




Article

# Enhanced Degradation of Phenol by a Fenton-Like System (Fe/EDTA/H<sub>2</sub>O<sub>2</sub>) at Circumneutral pH

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**Abstract:** This work deals with the degradation of phenol based on the classical Fenton process, which is enhanced by the presence of chelating agents. Several iron-chelating agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA), and ethylenediamine-*N,N'*-diacetic acid (EDDA) were explored, although particular attention was given to EDTA. The effect of the molar ligand to iron ratio, EDTA:Fe, initial pH, and temperature on the oxidation process was studied. The results demonstrate that the proposed alternative approach allows the capacity for degrading phenol to be extended from the usual acidic pH (around 3.0) to circumneutral pH range (6.5–7.5). The overall feasibility of the process depends on the concentration of the chelating agent and the initial pH of the solution. The maximum phenol conversion, over 95%, is achieved using a 0.3 to 1 molar ratio of EDTA:Fe, stoichiometric ratio of H<sub>2</sub>O<sub>2</sub> at an initial pH of 7.0, and a temperature of 30 °C after 2 hours of reaction, whereas only 10% of phenol conversion is obtained without EDTA. However, in excess of ligand (EDTA:Fe > 1), the generation of radicals seems to be strongly suppressed. Improvement of the phenol removal efficiency at neutral pH also occurs for the other chelating agents tested.

**Keywords:** phenol degradation; EDTA; circumneutral pH; Fenton system; ligands

## 1. Introduction

The treatment of wastewater has increasingly become a challenge for a number of industries. In many cases, biological treatment is sufficient and the most economical solution for this problem. Nevertheless, many industrial and some urban effluents contain refractory and/or biotoxic compounds, which need a specific chemical treatment in order to eliminate or partly reduce the concentration of contaminants to the required level allowing for direct discharge to conventional sewage plants [1,2]. Phenols are the major organic constituents found in effluents of petroleum refineries, phenolic resin manufacturing, herbicide manufacturing, and petrochemicals [3,4]. Phenol and its derivatives are a major source of environmental pollutants.

Most of the applied technologies to treat refractory compounds are based on expensive chemical oxidation, either because of the drastic operating conditions in catalytic wet air oxidation (CWAO), costly equipment (H<sub>2</sub>O<sub>2</sub>/UV), or dedicated oxidants (O<sub>3</sub>) [5]. In this regard, the well-known Fenton reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) has shown interesting results and some significant advantages: (i) iron is a widely available and a non-toxic element, (ii) H<sub>2</sub>O<sub>2</sub> is easy to handle and its decomposition leads to harmless

products [6], and (iii) the process can be applied at room conditions and with simple equipment [7–9]. However, its application to the treatment of real wastewater has so far been limited mainly due to the requirements of chemicals to acidify the wastewater, which results in major operational costs [10,11]. Classical Fenton-based process is restricted to an acidic pH range, the optimum pH being 3.0, due to the inability of the homogeneous iron catalyst to remain in solution at a pH beyond 4.0. This means that, as the pH increases from strongly acidic to neutral, the application of Fenton's reagent to wastewater remediation is hampered by the formation of amorphous iron oxide precipitates [12–14]. This reduces the efficiency of reagents during the reaction and generates a high amount of chemical sludge too [15].

Many studies have been devoted to applying modifications in order to circumvent the drawbacks associated with conventional Fenton and Fenton-like processes. Among many others, use of different sources of oxyradicals, photo irradiation, ultrasound, and electrochemical methods have been tested for their intensified performance [16–19]. In this sense, addition of chelating agents in the reaction system could prevent precipitation of iron in the solution at higher pH (6.0–7.0) by forming stable chelates with iron ions and promoting its availability for hydroxyl radical generation from peroxide in a wider pH range [13].

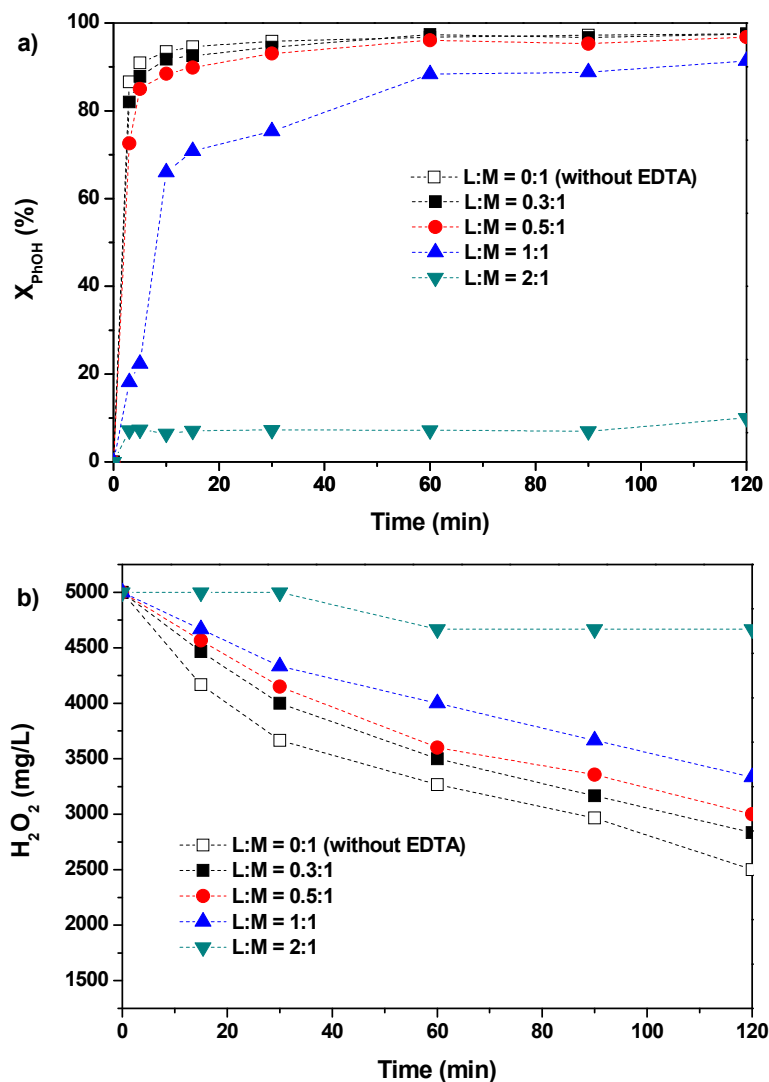
Some studies have reported a quick entire destruction of chlorophenols using hydrogen peroxide activated with iron catalysts complexed with tetraamidomacrocylic ligand (TAML). This provides an efficiency of one order of magnitude higher than the classic Fenton [20,21]. The route has also been tested for destruction of phenolic structures [22] and oxidation of the colorant Orange II [23]. Moreover, it has been demonstrated that other ligands like EDTA have been widely used to enhance the efficiency of Fenton's reaction due to their strong complexing ability with multivalent cation [24,25] and also their capability to activate the formation of hydroxyl radical when they are added in Fenton systems [26]. In addition, the capacity of the chelating ligands to activate the decomposition of the peroxides and to intensify the generation of radicals has been widely confirmed [27]. In recent studies [28], ligand enhanced Fenton reaction was successfully used for the oxidation of As(III) to As(V), but As(III) oxidation was inhibited in the presence of excess EDTA at acidic and neutral pH. Rastogi et al. [29] also reported the effect of inorganic, synthetic, and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols. Even though there are different studies that deal with how to overcome the drawbacks of the Fenton reaction, there is a lack of systematic investigation about the effect of different operational parameters and the possibilities of the addition of different ligands on the oxidation of phenol with Fenton process. Therefore, a comparison study in the oxidation of phenol under acidic and basic initial pH conditions was accomplished using different EDTA:Fe molar ratios. Furthermore, decomposition rate of  $H_2O_2$  during the reaction, effect of other iron-chelating agents, effect of iron concentration, and temperature were also investigated.

## 2. Results and Discussion

### 2.1. Effect of Ligand to Metal (L:M) Molar Ratio

The effect of EDTA:Fe molar ratio was investigated in the range from 0 to 2 in order to determine the optimum conditions for best phenol removal at initial phenol concentration of 1000 mg/L and 7 mg/L of  $Fe^{2+}$  for 2 hours at pH 3.0. The results are illustrated in Figure 1a. Similar phenol conversion (95%) was obtained for the free iron catalyst and for the  $Fe^{2+}$ -EDTA complexes in the range from 0 to 0.5 of L:M molar ratio after 2 hours of reaction. This implies that no improvement was obtained in acidic conditions due to the addition of EDTA. From the result, it is important to note that L:M molar ratios beyond 1:1 inhibited the oxidation of phenol. This fact can be related with the degradation of EDTA with  $H_2O_2$  in the presence of different catalysts [30–34]. Thus, the presence of excess EDTA does not improve the catalytic behavior; rather, it may inhibit the generation of radicals. It has been reported elsewhere that the ratio of ligand to metal is of significant importance since the generation of radicals can be reduced in the presence of excess ligand [35–37].

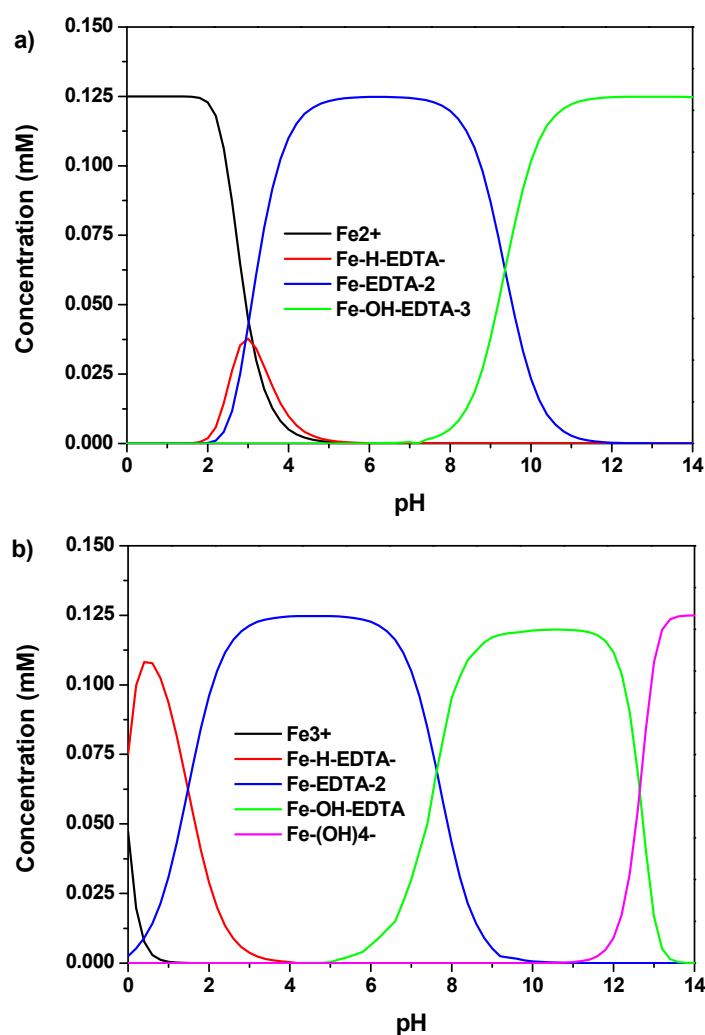
Figure 1b shows the consumption of hydrogen peroxide for different L:M molar ratio at pH 3.0 in the absence of phenol. At higher ligand concentration, hydrogen peroxide decomposition rate was negligible as the  $\text{H}_2\text{O}_2$  decomposition is inhibited with the presence of excess EDTA, as observed elsewhere [35]. Therefore, it shows the same tendency as the phenol removal efficiency, which depends on the L:M ratio.



**Figure 1.** Phenol (a) and  $\text{H}_2\text{O}_2$  (b) conversion versus time for different EDTA:Fe molar ratios. [Phenol] = 1000 mg/L,  $[\text{H}_2\text{O}_2] = 5000$  mg/L,  $[\text{Fe}^{2+}]_0 = 7$  mg/L,  $T = 30$  °C,  $[\text{pH}]_0 = 3.0$ , and  $t = 120$  min.

## 2.2. Speciation of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ in the Presence of EDTA

It is well-known that Fe and EDTA in solution form a diversity of species, whose distribution depends on the pH to a great extent. However, this speciation not only depends on the pH, but also on the complex formation kinetics [36,37] and the probability of EDTA degradation when exposed to  $\text{H}_2\text{O}_2$  [38]. The speciation diagrams of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  with EDTA as a function of pH were obtained using the thermodynamic data from the MINTQA2 [39] database and are shown in Figure 2 for an overall iron concentration range from 0 to 0.125 mM. As can be seen from Figure 2a,  $\text{Fe}^{2+}$  precipitates in the form of hydroxides at pH above 4.0. However, both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  form stable complexes in the presence of strong complex forming agents like EDTA in a wide pH range, up to pH 11 [9]. DTPA, EDDA, and NTA give similar behavior (diagrams not shown) too.



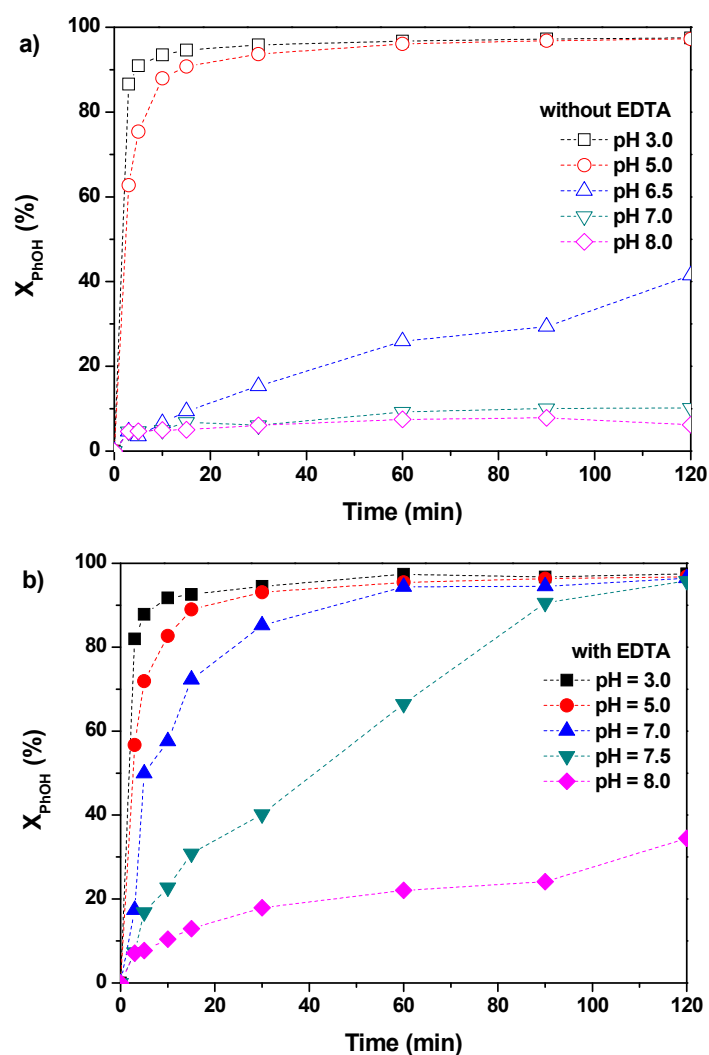
**Figure 2.** Equilibrium distribution of [Fe-EDTA] species as a function of pH for (a) Fe<sup>2+</sup> and (b) Fe<sup>3+</sup>, assuming 0.125 mM concentration of Fe and EDTA [40].

Furthermore, this distribution diagram shows that Fe<sup>3+</sup>-EDTA is the predominant species at a pH range of 2.0–7.0, whereas Fe<sup>2+</sup>-EDTA is the major species in the range of 3.0–9.0. Based on the speciation distribution in Figure 2b, pH range was divided into three regions, i.e., low pH (pH < 3.0, Region I), mid pH (3.0 < pH < 7.0, Region II), and high pH (pH > 7.0, Region III). The speciation in the low pH range contains protonated Fe<sup>2+/3+</sup>-EDTA complexes and free Fe<sup>2+</sup>, whereas the high pH range contains the hydroxyl complexes. The above experiments were conducted at pH 3.0, so there was already highly active free Fe<sup>2+</sup> and no possibility for Fe<sup>3+</sup> to form insoluble precipitate. Therefore, the presence of EDTA does not modify the conditions of the classical Fenton, hence the nil effect of the EDTA. However, at higher pH, where Fe<sup>3+</sup> precipitation in the form of hydroxide occurs, the addition of EDTA should play a relevant role. Thus, mid pH, where the Fe<sup>2+</sup>-EDTA and Fe<sup>3+</sup>-EDTA are predominant species, was chosen for the subsequent experiments.

### 2.3. Effect of Initial pH

Considering the Fe-EDTA species diagrams, different initial pHs were evaluated in order to explore the effect of pH over the Fenton process in the presence of EDTA. As can be seen in Figure 3b, only small performance changes were noted again for acidic conditions (pH 3.0 and 5.0) in the presence of EDTA (0.3:1 L:M ratio at 7 mg/L Fe<sup>2+</sup>, i.e., 0.125 mM) compared to the equivalent free Fe<sup>2+</sup> catalyst (Figure 3a), reaching a final 95% phenol conversion with both Fe<sup>2+</sup> and Fe<sup>2+</sup>-EDTA.

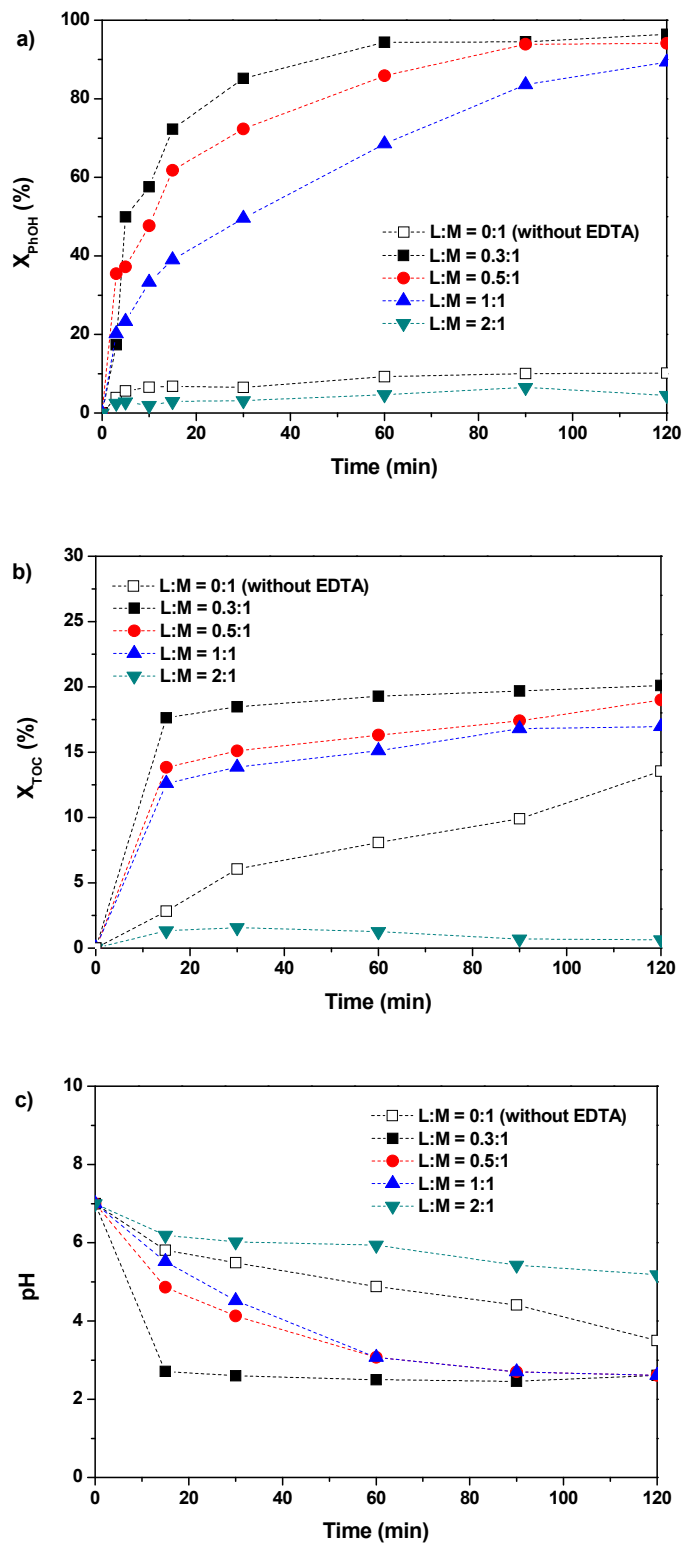
However, under circumneutral conditions (pH 6.5–7.0), the addition of EDTA brings to phenol conversion over 95% (Figure 3b). It is important to note that the conversion at circumneutral pH without EDTA only reaches 10% of phenol conversion (Figure 3a). As expected, at pH above 4–5 without EDTA, the reaction does not proceed because the iron precipitation yields inactive iron. Moreover, Figure 3a,b respectively show that at higher pH, e.g., 8.0, the conversion drops again both in the absence and in the presence of EDTA. For instance, under the same operating conditions, only 10% was achieved in the absence of EDTA and 35% in the presence of EDTA. The decrease in the reaction rates at pH 8.0 can be due to changes in the speciation of  $\text{Fe}^{3+}$  towards hydroxide complex species, which are probably not active for the generation of radicals and suppress the catalytic properties of iron. In this case, the presence of EDTA only partially prevents the formation of such less active iron species. In addition, hydrogen peroxide stability is also strongly affected by pH conditions [36]. Thus, a further increase of the pH above neutral values results in favoring the  $\text{H}_2\text{O}_2$  decomposition into water and molecular oxygen [41].



**Figure 3.** Phenol conversion versus time for different initial pH solution: (a) without EDTA (L:M = 0:1), (b) with EDTA (L:M = 0.3:1). [Phenol] = 1000 mg/L,  $[\text{H}_2\text{O}_2]$  = 5000 mg/L,  $[\text{Fe}^{2+}]_0$  = 7 mg/L,  $T$  = 30 °C, and  $t$  = 120 min.

Figure 4 shows the pH evolution, phenol, and TOC conversion against time for different L:M ratios under the same experimental conditions but at initial pH solution of 7.0. The result illustrates that the feasibility of the process mainly depends on both the chelating agent concentration used to

promote the reaction and the initial pH of the solution. This means that the presence of EDTA resulted in increased iron solubility at higher pH. Consequently, the Fenton reaction can be conducted over a broader range of pH when iron is complexed with EDTA.



**Figure 4.** Phenol conversion (a), TOC conversion (b), and pH evolution (c) versus time for different EDTA:Fe molar ratio. [Phenol] = 1000 mg/L,  $[\text{H}_2\text{O}_2]$  = 5000 mg/L,  $[\text{Fe}^{2+}]_0$  = 7 mg/L,  $T$  = 30 °C,  $[\text{pH}]_0$  = 7.0, and  $t$  = 120 min.

Figure 4a shows the degradation rate of phenol for each EDTA:Fe ratio, which follows the order 0.3:1 > 0.5:1 > 1:1. However, in excess of ligand (EDTA:Fe >1), only 10% of phenol conversion was achieved, because the presence of excess EDTA inhibited the generation of radicals, and this strongly negatively impacts the efficiency of phenol removal. Overall, the presence of EDTA highly increased the pH range where the classical Fenton system is feasible, which results in major cost savings as this eliminates the need for initial acidification.

Enhanced TOC removal was also observed during the oxidation. As can be seen in Figure 4b, the TOC reduction was 4.7%, 20.1%, 19.0%, 16.6%, and 0.6% for L:M ratio of 0:1, 0.3:1, 0.5:1, 1:1, and 2:1, respectively, after 2 hours of reaction. From the results, it can be seen that the amount of ligand also has a great effect on phenol total mineralization. Thus, the phenol and TOC conversion at initial pH of 7.0, in the absence (0:1) and excess (2:1) of EDTA is insignificant. However, the addition of small amounts of EDTA in the range of 0.3:1 to 1:1 EDTA:Fe ratio shows a significant improvement on the degradation.

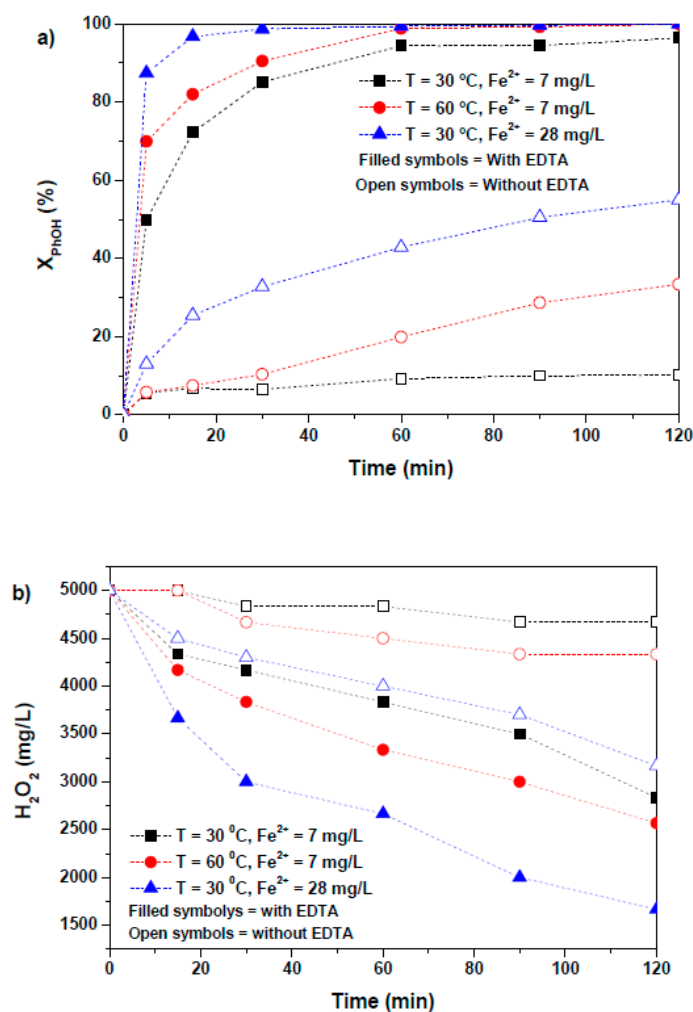
Figure 4c illustrates the pH variation of the solution during the reaction. After starting the reaction, the pH of the solution decreases dramatically in the first 15 min from original pH 7.0 to pH 5.8, 2.7, 4.9, 5.5, and 6.2 for L:M ratio of 0:1, 0.3:1, 0.5:1, 1:1, and 2:1, respectively. During the reaction, the decrease of the pH of the solution is very significant for the EDTA:Fe ratio of 0.3:1, 0.5:1, 1:1, which agrees with the formation of low molecular weight acid intermediates. For the EDTA:Fe ratio of 0.3:1, the solution pH plateaus after 30 min of reaction. In this experiment, the best results were obtained using 0.3:1 EDTA:Fe molar ratio (Figure 4), reaching over 95 % of phenol and 20.1% TOC conversion under neutral pH. Subsequently, the EDTA:Fe ratio was set at 0.3:1 in the following experiments.

#### 2.4. Effect of Temperature and Iron Concentration

The influence of two temperatures (30 °C and 60 °C) and two iron concentrations (7 mg/L and 28 mg/L) on the oxidation of phenol was studied under the optimal EDTA:Fe molar ratio previously found, i.e., 0.3:1, and without EDTA (0:1); in all cases, the initial pH of the solution was 7.0. Figure 5a clearly demonstrates that an increase in iron concentration and temperature favors phenol degradation. The phenol degradation profile obtained in the presence of EDTA at 30 °C and 7 mg/L of iron showed that, even at the lower temperature, 96% of phenol disappears after 2 hours of reaction. As expected, a higher temperature and iron concentration led to the increase of the reaction rate. At 60 °C with 7 mg/L of iron, the same conversion of 96% was found after only 60 min and the conversion was complete in just 30 min when 28 mg/L of iron was applied at 30 °C. Interestingly, without EDTA (L:M = 0:1), the results obtained for the phenol removal indicated a maximum phenol conversion of 10% and 36% for 7 mg/L of iron at 30 and 60 °C, respectively, whereas, at 30 °C and 28 mg/L of iron, the conversion was 58%. This confirms that, at neutral pH, the presence of EDTA plays a major role. Thus, the addition of EDTA at one-third of the molar stoichiometric ratio with respect to the iron is able to increase the phenol conversion from 10% to 96% at 30 °C with 7 mg/L of iron; this is almost ten times higher.

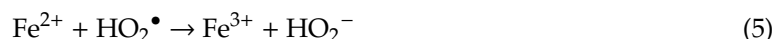
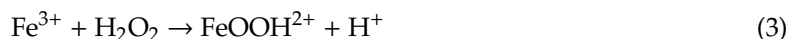
Figure 5b shows the hydrogen peroxide consumption at the two different temperatures and iron concentrations in the presence of EDTA using an EDTA:Fe molar ratio of 0.3:1 and without EDTA (0:1); in all the cases, the initial pH of the solution was again 7.0. At a higher temperature and iron concentration, the hydrogen peroxide decomposition rate also improved. Accordingly, phenol removal efficiency shows the same tendency as the peroxide decomposition rate, so small values of hydrogen peroxide conversion were encountered for the systems without EDTA at pH 7.0, even at a higher temperature and iron concentration.

This trend has already been reported in the literature for different cases. Walling [42] and Oakes and Smith [43] confirmed that while Fenton's reaction is effective in many cases, Fe<sup>2+</sup> catalyzed hydrogen peroxide decomposition rate takes feasible values only in a narrow pH range (3–4) where the activity is significant. However, it has also been reported that complexed forms of iron are active for hydrogen peroxide decomposition over a much wider pH range [44].



**Figure 5.** Effect of temperature and Fe concentration on (a) phenol and (b)  $\text{H}_2\text{O}_2$  conversion. [Phenol] = 1000 mg/L,  $[\text{H}_2\text{O}_2]_0 = 5000$  mg/L,  $[\text{pH}]_0 = 7.0$ , L:M = 0.3:1, and  $t = 120$  min.

There are several studies on the reaction between hydrogen peroxide and free or complexed iron ions in aqueous solution. Two different reaction mechanisms have been proposed. The first reaction pathway considers the generation of radicals through a classical set of reactions as proposed by Haber and Weiss [45].



In the presence of a radical scavenger, e.g., some organic compound, the radicals can attack it and this alternative pathway can compete, often favorably, with the self-decomposition of the hydrogen peroxide into water and molecular oxygen [46]. If  $\text{Fe}^{3+}$  is removed from the system,  $\text{Fe}^{2+}$  is progressively exhausted and the reaction stops, which occurs when the pH is not acidic enough for



preventing the formation of inactive, insoluble  $\text{Fe}(\text{OH})_3$ . Hence, the main role of the EDTA seems to be maintaining  $\text{Fe}^{3+}$  in solution even at neutral pH, without negative impact on the rest of steps.

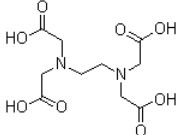
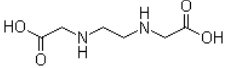
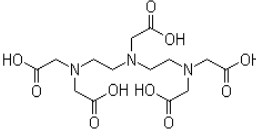
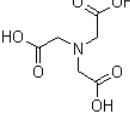
Although other researchers have alternatively suggested the intermediate generation of highly reactive ferryl ion ( $\text{Fe}^{4+}$ ) [46–48], in spite of their fundamental differences, the two schemes are surprisingly hard to distinguish. Rahhal and Ritcher [48] suggested that the pH of the system is the determining factor as to whether hydroxyl radicals or ferryl ions are generated.

Therefore, from our results, the addition of EDTA in the Fenton system indeed leads to a more efficient consumption of  $\text{H}_2\text{O}_2$ , which indicates an enhanced iron-catalyzed  $\text{H}_2\text{O}_2$  decomposition into radicals and, in accordance, an improved phenol removal rate. In conclusion, this can be considered as an intensification of the conventional Fenton process.

### 2.5. Effect of the Chelating Agent

To study the effect of the chelating agent over this oxidation process, four different chelating species were tested (EDTA, EDDA, DTPA, and NTA). These compounds were used in this study because they are commercially available, similar in structure, and represent a potentially useful class of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  chelate catalysts. Table 1 shows the structures of these compounds.

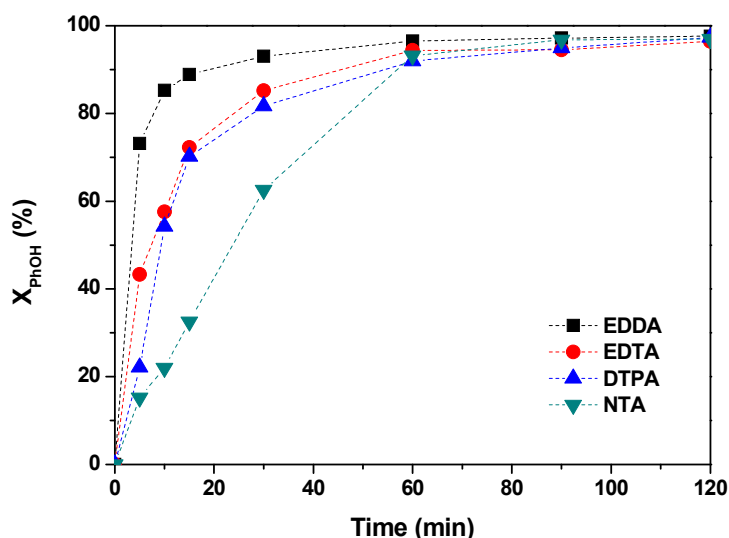
**Table 1.** Formula and structure of the different chelating agents tested.

Compound	Structure	Molecular Formula	Molecular Weight (g/mol)
Ethylenediaminetetraacetic acid (EDTA)		$\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$	292.24
Ethylenediamine- $\text{N,N}'$ -diacetic acid (EDDA)		$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$	176.17
Diethylenetriaminepenta-acetic acid (DTPA)		$\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$	393.35
Nitrilotriacetic acid (NTA)		$\text{C}_6\text{H}_9\text{NO}_6$	191.14

The tests were carried out for each chelating agent with an L:M ratio of 0.3:1 (except NTA 0.6:1, as NTA is tridentated) [13], 7 mg/L of iron concentration, an initial concentration of phenol of 1000 mg/L, a stoichiometric ratio of  $\text{H}_2\text{O}_2$ , at initial pH solution of 7.0, and a temperature of 30 °C.

As can be seen in Figure 6, the phenol degradation markedly depends on the chelating agent used for enhancing the oxidation. At 30 min of reaction, in terms of phenol conversion, the reactivity order observed was EDDA (93%) > EDTA (85%) > DTPA (81%) > NTA (63%). However, quite similar conversions (96%) were obtained for all chelating agents after 60 min of reaction. These results could be due to the fact that the stability of  $\text{Fe}^{2+}$  complex formed with each chelating agent could follow the speciation of  $\text{Fe}^{2+}$ , thus avoiding precipitation of iron at higher pH as suggested for EDTA. The pH evolution (data not shown) exhibits almost the same values, a minimum value (2.5) at approximately 120 min for all chelating agents, again suggesting the formation of organic acids. Although the identification of the partial oxidation products was not a main objective, we occasionally conducted a complete analysis of the treated samples. In such cases, the partial oxidation intermediates did not

differ from those identified in previous studies [49] conducted with powdered zero valent iron and air, which indeed included several short-chain organic acids present as later intermediates or end products.



**Figure 6.** Phenol conversion for different chelating agent. [Phenol] = 1000 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 5000 mg/L, [Fe<sup>2+</sup>]<sub>0</sub> = 7 mg/L, T = 30 °C, [pH]<sub>0</sub> = 7.0, L:M = 0.3:1, and t = 120 min.

Although the main role of the chelating agent is believed to be preventing the formation of Fe(OH)<sub>3</sub>, the complex formed must somehow modify the reaction steps where Fe<sup>3+</sup> participates, particularly in Eq. 3 where it is reduced back to Fe<sup>2+</sup>, allowing the generation of oxyradicals from the hydrogen peroxide to continue. This reaction is the slowest and often is the rate-controlling step for the overall process. Therefore, a too stable Fe(III)-chelant complex may slow down this step. From this point of view, EDDA seems to possess a structure less favorable to forming a very stable complex so the reduction of the Fe<sup>3+</sup> is facilitated, yet it is able to keep it in solution.

### 3. Materials and Methods

#### 3.1. Chemicals

Phenol (PhOH), used as model compound, was purchased from Panreac (>99% purity). Fenton reagents, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30% w/v solution), and Iron(II) sulphate heptahydrated (>98% purity) were also purchased from Panreac (Barcelona, Spain). The chelating agents used in this study were: ethylenediaminetetraacetic acid disodium salt dihydrate (98% purity) purchased from Panreac; nitrilotriacetic acid trisodium salt (98% purity) supplied by Sigma-Aldrich (St. Louis, MS, USA); diethylenetriamine pentaacetic acid (≥98% purity); and ethylenediamine diacetic acid (≥98% purity) obtained from Fluka (Seelze, Germany). Sulphuric acid (95-97% purity) and sodium hydroxide (98% purity) were also purchased from Sigma-Aldrich; these reagents were used to adjust the initial pH values. Deionized water was used to prepare all the aqueous solutions.

#### 3.2. Experimental Set-Up and Procedure

A magnetically stirred jacketed reactor was used for all oxidation reactions. The reactor has a 200 mL capacity. The reaction temperature was set and controlled by circulating deionized water from a thermostatic bath through a jacket.

The reactor was filled with 100 mL of solution containing 1000 mg/L of phenol, 7 mg/L of Fe<sup>2+</sup>, and a variable concentration of EDTA, selected to give the desired EDTA:Fe ratio (0:1, 0.3:1, 0.5:1, 1:1, and 2:1). The pH was adjusted by adding NaOH or H<sub>2</sub>SO<sub>4</sub>. Once the desired temperature was reached (30 °C), a small volume (1.7 mL) of concentrated hydrogen peroxide was added to provide the

stoichiometric amount of H<sub>2</sub>O<sub>2</sub> (5000 mg/L) and, thus, to start the reaction. All the experiments were carried out at a stirring rate of 300 rpm and for 2 hours.

During the reaction, 1 mL samples were withdrawn at 0, 3, 5, 10, 15, 30, 60, 90, and 120 min. Each sample was immediately quenched by using 40 µL of NaOH 6 N to stop the Fenton reaction. Then, it was filtered with a syringe filter of 0.45 µm nylon (Teknokroma, ref. TR-200101) and placed in a glass vial (Agilent) for immediate analysis. Some experiments were conducted three times to check the reproducibility of the results. The experimental error was within ±4%.

The main parameter used to compare the results in the discussion section is the conversion of phenol, X<sub>PhOH</sub>, defined as:

$$X_{\text{PhOH}}(\%) = \frac{[\text{PhOH}]_0 - [\text{PhOH}]_t}{[\text{PhOH}]_0}, \quad (8)$$

where [PhOH]<sub>0</sub> is the initial concentration and [PhOH]<sub>t</sub> is the concentration at time t.

### 3.3. Analytical Methods

The concentration of phenol was determined by HPLC (Agilent Technologies, model 1220 Infinity LC, Santa Clara, CA, USA) equipped with a C18 reverse phase column (Hypersil ODS, 5µm, 25 × 0.4 cm from Agilent technologies, Santa Clara, CA, USA). The analyses were performed with a mobile phase of a 40/60 mixture (volume %) of methanol and ultrapure water (Milli-Q water) at a flow rate of 1 mL/min. The pH of the water was adjusted at 1.41 with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The detection was performed using UV absorbance at a wavelength of 254 nm. The automatic injection volume was 20 µL of sample.

The total organic carbon (TOC) was measured in a TC Multi Analyzer 2100 N/C, equipment from Analytik Jena AG, with a non-diffractive IR detector (Jena, Germany). The non-purgeable organic carbon (NPOC) combustion infrared standard method 5310B [50] was used. TOC determination was performed using chemical oxidation of the sample in a high temperature furnace (800 °C) in presence of a platinum catalyst. The carbon dioxide produced during the oxidation was quantitatively determined by means of an infrared spectrophotometer detector. Sample acidification and aeration was carried out prior to analysis to eliminate inorganic carbon.

The TOC conversion, X<sub>TOC</sub>, was defined as:

$$X_{\text{TOC}}(\%) = \frac{[\text{TOC}]_0 - [\text{TOC}]_t}{[\text{TOC}]_0} \text{ and} \quad (9)$$

$$[\text{TOC}]_0 = [\text{TOC}]_{(\text{PhOH})_0} + [\text{TOC}]_{(\text{EDTA})_0}, \quad (10)$$

where [TOC]<sub>0</sub> is the initial total TOC according to Equation (10); [TOC]<sub>(PhOH)0</sub>, the initial TOC from phenol; [TOC]<sub>(EDTA)0</sub>, the initial TOC from EDTA; and [TOC]<sub>t</sub>, the total TOC at time t.

Finally, hydrogen peroxide concentration was determined by iodometric titration.

## 4. Conclusions

Aqueous phase oxidation of phenol solutions (1000 mg/L) was conducted from acidic up to circumneutral pH using a classical Fenton system (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) with or without the addition of a chelating agent in order to enhance oxidation performance. EDTA was selected for most of the tests under the same Fe<sup>2+</sup> catalyst load (7 mg/L) and H<sub>2</sub>O<sub>2</sub> dose (stoichiometric with respect to phenol).

In acidic conditions, close to the optimal pH (3–4), the presence of EDTA does not improve the phenol conversion achieved under classical Fenton conditions while, in EDTA excess, the phenol conversion becomes insignificant.

On the contrary, the phenol removal efficiency and peroxide decomposition rate significantly improved in the presence of EDTA at near circumneutral pH. Over 95% of phenol conversion was obtained using an EDTA:Fe ratio of 0.3:1 at pH 7.0, which is almost tenfold that obtained in the absence of EDTA. Among the different EDTA:Fe molar ratios tested, the ratio 0.3:1 was found to be the optimum.

Other chelating agents, like EDDA, DTPA, and NTA, were also tested in this study. They all enhanced the oxidation ability of the Fenton system at neutral pH, although EDDA provided the best oxidation performance.

Overall, the presence of a chelating agent in small quantities greatly broadens the pH range where the Fenton-like system is feasible, up to circumneutral pH. Thus, pH adjustment would not be required or would be just limited to caustic real wastewaters, which could result in major savings of operational costs.

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