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▶ **To cite this version:**

Muhammad Usman, Khalil Hanna, Stefan B. Haderlein. Fenton oxidation to remediate PAHs in contaminated soils: A critical review of major limitations and counter-strategies. Science of the Total Environment, 2016, 569–570, pp.179–190. 10.1016/j.scitotenv.2016.06.135 . hal-01338529

HAL Id: hal-01338529

https://univ-rennes.hal.science/hal-01338529

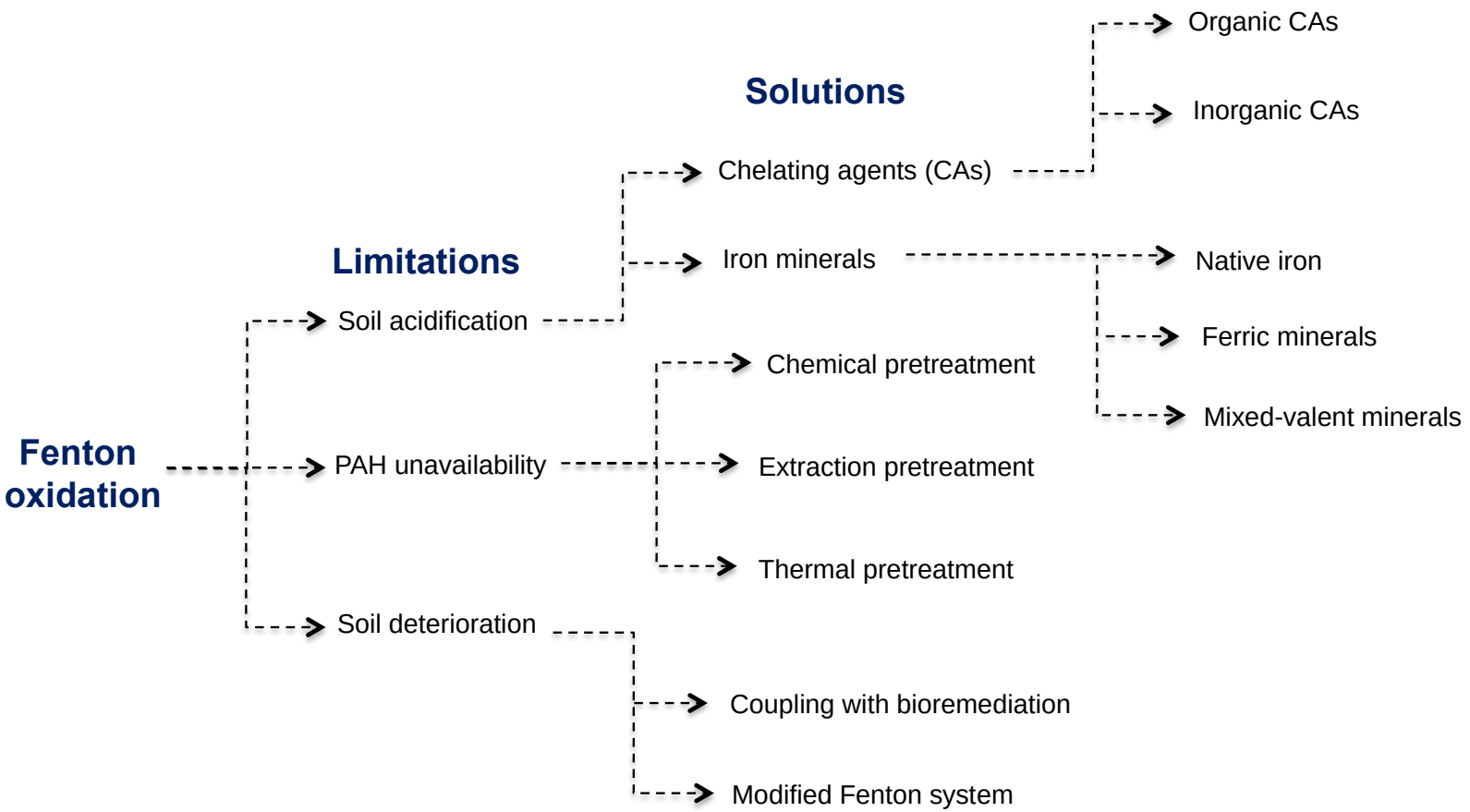
Submitted on 5 Dec 2016

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*Graphical Abstract

Graphical Abstract



Highlights

- 1st comprehensive review of major limitations of PAH removal by Fenton oxidation.
- Limitations under review are acidic pH, PAH unavailability and soil deterioration.
- Critical review of various strategies to address these limitations is presented.
- Gaps and future research needs are highlighted for application at field scale.

Fenton oxidation to remediate PAHs in contaminated soils: A critical review of major limitations and counter-strategies

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Abstract

Fenton oxidation constitutes a viable remediation strategy to remove polycyclic aromatic hydrocarbons (PAHs) in contaminated soils. This review is intended to illustrate major limitations associated with this process like acidification, PAH unavailability, and deterioration of soil quality along with associated factors, followed by a critical description of various developments to overcome these constraints. Considering the limitation that its optimal pH is around 3, traditional Fenton treatment could be costly, impractical in soil due to the high buffering capacity of soils and associated hazardous effects. Use of various chelating agents (organic or inorganic) allowed oxidation at circumneutral pH but factors like higher oxidant demand, cost and toxicity should be considered. Another alternative is the use of iron minerals that can catalyze Fenton-like oxidation over a wide range of pH, but mobility of these particles in soils (i.e. saturated and unsaturated zones) should be investigated prior to *in-situ* applications. The PAH-unavailability is the crucial limitation hindering their effective degradation. Research data is compiled describing various strategies to address this issue like the use of availability enhancement agents, extraction or thermal pretreatment. Last section of this review is devoted to describe the effects of various developments in Fenton treatment onto soil quality and native microbiota. Finally, research gaps are discussed to suggest future directions in context of applying Fenton oxidation to remediate contaminated soils.

Keywords

PAH Remediation; Fenton oxidation; pH; PAH unavailability; Soil quality

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds composed of two or more fused benzene rings. Their contamination in environment is of great concern due their high toxicity, carcinogenic effects and environmental persistence. There are sixteen PAHs that are considered as priority pollutants by United States Environmental Protection Agency (US EPA) and European community. For being recalcitrant in nature, PAHs tend to persist in the environment resulting in a ubiquitous distribution. The European Environment Agency (EEA) located about 1.5 millions of contaminated sites in Europe including 200,000 sites contaminated PAHs (E.E.A, 2012). Soil often acts as the ultimate depository of PAHs particularly due to their hydrophobic nature (Haritash and Kaushik, 2009). Owing to the strong persistence and ubiquitous occurrence, substantial research has been devoted to develop techniques to remove persistent PAHs from complex matrix like soil or sediments. Chemical oxidation has emerged as a viable remediation strategy to degrade PAHs in contaminated soils (Lee et al., 1998; Watts et al., 2002; Rivas, 2006; Ferrarese et al., 2008; Yap et al., 2011). The most common oxidants used in this technique are permanganate, ozone, persulfate and Fenton's reagent (H_2O_2 combining with iron) (ITRC, 2005). Among these oxidants, Fenton oxidation is showing promising potential to rapidly degrade PAHs in contaminated soils. Fenton treatments utilize the high reactivity of hydroxyl radical ($^{\bullet}OH$), a very reactive chemical species, which is generated by the decomposition of hydrogen peroxide (H_2O_2) by iron through following reaction (Fenton, 1894):

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III}OH^{2+} + HO^{\bullet} \quad (1)$$

Over the last two decades, use of Fenton oxidation has been well documented to treat PAHs in contaminated soils by numerous research studies. Apart from research data, few reviews focusing on chemical oxidation/Fenton-based treatments specifically for PAHs alone or along with other persistent organic pollutants in contaminated soils have been published (Rivas,

2006; Gan et al., 2009; Yap et al., 2011; Venny et al., 2012a). First review about chemical oxidation of PAHs was completed by F.J. Rivas (Rivas, 2006) where he focused mainly on the Fenton oxidation, ozone and high temperature pressurized water after a detailed discussion about sorption and extraction of PAHs from contaminated soils. Various techniques available for the remediation of PAH contaminated soils were reviewed by Gan and co-workers (2009) including bioremediation, solvent extraction, bioremediation, phytoremediation, chemical oxidation, photocatalytic degradation, electrokinetic remediation, thermal treatment and their integration. Yap and co-workers (2011) presented the first review specifically for the application of Fenton-based treatments (conventional, modified, Fenton-like along with integrated approaches) for PAHs-contaminated soils. Review by Venny and co-workers (2012a) described the fundamental principles and governing factors of Fenton oxidation to remediate soils contaminated with PAHs, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans and coupling of Fenton oxidation with other strategies like bioremediation and eletrokinetic remediation.

To the best of our knowledge, a systematic review illustrating the major limitations of Fenton treatment along with proposed solutions to overcome these constraints is still missing in literature. Thus, this review article is intended to collect research data related to potential constraints of Fenton oxidation in context of PAH contaminated soils. In addition, recent developments to overcome these limitations are critically evaluated along with associated factors in this review. These drawbacks would depend on the remedial strategy and scale, and the targeted zone in soils (e.g. aquifer or vadose zone). Despite the large amount of published studies related to Fenton treatments for PAH-contaminated soils at lab-scale (Yap et al., 2011), very limited data is available on the remediation performance at pilot/field scale (Liu et al., 1993; Brown, 1997; Lingle et al., 2001; ITRC, 2005; Taylor, 2012). Prior to the field or *in-situ* applications, feasibility studies are generally conducted at batch scale to determine the

extent and rate of PAH removal. However, few reports have investigated the Fenton oxidation under column dynamic conditions, which more closely mimic field conditions (Palmroth et al., 2006a; Laurent et al., 2012; Venny et al., 2012c; Lemaire et al., 2013b; Venny et al., 2014). Figure 1 shows the different experimental setups used to investigate Fenton oxidation in contaminated soils at laboratory scale. Column studies, which are better representative of real field conditions, can be carried out under water-saturated (that represents aquifer) and water-unsaturated conditions (that represent vadose zone).

We are convinced that this review article will be of significant interest for researchers working on chemical oxidation of PAHs-contaminated soils. Finally, the literature lack of information and data that is crucial prior to *in-situ* field applications is also highlighted.

2. Major limitations of Fenton oxidation in PAH-contaminated soil

Fenton oxidation has validated its potential as viable remediation technique for PAH-contaminated soils but there are various limitations associated with this process. This review article focuses on the three major limitations of this technique in context of PAH-contaminated soil including: i) acidification of medium, ii) PAH unavailability and iii) deterioration of soil quality, fertility and microbial community. These limitations are discussed in the following sections along with a critical discussion of their solutions proposed in literature.

2.1. Acidification of reaction medium

Traditional Fenton's reagent (Fe^{II}-H_2O_2) displays its maximum oxidation activity at a pH about 2.8 – 3 (Safarzadeh-Amiri et al., 1996; Pignatello et al., 2006). Thus, most of the remediation studies to remove PAHs in contaminated soils employed traditional Fenton reagent at acidic pH (Yap et al., 2011) which is probably the most important limitation of this

process. This initial acidification (optimum pH is 3) is required to keep Fe^{II} in its soluble form (Tamura et al., 1980). The iron precipitation occurring after pH 4.0 led to the obstruction of activation processes (Usman et al., 2012), through several parasite reactions including the decomposition of H_2O_2 to oxygen. In addition, sorption of Fe^{II} or Fe^{III} ions onto mineral or organic constituents in soil increases with increase in pH (Hanna et al., 2013; Catrouillet et al., 2014) and thus, rendering the Fe species less available for Fenton activation.

This acidification step is operated not only to keep Fe in dissolved form but also because the •OH generation in reaction (1) is highest at pH 3 that usually decreases at higher or lower pH values (Gallard et al., 1998). Furthermore, reaction (1) actually involves the formation of a highly oxidised Fe adduct, often indicated as ferryl (e.g. ferryl ion FeO^{2+}), which does not necessarily evolve into •OH (Pignatello et al., 1999).

Initial acidification required for optimum efficiency of Fenton's reagent is costly and impractical in soil system due to buffering capacity of soils (Ershadi et al., 2011). This could also create a hazardous situation for soil quality and microbes in soil buffered systems, where a circumneutral pH prevails (Nam et al., 2001; Sahl and Munakata-Marr, 2006; Sirguey et al., 2008; Valderrama et al., 2009). Therefore, traditional Fenton oxidation was found incompatible with subsequent biological treatment to remediate PAH contaminated soil (Nam et al., 2001). It may also increase mobilization of heavy metals that would devastate the soil ecosystem. Acidic pH along with high amount of Fe^{II} was also linked to a remarkable increase in available Fe and Al in treated soil, which reached the toxicity level (Gan et al., 2013). This decrease in pH during Fenton oxidation was also found as the major limiting factor for subsequent vegetation in treated soil (Sirguey et al., 2008). It was reported by Valderrama and co-workers (2009) that use of more aggressive traditional Fenton oxidation does not favor the subsequent biological treatment which was explained by the residual

oxidant that may remain in the soil and inhibit the biodegradation after the application of higher oxidant dose.

Therefore, various strategies were considered in literature that allows chemical oxidation at circumneutral pH but without compromising the oxidation efficiency for efficient PAH degradation like the use of chelating agents or iron minerals. These strategies will be detailed in the following paragraphs.

2.1.1 Use of Chelating agents

Use of chelating agents along with traditional Fenton treatment allows chemical oxidation at circumneutral pH and the reaction is termed as modified Fenton (MF) oxidation (Nam et al., 2001). Chelating agents (CAs) are mostly organic compounds that bind iron and therefore maintain in its dissolved form. By binding with Fe^{II} or Fe^{III}, CAs can maintain their ability to catalyze H_2O_2 at circumneutral pH. These chelating agents are used to extend the applicability of Fenton oxidation to native soil pH that has more practical implications for *in-situ* remediation. Different kinds of chelating agents have been explored in MF (Table 1) including cyclodextrines (CD), ethylenediaminetetraacetic acid (EDTA), catechol (CC), gallic acid (GA), citric acid (CA), oxalic acid (OA), humic acid (HA), malic acid (MA), sodium citrate (SC) and other amino-poly-acetic acids (Nam et al., 2001; Gryzenia et al., 2009; Veignie et al., 2009; Venny et al., 2012b).

For example, Nam et al. (Nam et al., 2001) showed that the addition of organic CAs (such as CC and GA) along with ferric ion during MF oxidation (pH 6.0–6.5) could have distinct advantages due to its compatibility with subsequent bioremediation as compared to the traditional Fenton oxidation at pH 2–3. Their results revealed that >80% of low molecular weight (LMW) PAHs and only 20-40% of high molecular weight (HMW) PAHs were degraded during traditional Fenton oxidation. In their attempt to overcome the limitations of

conventional Fenton oxidation, combined MF and biodegradation resulted in > 98% removal of LMW-PAHs and > 70% removal of HMW-PAHs. In their attempt to examine HA as iron chelator in MF oxidation, Georgi and co-workers (2007) reported that presence of HA (50–100 mg L^{-1}) in MF system greatly enhanced the degradation of organic compounds in the range of pH 5–7. They also highlighted that similar degradation extent can be obtained by MF oxidation at pH 5 in the presence of HA and traditional Fenton process at pH 3 in the absence of HA (Georgi et al., 2007).

In addition to binding Fe^{II} ion for enhanced solubility at circumneutral pH, CD (Veignie et al., 2009) or HA (Georgi et al., 2007) also resulted in improving availability of hydrophobic organic pollutants in contaminated soils by forming complexes with pollutants. Formation of pollutant-CD-iron or pollutant-HA-iron complex in microenvironment allows hydroxyl radicals to specifically target on pollutants by eliminating the detrimental soil matrix effect for improved oxidation efficiency (Lindsey et al., 2003; Georgi et al., 2007; Veignie et al., 2009). Owing to the ability of CD to improve pollutant availability, it was also employed in soil washing solution (Viglianti et al., 2006), bioremediation (Bardi et al., 2000) and chemical oxidation (Usman et al., 2012) that improved the removal efficiency many times. A detailed discussion about the use of CD to improve PAH availability is presented below in Section 2.2.1 (Chemical Pretreatment).

Despite the promising efficiency of chelating agents to promote pollutant oxidation, their use is limited by cost, toxicity and potential negative effects on oxidation efficiency due to the non-productive consumption of the CAs (Xue et al., 2009b; Pardo et al., 2014). For being organic in nature, CAs may compete with target pollutants for oxidant and thus act as radical scavenger by increasing oxidant demand (Georgi et al., 2007; Xue et al., 2009b; Pardo et al., 2014). Oxidation of CAs themselves will thereby lead to the loss of their chelating ability which is required to enhance pollutant degradation (Georgi et al., 2007). Moreover, chelating

agents like EDTA can also pose environmental risks because of their persistence in the environment and their contribution to improve heavy metal mobility/bioavailability (Sillanpaa and Pirkanniemi, 2001; Yang et al., 2001; Rastogi et al., 2009).

Recently inorganic CAs like sodium pyrophosphate (SP) were proposed as an alternative in MF oxidation of PAHs in contaminated soils at circumneutral pH (Venny et al., 2012b; Venny et al., 2012c; Jorfi et al., 2013). Comparison of various organic and inorganic CAs (Fig. 2a) to assist MF oxidation revealed the following efficiency order for PAH degradation: SP > EDTA > OA > MA > SC (Venny et al., 2012b). Other studies by this research group have established the higher efficiency of SP during Fenton oxidation and its compatibility with biological treatment to promote PAH degradation (Venny et al., 2012c; Venny et al., 2014). Similarly, Jorfi et al. (Jorfi et al., 2013) performed Fenton oxidation by employing iron nano-particles along with various CAs to remove pyrene in contaminated soil. They reported that removal efficiency was found to be maximum for SP (93%) compared to 86%, 75%, 72% and 71% for EDTA, SC, HA and FA, respectively at H_2O_2/Fe^{III} molar ratio of 10, pH 7 and the contact time of 6 h. Use of inorganic CAs could be advantageous since they are less likely to act as radical scavenger and do not increase the total organic carbon of system (Rastogi et al., 2009) although prolonged treatment could make SP to act as radical scavenger (Venny et al., 2012c). In addition to less oxidant scavenging, decomposition of H_2O_2 with SP was lower than with organic CAs (Fig. 2b) underscoring higher stability of oxidant when mixed with inorganic SP (Venny et al., 2012b).

2.1.2. Use of Fe-bearing minerals

In order to overcome the drawback of acidification employed in traditional Fenton oxidation, iron mineral can be used instead of soluble Fe^{II} at circumneutral pH, and the reaction is defined as a Fenton-like (FL) reaction. Iron minerals are able to catalyze Fenton-like

reactions over a wide range of pH values (Watts et al., 2002; Hanna et al., 2008; Jung et al., 2009). The water solubility of Fe-oxyhydroxides as well as the possible leaching of iron from their surface is low. The Fe-minerals catalyze oxidation mainly through heterogeneous reaction, i.e. activation of oxidant by Fe surface sites located on oxide surfaces. As a result, the ability of Fe to catalytically decompose H_2O_2 and generate hydroxyl radicals can be maintained with respect to traditional Fenton, but the overall oxidation kinetics is generally lower (Garrido-Ramírez et al., 2010). Various mechanisms are proposed for oxidative degradation of organic compounds on the surface of iron oxide catalysts during FL oxidation and are detailed elsewhere (Xue et al., 2009a; Garrido-Ramírez et al., 2010; Yap et al., 2011). There are various kinds of iron minerals including ferric-Fe^{III} (ferrihydrite, goethite, lepidocrocite, hematite etc.) and mixed Fe^{II} -Fe^{III} oxides (magnetite and green rust) (Cornell and Schwertmann, 2006). Heterogeneous catalysts including native or added iron oxides or certain transition metals can catalyze the FL oxidation in soils at circumneutral pH (Flotron et al., 2005; Usman et al., 2012), which may be especially advantageous for *in situ* remediation of contaminated soils where pH cannot be adjusted.

It was also reported by Jung and co-workers (2009) that H_2O_2 was more stable (as it has a ten times longer life time) under FL reaction (catalyzed by magnetite or hematite) than that with soluble Fe^{II}. Moreover, mineral-catalyzed oxidation system (3 ml of 30% H_2O_2 for 5 g contaminated sand) without pH adjustment showed better degradation (75.3%) of phenanthrene sorbed on sand (200 $mg.kg^{-1}$) than by Fenton activated by Fe^{II} (52.2%) (Jung et al., 2009).

Remediation of PAHs in contaminated soils was reported by Fenton-like oxidation catalyzed by native iron (Watts et al., 2002; Flotron et al., 2005) or iron minerals added into the system like goethite (Kanel et al., 2003; Kanel et al., 2004), hematite (Jung et al., 2009), iron oxyhydroxide/sodium dodecyl sulfate composites (Park and Kim, 2013) and magnetite

(Usman et al., 2012; Usman et al., 2013; Biache et al., 2015). Magnetite was found more effective than goethite and soluble Fe^{II} at acidic pH to remediate petroleum hydrocarbons in diesel and kerosene contaminated soil (Kong et al., 1998). Higher catalytic efficiency of magnetite, a mixed Fe^{II}-Fe^{III} oxide, as compared to the ferric minerals was correlated to its structural Fe^{II} (Matta et al., 2007; Hanna et al., 2008).

It was shown by Watts and co-workers (2002) that iron mineral present in solid matrix can allow the production of reactive oxidant species for strong degradation of PAHs. They reported that 85% of benzo[a]pyrene was removed when H_2O_2 (15 M) was catalyzed by naturally occurring iron minerals (33.52 $mg.g^{-1}$ of soil) while a degradation of 70% was achieved when H_2O_2 (15 M) was catalyzed by soluble Fe^{II} (6.6 mM) in sand. Role of endogenous iron minerals was highlighted when application of sole H_2O_2 resulted in PAH degradation almost equivalent to that obtained with H_2O_2 + soluble Fe^{II} without pH adjustment in sludge (pH 8.8) and sediment (pH 4.4) bearing 94 $mg.g^{-1}$, 30 $mg.g^{-1}$ and not determined total iron, respectively (Flotron et al., 2005). They reported similar findings in contaminated soil (pH 7.1) where Fe contents were not determined. Owing to the presence of native iron (16.4 $mg.g^{-1}$), application of Fenton oxidation (0.4 g $H_2O_2.g^{-1}$ soil) under saturated conditions resulted in significant degradation of PAHs (upto 52%) without any ferrous iron supplementation or initial acidification of soil (Palmroth et al., 2006a). Pardo and co-workers (2016) observed similar degradation of PAHs by Fenton oxidation (882 $mmol.L^{-1}$ without pH adjustment) obtained by adding 1 mmol L^{-1} Fe^{III} or without external addition of Fe highlighting the role of endogenous Fe. They noted a similar concentration of iron in solution after external addition of 1 mmol L^{-1} Fe^{III} or iron extracted from soil (Pardo et al. 2016)

Kanel and co-workers (2004) reported that goethite can successfully catalyze FL oxidation (33.5 g $goethite.kg^{-1}$ of soil and 5 M H_2O_2) with degradation extent of 73, 60, and 55% for

phenanthrene, anthracene, and pyrene, respectively in spiked sandy soil obeyed pseudo-first order kinetics at natural pH. Use of magnetite (Fig. 3) to catalyze FL oxidation (H_2O_2:Fe of 20, 10% w/w magnetite) at circumneutral pH (7 – 8) resulted in PAH degradation extent of 90% and 60% in spiked sandy soil and in historically contaminated soils (sandy loamy type) sampled from former coking plant site, respectively (Usman et al., 2012). Under the similar experimental conditions, soluble Fe^{II} was found unable to catalyze H_2O_2 as similar oxidation efficiency (20% in spiked sandy soil and 5% in real soil) was observed when H_2O_2 was used alone without iron activation and that was correlated to the precipitation of Fe^{II} at circumneutral pH in tested soils. Lower degradation in real soil samples as compared to the spiked sandy soil was related to the soil matrix effect. Magnetite-catalyzed FL oxidation (oxidant/Fe molar ratio equal to 10:1) also resulted in strong PAH removal (60–70 %) under flow through conditions (flow rate 0.1 mL min^{-1} under water-saturated columns) in spiked sandy soil having 10% of magnetite w/w (Usman et al., 2013). Biache and co-workers (2015) also highlighted the strong efficiency of magnetite-catalyzed FL oxidation (14.5 mL of H_2O_2 (30%wt), 500 mg magnetite for 5 g soil) to degrade PAHs in three contaminated soils sampled from former coking plant site (20% removal), former gas plant site soil (92%) and active wood treatment facility (50%). Recently, pyrite (FeS_2) showed strong reactivity to catalyze FL oxidation of PAHs in soil washing wastewater at circumneutral pH (Choi et al., 2014). They reported a sustainable reactivity of this process that was linked to slow but continuous Fe^{II} dissolution from the pyrite surface leads to the continuous formation of reactive radicals during the oxidation reaction (Choi et al., 2014).

Pardo and co-workers (2016) recently conducted a study to optimize the application of the Fenton oxidation to remediate PAH contaminated soils. They evaluated the suitability of nZVI particles and Fe^{III} salt at different concentrations of initial iron (1–5 mmol L^{-1}) and oxidant (88–1765 mmol L^{-1}) without pH adjustment. Almost similar degradation of PAHs

was achieved for the majority of the experiments. But, they reported that aqueous concentration of iron was lower in case of nZVI and they linked to its lower solubility as compared to Fe^{III} salt at circumneutral pH. Owing to this behavior, Pardo and co-workers (2016) suggested that nZVI could act as a continuous Fe source that can be advantageous for real field application.

Regardless of the investigated Fe-bearing minerals or nZVI particles to promote the *in-situ* application of the oxidation treatment, profound investigations are required to evaluate injection mode of these particles in soils. It will depend on the targeted area in soil whether saturated aquifer (pump and treat) or unsaturated zone such as vadose zone (e.g. lysimeter system). It is known that the efficiency of treatment significantly depends on the contact "pollutant/catalyst/oxidant" (Lemaire et al., 2013a), and therefore particles with a high mobility must easily reach the contaminated targeted zones (Johnson and Amy, 1995). This mobility is strongly related to the composition of particles including functionalized or not, particle size (micro- or nano-sized), concentration of suspension, etc. (Jiang et al., 2010). Despite the mobility and colloidal transport of natural particles and some manufactured nanoparticles have been already studied (Hannah and Thompson, 2008; Lowry et al., 2012), there is limited information on the transport and fate of the catalyst particles used for remediation purposes.

Apart from these strategies, few studies reported the use of Fenton's reagent (H_2O_2 + soluble Fe^{II}) to remove PAHs without adjusting the soil's pH to avoid this initial acidification but that leads to the partial degradation of PAHs (Kulik et al., 2006; Silva et al., 2009; Laurent et al., 2012).

2.2. PAH unavailability

Another major constraint associated with Fenton oxidation in aged contaminated soils is the poor availability of PAHs for remediation (Flotron et al., 2005; Usman et al., 2012; Lemaire et al., 2013a; Choi et al., 2014) due to their strong hydrophobicity and partitioning into soil constituents especially organic matter (Riding et al., 2013). This is caused by the deep diffusion of the contaminants into the organic material that renders them unavailable for the hydroxyl radicals, which are generated in the aqueous phase (Bogan et al., 2003). A strong connection was reported between PAH availability and remediation efficiency of Fenton oxidation (Usman et al., 2013; Biache et al., 2015; Usman et al., 2016). As a matter of fact, magnetite-catalyzed FL oxidation was not effective unless PAH availability was enhanced in two aged coking plant soils (Usman et al., 2012). Due to this strong correlation, Biache and co-workers (2015) proposed that efficiency of Fenton based oxidation could serve as a valid method to estimate PAH availability in contaminated soils. In order to suppress this limitation and thus effectively degrade PAHs in contaminated soils, various strategies were considered and are discussed below.

2.2.1 Chemical pretreatment

Chemical pretreatment involves the use of various chemical reagents to enhance the PAH availability in contaminated soils as a pretreatment for or in combination with Fenton oxidation. Four types of enhancement-solubility agents have been used including co-solvent, surfactant, cyclodextrin and vegetable oil to solubilize PAHs. Co-solvents like ethanol were used to increase solubility of PAH in soils that ultimately reduces the surface tension between the compounds in soil and aqueous phase, and increase in PAH availability (Bonten et al., 1999).

Ethanol-Fenton (ETF) treatment resulted in significant increase in PAH removal of 11–28% (Lundstedt et al., 2006), 97% (Lee et al., 1998) and 63-93% (Lee et al., 2002) than by Fenton alone in contaminated soils (Fig. 4). Application of ETF treatment in soil spiked with benz(a)anthracene (500 mg/Kg of soil) using optimized experimental conditions (1.0 ml of ethanol, 0.2 ml of 0.5 M Fe^{II}, and 0.3 ml of 30% H_2O_2 per g of soil) removed 97% of target PAH and that neither water nor sodium dodecyl sulfate (SDS as surfactant) show a substantial effect on removal (Lee et al., 1998). Ethanol was widely used as a solvent because of its safety, low cost, and excellent extraction ability (Lee and Hosomi, 2001a).

Recently, Yap and co-workers (2012) reported the use of a novel system, ethyl lactate-Fenton (ELF) treatment for soils artificially contaminated with four PAHs (500 mg/kg each of phenanthrene, anthracene, fluoranthene and benzo[a]pyrene). Their results (Fig. 4) indicate that ELF ($[H_2O_2]$ = 666 mM, Fe^{II} = 66.6 mM with ethyl lactate, pH = 3) resulted in higher PAH degradation (up to 97%) than ETF (70%) while conventional Fenton oxidation (without ethanol or ethyl lactate) resulted in 31–57% of untreated PAHs. A recent study by the same research group revealed the feasibility of using ELF to treat PAHs in aged soils (pH 4.4 and 6.2) having various quantities of soil organic carbon (Yap et al., 2015). Similar trend of higher PAH degradation by ELF (H_2O_2 = 667.6 mM, Fe^{II} = 16.7 & 66.7 mM with varying amounts of ethyl lactate) as compared to ETF or traditional Fenton (Fig. 4) was also indicated elsewhere (Gan et al., 2013). However, addition of co-solvents could change the general non-selective behavior of $^{\bullet}OH$ radicals towards selectivity as preferential degradation of anthracene > benzo[a]pyrene > phenanthrene > fluoranthene was observed by ELF and ETF treatments (Yap et al., 2012). They also suggested that degree of selectivity is co-solvent dependent as selectivity was more pronounced in the ETF treatment than in the ELF treatment. Moreover, presence of co-solvents during Fenton oxidation could also inhibit PAH degradation by acting as radical scavenger (Qiang et al., 2000; Lundstedt et al., 2006; Yap et

al., 2012). But scavenging effect was more pronounced for EL than ET and it was correlated to the higher bond ratio of C–O to C–H and higher oxidation state of EL (Yap et al., 2012). This scavenging effect associated with ethanol was avoided by its use as a pretreatment step (5 mL of ethanol/g soil for 24 h) where it was allowed to evaporate before soil samples were subjected to Fenton-like oxidation (Usman et al., 2012). Treating ethanol pre-treated soil by Fenton-like (FL) oxidation (magnetite + H_2O_2) caused 20% removal of PAHs (Fig. 5). It is worthy to note that no PAH degradation was observed when FL oxidation was used directly without any chemical pre-treatment (Usman et al., 2012). On the other hand, FL oxidation after pretreatment using cyclodextrin (CD, 10 mM, overnight mixing) resulted in slightly lower PAH degradation (15%) as compared to ethanol pretreatment (Usman et al., 2012) probably due to scavenging effect of CD (Hanna et al., 2005). This scavenging effect concerns only CD in study by Usman and co-workers (2012), as ethanol was allowed to evaporate from the reactor before applying oxidants.

Use of surfactants was also found effective to improve the PAH availability decreasing the interfacial tension and increasing their partitioning to the hydrophobic cores of surfactant micelles. First use of surfactants in combination with Fenton's reagent was reported by Martens and Frankenberger (Martens and Frankenberger Jr, 1995) who found that use of sodium dodecyl sulfate (SDS) before Fenton oxidation resulted in higher PAH degradation (30-45%) compared to without SDS. Application of cationic surfactant cetylpyridinium chloride (CPC) in the pyrite Fenton system enhanced the PAH oxidation efficiency from 91% (without CPC) to 97% at circumneutral pH (Choi et al., 2014). Recently, use of SDS as surfactant with H_2O_2 + Fe^{III} resulted in higher PAH removal than the systems without SDS including H_2O_2 + Fe^{III} or H_2O_2 + nanoparticles of zerovalent iron (nZVI) (Pardo et al., 2016).

It should be noted that surfactants can also be formed as a result of partial oxidation of hydrocarbons and/or native organic matter (Ndjou'ou and Cassidy, 2006; Gryzenia et al.,

2009). These authors demonstrated the potential of *in-situ* surfactant production during Fenton oxidation of hydrocarbon-contaminated soils. These surfactants accompanying the Fenton oxidation of hydrocarbons in soil are eventually removed by further chemical oxidation and/or biodegradation (Ndjou'ou and Cassidy, 2006; Gryzenia et al., 2009). Moreover, formation of reductants (e.g. superoxide) during Fenton oxidation could act as surfactant and contribute in enhanced desorption of PAHs (Watts et al., 1999). Non-selective degradation of PAHs was also linked to this probable production of surfactants during Fenton-like oxidation (Usman et al., 2012) that would have rendered HMW PAHs available for remediation (Gryzenia et al., 2009). Pretreatment of contaminated soils with vegetable oil prior to Fenton oxidation also improved the PAH degradation in contaminated soils (Bogan et al., 2003). They incorporated two different oils (corn oil and palm kernel oil) in Fenton treatment for PAH removal from highly contaminated aged soils. A significant increase in the PAH degradation (15–45%) was reported with 5% (per dry wt. of soil) oil addition, with a pronounced effect for HMW PAHs. On the other hand, Fenton treatment (without vegetable oil) could only degrade a few LMW PAHs.

2.2.2. Extraction pretreatment

It is well documented that artificially spiked PAHs (fresh contamination) are easier to oxidize than native PAHs because of their binding/sequestration onto soil constituents for years in later case (Nam et al., 2001; Flotron et al., 2005; Usman et al., 2012; Jorfi et al., 2013; Lemaire et al., 2013b). For example, Nam and co-workers (2001) described that Fenton treatment caused higher PAH removal in model spiked soil as compared to that in soil from former manufactured gas plant (MGP). They reported a highly efficient degradation of a mixture of PAHs in the model soil (noticeably, 84.5% and 96.7% of initial pyrene and Benzo(a)pyrene, respectively). In the MGP soil, the same treatment destroyed approximately

419 40% and 20% of pyrene and Benzo(a)pyrene, respectively. Flotron and co-workers (2005)
420 also reported more efficient degradation of spiked PAHs (onto soil, sediment and sludge)
421 than native PAHs in soil after Fenton oxidation.
422 Fenton oxidation (H_2O_2:Fe^{II} of 20:1) in column experiments under water-unsaturated
423 conditions caused significantly higher PAH degradation for spiked soils (55%) as compared
424 to aged soils (30%) (Lemaire et al., 2013b). In another work, removal of pyrene in freshly
425 contaminated soil was greater (91%) than that of the soil sample with aged pollution (43%)
426 when MF oxidation (300 mM H_2O_2, 5mM Fe^{III}) using iron nano-particles was applied (Jorfi
427 et al., 2013). The pyrene degradation extent decreased from 88.9% in freshly contaminated
428 soil to 74.7% in soil aged for 30 days although further increase in aging time did not
429 significantly decrease the removal efficiency (Sun and Yan, 2008). As a matter of fact,
430 incubation of a freshly contaminated coking plant soil by a ^{13}C-phenanthrene indicated that
431 bacteria rapidly degraded the freshly-added PAH whereas the native contamination of the
432 coking plant soil (including phenanthrene) is not affected (Cébron et al., 2011). But all these
433 studies using spiked soils were based upon the PAHs whose solutions were freshly prepared
434 in laboratory and were not extracted from the field soil.
435 This was done in a recent study where two ancient coking plant soils contaminated with 16
436 PAHs were extracted and solvent extractable organic matter (EOM) separated from these
437 soils was spiked on sand (Usman et al., 2012). Then, application of Fenton-like oxidation
438 (H_2O_2:Fe of 20:1, 10% magnetite w/w, neutral pH) (FL) resulted in significant degradation of
439 PAHs (90%) in sand spiked with EOM (Fig. 5). It should be noted that FL oxidation was
440 unable to degrade PAHs when applied directly in both soils. It might be correlated to the long
441 term aging of both soils as coking activities and steel industry continued on these soils from
442 the very beginning of the 20th century till 1983 (Ouvrard et al., 2011). As a next step of study,
443 Usman and co-workers (2012) applied extraction pretreatment to re-incorporate the PAHs

444 into the soil as fresh contaminants. It was done by following the same protocol as was used to
445 separate EOM (for spiking sand) but without separating it from the soil, rather it was allowed
446 to evaporate in soil. This procedure allowed PAH removal of 50-60% in re-contaminated
447 soils by successive Fenton-like oxidation (oxidation conditions similar to spiked sand) as
448 indicated in Fig. 5 (Usman et al., 2012). This drop in degradation efficiency between real soil
449 (50-60%) and spiked sand (90%) was correlated to soil matrix effect because of the insoluble
450 organic matter and mineral fraction (Flotron et al., 2005; Jonsson et al., 2007; Usman et al.,
451 2012). But, application of similar pretreatment allowed a six-times higher PAH availability
452 than raw soil measured by Tenax extraction that is closer to bioavailable fraction (Cébron et
453 al., 2013). This difference could be caused by different PAH availability levels including
454 bioavailable (Tenax available) and chemoavailable (deduced by FL oxidation) probably due
455 to higher accessibility for chemical oxidation as suggested elsewhere (Cébron et al., 2013).
456 Very few studies used the extraction pre-treatment to re-incorporate PAHs in same soil as
457 fresh contaminants (Usman et al., 2012; Cébron et al., 2013). Owing to its strong efficiency
458 to improve PAH availability, the *in-situ* feasibility of extraction pretreatment merits to be
459 explored at field scale. It should be noted that cyclodextrin or surfactant-enhanced *in-situ*
460 flushing and extraction of hydrocarbons compounds have been tested at the field scale
461 (McCray and Brusseau, 1999; McCray et al., 2000; Bardi et al., 2007; Chong et al., 2014).
462 However to the best of our knowledge, the use of solubility-enhancement agents in
463 combination with chemical oxidation has been never tested at field scale.
464
465 **2.2.3 Thermal pretreatment**
466 Pre-heating PAH contaminated soils also improved the remediation efficiency of successive
467 Fenton-like treatment (Biache et al., 2015; Usman et al., 2016). Recently, Usman and co-
468 workers (2016) pre-heated the two ancient coking plant soils at different temperatures (60,

100, and 150 °C for 1 week under inert atmosphere). Pre-heating resulted in slight removal of PAHs (6% for A soil and 9% for B soil even at 150 °C) but successive FL oxidation (H_2O_2:Fe of 20:1, 10% magnetite w/w, neutral pH) in pre-heated soils showed significant PAH degradation (19, 29, and 43 % in A soil and 31, 36, and 47 % in B soil pre-treated at 60, 100, and 150 °C, respectively, reference for degradation were pre-heated samples) (Fig. 5). No PAH degradation was reported when soils were subjected to chemical oxidation without pre-treatment (Usman et al., 2016). Similarly, Biache and co-workers (2015) reported an increase in PAH degradation in preheated soil samples (100 °C for 1 week under inert atmosphere) by H_2O_2 oxidation systems (including FL oxidation by 14.5 mL of H_2O_2 (30%wt), 500 mg magnetite for 5 g soil, neutral pH). Their experiments were based on three kinds of soils that were sampled from former coking plant, former gas plant and an active wood treating facility. Both coking and gas plant soils were characterized by similar EOM (10.3 and 11.5 mg/g, respectively) and PAH content (1146 and 1781 μg/g, respectively) while soil from wood-treating facility represented higher amount of EOM (81.94 mg/g) and PAHs (c.a. 12,000 $\mu g.g^{-1}$). The PAH distribution varied for each sample origin and was dominated by 4- and 5-ring PAHs (coking plant soil) or 2- to 4-ring PAHs (gas plant soil) or by pyrene and fluoranthene (wood treatment facility). Their results indicate that efficiency of FL oxidation varied according to the type of the soil. They did not report any PAH degradation by direct FL oxidation in coking plant soil unless the sample was pre-heated (20% degradation by successive FL oxidation). On the other hand, FL oxidation in the unheated and pre-heated gas plant soils showed the highest degradation rates (78% and 92%, respectively). The oxidative degradation of PAHs reached 49% and 50%, for the unheated and pre-heated wood-treating facility soils, respectively. Results obtained by Biache and co-workers (2015) clearly demonstrate that PAH unavailability was mainly related in coking plant soil due to its long-term aging (Ouvrard et al., 2011; Usman et al., 2012; Usman et al.,

494 2016). It was reported elsewhere that efficiency of Fenton oxidation was negatively
495 correlated to the age of the PAH contamination when experiments were performed by using
496 ten different soil samples originating from former gas plant, former wood-treating facility and
497 active coke production site and characterized by different contamination age ranging from 40
498 to 71 years (Jonsson et al., 2006; Jonsson et al., 2007). In aforementioned coking plant soil
499 (Biache et al. 2015, Usman et al. 2016), no such unavailability constraint was reported during
500 air oxidation of PAHs at 100 °C (Biache et al., 2011) which highlights the role of temperature
501 to control PAH availability. Similarly, heating aged PAH contaminated soils at higher
502 temperature (120 °C) prior to microbial incubation enhanced the PAH degradation due to an
503 increase in their bioavailability (Bonten et al., 1999). Mechanisms governing thermal pre-
504 treatment enhanced PAH availability has not been yet explored due to the limited number of
505 relevant studies. Moreover, further studies are required to test the upscaling of thermal
506 pretreatment for field applications while nature of the soil should be considered.
507
508 **2.3. Deterioration of soil quality and impacts on microbial community**
509 Fenton-based oxidation treatments helps to decrease the PAH load in contaminated soils but
510 it could negatively affect the soil quality and microbial community. This section illustrates
511 the effect of various Fenton-based strategies being used to remove PAHs from contaminated
512 soils.
513 Impact of Fenton oxidation (without pH adjustment or pH adjusted at 3 with H_2SO_4 1 N) onto
514 soil quality was investigated by Sirguey and co-workers (2008) in spiked agricultural soil and
515 coking plant soil. Significant degradation (75-97%) of PAHs was reported whereas
516 associated decrease in soil pH was found to be the limiting factor for plant growth. This
517 treatment resulted in a significant decline of organic C and N along with strong changes in

nutrient pool. Water retention capacity was however improved upon treatment that could encourage re-vegetation (Sirguey et al., 2008).

Laurent and co-workers (2012) applied MF oxidation (H_2O_2 + Fe^{II} without pH adjustment) under unsaturated conditions in industrial PAH-contaminated soil. A degradation of 14% and 22% of PAHs was obtained with addition of H_2O_2 at 6 and 65 g kg^{-1}, respectively. The results obtained at higher oxidant dose (65 g kg^{-1}) indicated a significant decrease in soil pH (4.8 decreased from 7.3), cation exchange capacity (2 units) and extractable phosphorus content (77% of initial content). Although drop in pH was not as harsh as it could be if initial acidification (low to 3) was adopted, it contributed along with higher oxidant amount to decrease bacterial, fungal, and PAH degrading bacteria population that rebounded after five weeks of incubation (Fig. 6). Plant growth was also negatively affected at higher oxidant dose. Treated soil also displayed a significant delay in seed germination and a decrease in root and shoot biomass (Laurent et al., 2012).

A column study was conducted by Palmroth et al. (Palmroth et al., 2006a) where soil pH was not acidified prior to MF oxidation (0.4 g H_2O_2/g soil without any ferrous iron addition) to minimize the stress on soil bacteria. Obtained results indicated a partial removal of PAHs (up to 52%). But toxicity of column leachate was increased towards *Vibrio fischeri* that was used to assess the effect of MF oxidation on microbial activity. Microbial activity and abundance of viable cells was lower in incubated MF-treated soil than in untreated soil. Still, incubation of MF-treated soil slightly improved the PAH-removal than in untreated soil highlighting its compatibility as also reported in another study (Palmroth et al., 2006b).

The high concentration of H_2O_2 used and the radicals formed in the Fenton's reaction are toxic to soil bacteria and, therefore, reduce the abundance of viable cells (Büyüksönmez et al., 1998). Apart from that, the acidic pH of 2–3 required for the traditional Fenton oxidation can disturb the soil ecosystem and thus, may be incompatible with biological treatment (Nam

et al. 2001). But application of this treatment at near neutral pH could be compatible with bioremediation (Nam et al., 2001). Ecological impacts and environmental concerns due to the presence of H_2O_2 can be significantly addressed by coupling with biological treatment. Moreover, combination of Fenton oxidation and bioremediation was found more efficient to degrade PAHs than sole process and thus, coupling was suggested to improve the removal efficiency and to minimize associated risks (Kulik et al., 2006; Palmroth et al., 2006a; Palmroth et al., 2006b; Valderrama et al., 2009; Venny et al., 2012c). A pilot scale study designed to treat MGP soil revealed that use of Fenton oxidation as the pre-treatment followed by biological treatment using an aerobic biosystem can decrease the PAHs to meet environmental standards (Liu et al., 1993). Moreover, no volatile organic compounds (VOCs) were observed during air monitoring from these experiments implying the safety of this process for environment. Integrated bioremediation and Fenton oxidation in bioslurry reactors also showed more than 80% degradation of PAHs while total microbial counts ranged up to 104 CFU/mL despite the sever oxidation conditions (Brown, 1997). Experimental conditions should be carefully optimized to improve compatibility of both processes as suggested in above studies. Moreover, it should be noted that microbes tend to restore their population and activity after few days (Sahl and Munakata-Marr, 2006; Sirguey et al., 2008). But, too much H_2O_2 during Fenton oxidation may potentially lead to undesired soil sterilization as it destroys the native micro-biota during the treatment (Valderrama et al., 2009).

Venny and co-workers (2012c) demonstrated the strong compatibility of MF oxidation (Fe^{III} + SP as chelating agent) with bioremediation (natural attenuation and biostimulation) for an efficient degradation of PAHs in column experiments simulating in-situ soil flushing. These authors, in another study in packed columns (Venny et al., 2014), described the impact of SP modified Fenton oxidation on soil functionality during remediation of PAHs in spiked and

aged soils. Use of optimized operating parameters during MF oxidation (H_2O_2/soil=0.081, Fe^{III}/soil=0.024, SP/soil=0.024, pH of SP solution=7.73) could make this treatment compatible with bioremediation and crop growth as the obtained values for pH, electrical conductivity, iron precipitation and soil respiration were within acceptable limits.

Gan et al. (Gan et al., 2013) compared the impact of ethyl lectate based Fenton (ELF) treatment onto soil quality with that of conventional water based Fenton treatment (CWF). It was found that ELF caused higher loss of soil organic matter than CWF that was correlated to its high efficiency. Moreover, a decrease in CEC, available P, Cu and Zn was observed in both treatments but to a greater extent in CWF, while ELF caused higher decrease in specific surface area and loss of N. Both treatments, when conducted at low pH (3-4) and high Fe^{II} dosage (H_2O_2:Fe^{II} = 10:1), caused Fe and Al toxicity. But no excessive Fe or Al was formed when ELF was employed at higher pH ($\gtrsim$ 6.2) and lower amounts of added Fe^{II}. This study suggested that ELF adopted for soil with such higher native pH could be compatible for revegetation purposes (Gan et al., 2013).

In addition, traditional Fenton oxidation has been known to frequently generate toxic transformation products due to partial mineralization of PAHs that could also contribute towards soil toxicity (Lee and Hosomi, 2001a; Flotron et al., 2005; Lundstedt et al., 2006). It has been reported that anthracene and benzo[a]anthracene were degraded by the Fenton oxidation by 97% and each target substance was further transformed to oxygenated PAHs by 68% (Lee and Hosomi, 2001b) and 39% (Lee et al., 1998), respectively. It has been reported that oxy-PAHs are more persistent than the target PAHs and some of them were not degraded any further during Fenton oxidation (Lundstedt et al., 2006). Moreover, owing to the higher solubility, these oxygenated PAHs (dibenzofuran, 9-H fluorenone and anthraquinone) are known to be more mobile than PAHs in US-EPA list (Lundstedt et al., 2014). Thus, their distribution and behavior was also focused along with target PAHs in many chemical

593 oxidation studies (Choi et al., 2014; Biache et al., 2015; Usman et al., 2016). No such by-
594 products were detected during magnetite-catalyzed FL oxidation (Usman et al., 2016) or
595 pyrite-Fenton system (Choi et al., 2014). A similar evolution observed for oxy-PAHs and
596 target PAHs suggested a non-preferential removal by FL oxidation (Usman et al., 2016).
597

598 **3. Conclusions and Outlook**

599 Fenton oxidation is widely used technique to remediate PAHs in contaminated soils but
600 various limitations are associated with its environmental application. This review is intended
601 to provide the readers a critical illustration of various limitations of this process along with a
602 brief discussion of strategies to overcome these limitations. The practical applicability of this
603 method strongly depends on the soil type and structure, history of contamination, and
604 concentration and physical state of the contaminants. A rigorous investigation of all these
605 parameters is a pre-requisite for effective application in soil remediation.
606 Considering the main drawback that its optimal pH is around 3, the traditional Fenton
607 treatment is costly and impractical due to high buffering capacity of soils and associated
608 hazardous effects. Use of modified Fenton oxidation by using chelating agents can allow its
609 use at circumneutral pH but chelating agents can also compete for $^{\bullet}OH$ radical with PAHs
610 and thus significantly affecting the oxidation efficiency. A recent approach in this regard is
611 the use of inorganic chelating agents that offers advantages over organic chelating agents for
612 oxidant consumption. Another possibility is the use of iron minerals, which are able to
613 catalyze Fenton-like oxidation over a wide range of pH. Due to the presence of structural Fe^{II},
614 magnetite showed strong reactivity to catalyze Fenton-like oxidation of PAHs at
615 circumneutral pH. Moreover, its catalytic stability can be maintained for multiple oxidation
616 cycles and it can be a promising treatment. Use of iron minerals or nanoparticles of ZVI
617 could provide a cost-effective alternative to the use of more than one reagent (e.g. chelating

618 agent + soluble Fe^{II}). Further studies are needed for a better understanding of Fenton-like
619 application in real field conditions, as injection of iron particles in unsaturated zone such as
620 vadose zone requires many investigations. Mobility, transport and fate of such particles
621 should be addressed on context of reactivity, stability and eco-toxicity. Detailed studies are
622 required to exploit the potential of endogenous iron minerals to catalyze chemical oxidation.
623 Another major limitation is the PAH unavailability during Fenton oxidation. Many strategies
624 are discussed including the use of availability enhancement agents, extraction or thermal
625 pretreatment. PAH availability is the crucial factor controlling its degradation in aged soils
626 and that should be considered while designing a remediation treatment. Use of suitable
627 pretreatment to enhance PAH availability can enhance the treatment efficiency. Most of the
628 studies are based on the batch experiments that should be up-scaled to column experiments
629 under saturated and unsaturated conditions to get closer to real field conditions. The field
630 application of certain pretreatments (extraction or thermal) seems difficult to implement that
631 merits to be resolved but they can serve as good approach for *ex-situ* application. Integration
632 of Fenton's treatment with bioremediation could become a suitable option to address the
633 detrimental effects associated with Fenton's application. The development of new modeling
634 approaches that account for the up-scaling of different involved reactions and complexity of
635 soil system becomes urgent in soil remediation science. More experimental work is also
636 needed to develop strategies with high remediation efficiency and yet are suitable for soil
637 quality so that contaminated sites can be restored to productive use.
638
639 **Acknowledgment**
640 This work was supported by a post-doctoral research fellowship from the Alexander von
641 Humboldt Foundation, which is gratefully acknowledged.
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907 **Figure captions**

908 **Figure 1:** Different phases of experimental setup used in laboratory to investigate application
909 of Fenton oxidation to remediate PAHs in contaminated soils.

910 **Figure 2. (a)** Removal of phenanthrene (PHE) and fluoranthene (FLUT) by using modified-
911 Fenton oxidation in the presence of inorganic chelating agent- SP (sodium pyrophosphate)
912 and organic chelating agents including EDTA (ethylenediaminetetraacetic acid), OA (oxalic
913 acid), SC (sodium citrate) and MA (malic acid). **(b)** H_2O_2 residual for MF treatment in the
914 presence of inorganic (SP) and organic chelating agents (EDTA, OA, SC and MA). Adapted
915 with permission from Figure 2 and Figure 5 of Venny et al. (2012b).

916 **Figure 3:** PAHs degradation in (a) organic extracts (spiked on sand) and (b) soil pretreated
917 with availability enhancement agent during oxidation experiments by: H_2O_2 alone without
918 iron activation (■-HP), H_2O_2 + soluble Fe^{II} (○-F) and H_2O_2 + magnetite (●-FL). Blank (▲)
919 experiment was performed in the presence of magnetite but without any oxidant. This
920 degradation is represented in terms of C_t/C_0 where C_t is the sum of 16 PAHs concentration at
921 specified oxidation time and C_0 is their concentration at t=0 (before oxidation) measured by
922 GC-MS. Adapted with permission from Fig. 2 and Fig. 6 of Usman et al. (2012).
923 Experimental conditions were: solid matrix = 2 g, volume of solution = 20 mL, magnetite
924 (10%, w/w) and equivalent amount of Fe^{II}.

925 **Figure 4:** Efficiency of ethanol in comparison with other PAH-availability enhancement
926 agent to assist Fenton oxidation where F: traditional Fenton, ETF: ethanol-Fenton system,
927 ELF = ethyl lactate-Fenton system, SDS-F = sodium dodecyl sulfate- Fenton system, CD-F =
928 cyclodextrin-Fenton system. Instead of traditional Fenton oxidation, Usman and co-workers
929 (2012) applied magnetite catalyzed Fenton-like oxidation (FL) assisted by ET and CD.

930

Figure 5: Degradation of 16 PAHs in former coking plant soil by Fenton-like oxidation assisted by various pretreatments and is represented by C/C_0 where C is the final concentration of PAHs after treatment and C_0 is the initial concentration. Where initial = PAH concentration before treatment and others represent application of Fenton-like oxidation direct (Direct oxidation = when soils were subjected to chemical oxidation without any pre-treatment), spiking/FL (when EOM was extracted from soils and spiked on sand), Ext-Pt/FL (extraction pretreatment to incorporate PAHs as fresh contaminants in soil as detailed in Section 2.2.2), and FL oxidation assisted by ethanol (ET-FL) or cyclodextrin (CD) or by thermal pretreatment at 60, 100, and 150 °C.

Figure 6. Density of cultivable bacteria, 16S rDNA, PAH-RDHα and 18s rDNA gene copy numbers in oxidized by Fenton treatment at low (L) i.e. 6 g kg^{-1} and high (H) i.e. 65 g kg^{-1} concentration of H_2O_2 and control soil (Control) at the start (T_0) and after 5 weeks (T5) of incubation. As the evolution of PAH-RHD_α GN and GP populations was not significantly different, the two populations were added to represent the global population of degraders. Mean ± SE (n = 3). LD: detection limit. Different letters within category data indicate significant differences between treatments; stars indicate significant differences between T_0 and T_6 by Mann and Whitney test. Reproduced with permission from Fig. 2 of Laurent et al. (2012).

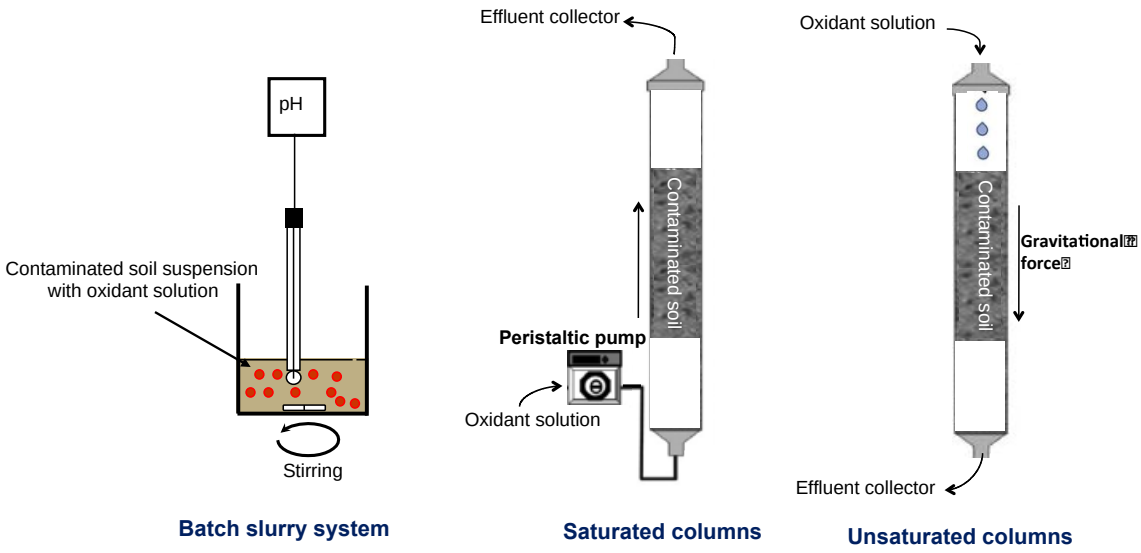
950 **Table 1:** Research studies using Fenton oxidation assisted by various kinds of chelating agents.

Focus of study	**Soil**	**Tested chelating agents (CA)**	**Experimental conditions**	**Important results**	**Reference**
To compare the efficiency of traditional Fenton and modified Fenton to couple with biodegradation for enhanced PAH removal	Spiked soil (PAHs = 600 mg/Kg), silt loam and soil sampled from former manufactured gas plant site, loamy sand	Catechol (CA) and gallic acid (GA)	5 g of MGP soil in 20 ml of distilled water, Fe^{III}; 82.5 mg of catechol or 141.0 mg of gallic acid and $Fe(ClO_4)_3 \cdot 6H_2O$ (0.07 M), 2 g of H_2O_2, neutral pH For traditional Fenton, experiments were performed at pH = 2-3 without chelating agents	Traditional Fenton was effective but required pH (pH 2–3) for optimum efficiency made the process incompatible with biological treatment. Efficiency was maintained by using chelating agents that allowed coupling with bioremediation.	Nam et al., 2001
Production of surfactants during various chemical oxidation strategies for PAH remediation	Soil sampled from former manufactured gas plant site, having sand:silt:clay =79:20:1%	EDTA	Laboratory slurry reactors, 4 kg of soil (dry weight) and 8.5 L of water (including the oxidant solutions), 200 mg of EDTA, 1 g Fe^{III} (as ferric sulfate), and 1 L of 50% H_2O_2, pH=8	All tested treatments resulted significant surfactant production and overall removal of PAHs. Modified Fenton with calcium peroxide exhibited better efficiency.	Gryzenia et al., 2009
Effect of various chelating agents on the efficiency of Fenton oxidation to remove PAHs	Spiked soil (loamy sand), containing 1000 mg/kg of two PAHs	Sodium pyrophosphate (SP) as organic CA, EDTA, Oxalic acid (OA),	Batch slurry system, 5 g of soil, 480 mM H_2O_2, 60 mM Fe^{3+}, solution:soil = 15 mL:5 g. Different doses of CAs: 0.1135–0.4015 g	Inorganic SP was demonstrated to be superior in efficiency to the tested organic CAs.	Venny et al., 2012c

		sodium citrate (SC) as inorganic CAs			
Optimization of experimental conditions for efficient coupling of Fenton's reagent with bioremediation	Soil (loamy sand) spiked with two PAHs, 500 mg the PAH/kg for each PAH,	SP	Unsaturated soil columns, 1.2 Kg soil, Various doses of oxidant, SP, Fe^{III} at different reaction times with soil pH of 4.07–5.41	An optimized operating condition of the modified Fenton was found at H_2O_2/soil 0.05, Fe^{III}/soil 0.025, SP/soil 0.04 and 3 h reaction time with 79.42% and 68.08% removal of tested PAHs. Use of SP assisted Fenton treatment and bioremediation serves as a suitable strategy to enhance soil quality.	Venny et al., 2012b
Role of various chelating agents to improve operating range of pH for degradation of PAHs by modified Fenton oxidation using iron nano particles	Spiked soil (silty sand), containing 100 mg of pyrene per kg of soil	SP as inorganic CA and EDTA, FA, HA and SC (as organic CAs)	Batch experiments, 5 g soil, 15 mL distilled water, iron nano-oxide = 5 – 60 mM, H_2O_2 = 0-500 mM, pH = 3 and 7	Application of modified Fenton treatment, with the following conditions (300 mM of H_2O_2, 30 mM of iron nano oxide, SP as CA, pH 7 after 6 h of reaction, removed 93% of tested PAHs that was higher than organic CAs.	Jorfi et al., 2013

951

952 **Figure 1:**

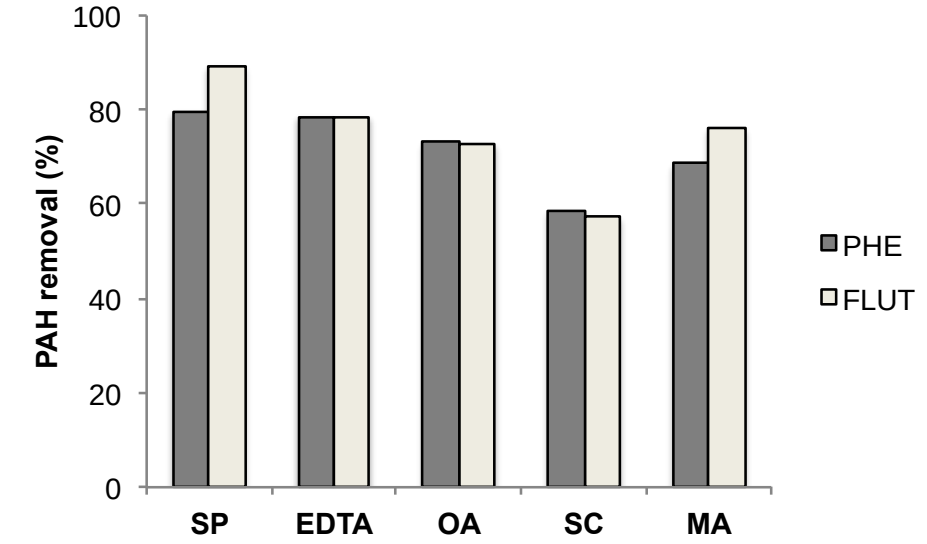


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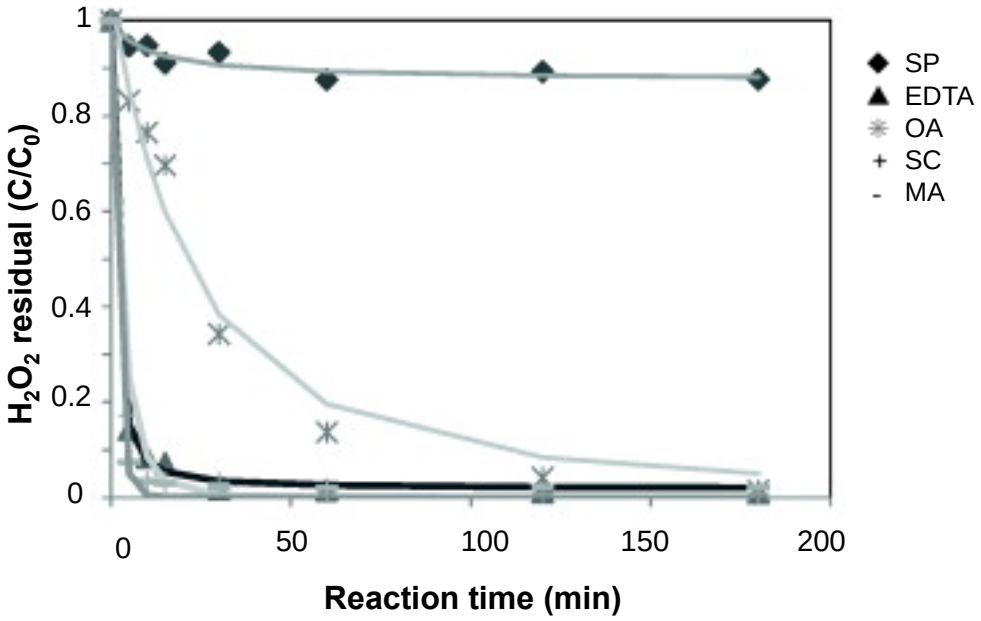
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955 **Figure 2:**

956 (a)



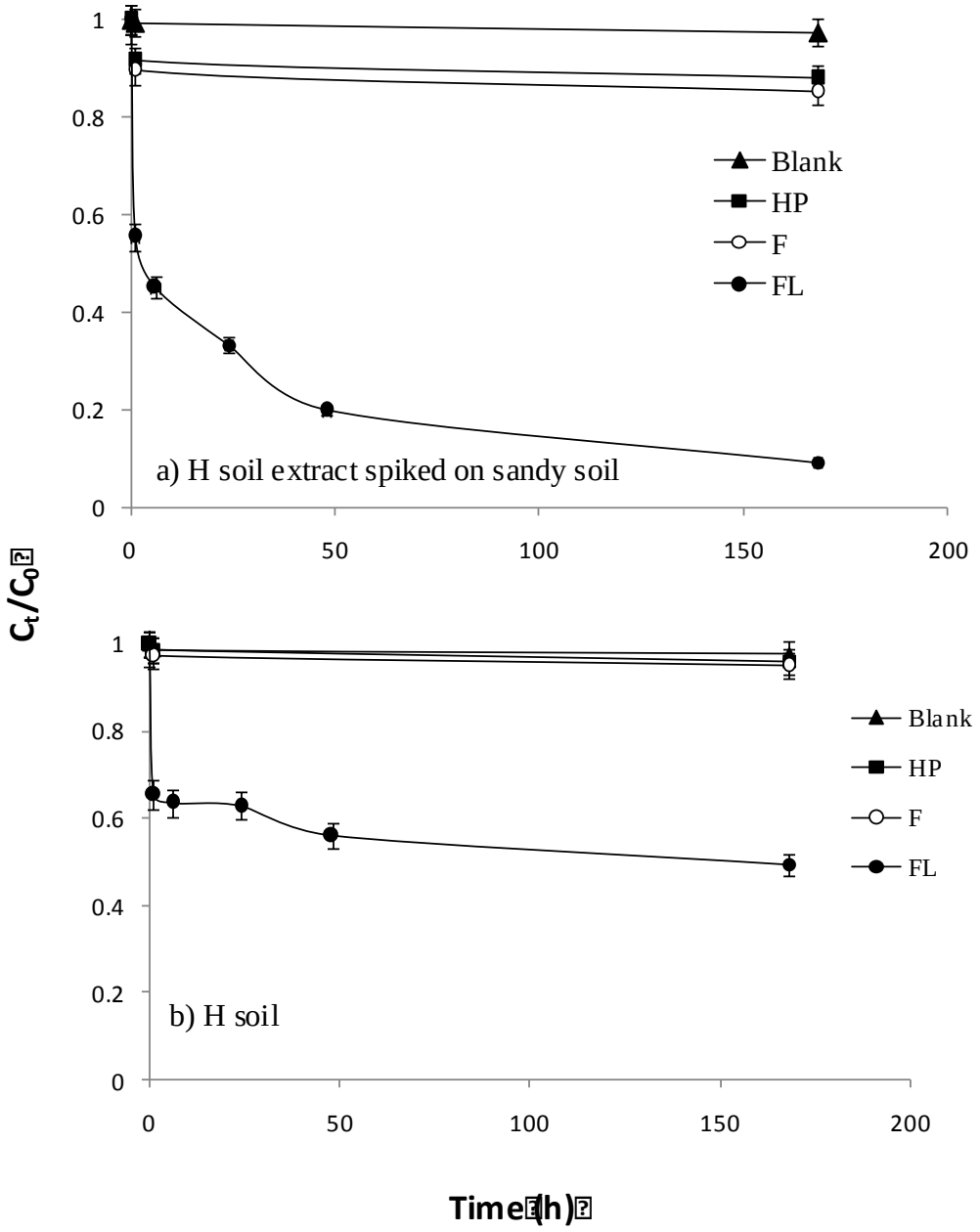
(b)



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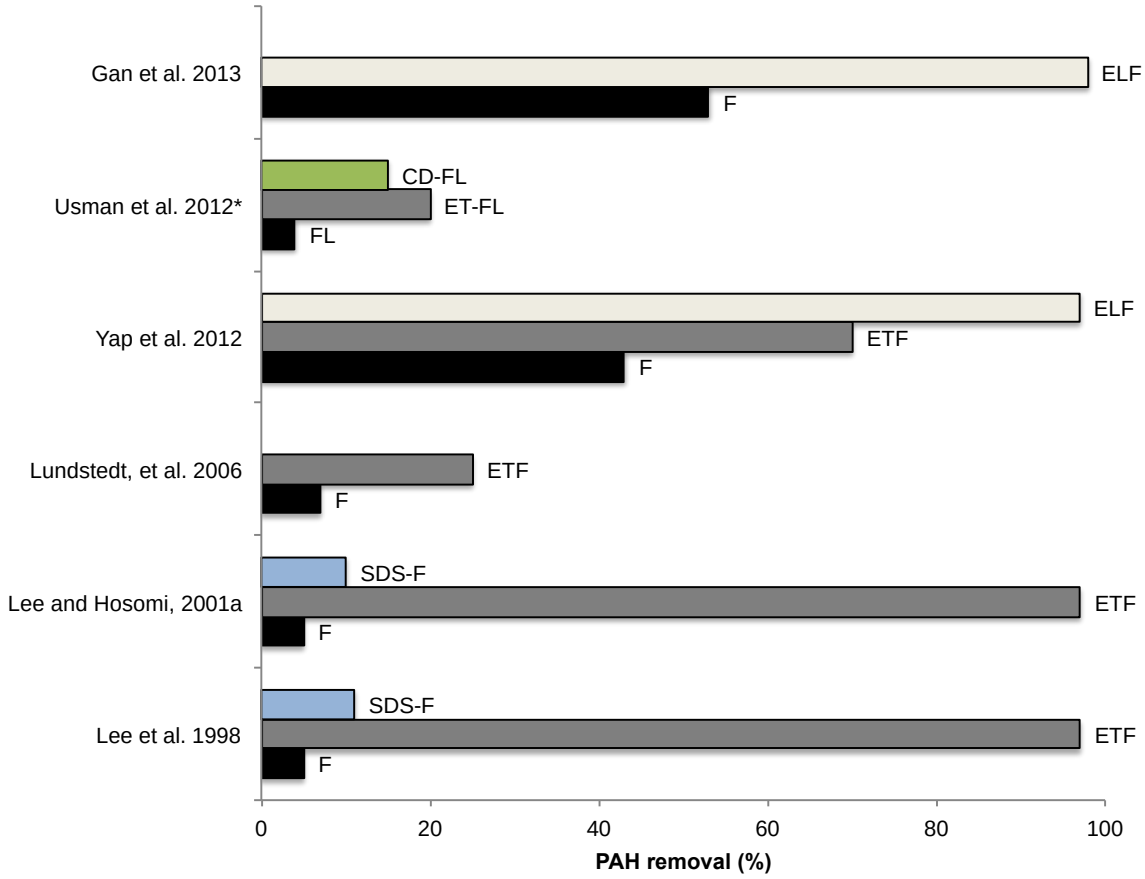
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959 **Figure 3:**



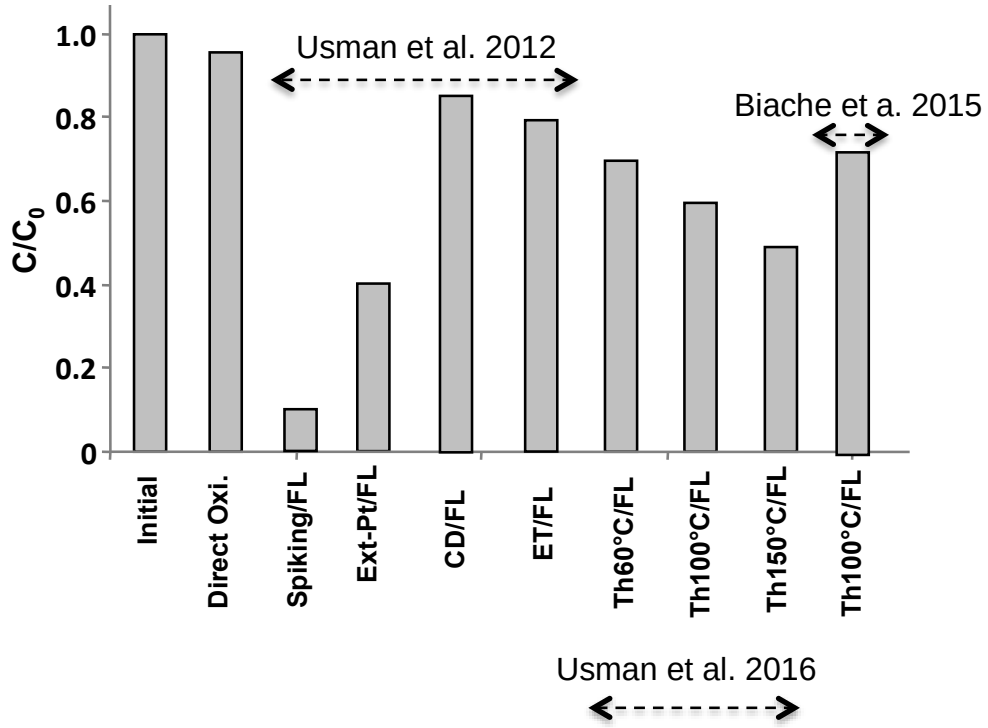
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961 **Figure 4:**



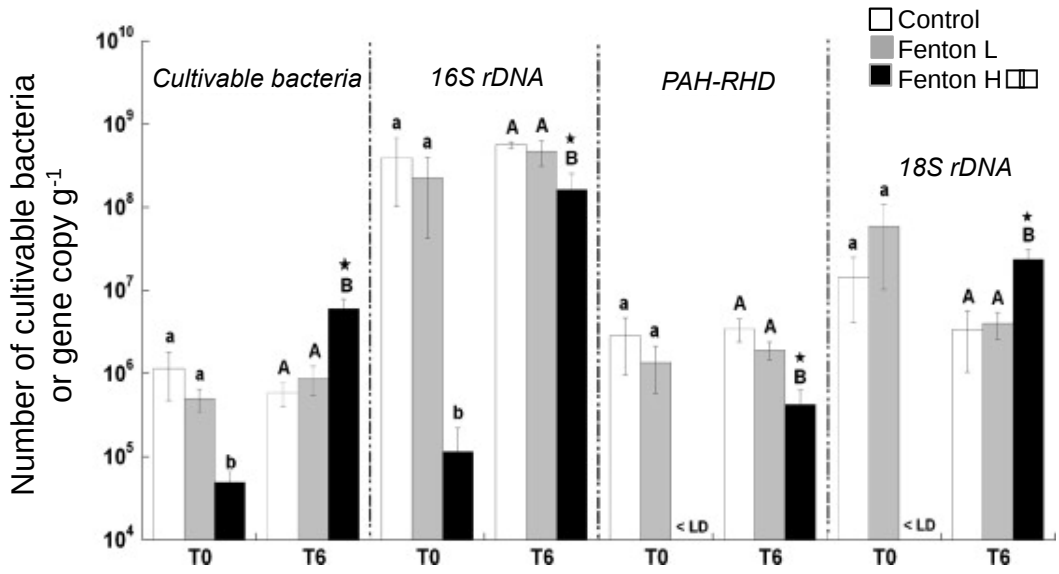
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963 **Figure 5:**



964

965 **Figure 6:**



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