Chelating Agents in Soil Remediation

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The Fenton process is an efficient treatment for removing many organics pollutants in aqueous systems at acidic pH (2.8-3.5). 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) makes iron soluble at circumneutral pH by forming complexes with Fe, and thus, enabling Fenton reactions under these conditions. This strategy, called chelate-modified Fenton process (MF), can be employed to overcome the challenges identified in conventional Fenton.

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

1. Introduction

Soil and sediments contamination by organic compounds, resulting from industrial and municipal waste discharge and improper use of chemical fertilizers and pesticides, is a widespread problem worldwide due to its great harm to the ecological environment and public health [1][2][3]. Nowadays, the principal organic 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].

Extensive work has been devoted to developing soil remediation techniques [5]. 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 [6]. The oxidants used in AOPs include hydrogen peroxide (H_2O_2), persulfate ($S_2O_8^{2-}$), permanganate (MnO_4^-), and ozone (O_3). One of the most frequently AOPs used is the Fenton process (H_2O_2 + Fe(II)), where H_2O_2 is the oxidant species and homogeneous Fe(II) acts as a catalyst for hydrogen peroxide decomposition [7][8].

Although the Fenton process has been proven to be a viable approach for remediating contaminated soils [9][10][11], there are various limitations associated with this treatment [10]. Fenton process displays its maximum $OH^\bullet$ production and the subsequent pollutant oxidation activity under acidic pH [12][13][14]. However, subsurface systems are often buffered in the neutral pH range (pH 6–8), which greatly complicates the implementation of this process. Different techniques can be used to ensure the efficient presence of catalysis at neutral pH such as a) the employment of iron minerals naturally occurring in soils instead of soluble iron (Fe(II)) [15], and b) deliver a soluble inorganic or organic ligand (L) (also named chelating agent, CA) to maintain iron in the solution, enhancing the Fenton reactions. This process is called chelate-modified Fenton (MF) 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 [10][16][17]. The extraction of the transition metals of the soil is also enhanced by the addition of chelating agents [18]. 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 [6].

In the simplified reaction scheme of chelate-modified Fenton (MF) it can be seen that the Fe-L complexes formed (Fe(II)-L and Fe(III)-L) would decompose H_2O_2 to generate radical species (hydroxyl and hydroperoxyl radicals) (Equations (14) and (15)), equivalent to classical Fenton reactions, 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 $O_2^{\bullet -}$ generated (Equation (18)) rather than from the direct Fenton reactions with H_2O_2 (Equation (15)) [19][20][21][22][23][24]. In this way, the MF acceleration is attributed to the positive effect of $O_2^{\bullet -}$ during regeneration of Fe(II)-L from Fe(III)-L.

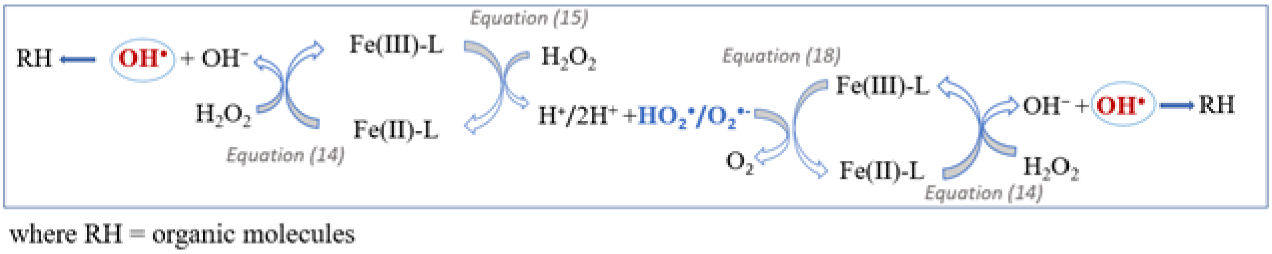

Figure 1. Simplified scheme summarizing the reactions involved in the chelate-modified Fenton process.

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

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 are summarized in Figure 2.

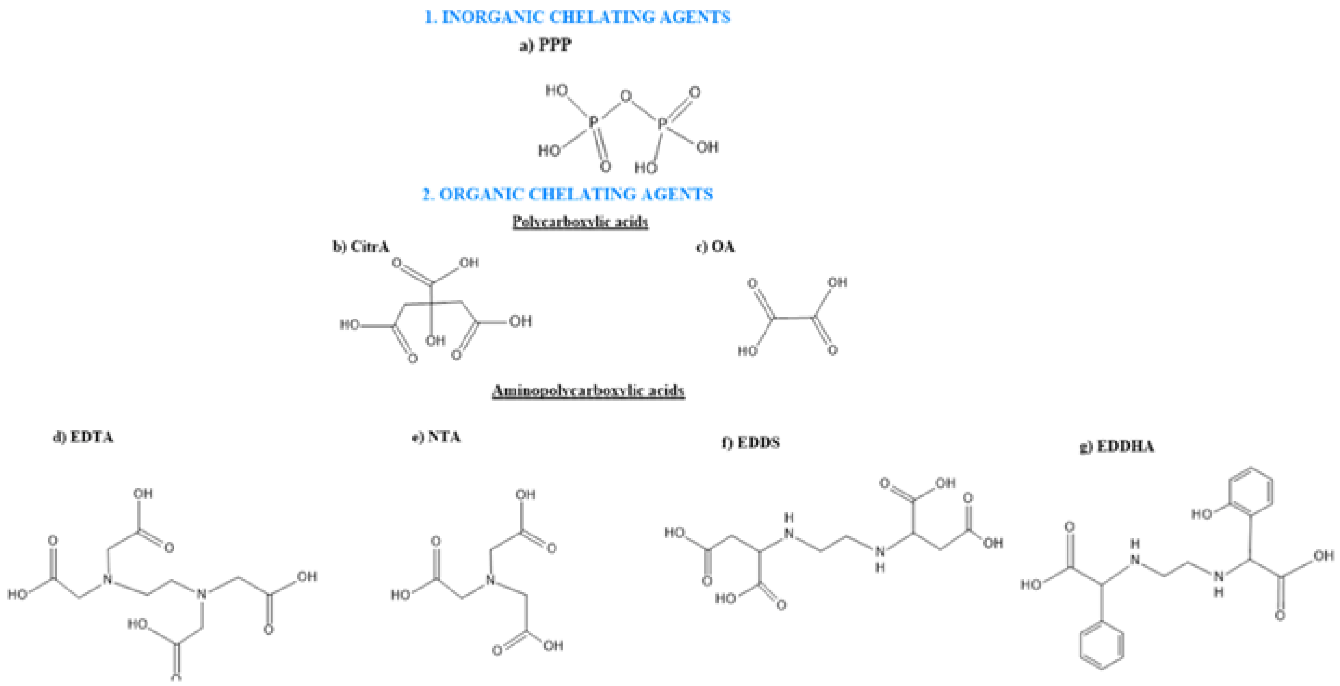

Figure 2. Structure of the investigated chelating agents: (1) inorganics; (**a**) pyrophosphate (PPP), and (2) organics; (**b**) citrate as citric acid (CitrA), (**c**) oxalate as oxalic acid (OA), (**d**) ethylenediaminetetraacetic (EDTA), (**e**) nitriloacetic acid (NTA), (**f**) ethylenediamine-N,N'-disuccinic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

2.1. Inorganic Chelating Agents: Pyrophosphate

Pyrophosphate (PPP) (Figure 2),, in the form of sodium pyrophosphate (SP), is the most used inorganic CA for iron stabilization [25][26][27][28][29] and oxidant stabilization [25][27][30] in Fenton-type systems. 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 [25][26][27][30]. Furthermore, the scavenging effect of this CA can be neglected due to the low reactivity of $OH^\bullet$ towards $P_2O_7^{4-}$, compared to other organic CAs (see Table 1) [31]. In addition, PPP can serve as phosphorus fertilizer to plants and environmental microorganisms [30][32], facilitating a subsequent bioremediation treatment.

Table 1. Kinetic constants for the Fenton process in the presence of different CAs.

Ligand (L)	ROS Involved in Pollutant Degradation	$k_{Fe(II)\text{-}L,\ H2O2}$ ($M^{-1}\ s^{-1}$) Equation (14)	$k_{Fe(III)\text{-}L,\ O2^{\bullet -}}$ ($M^{-1}\ s^{-1}$) Equation (18)	$k_{Fe(II)\text{-}L/Fe(III)\text{-}L,\ OH^{\bullet}}$ ($M^{-1}\ s^{-1}$) Equation (23)	$k_{L,\ OH^{\bullet}}$ ($M^{-1}\ s^{-1}$) Equation (24)
-	$OH^{\bullet}$ (acidic pH) or Fe(IV) (neutral pH) [33]	Equation (1): 40–80 [34][35]	n.f.	Equation (4): Fe(II): $2.5–5 \times 10^8$ [34][35]	-
PPP	$OH^{\bullet}$ [36]	1×10^5 [37][38][39]	n.f.	n.f.	2.2×10^5 [40] 9×10^5 [41]
Citrate	$OH^{\bullet}$ [42][36]	3.6×10^3 [42] 4×10^3 [43] 4.9×10^3 [38]	800 [43]	Fe(II)-L: 1.2×10^8 [43] Fe(III)-L: 1.2×10^8 * [44]	5×10^7 [41][45] 1.2×10^8 (pH = 3), 2.4×10^8 (pH = 6), 3.2×10^8 (pH = 6.6) [44]
Oxalate	$OH^{\bullet}$ [36]	3.1×10^4 [46]	$<1.0 \times 10^6$ [47]	Fe(II)-L: n.f. Fe(III)-L: 1×10^6[41]	1.4×10^6 [48] 7.7×10^6 [47] 1×10^7 [44]
EDTA	$OH^{\bullet}$ [36]	3.2×10^3 [43]	6×10^4 [43] 1.2×10^6 (pH = 7.3) [21]	Fe(II)-L: 5×10^9 [41] Fe(III)-L: 7.0×10^8–1.6×10^9 [41]	4×10^8 (pH = 4) [48] 2×10^9 (pH = 9) [48][49]
NTA	$OH^{\bullet}$ [19][36]	9.7×10^3–1.8×10^4 [50]	n.f.	Fe(II)-L: $2.3–5 \times 10^9$ [41] Fe(III)-L: 4.8×10^8 [19] 1.6×10^8 [50][41]	5.5×10^8 (pH = 6), 2.5×10^9 (pH = 9), 4.2×10^9 (pH = 10) [50]
EDDS	$OH^{\bullet}$ (80%) and $O_2^{\bullet -}$ (20%) [24]	n.f.	n.f.	Fe(II)/(III)-L: $2.0\text{-}5.2 \times 10^8$ [24]	2.5×10^9 [23]
EDDHA	$OH^{\bullet}$ (50%) and $O_2^{\bullet -}$ (50%) [27]	n.f.	n.f.	n.f.	n.f.
HA	$OH^{\bullet}$ [51] or $O_2^{\bullet -}$ [52]	n.f.	n.f.	n.f.	1.4×10^4 $LmgC^{-1}\ s^{-1}$ [51]

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

2.2. Organic Chelating Agents

2.2.1. Polycarboxylic acids (PCAs)

Citrate and **oxalate** ligands are the most commonly used PCAs. **Citrate** ligand can be generated from citric acid (CitrA) or sodium salts. CitrA is an environmental-friendly ligand consisting of three carboxyl groups and one hydroxyl group (Figure 2). The high-rate constant of citrate and Fe-citrate complex towards $OH^{\bullet}$ radicals leads to a significant scavenging effect at a high dose of this ligand. In this way, pH and citrate:Fe molar ratio have a decisive influence on the effectiveness of using this ligand in a MF process for soil remediation [53].

On the other hand, the ligand **oxalate** (in the form of oxalic acid $((C_2O_4)^{2-}$, OA) has been widely used to enhance the Fenton process for soil remediation [26][28][54][55]. The rate constant for the Fenton reaction in the absence of ligands is around 40–80 $M^{-1}s^{-1}$, whereas this value increases up to 3.1×10^4 $M^{-1}s^{-1}$ when the decomposition of H_2O_2 is catalyzed by Fe(II)-oxalate, which is 3 orders of magnitude higher [46][39], increasing process efficiency.

2.2.2. Aminopolycarboxylic Acids (APCAs)

- Ethylenediaminetetraacetic Acid (**EDTA**) (Figure 2) is one of the most popular APCAs and has been widely used as a chelating agent for soil remediation [56][57]. EDTA can strongly combine Fe(II) or Fe(III) to form a stable metal complex in solution. Fe(III)–EDTA can be reduced to Fe(II)–EDTA by $O2^{-}$. This radical is previously generated by a series of serial reactions initiated by the reaction between Fe(III)-EDTA and the oxidant (H_2O_2). Finally, Fe(II)–EDTA reacts with H_2O_2generating hydroxyl radicals [20][21]. Although EDTA enhances the Fenton effectiveness at near-neutral pH in soils [58][59][60][61], its use is limited due to its low biodegradability, contribution to heavy metal mobility/bioavailability, and persistence in the environment [62][63][64][65].

- Nitrilotriacetic acid (**NTA**) is one of the environmentally friendly CAs used to replace EDTA [17]. However, although NTA is biodegradable, its usage is controversial because it is moderately toxic to humans and mammals [66]. In addition, significant scavenging of the hydroxyl radicals generated is expected by NTA due to the high-rate constant between this CA and OH, especially significant at high pH values [50].

- Ethylenediaminedisuccinate (**EDDS**) has recently emerged as an alternative CA, this compound presenting properties similar to those of EDTA and readily biodegradable nature [24][63][67][68]. Since EDDS promotes the generation of superoxide radicals, the use of this new chelating agent in groundwater and soil remediation could be very effective [24]. Nevertheless, the application of EDDS should be limited by the fast reaction between EDDS and OH [23]. As mentioned above, apart from pH, the CA:Fe molar ratio greatly affects the efficiency of the process. It has been reported that EDDS showed a low ability to activate the oxidant at EDDS:Fe ratios higher than 1:1 [69].

- Ethylenediamine-N,N′-bis(2-hydroxyphenyl)acetic Acid (**EDDHA**) is a biodegradable ligand with two phenolic groups substituting the carboxylates of EDTA (Figure 2), which highly increase its stability. the application of the Fe(II)/EDDHA/H_2O_2 system has been shown to efficiently degrade soils contaminated with organic pollutants [27].

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. Humic substances are classified into humic and fulvic acids (HA and FA, respectively). Both are ubiquitous without potential toxicity, being considered “greener” amendments for the MF process [70]. The applicability of HA as a chelating agent in soil remediation greatly enhances the oxidation rate of organic compounds at neutral pH, the costs increase associated being negligible [55].

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 H_2O_2 to produce $OH^\bullet$ in the solid phase, which directly oxidizes the pollutant [71], as described in Figure 3a (adapted from Xu et al. [71]). This contrasted with the $OH^\bullet$ production and the oil degradation in the aqueous phase in the absence of Fe-SOM (Figure 3b).

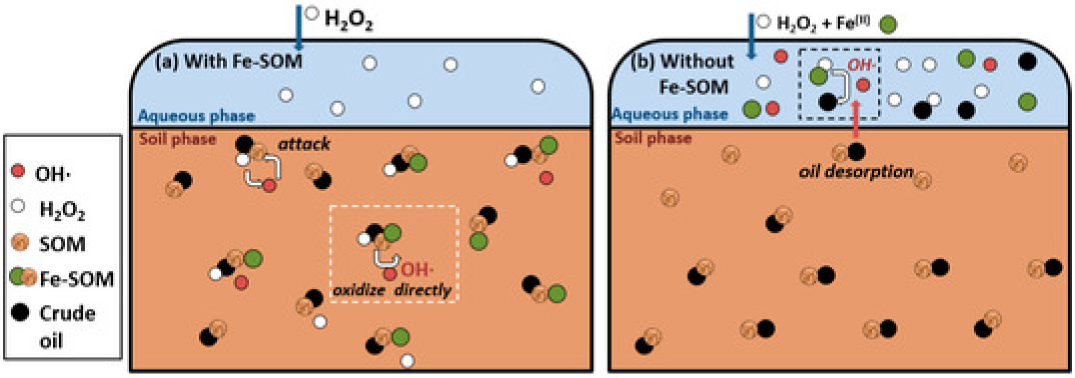

Figure 6. Schematic representation of different oxidation mechanisms in soil for crude oil degradation; (**a**) with Fe-SOM and (**b**) without Fe-SOM. Adapted from Xu et al. [71].

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

3.1. Factors Affecting Contaminant Removal

An important aspect in the remediation of contaminated soils derives from the **accessibility of the contaminants**. Pollution aging leads to the migration of contaminants from easily accessible to difficult sites, becoming sequestrated in the soil matrix [72], which reduces the chemical remediation efficiency of hydrophobic organic pollutants [73]. In this sense, CAs can enhance the desorption of the contaminants [72][74][75], and therefore, favor the accessibility of the contaminant towards the oxidant.

Another limiting factor in the remediation of soils 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 [30]. Moreover, the stability of H_2O_2 seems to be related to the properties of the soil. In this way, the specific characteristics of the soil should be considered to properly select the CA for the MF process.

The **soil texture** and **moisture** also influence the remediation process. Loose soil texture can help the mass transfer of reagents, while dense soil leads to large consumption of reagents [6]. Moreover, the application of low doses of oxidant at low soil-moisture levels has shown to be the most effective option [76].

The **adsorption** and **desorption of chemicals** (CA and catalyst) onto the soil is a limiting factor that should be considered when applying the MF process to remediate polluted soils.

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:

- BTEX and phenolic compounds
- Polycyclic aromatic hydrocarbons (PAHs)
- Total petroleum hydrocarbons (TPHs)
- Unsaturated chlorinated compounds and pesticides
- Saturated chlorinates compounds.

The reaction rate of each contaminant with the generated hydroxyl radicals ($k_{contaminant,\ OH^\bullet}$) will decisively influence the efficiency of its removal when applying the MF process. 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 $k_{contaminant,\ OH^\bullet}$ values found in the literature have been summarized in Table 2.

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

Group	Contaminant	$k_{contaminant,\ OH^\bullet}$ ($M^{-1}s^{-1}$), (Equation (22))	Ref.
BTEX/ phenolic compounds	Benzene	6.6×10^8	[77]
	Toluene	3.4×10^9	[77]
	Ethylbenzene	4.1×10^9	[77]
	Xylene	9.5×10^9	[77]
	Phenol	6.6×10^9	[77]

Group	Contaminant	$k_{\text{contaminant, OH}^\bullet}$ ($M^{-1}s^{-1}$), (Equation (22))	Ref.
	Bisphenol-A	9.8×10^9	[78]
PAHs	Acenaphthene	8.8×10^9	[79]
	Benzo[a]pyrene	2.53×10^{10}	[79]
	Chrysene	9.82×10^9 (20 °C, pH = 7)	[79]
	Fluorene	$2.8–9.9 \times 10^9$	[79]
	Naphthalene	$0.5–1.2 \times 10^{10}$	[79]
	Phenanthrene	1.34×10^{10}	[79]
Unsaturated chlorinated compounds and pesticides	Polychlorinated biphenyls (PCBs)	5×10^9	[80]
	Diuron	4.8×10^9	[41]
	Trichloroethylene (TCE)	$3–4 \times 10^9$	[41] [79]
	Tetrachloroethene (PCE)	2.8×10^9	[41]
	Pentachlorophenol (PCP)	4×10^9	[79]
	1,1-dichloroethene	6.8×10^9	[41]
	Vinyl chloride	1.2×10^{10}	[41]
	Atrazine, propazine, and terbuthylazine	$2.2–3.5 \times 10^9$	[51]
	1,2,3-trichlorobenzene	6.1×10^9	[79]
	1,4-dichlorobenzene	5.4×10^9	[79]
Saturated chlorinated compounds	γ-hexachlorocyclohexane (lindane)	5.8×10^8	[80]
	Trichloromethane	5.0×10^6	[24]

Extensive information on the use of different CAs for the remediation of soils contaminated with different types of organic pollutants has been summarized including 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 have been analyzed.

4. Potential Chelating Agents for Soil Remediation by Fenton Process

Apart from those mentioned above, other inorganics and 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 detailed below.

- Polyoxometalates (**POMs**), such as $PW_{12}O_{4}0^{3-}$and $SiW_{12}O_{40}^{4-}$, are inorganic CAs that form soluble complexes with Fe(III) under neutral pH conditions [81]. POM is biodegradable, non-toxic, and resistant to oxidation. Thus, its use presents significant advantages over most organic CAs [17].

- 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 [82][83].

- Other organics CAs such as **aspartic acid** and **glutamic acid** have shown promising results [84]. 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, making the application of these CAs a promising way to enhance the Fenton process [84]. Moreover, polyacrylic acids (**PAAs**) have been proven to be efficient CAs due to their multiple binding sites [85]. Applying the CAs mentioned above for the remediation of polluted soils has not been carried out, 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 most convenient CA:Fe molar ratio to employ depending on the CA properties, 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.

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