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Fenton oxidation for soil remediation: A critical review of observations in historically contaminated soils

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Abstract

Fenton-based treatments have received tremendous attention in recent decades as viable strategies for soil decontamination. Historically contaminated soils are characterized by particular contamination types, pollution composition patterns, soil constituents, and complex soil-pollutant interactions arising due to long-term pollutant aging. These major pitfalls dictate the remediation efficiency in a significantly different way in soils with a history of contamination than that in a spiked soil. It becomes, therefore, highly challenging to treat historically contaminated soils. Despite the immense amount of collected research data in these soils, to our knowledge, no comprehensive review of this topic has been published. This article is intended to provide a critical review of the applications, limitations, and implications of various Fenton-based processes exclusively in these soils. These processes are differentiated on the basis of experimental conditions, reaction chemistry, efficiency, and impacts on soil biota. These processes are critically evaluated to illustrate the promising techniques with a brief description of related challenges and their potential solutions. Moreover, coupling Fenton oxidation with other remediation techniques such as bioremediation, chemical reduction, and soil washing has also been discussed. The last part of this review describes the effects of these processes onto soil quality and native biota, and

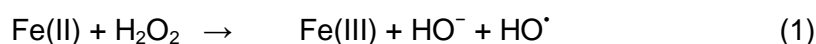
how they can be addressed. It is also highly demanding to identify the processes which are not likely to evolve in practice either due to their poor efficiency, treatment cost, or environmental impacts. Future critical research directions have been identified to promote research for the upscaling of this technique for real field application.

Keywords: Soil contamination; Soil remediation; Persistent organic pollutants; Advanced oxidation processes; Fenton oxidation

1. Introduction

Soil remediation has gained particular attention in recent decades due to its implications for food security and environmental health. Scientific community is continuously exploring suitable upgrades in conventional remediation strategies or their innovative alternatives. Advanced oxidation processes (AOPs) are emerging as viable remediation strategies for soils contaminated with organic pollutants. These AOPs rely on different oxidants which can completely mineralize the organic pollutants or improve their biodegradability for subsequent bioremediation in coupled remediation techniques.

Fenton oxidation is amongst the most popular AOPs owing to its high treatment efficiency, quick process, and wide application range. Fenton oxidation is based on the pioneering work of J.H. Fenton (1894) which suggested the application of a solution of H_2O_2 and Fe(II) salt (later termed as Fenton's reagent) for successful oxidation of tartaric acid. Hydroxyl radicals (HO^\bullet) are predominantly formed at acidic pH through this catalytic process. A large amount of research has been devoted to understanding its reaction mechanism but, the simplest and widely recognized representation of this reaction is the following:



Owing to its strong oxidation potential ($E^\circ = 2.8 \text{ V}$), the HO^\bullet radical is amongst the most reactive chemical species which is able to oxidize organic pollutants instantaneously in a non-selective way. There are many Fenton-based processes that are distinguished by

underlying reaction chemistry, treatment efficiency, and environmental impacts. A detailed description of different Fenton-based processes in the context of real soils is provided in the next section with an emphasis on their efficiency, advantages and challenges (Section 3, Table 1).

Fenton oxidation has been extensively used to remediate different organic pollutants in contaminated soils as evident from the immense amount of research in this field. It should, however, be noted that experiments denoting soil application have been performed in different contaminated matrices including artificially contaminated soils (pollutants spiked either on sand, synthetic soil composed of sand and minerals, or non-polluted real field soil) and historically contaminated real soils. All these matrices have been focused in reviews (mostly pollutant-specific) related to the Fenton oxidation without any particular distinction between different soil matrices while reviewing the existing literature (Cheng et al., 2016a; Sutton et al., 2011; Usman et al., 2016b; Venny et al., 2012; Yap et al., 2011). To our knowledge, this is the first review which is based exclusively on the observations regarding the applications of Fenton oxidation in real historically contaminated soils.

“Laboratory-spiked” contaminants are not sorbed in uncontaminated soils to the same extent as historically contaminated soils sorb their “native” pollutants (Arp et al., 2014). This is partly due to the absence of sufficient “aging” in laboratory studies (Arp et al., 2014; Usman et al., 2012). Once pollutants are discharged into the soil, they become sequestered in the soil, particularly in soil organic matter, and sorption strength increases over time (Jonsson et al., 2007). Moreover, these pollutants slowly start to diffuse into the organic soil fraction and/or penetrate into cavities (Figure 1). Soil organic matter is highly heterogeneous with varying proportions of organic phases having different affinities for contaminants. The presence of non-aqueous phase liquids (NAPLs) in soils presents specific challenges to any remediation technique (Pac et al., 2019). Moreover, the entrapment of pollutants in soil voids and pores may also affect their mobility and availability (Figure 1) (Jonsson et al., 2007). Similarly, soil mineral fractions and pollution characteristics have also shown strong impact on oxidation efficiency (Jonsson et al., 2007; Pac et al., 2019). Moreover, historically

contaminated soils tend to be near industrial sites (coking industry, gasworks, oil fields, etc.), where the soil can be enriched with strong-sorbing carbonaceous materials, which can decrease contaminant bioavailability (Arp et al., 2014). The contaminant contact time (i.e. aging effects) is also highly important in predicting the pollutant availability which is much lower in the historically contaminated soils compared with recently contaminated and spiked soils (Esmaeili et al., 2021). Owing to the long-term pollutant aging and soil heterogeneity, historically contaminated soils face particular pollution composition patterns, soil constituents, and complex soil-pollutant interactions. These major pitfalls pose particular challenges to soil decontamination as the treatment efficiency in historically contaminated soils can be significantly lower than that in spiked soil (Usman et al., 2012). Artificially contaminated soils can facilitate the preliminary investigations but are not the true representative of historically polluted soils under field settings. Owing to the recent advancements in this field and the amount of data in historically contaminated soils, it becomes essential to review the relevant literature to have better insights into the application of Fenton-based strategies for field application.

For this purpose, research data has been compiled from numerous publications dealing with the application of Fenton oxidation in historically contaminated soils. In the first part of this review, different Fenton-based processes are critically evaluated to illustrate the promising techniques and their appropriate applications with a brief description of related challenges and their key solutions. The coupling of this process with other treatment strategies like bioremediation, reduction, soil washing, is also discussed. Multiple experimental setups (batch, column, pot and field) have been used in soil remediation studies which are also discussed. The next sections describe the limiting factors associated with these processes in soil-plant system with a description of strategies to overcome these limitations. This review is intended to provide a unique reference to facilitate the upscaling of Fenton oxidation for real field application.

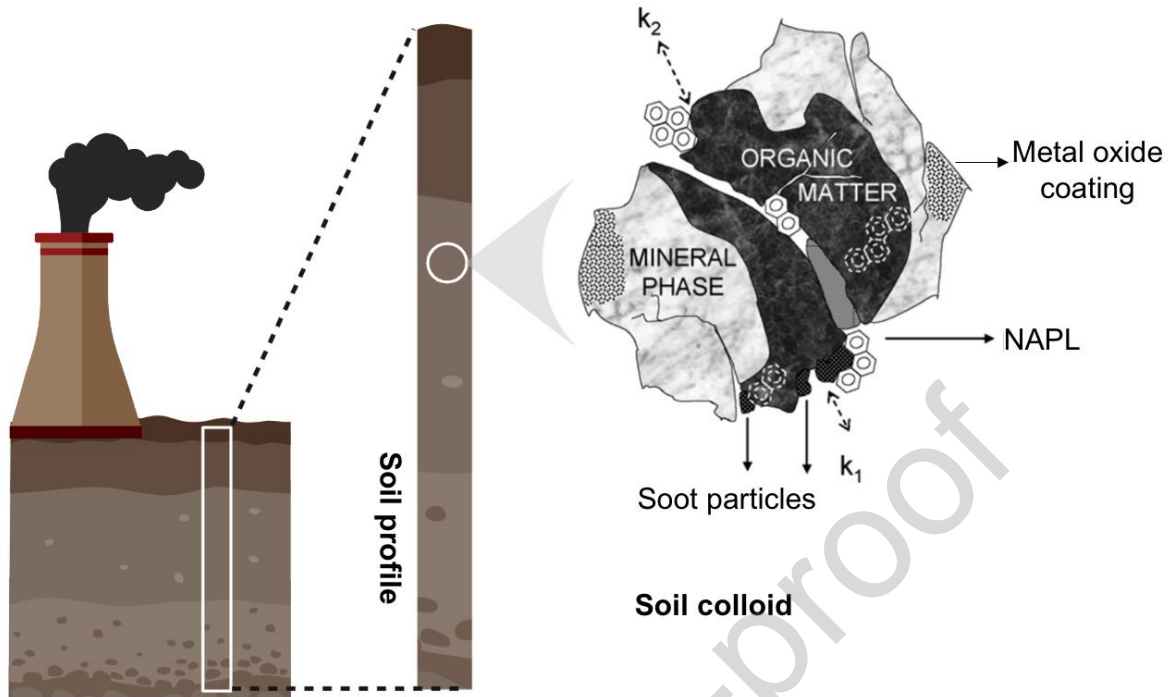


Figure 1: The conceptual model of a soil particle demonstrating different soil components that affect the remediation extent in historically contaminated soils. The image of soil colloid has been reproduced with permission from Ref. (Jonsson et al., 2007) whereas the rest of the figure has been prepared using Biorender app.

2. Literature search methodology

For this purpose, Web of Science database was searched (updated on March 16, 2021) by using the following keywords in manuscript titles: ("Fenton" or "chemical oxidation" or "H₂O₂") and ("soil" or "soils"). This search technique is often used in bibliometric analyses where the use of quotation marks (") ensures finding the exact phrases by deactivating the synonym feature of Web of Science (Usman and Ho, 2020; Vanzetto and Thomé, 2019). Term "or" was used to find different expressions which were connected by using "and" to ensure that these words appeared in the title of each article. This search yielded 309 articles and each article was read to identify if it focuses on the remediation of historically contaminated soils by using Fenton-based treatments. Articles presenting the application of Fenton oxidation in artificially contaminated soils (by spiking) were excluded. Studies

involving real contaminated soils were reviewed and are presented in the next sections. A separate search has also been performed by using TITLE ("Fenton" or "chemical oxidation" or "H₂O₂") and ("site" or "sites"). As, many irrelevant articles were found in this search (about reaction sites at catalysts), articles were first shortlisted by reading the article title on the basis of their applications in soils. Then, the shortlisted articles were read to identify the relevant articles. Table 2 provides a brief summary of all these studies.

3. Fenton oxidation-based strategies tested in historically contaminated soils

Different Fenton-based oxidation processes have been tested for the treatment of historically contaminated soils. These processes are categorized according to the associated number of publications in Figure 2. Among them, prominent strategies tested in real soils include modified Fenton oxidation followed by heterogeneous Fenton oxidation and traditional Fenton oxidation. However, photo-Fenton and electro-Fenton oxidation were mainly used to treat the soil washing extracts. These techniques which have been tested under different experimental conditions are described in the following sections. Table 1 provides a brief description of advantages and disadvantages of these techniques.

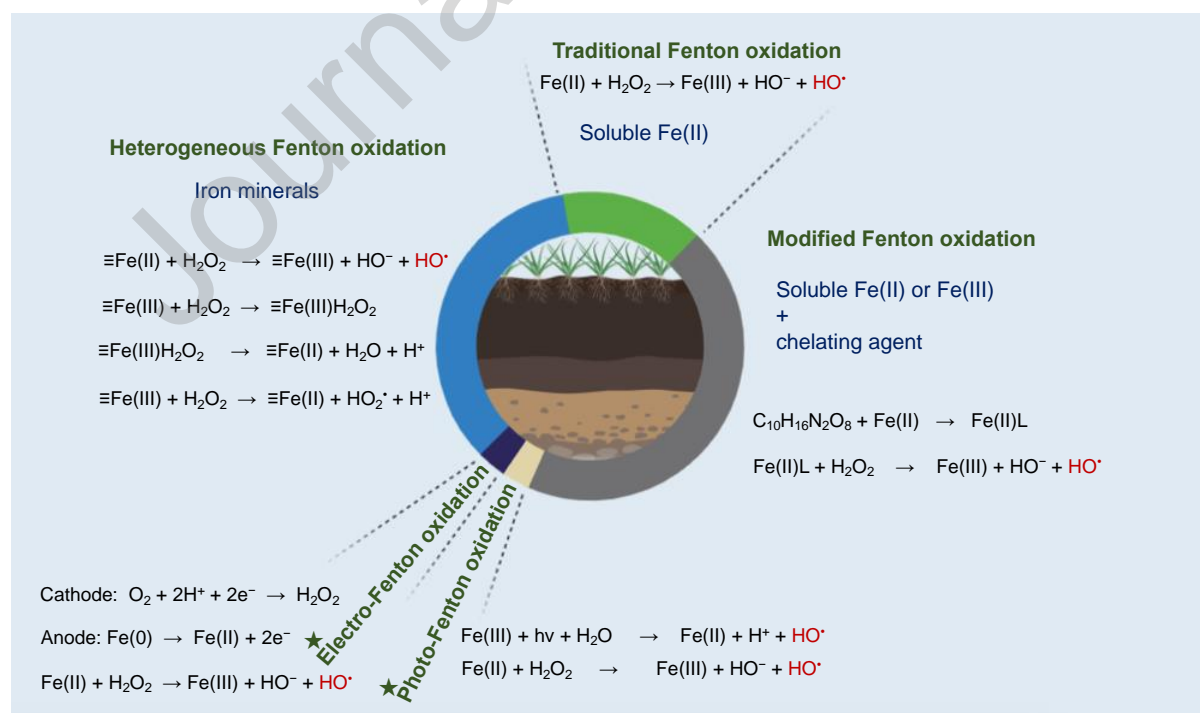


Figure 2: Fenton-based oxidation strategies tested for the remediation of historically contaminated soils. The size of each colored slice in pie chart is intended to represent the

share of publications in each theme. ☆: starred technologies (Photo-Fenton oxidation and electro-Fenton oxidation) were mainly used for the treatment of washing extracts of contaminated soils. (Figure prepared using Biorender app)

Table 1: A brief overview of the advantages and disadvantages associated with different Fenton-based oxidation strategies

Treatment	Activation agent	Advantages	Disadvantages/Challenges
Traditional Fenton oxidation	Soluble Fe(II)	<ul style="list-style-type: none"> • Comparatively simple operation. • Easy availability of reagents. 	<ul style="list-style-type: none"> • Requires acidic pH for optimum efficiency. • Maintaining this pH is costly and problematic in soil. • Iron catalysts cannot be separated from the reaction medium or reused.
Modified Fenton oxidation	Soluble Fe(II) with chelating agents (CAs)	<ul style="list-style-type: none"> • Wide working pH range. • Easy availability of reagents 	<ul style="list-style-type: none"> • Inclusion of CAs increases the treatment cost. • CAs, particularly organics, compete with pollutants and scavenge the oxidants. • Iron catalysts cannot be separated from the reaction medium or reused.
Heterogeneous Fenton oxidation	Solid iron minerals	<ul style="list-style-type: none"> • Wide working pH range • Low iron leaching • Iron minerals can be separated from the reaction medium or reused. • Endogenous iron minerals can also catalyze the oxidation and thus reduce the treatment cost. • Dual role of iron minerals can facilitate the coupling of Fenton oxidation with adsorption or chemical reduction. 	<ul style="list-style-type: none"> • Slow reaction rate, and low formation of reactive species • Stability and efficiency of iron minerals can decrease with the reaction time due to surface passivation • Injection of iron particles in contaminated soils is challenging and calls for further investigations.
Photo-Fenton process	UV–vis radiation	<ul style="list-style-type: none"> • Efficient cycling of Fe(II) and Fe(III) • Low input of initial Fe(II) • High radical production due to additional reactions 	<ul style="list-style-type: none"> • High treatment cost due to the use of light • Photoreactor must be designed prior • Has been applied only to treat the soil washing extract (no direct applications so far in the

			historically contaminated soils)
Electro-Fenton process	Relies on electro-chemistry for the on-site generation of H ₂ O ₂ and the supply of Fe(II) regenerated at the cathode.	<ul style="list-style-type: none"> • On-site generation of H₂O₂ and thus no risks with the transportation and handling of oxidant. • Continuous regeneration of Fe(II) at cathode. 	<ul style="list-style-type: none"> • High treatment cost • Complex process and reactor designing • Has been applied only to treat the soil washing extract (no direct applications so far in the historically contaminated soils)

3.1. Traditional Fenton oxidation

Traditional Fenton oxidation relies on soluble Fe(II) to catalyze H₂O₂ and requires an acidic pH (pH < 4) for optimum efficiency. This process has shown substantial potential to remove pesticides (Villa and Nogueira, 2006; Villa et al., 2008; Zhu et al., 2017), polycyclic aromatic hydrocarbons (PAHs) (Jonsson et al., 2006; 2007; Lundstedt et al., 2006), total petroleum hydrocarbons (TPHs) (Liu et al., 2019; Sutton et al., 2014b; 2014a) in industrially contaminated soils (Table 2). For example, Villa et al. (2008) reported 75% removal of a pesticide (DDT) when traditional Fenton oxidation (6 mM FeSO₄, 38.1 g H₂O₂ in increments) was applied in a soil obtained from a former pesticides warehouse in Brazil. Jonsson et al. (2007) evaluated its use in soils obtained from five Swedish industrial sites including three former wood impregnation sites, a former gas works, and a working coke plant. An overall degradation of 9-43% was observed in these soils though degradation efficiency varied according to the nature of PAHs i.e. 89%, 59%, and varying between 0-38% for PAHs with two, three, and more rings, respectively.

As soluble Fe(II) precipitates at higher pH values and loses its catalytic ability, most of the studies involving traditional Fenton oxidation were performed at acidic pH values (Table 2). However, maintaining such an acidic pH in soils could increase the treatment cost and can also cause adverse impacts on soil biota and quality (Sirguey et al., 2008; Villa et al., 2008). A separate section (No. 6.2) has been devoted to illustrating the impact and environmental implications of different Fenton-based processes in real contaminated soils. It is worth mentioning that few studies also assessed the efficiency of soluble Fe(II) at circumneutral

pH. However, under such conditions, either its efficiency was significantly affected (Usman et al., 2017), or it was completely unable to catalyze the chemical oxidation due to the precipitation of soluble Fe(II) (Usman et al., 2012). Performing this process at circumneutral pH exhibited negligible impacts on soil's indigenous microbes but its efficiency was declined (Liao et al., 2019). To summarize, optimum efficiency of soluble Fe(II) in contaminated soils requires acidic conditions which can have detrimental impacts on soil quality that should be considered. It is interesting to report that initial acidification can also improve the oxidation efficiency by the acid-induced dissolution of soil carbonate (complete or partial) which is otherwise considered as an oxidant scavenger (Usman et al., 2014).

3.2. Modified Fenton oxidation and role of chelating agents

To preclude the requirement of initial acidification, modified Fenton oxidation proposes the use of chelating agents (CAs) along with soluble Fe(II) to carry out the process at circumneutral pH (Zhang and Zhou, 2019). The CAs have a strong chelation ability for metal ions to keep them in solution even at higher pH values which extends the optimum range of reaction pH. As illustrated in Table 2, chelating agents have been used in Fenton oxidation of various pollutants such PAHs (Laurent et al., 2012; Lemaire et al., 2019; Liao et al., 2019; Zhao et al., 2019), TPHs (Chunyang et al., 2019; Liu et al., 2019; Martínez-Pascual et al., 2015; Sutton et al., 2014b; 2014a; Wang et al., 2015; Xu et al., 2011a; 2011b; 2016b; 2017a; 2018) or polychlorinated biphenyls (PCBs) (Ma et al., 2018). The use of CAs with soluble Fe(II) exhibited significant enhancement in oxidation efficiency. Two types of CAs have been employed in real contaminated soils. Their first type corresponds to organic CAs such as citric acid, citrate, ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-bis(o-hydroxyphenyl) acetic acid (EDDHA), oxalic acid, sodium citrate, sodium dodecyl sulfate, sodium N,N'-bis(carboxymethyl) glutamic acid (GLDA). Inorganic CAs are the other type of CAs where sodium pyrophosphate (SP) represent the sole example tested in the context of real soils. The EDTA has been used traditionally as a stable CA with high efficiency (Gryzenia et al., 2009; Lu et al., 2010a;

Ndjou'ou and Cassidy, 2006) but its application can be limited by its non-biodegradable nature (Ma et al., 2018). Therefore, Ma et al. (2018) suggested EDDS, a structural isomer of EDTA, as an alternative owing to its bridgeable nature. The addition of low-molecular weight organic acids such as citrate could also remarkably improve the oxidation efficiency (Sutton et al., 2014b; 2014a). Citric acid emerged as the most widely investigated CA in real contaminated soils (Table 2) probably because of its high efficiency, quick availability, and less environmental impacts. For example, in soil obtained from an oil tank storage site, Amsterdam, Xu et al. (2011b) reported that TPH degradation by modified Fenton oxidation was higher (51% removal) in the presence of citric acid than oxalic acid (9%). A similar trend was reported during the remediation of sorbed crude oil in contaminated soil (Xu et al., 2018). However, to remove bound PAHs by Fenton oxidation in a soil from an oil well in Chia, citric acid exhibited slightly lower efficiency than oxalic acid (Zhao et al., 2019). Recently, Ma et al. (2018) evaluated the removal of PCBs by modified Fenton oxidation activated by Fe(II) or Fe(III) chelated with five different CAs including organic (EDDS, EDDHA, GLDA, and sodium citrate) and inorganic CAs (like SP). They reported that PCB removal was higher in CA/Fe(II)/H₂O₂ system as compared to that by CA/Fe(III)/H₂O₂ due to the direct implications and greater reactivity of Fe(II). Efficiency of CAs varied in the following order: SP > EDDHA > sodium citrate > EDDS > GLDA (Figure 3). Organic CAs act as radical scavengers due to their competition with the target organic pollutants and thus decrease the oxidation efficiency (Usman, 2016). On the other hand, SP being an inorganic CA does not consume the oxidant. Findings of Ma et al. (2018) also revealed that the use of SP/Fe(II)/H₂O₂ slightly reduced the final pH (from 7.6 to 6.6) than EDDHA/Fe(II)/H₂O₂ that caused a remarkable decrease (from 7.6 to 2.7) which can be hazardous for soil quality and could contribute towards improving the metal solubility. Therefore, the use of SP and other inorganic CAs could be advantageous as compared to the organic CAs. But till now, only two studies have explored the efficiency of inorganic CAs in real contaminated soils (Jorfi et al., 2017; Ma et al., 2018). This should be further evaluated in the context of future studies.

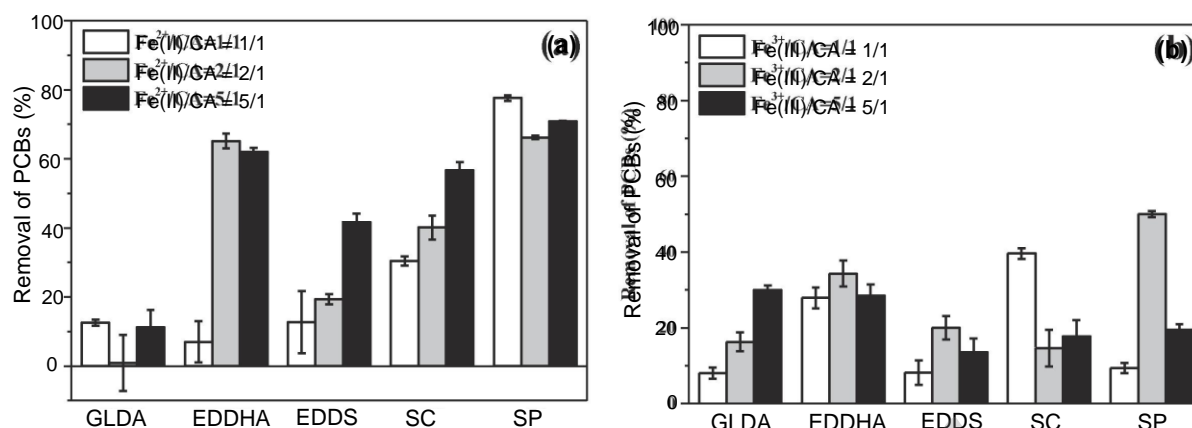


Figure 3: The removal of PCBs affected by the type and contents of different chelating agents (GLDA, EDDHA, EDDS, SC, SP) in the presence of (a) Fe(II) and (b) Fe(III). $[H_2O_2]_0 = 500$ mM, $[Fe]_0 = 50$ mM, $[PCB]_0 = 63.9$ mg kg⁻¹, and reaction time = 24 h. (Figure reproduced with permission from Ref. (Ma et al., 2018))

In addition to chelating soluble Fe(II) or Fe(III), CAs can also be advantageous in improving the catalytic ability of iron-based solids (hematite, zero-valent Fe etc.) or soil native Fe minerals (Polli et al., 2018; Popescu et al., 2017; Sherwood and Cassidy, 2014). These CAs facilitate the desorption of soil entrapped Fe allowing the formation of CA/soluble Fe complexes which can then participate in Fenton oxidation. It has been found that the use of EDTA resulted in significant improvement in TPH degradation (from <40% to >70%) when relied on native Fe or added ZVI (Ouriache et al., 2019). Soil organic matter (SOM) contains many natural CAs such as fluvic and humic acids which may also contribute in chelation. For example, in three arctic soils characterized by high SOM (10-15 wt.%) and Fe oxides, Sherwood and Cassidy (Sherwood and Cassidy, 2014) reported that relying on the SOM for chelation of the native Fe improved the stability and oxidation efficiency of H₂O₂ for diesel fuel degradation than by using EDTA as a chelate. However, it is usually difficult to achieve the optimum ratio of natural CAs (considering the small amount of SOM) to efficiently chelate the native Fe. Therefore, the addition of an appropriate amount of CA is usually required for an effective chelation of native Fe (Table 2). It should be noted that the use of these organic acids can also improve the availability of pollutants for higher removal efficiency by complexing with these pollutants (Zhao et al., 2019). Owing to this useful

feature, the use of cyclodextrin has been suggested as a pre-treatment before applying Fenton oxidation (Usman et al., 2012) that increased the oxidation efficiency of PAHs by increasing the pollutant availability. Though CAs enable the process to proceed at neutral pH, this process can be limited by higher treatment costs and elevated toxicity of CAs. Moreover, organic CAs can also increase the oxidant demand as they, being organic in nature, can consume the radicals by competing with the pollutants (Usman, 2016). This non-productive consumption would increase the treatment cost while decreasing the treatment efficiency. The use of inorganic CAs can be advantageous but limited amount of the associated literature calls for more studies to evaluate their efficiency and associated implications in soil system.

3.3. Heterogeneous Fenton oxidation and the role of iron minerals

Heterogeneous Fenton oxidation, also termed Fenton-like oxidation, is another important strategy where iron solids/minerals are used to catalyze the reaction at circumneutral pH (Usman et al., 2012; 2016b). Immobilization of Fe species within the structure of iron minerals prevents iron hydroxide precipitation. Thus, the catalytic ability of these iron minerals can be maintained at neutral pH. In this context, catalytic ability of following iron solids has been evaluated in the literature including iron oxides namely hematite (Jorfi et al., 2017), magnetite (Barzegar et al., 2017; Biache et al., 2015; Boulangé et al., 2019; Mirzaee et al., 2017; Rybnikova et al., 2016; 2017; Usman et al., 2012; 2014; 2016a; 2021), zero-valent Fe (ZVI) (Cao et al., 2013; Ouriache et al., 2019; Rybnikova et al., 2016; 2017), tourmaline (Jian et al., 2020; Li et al., 2016), steel slag (Cheng et al., 2016b) and endogenous iron (Table 2). It should be noted that the use of soluble Fe(III) has also been proposed as a Fenton-like catalyst in other environmental matrices but its use has never been evaluated in real soils. There exists only one study where Fe(III) bearing iron citrate has been used as a catalyst for heterogeneous Fenton oxidation of oil hydrocarbons in an oil field contaminated soil (Lu et al., 2010b). At the end of this treatment, total extractable organics were reduced from 32,400 to 21,800 mg kg⁻¹ soil. Provided below is a brief

description of the catalytic activity of different iron solids including native Fe species and exogenous iron minerals.

3.3.1. Use of endogenous Fe as a heterogeneous Fenton catalyst

Natural soils also contain a significant amount of iron ($2\text{--}50\text{ g kg}^{-1}$) in the form of different iron oxides which are capable of catalyzing the Fenton's process. Therefore, exploring the catalytic potential of endogenous Fe minerals is also gaining attention (Villa and Nogueira, 2006). The role of endogenous iron minerals was highlighted in PAH contaminated soils bearing 16.4 mg.g^{-1} of native Fe (Palmroth et al., 2006a). The addition of H_2O_2 alone (0.4 g.g^{-1} soil) removed $>50\%$ of PAHs under saturated conditions (Palmroth et al., 2006a). However, native Fe minerals may not be able to catalyze the Fenton oxidation despite their presence in sufficient amounts potentially due to their poor availability or existence as inactive forms (Usman et al., 2012). Therefore, most of the studies relying on the catalytic ability of native Fe suggested the use of chelating agents (Table 2). For example, in a highly contaminated soil obtained from pesticides warehouse, oxidation efficiency in the presence of native iron (hematite mainly) was 24% and 4% of DDT [1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane] and DDE [2,2-bis(4-chlorophenyl)-1,1-dichloroethylene], respectively (Villa and Nogueira, 2006). Degradation extent, however, increased to 53% (DDT) and 46% (DDE) by adding soluble Fe (3.0 mmol L^{-1}). Moreover, the use of chelating agents (Table 2) can also improve the availability and efficiency of native Fe species (Ouriache et al., 2019; Popescu et al., 2017; Sherwood and Cassidy, 2014). These agents enhance the desorption of the iron entrapped in soil and form soluble Fe-based complexes that remain available to catalyze Fenton's oxidation (Popescu et al., 2017). Endogenous iron exhibited higher catalytic ability to activate H_2O_2 in presence of EDTA (Ouriache et al., 2019). It is worth mentioning that owing to the catalytic ability of endogenous Fe, natural soils have been used as cost-free Fenton-like catalysts to degrade pollutants in water medium like pharmaceuticals and dyes (Aktas et al., 2017; Changotra et al., 2017; Khataee et al., 2015; Koottatep et al., 2017). Relying on endogenous Fe, if in sufficient quantities and with good

efficiency, can be economically feasible. However, the existence of endogenous Fe in sufficient amount is not the sole deciding parameter to rely on its role. Its type and the extent of its availability also dictate the efficiency of native Fe minerals which should also be assessed before implementing a treatment. In this context, it would be rewarding to make better efforts to improve the availability and efficiency of native Fe species in contaminated soils.

3.3.2. Use of exogenous Fe minerals as heterogeneous Fenton catalysts

To overcome the limitations associated with endogenous Fe, the use of exogenous Fe minerals has emerged as an efficient alternative. Among iron oxides, magnetite stands out owing to its higher catalytic ability as compared to other iron oxides, which, however, has only been compared in water medium (Matta et al., 2007). No such reactivity comparison has been made in real contaminated soils. The higher efficiency of magnetite has been linked to its structural Fe(II) which renders it more efficient than ferric (bearing Fe(III)) minerals (Usman et al., 2018a). Our previous studies reported that magnetite-catalyzed (10% w/w) Fenton oxidation was highly efficient to treat PAHs contaminated soils obtained from coking plant sites (Usman et al., 2012). It removed 70-90% of PAHs while soluble Fe(II) was unable to act as a catalyst at neutral pH (<10% of PAH removal). Rybnikova et al. (2017), however, reported the inefficiency of magnetite or nZVI (5 mg g⁻¹ of soil with 0.2-4 mM H₂O₂) at neutral pH to catalyze Fenton oxidation in PCP contaminated soil (timber mill) compared to the 36% removal in the presence of soluble Fe(II). Its use, however, decreased the pH of soil suspension was decreased to 5. The removal of PCP reached 43% with higher amounts of reagents (5 or 25 g of magnetite kg⁻¹ soil w/w with 200-500 mM H₂O₂) (Usman et al., 2021). This discrepancy in the remediation efficiency in the same soil has been correlated to different amounts of reagents tested in these studies (Rybnikova et al., 2017; Usman et al., 2021).

The use of ZVI-catalyzed Fenton oxidation has shown success in removing organochlorine pesticides (Cao et al., 2013) and petroleum hydrocarbons (Ouriache et al., 2019) in aged contaminated soils (Table 2). Both of these studies relied on the Fenton oxidation catalyzed

by ZVI applied along with EDTA, to prevent Fe precipitation at circumneutral soil pH. Rybnikova et al. (2016) reported that the catalytic ability of ZVI was slightly higher (18% pollutant removal) than magnetite (7% removal) in a historically contaminated PCB soil. It is worth mentioning that in spiked sand, degradation extent was up to 90% and 77% with ZVI and magnetite respectively. Though ZVI was more efficient, magnetite exhibited higher catalytic stability (Rybnikova et al., 2016). Indeed, the quick oxidation and surface passivation of nZVI are considered as the most significant challenges with its successful application for contaminant removal (Bae et al., 2018). However, the reduction potential of ZVI also enabled the coupling of reduction and Fenton oxidation in a PCP contaminated soil from a timber facility (Rybnikova et al., 2016). A detailed description of the coupling of Fenton oxidation with other strategies is provided in Section 4.

The use of steel slag-catalyzed Fenton-like process resulted in 93% removal of atrazine removal in soil obtained from contaminated load site of pesticide manufacturing plant (Cheng et al., 2016b). Its treatment efficiency was comparable to other catalysts like FeSO_4 and Fe_2O_3 . Contrary to these catalysts that decreased the soil pH from 5.4 to 3.4 (FeSO_4) and 4.6 (Fe_2O_3), the use of steel slag increased the soil pH to 6.2 which was beneficial for revegetation purposes. Therefore, the application of alkaline steel slag can be advantageous to avoid the limitations of the traditional Fenton process i.e. an acidic pH. A detailed description of the implications of Fenton-based processes on soil properties is provided in Section 6.2. It should be noted that heterogeneous catalysts reported in the context of real contaminated soils are very limited as compared to those tested in artificially contaminated soil or aqueous solutions which calls for further experiments in real soils. The catalytic ability of these minerals to catalyze Fenton oxidation strongly depends on their surface and structural characteristics and the nature of Fe species (Fe(II) or Fe(III)). The oxidation efficiency of iron minerals decreases by Fe leaching and surface oxidation/passivation which, if addressed, can improve the treatment efficiency. For example, in comparison to the 43% PCP removal by magnetite/ H_2O_2 system, the introduction of ascorbic acid improved the treatment efficiency to 95% (magnetite/ascorbic acid/ H_2O_2 system) (Usman et al., 2021).

The presence of ascorbic acid, a reducing agent, allowed magnetite to retain its structural Fe(II) contents and catalytic ability. However, this is the only study that used ascorbic acid in a historically contaminated soil (Usman et al., 2021) to enhance the catalytic ability of iron minerals in Fenton oxidation though its application has shown good efficiency in aqueous solution and spiked soils (Hwang and Kim, 2021). In this context, it is highly desirable to establish iron catalysts having higher stability and lower iron leaching but without compromising the treatment efficiency.

3.4. Photo-Fenton and Electro-Fenton oxidation

The application of Fenton's reagent with the UV-vis radiation (photo-Fenton oxidation) can trigger additional reactions to generate extra HO• radicals (Zhu et al., 2018). Electro-Fenton oxidation is another major Fenton-based process that involves the in-situ generation of H₂O₂ at the cathode with O₂ or air feeding in the presence of a suitable Fe catalyst (Zhou et al., 2017). On the other hand, the electro-assisted Fenton process comprises of the regeneration of catalyst by Fe(III) electrochemical reduction or the production of iron catalysts on the anode to form peroxi-coagulation process (Figure 2).

Despite the large number of studies using photo-Fenton or electro-Fenton oxidation to treat organics in aqueous solution or spiked soils, no study has reported their direct application in real contaminated soils. Both of these techniques were employed to treat the organic pollutants in soil extract in integration with soil washing of real contaminated soils (Huguenot et al., 2015; Safa and Mehrasbi, 2019; Villa et al., 2010). The readers are directed to Section 4.3 for further readings of this coupling.

4. Integration of Fenton oxidation with other remediation strategies

In coupled or integrated processes, two or more treatments, which are complementary to each other, are applied sequentially or simultaneously. Coupled treatment is intended to combine the advantages of individual techniques while overcoming their challenges. Fenton-based treatments can be integrated with other strategies for an improved treatment efficiency and to minimize the impacts of chemical oxidation on soil quality (Figure 4). A

major focus of such efforts was the coupling of Fenton oxidation with bioremediation (Table 2). Its coupling with other techniques like reduction and soil washing has also been investigated but there exist very few studies on this topic. Provided below is a brief description of different coupled processes tested in historically contaminated soils.

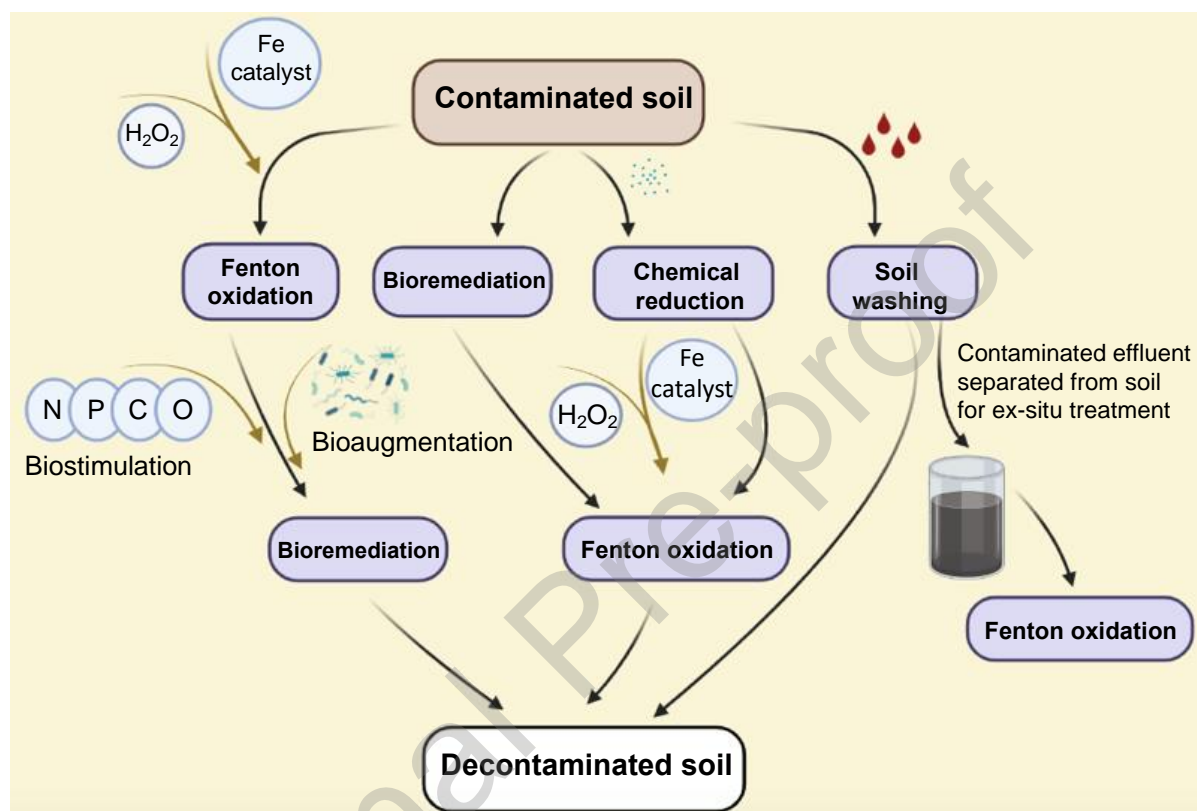


Figure 4: Integrated remediation of historically contaminated soils by coupling of Fenton oxidation with different remediation techniques. (Figure prepared using Biorender app)

4.1. Coupling of Fenton oxidation with bioremediation

Compared to the chemical oxidation, bioremediation is environment-friendly and more suitable for the bioavailable fraction of a contaminated site. For example, the majority of products in crude oil are biodegradable which can be removed by bioremediation alone. However, the existence of non-biodegradable residual contaminants after bioremediation prevents it from meeting the stringent environmental cleanup standards. Once the biodegradable fraction is eliminated, contamination level reaches a plateau as observed in oilfield contaminated soil after two years of bioremediation by Lu et al. (2010a). Therefore,

these researchers suggested the use of Fenton-like oxidation to eliminate the non-biodegradable residual contaminants after bioremediation (Lu et al., 2010a). Fenton oxidation is known for its rapid and extensive removal of pollutants. It has been suggested conventionally that Fenton oxidation is not compatible with bioremediation due to its negative impacts on microbes caused by acidic pH, oxidative stress, and changes in redox conditions. However, recent studies indicate that, although Fenton oxidation can temporarily decrease microbial activity, soil microbes can re-attain their populations and contaminant degradation ability (Sutton et al., 2011). Indeed, it has been reported in many studies (Table 2) that integration of both processes improves the treatment efficiency and soil quality issues traditionally associated with Fenton oxidation. For example, the application of a bioremediation pretreatment may improve the remediation and reduce the amount of oxidant required in subsequent oxidation as all biodegradable compounds have already been eliminated (Lu et al., 2010a; Usman et al., 2013; 2018b). After 20 weeks of bioremediation, the combined treatment removed 88.9% of TPHs whereas biological treatment alone removed 55.1%. Bioremediation may also lead to the formation of toxic byproducts which can also be toxic to the microbes. Therefore, the application of Fenton oxidation to bioremediation has been suggested to reduce soil toxicity and to improve treatment efficiency (Gong, 2012). For example, the removal of petroleum hydrocarbons increased from 55% (by 20 weeks of biostimulation alone) to 88% with the combined system where Fenton oxidation was applied to the biostimulation setup after 8 weeks (Gong, 2012).

Similarly, the application of Fenton oxidation as a pretreatment may improve overall remediation by (i) reducing the contamination to quantities less toxic for soil microbes, (ii) increasing the availability of pollutants for subsequent bioremediation, (iii) generating the biodegradable pollutant by-products, and (iv) providing oxygen and nutrients (by release from soil constituents) to improve the aerobic transformation of pollutants (as demonstrated in Figure 5 evaluating the interactions of oxidant species with soil constituents) (Sutton et al., 2011). Considering these advantages, the combination of Fenton oxidation with subsequent bioremediation (Table 2) has been tested in many studies by using Fenton oxidation as a

pre-treatment and bioremediation as a final polishing step. The use of an integrated system exhibited better treatment efficiency than either Fenton oxidation or bioremediation alone. For example, PAH removal by Fenton oxidation combined with bioremediation was higher (43–59%) than by bioremediation alone (22–30%) in a creosote oil-contaminated soil (Palmroth et al., 2006b). In another study, the application of Fenton oxidation as a pretreatment in an integrated system with bioremediation removed pyrene to a higher extent (82%) than by bioremediation alone (37%) (Jorfi et al., 2017). Similarly, PAH removal of 75% by the integrated system was noted in another creosote oil-contaminated soil with a 30% increase in removal contributed by the bioremediation step (Valderrama et al., 2009). In a petroleum-contaminated soil, the application of Fenton oxidation decreased the extractable organics from 32,400 to 21,800 mg kg⁻¹ soil which were further reduced to 5360 mg kg⁻¹ soil during 10 weeks of microbial treatment (Lu et al., 2010b). The major focus of the current research is to improve the microbial recovery and the efficiency of subsequent bioremediation. For this, there exist different strategies which are briefly described below:

(i) Reducing the oxidant dose during Fenton pre-oxidation: It has been found that lower amounts of oxidant (Fe/H₂O₂ ratio of 1:20) were sufficient to remove 43% of PAHs without inhibiting subsequent bioremediation, which caused to a total pollutant removal of 75%. However, aggressive pre-oxidation did not favor the subsequent bioremediation (Valderrama et al., 2009). A higher residual population of indigenous bacteria can be obtained by weak Fenton pre-oxidation (low H₂O₂ concentration) (Xu et al., 2016a; 2017a). As a consequence, the recovery period of microbes was shortened by 20-40 days and the efficiency of subsequent bioremediation was improved (Xu et al., 2016a). Therefore, the use of mild or weak Fenton peroxidation has been suggested for better efficiency of microbes in the subsequent bioremediation step (Valderrama et al., 2009; Xu et al., 2017a).

(ii) Shortening the contact time of the oxidant with microbes: Minimizing the amount of direct contact that soil microbes have with the concentrated oxidant can minimize the negative impacts of oxidation and can aid microbes to exhibit better bioremediation. This has been obtained by the incremental addition of H₂O₂ (Xu et al., 2011b) or by instant Fenton pre-

oxidation (Xu et al., 2020). The biodegradation of long-chain alkanes after instant Fenton pre-oxidation was two times higher than that after non-instant oxidation (Xu et al., 2020). In another effort to improve subsequent bioremediation, stepwise addition of H_2O_2 instead of adding all amount in the beginning has been suggested (Sutton et al., 2014a; Xu et al., 2011b). Incremental or sequential addition of chemical oxidant can provide mild oxidation conditions which prevent sterilization and a sudden increase in soil temperature (Xu et al., 2011b). In addition to its advantages in the coupled treatment process, the incremental addition of H_2O_2 also leads to higher oxidation efficiency (Lemaire et al., 2019; Xu et al., 2018). This has been attributed to the absence of scavenging reaction between H_2O_2 and HO^\bullet (that happens at high concentration) as H_2O_2 concentration remains low (Sutton et al., 2014a; Xu et al., 2018).

(iii) Biological stimulation after Fenton pre-oxidation: Biological stimulation is intended to provide nutrients to enhance the growth and activity of the existing microbes (Figure 4). A rebound in the bacterial communities and their activity has been noted when nutrients and air mixing were provided after preliminary Fenton pre-oxidation of an alkylbenzene-polluted soil (Martínez-Pascual et al., 2015). This rebound in microbial population allowed an efficient coupling of both techniques. Similarly, the use of nutrients and peanut hull in an oil-contaminated soil also allowed the microbes to recover their count and activities two weeks after Fenton oxidation (Gong, 2012). In addition to the use of a nutrient mixture, Valderrama et al. (2009) added a phosphate buffer in Fenton oxidation to control the reaction pH. The use of this buffer also provides phosphate to microbes and thus enhances their remediation potential (Sutton et al., 2011). Sutton et al. (2014a) noted that though microbial activity increased by the nutrients released during Fenton oxidation, a nutrient amendment was necessary to obtain diesel degradation by subsequent bioremediation. It should be noted that the addition of nutrients may not always be necessary as Fenton oxidation may release the nutrients by oxidizing the soil organic matter (Sirguyev et al., 2008). For example, phosphate concentration increased in soils after Fenton oxidation when the impact of

chemical oxidation was studied on plant growth (Sirguyev et al., 2008). A detailed description of the impact of Fenton oxidation on soil quality is provided in section 6.2.

(iv) Bioaugmentation by adding bacteria after Fenton pre-oxidation (Figure 4): Lu et al. (2010b) reported that Fenton-like oxidation reduced the microbial population from 3.45×10^6 CFU g⁻¹ to 4.21×10^3 CFU g⁻¹ soil. However, after inoculation with a mixed culture separated from the same contaminated soil, the microbial count increased gradually and attained a value of 2.19×10^8 CFU g⁻¹ after 4 weeks. The application of this treatment decreased the extractable organics by 84% (with 50% contributed by bioremediation). Similarly, the addition of indigenous microbes after Fenton pre-oxidation has also been tested in another pilot-scale study resulting in additional 19% removal of petroleum hydrocarbons (Kim and Lee, 2012).

4.2. Coupling of Fenton oxidation with chemical reduction

The coupling of Fenton oxidation with reduction has been mostly studied in aqueous solutions or spiked soils. However, the integration of both processes to remediate historically contaminated soil has been rarely investigated. There exists only one study that explored the removal of polychlorinated biphenyls (PCBs) in a historically contaminated soil by this coupled treatment (Rybnikova et al., 2016). This study relied on the use of four synthetic nanoparticles (Fe⁰, Fe/Ni, Fe₃O₄, Fe_{3-x}Ni_xO₄) which were firstly tested for the reductive transformation of PCBs followed by their use as catalysts in Fenton oxidation. In historically contaminated soil, only Fe⁰ and Fe/Ni particles exhibited better efficiency for reduction (13-18 %) and chemical oxidation (18-19%). It is worth mentioning that in PCBs spiked sand, the efficiency of Fe/Ni reached 97% (PCB28). This difference in treatment efficiency between spiked sand and historically contaminated soil has been linked to the soil matrix (Rybnikova et al., 2016). A detailed description of the impact of soil matrix is provided in Section 6.1 where various limiting factors are highlighted. The addition of oxidant after a preliminary reduction step could lead to the mineralization of the reduction by-products as the reactive oxidant species would react faster with low-chlorinated compounds or biphenyl, than with high-chlorinated compounds having greater stability (Rybnikova et al., 2016).

4.3. Coupling of Fenton oxidation with soil washing/soil flushing

Soil washing is an ex-situ process that involves the removal of contaminants from soil predominantly by washing with different liquids (extracting agents). In this process, different additives like surfactants and chelating agents are introduced into the washing solution to solubilize the soil pollutants which have low solubility and higher soil adherence. Similarly, soil flushing is an in-situ process where soils are flushed with extracting agents while the mobilized pollutants are collected in extraction wells. However, in both these processes, soil contaminants are only separated in soil solution. Therefore, contaminated washing effluents should undergo a suitable treatment before their discharge into the environment. Fenton oxidation has been successfully used as a post-treatment to decontaminate these contaminated effluents (Huguenot et al., 2015; Ma et al., 2016; Safa and Mehrasbi, 2019; Seo et al., 2015; Villa et al., 2010). For washing in historically contaminated soils, different extracting agents have been used like non-ionic surfactants (Dominguez et al., 2019; Huguenot et al., 2015; Ma et al., 2016; Seo et al., 2015; Villa et al., 2010), biosurfactant (Fanaei et al., 2020), cyclodextrins (Ma et al., 2016), and organic solvents (Usman et al., 2012).

Ma et al. (2016) compared the efficiency of non-ionic surfactants (Tween 80, Brij 58, and Brij 30) and cyclodextrin to enhance the washing efficiency of PCB (PCB28) in a soil contaminated with capacitor oil. The highest extraction efficiency (up to 61%) was observed with Brij 58 surfactant. However, the use of the surfactants and CD may contribute towards oxidant scavenging and thus can reduce the treatment efficiency of post-Fenton oxidation (Ma et al., 2016). Instead of separately treating the soil solution, Usman et al. (2012) spiked it on sand or the same soil sampled from a former coking plant site (as a pollutant availability enhancement strategy). It has been found that contrary to cyclodextrin, the scavenging effects can be avoided by using organic solvents (like chloroform or ethanol) as they can be evaporated after the extraction treatment (Usman et al., 2012). However, these solvents can have adverse impacts on the soil quality, and therefore, the use of vegetable oil has been suggested as an environment-friendly alternative for the desorption of pollutants (Bogan et

al., 2003; Gong et al., 2006). However, further studies are required to elaborate their role in historically contaminated soils.

It should be noted that coupling of soil washing/Fenton oxidation has also been studied with electrokinetic treatment (Table 2) (Popescu et al., 2017; Seo et al., 2015). The electrokinetic treatment relies on the low-density current generated by two electrodes introduced into contaminated soil. This current stimulates the transport of soil contaminants towards the electrodes where they are finally collected and treated (Popescu et al., 2017). The use of soil flushing and electrokinetic Fenton treatment removed about 58% of TPHs after 27 days of treatment in soil obtained from an area of high industrial activity in Spain (Popescu et al., 2017; Seo et al., 2015).

5. Experimental setups tested for Fenton oxidation of historically contaminated soils

Researchers have used different experimental setups to explore treatment efficiency in real contaminated soils such as batch, flow-through conditions (saturated, unsaturated, and closed-loop columns), and field application. Batch experiments are used to optimize the experimental conditions where oxidant solution is stirred with the contaminated soil ensuring an optimum contact between oxidant and contaminant for improved efficiency. Column experiments are considered as a better representative of field conditions and are usually performed on the basis of parameters derived from batch conditions (Usman et al., 2020; 2021). Oxidant solution is injected in soil columns under saturated (upward oxidant injection with a peristaltic pump) or unsaturated conditions (downward addition of oxidant where oxidant solution flows only due to gravity gradient). Preferential oxidant movement could leave the presence of preferential pathways and/or gas phase in the unsaturated columns because flow of water is mainly controlled by the gravity gradient (Rybnikova et al., 2017). Both these saturated and unsaturated systems represent open-loop setup where oxidant solution is flushed out of the system and thus any loss of unreacted oxidant would decrease the oxidation efficiency. Therefore, a closed-loop system was developed which is based on recirculation of injected oxidant solution which improves the oxidation efficiency. Generally,

treatment efficiency depends upon the oxidation system and follows this order: batch > closed-loop saturated column > saturated column > unsaturated column (Rybnikova et al., 2017).

Most of the remediation studies (Table 2) relied on batch experiments due to the simplicity of setup, better control over reaction conditions, and preliminary nature of investigations. Column systems are relatively complicated and were the subject of very few studies though they offer a better representation of the field conditions (Table 2). Closed-loop system has been tested by Rybnikova et al. (2017) to remediate a PCB-contaminated soil. A similar system has been applied by Talvenmäki et al. (2021) to treat a residential lot impacted by spills from a leaking light heating oil tank.

6. Major challenges and implications of Fenton oxidation in historically contaminated soils

Contrary to the aqueous solution or spiked soils, oxidation efficiency in historically contaminated soils could have different implications. Fenton oxidation can alter the physicochemical properties and microbial population of contaminated soils. Moreover, the efficiency of Fenton oxidation can be limited by poor pollutant availability in aged soils. Provided below is a brief description of these impacts and their potential solutions.

6.1. Poor pollutant availability and soil matrix effect

Poor pollutant availability is the major limitation in historically contaminated soils due to strong hydrophobicity and partitioning of pollutants into soil constituents especially organic matter (Figure 1) (Biache et al., 2015; Usman et al., 2013; 2016a). These contaminants are deeply diffused into the soil organic matter that renders them unavailable for the hydroxyl radicals (Bogan et al., 2003). Therefore, pollutant availability and Fenton oxidation efficiency have been strongly linked in PAH-contaminated soils (Biache et al., 2015; Lemaire et al., 2019; Usman et al., 2013; 2016a). Indeed, magnetite-catalyzed heterogeneous Fenton oxidation was not able to degrade PAHs unless their availability was increased in two coking plant soils (Usman et al., 2012). Due to this strong correlation, the efficiency of Fenton

oxidation efficiency has been proposed as a valid indicator to assess pollutant availability (Biache et al., 2015). This limitation in historically contaminated soils can be addressed by using different pretreatments including chemical, extraction, and thermal.

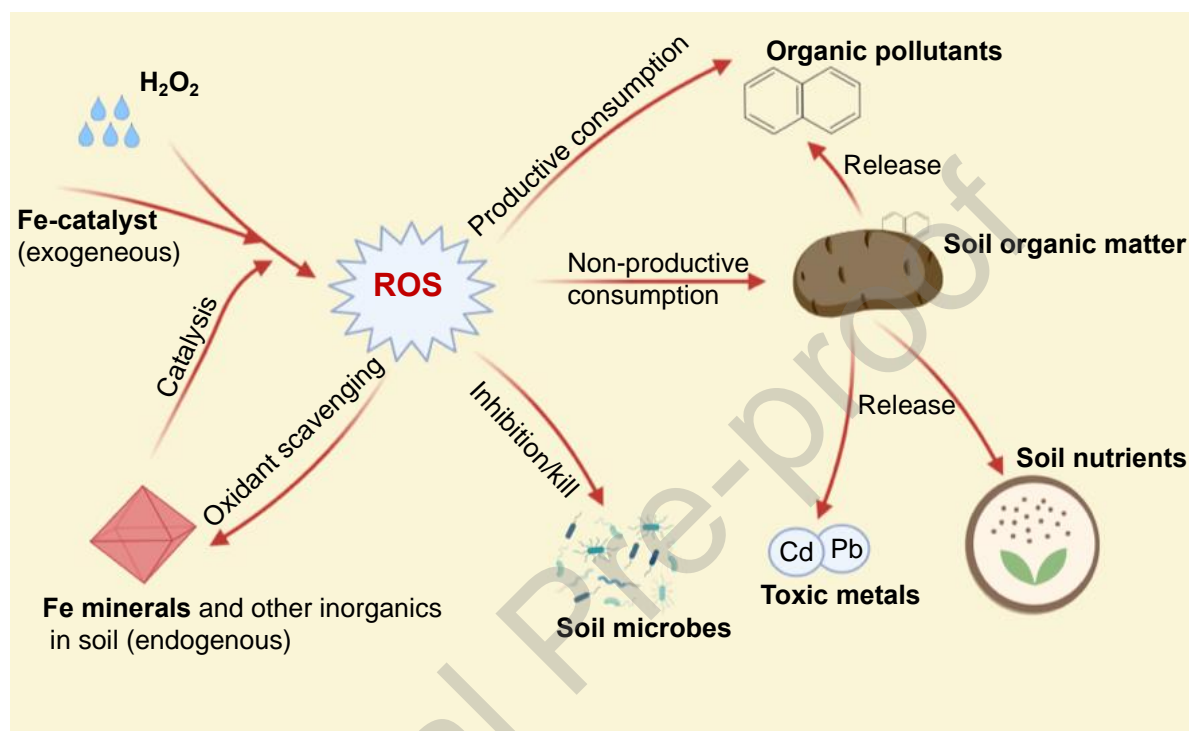


Figure 5: Interactions of reactive oxygen species (ROS) including with various soil constituents in historically contaminated soils. ROS predominantly include HO^\bullet along with other species like 1O_2 , H_2O_2 , $O^{\bullet-}_2$. After applications it interacts with soil pollutants (productive consumption) and non-productive consumption by soil organic matter and/or soil minerals. Among soil minerals, Fe minerals also contribute in the generation of ROS by catalyzing the added oxidant. (Figure prepared using Biorender app)

Chemical pretreatments are intended to enhance pollutant availability by using various chemical reagents like co-solvent, cyclodextrin, surfactant, and vegetable oil (Usman et al., 2016b). For example, treating ethanol pre-treated soil by Fenton oxidation increased the PAH removal by 11–28% (Lundstedt et al., 2006) and 20% in another study (Usman et al., 2012). However, ethanol can also act as a radical scavenger (Lundstedt et al., 2006). This scavenging effect was avoided by its evaporation in the soil before introducing the oxidant (Usman et al., 2012). In the same coking plant soil, the use of cyclodextrin as a pretreatment

of Fenton oxidation resulted in slightly lower PAH removal (15%) as compared to ethanol pretreatment due to its potential contribution to oxidant scavenging (Usman et al., 2012). Similarly, pretreating the PAH contaminated soil with vegetable oil also improved the efficiency of subsequent Fenton oxidation up to 45% (Bogan et al., 2003). It should also be noted that vegetable oil pretreatment rendered both heavy and light PAHs available for Fenton oxidation. On the other hand, only light PAHs were degraded by Fenton oxidation in the absence of this pretreatment.

It is well established that freshly-contaminated soils (artificially spiked) are easier to oxidize than historically contaminated soils as native pollutants in the latter case are strongly sequestered onto soil constituents for years (Jorfi et al., 2013; Lemaire et al., 2013; Nam et al., 2001; Usman et al., 2012). Against 84% and 96% removal of pyrene and Benzo(a)pyrene, respectively, in a spiked soil, only 40% and 20% of these pollutants were degraded when the same Fenton treatment was applied in a soil from former manufactured gas plant (Nam et al., 2001). Considering this, our group separated the extractable organic matter (EOM) by solvent extraction from two ancient PAH-contaminated coking plant soils and spiked it on sand as fresh PAH contamination (Usman et al., 2012). Application of Fenton-like oxidation in spiked sands removed more than 90% of PAHs whereas similar treatment was almost unable to degrade any PAHs when applied directly in soil. In the next step, instead of separating the EOM from the soil, it was allowed to evaporate in the same soil. This was done to improve the availability of PAHs as the fresh contamination in the same soils. This strategy removed up to 60% of PAHs in re-contaminated soils. This decrease in pollutant removal efficiency between spiked sand (90%) and real soil (60%) was attributed to non-productive oxidant consumption by insoluble organic matter and/or soil carbonates (Lemaire et al., 2019; Usman et al., 2012). These interactions of reactive oxygen species (ROS) with different soil constituents are shown in Figure 5. In general, soil organic matter can affect the Fenton oxidation in different ways: (i) as a surfactant and redox agent (Xu et al., 2017b), (ii) as a metal chelator (Sherwood and Cassidy, 2014), (iii) its competition with target pollutants for the oxidant (Lemaire et al., 2019; Usman et al., 2012). Therefore,

higher natural oxidant demand should be expected in real contaminated soils as compared to spiked sand or aqueous solutions.

Similarly, the pollutant availability and the efficiency of subsequent Fenton oxidation can be enhanced by pre-heating the contaminated soils. Pre-heating two ancient coking plant soils at different temperatures improved the subsequent Fenton oxidation of PAHs by 19, 29, and 43 % in A soil and 31, 36, and 47 % in B soil pre-treated at 60, 100, and 150 °C, respectively (Usman et al., 2016a). In another study (Biache et al., 2011), thermal pretreatment (100 °C for 1 week under inert atmosphere) was mainly found effective in soils from former coking and gas plants due to the long-term aging rendering PAHs unavailable. While the application of a similar pretreatment did not significantly enhance the Fenton oxidation of PAHs in soils sampled from an active wood treating facility (Biache et al., 2011). Mechanisms underlying an increased pollutant availability by thermal pretreatment have not been yet investigated due to limited research on this theme. Moreover, a better understanding of this process is required for its upscaling to the field with due consideration to the nature of the target soil. In any case, it is essential to thoroughly characterize the soil before applying Fenton oxidation as soil nature and pollutant interactions may necessitate extended contact for treatment or additional treatments.

6.2. Impacts of Fenton oxidation on soil quality and productivity

Fenton oxidation is highly efficient to decrease pollutant load in contaminated soils. However, it could also have negative effects on soil quality, microbial community and its productivity (Figure 6). This section describes the effects of Fenton oxidation reported in historically contaminated soils.

6.2.1. Impacts of Fenton oxidation on soil physico-chemical properties

Generally, the application of Fenton-based treatments in contaminated soils is accompanied by a decrease in soil's pH and a temporary increase in its temperature. The intensity of this variation is usually dependent on the dose of the reagents, the nature of the contaminated soil, and the treatment time (Cheng et al., 2016b; Ferguson et al., 2004; Liao et al., 2019;

Sirguey et al., 2008; Villa et al., 2008). For example, the decrease in the soil pH after oxidation varied between about 1.3 (Liao et al., 2019) to more than 5.5 units (Ferguson et al., 2004). Sirguey et al. (2008) studied, the efficiency of Fenton oxidation for the treatment of an alkaline PAH contaminated soil sampled from a coking plant site. A slight decrease in pH from 9.7 to 8.3 was reported after Fenton oxidation (H_2O_2 and Fe(II) at concentrations of 1.12 and 0.1 mol L^{-1} and UV irradiation). Laurent et al. (2012) also noted a prominent decrease in pH (from 7.3 to 4.8) and cation exchange capacity (CEC) (2 units) during the treatment of an industrial PAH-contaminated soil particularly at higher oxidant dose (65 g kg^{-1}). Similarly, for higher reagent concentrations (10 mol L^{-1} of H_2O_2 and 10 mol L^{-1} of FeSO_4), Ferguson et al. (2004) reported a temporarily pH decrease of 5.5 units (from 9.3 to 3.8) at the soil surface (<5 cm soil depth) in a field contaminated with petroleum products near the old Casey station, East Antarctica. This pH variation was found to be much lower (0.4 units) at a higher sampling depth (10 to 15 cm). During this field assay, a temporary but significant increase in soil surface temperature from 8 °C to 35-60 °C was reported due to the exothermic nature of Fenton oxidation. Similar increase in temperature was also observed by Villa et al. (2008) during the treatment of pesticide contaminated soil at laboratory scale by traditional Fenton process (20 mM H_2O_2 , 4 M soluble Fe(II) , pH 2.8). Temperature increased from 25 °C to about 55 °C during the first 30 min of the reaction and started gradually decreasing after 70 min of reaction. This temporary increase in temperature is mainly dependent on the concentration of H_2O_2 (Cheng et al., 2016b). Indeed, the average soil temperatures of 40.3, 48.4, 59.5, 66.2 and 71.1 °C were reported against H_2O_2 concentrations of 5, 10, 15, 20 and 30%, respectively in soil from a pesticide manufacturing plant treated by Fenton-like oxidation catalyzed by steel slag.

Though compared to the traditional Fenton oxidation, a modified Fenton treatment allows the oxidation to take place at neutral pH, the use of acidic chelating agents can lead to a prominent decrease in pH. For example, Liao et al. (2019) studied the remediation of a coking plant soil for three days using both Fenton oxidation (1 mM of H_2O_2 and 0.2 mM of FeSO_4 solution per g of soil) and modified Fenton treatment (2 mM of H_2O_2 , 0.4 mM of

FeSO₄ solution and 0.4 mM of citric acid per g of soil) which decreased the soil pH by about 1.3 and 5.7 units, respectively. However, the drop in pH was very small (from 7.20 to 7.10 in one soil and from 8.35 to 8.10 in soil) when Fenton-like oxidation (using magnetite) was applied in two coking plant soils (Usman et al., 2012). Interestingly, the use of steel slag-catalyzed Fenton-like oxidation slightly increased the soil pH from 5.4 to 6.2 due to the basic nature of steel slag (pH 12.3). It should be noted that in case of modified or Fenton-like oxidation, the decrease in pH is not as harsh as it could be in traditional Fenton oxidation where initial acidification (pH of 3) is required. Still, this small decrease in pH along with higher oxidant amount could significantly decrease the soil microbial count which, however, can be regenerated (as demonstrated in the section 6.2.4).

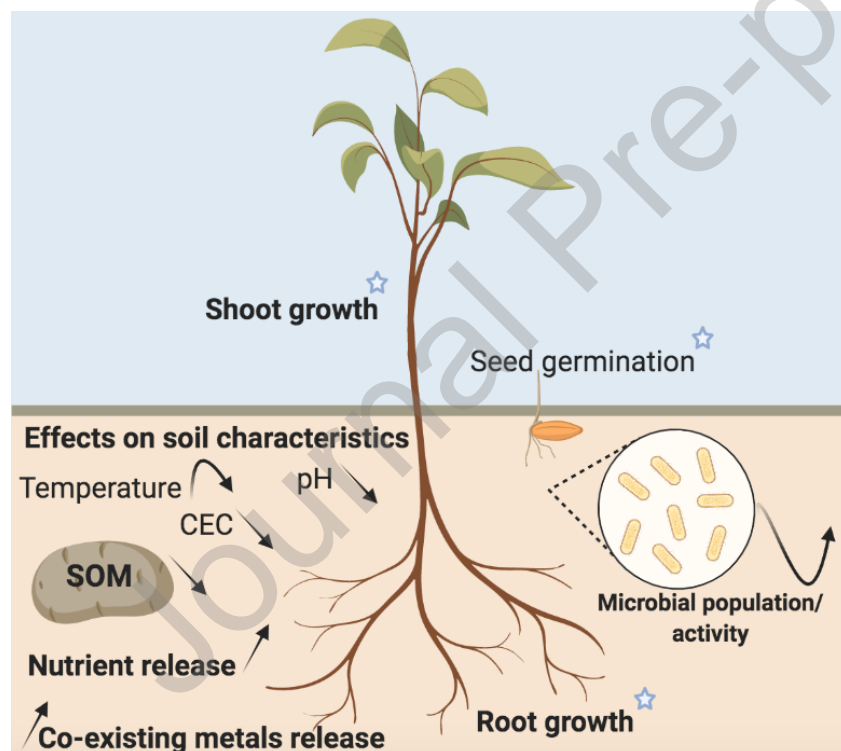


Figure 6: Impacts of Fenton oxidation on soil quality and plant growth. The parameters marked with an upward arrow indicate an increase while that with a downward arrow represent a decrease after Fenton oxidation. Contrasting findings have been reported for the starred parameters (☆). Microbial population decreases rapidly after Fenton oxidation but rebounds once the favorable conditions are restored. Temperature, however, represents a temporary increase that may be very harsh at strong oxidant doses. (Figure prepared using Biorender app)

6.2.2. Effects of Fenton oxidation on soil organic matter

Fenton oxidation, being a non-selective process, generally degrades both the target organic pollutants as well as the non-target SOM (Sutton et al., 2014a). The SOM is an extremely important soil constituent due to its role in maintaining soil quality and health. In historically contaminated soils, the organic matter bearing persistent pollutants can be more condensed than natural organic matter and thus may be recalcitrant to degradation. Moreover, Fenton oxidation can decrease the SOM contents to different extents depending upon the soil type, the reagents concentrations, and the treatment duration (Cheng et al., 2016b; Sirguyey et al., 2008; Sutton et al., 2014a; 2014b; Xu et al., 2017a). For example, a slight decrease in SOM contents from 4.7 to 4.3% was noted during Fenton-like oxidation of pesticide-contaminated soil (Cheng et al., 2016b) (Figure 7). Sirguyey et al. (2008), reported a slight decrease of the soil's total organic content (TOC from 9.9% to 8.7%) during the remediation of a coking plant soil (H_2O_2 1.12 M and Fe(II) 0.1 M). Similarly, Liao et al. (2019) reported that Fenton's reagent (H_2O_2 + soluble Fe(II) applied at neutral pH) had a negligible impact on TOC in two different soils from a coking plant and coal gas plant. However, the use of modified Fenton oxidation with citrate as an organic chelating agent significantly increased the TOC in both soils (from about 2.5 to 5% and from 0.3 to 1.5% in soils from coking and coal gas plants, respectively).

The degradation of SOM is also accompanied by an increase in dissolved organic carbon (DOC) due to the release of natural soil organics (Cheng et al., 2016b) (Figure 7). Soils intrinsically rich in organic matter exhibited an important SOM degradation as indicated by an increase in DOC from 69 mg kg^{-1} to 578 mg kg^{-1} (peat soil) and from 337 mg kg^{-1} to 3746 mg kg^{-1} (fill soil) by traditional Fenton oxidation ($150 \text{ mg L}^{-1} \text{ FeSO}_4$, 5 % H_2O_2 , pH < 3) (Sutton et al., 2014b). This increase in DOC contents was less prominent (2871 mg kg^{-1} in peat soil) with modified Fenton oxidation ($150 \text{ mg L}^{-1} \text{ FeSO}_4$, 5 % H_2O_2 , 1.2 g L^{-1} citrate, pH 6.8). Similar findings were observed by Sutton et al. (2014a) during oxidation of a contaminated soil collected from a railroad station in Poland. They reported that DOC concentrations were about 8 and 16 times higher after modified Fenton (pH 6.5-7) and the

traditional Fenton process (pH 3). An increase of 3.6 times in DOC was reported by Cheng et al. (2016b) using steel slag catalyzed Fenton-like process for the remediation of pesticides-polluted soil at natural conditions. The DOC concentrations were not significantly affected with sequential oxidant addition (three times over three days) (Sutton et al., 2014a). In another study, DOC contents increased by 15.1 times in oil-well contaminated soil (Yan'an, China) after Fenton pre-oxidation (900 mM H₂O₂, 2.9 mM Fe(II)) (Xu et al., 2017a). However, DOC concentration decreased from 7750 to 5940 mg kg⁻¹ when the H₂O₂ concentration was doubled (from 900 mM to 1800 mM) and to about 2600 mg kg⁻¹ when the pre-oxidation phase was performed without Fe(II). It is worth mentioning that most of these findings concern the coupling studies which are intended to provide mild treatment conditions. However, the loss of SOM could be more prominent when harsh oxidation conditions are used.

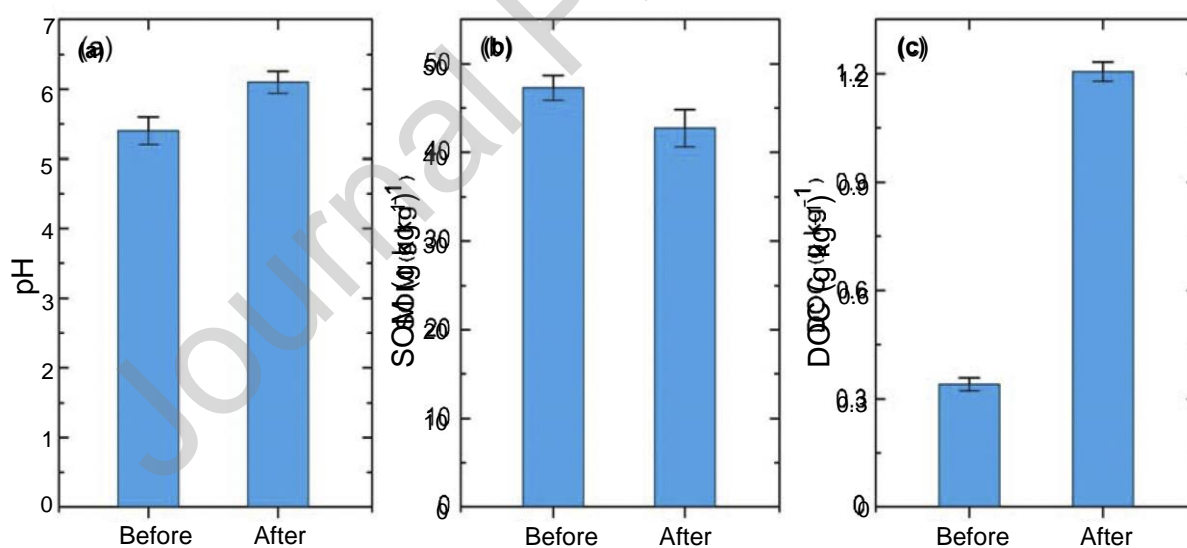


Figure 7: Effects of the Fenton-like treatment on the pH (a), soil organic matter – SOM (b), dissolved organic carbon – DOC (c) of a pesticide contaminated soil having 617.5 mg kg⁻¹ as the initial concentration of atrazine). converter slag dosage = 80 g kg⁻¹; H₂O₂ contents = 10%. This figure is reproduced with permission from Ref. (Cheng et al., 2016b).

6.2.3. Impacts on the release of nutrients and co-existing pollutants

There exists limited data on the effect of Fenton oxidation on the release of nutrients and co-existing pollutants in the target soils (Figure 6). For example, Sirguyev et al. (2008) reported that the Fenton oxidation of a PAH-contaminated coking plant soil caused an important decrease in contents of total N (from 2.20 to 1.51 g kg⁻¹), N-NO₃ (from 17.0 to 1.8 mg kg⁻¹), the available P (from 56 to 32 mg kg⁻¹). Moreover, this treatment also changed the aggregates structure due to SOM oxidation, and increased the surface area (from 16.8 to 21.5 m² g⁻¹) and the water retention capacity (from 9.1% to 22.8%). Furthermore, the exchangeable Ca and Mg were increased from 720 to 1280 mmol kg⁻¹ and from 9 to 14 mmol kg⁻¹, respectively. The N-NH₄ content was increased from 6.7 to 20.1 mg kg⁻¹. A similar trend was observed by Sutton et al. (2014a) after the treatment of a diesel-polluted soil by Fenton (H₂O₂/Fe(II) at pH 3) and modified Fenton oxidation (H₂O₂/Fe(II)/citrate at pH 6.5-7) oxidation. The N-NH₄ concentration in the polluted soil (0.5 mg kg⁻¹) increased by factors of 172 and 14 after Fenton and modified Fenton treatment, respectively. Moreover, the initial contents of total nitrogen (3.25 mg kg⁻¹) increased by about 62 and 13 times, respectively. Similarly, N-NH₄ content after Fenton pre-oxidation was enhanced from 15 mg kg⁻¹ to 763 mg kg⁻¹ with an increase in the H₂O₂ concentration from 0 mM to 1800 mM highlighting the role of oxidant dose in nutrient release (Xu et al., 2017a).

On the other hand, Fenton treatment was also found to increase the release of metals in co-contaminated soils (Villa et al., 2008). For example, Fenton oxidation of a pesticide contaminated soil increased the dissolution potential of 36%, 12%, 8.9%, 3.1%, and 0.9% for Zn, Cu, Ni, Mn, and Cr, respectively after 84 h of reaction. This high metal release was imputed to the SOM oxidation (leading to the release of metals, Figure 5) and acidic conditions that improve the solubility of immobilized metals. This increase in mobilization of pollutants has also been linked to the presence of H₂O₂ and other reactive species including oxidants and reductants formed during oxidation (Bennedsen et al., 2012). However, chelating agents like citrate, EDTA, and pyrophosphate did not seem to enhance metal mobilization (Bennedsen et al., 2012).

Further studies are, however, required to better understand the fate of different pollutants in co-contaminated soils and the mechanisms underlying metal mobilization. Along with that, field application also calls for the investigations into the evolution of SOM, DOC, nutrients, and co-existing pollutants following Fenton oxidation. This would be highly useful to better predict the efficiency of subsequent bioremediation.

6.2.4. Effects of Fenton oxidation on soil microorganisms

The application of oxidant affects the microbial community due to the combined effect of i) direct and harsh interactions of oxidant species with microbes, ii) generated heat, and iii) the acidic conditions during the Fenton oxidation. Several studies have studied the effect of Fenton-based processes on microbial communities' growth, diversity, and regeneration (Ferguson et al., 2004; Polli et al., 2018; Sutton et al., 2014a). Commonly, a dramatic decrease of the microbial community is observed after the oxidation, followed by a regeneration period of varying length (Liao et al., 2019; Sutton et al., 2014a). For example, the application of Fenton oxidation ($\text{H}_2\text{O}_2 + \text{Fe}^{\text{II}}$ without pH adjustment) decreased the bacterial, fungal, and PAH degrading bacteria population in a PAH-contaminated soil that rebounded after five weeks of incubation (Laurent et al., 2012).

The response and regeneration potential of microbes is usually dependent on the nature of tested soil, oxidation conditions, incubation duration, and the provision of favorable conditions for microbes like nutrients, air, etc. Depending on the experimental conditions (especially H_2O_2 concentration and treatment time), the total recovery of the microbial community could take longer time (Palmroth et al., 2006a; Sutton et al., 2014a). Indeed, even after 16 weeks of incubation, the soil previously treated for 10 days with a relatively high H_2O_2 amount (0.4 g per g of soil) had lower intact microbial cells (68%) than the untreated soil (95%) (Palmroth et al., 2006a). Likewise, Polli et al. (2018) investigated the impact of Fenton-like process at two H_2O_2 doses (2% and 6%) and two application modes (single and sequential addition) for the treatment of a diesel-contaminated soil collected from a gasoline station. The laboratory microcosms showed the devastating impact of all treatments on bacterial density and diversity (6S copy number decreased from $6.54 \times 10^8 \text{ g}^{-1}$

to about 1×10^5). But microbial community was partially recovered (16S copy number of 10^7 to 10^8) after 30 days of incubation of soil treated at lower oxidant dose (2%), while reaching a complete recovery in 03 months. Whereas for H_2O_2 dose of 6%, there was no recovery after 30 days and bacterial abundance was still two orders of magnitude lower than untreated soil even after 3 months of incubation.

Similarly, the nature of treatment and soil also affect the response of microbes. For example, Liao et al. (2019) reported that the microbial community began to grow after 7 and 10 days for the Fenton and modified Fenton treatments, respectively. Similarly, Sutton et al. (2014b) investigated the effect of both the soil nature (peat and fill) and oxidation method (Fenton and modified Fenton) on the bacterial activity for a period of 8 weeks. Both processes reduced the total bacterial 16S rRNA gene abundance by approximately one order of magnitude in both soils, confirming the moderate effect of the chemical oxidation on the indigenous soil microorganisms. Bacterial regeneration started after 1-4 weeks for the peat soil and 1-2 weeks for the fill soil. At the end of the incubation period (8 weeks), a quasi-full recovery of microbial biomass was reported for both soils. In contrast to the 16S rRNA gene measurements, for the two soils, no reduction of the monooxygenase gene (*alkB*) abundance was reported after chemical oxidation. Moreover, a rapid increase of the *alkB* gene contents was observed after 1 week of incubation, especially in the fill soil. The composition of microbial community was also found to be different depending upon the nature of treatment.

Results at the laboratory scale are generally different from the last field investigation. For example, Ferguson et al. (2004) in a field study (Casey station, East Antarctica), showed that the application of Fenton oxidation devastatingly reduced the contents of the total heterotrophs from 138×10^3 to below detectable levels within only 3 days. New microbial growth was detected after about 3 years. The authors explained this long-time recovery by the high sensitivity of the Antarctic ecosystems.

It is important to mention that the response of microbial community was much better after Fenton oxidation as compared to that after other oxidants including permanganate and

persulfate oxidation (Liao et al., 2019) (Figure 8). Permanganate was particularly harsh in inhibiting the microbial diversity and delaying their population recovery. Better response of microbial community to Fenton oxidation was linked to higher formation of biodegradable byproducts (used by microbes for their growth) during this process as compared to other oxidation methods. Likewise, Martínez-Pascual et al. (2015) reported that the provision of nutrients and air could improve the recovery of microbial population and community which was initially negatively impacted Fenton oxidation. The regenerated microbial community after 4 weeks was still different from the one present in the blank tests. They concluded that the impact of the Fenton oxidation on the microbiota lasts even after the disappearance of the added oxidants. To summarize, microbial population may be temporarily affected but their regeneration can be enhanced by applying strategies such as reducing the oxidant dose and or contact with the microbes, biological stimulation by providing nutrients after oxidation, and bioaugmentation by adding bacteria after Fenton treatment as demonstrated in Section 4.1.

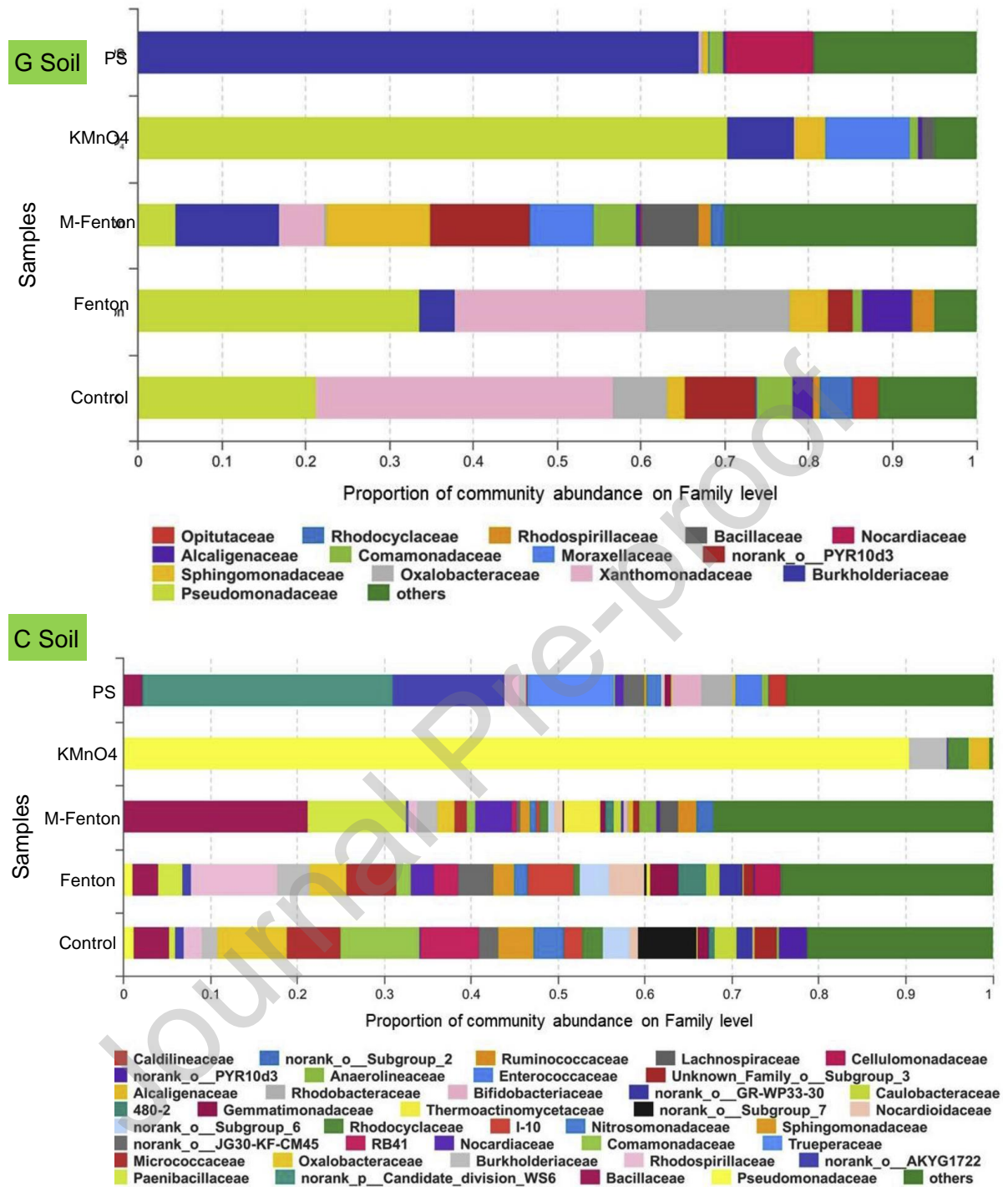


Figure 8: The structure of microbial community in a coal gas plant soil (G) and coking plant soil (C) after treatment by persulfate oxidation (PS), permanganate oxidation (KMnO₄), modified Fenton oxidation, (M-Fenton), Fenton oxidation (Fenton) and control. This image is reproduced with permission from Ref. (Liao et al., 2019).

6.2.5. Effects of Fenton oxidation on soil revegetation capacity

The impact of the Fenton-based technologies application on plants grown in real contaminated soils has been exclusively assessed at laboratory scale through petri dishes or pot assays (Figure 6). For example, Sirguy et al. (2008) reported that Fenton oxidation had a positive impact on the germination and growth of ryegrass (*Lolium multiflorum*, L.) in pot experiments. Indeed, the kinetic of seed emergence was higher in treated soil (former coking plant soil contaminated with PAHs) as maximum germination was achieved after 11 as compared to 18 days in non-treated soil respectively. Moreover, after a growth period of three weeks, compared to the blank assay, the Fenton treatment increased the average germination rate, the fresh and dry shoot biomass from 73%, 13.6 mg, and 3.0 mg to 90%, 119.0 mg, and 17.8 mg, respectively. Moreover, fresh root biomass and length have significantly increased from 1.1 mg and 0.8 mm to 17.7 mg and 4.2 mm, respectively. They imputed this positive effect to the decrease in the soil hydrophobicity and increase of the water availability. However, Laurent et al. (2012) noted that plant growth in a treated coking plant soil (contaminated with PAHs) was negatively affected at a higher oxidant dose (by modified Fenton oxidation with H_2O_2 at 65 g kg^{-1}). Moreover, treated soil also displayed a significant delay in seed germination and a decrease in root and shoot biomass. The decreased values of soil pH and higher oxidant concentration were found as the major limiting factors to affect plant growth (Laurent et al., 2012). Considering the contrasting results (performed at different oxidant doses) and very limited studies (only 02) on this topic, further studies are required to better evaluate the phytotoxicity of the reagents involved in Fenton oxidation.

7. Conclusions and outlooks

Fenton oxidation has been applied to decontaminate soils historically contaminated with various pollutants. However, the efficiency, reaction chemistry, and environmental impacts of Fenton oxidation is significantly altered depending on the nature of the Fenton process and catalyst type in particular. In comparison to the traditional Fenton oxidation, heterogeneous

processes have displayed better decontamination potential and less hazardous impacts on soil quality and native biota. The development of efficient and environment-friendly heterogeneous catalysts is a promising field. More efforts should be focused to improve catalyst stability and longevity in heterogeneous soil medium. Moreover, it is highly demanding to explore the fate of these catalysts in contaminated soils. Nanomaterials are gaining significant attention as heterogeneous catalysts recently but their injection into soil requires many investigations prior to their field application. Moreover, the toxicity of nanomaterials is itself a widely debated topic. Therefore, a comprehensive understanding of their interactions with soil biota is required. Owing to the substantial role of endogenous iron minerals, efforts are required to further improve their role. A thorough characterization of the soil before applying Fenton oxidation is essential due to the role of soil constituents and pollutant interaction as they may necessitate alterations in Fenton oxidation conditions (in oxidant doses, contact time or method of injection, etc.) or additional pretreatments (like availability enhancement of pollutants or iron minerals).

Similarly, the application of chemical oxidants leads to a dramatic decrease in soil microbial community which, however, can be regenerated if favorable conditions are provided after Fenton oxidation. However, extremely harsh oxidation conditions may completely destroy the soil structure making it very difficult to recover. Therefore, various strategies have been suggested to reduce the environmental impacts of oxidants like by reducing the oxidant dose and or contact time with the soil. In addition to this, biological stimulation by providing nutrients after oxidation, and bioaugmentation by adding bacteria can also facilitate soil recovery. These strategies have enabled the integration of Fenton oxidation with bioremediation that emerged as an environmental-friendly strategy. Maintaining a balance between the oxidation conditions, treatment cost, and environmental impacts would be crucial to design an environment-friendly and efficient treatment. Further studies are also required to assess the cost of this technology which is dictated by the site-specific geochemical and contaminant circumstances particularly for real field applications. To assess the cost of this treatment, the amount of pollution and the polluted soil volume must

be taken into account. While developing the cost information, it should be acknowledged that costs reported under a set of conditions at one site are very difficult to extrapolate to the other sites. Field scale applications are severely limited for Fenton oxidation in contaminated soils. Therefore, a thorough understanding of Fenton oxidation is required under field conditions to identify the true worth of the applicability and worth of this remediation strategy.

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Table 2: Summary of the prominent studies reporting the use of Fenton oxidation in historically contaminated soils. These studies are arranged chronologically according to the nature of pollutant.

Fenton oxidation strategy	Catalyst system	Pollutant type	Soil origin	Experimental setup	pH	Purpose of study	Ref.
Pesticides							
Traditional Fenton	Soluble Fe(II) and native Fe	DDT and DDE	Former pesticides warehouse, Mato Grosso, Brazil	Batch slurry	2.5-3	Oxidation of pesticides and evaluation of oxidation parameters particularly native Fe	(Villa and Nogueira, 2006)
Traditional Fenton	Soluble Fe(II)	DDT	Former pesticides warehouse, Mato Grosso, Brazil	Batch slurry	2.5-3	To evaluate treatment efficiency and impacts on metals and organic matter in soil	(Villa et al., 2008)
Soil washing followed by photo-Fenton oxidation	soluble Fe(II) with solar irradiation	DDT and DDE	Former pesticides warehouse, Mato Grosso, Brazil	Batch slurry	2.8	To test the feasibility of a coupled process	(Villa et al., 2010)
Fenton-like system	nZVI	DDT and DDE	Former organochlorine pesticide manufacturing plant, Jiangsu, China	Batch slurry	6.6	To test the efficiency of nZVI catalyzed chemical oxidation to degrade pesticides	(Cao et al., 2013)
Traditional Fenton and Fenton-like oxidation	Soluble Fe(II) or Fe ₃ O ₄	HCH	Former gravel pit of lindane manufacturing industry, Sierentz, France	Batch slurry	2 and 8	To evaluate the use of chemical oxidation to remediate HCH contaminated soils	(Usman et al., 2014)
Fenton-like oxidation	Steel converter slag	Atrazine	Site of pesticide manufacturing plant, Xiangtan,	Batch slurry	5.4	To assess the remediation efficiency and	(Cheng et al., 2016b)

			China			impact on soil	
Traditional Fenton oxidation	Soluble Fe(II)	Chloropyrifos and -bromo-2-chlorophenol	Insecticide factory, Jiangsu, China	Batch slurry	3	To compare the treatment efficiency of Fenton oxidation and persulfate oxidation	(Zhu et al., 2017)
Modified Fenton oxidation	Soluble Fe(II)	HCH	Former gravel pit of lindane manufacturing industry, Sierentz, France	Batch and column	8.05	To compare the efficiency of different oxidation systems (Fenton, persulfate, permanganate)	(Usman et al., 2017)
Polycyclic Aromatic Hydrocarbons (PAHs)							
Fenton-like oxidation	Relied only on soil indigenous Fe (16.4 g kg ⁻¹)	PAHs	Creosote oil contaminated soil from a wood impregnation site	Downflow soil columns	5 – 6	To evaluate treatment efficiency and effect on microbial activity	(Palmroth et al., 2006a)
Fenton-like oxidation + biodegradation	Relied only on soil indigenous Fe (16.4 g kg ⁻¹)	PAHs	Creosote oil contaminated soil from a wood impregnation site	Downflow soil columns	5 – 6	To evaluate the coupling of Fenton oxidation with bioremediation	(Palmroth et al., 2006b)
Ethanol pretreatment followed by traditional Fenton oxidation	Soluble Fe(II)	PAHs	Former gas work site, Sweden	Batch slurry	2-3	To test the efficiency of ethanol pretreatment on subsequent treatment by Fenton oxidation	(Lundstedt et al., 2006)
Traditional Fenton oxidation	Soluble Fe(II)	PAHs	Soils from industrial sites for wood preservation, coke	Batch slurry	pH 3, 70 °C,	Comparison of the treatment efficiency of Fenton and ozone	(Jonsson et al., 2006)

			production, gas work, Sweden			oxidation	
Traditional Fenton oxidation	Soluble Fe(II)	PAHs	Soils from industrial sites for wood preservation, coke production, gas work, Sweden	Batch slurry	pH 3, 25 °C	To study the role of soil properties and PAH characteristics in multiple soils	(Jonsson et al., 2007)
KH ₂ PO ₄ stabilized H ₂ O ₂ followed by bioremediation	Soluble Fe(II)	PAHs	Creosote oil contaminated soil samples from a wood preserving site, Spain	Batch slurry	3	To test the coupling of Fenton oxidation with bioremediation	(Valderrama et al., 2009)
Modified Fenton oxidation	Soluble Fe(III) + EDTA	PAHs	Former manufactured gas plant	Batch slurry	7.9	To test the formation of surfactants during chemical oxidation	(Gryzenia et al., 2009)
Modified Fenton oxidation	Soluble Fe(II)	PAHs	Former coking plant site, Neuves-Maisons, France	Unsaturated columns	7.3	To explore the effect of Fenton oxidation on soil properties	(Laurent et al., 2012)
Fenton-like oxidation	Fe ₃ O ₄ or soluble Fe(II)	PAHs	02 soils: Former coking plant sites, Neuves-Maisons and Homécourt, France	Batch slurry	7.2 – 8.3	To evaluate the catalytic ability of Fe ₃ O ₄ to promote Fenton-like oxidation	(Usman et al., 2012)
Modified Fenton oxidation	Soluble Fe(II)	PAHs	02 soils: Former coking plant sites, Neuves-Maisons and Homécourt, France	Unsaturated columns	7.4-8.4	To evaluate PAH oxidation under dynamic conditions and to see the role of PAH	(Lemaire et al., 2013)

						availability	
Thermal pretreatment followed by Fenton-like oxidation	Fe ₃ O ₄	PAHs	02 soils: Former coking plant, former gas plant, active wood-treating facility, France	Batch slurry	Natural	To evaluate the role of a pre-heating treatment (100 °C) on subsequent chemical oxidation	(Biache et al., 2015)
Thermal pretreatment followed by Fenton-like oxidation	Fe ₃ O ₄	PAHs	02 soils: Former coking plant sites, Neuves-Maisons and Homécourt, France	Batch slurry	7.2 – 8.3	To evaluate different temperatures (60, 100 & 150 °C) of thermal pretreatment on subsequent chemical oxidation	(Usman et al., 2016a)
Sono-Fenton-like oxidation	Fe ₃ O ₄ + ultrasonics	PAHs	Oilfield, Ahvaz city, Iran	Batch slurry	3.4	To evaluate the efficiency of sono-Fenton-like oxidation based on central composite design optimization approach.	(Barzegar et al., 2017)
Modified Fenton oxidation followed by bioremediation	Hematite + sodium pyrophosphate	Pyrene	Oil industrial zone, Iran	Batch slurry	7	To evaluate the efficiency of coupled system (bioremediation and Fenton oxidation)	(Jorfi et al., 2017)
Modified Fenton oxidation	Soluble Fe(II) + citric acid or oxalic acid	PAHs	Petrochemical plant, Nanjing, China	Batch slurry	3	To remove bound PAH residues in soil	(Zhao et al., 2019)

Traditional and modified Fenton oxidation	Soluble Fe(II) alone or with citric acid	PAHs	Coking plant field, Shijiazhuang and a coal gas plant field, Nanjing, China	Batch slurry	7.4 – 7.5	To evaluate the remediation potential and impact on soil quality	(Liao et al., 2019)
Modified Fenton oxidation	Soluble Fe(II)	PAHs	02 soils: Former coking plant sites, Neuves-Maisons and Homécourt, France	Batch slurry	7.4	To evaluate the limiting factors in chemical oxidation	(Lemaire et al., 2019)
Fenton-like	Fe ₃ O ₄	PAHs and PACs	02 soils: Former coking plant of Neuves-Maisons and former gas plant, Rennes, France	Batch slurry	7.4	To evaluate the behavior of PAHs and PACs	(Boulangé et al., 2019)
Oil hydrocarbons/Total petroleum hydrocarbons (TPHs)							
Modified Fenton oxidation	Soluble Fe(II)	TPHs, VOCs, SVOCs	North Creek Railroad Station' soil contaminated with diesel, New York, USA	In-situ application in saturated and unsaturated conditions	6-7	To remediate an historic site	(Vitolins et al., 2003)
Modified Fenton oxidation	Soluble Fe(II)		Diesel polluted soil, Old Casey Station, East Antarctica	small-scale field trial	9.3	To evaluate the field efficiency and impact on soil quality	(Ferguson et al., 2004)
Modified Fenton oxidation	Soluble Fe(III) + EDTA	TPHs	Sydney Tar Ponds site, Nova Scotia, Canada	Batch slurry	8	To evaluate the surfactant production during chemical oxidation	(Ndjou'ou and Cassidy, 2006)
Modified Fenton	Soluble Fe(III) +	Dichloromethane-	Soils adjacent	Batch slurry	7	To evaluate	(Lu et al.,

oxidation	EDTA	extractable organics	to oil wells in Dagang Oilfield, Tianjing, China			the remediation efficiency under different conditions	2010a)
Modified Fenton oxidation followed by bioremediation	Soluble Fe(III)	Dichloromethane-extractable organics	Soils adjacent to oil wells in Dagang Oilfield, Tianjing, China	Batch slurry	6.5	To evaluate the efficiency of coupled remediation strategy	(Lu et al., 2010b)
Modified Fenton oxidation followed by bioremediation	Soluble Fe(II) with citric acid or oxalic acid or SOLV-X	TPHs	Oil tank storage site, Amsterdam, Netherlands	Batch slurry	7.5	To study the role of various chelating agents and coupling with bioremediation.	(Xu et al., 2011b)
Modified Fenton oxidation	Soluble Fe(II) with citric acid	TPHs	Cable site, Arnhem, Netherlands	Batch slurry	7.5	Comparing the efficiency of Fenton oxidation with CaO and KMnO ₄ .	(Xu et al., 2011a)
Modified Fenton oxidation followed by bioremediation	Relied on native Fe	TPHs	Two oil contaminated soils, Finland	Batch slurry	6.2-7.7	To evaluate chemical oxidation in composted soil with bioremediation	(Cajal-Mariños et al., 2012)
Modified Fenton oxidation after bioremediation	Fe(III) with nitrilotriacetic acid	TPHs	Field site containing weathered petroleum oil-contaminated soil, Tianjing, China	Batch slurry	7.5	To evaluate the post-application of Fenton oxidation.	(Gong, 2012)
Modified Fenton oxidation	Native Fe with added EDTA or without it (relying on soil)	Diesel fuel	Three aged diesel fuel contaminated arctic soils	Batch slurry	3.9-4.2 (natural)	To evaluate the oxidation efficiency and to	(Sherwood and Cassidy, 2014)

	organic matter)		located in Pond inlet, Inuvik and Kugluktuk, Canadian Arctic			compare the chelating ability of native soil organic matter and added EDTA	
Traditional or modified Fenton oxidation followed by bioremediation	Soluble Fe(II) alone or with citrate	TPH	Diesel contaminated railway site, Węgliniec, Poland	Batch slurry	3 or 6.8	To evaluate the recovery of microbial population during this integrated treatment	(Sutton et al., 2014b)
Traditional or modified Fenton oxidation followed by bioremediation	Soluble Fe(II) alone or with citrate	TPH	Diesel contaminated railway site, Węgliniec, Poland	Batch slurry	3 or 6.8	To evaluate the effect of organic carbon and nutrients mobilized during Fenton oxidation on following bioremediation	(Sutton et al., 2014a)
Modified Fenton oxidation followed by biostimulation	Soluble Fe(II) with citric acid	alkylbenzene	Historically polluted soil from the leakage of an underground storage tank	Batch slurry		Spiking the naturally contaminated soil To evaluate the natural attenuation capacity and microbial resilience	(Martínez-Pascual et al., 2015)
Electrokinetic-Fenton process with soil washing	Citric acid or sodium dodecyl sulfate in anode chambers	TPHs and PAHs	Railroad adjacent polluted site, Seoul, Republic of Korea	-	8.6	To optimize the treatment efficiency and to study the impact on soil toxicity	(Seo et al., 2015)
Soil	Electroche	TPH	Urban	-	8.4	To	(Huguen

washing followed by electro-Fenton oxidation	mical reactor set at 1000 mA of power supply		TPH contaminated site			evaluate the remediation efficiency	ot et al., 2015)
Modified Fenton oxidation	Soluble Fe(II) with citric acid	TPHs	Two oil wells, Yan'An, China	Batch slurry	7.5	To optimize the oxidant dose	(Wang et al., 2015)
Modified Fenton oxidation	Soluble Fe(II) with citric acid	TPHs	Two oil wells, Yan'An, China	Batch slurry	7.5	To study the effect of oxidation conditions on the removal of TPHs and soil organic matter	(Xu et al., 2016b)
Fenton-like oxidation	Fe ₃ O ₄	TPHs	Petrochemical site, Mahshahr, Iran	Batch slurry	3	To optimize the treatment efficiency	(Mirzaee et al., 2017)
Electrokinetic Fenton oxidation	Citric acid as complexing agent of native Fe	TPHs	TPH polluted industrial site, Spain	-	5.7	To optimize the treatment efficiency and to study the impact on soil toxicity	(Popescu et al., 2017)
Modified Fenton oxidation	Soluble Fe(II) with citric acid	TPHs	Oil well, Yan'an, China	Batch	7.9	To investigate the effect of Fenton treatment on nutrient mobilization and subsequent remediation potential	(Xu et al., 2017a)
Modified Fenton oxidation	Soluble Fe(II) with citric acid or oxalic acid or SOLV-X	TPHs	Three soil samples obtained from Oil well, Yan'an, China	Batch	7.3-7.9	To evaluate stepwise Fenton oxidation in multiple steps	(Xu et al., 2018)
Modified Fenton	H ₂ O ₂ alone	TPHs	Site adjacent	Batch slurry,	8.2	To decrease	(Romero-

oxidation			to fuel storage tank of a thermoelectric power station, near Mexico City	manually mixed and allowed to stay		the leachability of TPH-contaminated soil	Frasca et al., 2018)
Fenton-like treatment (KH ₂ PO ₄ stabilized H ₂ O ₂) followed by natural attenuation	Relied on native Fe with added EDTA	Diesel organics	Gasoline station site contaminated with diesel	Saturated slurry	7.6	To explore the effect of chemical oxidation on soil native biota	(Polli et al., 2018)
Fenton-like oxidation	Native iron and added ZVI with EDTA	TPHs	Petroleum hydrocarbon contaminated site, Algiers	Batch	7.2	To assess the remediation potential of ZVI and native Fe-catalyzed process	(Ouriache et al., 2019)
Modified Fenton oxidation followed by bioremediation	Fe(II) with citric acid	TPHs	Xinjiang Oilfield, China	Batch	7.6	To evaluate the efficiency of coupled treatment	(Chunyang et al., 2019)
Traditional and modified Fenton oxidation followed by bioremediation	Soluble Fe(II) alone or with citric acid	Lubricant	Lubricant contaminated site in Southern Taiwan	Batch	pH 3 and 7	To evaluate the efficiency of coupled treatment	(Liu et al., 2019)
Fenton pre-oxidation followed by bioremediation	Soluble Fe(II) with citric acid (Fe bound to SOM)	Long chain crude oil	Oil well in Yan'an, northwestern China	Batch and field experiment	pH 7.2	To evaluate the efficiency of coupled treatment and its impact on microbial biodiversity	(Xu et al., 2020)
Explosives							
Traditional	Soluble	hexahydro-	Drainage	Batch	45	To test	(Bier et

I Fenton oxidation	Fe(II)	1,3,5-trinitro-1,2,5-tiazine	ditch of former munitions production site, Nebraska Ordnance Plant		°C, pH not specified	Fenton oxidation for RDX degradation in water and soil	al., 1999)
Polychlorinated biphenyls							
Coupling of chemical reduction and Fenton-like oxidation	Nanoparticles of Fe ⁰ , Fe/Ni and Fe ₃ O ₄	PCBs	PCB contaminated soil provided by INSA, Lyon, France	Batch	8.2	To test the efficiency of reduction coupled with chemical oxidation	(Rybnikova et al., 2016)
Soil washing coupled with Fenton-like oxidation	Soluble Fe(III)	PCB in capacitor oil contaminated soil	Transformer-filled landfill in Ningbo, China	Batch	3	To test the efficiency of soil washing coupled with chemical oxidation	(Ma et al., 2016)
Fenton-like oxidation	Fe ⁰ or Fe ₃ O ₄	PCBs	timber mill located in Waipa, New Zealand	Flow through columns under saturated and unsaturated conditions	7.2	To evaluate chemical oxidation of PCBs under flow through conditions	(Rybnikova et al., 2017)
Modified Fenton oxidation	Fe(II) or Fe(III) with inorganic CA (SP) and four organic CAs (EDDS, sodium citrate (SC), GLDA, and EDDHA)	PCB in capacitor oil contaminated soil	Transformer-filled landfill in Taizhou, China	Batch	7.6	To evaluate the role of different chelating agents in Fenton oxidation	(Ma et al., 2018)
Modified Fenton oxidation	Fe(II)	PCBs	Soil provided by French Environment and Energy Management Agency	Batch	9.9	To evaluate the efficiency of Fe(VI) with traditional oxidants	(Monfort et al., 2019)

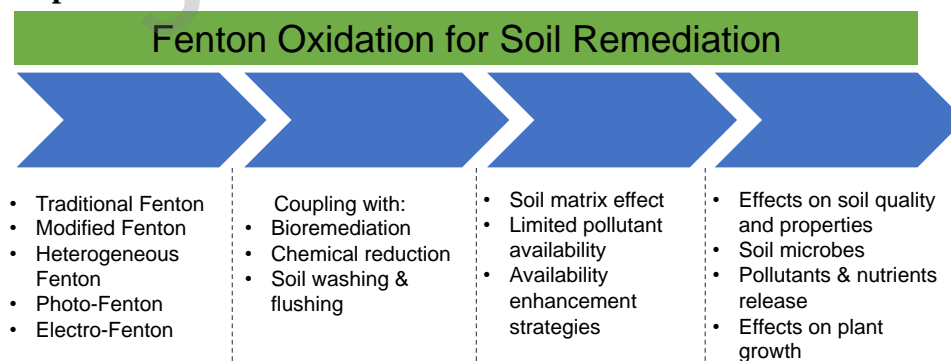
(ADEME)							
Flame retardants							
Fenton-like oxidation with bioremediation	Tourmaline	PBDEs	Electronic waste recycling plant, Tianjin city, China	Batch	7.2	To evaluate catalytic ability of tourmaline and its coupling potential	(Li et al., 2016)
MTBEs							
Fenton-like oxidation	Native Fe with EDTA and sodium citrate	MTBEs, TBA and TPHs	Fuel storage site, Italy	Lab-scale batch and In-situ pilot tests	6-7	To evaluate treatment efficiency at pilot level	(Innocenti et al., 2014)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Highlights

- 1st review evaluating the Fenton oxidation exclusively in real contaminated soils.
- These soils with complex pollution pose particular challenges to oxidation.

- Fenton-based techniques are critically reviewed along with the related challenges.
- Their implications and potential solutions in soil-plant system are evaluated.
- Future research needs are highlighted to facilitate upscaling at field scale.

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