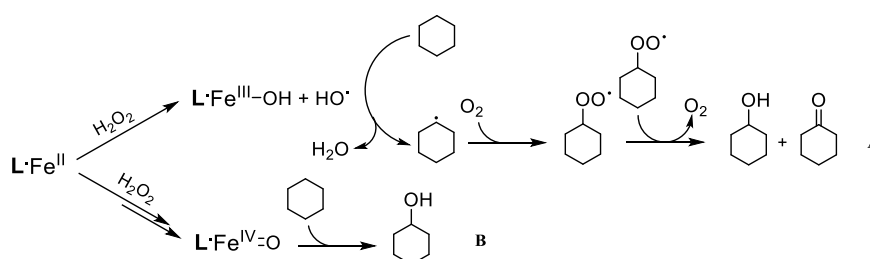
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117   **Scheme 1.** Proposed mechanism for cyclohexane oxidation. **A**: free radical path with Russel

118   termination type. **B**: a metal-based path.

119   By using this mechanistic tool based on Cy oxidation, in this work we develop a facile

120   method to provide evidence of the nature of Fenton reactive species in water in the presence

121   of several common Fe(II) ligands. Specifically, the A/K ratio is used as a selectivity proxy to

122   relate a structural parameter of the iron ligands (binding constants) with its influence on the

123   reaction. Furthermore, we demonstrate the possibility to control the reaction pathway by

124   adjusting the ligand concentration and other environmental conditions. One of the hypotheses

125   of this work is that numerous iron ligands can promote a metal-based reaction process. As

126   such, eight ligands are tested, namely, citric acid, tartaric acid, malic acid, quinic acid,

127   EDTA, EDDS, and NTA, as well as Fe-TAML[®] (see Figure S1 in the Supplementary

128   Material for its molecular structure). The first seven ligands are well-known iron chelators,

129   applied to perform oxidation reactions in water at near-neutral pH. Fe-TAML[®] and the classic

130   Fenton reagents (pH 3) are studied as standard controls for a metal-based and (supposed) free

131   radical process, respectively (Collins 2002; de Oliveira et al. 2007; Ghosh et al. 2008).

132   Through an active species linked to the iron-ligand complex, a metal-based mechanism can

133   modulate the path of the reaction and generate fewer and more predictable by-products.

134   Therefore, by verifying the involvement of a metal-based mechanism during a classic or

135   modified Fenton process in water, one can open the route toward a safer oxidation of

136   hazardous substances, e.g., phenols, pharmaceuticals, and pesticides.

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2. EXPERIMENTAL

2.1 Chemicals

140   Fe(III)-TAML[®] was purchased from GreenOx Catalysts Inc. (Pittsburgh, PA, U.S.A.).

141   Sodium phosphate tribasic was obtained from Carlo Erba (Italy). All the other reagents,

142   buffer solutions, and solvents were purchased from Sigma-Aldrich. Water was of Milli-Q

143   quality (TOC 2 ppb, resistivity $\geq$18.2 MΩ cm).

2.2 Reaction conditions

145   The reaction experiments were carried out at room temperature in a 20 mL solution for 10

146   min under continuous stirring, and were performed within 40 mL vials equipped by caps

147   provided with septum. The concentrations of the catalyst (computed in terms of iron

148   concentration), reagent (hydrogen peroxide), and substrate (cyclohexane) were 10^{-7}, 10^{-6},

149   and 10^{-4} mol/L, respectively, resulting in a relative ratio of 1:10:1000. While a 1:10

150   catalyst:oxidant ratio is typical of engineered applications, an excess of substrate was used

151   here to avoid the subsequent oxidation of one of the major by-products, namely,

152   cyclohexanol. Phosphate buffer (10 mM) or perchloric acid were used to fix the pH. Because

153   the value of the solubility constant of phosphate with iron is approximately 10^{-16}, significant

154   formation of iron phosphate can be ruled out in favor of the formation of iron-ligand

155   complexes. All the reactions were quenched by using *tert*-butyl alcohol (t-BuOH) as

156   scavenger of reactive species (excess concentration of 30 mM, thus 300:1 compared to

157   cyclohexane) for subsequent analysis (Rahhal and Richter 1988; Farinelli et al. 2019). The

158   iron-ligand complexes were prepared in equimolar ratio in a concentrated stock solution (0.01

159   mM) by stirring the mixture of the iron and ligand for 5 min, and were then diluted to 0.1

160   µM.

2.3 Analytical conditions

162   The headspace, solid phase microextraction technique (HS-SPME) was chosen as extraction

163   method before carrying out GC-MS analysis. This technique does not require solvents and

164   allows for highly sensitive analyses. Following each reaction experiment, the vials were left

165   in a thermostatic bath at 50 °C for 10 min to promote the transfer of all the relevant

166 compounds into the gas-phase headspace. Then, a SPME fiber (df 75 μm, fiber assembly

167 carboxen/polydimethylsiloxane) was injected through the septum of the cap and was left in

168 the headspace for 10 min, before withdrawing it for the subsequent GC-MS analysis. Samples

169 were analyzed on an Agilent 6890 GC system coupled with an Agilent 5973N mass selective

170 detector (MSD). For the chromatographic separation, a Zebron-5MS capillary column (30

171 m $\cdot \times$ 250 mm $\cdot \times$ 0.25 μm) was used. The injection port temperature was 280 °C, and the oven

172 temperature program was set as follows: 40°C for 5 min, then an increase to 310°C at a rate

173 of 15 °C/min (total run time 28.00 min). Helium was used as carrier gas at a constant flow of

174 1.2 mL/min, and the injector was held in splitless mode. The interface temperature was

175 280°C, the ionization energy was 70 eV, and the mass spectrometer operated in SIM mode

176 acquiring the following fragments: 84, 56, 41 (cyclohexane); 82, 67, 57 (cyclohexanol); 98,

177 55, 42 (cyclohexanone). Duplicate experiments for some of the tests discussed in this study

178 indicated high repeatability of the results; the error associated to the data and presented below

179 is related to the intrinsic uncertainty of the SPME technique, computed as the average among

180 the standard deviations reported in the 525.2 method provided by the EPA.

181 A few control experiments were carried out to study the Fenton degradation of phenol (by

182 both Fe^{2+} + H_2O_2 and Fe^{III}-TAML® + H_2O_2) using t-BuOH as scavenger, to take advantage of

183 the ability of this compound to react with $^\bullet$OH faster than with electron-capture oxidants,

184 such as ferryl (Buxton et al. 1988; Rahhal and Richter 1988). The time evolution of phenol

185 was monitored by liquid chromatography (see the Supplementary Material for additional

186 details).

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3. RESULTS AND DISCUSSION

3.1 Iron ligands promote the preferential formation of cyclohexanol

Eight widely available ligands able to complex iron in a stable fashion were tested, namely: citric acid, tartaric acid, malic acid, quinic acid, EDTA (ethylenediaminetetraacetic acid), EDDS (ethylenediamine-N,N'-disuccinic acid), NTA (nitrilotriacetate), and TAML (tetraamidomacrocyclic ligand). These ligands belong to two macro-categories: natural (citric, tartaric, malic, quinic acid) and artificial ligands (EDTA, EDDS, NTA, TAML). This choice was provisionally made to gain insight into any possible correlation between the two categories, or among ligands in the same category. The Fe-TAML® system is well-known to induce a metal-based oxidation process via a ferryl species, thus we expected an alcohol/ketone (A/K) product ratio different from 1 upon oxidation of cyclohexane (Collins 2002; de Oliveira et al. 2007). Conversely, the Fenton process at pH 3 generates mostly hydroxyl radicals, or at least the hydroxyl radical is the most reactive (although not the only one) species in the system. Therefore, the reaction should proceed mostly via a free radical mechanism, with an A/K ratio around 1 (Minero et al. 2013).

Figure 1 shows the A/K ratio values obtained with all the investigated ligands and in the absence of ligands, i.e., classic Fenton. The results obtained from oxidation tests are in line with expectations, thus attesting to the validity of the method. The classic Fenton process at pH 3 showed an A/K ratio around 1, while an A/K ratio significantly higher than 1 was obtained with all the other investigated ligands. Therefore, it is reasonable to hypothesize that the presence of an iron ligand in water promotes a metal-based oxidation.
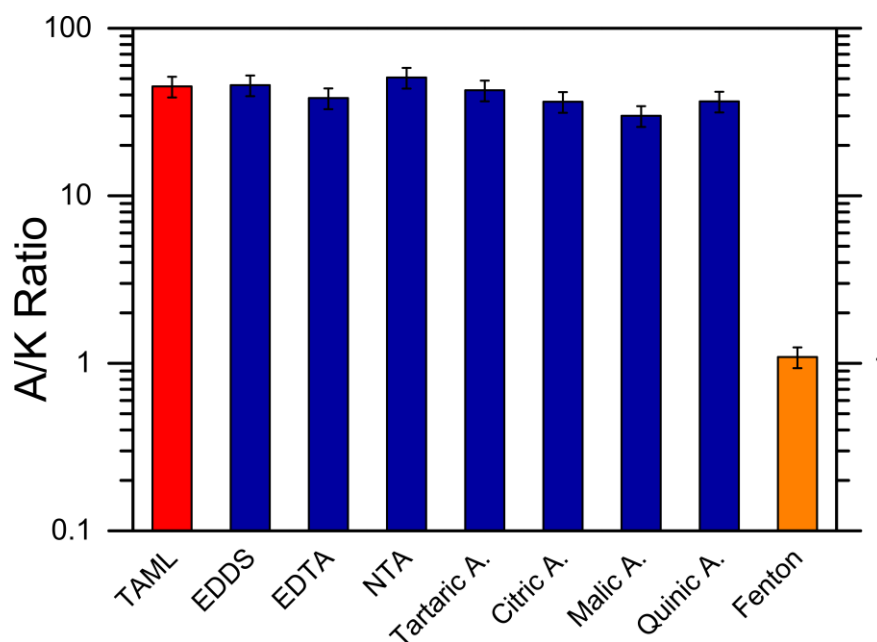
Figure 1. A/K ratio observed in the oxidation of cyclohexane with different iron ligands at pH 7 (phosphate buffer) and with the classic Fenton process at pH 3 (perchloric acid) after 30 min of reaction.

These conclusions are confirmed by the results of the degradation of phenol, with Fe^{2+} + H_2O_2 at pH 3 and with Fe-TAML$^®$ + H_2O_2 (see Figure S2 in Supplementary Material, as well as the related text). We carried out these experiments both in the absence and in the presence of t-BuOH, which reacts with $^•$OH faster than with ferryl (Buxton et al. 1988; Rahhal and Richter 1988). However, to avoid total quenching of the system by t-BuOH, the t-BuOH:phenol ratio was 40:1 and not 300:1 as per the Cy experiments. In the case of Fe^{2+} + H_2O_2, t-BuOH strongly inhibited phenol degradation, while in the case of Fe-TAML$^®$ the effect of the alcohol was practically negligible. These findings are consistent with $^•$OH being involved in phenol degradation by Fe^{2+} + H_2O_2 at pH 3, and with ferryl playing the same role with Fe-TAML$^®$ + H_2O_2. Indeed, the t-BuOH scavenging experiments agree with the A/K ratios derived from the Cy degradation experiments (**Figure 1**).

229   It is important to check for possible variations of the A/K ratio with reaction time, to ensure

230   that unbiased conclusions are obtained. **Figure 2** shows the kinetics of Cy degradation with

231   citric acid (**Figure 2a**), malic acid (**Figure 2b**), and quinic acid (**Figure 2c**) as iron ligands

232   (left Y-axis: A/K ratio, right Y-axis: Cy degradation). Cy degradation with citric and quinic

233   acids was very fast and the process reached completion after roughly 2 min of reaction. The

234   corresponding A/K ratio remained stable and significantly larger than 1 during the entire

235   duration of the test (30 min). On the other hand, **Figure 2b** (malic acid) shows slower

236   kinetics of degradation, with an A/K ratio reaching a peak value after 10 min of reaction. This

237   slower degradation allowed for an easier monitoring of the initial preferred formation of the

238   alcohol species (A/K > 1) and the subsequent oxidation of the alcohol into the ketone, which

239   caused a slight A/K reduction following the peak. The large excess of the initial Cy

240   consumed almost all the reactive species, thereby limiting their availability for alcohol

241   oxidation. By monitoring the A/K time evolution, one can thus be confident that there is

242   negligible bias linked to the further evolution of the system (A $\rightarrow$ K oxidation, or further

243   Fenton processes involving, e.g., Fe(III) after total Fe(II) consumption) after the initial

244   reaction step (Russell 1957).

245   The fact that the A/K ratio did not change much after the initial step suggests that the

246   mechanistic conditions reflect those of the initial reaction between Fe(II) and H_2O_2. Under

247   our experimental conditions and based on the stoichiometry of reaction (1), this process

248   would entail total consumption of Fe(II) that would be oxidized to Fe(III), and 10%

249   degradation of H_2O_2. Afterwards, Fe(III) would be recycled to Fe(II) at the expense of the

250   remaining H_2O_2.

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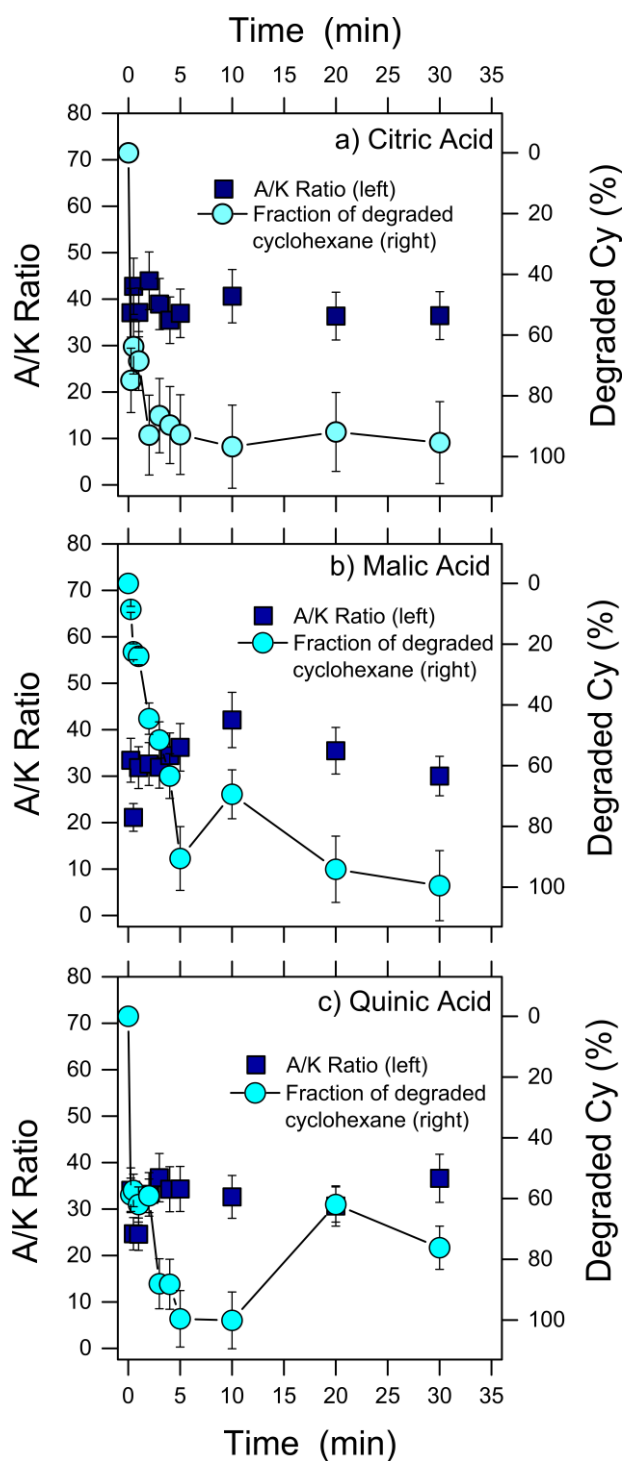
Figure 2. Fraction of degraded cyclohexane with respect to the total degraded amount

(circles, right axis) and trend of selectivity, i.e., A/K ratio (squares, left axis), as a function of

time in a system containing hydrogen peroxide as reactant and a) citric acid, b) malic acid, or

c) quinic acid as iron ligands. The pH of the aqueous system was buffered at 7 (phosphate

buffer). The solid lines connecting the circles are only intended as a guide for the eye.

The influence of the reaction environment was also studied by following the A/K ratio in the oxidation of Cy at different pH values (3-7) (**Table 1**). All the individual concentrations of alcohol and ketone products obtained during the experiments are presented in the Supplementary Material (Tables S1-S3). Citric, malic, and quinic acid were chosen as iron ligands because the iron binding constant of these compounds would not change significantly within the explored pH range, thereby allowing for the pH value to solely affect the Fenton process (Supplementary Material, Figure S3). Phosphate (10 mM) was used to buffer the pH at values of 5, 6, and 7, while perchloric acid (1.16 M stock solution) was employed in tests performed at pH 3. In all these cases, the A/K ratios were higher than 1, independently of the pH values. This finding suggests that a metal-based mechanism in the presence of the three ligands was observed regardless of the acidity of the solution. Although acidity has no direct effect on the mechanistic path, the conditional binding constant may be function of the pH and this indirect effect of the solution acidity is discussed below.

Table 1. A/K ratio for the oxidation of cyclohexane at different pH values with citric, malic and quinic acid as iron ligands. The pH was fixed with phosphate buffer except for pH 3 (HClO$_4$). The reaction time was 30 min.

	pH 3	pH 5	pH 6	pH 7
Citric acid	10±1	7.4±1.0	8.5±1.2	8.6±1.2
Malic acid	18±3	15±2	16±2	15±2
Quinic acid	28±4	31±4	23±3	28±4

**3.2 Switching the mechanism from free radical to metal-based catalysis**

In the previous section, we hypothesized that the mechanistic degradation path depends on the presence of the ligand, and possibly on its concentration and conditional binding constant. In order to investigate the influence of the ligand concentration and of its conditional binding constant with the metal (i.e., the value of the binding constant that takes into account the protonation of the ligand at the given pH value), EDTA and EDDS were chosen as iron ligands and applied at acidic pH. Despite their structural similarity, these two ligands behave differently in terms of their conditional binding constant as a function of pH. Specifically, while the conditional binding constant at pH 7 is high for both EDTA and EDDS ($\sim 10^{11}$ and 10^6, respectively), at pH 3 EDDS features a low conditional binding constant (10^{-3}), while that of EDTA is still relatively high ($\sim 10^4$) (see Supplementary Material, Figure S3). Therefore, when using EDDS as iron ligand at pH 3, one expects a high amount of free iron to occur in solution, which could reasonably induce a classic Fenton process (free radical mechanism). In this series of experiments, the pH value was fixed at a value of 3 by addition of perchloric acid.

Figure 3 reports the A/K ratios observed when EDDS and EDTA were used as ligands at pH 3, at various [Ligand]:[Fe(II)] ratios. All the individual concentrations of alcohol and ketone products obtained during the experiments are presented in the Supplementary Material (Tables S4-S5). Please note that **Figure 1** summarized instead the A/K ratios measured at 1:1 [Ligand]:[Fe(II)] ratio and at pH 7. Consistently with the hypotheses, at 0:1 ligand:iron ratio (i.e., with no ligand in solution) we observed the classic Fenton process and the A/K ratio was close to 1. The A/K ratio remained always close to 1 with EDDS, regardless of its concentration. Based on the conditional binding constants, when using EDDS as iron ligand at pH 3, one expects free iron to occur in solution, which could reasonably promote a process similar to a classic $^{\bullet}$OH-based Fenton reaction. In contrast, with EDTA the reaction clearly

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switched from a free radical mechanism to a metal-based one when the ligand concentration

increased (Bernasconi and Baerends 2009; Mang et al. 2016). These results strongly suggest

that the presence of a bonded Fe(II)-ligand complex plays a crucial role in the direction of the

mechanistic path. This parameter is a strong function of the concentration of the ligand as

well as of the conditional binding constant of the complex metal/ligand. Therefore, one can

generalize that the mechanistic path may be mostly imputable to the concentration and to the

conditional binding constant of the ligand, and that the environmental conditions have

importance only if they affect complex formation.
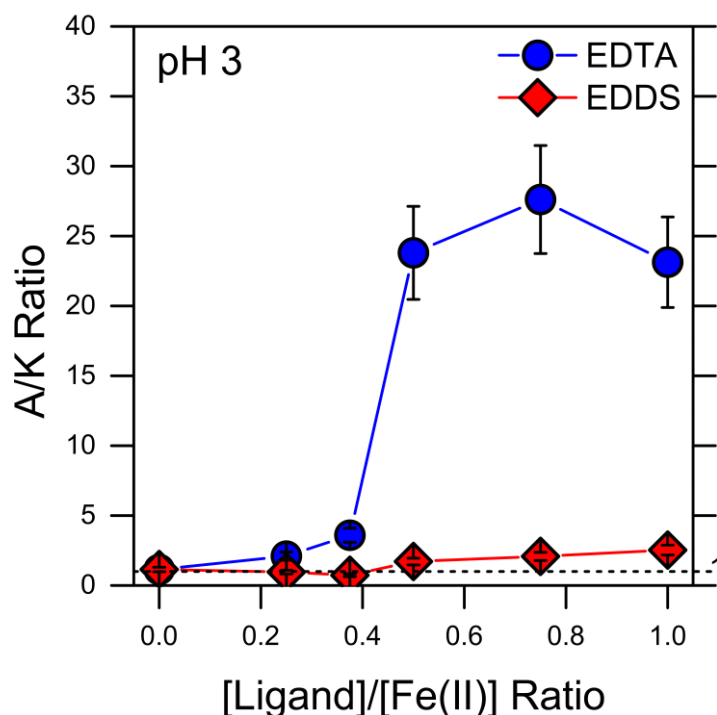
**Figure 3.** A/K ratio observed after 30 min of reaction in the oxidation of cyclohexane with

EDTA and EDDS as iron ligands, added at different concentrations. The runs were carried

out at pH 3. The condition of no added Ligand ([Ligand]/[Fe(II)] = 0) corresponds to the

classic Fenton process. The solid lines are only intended as a guide for the eye. The dashed

line depicts the expected A/K ratio for a pure free radicals-based catalysis.

3.3 Evidence of the effect of pH on the traditional Fenton process

Finally, we provide some insight into the Fenton mechanism at different pH values. **Figure 4** shows the A/K ratio obtained with the classic Fenton process in the 3-7 pH range, fixed by use of phosphate buffer (PBS). Additional experiments were also conducted by fixing the pH at 3 and 4 using perchloric acid instead of phosphate buffer. Please note that Fe(II) was dosed at low concentration (0.1 μM) to avoid its precipitation as hydroxide, which would otherwise take place at near-neutral pH ($pKs^{Fe(OH)_2}$ = 15.1 (Harris 2006)). The results obtained in the absence of ligands imply that the classic Fenton reaction proceeds through a free radical or mixed mechanism up to pH 5. Above this value, the mechanism switched to a preferential metal-based one. This result is supported by previous reports proposing that a ferryl species is involved in the Fenton reaction at near-neutral pH (Rush et al. 1990; Bossmann et al. 2004; Bataineh et al. 2012). The presence of a ferryl species at pH 6-7 means that the classic Fenton reaction will be less reactive under near-neutral conditions, since the non-coordinated ferryl species is considered less reactive than the hydroxyl radical (Bataineh et al. 2012).
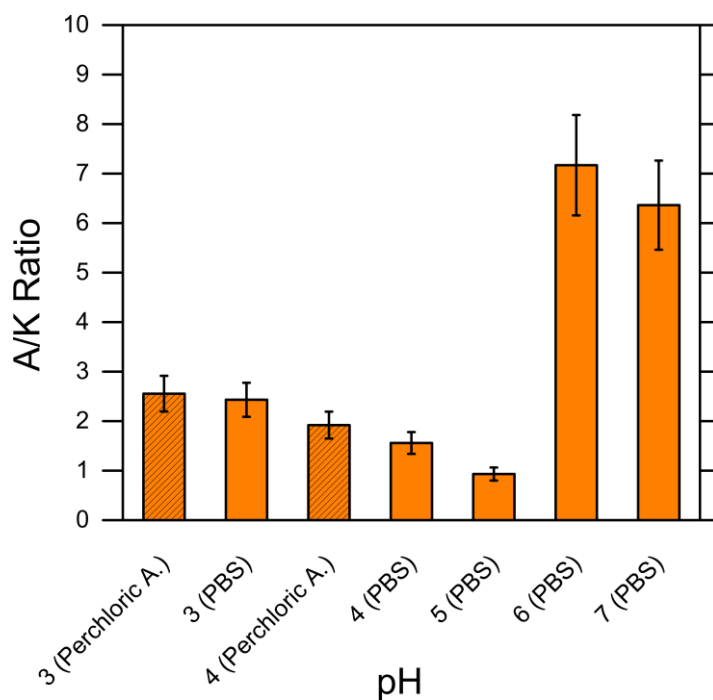
Figure 4 A/K ratio observed in the classic Fenton process performed at different pH values.

4. CONCLUSIONS

The oxidation mechanism of the Fenton reaction was here investigated with and without iron ligands in solution. Eight widely common ligands that are able to complex iron(II) were studied, namely, citric acid, tartaric acid, malic acid, quinic acid, EDTA, EDDS, and NTA, plus the Fe-TAML® system. The ligand performance was tested toward the oxidation of cyclohexane by following the formation of the main products, namely, cyclohexanol (A) and cyclohexanone (K). Measurement of the concentration ratio between these two species (A/K ratio parameter) during the reaction provides evidence of the mechanism involved in the oxidation of the substrate. This simple method was proven effective to discriminate in water between the predominance of a non-selective active species, free radicals, or of a more selective ferryl species.

All the tested ligands showed high A/K ratios, which is a proper index of a metal-based behavior, including the well-known Fe-TAML® system that was expected to behave in this fashion. Also expected was the fact that the classic Fenton process was associated with an A/K ratio of approximately 1, evidence of a free radical process, which adds further evidence in favor of cyclohexane as suitable probe when coupled with the A/K ratio. The results suggested that the ligand/iron concentration ratio plays a role in the mechanism of reaction and this parameter may be thus exploited to control the pathways of contaminant degradation in water. Also, if the ligand-specific binding constant changes with environmental conditions, e.g., the pH, the reaction mechanism may be controlled by adjusting such conditions.

This work proves the ability of simple iron ligands to drive the reaction pathway towards selective metal-based catalysis. Selective catalysis allows for better control of the degradation pathway of harmful contaminants, to avoid the formation of toxic by-products. The ubiquitous character of the Fenton process in nature and of iron complexes formed in water

360 (e.g., citrate), alongside the generation of H_2O_2 in illuminated NOM-containing

361 environments, lead to (photo)Fenton reactions during the diurnal cycles. As such, the present

362 study holds important implications in the elucidation of the Fenton process that occurs both in

363 nature and in engineering applications, and represents a step further in understanding the

364 effectiveness of ligand-mediated oxidation of natural and anthropogenic contaminants.

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ASSOCIATED CONTENT

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367 **Supporting Information.** The Supporting Information is available free of charge on the ACS

368 Publications website

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373 **Notes**

374 The authors declare no competing financial interest.

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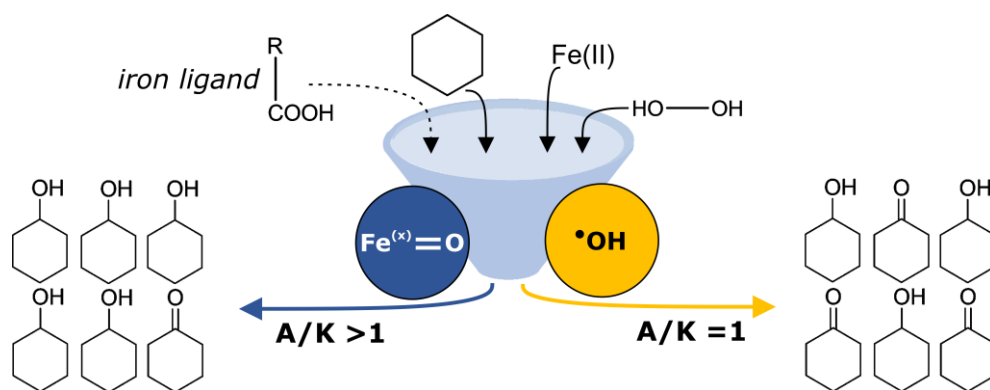524 https://doi.org/10.1016/0003-9861(87)90603-5

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543 **Graphical Abstract**

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