

Review

Application of Chelating Agents to Enhance Fenton Process in Soil Remediation: A Review

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Abstract: Persistent organic contaminants affecting soil and groundwater pose a significant threat to ecosystems and human health. Fenton oxidation is an efficient treatment for removing these pollutants in the aqueous phase at acidic pH. However, the in-situ application of this technology for soil remediation (where pHs around neutrality are required) presents important limitations, such as catalyst (iron) availability and oxidant (H₂O₂) stability. The addition of chelating agents (CAs), forming complexes with Fe and enabling Fenton reactions under these conditions, so-called chelate-modified Fenton process (MF), tries to overcome the challenges identified in conventional Fenton. Despite the growing interest in this technology, there is not yet a critical review compiling the information needed for its real application. The advantages and drawbacks of MF must be clarified, and the recent achievements should be shared with the scientific community. This review provides a general overview of the application of CAs to enhance the Fenton process for the remediation of soils polluted with the most common organic contaminants, especially for a deep understanding of the activation mechanisms and influential factors. The existing shortcomings and research needs have been highlighted. Finally, future research perspectives on the use of CAs in MF and recommendations have been provided.

Keywords: chelating agents (CAs); modified Fenton (MF); soil remediation; organic pollutants; H₂O₂ stability; reactive oxygen species (ROS); ligand



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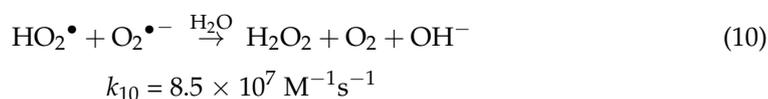
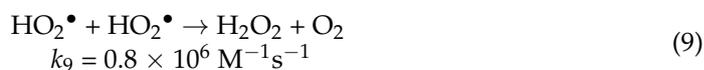
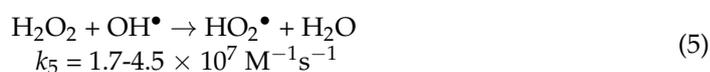
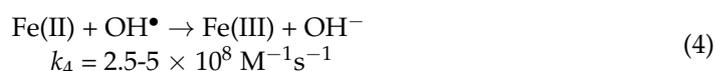
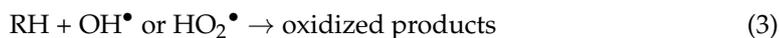
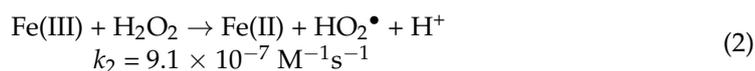
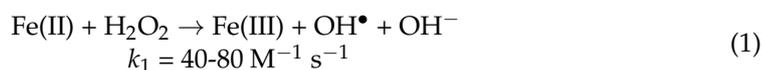
1. Introduction

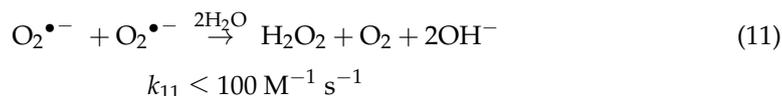
In recent years, many persistent and toxic contaminants found in soils have attracted the attention of the scientific community. Soil and sediment contamination by organic compounds, resulting from industrial and municipal waste discharge and improper use of chemical fertilizer and pesticides, is a widespread problem worldwide due to its great harm to the ecological environment and public health [1–3]. Nowadays, the principal substances contributing to soil pollution are petroleum oil hydrocarbons (e.g., aliphatic, aromatic, polycyclic aromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethylbenzene, and xylenes), chlorinated hydrocarbons like polychlorinated biphenyls (PCBs), trichloroethylene (TCE), and perchloroethylene, nitroaromatic compounds, organophosphorus compounds), solvents, and pesticides [4]. In China, 2.5% of total farmland is too contaminated to be used [5], whereas more than 80,000 sites suffer from soil pollution in the European Union [6]. In this context, the remediation of organic-contaminated soils is crucial, becoming a priority objective for both government institutions and society [3,7].

Extensive work has been devoted to developing soil remediation techniques [8], which mainly involves physical, chemical, and biological processes or/and their combinations. Advanced oxidation processes (AOPs) are powerful chemical methods with growing popularity for organic-contaminated soil remediation, being considered more effective than physical and biological approaches [9]. AOPs are considered capable of oxidizing different classes of organic pollutants by reactive radical species, achieving high levels

of mineralization [8,9]. The oxidants used in AOPs include hydrogen peroxide (H_2O_2), persulfate ($\text{S}_2\text{O}_8^{2-}$), permanganate (MnO_4^-), and ozone (O_3). One of the most frequently AOPs used is the Fenton process ($\text{H}_2\text{O}_2 + \text{Fe(II)}$), where H_2O_2 is the oxidant species and homogeneous Fe(II) acts as a catalyst for hydrogen peroxide decomposition [7,10]. Alternatively, the catalyst used can be homogeneous Fe(III), giving rise to the Fenton-like process [11]. The interest in using heterogeneous catalysts in the Fenton process (known as catalytic wet peroxide oxidation process, CWPO) has significantly increased in recent times [12]. CWPO uses natural iron-containing materials [12–14], supported catalysts with high surface area-supports (pillared clays, zeolites, silica, activated carbon, etc.), allowing the dispersion of the active phase (mainly Fe, but also Cu, Mn, Au, etc.) and metal-free-catalysts (carbonaceous materials) [15,16] to generate highly oxidizing species.

Many recalcitrant organic compounds (e.g., benzene, phenol, PAHs) have been efficiently degraded by the Fenton process and converted into low toxicity compounds [17,18]. The generally accepted mechanism of the Fenton process proposes that the reaction between Fe(II) and H_2O_2 first leads to the formation of hydroxyl radical (OH^\bullet , redox potential E_0 of 2.80 V) and Fe(III) (Equation (1)). Then, the generated Fe(III) can be reduced by reaction with excess hydrogen peroxide, generating Fe(II) and hydroperoxyl radical (HO_2^\bullet) (Equation (2)). This step allows the regeneration of the catalyst in a cyclic mechanism. Since the regeneration of Fe(II) (Equation (2)) is several orders of magnitude slower than its oxidation (Equation (1)), it is considered as the rate-limiting step of the reaction chain in catalytic Fenton systems. Once the radical species are formed (OH^\bullet and HO_2^\bullet), they react with organic pollutants (RH) as presented in Equation (3). Moreover, several competitive reactions (radicals recombination, reaction of hydroxyl radicals with hydrogen peroxide and with Fe(II)) can also occur (Equations (4)–(7)), negatively affecting the oxidation process [19–23]. The rate constants of these reactions (Equations (4)–(7)) have been reported in the literature [21,24]; as well as the hydroperoxyl radical (HO_2^\bullet) and its conjugated base ($\text{O}_2^{\bullet-}$) dissociation rate constants (Equation (8)) [25] and k values have been numbered according to their corresponding equation. According to Equations (9)–(11), it should be considered that $\text{O}_2^{\bullet-}$ and HO_2^\bullet can act as scavengers of the $\text{O}_2^{\bullet-}$ formed [26].





Although the Fenton process has been proven to be a potentially viable approach for remediating contaminated soils [27–29], there are various limitations associated with this treatment [28]. These limitations, along with possible solutions proposed in the literature, will be examined in the following sections.

1.1. Major Limitations of Fenton Oxidation in Contaminated Soils

The Fenton process displays its maximum OH^\bullet production and the subsequent pollutant oxidation activity under acidic pH, in the range 2.8–3.5 [19,30,31]. The system reactivity decreases with increasing pH above the value of 3.5 due to a decrease in dissolved iron concentration, which precipitates as ferric hydroxide ($\text{Fe}(\text{OH})_3$) [32]. Moreover, the adsorption of Fe(II) and Fe(III) ions onto mineral and organic constituents in the soil increases with the pH increase [33], resulting in less dissolved Fe available as catalyst for hydrogen decomposition, and consequently, Equation (1) would end. Hence, most of the research on the Fenton process application in aqueous systems has focused on the acidic pH range [34]. However, subsurface systems are often buffered in the neutral pH range (pH 6–8), which greatly complicates the implementation of this process. When treating in situ calcareous soils by the Fenton process, the initial pH adjustment of the soil by injecting an acid into the subsurface is expensive and impractical because of the buffer capacity of the soil [8,35,36]. Moreover, an acidified soil environment may also cause permanent damage to the soil ecosystem, preventing further biological treatments application [37,38].

To ensure the efficient presence of catalysis at neutral pH despite the low solubility of Fe(III), iron minerals naturally occurring in soils (normally iron in its oxidized state Fe(III)) have also been used as catalysts instead of soluble iron (Fe(II)) [39]. The progressive solubilization of the native iron minerals allows the decomposition of H_2O_2 and pollutants oxidation in soils without pH adjustment [22,35]. Similarly, heterogeneous Fenton reactions can effectively degrade refractory organic pollutants in soils at even circumneutral pH ranges [19]. Another possibility to overcome the constraint mentioned above is to deliver a soluble inorganic or organic ligand (also named chelating agent, CA) to maintain iron in the solution, enhancing the Fenton reactions. This process is called chelate-modified Fenton (MF; Fe(II)/Fe(III) + H_2O_2 + CA) process. Inorganic and organic CAs form complexes with Fe(II)/Fe(III) at neutral pH, keep it soluble, and thus enhance the production of oxidative species and extend the applicability of Fenton oxidation to a wider range of pH [28,40,41]. The extraction of the transition metals of the soil is also enhanced by the addition of chelating agents [42]. Furthermore, some authors proposed that CAs can also improve the persistence of H_2O_2 , allowing the radical species generated to flow through the soil, reaching the target contaminants [9]. Thus, CAs addition has practical implications for enhancing the Fenton and Fenton-like processes in soil remediation. The main characteristics of the chelating agents applied in Fenton process have been summarized in Table 1 (Section 2.3).

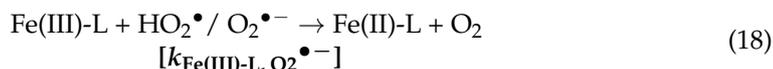
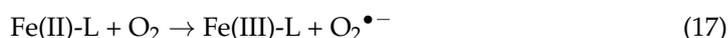
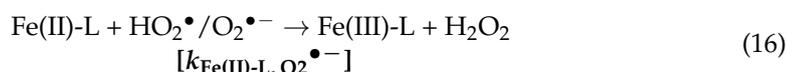
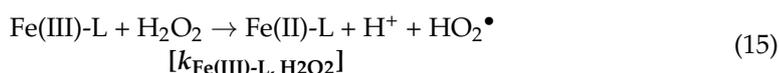
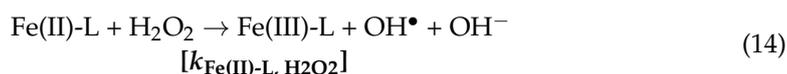
1.2. Use of Chelating Agents in Soil Remediation by Modified Fenton Process: Reaction Mechanism

A simplified reaction mechanism showing the reversible binding between the ligand and iron (Fe(II)/Fe(III)), which results in the formation of a complex (expressed as Fe(II)-L and Fe(III)-L, respectively), is proposed in Equations (12) and (13). It should be considered that the complexation of Fe species with ligands is more complicated than shown, and a wide variety of complexes, such as FeL_2 , FeHL , FeHL_2 , etc., can be formed. Their generation depends on several factors, such as the type of CA used, the CA:Fe molar ratio, and the pH, among others. For simplicity, Fe(II)/Fe(III)-L (abbreviated as Fe-L) is used to represent

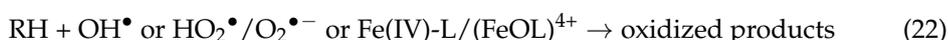
all the forms of the possible complexes formed between the ligand corresponding to each CA and Fe, which stability constants have been summarized in Table 2.



In a simplified reaction scheme of chelate-modified Fenton (MF), the Fe-L complexes formed (Equations (12) and (13)) would decompose H_2O_2 to generate radical species (hydroxyl and hydroperoxyl radicals) (Equations (14) and (15)), equivalent to classical Fenton reactions (Equations (1) and (2), respectively), being the catalytic regeneration (Equation (15)) the limiting stage of the process. However, in the presence of most organic CAs, it has been suggested that H_2O_2 was unlikely to reduce complexed iron, and the reduction of Fe(III)-L was mainly produced through $\text{O}_2^{\bullet-}$ generated (Equation (18)) rather than from the direct Fenton reactions with H_2O_2 (Equation (15)) [26,43–47]. In this way, the MF acceleration is attributed to the positive effect of $\text{O}_2^{\bullet-}$ during regeneration of Fe(II)-L from Fe(III)-L. Following the catalytic cycle, the reduced Fe(II)-L can be reoxidized by H_2O_2 (Equation (14)), reactive species ($\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$) (Equation (16)) or O_2 (Equation (17)). The nomenclature of the kinetic constants corresponding to each reaction has been included. The values of these constants are listed in Table 3 (Section 2.4).

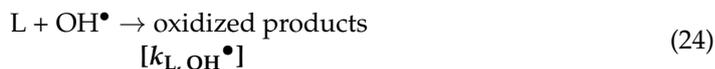
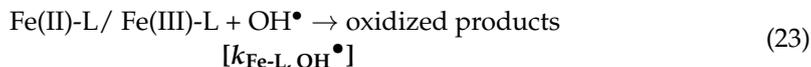


In the MF system, different reactive oxygen species (ROS) can be responsible for the degradation of organic contaminants, being the main types: hydroxyl radical (OH^{\bullet}), superoxide radical ($\text{O}_2^{\bullet-}$) (and its conjugated base, hydroperoxyl radical (HO_2^{\bullet})), and high-valent iron species [48]. Indeed, there has been considerable debate as to whether the main ROS in the MF process are hydroxyl radicals or higher oxidation states of iron (such as Fe(IV) or ferryl ($\text{FeO}^{\bullet 2+}$) complexes) (Equations (19)–(22)) [49]. In the presence of some CAs, rather than the direct generation of hydroxyl radicals (Equation (14)), the initial step is likely the formation of a ferrous peroxide (Fe(IV)) complex (Equation (19)). This complex can convert to ferryl species (Equation (20)), breakdown to give hydroxyl radicals (Equation (21)), or directly oxidize an organic substrate. Thus, in different circumstances, one or all three of the reactive species (or the combination of them) may oxidize the organic pollutants (RH) (Equation (22)).



As mentioned above, the addition of CAs in the Fenton process allows the extent of its pH application range to approximately neutral conditions and decreases oxidant consumption [50]. However, the use of CAs has some disadvantages that must be considered

before its implementation. CA and pollutant can compete for the hydroxyl radicals (or the other reactive species) formed with a significant loss of the process efficiency [51]. In this regard, the scavenger effect of the CA should be considered. The reactions between Fe-L and ligands (L) with OH• are reflected in Equations (23) and (24), respectively.



Even though the possible oxidation of ligands by the radical species generated is of great importance, this aspect has not been deeply analyzed in the literature, where attention has been mostly paid to the pollutant abatement. The OH• or other reactive species yield in the MF process depends on the pH value, the H₂O₂:Fe ratio, and the CA:Fe ratio [52]. Moreover, when choosing the CA, different factors, such as the contaminant accessibility, soil matrix content, soil texture and moisture, the adsorption of the catalyst and the CA onto the soil, intraparticle diffusion and removal of chemicals added by leaching can significantly affect the contaminant removal, and thus, should be considered. In the same direction, it should be considered that the type of soil will determine the kinetics of the process and even the mechanism scheme.

Applying different CAs to make iron soluble at circumneutral pH (as catalyst for hydrogen peroxide decomposition) has been recently reviewed for Fenton and photo-Fenton processes in the aqueous phase [32,40,41]. The authors affirmed that the contaminants are efficiently degraded by this process (MF), highlighting a potential treatment approach for the degradation of different pollutants (including emerging contaminants, aromatic compounds, pesticides, dyes, etc.) at neutral pH.

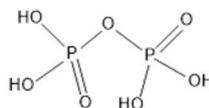
However, to the best of our knowledge, a critical review illustrating the use of different chelating agents in Fenton treatment for soil remediation is still missing in the literature. Thus, this article reviews the most common CAs and their employment for soil remediation by the Fenton process (MF process). Four aspects have been considered: the main characteristics of the CAs, the stability constants of the Fe-L complexes formed (Fe(II)-L and Fe(III)-L, respectively), the reaction mechanism of Fe(II)-L oxidation (and potentially Fe(III)-L reduction) in the presence of different ligands, and the negative hydroxyl radical scavenger effect of the ligand. Finally, this review analyzes the results obtained when using different CAs to enhance the Fenton process in soil remediation, giving practical information on which type of CA to use depending on the pollutant type and the real matrix soil's characteristics. Moreover, this review has identified the unexplored areas in this topic which will give readers insight into future studies.

2. Chelating Agents Commonly Used in Modified Fenton Process for Soil Remediation

Many compounds strongly complex with Fe and, therefore, can be used as chelating agents in the MF process. CAs used in soil remediation may be classified into inorganic and organic compounds. The most used inorganic compound is pyrophosphate (PPP). Among organic CAs, three main types may be considered according to their coordination sites: polycarboxylates (citrate (in the form of citric acid (CitrA) or its salt) and oxalate (in the form of oxalic acid (OA) or its salt), aminocarboxylates (ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-bis(2-hydroxyphenyl)acetic acid (EDDHA)) and humic substances (humic (HA) and fulvic acids (FA)). The structure of the CAs most used for the remediation of soils contaminated with organic pollutants, and therefore considered in this review, is summarized Figure 1.

1. INORGANIC CHELATING AGENTS

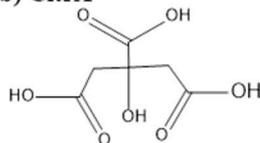
a) PPP



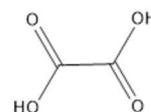
2. ORGANIC CHELATING AGENTS

Polycarboxylic acids

b) CitrA

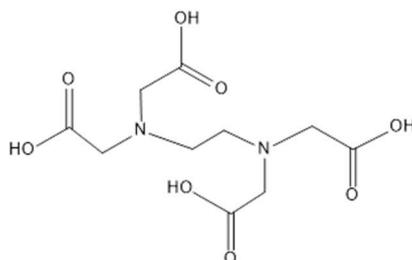


c) OA

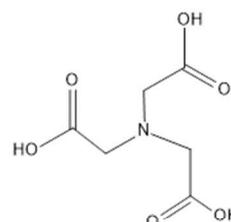


Aminopolycarboxylic acids

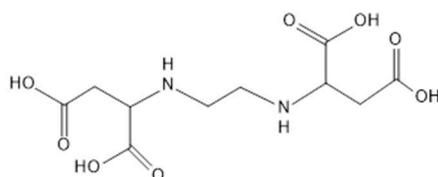
d) EDTA



e) NTA



f) EDDS



g) EDDHA

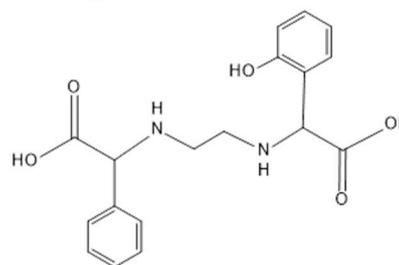


Figure 1. Structure of the investigated chelating agents: (1) inorganics; (a) pyrophosphate (PPP), and (2) organics; (b) citrate as citric acid (CitrA), (c) oxalate as oxalic acid (OA), (d) ethylenediaminetetraacetic (EDTA), (e) nitriloacetic acid (NTA), (f) ethylenediamine-*N,N'*-disuccinic acid (EDDS) and (g) ethylenediamine-*N,N'*-bis(2-hydroxyphenyl)acetic acid (EDDHA).

In addition to the CAs above-mentioned, other organics CAs less frequently used for soil remediation are catechol (CC), L-Ascorbic acid (L-AA), gallic acid (GA), picolinic acid (PA), sodium *N,N'*-bis(carboxymethyl) glutamic acid (GLDA), and cyclodextrins (CD).

The capability of a single ligand to form strong complexes with Fe is essential to prevent the precipitation of Fe(III) as iron hydroxide [32]. The binding Fe-L influences the characteristics and reactivity of the complex with substrates [53]. The stability constant of Fe(II)-L and Fe(III)-L is defined as the equilibrium constant for the complex formation in solution (Equations (12) and (13)), and it indicates the strength of the interaction between CAs and Fe. The complex formation equilibria can be written as the sum of each stage (generation of ML, ML₂, ML₃, etc.), giving rise to overall stability constants (β). Except for the first stage (ML), in which β_1 corresponds to K_1 , the overall stability constants are

products of the successive formation constants of each of the stages. CAs with lower stability constants (expressed as its logarithmic value, $\text{Log } \beta$) would need higher CA:Fe molar ratios to form stable Fe-L complexes. The higher the stability constant of a complex is, the higher the tendency of forming the Fe-L complex will be. In this way, higher stability constants of Fe(III)-L than Fe(II)-L suggested higher reaction rates of Fe(II)-L with H_2O_2 (Equation (14)), and accordingly, lower reduction rates of Fe(III)-L to Fe(II)-L (Equation (15) or Equation (18)) [41].

Another interesting feature of each CA is its acid ionization constant values (pK_a). pK_a is a quantitative measure of the strength of an acid that dissociates into the conjugate base and a hydrogen ion (H^+). Depending on the charges, each ligand will have corresponding pK_a values, e.g., a polyprotic CA with four protons will have four pK_a values, corresponding to Equations (25)–(28). pK_a values represent the tendency of the donor atoms of the ligand to donate electrons to metal atoms: thus, directly affecting the Fe-L formation, and consequently, the stability constant. The lower the value of pK_a is, the stronger the acid is. The addition of CAs with low pK_a values will tend to decrease the pH of the Fenton system, and it would correspond with lower stability constants of Fe-L complexes [41].



The Fe-L formed will depend on the reaction conditions, such as CA:Fe molar ratio and pH. Therefore, a systematic review of each ligand, including its main characteristics, the Fe-L formation, the reaction mechanisms between Fe-L and H_2O_2 , the reactive species generated in the system and their role in contaminant degradation, has been carried out in the following subsections. However, it should be considered that the chemical kinetics and mechanism controlled by stoichiometry can vary significantly depending on the type of soil treated and its characteristics, as further detailed in Section 3.1.

2.1. Inorganic Chelating Agents: Pyrophosphate

Pyrophosphate (PPP) contains two dentates, as can be seen in Figure 1. PPP, in the form of sodium pyrophosphate (SP), is the most used inorganic CA for iron stabilization in Fenton type systems [54–58]. Moreover, the addition of SP has shown an oxidant stabilizer effect, slowing down its decomposition [54,56,59]. The Fe-L formed between Fe and SP are $\text{Fe}(\text{HP}_2\text{O}_7)_2^{3-}$, in the pH range of 2–8, and $\text{Fe}(\text{OH})_2\text{P}_2\text{O}_7^{3-}$, at $\text{pH} > 8$ [59,60].

Contradictory results have been found in the literature regarding the Fe/PPP/ H_2O_2 mechanism. Ma et al. proposed a plausible reaction mechanism for the degradation of organic compounds by MF in the presence of PPP (in the form of SP), as shown in Figure 2, where the main reactions of the process are schematized (adapted from Ma et al. [56]). Fe(III)-PPP is reduced to Fe(II)-PPP by hydrogen peroxide. The authors found that $\text{O}_2^{\bullet-}$ and OH^\bullet contributed to the degradation of polychlorinated biphenyls (PCBs) by 10% and 90%, respectively [56]. Rachmilovich-Calis et al. determined the rate constant of Fe(II)-PPP with H_2O_2 (Equation (14)), which was at least 20 times higher than in the absence of ligands [53] (see Table 3, Section 2.4, where the kinetic constants of the different reactions involved in MF process have been summarized). However, Fischbacher et al. suggested that Fe(III)-PPP did not react with H_2O_2 (Equation (15)), and thus, catalyst regeneration is not produced [52]. This finding is in accordance with the high stability constant of Fe(III)-PPP (included in Table 2, Section 2.3, where the main properties of the CAs studied have been summarized), which favors the oxidation of Fe(II)-PPP to Fe(III)-PPP by H_2O_2 (Equation (14)) while dramatically hinders the reduction of Fe(III)-PPP to Fe(II)-PPP (Equation (15) or Equation (18)) [44,59]. Although some authors supported that the reduction of Fe(III)-PPP was limited, the delays in the rate of H_2O_2

decomposition, the increase in OH^\bullet production and the amount of soluble iron, lead to an increase in pollutant conversion when this ligand is used in soil remediation under near-neutral conditions [54–56,59]. Furthermore, a positive aspect of PPP is its inorganic nature. The scavenging effect of this CA can be neglected due to the low reactivity of OH^\bullet towards $\text{P}_2\text{O}_7^{4-}$, compared to other organic CAs (see Table 3) [61]. In addition, after its hydrolysis to orthophosphate, PPP can serve as phosphorus fertilizer to plants and environmental microorganisms [59,62], facilitating a subsequent bioremediation treatment after the application of the MF process.

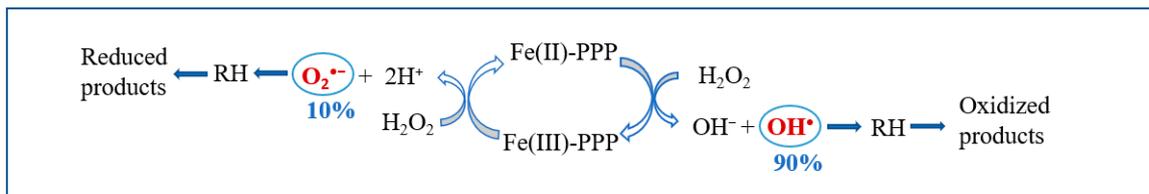


Figure 2. Simplified mechanism of organic pollutant degradation (RH) in the Fe/PPP/H₂O₂ system. Adapted from Ma et al. [56].

On the other hand, factors such as CA:Fe and H₂O₂:Fe ratios can decisively influence the process efficiency and therefore, they should be considered. In this way, it has been reported that the combination of Fe(II) with an equal molar amount of PPP enhanced the production of OH^\bullet [63], while the use of PPP concentrations considerably higher ($[\text{CA}] \gg [\text{Fe}]$) decreased the yield of hydroxyl radicals formed [52]. In this case, the strong steric hindrance by PPP impeded the interaction between H₂O₂ and the catalyst [61].

2.2. Organic Chelating Agents

2.2.1. Polycarboxylic acids (PCAs)

Citrate/Citric acid (CitrA)

Citrate ligand can be generated from citric acid (CitrA) or sodium salts, such as sodium citrate mono-hydrate (SC_m) and trisodium citrate (SC). CitrA is an environmental-friendly ligand consisting of three carboxyl groups and one hydroxyl group (Figure 1). This tricarboxylic acid has relatively low *pKa* values (Table 2, Section 2.3). Thus, its addition tends to decrease the pH of the reaction mixture. The pH decline can be associated to a possible dramatic ecological impact on the soil, and, therefore, the use of CitrA should be carefully evaluated. To avoid this effect and maintain the natural pH of the soils, sodium salts (SC_m and SC) which act as a buffer, can be used instead of CitrA [35]. The ligand citrate interacts with Fe to generate the complex Fe-citrate. The reaction of Fe(II)-citrate with H₂O₂ at neutral pH has been illustrated in a simplified scheme (Figure 3, adapted from Zeng et al. [64]), where the main reactions involved in the process have been schematized.

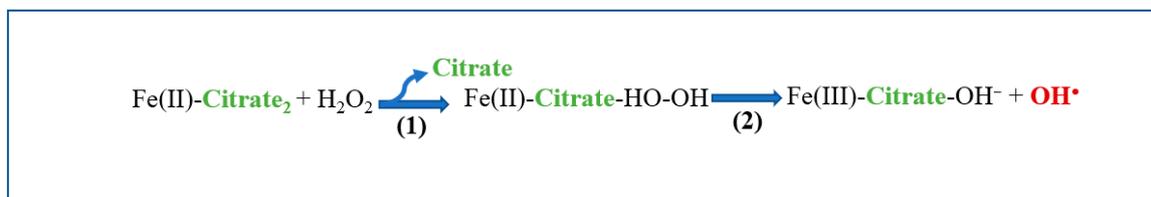


Figure 3. Simplified scheme of MF mechanism in the presence of citrate. Adapted from Zeng et al. [64].

In this reaction, H₂O₂ substitutes a citrate ligand from Fe(II)-citrate₂ to form Fe(II)-citrate-H₂O₂ (step 1). The ligand-exchange rate determines this reaction and thus is the rate-limiting step. Then, an intramolecular transfer from the Fe(II) to the H₂O₂ bound occurs, producing Fe(III)-citrate-OH⁻ and hydroxyl radicals (step 2), much faster than step 1 [64]. Adversely, the kinetic model proposed by Miller et al. supported that superoxide radicals

($O_2^{\bullet-}$) are produced by the reaction between Fe(II)-citrate and oxygen (Equation (29)). After that, the Fe(III)-citrate is reduced by $O_2^{\bullet-}$ (Equation (30)) [25].



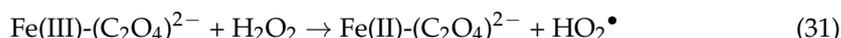
The ability to maintain Fe in solution in the Fe/citrate/ H_2O_2 system depends on the reaction pH and the reagents molar ratio. Soluble Fe(III)-citrate complexes are formed at pH above 3.0, and iron dramatically precipitates at pH > 7 [32,65]. At low citrate:Fe molar ratios and low pH values, the speciation of these systems is dominated by the dinuclear and trinuclear complexes (Fe_2L_2 and Fe_3L_3 , respectively) [66]. However, at low citrate:Fe molar ratios and neutral pH, each iron atom binds with two citrate ligand to form the mononuclear dicitrate complex (FeL_2) [67]. Moreover, the reaction pH and the CA:Fe molar ratio also affects the amount of the oxidizing species generated in the system [68]. The oxidation of Fe(II)-citrate resulted in substantial OH^\bullet production, and a rate constant of the Fe(II)-citrate reaction with H_2O_2 ($k_{\text{Fe(II)-L}, H_2O_2}$, Equation (14)) of $4.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ has been reported [25,69]. The reaction rate constant obtained is in accordance with those obtained elsewhere [64,69] (included in Table 3, Section 2.4).

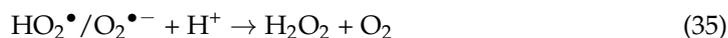
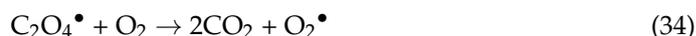
Zepp et al. [70] determined the reactivity of citrate with OH^\bullet , suggesting relatively high values for the kinetic constant ($k_{\text{citrate}, OH^\bullet}$, $\text{M}^{-1}\text{s}^{-1}$) (Equation (24)) at 25 °C, depending on the reaction pH: 1.2×10^8 (pH = 3.0), 1.5×10^8 (pH = 3.6), 2.4×10^8 (pH = 6.0), and 3.2×10^8 (pH = 6.6). The increase in reactivity with pH is attributable to the citrate deprotonation (as CitrA) to its more reactive dissociated species [70]. These authors estimated that the hydroxyl radical scavenging rate constant for the Fe-L complex ($k_{\text{Fe-citrate}, OH^\bullet}$) was $1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Equation (23), Table 3, Section 2.4). Thus, the high-rate constant of citrate and Fe-citrate towards OH^\bullet radicals lead to a significant scavenging effect (related to low pollutants degradation) at a high dose of this ligand. However, the relatively low stability constant of Fe-citrate (especially when CitrA is used, Table 3, Section 2.3) requires high proportions of this ligand to chelate the catalyst [41]. In this way, the concentration of citrate should be high enough to favor the formation of the Fe-citrate complex but not so high as to cause a significant scavenging effect on the OH^\bullet radicals produced. For all of the above, it can be concluded that pH and citrate:Fe molar ratio has a decisive influence on the effectiveness of using this ligand in a MF process for soil remediation [71].

On the other hand, Fe-citrate complexes produce a significant stabilization effect of H_2O_2 [35,72,73]. For example, Vicente et al. reported that citrate, both as CitrA and citrate salts (SC_m and SC), reduced the H_2O_2 conversion significantly, following a decreasing order at 1 h of reaction time: no citrate addition (75%) > SC(60%) > SC_m (50%) > CitrA(20%) [35].

Oxalate/Oxalic Acid (OA)

The ligand oxalate is mainly used as oxalic acid ($(C_2O_4)^{2-}$, OA). OA is the simplest existing dicarboxylic acid and has been widely used to enhance the Fenton process for soil remediation [55,57,74,75]. In the MF process, OA binds to the iron ion to form Fe-oxalate ($Fe(III)(C_2O_4)^{2-}$ [76]). This facilitates the reduction of ferric ion to ferrous ion by H_2O_2 (Equation (31)). Meanwhile, Fe(III)-OA can also be reduced by superoxide ($O_2^{\bullet-}$) and hydroperoxyl (HO_2^\bullet) radicals (Equation (32)). The catalyst regeneration (giving rise to Fe(III)-OA) contributes to the decomposition of H_2O_2 and generation of hydroxyl radicals (Equation (33)) [76]. In addition, oxalate can react with dissolved oxygen to form superoxide radicals ($O_2^{\bullet-}$) (Equation (34)), which in turn can produce H_2O_2 according to Equation (35). In this way, the hydrogen peroxide generated can yield more hydroxyl radicals [45]. Thus, oxalate enhances the production of hydroxyl radicals. The following scheme has been proposed by Wang et al. [76].





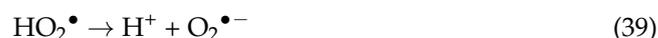
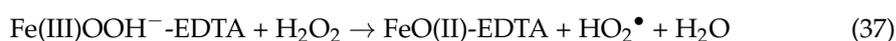
The rate constant for the Fenton reaction (Equation (1)) in the absence of ligands is around $40\text{--}80 \text{ M}^{-1}\text{s}^{-1}$, whereas this value increases up to $3.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ when the decomposition of H_2O_2 is catalyzed by Fe(II)-oxalate, which is 3 orders of magnitude higher [77,78].

Moreover, OA (and its dissociated species) can be considered almost unreactive with hydroxyl radicals ($k_{\text{oxalate, OH}^\bullet}$ values in the range of $1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [79]– $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [70]) compared to other organic CAs, such as citrate, EDTA and EDDS (the kinetic constant between OA and hydroxyl radicals is 1 or 2 orders of magnitude lower than the corresponding to other CAs, as can be seen in Table 3, Section 2.4). Thus, the competition of oxalate with target pollutants for OH^\bullet is minimized. The lower scavenging effect of this ligand towards OH^\bullet is especially interesting for the remediation of recalcitrant organic contaminants (with relatively low pollutants- OH^\bullet rate constants). Otherwise, the low stability constant of Fe-OA (Table 2, Section 2.3) highlights the need to use a high concentration of this ligand to chelate the iron. Furthermore, similarly to citrate ligand, the addition of OA might decrease the reaction pH due to the relatively low pK_a value of this compound (Table 2, Section 2.3).

2.2.2. Aminopolycarboxylic Acids (APCAs)

Ethylenediaminetetraacetic Acid (EDTA)

This hexa-dentate aminocarboxylate CA has two N and four O donors (Figure 1). This is one of the most popular APCAs and has been widely used as a chelating agent for soil remediation [80,81]. EDTA can strongly combine with Fe(II) or Fe(III) to form stable metal complex in solution ($\log \beta$ (Fe(II)) = 14.3; $\log \beta$ (Fe(III)) = 25.1 [82], Table 2, Section 2.3). Fe(III)-EDTA can be reduced to Fe(II)-EDTA by $\text{O}_2^{\bullet-}$ (Equation (40)). This radical is previously generated by a series of serial reactions (Equations (36)–(39)) initiated by the reaction between Fe(III)-EDTA and the oxidant (H_2O_2). Finally, Fe(II)-EDTA reacts with H_2O_2 generating hydroxyl radicals (Equation (41)) [43,44].



This mechanism supported that the interaction of Fe-EDTA and $\text{O}_2^{\bullet-}$ strongly influences OH^\bullet production. Consequently, the summarized complex reaction proposed in Equation (15)), where a direct reduction of Fe(III)-L by H_2O_2 is assumed, is not applicable for EDTA-chelated systems.

Conflicting conclusions on the nature of ROS formed in the Fe/EDTA/ H_2O_2 system were reported in the literature. For example, some authors reported that Fe(IV) was the reactive intermediate produced at near-neutral pH [83], whereas others identified OH^\bullet as the primary intermediate [25].

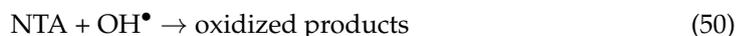
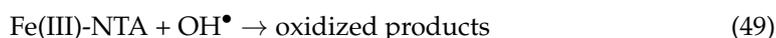
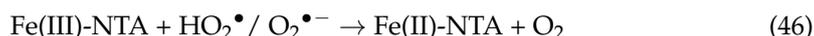
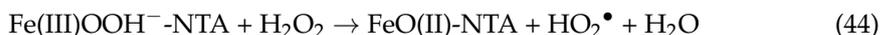
Although several authors corroborated the significant effect of EDTA in the improvement of Fenton effectiveness at near neutral pH in soils [84–87], its use is being limited since it has been recently considered an emerging contaminant of concern due to its low biodegradability, its contribution improving heavy metal mobility/bioavailability, and persistence in the environment [73,88–90]. Therefore, there is a long term need to replace

the conventional complexing agent EDTA with better compounds, which are not only more biodegradable, but also provide improved technical performance [91].

Nitrilotriacetic Acid (NTA)

The tetra-dentate aminocarboxylate chelating agent (NTA) is one of the environmentally friendly CAs used to replace EDTA [41]. However, although NTA is biodegradable, its usage is controversial because it is moderately toxic to humans and mammals [92].

When using a NTA:Fe ratio of 1:1, 95% of NTA was bound in the Fe(III)-NTA complex [26]. Motekaitis et al. (1994) indicated that Fe(III)-NTA predominates at pH below 3 [93], while the main species at pH around 8 was reported to be $[\text{Fe}(\text{OH})_2\text{NTA}]^{2-}$. This complex activates H_2O_2 to produce OH^\bullet , presenting a lower OH^\bullet scavenging effect than the other species of Fe(III)-NTA complexes [94]. The reaction sequence for NTA-modified Fenton is summarized in Equations (42)–(50) [26]. Moreover, other oxygen radical competitive reactions (radicals recombination, reaction of hydroxyl radicals with H_2O_2 and with Fe(II), $\text{O}_2^{\bullet-}$ scavenger ability, etc.) corresponding to the previously reported for the homogenous Fenton (Equations (4)–(11)) should also be considered. Zhang et al. suggested that Fe(II)-NTA is instantaneously oxidized to Fe(III)-NTA at the beginning of the reaction (Equation (42)), and after that, OH^\bullet is generated by using $\text{O}_2^{\bullet-}$ as an intermediate (Equation (46)) and not directly through the reaction of Fe(III)-NTA and H_2O_2 (Equation (43)) [26]. In this way, as for the EDTA ligand, it was suggested that H_2O_2 was unlikely to reduce complexed iron [43], and the reduction of Fe(III)-L was superoxide-dependent not H_2O_2 -dependent. However, no Fe(II) was detected in the Fe(III)/NTA/ H_2O_2 modified Fenton system [26,43], and this could be attributed to three reasons: (1) too low reactivity of $\text{O}_2^{\bullet-}$ in the buffer solution, (2) short life-time of $\text{O}_2^{\bullet-}$ and (3) Fe(II)-NTA was generated by the Equation (46), but it was instantaneously oxidized to Fe(III)-NTA (Equation (42)) [26].



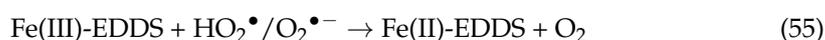
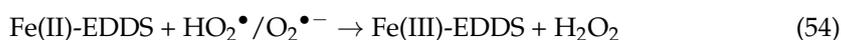
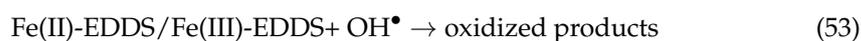
Values reported in the literature for the rate constant between Fe(III)-NTA and OH^\bullet are in the range $1.6\text{--}4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [26,95] (Table 3, Section 2.4). In addition, significant scavenging of the hydroxyl radicals generated is expected by NTA due to the high rate constant between this CA and OH^\bullet , especially significant at high pH values [95], as seen in Table 3.

Ethylenediaminedisuccinate (EDDS)

EDDS has recently emerged as an alternative chelating agent, this compound presenting properties similar to those of EDTA and readily biodegradable nature [47,88,91,96]. EDDS is a hexa-dentate aminocarboxylate soluble in water in any ratio [91].

The formation of different Fe-EDDS complexes as a function of pH has been reported elsewhere [97]. These authors stated that Fe(III)-EDDS⁻ (with $\log \beta = 20.6$) is predominant at acid pHs ($\text{pH} \leq 7$) and hydrolyzed complex species (Fe(OH)-EDDS²⁻ and Fe(OH)₂-EDDS³⁻ with $\log \beta = 7.9$ and 9.9, respectively) at higher pH values. It has been reported that the suitable pH range for EDDS is from 3 to 9 [47]. The Fe(III)-EDDS complex has

shown to be unstable at $\text{pH} > 8$, suggesting that the addition of EDDS does not significantly shift the precipitation of Fe(III) as iron hydroxide ($\text{Fe}(\text{OH})_3$) under these conditions [32]. As mentioned above, apart from pH, the CA:Fe molar ratio greatly affects the efficiency of the process. In this way, Fe(II)-EDDS complex showed low ability to activate the oxidant at EDDS:Fe ratios higher than 1:1, due to the fact that the complete coordination of Fe(II) with an excess of EDDS forms a bulky hexacoordinated complex which hinders the attachment of Fe(II) by the oxidant [98]. The main reactions involved in the EDDS-MF process are summarized as follows (Equations (51)–(55) [46]):



The generation of Fe(II)-EDDS from Fe(III)-EDDS reduction is the rate-limiting step, and any factor that can raise the corresponding rate constant (Equation (52)) would probably accelerate the formation rate of OH^\bullet (Equation (51)). Huang et al. suggested that bisphenol A degradation was mainly attributed to the action of OH^\bullet rather than $\text{HO}_2^\bullet / \text{O}_2^{\bullet-}$ at $\text{pH} = 6.2$ [47]. However, it was determined that the formation of hydroxyl radicals strongly depends on the presence of $\text{O}_2^{\bullet-}$ (Equation (55)). Indeed, 20% of OH^\bullet generated comes from the classical Fenton reactions (Equations (51) and (52)), without the need for superoxide radical, whereas the other 80% of OH^\bullet comes from the reduction of Fe(III)–EDDS with superoxide radical anions (Equation (55)) (Figure 4, adapted from Huang et al. [47]).

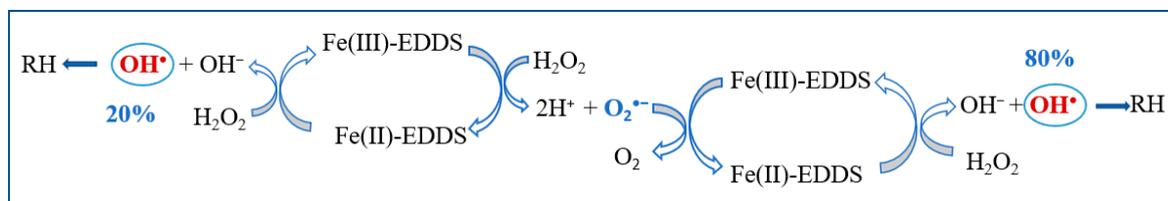


Figure 4. Simplified mechanism of organic pollutant degradation (RH) in the Fe/EDDS/ H_2O_2 system at $\text{pH} = 6.2$. Adapted from Huang et al. [47].

Since EDDS promotes the generation of superoxide radicals, the use of this new chelating agent in groundwater and soil remediation could be very effective [47]. Nevertheless, the application of this CA should be limited by the fast reaction between EDDS and OH^\bullet [46], (Table 3, Section 2.4).

Ethylenediamine- N,N' -bis(2-hydroxyphenyl)acetic Acid (EDDHA)

EDDHA is a biodegradable ligand with two phenolic groups substituting the carboxylates of EDTA (Figure 1), which highly increase its stability (Table 2, Section 2.3). Ma et al. proposed the oxidation mechanism of this CA based on a catalytic cycle (Figure 5, adapted from Ma et al. [56]), where the main reactions of the MF process in the presence of this CA are detailed. As can be seen, both OH^\bullet and $\text{O}_2^{\bullet-}$ radicals are of equal importance (50% each one) in the degradation of PCBs in the Fe(II)/EDDHA/ H_2O_2 system [56]. Nahim-Granados et al. stated that the presence of light in the Fe/EDDHA/ H_2O_2 system favors the reduction of Fe(III) to Fe(II) [99].

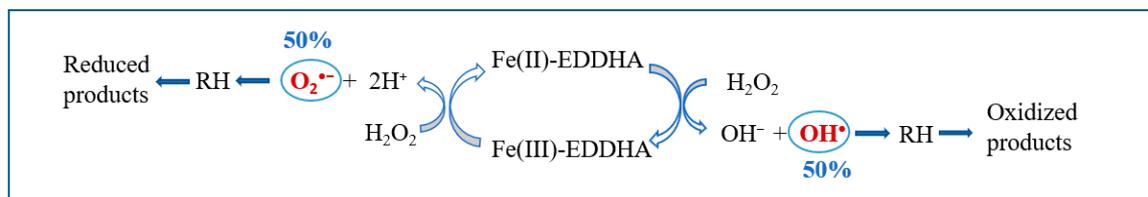


Figure 5. Simplified mechanism of organic pollutant degradation (RH) in the Fe/EDDHA/H₂O₂ system. Adapted from Ma et al. [56].

2.2.3. Humic Substances (HS) and Soil Organic Matter (SOM)

Humic substances are the major constituents of the organic matter of soils and sediments. HS are naturally occurring organic compounds that arise from the decomposition and transformation of plant, animal, and microbial residues [100]. They are organic substances of high molecular weight and refractory to biodegradation. Humic substances are classified into humic and fulvic acids (HA and FA, respectively). Both are ubiquitous without potential toxicity. Thus, these compounds can be considered “greener” amendments for the MF process [101].

Humic acids are composed of molecules rich in acidic functional groups, mainly carboxyl and phenolic groups, and hydrophobic moieties such as alkyl chains and aromatic cores. These substances have been used in literature as an amendment to improve the abatement of organic compounds by the Fenton reaction, especially in aqueous phase [75,102–104], although the reaction mechanism is not completely understood.

The applicability of HA as chelating agent in soil remediation greatly enhances the oxidation rate of organic compounds at neutral pH, the costs increase associated being negligible [75]. Georgi et al. suggested that OH[•] are the main reactive species in the HA-modified Fenton system [75], whereas Yang et al. reported that superoxide was also a dominant ROS [105]. In the same way, the addition of FA as CA increases the rate constant of Fenton’s reaction as a result of the formation of Fe(II)-fulvate at near circumneutral pH [106]. Moreover, it has been demonstrated that HAs act as sorbents for hydrophobic organic compounds from soil [101].

Recently, the research interest is focused on the possibility of extract these substances from organic wastes. In this way, Zingaretti et al. tested the use of HAs extracted from compost in a MF process, and the obtained results were equivalent to those achieved applying commercial HAs or traditional amendments (KH₂PO₄ and EDTA) [101]. HAs extracted from compost were able to chelate 0.04 mg iron mg_{HA}⁻¹ and increased the lifetime of the oxidant similarly to the traditional stabilizers used. Moreover, the extracted humic acids allowed to obtain a normalized radius of influence higher than those observed using EDTA. Therefore, it was demonstrated that extracted HAs could be simultaneously used as H₂O₂ stabilizer and chelating agent [101]. The use of these natural substances (HAs extracted from compost) was also evaluated for the remediation of diesel-contaminated soil [107]. The addition of HAs (10 g L⁻¹) showed a beneficial effect on the hydrogen peroxide stability, especially when combined with KH₂PO₄. In the same line, Zingaretti et al. have also explored the possibility to extract HAs from the bio-stabilized waste produced from a Mechanical Biological treatment plant [108]. The HAs obtained showed high functional group contents and aromaticity, equivalent to the characteristics of commercial HAs, allowing to consider these substances for different applications such as the MF process [108].

SOM, the organic fraction of the soil, which includes humic substances, can also develop an important role as CA. Xu et al. reported that SOM can combine with iron ions to form Fe-SOM, catalyzing the decomposition of H₂O₂ to produce OH[•] in the solid phase, which directly oxidizes the pollutant (crude oil) [109], as described in Figure 6a (adapted from Xu et al. [109]). This contrasted with the OH[•] production and the oil degradation in the aqueous phase in the absence of Fe-SOM (Figure 6b).

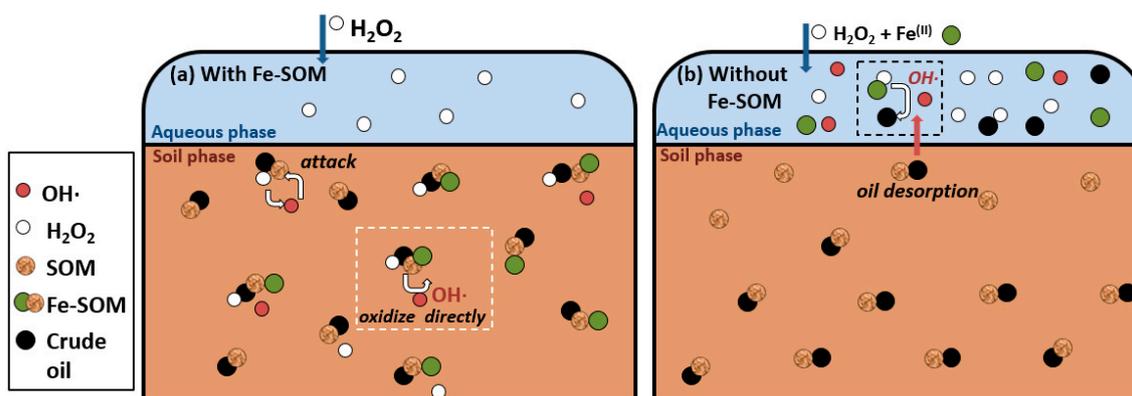


Figure 6. Schematic representation of different oxidation mechanism in soil for the degradation of crude oil; (a) with Fe-SOM and (b) without Fe-SOM. Adapted from Xu et al. [109].

2.3. Chelating Agents' Properties

For each CA considered in the present review (those most commonly used for soil remediation in the MF process), an overview on the most relevant properties, such as the type of ligand (inorganic/organic), the cost, biodegradability, and toxicity, has been performed and the information found in the literature has been summarized in Table 1. As previously stated, the presence of some CAs increases the stability of hydrogen peroxide. This important issue has also been considered in Table 1.

Table 1. Summary of the main characteristics of the chelating agents applied in Fenton process.

Ligand	Type	Biodegradability	Toxicity	Cost	Stabilizing Effect
PPP	Inorganic	Biodegradable	Non-toxic	597 \$ t ⁻¹ (SP) [56]	Yes [54,56,59]
Citrate	Organic	Biodegradable [35]	Non-toxic	450–590 \$ t ⁻¹ (SC)	Yes [35,72]
Oxalate	Organic	Biodegradable	Non-toxic	450–510 \$ t ⁻¹ (OA)	Yes (moderate) [55]
EDTA	Organic	Non-biodegradable [110]	Toxic [110]	4 € L ⁻¹ (solution at 40%) [86]	No [35]
NTA	Organic	Biodegradable [92]	Moderately toxic [92]	n.f.	n.f.
EDDS	Organic	Biodegradable [91,111]	Non-toxic [110]	n.f.	Yes [72,88]
EDDHA	Organic	Biodegradable [111]	Non-toxic [111]	n.f.	Yes [56]
HA	Organic	Biodegradable [101]	Non-toxic [75]	1000 € t ⁻¹ (sodium humate)	Yes [101,107]

n.f. = not found.

Other aspects, such as the *pKa* values and the stability constants of the complexes (Fe(II)-L and Fe(III)-L) formed, have been summarized in Table 2. As previously stated, the stability constant indicated the tendency of forming the Fe-L complex. From the results summarized in Table 2, citrate and oxalate ligands present relatively low stability constant, and thus, higher CA:Fe ratios would be needed when using these CAs compared to others having higher stability constants, such as PPP, EDDHA or EDTA. On the other hand, as previously mentioned, it can be observed that those CAs presenting lower stability constants of Fe-L complexes (citrate and oxalate) have lower *pKa* values. It should be considered that the addition of CAs with low *pKa* values would decrease the pH of the MF system. In this way, the possible ecological impact on the soil should be considered before selecting these CAs.

Table 2. pKa values of CAs and stability constants (Log β) of the Fe(II)/(III)-L formation.

	PPP	Citrate (CitrA)	Citrate (SC)	Oxalate (OA)	EDTA	NTA	EDDS	EDDHA	HA
pKa: pKa ₁	0.8 [53]	3.0 [112]		1.2 [113]	2.0 [114]	1.8 [95]	2.4 [114]	6.3 [115]	4.1–8.8
pKa ₂	2.3 [53]	4.6 [112]		4.2 [113]	3.0 [114]	2.3 [95]	3.9 [114]	8.6 [115]	[116]
pKa ₃	6.7 [53]	5.8 [112]			6.4 [114]	9.4 [95]	6.8 [114]	10.2 [115]	
pKa ₄	9.5 [53]				10.4 [114]		9.8 [114]	11.7 [115]	
Log β of Fe(II)-L	18.4 [56,117]	3.2 [118]	15.5 [55,65]	4.5 [55]	14.3 [55,82]	8.1 [82]	n.f.	14.3 [119]	1.3 [116]
Log β of Fe(III)-L	39.2 [55]	11.5 [120] 11.9 [118]	25 [55,65]	7.5 [55]	25.1 [55,82]	15.9 [82,92]	20.6 [97] 22.0 [121]	33.9 [119]	2.5 [116]

n.f. = not found. pKa₁₋₄ are the acid ionization constant values for a polyprotic acid, which corresponds to Equations (25)–(28), Log β of Fe(II)-L correspond to Equation (12) and Log β of Fe(III)-L, to Equation (13).

2.4. Kinetic Constants of Chelate-Modified Fenton Process

The kinetic constants found in the literature for the main CAs studied in the MF process (Equations (14), (18), (23), and (24)) and the corresponding to the homogeneous Fenton reaction (in the absence of CA), have been summarized in Table 3. In addition, the main reactive oxygen species (ROS) involved in these reactions have also been included.

Regarding radical species, it has been reported that under acidic conditions OH[•] was the main oxidizing intermediate generated in the Fenton system. However, at near-neutral pH, the reactive intermediate shifted to Fe(IV) compounds [122]. However, contradictory conclusions on the nature of reactive intermediate formed in MF systems have been obtained in the literature [123]. To clarify this aspect, a recent study carried out by Wang et al. supported that Fe(II)-L (L= OA, CitrA, NTA, EDTA, PPP, and tetrapolyphosphate (TPP)) tended to catalyze H₂O₂ to generate OH[•] rather than Fe(IV) [123]. Moreover, some authors have recently clarified the role of the O₂^{•-} in the EDDS-MF [47] and EDDHA-MF systems [56].

A major effort has been made to find as much data as possible with respect to the kinetic rate constants of the reaction mechanism of Fe(II)-L oxidation (and potentially Fe(III)-L reduction) in the presence of different CAs, and the negative hydroxyl radical (from H₂O₂ decomposition) scavenger effect of the ligand. However, no values have been found for many of the cases (mainly those related to EDDS, EDDHA and HA ligands), highlighting the need for further research in this field. It has also been difficult to obtain a reliable literature estimate for the reduction rate constant of Fe(III)-L to Fe(II)-L by superoxide radicals (Equation (18)).

As shown in Table 3, the addition of CAs significantly increases the reaction rate constant of Equation (14), compared to the corresponding traditional Fenton Equation (1). As previously reported, the higher stability constant of Fe(III)-L indicates a higher reaction rate of Fe(II)-L with oxidant [41,124].

Concerning the scavenger effect of the CAs under study, oxalate has the lowest reaction rate constants corresponding to Equations (23) and (24), respectively. This would justify its use for treating more recalcitrant pollutants (with low $k_{\text{contaminant, OH}^{\bullet}}$ values).

Table 3. Kinetic constants for the Fenton process in the presence of different CAs.

Ligand (L)	ROS Involved in Pollutant Degradation	$k_{\text{Fe(II)-L, H}_2\text{O}_2}$ ($\text{M}^{-1} \text{s}^{-1}$) Equation (14)	$k_{\text{Fe(III)-L, O}_2^{\bullet-}}$ ($\text{M}^{-1} \text{s}^{-1}$) Equation (18)	$k_{\text{Fe(II)-L/Fe(III)-L, OH}^\bullet}$ ($\text{M}^{-1} \text{s}^{-1}$) Equation (23)	$k_{\text{L, OH}^\bullet}$ ($\text{M}^{-1} \text{s}^{-1}$) Equation (24)
-	OH [•] (acidic pH) or Fe(IV) (neutral pH) [49]	Equation (1): 40–80 [21,24]	n.f.	Equation (4): Fe(II): 2.5–5 × 10 ⁸ [21,24]	-
PPP	OH [•] [123]	1 × 10 ⁵ [53,69,78]	n.f.	n.f.	2.2 × 10 ⁵ [125] 9 × 10 ⁵ [126]
Citrate	OH [•] [64,123]	3.6 × 10 ³ [64] 4 × 10 ³ [25] 4.9 × 10 ³ [69]	800 [25]	Fe(II)-L: 1.2 × 10 ⁸ [25] Fe(III)-L: 1.2 × 10 ⁸ * [70]	5 × 10 ⁷ [126,127] 1.2 × 10 ⁸ (pH = 3), 2.4 × 10 ⁸ (pH = 6), 3.2 × 10 ⁸ (pH = 6.6) [70]
Oxalate	OH [•] [123]	3.1 × 10 ⁴ [77]	<1.0 × 10 ⁶ [128]	Fe(II)-L: n.f. Fe(III)-L: 1 × 10 ⁶ [126]	1.4 × 10 ⁶ [79] 7.7 × 10 ⁶ [128] 1 × 10 ⁷ [70]
EDTA	OH [•] [123]	3.2 × 10 ³ [25]	6 × 10 ⁴ [25] 1.2 × 10 ⁶ (pH = 7.3) [44]	Fe(II)-L: 5 × 10 ⁹ [126] Fe(III)-L: 7.0 × 10 ⁸ – 1.6 × 10 ⁹ [126]	4 × 10 ⁸ (pH = 4) [79] 2 × 10 ⁹ (pH = 9) [79,129]
NTA	OH [•] [26,123]	9.7 × 10 ³ – 1.8 × 10 ⁴ [95]	n.f.	Fe(II)-L: 2.3–5 × 10 ⁹ [126] Fe(III)-L: 4.8 × 10 ⁸ [26] 1.6 × 10 ⁸ [95,126]	5.5 × 10 ⁸ (pH = 6), 2.5 × 10 ⁹ (pH = 9), 4.2 × 10 ⁹ (pH = 10) [95]
EDDS	OH [•] (80%) and O ₂ ^{•-} (20%) [47]	n.f.	n.f.	Fe(II)/(III)-L: 2.0–5.2 × 10 ⁸ [47]	2.5 × 10 ⁹ [46]
EDDHA	OH [•] (50%) and O ₂ ^{•-} (50%) [56]	n.f.	n.f.	n.f.	n.f.
HA	OH [•] [130] or O ₂ ^{•-} [105]	n.f.	n.f.	n.f.	1.4 × 10 ⁴ LmgC ⁻¹ s ⁻¹ [130]

n.f. = not found. * These authors supposed that $k_{\text{Fe(III)-L, OH}^\bullet}$ was like $k_{\text{L, OH}^\bullet}$.

3. Application of Chelating Agents in Soil Remediation by Modified Fenton

3.1. Factors Affecting Contaminant Removal

When applying chelate-modified Fenton technology for the remediation of contaminated soils, some common factors can affect the effectiveness of the process. The most important ones are detailed below.

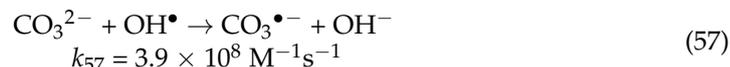
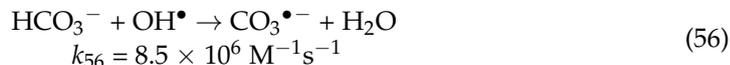
3.1.1. Contaminant Accessibility

An important aspect in the remediation of contaminated soils derives from the accessibility of the contaminants. Pollution ageing leads to the migration of contaminant from easily accessible to difficult sites, becoming sequestered in the soil matrix [35], which reduces the chemical remediation efficiency of hydrophobic organic pollutants [131]. Consequently, several authors have reported that pollutant removal by the Fenton process decreases with contamination ageing [85]. For example, Jorfi et al. observed that working under the same experimental conditions, removing of pyrene in spiked contaminated soil was 91% compared to the 43% obtained in a real soil sample [85]. Thus, one of the most limiting factors in soil remediation is the low availability of contaminants, partly sequestered in the aged soils. Although some authors proposed that Fenton reaction can improve the remediation process due to the desorption of hydrophobic contaminants [85,132], a refractory fraction of the contaminant remained in the solid phase after the treatment [133]. In this sense, chelating agents can also enhance the desorption of the contaminants [35,134,135], and therefore favor the accessibility of the contaminant towards the oxidant.

3.1.2. Soil Matrix: Organic Matter, Carbonates and Metals Content

Another limiting factor in the remediation of soils when using CAs is the negative effect of the soil matrix. It has been reported that the soil type determines the concentration of soluble Fe(III) in soil slurry systems, probably through hydrolysis and adsorption [59]. Meanwhile, the stability of H₂O₂ seems to relate not only to the stability of Fe(III) complexes

but also to the properties of the soil system [55]. Bicarbonate and carbonate are present in high concentrations in calcareous soils. Their presence has been reported to cause competitive reactions with hydroxyl radicals, inhibiting the degradation of the contaminant by the OH• (Equations (56) and (57), with the corresponding k_{56} and k_{57}) [136], generated in the MF process.



In this way, Lemaire et al. reported that the degradation rate of PAH did not increase significantly with the addition of citric acid [137]. The high carbonate content of the soil (35 g kg^{-1}) led to hydrogenocarbonate and carbonate ions transfer to the liquid phase, increasing hydroxyl radical scavenging (Equations (56) and (57)). The high content of soil organic matter (SOM) also increases oxidant consumption [35,59,88]. Moreover, when the concentration of SOM is high, part of the hydroxyl radicals generated is consumed by side reactions, decreasing the pollutants' degradation [137]. CAs might alter the association between SOM and the inorganic matrix or affect the SOM structure itself [138], and this should also be studied before selecting a chelating agent. As stated in Section 2.2.3, in the case of soil with high content of SOM, it could combine with iron ions to form Fe-SOM and catalyze the decomposition of H_2O_2 to produce OH•, avoiding the use of other chelating agents [81,109].

On the other hand, the intrinsic minerals in soil can be positive for soil remediation by MF. These minerals can serve as catalysts for the oxidant, increasing the removal of the pollutants. For all those mentioned above, the specific characteristics of the soil should be considered to properly select the CA for MF process. In this way, the reaction mechanisms previously reported and most of them obtained performing experiments in the aqueous phase will be more complex. Although the experiments to elucidate the reaction mechanisms and kinetics for constructing predictive models for soils have been carried out using correct chemical stoichiometry, the study of some important aspects is still missing in the literature. This is the case of separate measurements of adsorbed and dissolved chemicals (CAs and catalysts), determination of proper chemical stoichiometry depending on soil matrix, measurements of filled and empty adsorption sites, calculation of time-dependent kinetic rate coefficients for each reaction or process, etc.

3.1.3. Soil Texture and Moisture

Loose soil texture can help the mass transfer of reagents, while dense soil leads to large consumption of reagents [9]. In this way, the Fenton process is favored in soils containing higher surface area and high pore volumes due to enhanced accessibility [35]. Peluffo et al. explored the effect of moisture content in the presence of chemical oxidants [139]. These authors demonstrated that an increase in soil moisture (from 25% to 37%) greatly increased the pollutant removal (phenanthrene) when a low oxidant dose was employed, whereas the results with a high oxidant dose were reversed. Moreover, the oxidant decomposition rate decreased at high moisture levels, possibly through diluting H_2O_2 -activators within the soil. Thus, for oxidative treatments of contaminated soil, the application of low doses of oxidant at low soil-moisture levels seems to be the most effective option.

3.1.4. Adsorption and Desorption of Chemicals onto the Soil

The adsorption and desorption of chemicals (chelating agent and catalyst) onto the soil is a limiting factor that should be considered when applying MF process to remediate polluted soils. Some authors observed a significant dependence of the liquid/soil phase ratio (V_L/W) on the amount of adsorption of chemicals. Adsorption is often increased with decreasing the V_L/W ratios, being the recommended ratio from 2 to 4 [140]. However, the chemicals (CAs, catalyst, etc.) mobility through the soil and the optimum V_L/W ratio

can vary depending on the type of soil studied and its composition. For example, in the Fe(III)/EDDHA system, organic matter and iron oxides or hydroxides have been identified as the most reactive soil constituents and calcium carbonate and clay as the least reactive ones for Fe-EDDHA adsorption onto the soil [140]. Determining the amount of soluble CA and Fe-L in batch and columns is a useful tool to compare the reactivities of different CAs and establish the CAs long-lasting effect on the soil solution. In this way, although several investigations have been carried out to study the Fe-L retention by the soil when using different CAs (such as EDDHA, EDTA, diethylenetriaminepentaacetic acid (DTPA), etc.) [140–142], further research is needed concerning this aspect when applying CAs to enhance Fenton process in soil remediation. To the best of our knowledge, adsorption of CAs has been scarcely studied in the literature. Rosas et al. studied the adsorption of an organic CA (citrate) and diuron, which was much lower than that of the organic pollutant [143]. To further explore this aspect, future investigations should include a detailed study of the interactions of the CA and Fe-L complexes with soil and soil constituents and its diminution from the solution related to possible degradation or adsorption mechanisms.

3.2. Results of Modified Fenton Obtained according to the Contaminant Type

The review of CAs application in the MF process will be carried out according to the main types of contaminants found in the literature for soil remediation. According to their characteristics, pollutants have been divided into the following groups: (i) BTEX and phenolic compounds, (ii) polycyclic aromatic hydrocarbons (PAHs), (iii) total petroleum hydrocarbons (TPHs), (iv) unsaturated chlorinated compounds and pesticides, and (v) saturated chlorinated compounds. The reaction rate of each contaminant with the generated hydroxyl radicals ($k_{\text{contaminant, OH}^\bullet}$, Equation (22)) will decisively influence the efficiency on its removal when applying the MF process. In this way, the $k_{\text{contaminant, OH}^\bullet}$ values found in the literature have been summarized in Table 4. It should be noted that other reactive oxidants such as superoxide radical, hydroperoxyl radical, and Fe(IV) have not been included since OH^\bullet can be considered as the dominant ROS (Table 3). However, it is noteworthy that exploring the nature of the Fe(IV) species from the MF reactions (including issues on the distinguishment from OH^\bullet) is a challenging task nowadays [144], and further research is needed to clarify the chemistry of Fe(IV).

Table 4. Kinetic constants of different organic contaminants with hydroxyl radicals.

Group	Contaminant	$k_{\text{contaminant, OH}^\bullet}$ ($\text{M}^{-1}\text{s}^{-1}$), (Equation (22))	Ref.
BTEX/phenolic compounds	Benzene	6.6×10^8	[145]
	Toluene	3.4×10^9	[145]
	Ethylbenzene	4.1×10^9	[145]
	Xylene	9.5×10^9	[145]
	Phenol	6.6×10^9	[145]
	Bisphenol-A	9.8×10^9	[146]
PAHs	Acenaphthene	8.8×10^9	[147]
	Benzo[a]pyrene	2.53×10^{10}	[147]
	Chrysene	9.82×10^9 (20 °C, pH = 7)	[147]
	Fluorene	$2.8\text{--}9.9 \times 10^9$	[147]
	Naphthalene	$0.5\text{--}1.2 \times 10^{10}$	[147]
	Phenanthrene	1.34×10^{10}	[147]
Unsaturated chlorinated compounds and pesticides	Polychlorinated biphenyls (PCBs)	5×10^9	[148]
	Diuron	4.8×10^9	[126]
	Trichloroethylene (TCE)	$3\text{--}4 \times 10^9$	[126,147]
	Tetrachloroethene (PCE)	2.8×10^9	[126]
	Pentachlorophenol (PCP)	4×10^9	[147]
	1,1-dichloroethene	6.8×10^9	[126]
	Vinyl chloride	1.2×10^{10}	[126]
	Atrazine, propazine, and terbuthylazine	$2.2\text{--}3.5 \times 10^9$	[130]
	1,2,3-trichlorobenzene	6.1×10^9	[147]
	1,4-dichlorobenzene	5.4×10^9	[147]
Saturated chlorinated compounds	γ -hexachlorocyclohexane (lindane)	5.8×10^8	[148]
	Trichloromethane	5.0×10^6	[47]

3.2.1. BTEX and Phenolic Compounds

BTEX (benzene, toluene, ethylbenzene and xylenes) and phenolic compounds are organic compounds identified as hazardous chemicals due to adverse effects on human health at very low concentrations [149]. In addition, the high-water solubility and volatility of BTEX enable them to migrate in the subsurface and contaminate soils. In this way, a great effort has been made to remediate soils contaminated by these compounds [150]. However, the application of Fenton enhanced by the addition of chelating agents (MF process) for the remediation of soils polluted with BTEX and phenolic compounds has been poorly studied to date.

The limited number of works found in the literature concerning the remediation of this pollutants group by the MF process have been summarized in Table 5. This table contains information about the CAs tested, the oxidation process and the reagents molar ratios selected as the most convenient, the type of soil treated (spiked or real), the type of experiments (batch or column), the pollutant and its concentration in the contaminated soils, the liquid to soil mass ratio (V_L/W) and the system pH, the reaction time and, finally, the main results obtained concerning the pollutants, hydrogen peroxide, and CA conversions. The same information (for the corresponding pollutants group) is collected in Tables 6–8.

Table 5. Research studies for BTEX and phenolic compounds degradation in soils using MF process.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
(a) H ₂ O ₂ Stabilizer: DP (b) Chelant: EDTA, l-AA GA, CitrA, SC _m , SC (c) Chelant: EDTA, SC	(a) Stabilization study (DP): [H ₂ O ₂] = 290–580 mM, [DP] = 58–116 mM Natural Fe species present in the soil H ₂ O ₂ :DP = 5:1	80 mg kg ⁻¹ 2,4-DMP	EDTA: 7.7 l-AA: 5.8 GA: 5.5 CitrA: 5.2 SC: 8.3 SC _m : 7	Spiked soil (3 calcareous loamy sand soils with SOM: S1: 15.2% S2: 10.1% S3: 6.4%) Batch slurry	2	(a) 24 h	(a) X _{H₂O₂} : [H ₂ O ₂] ₀ = 290 mM: S1(100%) > S2(95%) > S3(90%) [H ₂ O ₂] ₀ = 580 mM: S1(100%) > S2(60%) > S3(70%) Obs: no stabilization effect of DP with S1 X _{CA} : No data	[35]
	(b) Stabilization study (6 CAs): [H ₂ O ₂] = 290 mM, [CA] = 50 mM H ₂ O ₂ :CA = 5.8:1					(b) 1 h	(b) X _{H₂O₂} : S2 (selected) (EDTA(80%) > no CA (75%) > SC(60%) > SC _m (50%) > GA ≈ l-AA(35%) > CitrA (20%)) X _{CA} : No data	
	(c) Contaminant removal [H ₂ O ₂] = 290 mM [EDTA] or [SC] = 50 mM H ₂ O ₂ :CA = 5.8:1					(c) 1 h	(c) X _{2,4-DMP} : SC (90%) ≈ EDTA (90%) > no CA (63%) X _{CA} : No data. Obs: Fe solubilization (mM): SC(0.27) > EDTA(0.11). 2,4-DMP extraction: EDTA (34%) > SC (26%)	
SC	(a) [H ₂ O ₂] = 1470 mM, [CA] = 50 mM, [Fe(III)] = 27 mM H ₂ O ₂ :CA:Fe:EB = 313:11:6:1 (b) [H ₂ O ₂] = 4410 mM, [CA] = 47 mM, [Fe(III)] = 5 mM H ₂ O ₂ :CA:Fe:EB = 47:0.5:0.1:1	(a) 1996 mg kg ⁻¹ EB (b) 19960 mg kg ⁻¹ EB	6	Spiked soil Batch slurry	2	120 h	(a) X _{EB} : 100% X _{H₂O₂} : 100% X _{CA} : 80% Obs: soluble Fe decays as citrate disappears, H ₂ O ₂ and EB disappeared faster when [Fe(III)] was higher. (b) X _{EB} : 60% X _{H₂O₂} : 100%; X _{CA} : 100%	[50]
KH ₂ PO ₄ EDTA HAs (commercial and from compost)	[KH ₂ PO ₄] = 59 mM, [EDTA] = 10 mM, [HAs] = 1000 mg/L [H ₂ O ₂] = 1765 mM Natural Fe species present in the soil	5 mg kg ⁻¹ chlorophenol	HA and KH ₂ PO ₄ : 5.5 EDTA: 8	Spiked soil (Fe = 29.7 g kg ⁻¹ and Mn = 0.8 g kg ⁻¹) Batch slurry	5	3 h	X _{chlorophenol} : HA _{extracted} (95%) ≈ EDTA(95%) > HA _{commercial} (90%) > KH ₂ PO ₄ (78%) > no CA (76%) X _{H₂O₂} (24 h): no CA(95%) > EDTA(90%) > HA(62%) > KH ₂ PO ₄ (78%) X _{CA} : No data	[101]

DP = Potassium dihydrogen phosphate; EDTA = Ethylenediaminetetraacetic acid; l-AA = l-Ascorbic acid; GA=Gallic acid; CitrA=Citric acid; SC_m = Sodium citrate mono-hydrate; SC = Sodium citrate; S1, S2 and S3 = soils; DMP = Dimethylphenol; EB = Ethylbenzene; SOM = Soil organic matter; BTEX = Benzene, toluene, ethylbenzene and xylenes. Obs = Observations, n.f. = not found.

Vicente et al. analyzed the influence of a H_2O_2 -stabilizer (potassium dihydrogen phosphate, DP) and different CAs on the consumption of H_2O_2 and the remediation efficiency of a soil contaminated with 2,4-dimethylphenol (2,4-DMP) [35]. The application of DP reduced the H_2O_2 consumption by 40% in soils with high surface area and low SOM content. On the contrary, these authors found a negligible stabilization effect when treating soils with high SOM content, consistent with that previously reported in Section 3.1. Moreover, these authors studied the destabilization effect of H_2O_2 in the presence of different CAs, reporting the following order: EDTA < SC < SCm < l-ascorbic acid (l-AA) \approx gallic acid (GA) < CitrA. The high oxidant consumption when using EDTA can be explained by attending to the high value of the stability constant of Fe(III)-EDTA (Table 2).

On the other hand, the major H_2O_2 stabilization effect achieved in the case of CitrA can be related to the low pH obtained in this CA/soil suspension, as can be seen in Table 5, suggesting that the pH of the system notably influences H_2O_2 stability. Regarding pollutant removal efficiency (only studied in the presence of EDTA and SC), these authors reported that the addition of EDTA or SC increased the degradation of the pollutant (2,4-DMP) by 27%. The results indicated that the presence of these CAs favors the desorption of the entrapped pollutant and solubilizes part of the iron from the soil, resulting in a significant increase in 2,4-DMP degradation [35].

Similarly, Pardo et al. reported an increase in ethylbenzene (EB) conversion when SC was used as CA [50]. Besides, citrate as sodium salt controlled the H_2O_2 decomposition rate and maintained a neutral pH. However, the concentration of soluble iron decayed as citrate disappeared from the reaction media [50]. This fact highlights the importance of studying separately the concentration of the chemicals (CA and catalyst) both dissolved in the aqueous phase and adsorbed onto the soil, aspects rarely reported in the literature.

The remediation of soils artificially contaminated with 3-chlorophenol was explored using extracted humic acids from compost as CA and H_2O_2 stabilizer [101]. The extracted HAs allowed to achieve a H_2O_2 lifetime close to the one obtained with a traditional stabilizing agent, being effective in removing the pollutant (95% in the test carried out with 1000 mg/L of extracted HAs at 3 h of reaction time). The contaminated soils were also treated by MF using a traditional chelating agent (EDTA) and commercial HAs. The test performed with EDTA led to more equivalent results than extracted HAs, whereas the 3-chlorophenol removal achieved with commercial HAs was lower [101].

Therefore, based on the limited results found for this group of contaminants, the CAs recommended for BTEX and phenolics compounds removal from soil are: Citrate > HAs > EDTA. Citrate (as CitrA and SC) stands up as a more suitable stabilizer and CA than EDTA in the MF process because the last one reacts with hydroxyl radicals 10 times faster than citrate (see kinetic constants, corresponding to Equation (24), summarized in Table 3), showing high OH^\bullet scavenging effect. Moreover, the citrate use leads to higher iron solubilization, a hydrogen peroxide stabilization effect [35], and entails fewer environmental problems than EDTA. Finally, it is preferable to use citrate as sodium salt (SC) instead of the acidic form (CitrA) because this CA promotes a near-neutral soil pH during the reaction, minimizing the environmental impact of the remediation technique [35,50]. On the other hand, although similar contaminant removal was obtained with HAs and EDTA [101], using compounds with lower environmental impacts is highly recommended, as is the case of HAs.

A second dose of oxidant and Fe-citrate increases the target pollutant degradation [151], although this option would be only recommended when treating recalcitrant pollutants with low hydroxyl radical reaction rate constants. In this way, Liang et al. reported that among four BTEX compounds, benzene was the most resistant to oxidation in the aqueous phase [152], the reaction rate constant of benzene with hydroxyl radicals ($k_{\text{benzene, OH}^\bullet} = 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [145]) being one order of magnitude lower than those of toluene, ethylbenzene, and xylene, as summarized in Table 4. In this study, benzene conversion increased when using different CAs, following the descending order (at the same operating conditions): CitrA (100%) > EDTA (50%) [152], which is in line with the above mentioned.

An alternative to EDTA is the use of the environmentally friendly ligand EDDS. Huang et al. demonstrated the effective removal of Bisphenol-A by Fenton-EDDS application when treating polluted waters [47]. In this way, it would be interesting to test the efficacy of the EDDS removing BTEX and phenolic compounds in real soil matrices, which has not been reported in the literature so far. However, it should be considered that the reaction rate constant of EDDS with OH^\bullet is relatively high ($k_{\text{EDDS}, \text{OH}^\bullet} = 2\text{--}5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [47], Table 3) and, therefore, EDDS application would not be recommended for the remediation of highly refractory pollutants, such as benzene ($k_{\text{benzene}, \text{OH}^\bullet} = 6.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [145], Table 4), due to the high possibility for competition between EDDS and the pollutant for the hydroxyl radicals formed (Equations (23) and (24)).

3.2.2. Polycyclic Aromatic Hydrocarbons (PAHs)

The polycyclic aromatic hydrocarbons (PAHs) contamination is of great concern due to the high toxicity, mutagenic and carcinogenic effects of these pollutants. PAHs can be strongly adsorbed to soil organic matter, encapsulated in soil mineral, and presented in the form of dense non-aqueous phase liquid (DNAPL), which makes the remediation process difficult [153]. Therefore, substantial research has been undertaken to develop efficient techniques to remove persistent PAHs from soils or sediments [28]. The most commonly studied PAHs are: naphthalene (NAP), phenanthrene (PHE), benzo(a)fluoranthene (Baft), 2-methylnaphthalene, anthracene (ANT), benzo(k)fluoranthene (Bkf), fluoranthene (FLUT), benzo(a)pyrene (BaP), acenaphthylene (ACEL), pyrene (PYR), indeno (1,2,3-cd)pyrene (INDE), acenaphthene (ACE), fluorene (FLU), dibenzo(a,h)anthracene (BaT), chrysene (CHR), benzo (g,h,i)perylene (BghiP), and benzo(a)anthracene (BaA) [154]. A wide variety of CAs has been explored in MF process to remediate PAHs (Table 6), including sodium pyrophosphate (SP), EDTA, oxalate (as oxalic acid (OA) and sodium oxalate (SO)), citrate (as citric acid (CitrA) and sodium citrate (SC)), malic acid (MA), humic acid (HA), cyclodextrins (CD), catechol (CC), and gallic acid (GA), most of which are discussed in Section 2.

Venny et al. performed a comparison of various organic and inorganic CAs to assist MF oxidation [55]. Their results revealed that inorganic SP was superior in pollutant removal efficiency (79.5% and 89.1% of conversion for PHE and FLUT, respectively) and the application of SC resulted in lower PAH removal (58.5% and 57.5% of pollutant conversion for PHE and FLUT, respectively at 24 h of reaction time) (Table 6). Similar findings were obtained by Jorfi et al., reporting the maximum pollutant removal efficiency by employing SP, 93%, compared to 86%, 75%, 72%, and 71% achieved at the same conditions for EDTA, SC, HA and FA, respectively [85]. In both studies, the higher conversion of PAHs achieved when using an inorganic CA (SP) than the organic ones was probably due to the lower competition of this ligand for the OH^\bullet , as indicated by the respective $k_{\text{L}, \text{OH}^\bullet}$ and $k_{\text{Fe-L}, \text{OH}^\bullet}$ values for these CAs in Table 3. Contrary to the results mentioned above [55,85], the use of inorganic CAs (SP and DP) was not effective in hydrogen peroxide activation in the study carried out by Shih et al., where the PAHs degradation pursued the following descending order: SC (68%) > OA \approx DP (51%) > EDTA (44%) > SO (36%) > SP (32%) (Table 6) [57]. Different factors can justify such variations in the results reported in the literature.

Firstly, the differences in the chemical composition of the soil may play a crucial role, as previously mentioned in Section 3.1.2. In this way, although pyrophosphate is not oxidized by hydroxyl radicals [73], when phosphates are added to soils containing calcium carbonate adsorption, and precipitation of phosphate-containing minerals occur, which in turn reduced soil permeability and led to the ineffectiveness of the Fenton treatment [155]. Thus, SP and DP may combine with both natural mineral components of soils and Fe(III) in solution in the aqueous phase, forming stable complexes. However, the Fe-monophosphate complex is insoluble. Hence, the concentration of dissolved Fe(III) decreases with time [54], reducing the efficiency of inorganic CAs in some matrix soils. In this way, as stated previously in Section 3.1.4, future studies should investigate the interactions of CAs and Fe-L formed with soil and the different soil components, as well as the CA and Fe-L

diminution from the solution related to a possible degradation, or adsorption mechanisms, due to the strong influence of these factors on process performance.

Secondly, the significant differences obtained in the pollutant removal may be explained by the concentration of the inorganic CA (SP) used in these studies. For example, in the work carried out by Venny et al., SP was added in a CA:Fe molar ratio of 0.8:1 [55], whereas the ratio used by Shih et al. was 5:1 [57]. At high SP concentration, the strong steric hindrance impeded the interaction between oxidant and Fe(II)-SP, decreasing the yield of OH^\bullet . Moreover, the reduction rate of Fe(III)-SP also decreases [52], which may be the reason for the low efficiency obtained by Shih et al. for the use of SP in the MF process [57].

Regarding the use of SC and Citra, controversial results have been found in the literature. For example, Shih et al. found that SC was the most effective of four CAs used to stabilize ferrous iron [57]. However, the use of this CA, led to poor results for other researchers [55]. As stated above, the CA:Fe ratio is an important factor conditioning the nature and concentration of the oxidizing species generated. For example, the relatively low stability constant of Fe-citrate requires high CA:Fe ratios, which justifies the low pollutant conversions achieved in the study carried out by Venny et al. by using a low SC:Fe ratio of 0.5:1 [55]. In the same way, the degradation rate of PAHs did not significantly increase with the addition of Citra [137], which was justified by the low Citra:Fe molar ratio employed in this case (0.5:1). However, although the use of high citrate:Fe ratios (from 1:1 to 25:1) coincides with high contaminant conversion values [57,151,156], if this CA is present in relatively high concentrations, it can also compete with the pollutant for hydroxyl radicals ($k_{\text{Fe-citrate, OH}^\bullet} = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{citra, OH}^\bullet} = 5 \times 10^7 - 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, as summarized in Table 3), reducing the pollutant degradation efficiency [73]. Therefore, an optimal concentration of citrate should be high enough to favor the formation of the Fe-citrate complex but not too much to cause an important scavenging effect on the OH^\bullet produced.

As in the case of the previous CAs, controversial results have been found in the literature regarding the use of EDTA. As summarized in Table 6, some authors have obtained good results when using this CA for PAHs degradation [55,85]. However, no significant improvement associated with its use was observed in other studies [57,157]. The differences could reside in the presence of heavy metals (HM) in real contaminated sediments, with higher stability constants with EDTA than iron ($\text{Log } \beta_{\text{HM-EDTA}} > \text{Log } \beta_{\text{Fe-EDTA}}$), and thus being responsible for the moderate efficacy of this CA in the mentioned works.

As for the case of SC, the slower rate of PAHs degradation when using OA compared to SP and EDTA in the study of Venny et al. could be attributed to the fact that higher CA:Fe molar ratio than the used (OA:Fe > 1) is needed, owing to the weaker complexation ability of oxalate with iron ions in contrast to SP and EDTA (Table 2). Accordingly, better results were obtained with OA compared to EDTA and SP by Shih et al., who used a higher CA:Fe molar ratio (OA:Fe = 2:1) [57].

Regarding the use of less common organic CAs (not covered in Section 2), such as catechol (CC), the addition of this CA resulted in a significant increase in the degradation of heavy PAHs [158]. On the contrary, in the study carried out by Nam et al., the addition of CC and GA resulted in a decline in the overall performance of the process compared to the unmodified Fenton process [37]. However, the system's pH was maintained at neutral values, which allowed the combination of the chemical oxidation process with subsequent biodegradation. In this way, combined MF and biodegradation resulted in approximately 98% removal of low molecular weight PAHs and 70% removal of high molecular weight PAHs.

In addition to all the above, excellent performance in the remediation of PAHs-contaminated soils has been reported by means of persulfate enhanced MF (PS-MF) treatment [55,158]. These findings imply the compatibility of $\text{SO}_4^{\bullet-}$ radical anion (coming from PS decomposition) in enhancing the MF treatment coupled with CAs even at remarkably low concentration. However, there is not much information in the bibliography regarding the application of this treatment and further research is required.

Table 6. Research studies for PAHs degradation in soils using MF process.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
SP EDTA OA SC MA	(a) <i>Fenton</i> [H ₂ O ₂] = 480 mM, [Fe(III)] = 60 mM H ₂ O ₂ :SP:EDTA:OA:SC:MA:Fe = 8:0.8:0.7:0.7:0.5:0.5:1 (b) <i>Fenton + PS</i> [H ₂ O ₂] = 324 mM, [PS] = 120 mM, [CA] = 60 mM, [Fe(III)] = 60 mM PS:H ₂ O ₂ :CA:Fe = 2:5.4:1:1	1000 mg kg ⁻¹ of PHE and FLUT	7	Spiked soil (loamy sand) Batch slurry	3	24 h	(a) X _{PHE} : SP(79.5%) > EDTA(78.7%) > OA(73.1%) > MA(68.5%) > SC(58.5%) X _{FLUT} : SP(89.1%) > EDTA(78.5%) > MA(76.0%) > OA(72.7%) > SC(57.2%) X _{H₂O₂} (3 h): SP(10%) < OA(95%) < SC(100%) < MA(100%) < EDTA(100%) X _{CA} : No data (b) X _{PHE} : SP(95.4%) X _{FLUT} : SP(92.3%) X _{H₂O₂} : No data, X _{CA} : No data	[55]
SP SC EDTA FA HA	[H ₂ O ₂] = 300 mM, [CA] = No data, [iron nano-oxide] = 30 mM H ₂ O ₂ :Fe = 10	100 mg kg ⁻¹ PYR	7	(a) Spiked soil (silty sand) (b) Aged soil (1 year) (c) Real soil Batch slurry	3	6 h	(a) X _{PYR} : SP(93%) > EDTA(86%) > SC(75%) > HA(72%) > FA(71%) (b) X _{PYR} : SP(91%) (c) X _{PYR} : SP(43%) X _{H₂O₂} : No data, X _{CA} : No data	[85]
SP SO EDTA OA SC DP	[H ₂ O ₂] = 50 mM [Fe(II)] = 0.25–2.5 mM SP:EDTA:SO:OA:SC:MP:Fe = 5:5:2:2:4:2:1 CA:Fe(w:w) = 1:1	4.23 mg kg ⁻¹ PAHs (16 types)	7.2	Real sediments TOC = 8.5% SOM = 10.5% Batch slurry	25	24 h	X _{PAHs} : SC(68%) > OA ≈ DP(50.5%) > EDTA(44%) > SO(36%) > X _{SP} (32%) X _{H₂O₂} : No data, X _{CA} : No data	[57]
CitrA	[H ₂ O ₂] = 1800 mM (15-fold SMR), [CA] = 90 mM, [Fe(II)] = 180 mM H ₂ O ₂ :CA:Fe = 20:1:2	1550 mg kg ⁻¹ PAHs (16 types)	7.4	Real soil (sandy loam) Batch slurry	2	4 d	X _{PAHs} : 45% X _{H₂O₂} : No data, X _{CA} : No data Obs: cyclodextrin and/or CAs did not improve the oxidation process. Limiting factors: low PAHs availability	[137]
EDTA	[H ₂ O ₂] = 570 mM, [CA] = [Fe(II)] = 26 mM H ₂ O ₂ :CA:Fe = 22:1:1	1200 and 2800 mg kg ⁻¹ PHE and PYR	5.2	Aged soil (15 month) (109 mg kg ⁻¹ Fe) Batch slurry	2	7 d	X _{PHE} : 10% X _{PYR} : 37% X _{H₂O₂} : No data, X _{CA} : No data	[157]
EDTA	[H ₂ O ₂] = 1730 mM, [CA] = 0.08 mM, [Fe(III)] = 2.1 mM H ₂ O ₂ :CA:Fe = 21900:1:27	21420 mg kg ⁻¹ PAHs (16 types)	8	Real soil Batch slurry	2.5	2 d	X _{PAHs} : 71.3% X _{H₂O₂} : 100% (2 h) X _{CA} : No data Obs: PAHs with 5 and 6 rings showed lower removal rates	[159]

Table 6. Cont.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
15 CAs tested *: CC and GA selected	[H ₂ O ₂] = 882 mM, [CC] = 37 mM, [GA] = 41 mM, [Fe(II)] = 35 mM H ₂ O ₂ :CA:Fe = 24:1:1	3724 mg kg ⁻¹ PAHs (NAP, FLU, PHE, ANT, PYR, CHR, BaP)	6–6.5	Real soil (loamy sand) Batch slurry	4	24 h	CC: X _{NAP} (84.7%), X _{FLU} (32.8%), X _{PHE} (31.7%), X _{ANT} (29.2%), X _{PYR} (41.7%), X _{CHR} (12%), X _{BaP} (45.2%) GA: X _{NAP} (89%), X _{FLU} (36.2%), X _{PHE} (29.9%), X _{ANT} (33.2%), X _{PYR} (41.1%), X _{CHR} (8.9%), X _{BaP} (50.4%) X _{H₂O₂} : No data, X _{CA} : No data Obs: X _{pollutant} > in Fenton (pH = 2–3 acid soil) than MF but MF allowed the combination of the treatment with biodegradation.	[37]
CC	(a) Fenton [H ₂ O ₂] = 100 mM, [CA] = 2 mM, [Fe(II)] = 2 mM H ₂ O ₂ :CA:Fe = 50:1:1 (b) Fenton + PS [H ₂ O ₂] = 50 mM, [PS] = 50 mM, [CA] = 2 mM, [Fe(II)] = 2 mM PS:H ₂ O ₂ :CA:Fe = 25:25:1:1	16 PAHs (light 700 mg kg ⁻¹ , heavy 1700 mg kg ⁻¹)	7.7	Real soil Batch slurry	3.3	n.f.	(a) Ligth: 98%, Heavy: 97%, Total PAHs: 98% (b) Ligth: 93%, Heavy: 90%, Total PAHs: 92% X _{H₂O₂} : No data, X _{CA} : No data	[158]

SP = Sodium pyrophosphate; EDTA = Ethylenediaminetetraacetic acid; OA = Oxalic acid, Citra = Citric acid; MA = Malic acid; SC = Sodium citrate; FA = Fulvic acid; HA = Humic acid; GA = gallic acid; EDDS = Ethylenediaminedisuccinic acid; SO = Sodium oxalate; DP = Potassium dihydrogen phosphate; CC = Catechol; PAH = Polycyclic aromatic hydrocarbon; PHE = Phenanthrene; FLUT = Fluoranthene; PYR = Pyrene; NAP = Naphthalene; CHR = Chrysene; BaP = Benzo(a)pyrene; BaA = Benzo(a)anthracene; Baft = Benzo(a)fluoranthene; FLU = Fluorene; 2-MET = 2-Methylnaphthalene; * 15 potential CAs were tested. Among them, catechol (CC) and gallic acid (GA) were chosen based on the degradation efficiency of PAHs. Obs = Observations, n.f. = not found.

3.2.3. Total Petroleum Hydrocarbons (TPHs)

Total petroleum hydrocarbons (TPHs) are one of the most common pollutants in the environment. TPHs include a broad family of several hundred hydrocarbon compounds, including volatile petroleum hydrocarbons (VPHs, C₂–C₅) and extractable petroleum hydrocarbons (EPHs, C₆–C₄₀) that originally come from crude oil, which is used to make petroleum products: gasoline, kerosene, diesel fuels, jet fuels, mineral-based motor oils, fuel oils, etc.

Conflicting results on the use of citrate in MF process for the remediation of TPHs contaminated soils have been found in the literature. As summarized in Table 5, some authors have obtained interesting results when using CitrA [38,72,74,160,161]. Chang et al. reported that the stabilizing effect order for different CAs on the decomposition of hydrogen peroxide and TPHs removal was: Citrate > Phosphate > EDDS > EDTA, as summarized in Table 7 [72]. These results agree with those obtained by Vicente et al., who reported a higher H₂O₂ stabilizing effect and chelating efficacy of citrate than EDTA when treating 2,4-DMP polluted soils [35]. In contrast, Pardo et al. stated that higher TPHs removal efficiencies were obtained (up to 75%) after the treatment of a diesel-polluted soil in the absence of citrate (coming from SC) [51] than in the presence of this CA ($X_{\text{TPHs}} = 37\%$). This fact could be explained by the pH of the system (pH = 6). As indicated in Citrate/Citric acid (CitrA) Section (Table 3), as the pH of the reaction medium increases, the rate constant of citrate with OH• increases. Consistently, at these conditions, the CA (citrate) competes with the pollutant for the hydroxyl radicals generated, decreasing the efficiency of the remediation treatment [51].

For their part, Ouriache et al. and Polli et al. suggested that the use of EDTA improved the removal of TPHs from polluted soils [84,162]. On the contrary, other authors reported that the presence of EDTA in the MF process was not beneficial for the degradation of these pollutants (hydrocarbon fractions treated: C₁₀–C₄₀ and C₁₀–C₁₆) [81,163]. All these studies were conducted with real contaminated soils. However, such variations in the results obtained can be justified by the differences in the SOM and total organic carbon (TOC) content of the soils treated. Therefore, the EDTA application has been considered suitable for remediating soils with relatively low TOC and SOM contents [84,162].

Conversely, when soil TOC and SOM content was higher than 10%, the efficiency of the treatment decreased by adding EDTA [81,163]. This fact can be attributed to the formation of the complex Fe(III)-SOM, which presents a stability constant 20 orders of magnitude lower than Fe(III)-EDTA (Table 3). Fe(III)-EDTA is less available for decomposing hydrogen peroxide than Fe(III)-SOM. Thus, the presence of EDTA inhibits the participation of native Fe oxides in the Fenton reactions, decreasing the efficiency of remediation treatment. These findings highlight the importance of studying and knowing the characteristics of the contaminated soil before selecting the CA. In the case of soils with high SOM content, humic and fulvic acids can act as CAs, increasing iron availability.

HAs can also be obtained from organic wastes. In this line, a diesel-contaminated soil collected in a former gasoline station was treated by the MF process using HAs extracted from compost [107]). A traditional stabilizer of hydrogen peroxide (KH₂PO₄) was also used in this work. The authors observed a beneficial effect of extracted HAs in terms of diesel removal (90% of diesel elimination when using KH₂PO₄ together with the HAs extracted from compost vs 55% without any amendment) [107]).

Some studies concerning the application of MF process have been focused on the degradation of methyl tert-butyl ether (MtBE), a fuel additive. Without the addition of an external iron source, the effectiveness of a MF process was investigated by performing column tests on an artificially MtBE contaminated soil [87]. The obtained results showed that preconditioning soil with EDTA significantly enhanced MtBE oxidation. Moreover, no pollutant by-products were detected, suggesting that the tert-butyl group of MtBE was completely degraded [87]. This process was also successfully applied to the pilot-scale treatment of a site contaminated by MtBE, using hydrogen peroxide catalyzed by naturally occurring iron mineral, chelating agents (EDTA and SC) and hydrogen peroxide stabilizer

(potassium hydrogen phosphate). The remediation process allowed to meet the clean-up goals in an area of 75 m² [86].

Six iron compounds were tested as catalysts for the remediation of a diesel contaminated soil by MF (one of them, Fe(III)-NTA). In the presence of the Fe-CA, 80% of pollutant removal was achieved after 1 h of reaction [164]. Gong et al. studied the application of a MF process, using Fe(III)/NTA in a molar ratio of 1:1 as a catalyst, coupled with a bioremediation treatment [165]. A TPHs conversion of 89% was obtained in the combined treatment (after bioremediation for 20 weeks) compared with 55% in the biological treatment alone without EDTA addition.

Additionally, as stated in the case of PAHs, some authors have studied the sequential addition of hydrogen peroxide (stepwise addition of H₂O₂), reporting that following this remediation strategy, the elimination of TPHs can considerably increase [72,74]. After the sequential addition of the oxidant, the three-time addition of H₂O₂ was the optimal dose considering treatment efficiency and economic aspects. In the presence of citrate, Xu et al. achieved a TPHs degradation of 51%, which increased up to 93% after applying a biological treatment [74].

The remediation of these compounds has been recently studied, combining the MF process and bioremediation. For example, Guzmán-López et al. evaluated the degradation of TPHs from soil artificially contaminated with crude oil by MF with citrate as a CA followed by a biostimulation treatment (with nutrients and oil palm bagasse used as an amendment), obtaining exciting results [166].

Table 7. Research studies for TPHs degradation in soils using MF process.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
SC	[H ₂ O ₂] = 2000–4000 mM, [CA] = 50 mM, [Fe(III)] = 20 mM H ₂ O ₂ :CA:Fe = 200–100:2.5:1	1000 and 10,000 mg kg ⁻¹ B20 biodiesel blend (20% FAME)	4.5–6	Spiked soil (sandy clay loam) Batch slurry	2	300 h	X _{TPH} : 37% and 35% (H ₂ O ₂ 4M and 2M, respectively) Obs: in the absence of SC, X _{TPH} up to 75% X _{H₂O₂} : 20% (120 h), 40% (200 h) and 100% (240h) Obs: in the absence of SC, X _{H₂O₂} ≈ 90% (<4 h) X _{CA} : 30% (120 h), 60% (240 h) and 100% (300h)	[51]
CitrA	[H ₂ O ₂] = 980 mM, [CA] = 500 mM, [Fe(II)] = 250 mM H ₂ O ₂ :CA:Fe = 4:2:1	10,000 mg kg ⁻¹ of lubricant	Neutral	Spiked soil (clay loam) Batch slurry	3	5 h	X _{lubricant} : 74.5% X _{H₂O₂} : No data, X _{CA} : No data	[38]
Citrate Phosphate EDDS EDTA	[H ₂ O ₂] = 4400 mM, [CA] = 50 mM Natural Fe species present in the soil H ₂ O ₂ :CA = 88	(a) 8000 mg kg ⁻¹ diesel oil (70% alkanes-30% aromatic HCs) (b) 1–2 and 1823 g kg ⁻¹ (soils A, B, C and D)	n.f.	(a)Spiked soil (Slightly acidic loamy sand) (b)Real soil (A,B,C,D) (Sandy loam) Column	0.375	2 h	(a) X _{TPH} : Citrate(80%) > Phosphate (60%) > EDDS(58%) > EDTA(41%) X _{H₂O₂} : Citrate (55%) < Phosphate (65%) < EDDS(85%) < EDTA (90%); X _{CA} : No data (b) X _{TPH} (Citrate): soil A (65%) and soil B (75%) 3-Consecutive H ₂ O ₂ addition (24-48-72h, Citrate: soil C (94%) and soil D (93%).	[72]
CitrA	ElectroFenton [H ₂ O ₂] = 3000 mM, [CA] = 100 mM H ₂ O ₂ :CA = 30	10,000 mg kg ⁻¹ petroleum (TPHs)	2–4	Spiked soil (kaolin, low permeability)	n.f.	15 d	X _{TPH} : 89% Obs: In the absence of CitrA, X _{TPH} 27%. X _{H₂O₂} : No data, X _{CA} : No data	[160]
CitrA	ElectroFenton [H ₂ O ₂] = 2200–2900 mM [CA] = 100 mM H ₂ O ₂ :CA = 22–29	80.4 mg kg ⁻¹ TPH	<5	Real soil 7632 mg kg ⁻¹ Fe	n.f.	15-27d	X _{TPH} : 54.4% and 58.2% after 15 and 27 days X _{H₂O₂} : No data, X _{CA} : No data	[161]
CitrA SOLV-X OA	[H ₂ O ₂] = 490 mM/doses (5 doses) [Fe(II)] = 7 mM, [CitrA] = 15 mM, [OA] = 22 mM, [SOLV-X] = 32 g L ⁻¹ H ₂ O ₂ :Fe = 70:1 (1 doses) H ₂ O ₂ :Fe = 350:1 (5 doses)	4840 mg kg ⁻¹ TPHs (78% of C ₁₀ –C ₂₀)	7.5	Real soil (few months contamination) Batch slurry	6.25	4 d	X _{TPHs} : CitrA (51%) > SOLV-X (44%) > OA (9%) Obs: 3-time addition of H ₂ O ₂ was favorable X _{TPHs} : CitrA (59%) X _{H₂O₂} : No data, X _{CA} : No data Obs: Biological treatment after MF, X _{TPH} = 93% (4 weeks)	[74]
EDTA	(a) [H ₂ O ₂] = 2700 mM, [CA] = [Fe _{mZVI}] = 720 mM H ₂ O ₂ :CA:Fe _{mZVI} = 15:4:4 (b) H ₂ O ₂ :CA:Fe _{soil} = 20:1:1	30,510 mg kg ⁻¹ TPHs	7.3	Real soil 16.8 g kg ⁻¹ Fe SOM 5.9% TOC 2.1% Bach slurry	1.7	48 h	(a) X _{TPHs} : 72.2% (b) X _{TPHs} : 79.3% X _{H₂O₂} : No data X _{CA} : No data Obs: no EDTA (H ₂ O ₂ :Fe =15:4), X _{TPH} = 39.3%	[84]
DP (Stabilizer) EDTA (CA)	[H ₂ O ₂] = 5900 + 5900 mM [EDTA] = 5 mM H ₂ O ₂ :DP = 30:1 Natural Fe species present in the soil	1850 mg kg ⁻¹ diesel (C ₈ –C ₂₈)	7.6 ¹	Real soil 42 mg kg ⁻¹ Fe TOC = 0.83% Bach slurry	2	13 d	X _{diesel} : 75% X _{H₂O₂} : 90% (13 d) X _{CA} : No data Obs: MF treatment was equally effective one H ₂ O ₂ (17.6 M), two H ₂ O ₂ (5.9 + 5.9 M) injections or one (5.9 M) injection + bioattenuation (90 d).	[162]

Table 7. Cont.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
EDTA SOM	(a) [H ₂ O ₂] = 5000 mM, [EDTA] = 100 mM, [SOM] = 102–150 g kg ⁻¹ Natural Fe species present in the soil (b) Without EDTA: [H ₂ O ₂] = 5000 mM, [SOM] = 102–150 g kg ⁻¹ Natural Fe species present in the soil	10,250–14,270 mg kg ⁻¹ F ₂ (C ₁₀ –C ₁₆)	4	Real soil (10–12 years, rich in SOM and Fe) Batch slurry	0.4	70 h	(a) X _{F2} : 27–40% (3 soils) X _{H2O2} : (100%, 10 h) X _{CA} (EDTA + SOM): No data (b) X _{F2} : 98% X _{H2O2} : (40–60%, 10 h and 100% > 50 h) X _{CA} (SOM): 3.2–9.8% (3 soils) Obs: stability constant of SOM-Fe(III) 20 orders of magnitude < than EDTA-Fe(III)	[81]
Phosphate EDTA CitrA	[H ₂ O ₂] = 1470 mM, [phosphate] = 20 mM [Fe(II)] = 90 mM H ₂ O ₂ :phosphate:Fe = 73.5:1:4.5 [CitrA] = 90 mM H ₂ O ₂ :CitrA:Fe = 16.3:1:1	62.2 g kg ⁻¹ C ₁₀ –C ₄₀ (95 mg kg ⁻¹ PAHs)	7.2–7.5	Real soil TOC = 13.6% Batch slurry	1.2	12 d	X _{C10-C40} : Phosphate(21.4%) >CitrA(6.7%) X _{H2O2} : No data, X _{phosphate} :No data, X _{CitrA} : 51.8% Obs: Without phosphate or CitrA: X _{C10-C40} = 0%	[163]
EDTA	[H ₂ O ₂] = 2.3 g _{ox} kg _{soil} ⁻¹ [EDTA] = 7.5 g _{ox} kg _{soil} ⁻¹ H ₂ O ₂ :DP = 5:1	1855 g (MtBE + TBA + TPH)		Real soil Pilot-scale	-	16 h	X _{pollutants} : 78% X _{CA} : No data	[86]
SOM	[H ₂ O ₂] = 900 mM Fe-SOM = 837 mg kg ⁻¹ Natural Fe species present in the soil	4.7 g kg ⁻¹ TPHs	7.5	Spiked soil Batch slurry	12	22 h	X _{TPHs} : 67% (without Fe-SOM only 6%). X _{H2O2} : 100%	[109]
DP (Stabilizer) Extracted HAs (CA)	[H ₂ O ₂] = 1765 mM, [HAs] = 10 g L ⁻¹ , [DP] = 60 mM H ₂ O ₂ :DP = 29:1 Natural Fe species (20 g kg ⁻¹) present in the soil	3760 mg kg ⁻¹ diesel	5.5	Real soil TOC = 0.6% Batch slurry	5		X _{diesel} : 90% (without HAs and DP addition only 55%). X _{H2O2} : 100% (at 150 h) (without HAs and DP addition at 1 h) X _{DP} : No data	[107]
NTA	Bioremediation + MF [H ₂ O ₂] = 30 mmol kg _{soil} ⁻¹ [CA] = [Fe] = 0.6 mmol kg _{soil} ⁻¹ Soil/penaut hull = 10%(w/w) H ₂ O ₂ :CA:Fe = 50:1:1	38.3 g kg ⁻¹ TPHs	7.9	Real soil Batch slurry	5–6.7	8 weeks (Bio) + 12 weeks (MF)	X _{TPHs} : 89% (whitout EDTA addition 55%) X _{H2O2} : 100% (24 h) X _{CA} : No data	[165]

SC = Sodium citrate; CitrA = Citric acid; DP = Potassium dihydrogen phosphate; EDTA = Ethylenediaminetetraacetic acid; EDDS = Ethylenediaminedisuccinic acid; OA = Oxalic acid, SOM = soil organic matter; TPHs = total petroleum hydrocarbons; FAME = Fatty acid methyl esters; F2 = Fraction 2 diesel hydrocarbons from C₁₀–C₁₆. Obs = Observations, n.f. = not found.

3.2.4. Unsaturated Chlorinated Compounds and Pesticides

Unsaturated chlorinated compounds are organic molecules with at least one multiple bond (double or triple) and at least one chlorine atom substituent. The more chlorine substituent on unsaturated carbon compounds decreases the reaction rate of the pollutant with OH^\bullet , as can be seen in Table 4.

Ko et al. used SC to enhance the oxidation of soil polluted with a non-aqueous phase liquid (NAPL) [167]. However, their results revealed that the application of SC with H_2O_2 did not improve the removal of the pollutants (chlorinated volatile organic compounds (CVOCs), among them, several chlorinated ethenes (tetrachloroethene (PCE), trichloroethene (TCE)) and ethanes (saturated compounds such as 1,1,2,2-tetrachloroethane (TeCA), 1,2-dichloroethane (DCA) and 1,1,2-trichloroethane (TCA)), as shown in Table 8) present in the groundwater. This result may be partially attributed to the high pH of the system ($\text{pH} > 8$) and the scavenging of OH^\bullet by citrate. Although the rate constants of citrate and Fe-citrate with OH^\bullet are relatively low ($k_{\text{citrate}, \text{OH}^\bullet} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [126,127] and $k_{\text{Fe-citrate}, \text{OH}^\bullet} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [70]) compared to the rate constant of the studied pollutants (chlorinated ethanes and ethenes) with OH^\bullet (in the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$, Table 4), the chelating agent scavenger effect cannot be assumed to be negligible due to the high concentration of citrate used in these experiments (approximately eight times higher than the pollutants).

Conversely, other authors have reported a significant increase in pollutant conversion (the pesticide diuron) using SC as a CA [135,143], as shown in Table 8. Vicente et al. reported an increase in the diuron conversion from 55% (without SC addition) to 80% (in the presence of this CA) [135]. These results can be explained attending, on the one hand, to the slightly higher reactivity of diuron with OH^\bullet radicals than the contaminants considered in the previous works (such as TCE and PCE [167]; $k_{\text{diuron}, \text{OH}^\bullet} = 4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} > k_{\text{TCE}, \text{OH}^\bullet} = 3\text{--}4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} > k_{\text{PCE}, \text{OH}^\bullet} = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [126], Table 4). On the other hand, the concentration of SC may play a determining factor. Tan et al. reported a maximum of 80% of diuron degradation when the citrate:Fe ratio was 1:1 [168]. However, the degradation of diuron was only 57% when the citrate:Fe ratio was 5:1, which was even lower than the diuron degradation achieved without CA addition. This was because, as previously stated, when SC (the CA used in this case) is added in relatively high concentrations, it can compete with contaminant for OH^\bullet . Moreover, in the presence of CA excess, the possible formation of plentiful hexa-coordinated complexes of iron hinders the accessibility of the iron center for hydrogen peroxide attachment [169], resulting in decreased degradation efficiency of the contaminant. In this way, as previously explained in the case of PAHs (Section 3.2.2), an optimal concentration of citrate should be high enough to favor the formation of the Fe-citrate complex (mainly due to its relatively low stability constant, Table 2) but not too high to cause an important scavenging effect on the hydroxyl radicals produced or to hinder the accessibility of the iron. Additionally, Ko et al. tested the addition of persulfate combined with hydrogen peroxide in a PS-MF system using citrate as CA. Regrettably, a lower removal of the CVOCs was achieved in this system, suggesting that citrate may scavenge hydroxyl radicals [167].

The use of pyrophosphate (SP) was a promising option for the remediation of soils polluted with polychlorinated biphenyls (PCBs) and PCE in the MF process [54,56,59]. Ma et al. reported that PCBs degradation followed the descending order with different CAs and the same reaction conditions: EDDHA (63%) > SP (62%) > SC (33%) > EDDS (18%) > GLDA (sodium N,N'-bis(carboxymethyl) glutamic acid) (1%) [56]. A SP:Fe(II) molar ratio of 1:1 resulted in the highest removal rate of PCBs. The inhibitory effect of the CA was noticed when the SP concentration was too high, in this case, the complex Fe-SP precipitated, decreasing the efficiency of the remediation treatment, which is in accordance with the results reported by Venny et al. in the remediation of other pollutants (PAHs, (the optimal SP:Fe molar ratio was 1:1) [55]. Moreover, the study carried out by Ma et al. revealed that not only inorganic CAs (SP), but also organic CAs such as EDDHA can markedly enhance the removal of PCBs from capacitor-oil-contaminated soil slurry [56].

In the last case, the soil pH dropped significantly from neutral values up to 2.7. The pH decrease can be due to the generation of important concentrations of organic acids as intermediate oxidation by-products from the incomplete oxidation of refractory pollutants. In the case of Fe(II)/PPP/H₂O₂ system, the ROS mainly produced are hydroxyl radicals (90%) (as schematized in Figure 2). In this way, hydroxide groups are generated in excess (Equation (14)) which are able to neutralize the acid compounds produced during the degradation of the pollutant. However, in the Fe(II)/EDDHA/H₂O₂ system, insufficient hydroxyl groups were produced (Equation (14)) to balance the acids generated (both OH[•] and O₂^{•-} radicals are important (50% of the ROS generated), as schematized in Figure 5), and, consequently, the pH of the reaction medium declined more in this system.

This is the only work found in the literature using EDDHA as CA to improve the Fenton process in soils remediation [56]. In this way, it would be of interest to investigate its potential use to remediate soils polluted with other types of contaminants or soil matrix. For example, if EDDHA was used for the in-situ remediation of calcareous soil, the buffer effect of the soil would probably prevent the pH drop produced by this CA. Moreover, there is limited information in the literature regarding the mechanism of this CA and the different rate constants involved in the process, and thus, more research is needed.

Therefore, based on the results obtained for this group of contaminants, an optimal order of use of the different CAs to obtain a higher removal of unsaturated chlorinated compounds and pesticides can be as follows (the optimal CA:Fe ratio reported has been included for each CA): Citrate (Citrate:Fe = 1:1) > SP (SP:Fe = 1:1) > EDDHA (0.5:1) > EDTA > EDDS > GLDA. However, it should be considered that this order is only indicative. In this way, for each specific case, the rate constant of the contaminant with the OH[•] radicals generated (Table 4) and the scavenging effect of the CA (Table 3) should be considered, as well as the specific soil matrix characteristics.

Table 8. Research studies for unsaturated chlorinated compounds degradation in soils using MF process.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
SC	(a) [H ₂ O ₂] = 880 mM, [CA] = 5.2 mM, H ₂ O ₂ :L = 170:1 Natural Fe species present in the soil (b) [H ₂ O ₂] = 880 mM, [CA]=[Fe(III)] = 5.2 mM mMH ₂ O ₂ :CA:Fe = 170:1:1	40 mg kg ⁻¹ diuron	4.5–6	Spiked soil (sandy clay loam, 18.2 mg kg ⁻¹ Fe) Batch slurry	2	48 h	(a) X _{diuron} : 73% X _{H₂O₂} : 50% X _{CA} : 40% (b) X _{diuron} : 80% X _{H₂O₂} : 65% X _{CA} : 100% Obs: X _{diuron} = 55%, X _{H₂O₂} = 40% without SC or Fe addition.	[135]
SC	[H ₂ O ₂] = 294 mM, [CA] = 50 mM, [Fe(II)] = 5 mM mMH ₂ O ₂ :CA:Fe = 58.8:10:1	39 mg kg ⁻¹ diuron	Neutral	Spiked soil (sandy clay loam, 8.3 mg kg ⁻¹ Fe) Batch slurry	2	48 h	X _{diuron} : 90% X _{H₂O₂} : 100% X _{CA} : 20%	[143]
SC	(a) Fenton [H ₂ O ₂] = 441 mM, [CA] = 136 mM, [Fe(II)] = 45 mM H ₂ O ₂ :CA:Fe = 9.3:3:1 (b) H ₂ O ₂ + PS [H ₂ O ₂] = 147 mM, [PS] = 63 mM, [CA] = 68 mM, [Fe] = 0 mM H ₂ O ₂ :PS:CA = 2.2:1:1	1228 mg kg ⁻¹ NAPL: 30% of 5 CVOCs (DCA, TCE, TCA, PCE, and TeCA) and 70% chlorinated aliphatic organics, chlorinated aromatics, BTEX, styrene and TPH.	8.1	Spiked soil Batch slurry	1.9	48 h	(a) X _{CVOCs} : 46 %, X _{NAPL} : 52% X _{H₂O₂} : 98% X _{CA} : No data Obs: Without SC addition, X _{CVOCs} = 76% and X _{NAPL} = 40% (pH = 2.4) (b) X _{CVOCs} : 40%, X _{NAPL} : 57% X _{Oxidant (PS+H₂O₂)} : 57% X _{CA} : No data Obs: Without SC addition, X _{CVOCs} = 64% and X _{NAPL} = 74% (pH = 2.6) Efficiency removal a) and b): TCE > PCE > DCA > TCA > TeCA	[167]
SP	[H ₂ O ₂] = 250 mM, [CA] = [Fe(III)] = 25 mM H ₂ O ₂ :CA:Fe = 10:1:1	80 mg kg ⁻¹ of PCBs for RS, PS, and FS, and 70.67 mg kg ⁻¹ of PCBs for BS	7	Spiked, 4 soils: RS, PS, FS, BS. Batch slurry	20	24 h	X _{PCBs} : RS (91.3%) > BS (81.3%) ≈ PS (81.0%) > FS (77.6%) X _{H₂O₂} (8 h): FS(97%) > PS (93%) > BS (87%) > RS (78%) X _L (hydrolysis) (8 h): RS(14%) > FS(13%) > PS(8%) > BS (6.5%) Obs: production of OH• (RS > BS > PS > FS)	[59]
SP GA PA	[H ₂ O ₂] = 146 mM, [Fe(II)] = 10 mM, [SP] = 20 mM H ₂ O ₂ :CA:Fe = 14.6:2:1	8109 mg kg ⁻¹ PCE	6–5.2	Spiked (2 sandy soils) Batch slurry	5	120 h	X _{PCE} : SP(18%), GA and PA (no data) X _{H₂O₂} : No data, X _{CA} : No data Obs: X _{PCE} = 0% without SP addition Cl ⁻ released (mmol): SP (2.75) > PA (2) > GA (1.5) Fe (mg L ⁻¹): 30 mM SP(125) > 20 mM SP(50) > 10 mM SP(25) > without SP(0)	[54]

Table 8. Cont.

Tested CA	Treatment and Optimal Reagents Dose Concentration (mM) and Molar Ratio	Pollutant cc. (mg kg ⁻¹)	pH	Soil Type/Reaction System	V _L /W(mL/g)	Reaction Time	Conversion (%)	Ref
SP EDDS SC GLDA EDDHA	(a) CA screening [H ₂ O ₂] = 500 mM, [CA] = 25 mM, [Fe(II)] = 50 mM H ₂ O ₂ :CA:Fe = 10:1:2 (b) Optimal [H ₂ O ₂] = 1000 mM, [EDDHA] = 25 mM, [SP] = [Fe(II)] = 50 mM H ₂ O ₂ :SP:Fe = 20:1:1 H ₂ O ₂ :EDDHA:Fe = 20:0.5:1	63.9 mg kg ⁻¹ PCB	6.6 (SP) 2.7 (ED- DHA)	Real (sandy soil) (4465 and 812 mg kg ⁻¹ Fe and Ca, respectively) Batch slurry	20	(a) 24 h (b) 48 h	(a) X _{PCB} : EDDHA(63%) > SP(62%) > XSC(33%) > EDDS(18%) > GLDA(1%) Obs: Optimum SP:Fe = 1:1, X _{PCB} = 75% X _{PCB} removal higher in Fe(II) system than that in the Fe(III) system. X _{H₂O₂} : No data, X _{CA} : No data (b) X _{PCB} : SP(87.5%) > EDDHA (77.1%) X _{PCB} : 53% without SP/EDDHA (15 min) X _{H₂O₂} (10 min): without SP/EDDHA (99%) > EDDHA (39%) > SP (37%) X _{CA} : No data	[56]

SC = Sodium citrate; Citra = Citric acid; EDTA = Ethylenediaminetetraacetic acid; SP = sodium pyrophosphate; EDDS = Ethylenediaminedisuccinic acid; GLDA = Sodium N,N'-bis(carboxymethyl) glutamic acid; EDDHA = Ethylenediamine-N,N'-bis(o-hydroxyphenyl) acetic acid; GA = Gallic acid; PA = Picolinic acid; RS = Red soil; PS = Paddy soil; FS = Fluvo-aquic soil; BS = Black soil; DCA = 1,2-dichloroethane; TCE = Trichloroethene/trichloroethylene; TCA = 1,1,2-trichloroethane; PCE = Tetrachloroethene TeCA = 1,1,2,2-tetrachloroethane; AA = Aristolochic acid; PCBs = Polychlorinated biphenyls. Obs = Observations, n.f. = not found.

3.2.5. Saturated Chlorinated Compounds

Saturated chlorinated compounds are organic molecules with single bonds and at least one chlorine atom substituent. The use of CAs to enhance the remediation of saturated chlorinated contaminated soils has been very scarcely studied in the literature.

In the case of chlorinated ethane compounds, it has been demonstrated that the higher the number of chlorine substituents on the ethane molecule, the more difficult it is the pollutant to oxidize: tetrachloroethane (TeCA) (4) < trichloroethane (TCA) (3) < dichloroethane (DCA) (2) [167], which is related to the rate constants of these compounds with hydroxyl radicals. In this way, depending on the type of unsaturated chlorinated compound, different CAs should be selected. As previously stated, Ko et al. performed a comparative study on oxidative treatments (Fenton, PS, and MF) of chlorinated ethanes and ethenes. The CA selected in the mentioned study was SC [167]. Regardless of the oxidation treatment, the ethane's degradation was always lower than the corresponding to ethenes, highlighting the high refractoriness of these pollutants. Furthermore, these authors found that the addition of citrate kept post-treatment pH near neutral values. However, the use of SC resulted inefficient due to the hydroxyl radicals scavenging effect of this CA [167].

Dominguez et al. reported that the application of the Fenton process was unappropriated for the elimination of hexachlorocyclohexanes (HCHs) from a real polluted soil with a high concentration of carbonates (>40%). Carbonates (and bicarbonates) acted as a buffer, maintaining the pH of the system at around neutrality, and at these conditions, the catalyst precipitated in the form of $\text{Fe}(\text{OH})_3$, and it was rapidly removed from the reaction medium [36]. Moreover, H_2O_2 was quickly decomposed because of unproductive reactions. The concentration of iron in this real soil was high, and to increase the concentration of iron available at neutral pH, these authors tested SC (10 mM). However, a negligible concentration of iron was found to be available at these conditions (<2 mg L⁻¹ after 24 h), highlighting the need of adding the catalyst externally.

On the other hand, it should be considered that the rate constant of lindane (one of the HCHs isomer, g-HCH) with the hydroxyl radicals is relatively low ($k_{\text{HCH}}(\text{lindane}), \text{OH}^\bullet = 5.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [148]) compared to the values reported for other organic pollutants (Table 4). For this reason, the application of the Fenton process for the remediation of soils contaminated with saturated chlorinated compounds requires further research to find a feasible CA able to keep the iron available at neutral pH and achieve an acceptable hydrogen peroxide stabilization. For example, among the organic CAs considered in this review, the low scavenging effect on OH^\bullet of oxalic acid (Table 3) might be interesting for its application in the oxidation of these recalcitrant organic contaminants (HCHs). However, the addition of OA might decrease the reaction pH due to the relatively low pK_a value of this compound, and a detailed study of the soil type must be carried out before the selection of the CA. In this way, inorganic CAs (such as SP) could also be tested to enhance the degradation of these pollutants by the Fenton process, considering the advantages of these CAs over the organic ones. Firstly, $\text{Fe-L}_{\text{inorganic}}$ complexes have lower reaction rates with hydroxyl radicals than $\text{Fe-L}_{\text{organic}}$ (Table 3) and, therefore, they will compete less for the generated radical species, which can be of great interest for the remediation of such refractory compounds. Secondly, inorganic CAs are generally nontoxic and stable, unlike many organic ligands.

4. Potential Chelating Agents for Soil Remediation by Fenton Process

In previous sections, the main chelating agents used to eliminate contaminants in soils have been described. As earlier mentioned, the organic CAs can significantly scavenge the radical species produced in the system, lowering their availability to further oxidize the recalcitrant organic compounds, resulting in lower contaminant conversion. Consequently, the continuous supply of oxidant and CA to the reaction medium is required. Furthermore, some of the organic CAs studied also pose secondary environmental risks. Thus, the use of inorganic CAs (apart from the commonly used pyrophosphate) may provide a promising alternative approach for extending the pH range of the Fenton system to neutral values.

Considering the above, some CAs that have been successfully used in the aqueous phase are exposed as potential CAs for soil application.

4.1. Polyoxometalate

Considering the above, polyoxometalates (POMs), such as $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$, are inorganic CAs that form soluble complexes with Fe(III) under neutral pH conditions [170]. POM is biodegradable, non-toxic, and resistant to oxidation. Thus, its use presents significant advantages over most organic CAs [41]. Some reports involving the use of POM in the Fenton process in aqueous solution have been published with exciting results [170–174]. For example, Lee et al. [170] found that $\text{PW}_{12}\text{O}_{40}^{3-}$ in the homogeneous Fe(III)/ H_2O_2 system significantly enhanced the oxidation of recalcitrant organic compounds even at pH values of 8.5. These authors suggested that coordination of POM with iron converted the active oxidant from Fe(IV) to hydroxyl radical at circumneutral pH values. Lee et al. [174] reported that the presence of POM in the zerovalent iron (ZVI)/ H_2O_2 system enhanced the efficiency of 12 organic contaminants abatement and oxidant utilization under circumneutral pH values. In the mechanism proposed by Lee et al. [170], the catalyst forms complexes with POM, preventing its precipitation on the ZVI surface or in bulk solution and, therefore, enhancing the Fenton process. Regrettably, the reaction mechanism of organic contaminant degradation in the Fe(III)/POM/ H_2O_2 system and the nature of the reactive radicals produced are not fully understood, and much work is still needed. It should be considered that POM anion in the aqueous phase gradually hydrolyses at neutral and alkaline pH values (making difficult its recovery from the medium after the reaction) [170,171]. Nevertheless, the POM-Fe complex is relatively more stable [170]. In this line, heterogeneous catalysts such as ZVI and other iron-containing materials are catching the attention of researchers for the treatment of polluted waters. However, no reports regarding the remediation of soils contaminated with organic pollutants using the relatively new POM/ H_2O_2 system have been found. In this way, further research to develop more stable forms of iron-polyoxometalate catalysts or less expensive ways of producing POM is required [170].

4.2. Tripolyphosphate

Tripolyphosphate (TPP), one of the commonly used polyphosphates, had proved to be a promising inorganic CA for iron stabilization in Fe-based AOPs for the abatement of organics pollutants in aqueous systems [175,176]. Deng et al. studied the treatment of coking wastewater (containing phenols, PAHs, pyridine, and indole) in a novel electro-Fenton (EF) process at pH = 6.8 by using TPP [176]. Their results showed that total organic carbon (TOC) decay in the presence of TPP was 2.1 times higher than that of conventional EF. As for PPP and POM, this CA has no scavenging ability [61]. Nevertheless, this compound has been scarcely used to remediate polluted soils.

4.3. Other Organics CAs

Apart from those mentioned above, other organics CAs not considered in the review have shown promising results in removing organics pollutants from the aqueous phase, and they could be tested for soil remediation. Some of them are aspartic acid and glutamic acid [177]. The formation of Fe(II)-aspartate and Fe(II)-glutamate complexes has been proved to extend and improve the rate of p-nitrophenol degradation process to neutral pH conditions. The very fast removal (minutes) of this pollutant makes the application of these CAs a promising way to enhance the Fenton process [177]. Moreover, polyacrylic acids (PAAs) have been proven to be efficient CAs due to their multiple binding sites [178]. Applying the CAs mentioned above for the remediation of polluted soils has not been carried out to the best of our knowledge, and further research is needed.

5. Conclusions

The addition of chelating agents (CAs) allows overcoming some of the main limitations of conventional Fenton in soil remediation, such as the possibility to operate at circumneutral pH, maintaining the catalyst (Fe) available and increasing the oxidant (H_2O_2) stability. CAs, forming complexes with Fe, allow extending conventional Fenton pH to neutral or near-neutral pH. The selection of the CA is not trivial and several aspects should be considered, such as the pollutant type and its accessibility, the characteristics of the soil matrix (SOM and TOC content, presence of natural iron oxides and other metals, carbonates, etc.), and the future use of the soil, among others. This paper systemically reviewed the application of chelate-modified Fenton (MF) systems using inorganic (pyrophosphate) and organic (polycarboxylic acids, aminopolycarboxylic acids and humic substances) CAs in the remediation of soils contaminated with organics compounds (BTEX, phenolic compounds, PAHs, TPHs, saturated and unsaturated chlorinated compounds and pesticides). The main conclusions are as follows:

- More than 50% of the papers found in the literature focused on the treatment of artificially contaminated soils (spiked soils). However, the results obtained with these soils cannot be directly extrapolated to real soils. Moreover, most of them have been carried out batch-wise. Therefore, for future research, the remediation of real polluted soils would be recommended, and for more realistic conditions (dynamic conditions), column experiments would be preferred.
- Many factors affect the efficiency of the MF process, including the type of the CA, the molar ratio CA:Fe, the H_2O_2 dose, the reagents dosing mode, the reactivity of CA and Fe-CA for the reactive radical species generated, the pH, the soil matrix characteristics, the pollutant ageing, and accessibility, etc.
- Other factors, such as the adsorption of CAs onto the soil (which is usually non-negligible) have been scarcely studied in the literature. In this way, further attempts to study the application of CAs to enhance the Fenton process in soil remediation should not be based solely on the degradation of the pollutant. Additionally, they should include a detailed study of the interaction of the CA and Fe-L complexes with soil and soil constituents and its diminution from the solution related to possible degradation or adsorption mechanisms.
- Inorganic CAs are generally nontoxic and non-reactive with the radical species generated, and therefore, present significant advantages over the organic CAs.
- The system pH and CA:Fe molar ratio affect the nature and amount of the reactive oxygen species (ROS: OH^\bullet , $\text{O}_2^{\bullet-}$, HO_2^\bullet , Fe(IV), $(\text{FeO})^{2+}$) generated in the MF process.
- For most of the CAs reviewed, Fe(III)-L is reduced to Fe(II)-L by superoxide radicals and not by the direct reaction with H_2O_2 . However, some contradictory results have been found in the literature regarding the MF mechanism and further research is needed.
- The evolution of CA, H_2O_2 and catalyst during the reaction time in the MF system is a critical factor determining the pollutant removal and, therefore, should be systematically evaluated. Nevertheless, it has been scarcely considered in the literature and requires further research. Thus, future papers should include experimental measurement of chemical evolution in the system (soil and aqueous phases) and calculate time-dependent kinetic rate coefficients for each reaction.
- Additional research studies are required to determine the optimum molar ratios of CA:Fe and Fe: H_2O_2 in the MF system as there is no agreement among researchers. In the case of inorganic CAs such as PPP, when a high CA:Fe molar ratio is used, steric hindrance is produced, inhibiting the Fenton catalytic cycle. Therefore, the use of a low CA:Fe molar ratio is recommended. However, when using CAs with low stability constants (as CitrA and OA), high CA:Fe molar ratios are needed.
- The radical scavenging effect of CA (and the corresponding Fe-L complex) is decisive. Therefore, to achieve an efficient pollutant degradation, the kinetic constant of the

pollutant with OH^\bullet should be significantly higher than the kinetic constant of CA (and Fe-L) with these radicals.

- The application of CAs that have been successfully used in the aqueous phase, such as polyoxometalate, tripolyphosphate (inorganic CAs) or polyacrylic acids, and aspartic and glutamic acids (organic CAs), should be tested in soil remediation.
- Engineering cost studies for applying bench-scale laboratory experiments to field conditions are missing in the bibliography, and consequently should be included in future investigations.

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