

Review

Activation of Persulfate for Groundwater Remediation: From Bench Studies to Application

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Abstract: Persulfate-based in situ chemical oxidation (ISCO) has been increasingly used for the remediation of contaminated groundwater and soil. In recent years, there have been numerous studies in the literature on all aspects of the activation of persulfate for contaminant removal at the laboratory scale, including the ways and mechanisms for the activation, the pathways of contaminant degradation, the factors associated with the activation performance, the methods characterizing the processes, etc. In contrast, studies in the literature on the practical use of the activated persulfate at the field scale are fewer, and at the same time have not been reviewed in an organized way. This review was initiated to summarize on the current research on the applications of activated persulfate for actual site remediation, and to extract the knowledge necessary for the formation of applicable technologies. The remediation efficiency and mechanism of activated persulfates by heat, alkaline, metal-based, and electrokinetic activated technologies are described. The major factors including pH, the persistence of persulfate, and the radius of influence and soil property during ISCO remediation applications were presented and discussed. Finally, the rebound process and impact towards microbial communities after in-situ chemical oxidation on site application were discussed.

Keywords: persulfate activation; in situ chemical oxidation; degradation of organic pollutants; groundwater remediation



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1. Introduction

A global potable water deficit has been caused by rising soil and groundwater organic contamination [1,2]. Nearly two and a half billion people lack adequate sanitation, and more than a billion live without a potable water supply [3]. Therefore, the effective remediation of organically contaminated soil and groundwater has become a critical issue in need of being addressed. However, due to the persistence of organics, typical physical remediation approaches (e.g., thermal desorption), it is challenging to efficiently remove organic contaminants from soil and groundwater [4].

The in situ chemical oxidation (ISCO) method has become increasingly popular for the remediation of organically contaminated soils and groundwater due to its efficiency and environmental friendliness [5]. When introduced directly into the contaminated source, chemical oxidants convert organic pollutants into harmless chemicals [6]. Permanganate (MnO_4^-) [7], catalyzed H_2O_2 propagations (CHP) [8] and persulfate [9] are widely used in ISCO practices. Hydrogen peroxide (H_2O_2) is unstable and readily decomposed, which translates to very low persistence and higher application costs [10]. Permanganate is stable; however, target organic contaminants are limited to alkenes, benzenes, and their derivatives. Furthermore, manganese dioxide (MnO_2), as a product of the reaction, can reduce the soil permeability and inhibit the transport of oxidants in the subsurface [11]. Recently, persulfate has become an agent oxidant used in ISCO [12]. In contrast to hydrogen peroxide, persulfate has the advantages of relative stability for long distance transport, a low price for commercial products, a high reaction rate, and efficiency [6,13]. Most importantly,

persulfate is effective for recalcitrant compounds for which most other oxidants (such as permanganate) are not, which enables it to degrade a broad range of organic contaminants, such as petroleum hydrocarbons [14,15], chlorinated ethylene [16], chlorinated alkanes [12], dioxane [17,18], methyl tert-butyl ether (MTBE) [19,20], polycyclic aromatic hydrocarbons (PAHs) [21–23], and per- and polyfluoroalkyl substances (PFAS) [24,25].

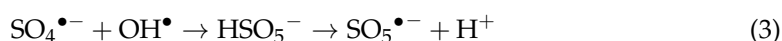
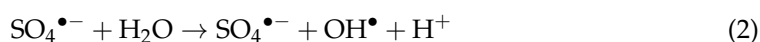
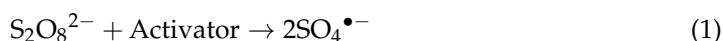
Although persulfate ($S_2O_8^{2-}$) is an oxidant with a redox potential of 2.01 V, its reaction with many refractory contaminants is slow and activation is usually required for optimal performance [26]. In general, activation of persulfate means production of sulfate radical ($SO_4^{\bullet-}$), a much stronger oxidant species with a redox potential of 2.5–3.1 V depending on the solution conditions [27]. The common approaches for activating persulfate are the use of bases [28], UV irradiation [29], heat [29], and transition metal and metal oxides [30,31]. Some novel approaches include the use of phenols [32], quinones [33], naturally occurring metal oxides [34,35], and iron filings [18] as activators.

For the successful application of persulfate to degrade contaminants, some crucial points, such as the activation of persulfate, the dosage of persulfate, the physicochemical properties of soil, and the monitoring of soil and groundwater during and after remediation should be considered. Because the application of this method is mainly through activating persulfate to produce a sulfate radical to degrade pollutants, a mechanistic understanding of the activation of persulfate by different methods, e.g., the use of bases, heat and transition metal and metal oxides, is of great significance. Some parameters, including persulfate dosage, transport distance of persulfate in soil, and pH of groundwater and soil, determine the remediation efficiency. Indeed, there are some review studies about the activation mechanism and application of persulfate and influencing factors at the laboratory scale [4,6,36–44]. To the best of our knowledge, few reviews have focused specifically on applications of persulfate at pilot and field scales [44]. Tsitonaki et al. (2010) discussed the mechanism of persulfate for remediation of contaminated soils and groundwater, activation methods including heat, iron, and alkaline activation, and in-situ oxidation effects [44]. However, some recent achievements in the laboratory and the development of on-site applications have not been included. Recently, the development of the persulfate activation by iron-based materials for the decontamination of water and soil was reviewed by Karim et al. (2021) [5], and the mechanism of the degradation of various pollutants by the activated persulfate have been reviewed in the literature [6,36,41,45]. However, these reviews did not discuss the main factors of the persulfate-based ISCO applications, and the impact after remediation.

Hence, this review aimed to focus on the recent achievements in bench-scale studies and the key parameters in pilot-and field-scale applications of activated persulfate to degrade organic pollutant, in order to provide a theoretical reference for field remediations in the future. The degradation and mechanisms of the persulfates activated by various methods on the pollutants at the laboratory scale were summarized, as well as the application and remediation efficiency of activated persulfates at the pilot scale and field scale were described and summarized. The major influencing factors and parameters of persulfate-based ISCO remediation, and the impact after application were discussed.

2. Activation Mechanism of Persulfate for ISCO Application

Persulfate anion ($S_2O_8^{2-}$) can be converted into reactive radicals, including sulfate radical ($SO_4^{\bullet-}$), peroxymonosulfate radical ($SO_5^{\bullet-}$) and sulfite radical ($SO_3^{\bullet-}$), depending on the activation methods and conditions. The above mechanism can be described as follows [46]:



Common activation methods include alkali treatment [28], metal catalyzed processes (chelated and unchelated, homogeneous and heterogeneous) [47–49], heat [36,50], radiation

(UV, visible light) [51], H₂O₂ [52] and electrical activation [53]. While some of the activation methods, e.g., UV and visible light, have proven to be successful to some degree at the laboratory scale, challenges in field applications remain due to the lack of perfect supporting equipment and feasible pathways [29,52]. Heating and electrokinetic activation are widely used activation technologies in field practices for the temperature of soil and groundwater to be controlled and monitored [54–56]. Alkaline- and metal-based materials were also widely used to activate persulfate in field applications because they can directly be injected into the polluted designation together with persulfate [57–59].

2.1. Heat Activation

The activation of persulfate by heating can be described as Equation (4) [36]. As a result of heat absorption, sulfate radicals (SO₄•[−]) can be generated by the breakdown of sulfate bonds in persulfate [45]. The energies for heat activation under acidic, neutral, and basic conditions are in the range of 100–116 kJ/mol, 119–129 kJ/mol, and 134–139 kJ/mol, respectively [60].



Extensive bench-scale studies have reported that heat activation significantly enhanced the degradation of the organic pollutants by persulfate, with a considerable removal rate (Table 1). Zhao et al. (2013) studied the degradation of polycyclic aromatic hydrocarbons (PAHs) using persulfate activated by heat, alkaline, and iron activations [21]. The results showed that among the three activation methods tested the heat activation was the best and the removal rate of PAHs reached 99.1% at a temperature of 60 degrees C. According to Gu et al. (2011) [61], only 7.6% of TCE was degraded after 10 h of reaction at 20 degrees C. When the temperature was raised from 30 degrees C (31.6%; 10 h) to 50 degrees C (100%; 2 h), TCE degradation was significantly accelerated and TCE was totally removed after two hours. This suggests that the increase of temperature can significantly enhance TCE removal and shorten the remediation time. While extreme temperature speeds up the activation of persulfate, it reduces the degradation efficiency of contamination by persulfate [24]. This has been demonstrated in the study of Yu-Chi Lee (2009) [24], where it was reported that the decomposition rate of perfluorooctanoic acid (PFOA) was 99.3% at a temperature of 90 degrees C, while it decreased to 94.1 at a temperature of 130 degrees C [24]. This is because extreme temperatures lead to the formation of significant amounts of radical oxidants that are released rapidly to consume most of the remaining persulfate, thus causing a lower degradation efficiency. To prevent excessive consumption of persulfate at the injection stage, excessive high temperatures should not be adopted in field practices.

In addition, the optimum temperature that provided the best degradation efficiency appears to differ between pollutants. For instance, Bisphenol A was totally degraded by persulfate at 30 degrees C [62], PAHs were completely degraded by persulfate at 40 degrees C [21] and PFOA was completely degraded by persulfate at the temperature of 70 degrees C [24]. Therefore, the optimal temperature should be set according to the characteristics of pollutants when heat-activated persulfate is applied to the actual site remediation. For some pollutants, temperature in the field is difficult to increase to the optimum value, it is necessary to use a combination of other activation methods to achieve a considerable remediation.

Table 1. Bench scale and laboratory studies with heat-activated persulfate.

Target Contaminants	Reaction Conditions			Removal Efficiency (%)	Ref.
	Persulfate Conc.	Reaction Duration (d)	Temperature (°C)		
PAHs	0.5 mmol L ⁻¹	3	40	87	[21]
			50	96	
			60	99	
TCE	20 mmol L ⁻¹	1	20	7.6	[61]
			30	31.6	
			40	100	
			50	100	
TCE	15 mmol L ⁻¹	32	20	100	[9]
		0.12	40	100	
		0.35	50	100	
		0.013	60	100	
PCE	15 mmol L ⁻¹	0.063	50	92	[63]
TPHs	1000 mmol L ⁻¹	2	55	72.64	[64]
HCHs	10 mmol L ⁻¹	9	55	83	[65]
Chlorinated Solvents	100 mmol L ⁻¹	3	50	79.5	[66]
BPA	8 mmol L ⁻¹	0.013	30	98.5	[62]
DDTs	100 mmol L ⁻¹	7	50	92–94	[67]

Note: PAHs—Polycyclic Aromatic Hydrocarbons; TCE—Trichloroethylene; PCE—Perchloroethylene; TPHs—Total petroleum hydrocarbon; HCHs—Hexachlorocyclohexane; BPA—bisphenol A; DDTs—Dichlorodiphenyltrichloroethane.

2.2. Alkaline Activation

Persulfate is slowly activated under acidic and weak alkaline conditions, while it is rapidly activated under strong alkaline conditions [68]. The reaction mechanism of base activation can be described as Equations (5)–(8). The sulfate radical ($\text{SO}_4^{\cdot-}$), hydroxyl radical ($\text{OH}^{\cdot}$) and superoxide radical ($\text{O}_2^{\cdot-}$) are generated during base activation. $\text{SO}_4^{\cdot-}$ can directly react with OH^- and H_2O to produce $\text{OH}^{\cdot}$, which results in a large amount of $\text{OH}^{\cdot}$ in the system at a pH higher than 12 [6]. $\text{O}_2^{\cdot-}$ is quickly scavenged by $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ [28], which is described in Equations (9) and (10), respectively.

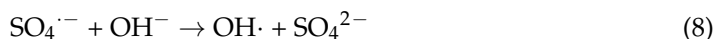
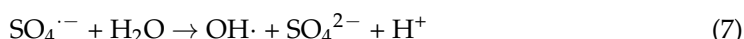
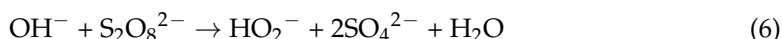
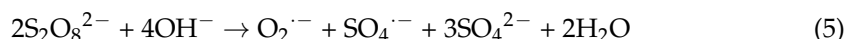


Table 2 summarizes various studies of the use of alkali-activated persulfate to degrade organic contaminants. Zhao et al. (2013) reported that the base-activated persulfate showed a good performance for remediation of the PAH-contaminated soil. When the initial pH was raised from 10 to 12, the removal efficiency of PAHs increased from 55% to 65% [21]. García-Cervilla (2020) reported that the alkali can not only promote the degradation of HCHs by activating persulfate, but also directly lead to the rapid dehydrochlorination of HCHs and HeptaCHs, which are converted into trichlorobenzenes (TCBs) and tetrachlorobenzenes (TetraCBs), respectively [57]. After 21 days of treatment, the chlorinated organic compounds (COCs) conversion reached about 96% and 70% in two different soil fractions ($2\text{ mm} < \text{dp} < 0.25\text{ mm}$, $\text{dp} < 0.25\text{ mm}$) when using PS and NaOH concentrations of 400 mmol L^{-1} [57]. Great degradation efficiency were also observed when alkaline-activated persulfate was used for 4-bromo-2-chlorophenol (BCP) [13] and TPH [58].

Several studies in the literature showed that an increase of the ratio of base to persulfate increased the degradation of the pollutants in the soil [57–59]. However, due to the natural buffering capacity of the water and soil as well as the sulfuric acid generated from persulfate reactions, high base conditions require a large amount of alkali to be injected in field practices [41]. Furman (2011) demonstrated that the most proper molar ratio of alkaline to persulfate may be 2:1 when alkaline-activated persulfate is used [28,34]. Moreover, the elevated base levels may change the soil dispersion, resulting in a decrease in remediation efficiency [34,69]. Therefore, base activation is often coupled with other activation methods, which can significantly enhance the remediation of organic contaminated soil. Lominchar (2018) used zerovalent iron (nZVI) and H₂O₂ combined with alkaline to activate persulfate and had a considerable removal efficiency of phenol [59]. Similar trend was observed when alkaline was coupled with heat, Fe²⁺ and ultrasonic activation [70]. Only 30.8% of BDE was degraded by persulfate at ambient temperature (25 °C), while 46.6% of BDE was removed when the temperature was raised to 40 °C. Alkaline activation with the addition of Fe²⁺ and with the assistance of an ultrasonic application also enhanced the degradation of BDE, with removal efficiencies of 51.5% and 49.2%, respectively [70]. When coupled with other technologies to activate persulfate, the role of the alkaline environment in the degradation process is altered in the system. Huang et al. (2022) combined alkaline with heat-activated persulfate to degrade TCA and TCE, and demonstrated that the main role of alkaline was to hydrolyze the chlorinate alkanes rather than activate the persulfate in a base-heat combined activation system [71].

Table 2. Bench scale and laboratory studies with alkaline-activated persulfate.

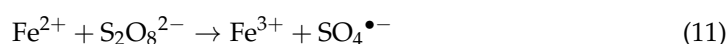
Target Contaminants	Reaction Conditions				Removal Efficiency (%)	Ref.
	Persulfate Conc.	Reaction Duration (d)	pH	Type of Base		
PAHs	0.5 mmol/L	3	10 11 12	NaOH	55 62 65	[21]
HCHs and HeptaCHs	100–400 mmol/L	21	Above 12	NaOH	HCHs -90 HeptaCHs -70	[57]
TPHs	420 mmol/L	56	12	NaOH	98	[58]
BCP	0.21 mol/L	3	>10	NaOH	97	[13]
Phenol	210/420 mmol/L	7	12	NaOH	100	[59]
BDE	0.2 mol/L	0.25	12	NaOH	30.9	[70]
			With 55 °C	NaOH	46.6	
			With Fe ²⁺	NaOH	51.5	
			With ultrasonic	NaOH	49.2	
TCA and TCE	10–75 mmol/L	2	12 with 50 °C	NaOH	100	[71]

Note: PAHs—Polycyclic Aromatic Hydrocarbons; TPHs—Total petroleum hydrocarbon; BDE—brominated diphenyl ethers; HCHs—Hexachlorocyclohexane; BCP—Bromocresol purple; TCE—Trichloroethylene; TCA—Trichloroanisole.

2.3. Iron Activation

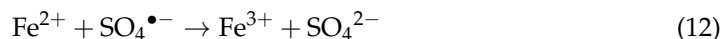
The transition metals and metal–chelate complexes can activate the persulfate at ambient temperatures and neutral pH without the need for additional additives or energy to regulate pH or temperature [5]. Fe²⁺, Ag⁺, and Cu²⁺ metal ions have all been reported to significantly activate persulfate [31,72]. Fe²⁺ is widely used for persulfate-based ISCO, which is in contrast to Ag⁺ and Cu²⁺ of high toxicity and high cost [73].

The mechanism of Fe²⁺ activate persulfate involves a one-electron transfer in which Fe²⁺ provides an electron to persulfate anion, as shown in Equation (11) [74,75].



Iron-activated persulfate has been shown to be suitable for the degradation of most refractory pollutants including PAHs [74], TCE [76], TPHs [75], HCHs [77] and PCBs [78] etc.

(Table 3). It was shown that the removal efficiency of organic pollutants increased first and then decreased with the increase the concentration of Fe^{2+} [31,73]. This is because the low concentration of Fe^{2+} would cause inefficient utilization of persulfate, while a high concentration of Fe^{2+} would lead to consumption of sulfate radicals by Fe^{2+} (Equation (12)) [40].



To minimize the scavenging of $\text{SO}_4^{\bullet-}$ by Fe^{2+} , the molar ratio of Fe^{2+} to persulfate must be optimized. Matzek and Carter (2016) and Zhu et al. (2019) reported considerable contaminants degradation when the mole ratio of Fe^{2+} to persulfate was 1:1 and 1:2 [41,79]. In addition, multiple additions of Fe^{2+} is another option. Several studies reported that multiple additions of Fe^{2+} can maintain the continuous generation of $\text{SO}_4^{\bullet-}$ and has a higher pollutant degradation efficiency than a one-time addition of Fe^{2+} [76,80,81]. Liang et al. (2004) proved that the TCE removal efficiency reached 92% with two sequential additions of Fe^{2+} , which was higher than that of one addition of the equivalent dose of Fe^{2+} (47%). Jiang et al. (2013) obtained a similar trend when multiple additions of Fe^{2+} were applied to degrade bisphenol A.

Due to the rapid reaction between metal ions and persulfate, the homogenous activation method is unable to achieve in situ and sustainable activation in the field practice [82,83]. In addition, the addition of metal ions will introduce anions, which will involve in the homogenous reaction between the persulfate and metal ions, and thus affect the activation effect [84]. In contrast, the metal-based heterogeneous reaction system has the advantage of long-lasting activity for persulfate activation, which is associated with the solid form of the activators [38]. Natural minerals including goethite, hematite, pyrite, ilmenite, ferrihydrite, lepidocrocite and magnetite, have been shown to activate persulfate to degrade pollutants [85–87]. While the iron-contained minerals were proven to significantly activate persulfate, the powder form of those minerals are basically large, thus caused clogging when injected into the subsurface [40,88]. In addition, the mineral content in some contaminated areas is too low to activate persulfates effectively to degrade contaminants [85]. Engineered nanoparticles are widely studied, such as the nanoparticles of zerovalent iron (nZVI), Fe_3O_4 (n Fe_3O_4), and ZVI based bimetal materials [89–91]. Among these engineered nanoparticles, nZVI seems to be more appropriate in in situ oxidation applications for its low cost and high activation efficiency [77]. Kim et al. (2018) used nZVI particles as the activator for persulfate to achieve a complete removal of phenol [92]. Yuan (2021) also applied nZVI-activated persulfate to degrade TBBPA. Laboratory data showed under the set condition (25 mM persulfate, pH 5.5, and 3 g/kg nZVI) that the degradation efficiency of TBBPA (5 mg/kg) was 78.32% after 12 h [93]. The reaction in a persulfate/nZVI system involved two stages (fast reaction stage and slow reaction stage) [92]. In the early step, $\text{Fe}^0(\text{s})$ was quickly consumed, and the aqueous Fe^{2+} activated persulfate to generate large amounts of sulfate radicals. When controlled by Fe catalyzed activation in the presence of aqueous Fe^{3+} and iron (oxyhydr)oxides in the nZVI shells, the second stage moved significantly more slowly than the first stage [92]. Although there are few studies in the literature reporting the successful application of nZVI in site remediations yet, they have broad application prospects in future site remediation based on their rheological properties and effective persulfate activation characteristics.

Table 3. Bench scale and laboratory studies with iron-activated persulfate.

Target Contaminants	Reaction Conditions					Removal Rate (%)	Ref.
	Persulfate Conc.	Reaction Times (d)	Iron-Selected	pH	Temperature (°C)		
PAHs	1.85 mol/kg soil	1	Fe ²⁺	7.2	25 ± 1	65	[94]
TCE	0.009 mol/kg soil	1	Fe ²⁺	4.2	20	100	[76]
TPHs	0.021 mol/kg soil	30	Fe ²⁺	5.63	25 ± 1	40	[15]
HCHs	0.3 mol/kg soil	1	Fe ²⁺	2	25 ± 1	89	[95]
PCBs	1 mol/L	3	Fe ²⁺	6.61	25	81	[78]
Atrazine	50 mmol/L	0.42	Fe ²⁺	3.0	23	80	[96]
PAHs	200 mmol/L	25	Fe ³⁺ /nZVI	7.5	25	81.42	[97]
PHE	12 mmol/L	2	nZVI	2.8	25	76	[92]
TBBPA	25 mmol/L	0.5	nZVI	5.5	25	78.3	[93]
PAHs	1.2	7	nano-Fe ₃ O ₄	1.3 ± 0.2	24 ± 2	63	[98]

Note: PAHs—Polycyclic Aromatic Hydrocarbons; TCE—Trichloroethylene; TPHs—Total petroleum hydrocarbon; HCHs—Hexachlorocyclohexane; PCBs—Polychlorinated biphenyls; PHE—Phenanthrene; TBBPA—Tetrabromobisphenol A.

2.4. Electrical Activation

The electrochemical activation of persulfate is a novel green technology. By applying a positive current using an iron anode, Fe²⁺ is continuously produced by anodic corrosion (Equation (13)). The regeneration of Fe²⁺ from Fe³⁺ can be enhanced by the reduction of Fe³⁺ on the cathode (Equation (14)), which further improves the utilization of Fe²⁺ [99,100]. As the production of Fe²⁺ is proportional to the current based on Faraday law, in situ manipulation (i.e., increasing or inhibiting) of persulfate reactivity is theoretically made feasible by adjusting the current [101]. In addition, persulfate was injected to a subsurface matrix such as clay. The transport distance may be extremely low due to a low hydraulic conductivity [102]. Electrical activation seems to be a promising technology in in situ persulfate-based applications when facing such circumstances, since persulfate can be delivered under an electrical current [53].



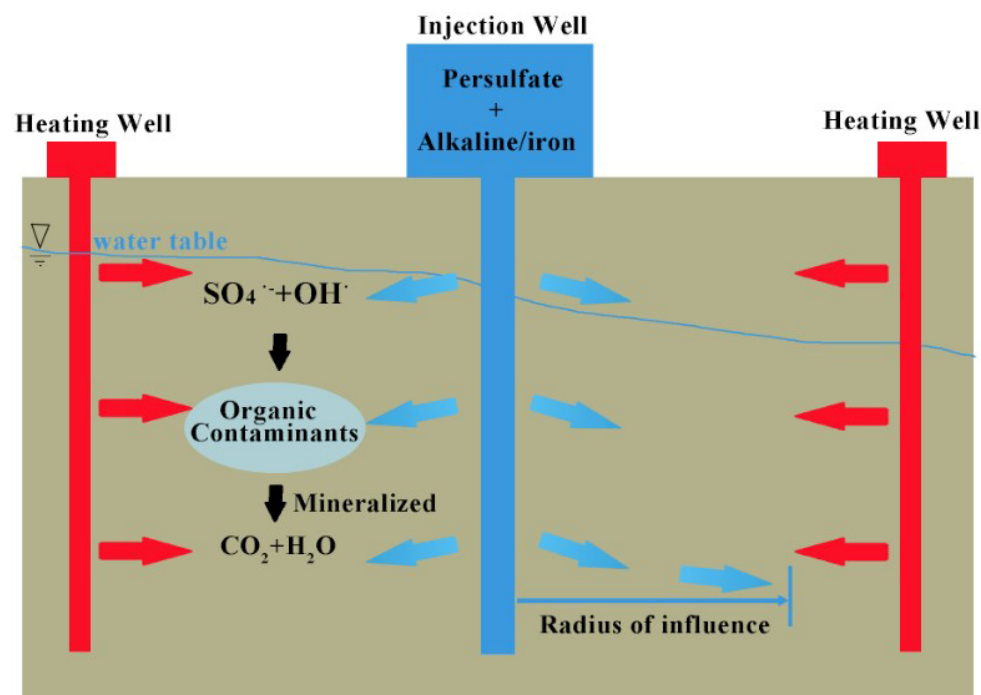
For this technology, which was only developed a few years ago, a handful of studies in the literature reported the applications in groundwater remediation (Table 4). Isosaari P et al. (2007) used electro-activated persulfate to degrade PAHs, which was further compartmented with electrokinetic and persulfate oxidation systems [103]. The results showed that the removal efficiency of PAHs in the electro-activated persulfate system was 35%, which was higher than that in electrokinetic (24%) and persulfate oxidation (12%) systems [103]. Yang et al. (2015) studied the in situ persulfate oxidation process of TCE by electrical activation, which significantly improved the transfer of injected persulfate from the anode reservoir to the cathode reservoir via the soil compartment resulting in a good remediation efficiency [102]. Electrical activated persulfate coupled with NaNO₃ to flush the cathode and attain a higher conductivity, achieved a good removal efficiency for BDE (88.6% was removed) [104] and PHE (78.8% was removed) [54]. When electro-activation is used with persulfate, the location of the injection wells should be considered properly as the transport rates of persulfate ions in the subsurface are different, and mainly dominated by electroosmosis and electromigration. Fan et al. (2014) pointed out that the preferred location for persulfate injection may be the cathode reservoir after comparing the transport distance of persulfate and degradation of the contaminant (PCB) under different persulfate injection locations including anode, cathode and both electrodes [101].

Table 4. Bench-scale and laboratory studies with electrically activated persulfate.

Target Contaminants	Reaction Conditions					Removal Efficiency (%)	Ref.
	Persulfate Conc.	Reaction Duration (d)	Coupling Method	pH	Temperature (°C)		
PAHs	223 mmol/L	56		6.5	20	35	[103]
TCE	1 g/L	14		7.23	25	92.4	[105]
	1 g/L	14	nano- Fe ₃ O ₄	7.23	25	97.4	
PCBs	30% by weight	10		4.9	23	77.9	[106]
Dimethyl phthalate	3.14 g/L	28	nano- Fe ₃ O ₄	7.7	20	97.92	[102]
PCBs	20% by weight	15	pH = 12	12	-	40.5	[107]
BDE-209 and Cu	0.1 mol/L	10	Coupled with NaNO ₃	5.1	-	88.6	[104]
PHE	10%	25	0.01 mol/L NaNO ₃	7.99	15	78.8%	[54]

3. Applications and Development of Persulfate in ISCO

In clean-up activities at numerous contaminated sites over the past 20 years, persulfate activated by various techniques has been employed with a satisfactory removal result. To improve the remediation efficiency, the multiple activation methods discussed above are usually combined (Table 5). The application mechanism of ISCO using persulfate is shown in Figure 1.

**Figure 1.** The application mechanism of ISCO using persulfate.

Because only the activator and persulfate need to be injected into the underground through injection well, chelated iron activation and alkaline activation are currently the two most widely employed technologies for persulfate-based ISCO applications. The base is often sodium hydroxide (NaOH) or potassium hydroxide (KOH), and typically very high concentrations are needed to obtain good remediation results at the field application [69]. A considerable removal efficiency was obtained in several site remediation cases with alkaline activations. After three months of persulfate and hydroxide injection in the vadose zone and treatment region, TPH in existing wells were completely depleted, and TPH mass was reduced by 84% [108]. Over 90% of ethylbenzene and 87% of benzene were removed from PAHs and BTEX-contaminated areas in Brownfield, New York, following the application of

alkaline activation [109]. To obtain a satisfactory remediation performance from the alkaline activation, the pH needs to be raised to more than 12. However, the pH in actual soil cannot reach the desired value due to the strong buffering capacity of the soil. For example, the pH was raised to 9.1 after 6.5 weeks injection and then decreased to 6.8 in 2 months [110]. It is a feasible way to maintain the alkaline conditions of the site by constructing a waterproof curtain to prevent the dilution of groundwater.

The use of thermally activated persulfate to degrade organic pollutants has good application prospects for site remediation. Depending on the features of the remediation site, different heating techniques are applied, such as steam-enhanced heating, electrical resistance heating, and thermal conductive heating [44]. To reduce the high cost of heating, the temperature of approximately 40 degrees C was recommended in the field [111]. Electro-activated remediation has only recently been used in site remediation, and most of the cases were on a pilot scale. Nicholas A (2020) applied electrokinetic-activated persulfate for chlorinated solvents remediation in a clay site [56]. It was reported that the subsurface temperatures along the transect were higher than the 35–40 degree C target range for persulfate activation. Substantial decreases (over 80%) in total CVOCs were observed at the monitoring well with the persulfate breakthrough. Another way to add heat is by adding CaO, which can react with H₂O to release a large amount of heat, and increases the site temperature. Kabir et al. (2004) used CaO with persulfate to remediate BTEX and naphthalene in a site application and 93% of the contaminant was removed [112].

In practical site remediation projects, persulfate is often activated by a combination of multiple methods rather than a single method. Thompson (2006) used the iron-heat-peroxide combined methods to activate persulfate and successfully reduced the contaminants concentration below the risk-based target (86–96% removal) [113]. Hydrogen peroxide and Fe²⁺ were also used in combination when persulfate was applied to remediate TCE [114]. The persulfate-based ISCO technology can be enhanced by the use of surfactants, which increase the solubility of hydrophobic contaminants and thus better enable them to come into contact with free radicals [115]. At a former truck service facility site in New Jersey, surfactant-enhanced ISCO technology was used with a low persulfate to contaminants ratio (4.2:1) to clean up the extractable petroleum hydrocarbon (EPH). After seven days, the average concentration of the EPH in the soil was decreased from 5075 mg/kg to 3098 mg/kg [109].

Table 5. Pilot scale and site applications with persulfate.

Target Contaminates	Activation Method	Persulfate Dosage	Duration	Removal Efficiency (%)	pH	Temperature (°C)	Ref.
PAHs, BTEX	Surfactant-alkaline	Na ₂ S ₂ O ₈ -15,200 kg (25–50 g/L) NaOH-61,950 kg (20 g/L) VerSOL-329,545 kg (5 g/L)	5 months	90.3	-	-	[108]
PAHs, BTEX, TPH	hydrogen peroxide	Na ₂ S ₂ O ₈ -50–100 g/L H ₂ O ₂ -0.5–4% (wt)	6.5 weeks	TPH-97 PAHs-73 DNAPL-950 L	-	-	[116]
Cl-ethenes, dichloro-methane	Iron, peroxide, heat	Na ₂ S ₂ O ₈ -48,500 L (10.5%wt) Iron-13,750 L (0.07%wt)		86–96	-	45	[113]
TPHs, VOCs & SVOCs	Surfactant-alkaline	VeruSol-2021 L Na ₂ S ₂ O ₈ -17,413 L NaOH-17,034 L	7 days	TPH-92	-	-	[109]

Table 5. Cont.

Target Contaminates	Activation Method	Persulfate Dosage	Duration	Removal Efficiency (%)	pH	Temperature (°C)	Ref.
TCE, TCA, DCE	Alkaline (KOH), Fe^{2+}	$\text{Na}_2\text{S}_2\text{O}_8$ -4221.9 L (10%wt)	4 months	100	-	-	[114]
Diesel & Gasoline LNAPL	Peroxide	-	-	99.33	-	-	[117]
PAHs, BTEX	Surfactant-iron	-	70 days	BTEX -92 VOCs -91	-	-	[118]
BTEX, naphthalene	CaO	-	-	42–93	-	-	[112]
TPH	none	$\text{Na}_2\text{S}_2\text{O}_8$ -20 g/L	120 days	98	-	-	[119]
TCA, DCE, DCA	electrokinetically	40 g/L	208 days	80	-	5–40	[56]
PCE, TCE, BTEX	Alkaline (NaOH)	$\text{Na}_2\text{S}_2\text{O}_8$ -26% (wt) NaOH-25% (wt) $\text{Na}_2\text{S}_2\text{O}_8$:NaOH = 2:1	12 weeks	over 90	4.9–9.1	-	[110]
TCE		5500 L of 5% persulfate solution	75 days	95–100	6.70–7.22	30.4–31.6	[120]
TPHs, PAHs	CaO	$\text{Na}_2\text{S}_2\text{O}_8$ -249.76 t CaO-404.6 t	-	60–99%	1.9–9.3	-	[121]

4. Factors Affecting the Application of Persulfate in ISCO

For practical field applications, many factors affect the efficiency of persulfate in degrading target organic pollutants. As is shown in Figure 2, the main influencing factors to be considered in field applications of persulfate are the dosage of persulfate, the persistence and the radius of influence of persulfate, and the physicochemical properties of soil, pH and dissolved ions in groundwater (Figure 2).

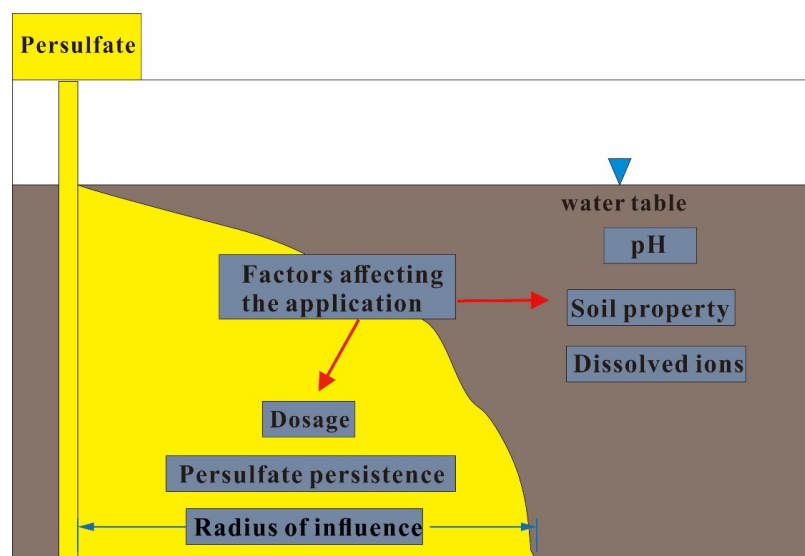


Figure 2. Factors affecting the application of persulfate in ISCO.

4.1. pH

The reaction of persulfate with pollutants in soil and groundwater is closely related to pH. The pH of the solution is impacted by persulfate reactions, which makes it difficult to quantify. Sulfate, a very weak conjugate base, is the main inorganic result of persulfate reactions. As a result, the pH drops when persulfate reactions produce protons, as has been reported in many persulfate systems [73,122,123]. Wu et al. (2020) reported that, as a result of proton generation, persulfate caused the pH to drop to acidic levels (3–4) [123]. A similar

result was observed by Waisner (2008), wherein pH decreased from 7 to roughly 2 (except alkaline activation) in unbuffered treatment systems [122]. The pH variations observed in the field were not as significant as those in the laboratory research. Sperry et al. (2002) observed a drop in pH from 5.7 to 5.3 in monitoring wells [124]. Results obtained from Yu-Chen Chang (2018) showed that when the persulfate was injected, the pH was firstly decreased from 7.0 to 6.2, but recovered to 7 in the next few days and the groundwater in each injection well remained at a near-neutral pH (6.70–7.22) [120].

4.2. Persulfate Dosage

The dosage of persulfate is an important parameter affecting the effectiveness of a site remediation. A low dosage of persulfate may not achieve the intended remediation purpose, while an excessive dosage will not only result in higher remediation costs, but also cause damage to groundwater and soil [4,39]. In laboratory-scale studies, it has been proven that the higher the concentration of persulfate, the more effective it is in degrading the contaminants [36,55,96,125–127]. Due to the diffusion of persulfate in groundwater and the complex contaminants in actual spiked sites, however, the concentration of persulfate used in the laboratory may not be properly matched when applied to site applications. For instance, the concentrations of persulfate used in the laboratory typically ranged from 10 mmol/L to 100 mmol/L and can obtain a promising removal efficiency, whereas the concentrations of persulfate used in field applications need to reach 1000 mmol/L to meet the same removal efficiency [120]. For this reason, bench-scale studies or pilot-scale studies were needed using the site contaminated soils to evaluate the optimal persulfate concentration prior to field-scale site remediation. However, due to the different types of target pollutants and the varying severity of contamination at each site, the dosage of persulfate varies greatly from sites to sites. Few studies have unified the large amount of data and arrived at a reasonable range of values for the dosage of persulfate. Therefore, more in-depth research is still needed in this area.

4.3. Persulfate Persistence

The persistence of the persulfate in porous media after injection into the subsurface is crucial. The persistence of persulfate is frequently determined by tracking the decomposition of persulfate at a specific region over time [26]. In a practical remediation project, the decline of groundwater quality parameters (e.g., ORP) are also sometimes employed as indirect indicators of persulfate persistence [128].

The persistence of persulfate varies greatly in subsurface and is affected by the activation methods. Sra et al. (2010) evaluated the stability of the inactivated persulfate in the presence of multiple aquifer solids and the result showed that the decomposition of inactivated persulfate remained sluggish in all aquifer, with half-lives ranging from 2 to 600 d [129]. The stability of persulfate will rise with either an increase in ionic strength or the concentration of persulfate per unit mass of aquifer solids [119]. Johnson (2008) studied the persulfate persistence under thermal-activated conditions, and observed that the thermolysis half-life of persulfate was over 143.6 days, which was reduced to 4.1 days at 50 °C and 0.36 day at 70 °C [26]. Sra (2014) further compared the stability of persulfate under peroxide activation and alkaline activation methods [130]. A rapid decrease in persulfate concentrations was observed at peroxide activation and the consumption rate of persulfate (k_{obs}) was 100 times higher than inactivated persulfate. In contrast, alkaline activation had a much smaller effect on the stability of persulfate since k_{obs} was only a quarter times higher than inactivated persulfate [130].

For site applications, several pilot and field tests of persulfate persistence were also employed. For persulfate under the alkaline activation, the concentration of persulfate was reduced from 28 g/L to 2 g/L after 40 days [108]. Another report demonstrated that the persulfate can be sustained for nearly one week when heat was applied as an activator [118]. Yu-Chen Chang (2017) demonstrated that even without activation, the persulfate was almost completely depleted after 14 days of injection [120]. In comparison to the outcomes of

laboratory-scale investigations, the persistence of persulfate in practical applications is significantly lower. The main reason is probably due to the groundwater movement and the substantial consumption by soil organic matter in the aquifer sediment.

4.4. Radius of Influence of Persulfate

The radius of influence (ROI) of persulfate is significantly related to the soil permeability and transport ability of persulfate in the soil, which affects the transport length of the persulfate around the injection well, and thus determines the placement of injection wells. In laboratory studies, ROI of persulfate is mainly evaluated from the breakthrough curves of persulfate in the flow field column. Even more, the convective and dispersion coefficients can be also obtained and used to calculate the ROI. In practical remediation sites, ROI is usually calculated from groundwater persulfate concentrations in observation wells constructed at different distances from the injection well in different directions.

The main processes associated with persulfate transport include advection and diffusion. Several studies in the literature have tested the diffusion process of persulfate in column experiments. One-dimensional column experiments combined with tracer tests after persulfate injection were performed in a relatively high hydraulic conductivity medium by Favero (2016) and the longitudinal dispersity ($\alpha_L = 2.431 \pm 0.002$ cm) and retardation factor ($R = 1.10$) were obtained [131]. Merker et al. (2010) tested the persulfate transportability in two low-permeability soils (kaolin and Palouse loess). The results showed that persulfate diffused into both soil types under each treatment condition and the transport distance of persulfate in the kaolin (4 cm after 82 days) was relatively shorter than that in the Palouse loess (12 cm after 70 days). In addition, the higher persulfate concentrations and the longer transport time enhanced the persulfate diffusion process [132]. Persulfate diffusion can be enhanced by electrokinetic delivery [133]. The longest delivery distance reached 10 cm after 10 days when electrokinetic delivery was coupled with alkaline activation [133].

ROI of persulfate in practical field applications can be calculated by measuring persulfate concentrations in monitoring wells placed in various directions at the injection site. The transport length of persulfate was estimated by Tsitonaki et al. (2010) and ranged from 0.1 m to 23 m, however very little data were used, even without mentioning the kind of soil media [44]. Chang et al. (2017) estimated the ROI of persulfate was 3.6 m to 4.5 m in a loamy sand remediation site wherein the groundwater velocity was 0.5 m per day [120]. Sutton et al. (2014) reported that a slight rise of persulfate was observed in downstream monitor wells which was 4.8 m far from the injection well [134]. Krembs et al. (2010) reviewed 29 ISCO cases and concluded the median value of the observed ROI was 7.62 m and the design ROI was 4.27 m, which indicated that the spread of oxidants in the soil was wider than anticipated [128]. Groundwater quality such as ORP, DO, temperature, and conductivity are sometimes employed as indirect indicators of oxidant ROI. After the oxidant has fully reacted, these parameter values can spike in groundwater, but the residual effects of the oxidant can still be determined, resulting in ROI false positives [128]. The hydraulic conductivity (K) profile can vary by an order of magnitude over brief vertical sections when measured across screened intervals in groundwater wells [135]. Under these circumstances, an ROI artifact and an excessive amount of oxidant may be delivered into high K layers [128]. For a more precise evaluation of oxidant transport and ROI, injection and monitoring well screens that are representative of discrete vertical intervals would be helpful in diagnosing this condition.

4.5. Soil Property

The capacity to distribute and use oxidants in the subsurface depends heavily on how persulfate interacts with a porous medium. The main factors influencing the effect on the degradation by persulfate are soil texture, minerals, and soil organic matter (SOM) content.

The soil texture not only affects the transport of persulfate but also can affect the degradation of contaminants. Crimi and Taylor (2007) conducted alkaline, hydrogen peroxide, and chelated iron activation methods and evaluate the degradation efficiency in

a variety of five porous media [125]. They found that the efficiency of persulfate activated by different methods differed in each porous medium, indicating that the characteristics of the porous media affect treatment effectiveness [125]. Yeliz and Reddy (2012) also reported that the PCB can be better degraded in kaolin, while the degradation was insignificantly in glacial till when electro-activated persulfate was applied [106]. The final pH of these two soils was different after remediation. The values of the final pH were around 1 in kaolin but were 7 in glacial till. The low pH also indicated the high consumption of persulfate and better degradation of PCB in kaolin. However, the mechanism of different types of soils impacting the oxidation and the role that soil texture plays in the oxidation process still have not been studied in those studies and need to be further revealed.

The SOM may have a negative impact on persulfate oxidation for its ability to compete with soil pollutants, resulting in a significant consumption of persulfate [42,136]. Even more, according to electron paramagnetic resonance (EPR) spectroscopy analysis, Fang (2018) demonstrated that sulfate radicals and hydroxyl radicals can react with SOM and decrease the degradation efficiency [137]. While another study reported that SOM can enhance the degradation of certain pollutants by activating persulfate processes rather than simply exerting a negative effect by consuming persulfate when persulfate was used to remediate benzene in clays, and aquifer solids [74]. Additionally, considerable SOM content has been reported to still be present in the persulfate solution, suggesting that certain organic carbon content may actually be nonreactive with persulfate and its free radical chemistry [138]. Therefore, the effect of SOM on the degradation of persulfate still needs to be further explored, and the types of target pollutants should also be considered in actual remediation applications.

The mineral phase is a crucial part of the soil because it can interact with organic substances to stabilize organic carbon in soils [139]. Mineral transition metals may react with persulfate to affect contaminant removal efficiency further by either promoting activation or lowering oxidant persistence [85,86,140]. There are many iron minerals, such as ferrihydrite, ilmenite, hematite, pyrite, goethite, magnetite, and lepidocrocite in the soil, which were observed to have the potential to activate persulfate and make persulfate consumption [85,86]. For example, the highest consumption of persulfate was observed when pyrite was applied to activate persulfate in a study by Teel et al. (2011). The main reason was that pyrite can be decomposed rapidly in weakly acidic water, providing Fe^{2+} to activate persulfate.

4.6. Dissolved Ions

Groundwater contains far more dissolved anions and cations than the deionized water used in laboratory studies and these ions will somewhat impact the remedial effect of persulfate on the target contaminants.

Groundwater contains a high concentration of anions such as chloride (Cl^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and other anions are frequently found in groundwater, which may have an impact on the remediation. When various activation techniques are used, chloride, the most dissolved inorganic ion in groundwater, can have a variable impact on the effectiveness of organic pollutant degradation. Bennedsen (2012) reported that the degradation efficiency of p-nitrosodimethylaniline was enhanced when heat and alkaline was applied to activated persulfate, while there was no influence on the degradation efficiency when iron activation was applied at neutral pH. To make matters worse, when the pH was buffered to acidic conditions (pH = 2) with iron activated persulfate, the degradation efficiency of p-nitrosodimethylaniline was significantly decreased in the presence of chloride [141]. Li (2013) pointed out that the presence of anions including chloride (Cl^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-) can decrease the degradation efficiency of TCA. He demonstrated that the presence of these anions can quench hydrogen radicals ($\text{OH}\cdot$) and sulfate radicals ($\text{SO}_4^{\cdot-}$) and decrease the degradation efficiency [142]. In addition, groundwater contains many types of cations including potassium ion (K^+), sodium ion (Na^+), ferric ion (Fe^{3+}), ferrous ion (Fe^{2+}),

ammonium ion (NH_4^+). Most existing cations (e.g., K^+ , Na^+) have no influence on the degradation efficiency of organic pollutants [85]. However, the dissolution of ferric and ferrous ion can somewhat activate persulfate and enhance the degradation efficiency [140]. Mustapha (2021) demonstrated that the dissolved ferric ion and ferrous ion from subsurface sediments can effectively activate persulfate to degrade aniline [140].

5. Impact of Environmental Application

5.1. Rebound

When ISCO implementation has been completed, there may be an increase of target pollutants in groundwater concentrations, which was observed at a given location and referred to as rebound [128]. Rebound generally occurs in the remediation of low permeable areas contaminated by non-aqueous phase liquid (NAPL) contaminants, which are slowly released into groundwater. It exhibited an initial decrease in groundwater contaminants concentrations during and after site remediation, followed by an increase in groundwater contaminants concentrations over a longer period. Sra (2013) observed that the ethylbenzene and naphthalene were first declined to 10 $\mu\text{g/L}$ and 53 $\mu\text{g/L}$ during the injection time, but were finally raised to 2000 $\mu\text{g/L}$ and 360 $\mu\text{g/L}$ after 300 days which were even a little higher than the levels before remediation [119]. The same trend was also reported in Superfund Site Louisiana (USEPA), where the TPH concentrations in observing wells rebounded to the pre-remediation level when the injection was ended after 60 days [117]. Krembs et al. (2010) reported that rebound occurred at over half (62%) of the sites for over 71 remediation sites. Nearly half (49%) of the monitoring wells at those locations that experienced rebound observed the rebound process [128]. Any leftover sorbed, or NAPL phase contaminants, may re-equilibrate with the groundwater once the oxidant is depleted, which could lead to a rise in aqueous phase contamination, as seen during the post-ISCO monitoring period. Another potential pathway for contamination rebound is back-diffusion from low permeability media that were not properly treated during ISCO deployment. A third mechanism is insufficient source zone demarcation, which prevents ISCO applications from properly targeting the source zone. An influx of contaminated groundwater from untreated upgradient regions at the site could potentially result in an increase in pollutant concentrations.

5.2. Microbial Communities

The microbial community is an essential sign of the health of the soil and can be closely related to soil remediation equality [143]. The use of persulfate may significantly affect the population and diversity of microbial communities [43]. Mora et al. (2014) pointed out that the injection of persulfate may decrease the number of cultivable heterotrophic bacteria populations [144]. Sutton N B (2015) also observed a significant reduction of microbial communities in all three wells after 21 days persulfate remediation. The possible reason for the decrease in microbial communities appeared to be positively correlated with the negative effects of persulfate on soil acidification [144]. Luo (2022) pointed out that the sulfate radicals ($\text{SO}_4^{\cdot-}$) and the hydroxyl radical ($\text{OH}^{\cdot}$) generated by persulfate had strong oxidative potential in activated persulfate systems, which would cause harm to anaerobic microbes to some extents and reduce fragile microbes in the soil systems [145]. Even more, after persulfate oxidation, the high sulfate concentrations could encourage sulfate-reducing bacteria, which produces hazardous H_2S , which is harmful to public health [146].

6. Conclusions and Outlooks

Persulfate, a potential oxidant, is increasingly used in persulfate-based advanced oxidation for the remediation of groundwater and soil contaminated by organic chemicals. Multiple methods, including heat, alkaline, iron-based and electrokinetic were applied to activate persulfate successfully in site remediation. The alkaline and iron-based activation technologies seem to be the most used in site applications, while heat-activated persulfate consumes more energy and extra equipment is required, resulting in a high cost. The

combination of multiple methods to activate persulfate and surfactants to enhance the oxidation process has become a trend in recent years. Since every activated method has its shortcomings, how to overcome those shortcomings by coupling with other remediation technologies remains to be explored.

At present, although a number of remediation projects are carried out by using persulfate as oxidant, the parameters obtained from site applications are still inadequate. The dosage demand, the persistence, and the radius of influence of persulfate in field-scale applications varies at each site for different activation methods. Soil texture, minerals, and soil organic matter (SOM) content can affect the remediation efficiency when ISCO is applied to site remediation. The mechanism of persulfate-based ISCO still needs to be further explored and more attention should be paid to the transformation of achievements from laboratory research to field applications.

ISCO remediation is a long-term project and often cannot achieve the purpose of remediation at one time, compared with traditional physical methods. Nearly 50 percent of applications were observed to have a rebound process and needed extra remediation. Therefore, long term groundwater observation should be carried out when the ISCO applications are used. Persulfate treatments not only have a negative impact on the population and diversity of soil systems, but also cause a disruption of the biological natural attenuation capacity. Further attention should be paid to changes in soil microbial communities during and after remediation.

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