Global NEST Journal, Vol 24, No 1, pp 74-86
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An overview of chemical oxidation-based remediation technologies for non-aqueous phase liquids removal from soil

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Received: 21/08/2021, Accepted: 09/11/2021, Available online: 17/01/2022
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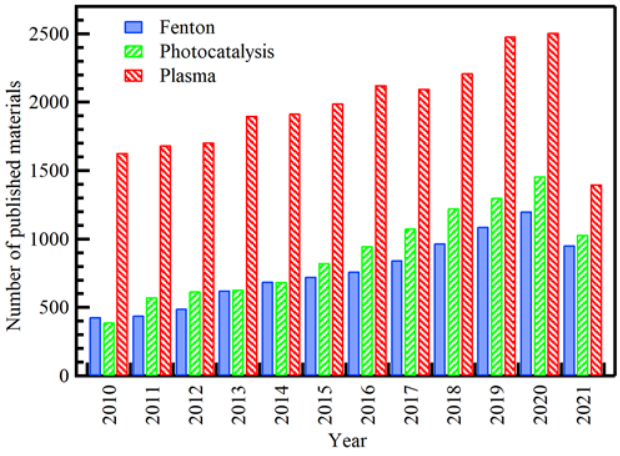
https://doi.org/10.30955/gnj.003909

Graphical abstract



Abstract

This review provides a general overview of the application of chemical oxidation to hydrophobic contaminants in the form of non-aqueous phase liquids (NAPLs). Six types of chemical oxidation processes, three conventional process: activated persulfate, permanganate, and ozonation, along with three advanced oxidation processes (AOPs):Fenton process, photocatalysis, and plasma oxidation are presented discussed. In addition, this paper provides a brief insight into the combination of chemical oxidation with other remediation technologies for the efficient removal of NAPLs. The common and wide use of activated persulfate for soil remediation is hindered by the fact that it needs heat activation, whereas the main drawback of using permanganate is the precipitation of manganese oxide at the NAPLs face. In addition, the high cost of equipment at the site restricts the ozone application for in-suit soil remediation. The application of AOPs processes such as Fenton and plasma oxidation has received great attention due to its high removal efficiency. However, photocatalysis technology in the field is difficult because it needs photo energy to run the oxidation process. Although plasma oxidation can degrade contaminants in minutes, some active species have short-lived time that could disappear before entering the soil layer. Ozonation is efficient in treat soils with low moisture and large pore spaces. Nevertheless, the optimal pH for ozonation oxidation is 3, which is hard to achieve in real-world applications. Combining chemical oxidation with other remediation technology, especially biological remediation, is a valuable technique of soil remediation as the synergetic effects may increase the sustainability of the applied process towards green technology for soil remediation.

Keywords: Advance oxidation process, fenton oxidation, plasma oxidation, NAPLs, soil remediation, combined remediation process.

1. Introduction

Soil and groundwater contamination by petroleum hydrocarbon products is a global common problem separate immiscible phase in the subsurface referred to as light non-aqueous phase liquids (NAPLs) (Mateas *et al.*, 2017). Behaviour of NAPL-derived organic pollutants in aquifer systems mainly depends on dissolution of the contaminants within the source zone, the mass transfer to the flowing groundwater, advection, dispersion, diffusion, sorption (retardation) and biodegradation (Aminnaji *et al.*, 2020). The contamination of groundwater by NALPs is a challenging environmental problem that poses risks to

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both human and the environment (Tsai *et al.*, 2008); thus, soil and groundwater remediation, to achieve environmental sustainability and protect human health, has become the shared vision of various stakeholders, including governments, world organizations, and the public (Honetschlägerová *et al.*, 2019). Numerous remediation technologies have been employed to remove NAPLs from soil and groundwater during the last few decades. The mechanism of these technologies can be broadly classified as physical, often due to accidental releases, such as spills during product transportation and storage tanks and pipelines leakage (Cheng *et al.*, 2016). Most petroleum hydrocarbons are lighter than water. Because of their low solubility, they are often present and act as a chemical, and biological whereas and depending on the site of treatment, it is divided as in-situ and ex-situ remediation (Liu *et al.*, 2020a).

The chemical oxidation process aims to be defined as an oxidizer (oxidant) ability to mineralize the organic compounds to carbon dioxide, inorganic, and water or transform harmful ones into harmless or biodegradable compounds (McKenzie *et al.*, 2016). In the last 20 years, In-Suite Chemical Oxidation (ISCO) has become a promising technology for soil and groundwater remediation where the site is contaminated by NAPLs (Ranc *et al.*, 2016). The advantages of chemical oxidation for NAPLs can be summarized as high ability to oxidize NAPLs, relatively an affected by pollutant characteristics and concentration, rapid degradation/destruction of contaminants (measurable result in a short time), competitive cost relative to intensive pump-and-treat systems, non-destructive (no need to disturbing aboveground structure), and can be used in combination with other remediation technology (Tsai *et al.*, 2008; Mdlovu *et al.*, 2019; Martínez-Pascual *et al.*, 2015).

Hydrogen peroxide (H_2O_2) was the first oxidant used in full-scale ISCO. Shortly after that, potassium or sodium permanganate ($KMnO_4$, $NaMnO_4$) and ozonation were used to oxidize full-scale remediation (Liu, 2017).. Recently, persulphate has become another alternative for soil and groundwater remediation by ISCO (Bennedsen, 2014). The redox potentials (E_0) for this oxidant are: persulfate (2.01 V), permanganate (1.70 V), hydrogen peroxide (1.80 V), and ozone (2.10 V) (Liu, 2017). The hydrogen peroxide solution has been used widely because it dissociates into many strong oxidants to destroy many contaminants quickly. In addition, in the presence of catalyst ions in soil (such as ferrous ions), the production of hydroxyl radicals, which are considered powerful oxidants (2.86 V), can be accelerated as a Fenton reagent reaction can take place (Kim and Lee, 2012).

The use of permanganate in ISCO is fully developed, and its application in soil and groundwater remediation is well documented as it has been used in numerous sites (Baciocchi, 2013). The main advantages of using permanganate as an oxidant for ISCO are the stability of the oxidant which means it can stay in the subsurface for months and has good distribution due to both diffusive and advective transport. Furthermore, its distinctive purple color makes it notable visually, allowing measuring quantitatively (Anvarov *et al.*, 2019). On the other hand, one of the main drawbacks of using permanganate is the precipitation of manganese dioxide (MnO_2) at the NAPLs interface and injection wells, respectively, in addition, permanganate alone is an ineffective NAPLs oxidant because of its inability to oxidize benzene rings (Heiderscheidt *et al.*, 2008). Persulfate has been used in ISCO application as it produces sulfate radical, which is considered a strong oxidant where the most known activators of persulfate are heated, chelated iron, and iron (Ko *et al.*, 2012; Wang *et al.*, 2017; Solano *et al.*, 2017; Yang *et al.*, 2020). Sodium persulfate ($Na_2S_2O_8$) is widely used as persulfate salts, while the use of potassium persulfate ($K_2S_2O_8$) is limiting its application as a remediation agent due to its low solubility (Cavanagh *et al.*, 2017; Jousse *et al.*, 2017). As heat can readily activate sulfate radicals, chemical oxidation by persulfate is feasible remediation technology for soil and groundwater pollutants under thermal conditions. However, overuse of persulfate on groundwater remediation, especially those used for drinking purposes, can cause human health problems such as diarrhea (Bennedsen, 2014; Tsai *et al.*, 2008). Finally, chemical oxidation by ozone is advantageous compared to other oxidation processes, such as permanganate, persulfate, and hydrogen peroxide, due to its highest redox potential compared to others. Two ways to apply ozone for soil and groundwater remediation are ozone gas injection in the vadose zone and sparging the ozone gas under the water table (Rivas, 2006). Nevertheless, ozone application in ISCO can be hindered by the capital equipment cost at the site and the limited ozone stability. Degradation of NAPLs may occur either through direct oxidation with ozone or indirectly by hydroxyl radical, which can be generated by ozone's reaction with hydrogen peroxide (Bennedsen, 2014).

In the past few decades, some reviews regarding applying different technologies for NAPLs remediation were documented in the literature. Mulligan *et al.* (2001) evaluated the effectiveness of three types of biosurfactants on the remediation of contaminated soil in laboratory scale, field, and full-scale applications. They concluded that removing the metals with the anionic biosurfactants even though the exchangeable fractions were not significant. Rivas (2006) reviewed and compared the efficiency of ozone, hydrogen peroxide, and high-temperature pressurized water for Polycyclic aromatic hydrocarbons removal from soil and groundwater. Besha *et al.* (2018) reviewed the recent advances in surfactant enhanced ISCO to remediation NAPLs in contaminated soils. They focused on three important components of surfactant ISCO includes surfactant/co-solvent mixtures, the catalyst and/or the oxidant, and the free radicals.

The main objective of this review is to evaluate the recent research and development regarding the application of ISCO by both conventional chemical oxidation methods and advanced chemical oxidation. The focus is primarily on the advance oxidation process (AOPs): Fenton, photocatalysis and plasma oxidation. Moreover, the results from recent studies are discussed and summarized. This review also comprehensively discusses the the implementation of chemical oxidation in combination with other remediation technology for effective soil and groundwater remediation. Finally, a recommendation for the research needs regarding using chemical oxidation in NAPLs remediation is presented.

2. The advanced chemical oxidation process

AOPs is a process of generation of the highly reactive hydroxyl radical ($^{\cdot}OH$) (Flotron *et al.*, 2005; Kang *et al.*, 2006). Different chemical processes can generate $^{\cdot}OH$ such as the Fenton process, photocatalysis, plasma oxidation, UV with ozone, and hydrogen peroxide. The process verity allows competing with the complicity of many treatment systems (Burbano *et al.*, 2005; Venny *et al.*, 2012; Matta *et al.*, 2008; Watts *et al.*, 2002; Yap *et al.*, 2011).

The interest in AOPs started around 1995 and has continued to focus on numerous studies dealing with contaminants and pollutants in the environment (Wang *et al.*, 2009; Quiroga *et al.*, 2009; Zepp *et al.*, 1992). Figure 1 presents the number of publications about AOPs from 2010 to 2020 using AOPs as a searched keyword. The photocatalysis oxidation process for soil remediation is at the top, with around 22038 research in the last 10 years, followed by plasma oxidation with 10386 research articles. The Fenton process for soil remediation is at the top, with around 8280 research in the last 10 years. The following sections describe the key processes involved in these oxidation technologies. Overall, all methods have great attention, and many works are published recently.

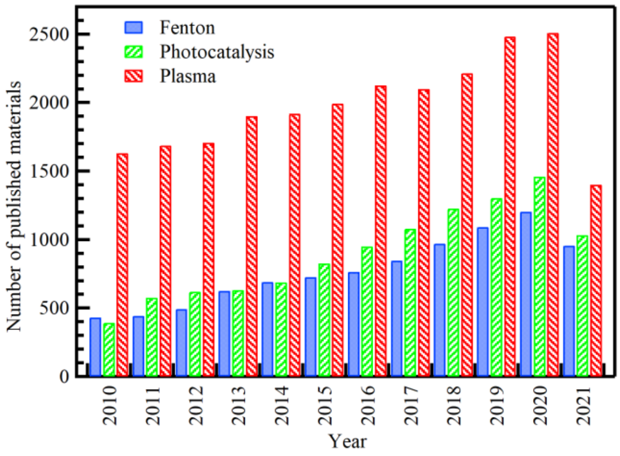

Figure 1. Numbers of articles published from 2010 to 2021 apply advanced oxidation technologies for soil remediation (Scopus, October 2021).

2.1. Fenton process

Fenton oxidation involves the generation of hydroxyl radicals by the combination of hydrogen peroxide (H_2O_2) with soluble catalyst (ferrous ion (Fe(II) or ferric ion (Fe(III)) (Haber and Weiss, 1934). The produced hydroxyl radical is considered among the strongest oxidant (E_0=2.73 V), which can oxidize a large list of organic compounds (Flotron *et al.*, 2005; Kang *et al.*, 2006). As seen in Equation 1, the H_2O_2 decomposition under the Fenton reaction can produce $^{\cdot}OH$ (Haber and Weiss, 1934). RH and R in Equations 2 and 3 (Flotron *et al.*, 2005; Kang *et al.*, 2006).represent the organic compounds that can be oxidized by $^{\cdot}OH$ using hydrogen abstraction ($R^{\cdot}$) Equation 2 or hydroxyl addition ($^{\cdot}ROH$) in Equation 3. In addition, the formed ferric ions from Equation 1 (Haber and Weiss, 1934) can catalyze H_2O_2, as seen in Equation 4 (Haber and Weiss, 1934); this reaction is known as a Fenton-like reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + {}^{\cdot}OH \quad (1)$$

$$RH + {}^{\cdot}OH \rightarrow H_2O_2 + R^{\cdot} + further\ oxidation \quad (2)$$

$$R + {}^{\cdot}OH \rightarrow {}^{\cdot}ROH + further\ oxidation \quad (3)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + H^{+-} + HO_2^{\cdot} \quad (4)$$

Fenton/Fenton-like reactions can proceed at atmospheric pressure and room temperature but are highly pH-dependent due to the iron ions (Fe(II) and Fe(III) and the speciation factors of the H_2O_2 whereas they (Burbano *et al.*, 2005). The Fenton reaction can be carried out effectively at pH around 3; a significant reduction in the efficiency can occur with both a small increase or decrease in the pH value (Venny *et al.*, 2012; Matta *et al.*, 2008). For example, when pH is below 3, oxonium ions ($H_3O_2^{+}$) can be formed when H_2O_2 solvate protons. Oxonium ions may enhance the stability of H_2O_2, thus, reduce the reactivity of H_2O_2 with ferrous ions. For pH higher than 3, the colloidal ferric species appear as the dissolved fraction of iron ions decrease (Watts *et al.*, 2002).

To deal with this shortcoming, modifications have been proposed for the Fenton reaction to increasing the pH range. These modifications involve amendments to increase the applicability of the Fenton process in native soil to neutral conditions. Chelators, including nitrilotriacetic acid, cyclodextrin, ethylenediamine tetra acid, and catechol, have been particularly used as modified Fenton reagents. The chelating agents are able to dissolve Fe^{3+} precipitation by forming complexes (Yap *et al.*, 2011; Rivas, 2006).

Studies have shown that ultraviolet-visible (UV-Vis) light irradiation can facilitate the degradation of organic contamination by Fenton reaction at wavelength values higher than 300 nm (Wang *et al.*, 2009; Quiroga *et al.*, 2009). In this case, Fe^{2+} is generated by the photolysis of Fe^{3+} in the presence of H_2O_2 (Zepp *et al.*, 1992). These two reactions are known as the photo-Fenton (Equations 5 and 6) (Burbano *et al.*, 2005). Moreover, $^{\cdot}OH$ also is formatted in photo-Fenton reaction (Equation 7) (Pignatello, 1992; Khataee *et al.*, 2015). However, the photo-Fenton reaction is highly pH-dependent. The optimum pH value for the photo-Fenton reaction is 2.8, with 50% of the Fe(III) present as Fe^{3+} and 50% as Fe $(OH)_2$ (Pignatello, 1992; Khataee *et al.*, 2015). When the pH is lower than 2.8, the concentration of $Fe(OH)_2^{+}$ will decrease, whereas at pH greater than 2.8, precipitated

Fe(III) as oxyhydroxides are observed (Khataee *et al.*, 2015; Kavitha and Palanivelu, 2004).

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + {}^{\cdot}OH \tag{5}$$

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\cdot}OH \tag{6}$$

$$H_2O_2 + h\upsilon \rightarrow 2\ {}^{\cdot}OH \tag{7}$$

Another type of Fenton reaction is Electro-Fenton which has attracted more interest in remediation of contaminated soil remediation (Rodrigo *et al.*, 2014; Sirés *et al.*, 2014). The electro-Fenton process can be applied by passing a direct current across transplanted electrodes in the contaminated soil, as shown in Figure 2 and Equation 8(Mousset *et al.*, 2016).

$$M + H_2O \rightarrow M({}^{\cdot}\mathrm{OH}) + H^+ + e^- \tag{8}$$

In contrast to the general Fenton process, H_2O_2 is produced in situ at the cathode as O_2 or air pumping near the cathode electrode, whereas the ˙OH is generated on the anode electrode (Mousset *et al.*, 2016). As the ˙OH is generated at the bulk, the contamination is destroyed by the Fenton reaction (Mousset *et al.*, 2014b).

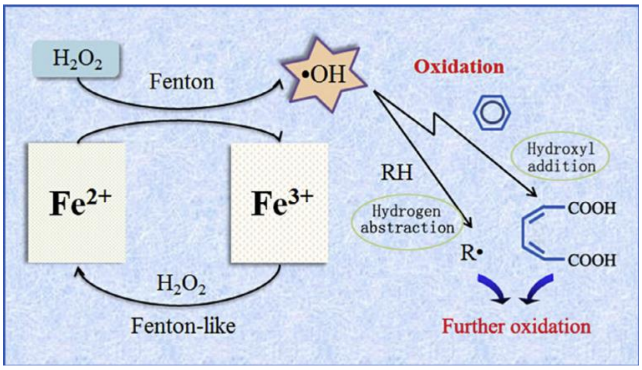

Figure 2. Decomposition of organic compounds by Fenton process (Cheng *et al.*, 2016).

In the Electron-Fenton process, no sludge is generated; thus, this process is considered a green technology for soil remediation as no harmful product is generated (Mousset *et al.*, 2014a, Martínez-Huitle and Brillas, 2009). Moreover, when soil composition has iron ions, no iron addition is needed. Therefore, in certain circumstances, the modified Fenton process is preferred over the traditional Fenton treatment. In addition, in some cases, the modified Fenton process can enhance the contaminant's solubility, increasing the Fenton oxidation efficiency by lowering the interfacial tension (Nam *et al.*, 2001).

2.2. Photocatalysis

During the last 40 years, the photocatalysis process for oxidation has been studied extensively (Chen and Mao, 2007; Yu and Yu, 2008). In this process, a metal-semiconductor such as Zinc oxide (ZnO), Tungsten trioxide (WO_3), Cadmium sulfide (CdS), Nickel oxide (Nio), Gallium phosphide (GaP), and Titanium dioxide (TiO_2) is used (Yu and Yu, 2008; Iwasaki *et al.*, 2000; Chen *et al.*, 2012). Due to its characteristics, TiO_2 in the anatase form has been proven as the most suitable semiconductor as it has high photoactivity, low coast, chemical inertness, easy to produce, and non-toxic. On the other hand, ZnO, GaP, and CdS can dissolve and produce toxic by-products when used in environmental remediation during the photocatalysis process (Chen *et al.*, 2012).

A research involved the preparation of a thin TiO_2 film of photonic structure by a sol-gel technique, using PS spheres as a template, with alternating air and TiO_2 spaces with a periodicity of approximately 150 nm. The band gap of anatase TiO_2 is 3.2 eV and so a photonic band gap in the mid-to-high UV wavelength range (280–380 nm) was required to increase the quantum efficiency of the photo-catalyst. (Nakata and Fujishima, 2012; Fujishima *et al.*, 2008). Many investigations on various substrates have well established removing organic contaminants in soils using TiO_2 combined with solar light or UV-irradiation (Ochiai and Fujishima, 2012; Kumar and Devi, 2011).

When suitable scavengers (HO^- and/or H_2O) are available, ˙OH can be formed from oxidation reactions as shown in Equations 9 and 10 (Hoffmann *et al.*, 1995). Superoxide radical anion (O_2^-) is another reactive radical that can be formed during the photocatalytic process in Equation 11 (Linsebigler *et al.*, 1995; Giahi *et al.*, 2019; Sharifi *et al.*, 2019; Ethiraj *et al.*, 2020). In addition, O_2^- can lead to the formation of ˙OH according to Equations 12, 13, and 14 (Ognier *et al.*, 2014). In addition, some adsorbed pollutants may react directly with e- through reductive processes, as shown in Equation 15 (Fox and Dulay, 1993). Figure 3 represents the mechanism of contaminant removal by TiO_2 photocatalysis.

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + H^+ + {}^{\cdot}\mathrm{OH} \tag{9}$$

$$TiO_2(h^+) + HO^- \rightarrow TiO_2 + {}^{\cdot}\mathrm{OH} \tag{10}$$

$$O_2 + e^- \rightarrow O_2^- \tag{11}$$

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \tag{12}$$

$$HO_2^{\cdot} + H^+ + TiO_2(e^-) \rightarrow + TiO_2 \tag{13}$$

$$H_2O_2 + TiO_2(e^-) \rightarrow {}^{\cdot}\mathrm{OH} + HO^- + TiO_2 \tag{14}$$

$$RH + h^+ \rightarrow H^+ + R^{\cdot} \tag{15}$$

UV light irradiation is required to activate the photoreaction with conventional TiO_2, a bandgap of 3.2 eV. However, since less than 6% of the light reaching the Earth is UV light (Pelaez *et al.*, 2012), the photoreaction using sunlight as an energy source may hinder the entire process due to low UV light (Ethiraj *et al.*, 2020; Solehudin *et al.*, 2020; Laouini *et al.*, 2021). Therefore, significant efforts have been directed towards increasing the energy efficiency of photocatalysis reactions. As a result, the photo-response region range of TiO_2 has been successfully increased in many studies to reach visible light. This process can be accomplished by introducing additional components into the lattice structure (Zhang *et al.*, 2015; Sacco *et al.*, 2015). Metal (e.g., Fe, Cr, V, Co) doping and non-metal (e,g., S, C, F, N) doping has been investigated in this domain. Both have successfully extended the visible light response of the TiO_2 to photocatalyst reaction (Sacco *et al.*, 2015; Iwasaki *et al.*, 2000).

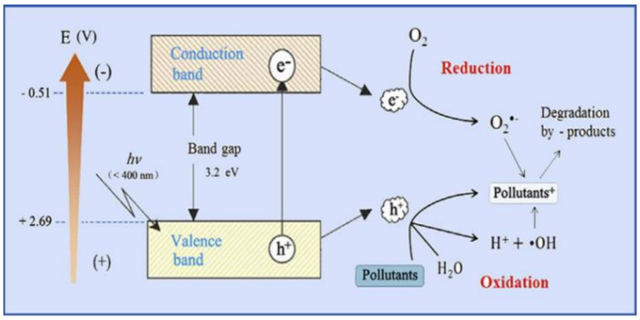

Figure 3. Decomposition of organic compounds by photocatalysis process(Cheng *et al.*, 2016).

2.3. Plasma oxidation

Plasma oxidation is considered a competitive technology for organic pollutants removal from soil. Recently, plasma oxidation was investigated as an eco-innovative technology for soil remediation. Low-temperature plasma (LTPs) techniques have received great attention for soil remediation due to the following advantages (1) rapid start and low energy consumption; (2) long service life of equipment; (3) wide application range and high purification efficiency; and (4) lack of additional additives and secondary pollution (Zhao *et al.*, 2019). LTPs methods such as dielectric barrier discharge (DBD) (Ognier *et al.*, 2014; Aggelopoulos *et al.*, 2015) and pulsed corona discharge (PCD) (Wang *et al.*, 2014a) are most investigated. When plasma production occurs, electrons with high energy are produced, affording highly reactive species and space charge. Highly reactive species include $^{\cdot}OH$, O and H radicals, and ozone, H_2O_2 molecules (Lou *et al.*, 2012; Wang *et al.*, 2015; Wang *et al.*, 2014b).

3. Conventional chemical oxidation process for NAPL remediation

3.1. Permanganate

Table 1 presents the overview of the previous work carried out in the remediation of NAPLs by conventional chemical oxidation methods. Some of these studies are discussed below.

Soil and groundwater remediation with permanganate involves injecting permanganate in the form of sodium or potassium permanganate ($NaMnO_4$ or $KMnO_4$) in the contaminated site to degrade the pollutant such as NAPLs (Zhang *et al.*, 2020). In a recent study, Bajagain *et al.* (2019) studied potassium permanganate with bioaugmentation foam for diesel contaminated soil for the first time. Results showed that combining two methods achieved up to 92.1% removal efficiency of diesel from the initial concentration of 5542 mg/kg). These methods separately achieved 37% removal efficiency for the potassium permanganate and 72.1% for bioaugmentation foam. In an earlier study, Matta and Chiron (2017) examined the performance of permanganate for the oxidation of pentachlorophenol in contaminated soil. The results showed that permanganate has a good ability to oxidize pentachlorophenol. The removal efficiency reached around 77% after 24 h, demonstrating the ability of permanganate as an ISCO reagent.

3.2. Activated persulfate

Recently, activated persulfate has been used for soil and ground remediation due to its high redox potential (E=2.01 V). Persulfate can be activated by ferrous ions or heat to generate sulfate free radicals ($SO_4^{-\cdot}$), which is considered a strong oxidizer. Many studies used activate persulfate to degrade contaminants such as petroleum hydrocarbons and chlorinated organic compounds. Chang *et al.* (2018*)* investigated the efficiency of activated persulfate for remediation of Trichloroethene (TCE). Results showed 100% TCE removal from the first site and around 95% in the second site. The result indicated that one injection of 275 Kg of 5% persulfate was better than two injections in sequence with 137.5 kg.

In another study, Li *et al.* (2017*)* studied the effect of alkalinity, chloride, and pH on benzene degradation from contaminated groundwater. The results showed that an increase of pH accelerated persulfate decomposition because of the formation of reactive surface hydroxy complexation at high pH, whereas the increase of the alkalinity decreases the rate of persulfate decomposition, consequently, the degradation of benzene. The change in chloride concentration in the groundwater sample had no significant effect on the decomposition of persulfate nor benzene degradation. In a recent study, Liu *et al.* (2020b) studied the performance of biochar activated persulfate on the degradation of bisphenol in contaminated soil. For soil spiked with 31.93 mg kg^{-1} bisphenol, the result pointed out that biochar can effectively activate persulfate to produce activated persulfate and hydroxyl radicals to remove bisphenol from contaminated soil.

3.3. Ozone Treatment

Soil remediation by O_3 is considered one of the most promising technologies among the technologies that can be applied “on-site” or “in situ”. Two methods of O_3 an applied; the first one uses O_3 as an oxidation agent for contaminant decomposition (direct method), whereas the second one uses O_3 to generate $^{\cdot}OH$, which can oxidize the organic contaminants better than O_3 itself (Andaluri and Suri, 2017). Forming $^{\cdot}OH$ by ozone decomposition at pH greater than 6 is formulated to follow the indirect reaction pathway. In soil remediation, many studies have demonstrated the feasibility of using O_3 to degrade pesticides, PCBs, hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) in soil (Andreozzi, 1999; Yu *et al.*, 2007; Pierpoint *et al.*, 2003).

Tamadoni and Qaderi (2019) investigated the removal of phenanthrene, anthracene, and benz(a)anthracene from contaminated soil by ozonation. They found that the removal efficiency of anthracene, phenanthrene, and benz(a)anthracene were 67.87, 85.2, and 45.9%, respectively. Remarkably, the results showed that better removal of PAHs contaminants from soil and groundwater is achieved when the fine-grained soil particle fraction is less and for higher aqueous phase solubility.

Table 1. Recent studies applied conventional chemical oxidation methods for NAPLs remediation

Technology	Contaminate	Experimental Condition	Important results	References
Activation of persulfate with biochar	Bisphenol	pH 7 Biochar dose (0.25-2.0)1 g L^{-1} Persulfate concentration (2-15 mM).	Increasing persulfate and biochar dosage increased the degradation of bisphenol where the higher dosage of persulfate or biochar may decrease bisphenol removal due to the consumption of hydroxyl radicals and sulfate radicals in the spiked soil remediation, The acidification of the soil due to the drop of pH can be mitigated by adding biochar.	(Liu et al., 2020b)
Ozonation	Phenanthrene, anthracene, benz(a)anthracene	Ozone concentration (0.1-5.5 g/h) Contaminants concentrations (7.5 mg/kg and 517.5)	The Removal efficiency of phenanthrene was 67.87%, where the removal efficiency of anthracene and benz(a)anthracene was 85.2% and 45.9%, respectively For ozonation remediation: less fine-grained soil and high-water solubility cantonment are the results in high remediation	(Tamadoni and Qaderi, 2019)
Potassium permanganate	Pentachlorophenol	pH 7 pentachlorophenol initial concentration 50 mg L^{-1} concentration of $KMnO_4$ = 5.6 mM Experiment time 24 h temperature range of 20–22° C	Permanganate oxidation has a high potential for in situ renditions of aromatic organochlorine such as pentachlorophenol.	(Tamadoni and Qaderi, 2019)
Activated persulfate	Trichloroethene	TCE initial concentration (0.26 and 0.361) mg L^{-1} in the first and second per hole, respectively.	The removal efficiency of 100% in the first per hole and 95% in the second per hole One injection of 275 kg of 5% persulfate was better than two injections of 137.5 kg in TCE removal. Persulfate is still active for 14 days in the aquifer	(Chang et al., 2018)
Activated Persulfate	Benzene	Initial concentration 1 mM benzene Chloride concentrations (0- 5) mM pH was adjusted between 8 and 13.	Higher pH enhances remediation throughout the formation of hydroxo complexes, whereas higher alkalinity decreases the persulfate activity by forming an unreactive surface carbonate complex. No effect of Chloride on the persulfate decomposition	(Li et al., 2017)
Permanganate with bioaugmentation.	Petroleum hydrocarbons	TPH concentration (5542 mg/kg). Permanganate dosage (0.5-pore-volume). Treatment time 1 month.	TPH removal efficiency was around 92% through permanganate and bioaugmentation, while 72% removal efficiency was achieved by permanganate alone.	(Chowdhury et al., 2017)
Electrokinetic-enhanced permanganate (EK-PM)	Trichloroethene	Permanganate concentration 30 g/L 25 mA direct current (DC) Experiment time 50 h Initial concentration 771 mg/L	EK-PM system enhanced the delver of permanganate to dense strata layer, which increases the removal efficiency of TCE.	(Chowdhury et al., 2017)
Ozone and peroxide	1,4-dioxane	Ozone dosage (1- 20) mg L^{-1} Peroxide dosage (1, 5, and 10) mg L^{-1} Initial concentration of 1,4-dioxane 100 mg L^{-1}	Low removal efficiency at an acidic condition where high removal efficiency was observed at pH between 8 and 10 Mass transfer of ozone into water is gas flow rate dependent. Therefore, to increase the mass transfer of ozone, the gas flow rate should be increased	(Andaluri and Suri, 2017)

4. Advance chemical oxidation process for NAPL remediation

4.1. Fenton process

Table 2 summarizes the previous works conducted in the remediation of NAPLs by the Fenton process. Among the AOP process, the Fenton process is considered the most popular one in the remediation of NAPLs. Farzadkia *et al.* (2014) studied the effect of the Fenton process to remove total petroleum hydrocarbons (TPH) from oily sludge. Results revealed that at the operating condition: reaction time 1 h, H_2O_2 to Fe(II) molar ratio of 10, H_2O_2 to sample mass ratio of 15, and pH of 5, the removal efficiency of TPH was 36.5%. Xu *et al.* (2018) used a stepwise oxidation process to remove adsorbed THM on soil. After 3 steps of adding H_2O_2 the total TPH removal efficiency was 49.6%, with around 20% increase compared to adding H_2O_2 initially in conventional Fenton oxidation. In another study, Qin *et al.* (2019) conducted batch experiments to investigate the effect of the ferrous ion source in the degradation of long-chain petroleum hydrocarbon from the soil. The results showed that the decomposition rate of petroleum hydrocarbons, ferrous sulfate, and magnetite was the same at H_2O_2 dose of 1.5%, whereas the ability of pyrite to start Fenton like reaction was weaker than ferrous sulfate and magnetite. In another study, Chok *et al.* (2020) investigated the removal of two TPH from the groundwater by Fenton oxidation. The study reported that the Fenton process could remove more than 47% of COD at the operation condition; H_2O_2 (0.1 g/L), Fe (0.01 g/L), pH 6, and reaction time of 120 minutes. Santos *et al.* (2018) used four soil samples to investigate the effect of soil physicochemical properties on gasoline contaminated soil treated by Fenton oxidation process. The results showed that soil samples, such as Red Argisol, Red-Yellow Argisol, and Red Latosol, with high iron content, were more remediable because ion minerals content enable the Fenton process.

Rodríguez *et al.* (2018) used three approaches in the same reactor (microfluidic cells, anodic oxidation with diamond anodes, and an electro-Fenton process). The authors reported that using those systems in the same reactor can increase the removal efficiency of clopyralid from the soil compared to the conventional treatment technologies in terms of high treatment efficiency and short treatment time. In another study, Roohi and Fatehifar (2019) investigated the removal of tert-butyl mercaptan from contaminated soil using bimetallic Fenton treatment that included $Fe^{2+}/Fe^{3+}/Fe^{0}/Cu^{2+}$ in the presence of gasoline. They found that to reach approximately full removal of tertbutyl mercaptan, the optimum conditions should be: initial gasoline concentration (2.5% w/w), $CUSO_4$ (0.12% w/w), H_2O_2 (8.92% w/v), nano-ZVI (0.1194% w/w) and nano-Fe_3O_4 (0.899% w/w). Sun *et al.* (2021) investigated the removal efficiency of 2,3,4,5-tetrachlorobiphenyl from contaminated soil using the heterogenous Fenton process. A high removal rate was obtained (76.3%) after 80 min of reaction at operating condition of montmorillonite supported nanoscale zero-valent iron 29.88 g kg^{-1}, H_2O_2 45.99 g $kg^{-1,}$ and initial pH 3.5. Zhang *et al.* (2015) investigated the efficiency of three-electrode electro-Fenton for groundwater remediation where Rhodamine B was used as a contaminant. Introducing the third electrode increased the H_2O_2 formation to reach around 20.9 ml L^{-1}, yielding a removal efficiency of 97.4%. They conclude that the obtained result is higher than the two-electrode E-Fenton systems without aeration by 5%. Another modified Fenton process was developed by Huang *et al.* (2020) by the reaction between using glucose oxidase and glucose in combination with Fe(II) (GMFs) to in-situ H_2O_2 generation (Figure 4). The developed process was applied to remove TCE from groundwater. Within 8 h, the removal efficiency of TCE reached around 78%.

Table 2. Recent studies using the Fenton process for NAPLs remediation

Technology	Contaminate	Experimental Condition	Main results	References
Heterogenous Fenton process	2,3′,4,5-tetrachlorobiphenyl (PCB67)	Montmorillonite supported nanoscale zero-valent iron concentration 29.88 g kg^{-1}. H_2O_2 concentration 45.99 g kg^{-1}. pH 3.5 Treatment time 80 minutes.	High removal efficiency (76.38%) of 2,3′,4,5-tetrachlorobiphenyl at the investigated condition	(Sun et al., 2021)
Fenton oxidation	Total petroleum hydrocarbon (TPH)	H_2O_2 concentration (0.01-0.1) mg L^{-1} pH range (3-6), Fe(II) concentration (0.01-0.5) mg L^{-1} Fenton oxidation reaction time (30-120) minutes.	COD removal from 5.61% to 47.16%.	(Chok et al., 2020)
Glucose oxidase modified Fenton reactions (GMF)	Trichloroethene (TCE)	Modified Fenton system was formed by the combination of Fe(II) and the reaction between glucose oxidase and glucose.	The removal efficiency of TCE was 78% within 8 h.	(Huang et al., 2020)
Fenton process	Total petroleum hydrocarbons (TPH)	Reaction time 1 h. H_2O_2 mass ratio 15%. pH 5 Molar ratio of H_2O_2 to Fe(II) was 10%.	The low removal efficiency (36.47%) of TPH was attributed to the semi-solid nature of the sample where the hydroxyl radicals were produced in the aqueous solution. Thus, adding water to the sample enhanced the removal efficiency of TPH.	(Santos et al., 2018)
Fenton-like processes	long-chain petroleum hydrocarbons	H_2O_2 dosage (1.5%)	The removal efficiency of the aliphatic C35-C40, C21-C35, and C16-C21 was 25%, 50%, and 70%, respectively. The decomposition rate of petroleum hydrocarbons ferrous sulfate and magnetite was the same at an H_2O_2 dose of 1.5%, whereas the ability of pyrite to start Fenton like reaction was weaker than ferrous sulfate and magnetite	(Qin et al., 2019)
Microfluidic cells coupled with diamond anodes and electro-Fenton process.	Clopyralid	pH 3 Initial concentration of clopyralid 100 mg kg^{-1}	High treatment efficiency in a short time rivaling that the investigating coupled system is a promising technology for soil remediation,	(Rodríguez et al., 2018)
Electro-Fenton (E-Fenton)	Rhodamine B	Current at (-1, -3 and -5) mA. The rhodamine initial concentration (5 mg L^{-1}) Fe(II) ion concentration (0.5 mM). Reaction time 120 minutes.	High removal efficiency of rhodamine (97.4%)	(Zhang et al., 2017)

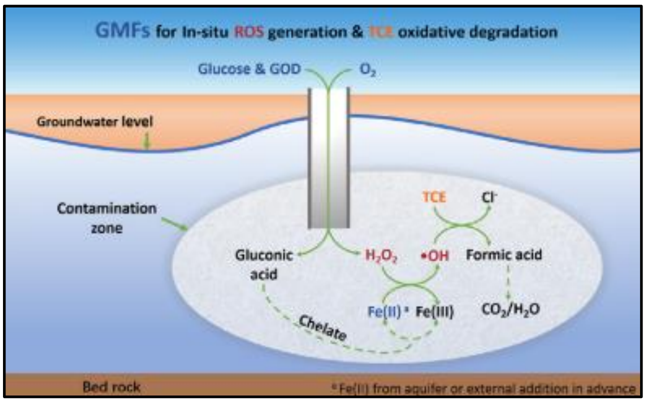

Figure 4. Glucose in combination with Fe(II) (GMFs) remediation technology (Huang *et al.*, 2020).

4.2. Photocatalysis

In a recent study, Satyro *et al.* (2016) studied the performance of TiO_2^- photocatalytic treatment of soil washing effluent. Different artificial sunlight was used to remove Fe, Zn, Cu, and ethylenediamine succinic acid (EDDS). The results showed that, for effluent produced from the soil washing process, TiO_2 based photocatalytic process could remove both heavy metals and organic chelate simultaneously. In addition, using artificial solar light on the photocatalytic process can be efficient. In another study, Wang *et al.* (2016a) investigated the photocatalytic oxidation pathway of diphenylarsinic acid (DPAA) contaminated soil by nano-sized titanium dioxide (TiO_2). They found that soil: water ratio has a greater effect on DPAA removal efficiency than other characteristics. Gunti *et al.* (2015) pointed out that UV and visible radiation can remediate organic compounds (methyl orange and naphthalene) when combined with graphed doped TiO_2 nanostructured photocatalytic materials. Another attempt has been presented by Hsu *et al.* (2019), who synthesized $LaFeO_3$ by sol-gel method and studied the removal of Trichlorethylene (TCE) from groundwater by $LaFeO_3$ photocatalytic oxidation. A 95% removal efficiency of TCE was achieved in an aqueous solution where the operating parameters were $LaFeO_3$ concentration of 2 g L^{-1} and 1 h Xenon lamp illumination.

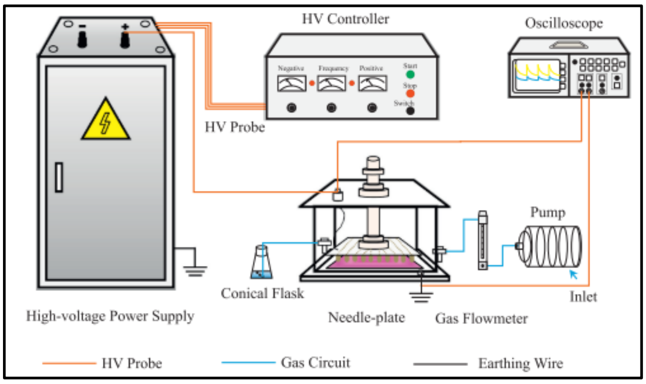

Figure 5. PCD reactor for soil remediation (Zhan *et al.*, 2019).

4.3. Plasma oxidation

Redolfi *et al.* (2010) was the first researcher who used LTP discharges to treat contaminated soil. The kerosene oxidation in the soil matrix was investigated by using a DBD reactor at atmospheric pressure. Results showed that the kerosine removal efficacy reached 90% in the soil matrix. In another study, Mu *et al.* (2016) investigated the influence of treatment time, electrode gap initial contaminated concentration, discharge voltage, gas flow rate, and pH of the soil on the performance of a DBD plasma reactor. The result indicated that the soil pH has a small effect on the removal efficiency of pyrene, whereas the increase of the applied voltage and decrease of electrode gap enhances the removal efficiency. In another study, Wang *et al.* (2015) examined the effect of gas vasculitis, species scavengers, and airflow rate on H_2O_2 formation during the use of a multi-channel pulsed discharge plasma for removal of p-nitrophenol from contaminated soil. The results showed that the formation rate of H_2O_2 in O_2 plasma atmosphere was higher than Ar, N_2, and air atmospheres. In addition, hydroxyl radical's formation was obtained in the O_2 atmosphere case. Zhan *et al.* (2019) used a PCD reactor (Figure 5) to degrade gasoline from soil and fix nitrogen. The results indicated that removal rate was affected by input power, gas flow rate, electrode gap, soil moisture, pH, and initial gasoline concentration. They found that PCD technology was able to remediate gasoline contaminated soil and improve soil nitrogen content and physical characteristics simultaneously.

In another study, Wang *et al.* (2016c) explored the feasibility of using atmospheric pressure DBD to remediation glyphosate-contaminated soil. It was reported that around 93% removal efficiency of polyphosphoric was removed from contaminant soil after 45 min with an energy yield of 0.47 g KW L^{-1}. Table 3 summarizes some representative studies focused on plasma oxidation. Lu *et al.* (2016) studied the degradation of PAHs contaminated soil using a pulsed corona discharge plasma system. The results showed that under optimum conditions (treatment time 40 min, voltage 18 kV, airflow rate 0.8 L/min, and frequency 70 Hz) the removal efficiency was around 70%; this result suggests pulsed corona discharge plasma was a potential method for remediation of PAH-contaminated soil. Furthermore, it was reported that pyrene removal was higher at neutral pH, whereas p-nitrophenol was more degradable at basic soil.

5. Combined chemical oxidation with other mitigation methods for NAPL remediation

Synergetic studies can be characterized as: combination with soil flushing, a combination with biotreatment, and a combination of much chemical oxidation at the same time. Recently, a combination of chemical oxidation with other mitigation methods has received more attention. In this section, an over the review of the recent works in this domain is presented.

Several studies combined chemical oxidation and soil washing; Huguenot *et al.* (2015) proposed a new system to enhance the remediation of hydrocarbon contamination from soil. They use soil washing followed by Electro-Fenton oxidation. First, an ex-situ soil column washing experiment was conducted using Tween 80 as a washing solution. Then, the collected leached from the bottom of the column was treated by Electro-Fenton technology. The result showed that complete mineralization (more than 99%) of the hydrocarbons was observed after 32 h treatment by Electro-Fenton oxidation. In a subsequent study, Seo *et al.* (2015) studied the combination of an enhanced electrokinetic-Fenton process with soil washing to remove TPHs and zinc from polluted soil. The result pointed that the removal of TPHs and zinc enhanced using 10% H_2O_2 in synthetic soil, whereas in a real soil sample, the removal efficacy decreased due to the complexity of real contaminated soil. Subsequently, Popescu *et al.* (2017) evaluated the combination of electrokinetic technology and the Fenton process for the simultaneous soil flushing and degradation of TPH. It was reported that, after 15 and 27 days, the removal efficiency of TPH reached 54.4 and 58.2%, respectively, for an initial concentration of TPHs of 80.4 g kg^{-1}.

Another approach has been developed for the combination of chemical oxidation technology and bioremediation. For example, Liu *et al.* (2020c) developed a combined Electro-Fenton and bioslurry (EF-bioslurry) combined process for remediation of PAHs contaminated soil with an initial concentration of 3605 mg Kg^{-1}. After 24 h treatment by electro-Fenton, the removal efficiency was 92.5%. Remarkably, the removal efficiency increased to 99% after 40 days of bio-slurry treatment.

Table 3: Recent studies used plasma oxidation for NAPLs remediation

Technology	Contaminate	Experimental Condition	Important results	Ref.
Pulse corona discharge (PCD)	Gasoline	Voltage 0-40 kV Room temperature around 25 °C pH 7.2 Gasoline concentration (2000 mg/kg)	Under the optimal condition, the gasoline removal efficiency was 90%; simultaneously, the nitrogen concentration was increased from 0 to 14 ppm.	(Zhan et al., 2019)
Dielectric barrier discharge (DBD) plasma	Pyrene	The initial concentration of pyrene was 100 mg kg^{-1} Peak to peak voltage 31.6, 33.8, and 36.2 kV Reaction time (10, 20, 30, 40, 50 and 60) min	DBD can remove pyrene over a wide range of pH. The removal efficiency was 60% at 36.2 kV peak to peak voltage and 60 min reaction time.	(Mu et al., 2016)
Atmospheric pressure dielectric barrier discharge (DBD)	Glyphosate	Airflow rate 1.5 L min^{-1} Glyphosate initial concentration 200 mg kg^{-1}	Around 93% removal efficiency of polyphosphoric was removed from contaminant soil after 45 min with an energy yield of 0.47 g KW/L The degradation efficiency was enhanced by increasing the discharge voltage.	(Wang et al., 2016c)
Pulsed corona discharge plasma system.	Polycyclic aromatic hydrocarbons (PAHs)/ Phenanthrene (Phe)	Initial concentration 100 mg/kg Pulse frequency 70 Hz, 40 min of discharge treatment Airflow rate 0.8 L/min, Pulse voltage 18 kV, Pulse frequency 70 Hz	The degradation efficiency of Phe approached approximately 70%.	(Lu et al., 2016)
A pulsed discharge plasma (PDP)	P-microphone and Pyrene	pyrene initial concentration 100 mg kg $^{-1}$ P-nitrophene initial concentration 300 mg kg^{-1} Peak voltage 16.5 kV Airflow 1 L min^{-1} Pulse frequency 50 Hz	removal of pyrene was higher at neutral pH, whereas p-nitrophenol was more degradable at basic soil For PDP systems, the most important parameter was pulse discharge time which significantly affects the energy utilization efficiency.	(Wang et al., 2016b)
Pulsed corona discharge plasma	Petroleum hydrocarbons	Contaminant initial concentration 5000 mg kg^{-1} Peak to peak voltage 30 kV Treatment time 60 min Soil moisture 1.44% Pulsed frequency 50 Hz Discharge gap distance 14 cm	Around 76% of the petroleum contamination was removed within 60 min from an initial concentration of 5000 mg kg^{-1} and with an energy efficacy of 0.2 mg kJ^{-1}. Soil with high moisture are favorable to remediation by pulsed corona discharge plasma.	(Li et al., 2016)
A multi-channel pulsed discharge plasma	p-nitrophenol	Gas atmosphere (air, O_2, Ar, and N_2), airflow rate (0, 0.4, 0.8, 1.2) (L/min)	Compare to N_2, Ar, and air, the O_2 plasma atmosphere was more efficient in p-nitrophenol remediation due to the formation of hydroxyl radicals and H_2O_2.	(Wang et al., 2015)

In some cases, more than one chemical oxidation method may use at the same time. For example, Liu *et al.* (2016) studied the combination of catalyzed H_2O_2 and activated persulfate to remediation of ortho-nitro chlorobenzene (o-NCB) contaminated soil. The result indicated that combining both oxidation processes enhanced the degradation of o-NCB in soil compared to using these two methods separately. Cui *et al.* (2017) investigated a novel approach for combining the oxidation process using permanganate and peroxymonosulfate to remediation trichloroethylene and benzene in simulated groundwater. They found that the removal of benzene was related to the activated peroxymonosulfate, where the intermediates competed with trichloroethylene for permanganate.

6. Conclusion

This article presents a review of the late advances on the chemical oxidation technologies for NAPLs contaminated soil remediation. The main findings can be itemized as follows:

- Fenton process has received more attention in the last 10 years due to the following advantages: (1) it can degrade a wide range of contaminants, (2) easy to implement, (3) sub-products are usually harmless or biodegradable. However, the main disadvantages of the conventional Fenton process are the huge amounts of chemicals involved and the requirement to decrease soil pH. In addition, H_2O_2 injection is often a challenge because enzymes and iron oxides can decompose it.
- The application of TiO_2 photocatalyst was largely examined due to its safety, low cost, and high photocatalytic activity (Giahi *et al.*, 2019). However, the main drawback is that photocatalytic degradation only happens in the upper layer of the soil, whereas the efficiency of this technology decreases as it goes deeper into the soil.
- Although plasma oxidation can degrade contaminants in minutes, some active species have short-lived time that could disappear before entering the soil layer. On the other hand, ozonation is efficient in treating soils with low moisture and large pore spaces. Nevertheless, the optimal pH for ozonation oxidation is 3, which hard to achieve in real sites.

Combine chemical oxidation with other remediation technology seems to be the future of soil remediation as the combination process may increase the sustainability of the applied process towards green technology for soil remediation.

7. Recommendations

This review provides readers with a general overview of chemical oxidation for the remediation of NAPLs contaminated soil. With a special address to AOPs, especially the Fenton process and plasma oxidation process. The main recommendations is pointed as fellows:

- More work needs to be done on modified and combination processes. For example, chemical oxidation and biological, especially Fenton process and bioremediation, seems effective because it is environmentally friendly and low cost.
- Using more than one chemical oxidation method appears to be promising for quick and efficient soil remediation. However, the conflict between the various oxidant must be taken into consideration.
- Another promising strategy is the development of new modifications to increase TiO_2 catalysis using sunlight to increase the photo efficiency of the TiO_2 and decrease costs. Future studies can also focus on the chemically modified TiO_2 for the visible activated photocatalysis.
- Concerning plasma oxidation, although the recent studies demonstrate the efficiency of plasma oxidation on NAPLs remediation, more work is needed to upscale this technology to the field scale.

Acknowledgment

The research leading to these results has received funding from the Ministry of Higher Education, Research and Innovation (MoHERI) of the Sultanate of Oman under the Block Funding Program, MoHERI Block Funding Agreement No. MoHERI/BFP/ASU/01/2020.

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