



Effect and mechanism of persulfate activated by different methods for PAHs removal in soil



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HIGHLIGHTS

- Oxidative capability and mechanism of activated persulfate were investigated.
- Thermal and chelated ferrous activated persulfate showed high removal of PAHs.
- Thermal activation facilitated high molecular weight PAHs removal by persulfate.
- Hydroxyl radicals in thermal activated systems contribute to high PAHs removal.

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ABSTRACT

The influence of persulfate activation methods on polycyclic aromatic hydrocarbons (PAHs) degradation was investigated and included thermal, citrate chelated iron, and alkaline, and a hydrogen peroxide (H_2O_2)-persulfate binary mixture. Thermal activation (60°C) resulted in the highest removal of PAHs (99.1%) and persulfate consumption during thermal activation varied (0.45–1.38 g/kg soil). Persulfate consumption (0.91–1.22 g/kg soil) and PAHs removal (73.3–82.9%) varied using citrate chelated iron. No significant differences in oxidant consumption and PAH removal was measured in the H_2O_2 -persulfate binary mixture and alkaline activated treatment systems, relative to the unactivated control. Greater removal of high molecular weight PAHs was measured with persulfate activation. Electron spin resonance spectra indicated the presence of hydroxyl radicals in thermally activated systems; weak hydroxyl radical activity in the H_2O_2 -persulfate system; and superoxide radicals were predominant in alkaline activated systems. Differences in oxidative ability of the activated persulfate were related to different radicals generated during activation.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of hydrophobic organic molecules consisting of 3–6 benzene rings and are highly toxic, carcinogenic, and environmentally persistent. PAH contamination exists in industrial areas and sewage-irrigated farmland in Poland, Spain, Germany, and China [1–4], and represents significant risk to the surrounding ecological environment

and to human health. Given these risks, immediate remediation is required. In situ chemical oxidation (ISCO) is an effective soil remediation technology, has a high removal efficiency of the contaminants [5–7], and has been applied under a broad range of soil types and hydrogeological conditions. In a recent survey, PAHs were the predominant contaminant found in 7% of all ISCO sites (223 total sites) investigated in the US [8].

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is an oxidant used at ISCO sites to transform a wide range of environmental contaminants under a broad spectrum of environmental conditions [6,9]. After activation (i.e., thermal, metal ion, base activation), more powerful oxidant (i.e., $\cdot\text{SO}_4^-$, $\cdot\text{OH}$) can be generated [9,10]. In addition, the persulfate anion can persist in subsurface systems longer than ozone and hydrogen peroxide [11], giving this oxidant several advantages over other oxidant candidates used in ISCO. Persulfate has

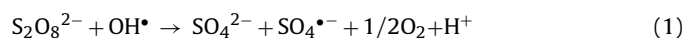
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been applied to remediate many organic pollutants, including the gasoline compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) [11–13], chlorinated volatile organic compounds (CVOs) [14–16], PAHs [17,18], petroleum hydrocarbons [19,20], methyl *tert*-butyl ether (MTBE) [21,22], and many others.

The rate of oxidant reaction is functionally dependent on the method of persulfate activation [23]. Some studies have investigated the effect of activated persulfate to destroy PAHs in soil, sediment or water. In these studies, persulfate activation was generally achieved using EDTA- and citrate-chelating ferrous iron [5,17,18,24]. It has been proposed in various studies that hydrogen peroxide (H_2O_2) may serve as an activator of persulfate. However, the role of H_2O_2 in a binary mixture of H_2O_2 and persulfate is poorly understood and not well documented [21]. Specifically, it has not been demonstrated whether H_2O_2 activates persulfate, or whether H_2O_2 is indirectly involved in other contaminant fate mechanisms such as Fenton-like oxidation. Reaction of hydrogen peroxide with the catalytic minerals in natural soils may initiate the formation of radicals, such as hydroxyl or superoxide radicals, which can directly react with pollutants, or interact with persulfate to form sulfate radicals through propagation reactions such as the reaction in reaction (1) [21,25,26]. It was also reported that hydrogen peroxide could support persulfate activation by elevating subsurface temperatures and then thermal-activation of persulfate [21,27]. Another possible role of H_2O_2 was Fenton-driven reduction of Fe(III) to Fe(II), and subsequent Fe(II)-activation of persulfate [21]. Here, we refer to the combined use of H_2O_2 and $Na_2S_2O_8$ as a binary mixture rather than H_2O_2 activation of persulfate. Further investigation is needed to assess and differentiate the activation and destruction mechanisms. Although Sra studied the treatability of gasoline compounds by persulfate using different activation strategies [28], limited research involves a comparison of the feasibility and mechanism of PAH destruction by persulfate activated using different methods.



The oxidant demand for persulfate in soil is variable (0.1–0.3 g/kg [29]; 1.4–6.0 g/kg [13]), and not often reported. The soil oxidant demand for persulfate is partially dependent on site specific soils, but it also dependent on the activation conditions for each specific application. The oxidant demand for persulfate as it relates to contaminant destruction is needed to assess the general feasibility of persulfate oxidation of contaminants, and to explore the persulfate reaction and oxidation mechanisms under different activation conditions.

In this study, persulfate was activated under different conditions to examine the effects of PAH transformation, PAH removal, identification of radical intermediates, and the mechanism of radical-contaminant transformation. Through these experiments, a theoretical basis for optimizing persulfate remediation is established where oxidant consumption, remediation effectiveness and cost can be more thoroughly examined.

2. Materials and methods

2.1. PAH contaminated soil

Soils contaminated with PAHs were collected from a coking plant in Beijing, China. Upon collection, the soil samples were homogenized and sieved (20-mesh sieve) to assure uniformity, freeze-dried, and stored in a refrigerator (-60°C) until used. The initial concentrations of PAHs are shown in Table 1.

Table 1

Concentration of PAHs in soil samples collected from the former coking plant (Beijing, China).

Compound name	Compound abbreviation	Number of rings	[PAHs] _{soil} (mg kg ⁻¹)
Naphthalene	Nap	2	6.3
Acenaphthylene	ANY	3	2.8
Acenaphthene	ANE	3	181.1
Fluorene	FLE	3	90.7
Phenanthrene	PHE	3	29.0
Anthracene	ANT	3	14.1
Fluoranthene	FLA	4	3.9
Pyrene	PYR	4	2.3
Benz[a]anthracene	BaA	4	0.6
Chrysene	CHR	4	1.8
Benzo[b]fluoranthene	Bbf	5	0.8
Benzo[k]fluoranthene	Bkf	5	0.9
Benzo[a]pyrene	Bap	5	1.1
Dibenz(a,h)anthracene	DahA	5	0.1
Indeno(1,2,3-cd)pyrene	IcdP	6	0.2
Benzo[ghi]perylene	BghiP	6	0.4
Total			340.0

2.2. Experiment design and sample analysis

2.2.1. Persulfate oxidation parameter screening experiments

Fourteen experiments were conducted to independently investigate the role of persulfate activation conditions including temperature (40, 50, 60 °C); citrate-chelated iron (mole ferrous iron/mole persulfate = 1/10, 1/4, 1/2); alkaline conditions (pH 10, 11, 12), and persulfate- H_2O_2 binary mixtures (mole H_2O_2 /mole $Na_2S_2O_8$ = 1/100, 1/10, 1/1) (Table 2). The ranges of temperature, mole ferrous iron/mole persulfate, mole H_2O_2 /mole $Na_2S_2O_8$, pH were determined according to the previous studies and results [12,13,25,30–32]. In this testing system, oxidant-free and activator-free conditions served as controls to assess treatment performance of the persulfate activation treatments. All experiments were performed in triplicate.

Contaminated soil (5 g) was loaded into 40-mL borosilicate glass volatile organic analysis (VOA) vials, and 7.5 mL of persulfate (0.5 M) or deionized (DI) water was added, supplemented with DI water to give a total volume of 15 mL. After addition of each solution, the test reactors were completely mixed to assure uniform reaction conditions. Subsequently, activation reagents were added, or the activation treatments were performed. For example, heat activation involved placing the reaction system into a constant temperature (40–60 °C) water bath; citrate-chelating iron activation involved dissolving citric acid in a ferrous sulfate solution and adding it to the test reactor; H_2O_2 –persulfate binary mixtures were prepared through the addition of H_2O_2 ; and alkaline activation involved adjusting the pH to 10, 11, or 12 using sodium hydroxide (3 M).

During the first 6 h of reaction, the test reactors were manually shaken once every hour, and then, placed static. After 72 h, the VOA vials were placed in an ice bath for 2 h to terminate the reaction. Subsequently, the E_h of the soil slurries in the test reactors were measured. Subsequently, the soil and supernatant were separated and the concentrations of PAHs and oxidant in the supernatant, and the concentrations of PAHs in the soil were analyzed.

2.2.2. Oxidant and PAH analysis and E_h measurement

Persulfate concentrations in aqueous samples were measure by placing the aqueous sample (0.1 mL) into a test tube (20-mL). Subsequently, DI water (0.9 mL), 2.5 N H_2SO_4 (10 mL), and 0.4 N ferrous ammonium sulfate (FAS) (0.1 mL) were added. The contents were mixed and allowed to react (40 min). Finally, 0.6 N ammonium thiocyanate (NH_4SCN) (0.2 mL) was added, and the absorbance was

Table 2

Parameters, conditions, and nomenclature used in persulfate oxidation parameter screening experiments.

Activator	Dosage of activator	pH	Temperature	Remarks
–	–	–	20 °C	Oxidant free
–	–	–	20 °C	Un-activated persulfate
–	–	–	40 °C	Constant temperature water bath
–	–	–	50 °C	Constant temperature water bath
–	–	–	60 °C	Constant temperature water bath
Citratechelated ferrous iron(0.5M)	1/10 ^a	–	20 °C	Mixed citrate and ferrous sulfate
Citratechelated ferrous iron (0.5M)	1/4 ^a	–	20 °C	Mixed citrate and ferrous sulfate
Citratechelated ferrous iron (0.5M)	1/2 ^a	–	20 °C	Mixed citrate and ferrous sulfate
Hydrogen peroxide (12.5%)	1/100 ^b	–	20 °C	Mixed hydrogen peroxide and persulfate
Hydrogen peroxide (12.5%)	1/10 ^b	–	20 °C	Mixed hydrogen peroxide and persulfate
Hydrogen peroxide (12.5%)	1/1 ^b	–	20 °C	Mixed hydrogen peroxide and persulfate
–	–	10	20 °C	Adjust pH using NaOH(3M)
–	–	11	20 °C	Adjust pH using NaOH(3M)
–	–	12	20 °C	Adjust pH using NaOH(3M)

^a Citrate chelated ferrous iron(mol)/persulfate (mol), note: citrate(mol)/ferrous iron(mol) = 1:1.^b H₂O₂(mol)/persulfate (mol).

measured with a spectrophotometer (2800 UV/Vis Spectrophotometer, Shanghai) at a wavelength of 450 nm. A calibration curve established by these procedures ranged from 60 to 1800 mg/L with a linear correlation coefficient ($R^2 > 0.99$).

Soil samples from each test reactor were freeze-dried, and sub-samples (2 g) were collected, weighed, and mixed with dichloromethane (10 mL). The mixture was ultrasonically extracted (1 h) and centrifuged. An aliquot (2 mL) of the supernatant extract was collected, added to a silica gel column extraction cell (10 g of 200–300 mesh silicone, with anhydrous sodium sulfate) for purification, and eluted with n-hexane/dichloromethane (1:1, v/v). The purified extract was condensed to approximately 0.5 mL using a rotary evaporator (RE-52AA, Shanghai), and internal standard (125 μ L) was added and the volume adjusted to 1 mL with n-hexane for quantitative analysis. PAHs concentrations were analyzed by gas chromatography (GC) (Agilent 7890A) under the following conditions: HP-5MS 30 m \times 0.25 mm capillary column; helium as carrier gas; inlet pressure 0.03 MPa; linear velocity 37 cm/s; inlet temperature 300 °C; start temperature 60 °C; programmed to 300 °C at a rate of 5 °C/min; retained for 20 min until complete elution of all species.

The concentration of PAHs in the supernatant was measured using a liquid–liquid extraction method. A mixture of the supernatant (5 mL) and N-hexane (5 mL) were placed in a glass centrifuge tube, and shaken (1 h; 250 rpm). The N-hexane extract (1 mL) was direct injected into a GC–mass spectrometer (MS) for analysis.

The E_h of the soil slurries in the test reactors were measured using a pH510 meter.

2.3. Mechanistic Investigation- radical intermediates

Based on the results of the persulfate oxidation parameter screening experiments, the most effective activation conditions for PAH oxidation were identified and used for further study. Specifically, the detection and identification of radical intermediates was performed using electron spin resonance (ESR) to help assess the mechanisms involved in PAH transformation. The quantity of different radicals cannot be calculated by ESR, which can only be roughly judged by the intensity of radicals in the spectra, therefore the ESR results was used for qualitative analysis of reaction mechanism of activated persulfate with PAHs.

An aqueous sample of the persulfate solution (1 mL) was activated using various methods for a short period (5 min), and then sampled (200 μ L) for further analysis. The spin trap compound, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used in this analysis. DMPO reacts with radical intermediates in oxidation systems and forms a unique radical adduct that is stable, relative to the hydroxyl,

sulfate, and superoxide radicals, and can be detected through electron spin resonance instrument. A small solution (10 μ L) of DMPO was added to the oxidant solution, mixed, and then injected into the ESR instrument for detection of the DMPO radical adduct. The analytical conditions of the ESR instrument were: modulation amplitude of 3.08 G, time constant of 10.24 ms, conversion time of 20.48 ms, sweep width of 100 G, a resonance frequency of 9.75 GHz. Simulated by WINEPR software, standard spectra of hydroxyl radicals (hydroxyl radical adduct with hyperfine splitting constants of AN=14.96 and AH=14.78), sulfate radicals (sulfate radical adduct with hyperfine splitting constants of AN=13.51, AH=9.93, $A_{\gamma 1}H=1.34$, and $A_{\gamma 2}H=0.88$ and superoxide radical (superoxide radical adduct with hyperfine splitting constants of AN=14.49, $A\beta H=10.83$, $A\alpha H=1.31$ -gauss) were obtained and illustrated in Fig. 1.

2.4. Statistical analysis

SAS software (Version 8) was used for statistical analysis of the data, including significance tests and multiple comparisons.

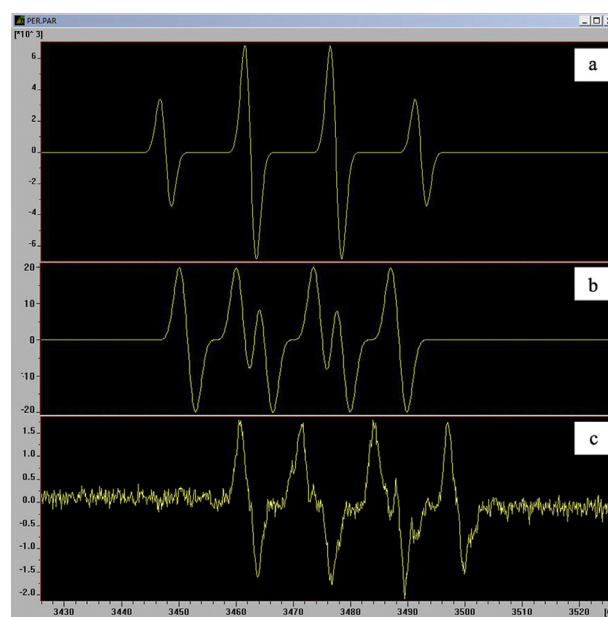


Fig. 1. Electron spin resonance characteristic spectra of the DMPO-radical adducts for (a) the hydroxyl radical, (b) the sulfate radical, and (c) the superoxide radical.

Table 3
Persulfate consumption and E_h in reaction systems activated by different methods.

Treatment	Persulfate consumption (g/kg soil)	E_h (mV)
Deionized water	N/A	367
Unactivated persulfate	0.25 ± 0.28	573 ± 5
Heat-activated persulfate		
40 °C	0.45 ± 0.25	656 ± 45
50 °C	0.84 ± 0.24	746 ± 14
60 °C	1.38 ± 0.35	762 ± 5
Citrate-chelated ferrous iron ^a		
1/10	0.91 ± 0.06	680 ± 5
1/4	1.03 ± 0.13	682 ± 2
1/2	1.22 ± 0.07	678 ± 5
H ₂ O ₂ –persulfate binary system ^b		
1/100	0.22 ± 0.31	509 ± 8
1/10	0	522 ± 34
1/1	0	527 ± 3
Alkaline activated persulfate ^c		
10	0.06 ± 0.09	555 ± 4
11	0.35 ± 0.26	560 ± 2
12	0.25 ± 0.36	562 ± 17

^a Ferrous iron (mol)/persulfate (mol).^b H₂O₂ (mol)/persulfate (mol).^c pH adjusted with NaOH.

3. Results and analysis

3.1. Oxidant consumption and E_h of persulfate activated by different methods

The redox potential (E_h) measured after reaction in test reactors represents the oxidative capacity of the reaction system and a general indicator of the potential for PAH oxidation transformation. A reliable correlation was not established between the mass of oxidant reacted and E_h values measured in the test reactors. E_h in the DI water amended reactor (367 mV) represents background and all E_h values in oxidant amended reactors exceeded this value (Table 3).

Oxidant consumption and E_h values increased as the temperature increased in heat-activated persulfate. Persulfate consumption and E_h in 60 °C activated persulfate was 5.6 and 1.3 times higher than the unactivated persulfate reactor, respectively, indicating the significant role of thermal activation. Persulfate consumption and E_h in citrate-chelated ferrous activated persulfate was also greater than the unactivated system but less than 60 °C thermal activation. A small increase in persulfate consumption was measured between increasing citrate chelated ferrous iron ratios, however, negligible differences in E_h were measured. Both E_h and persulfate consumption in the citrate chelated ferrous iron test reactors were higher than in the unactivated system indicating the important role of ferrous iron persulfate activation.

E_h values in the H₂O₂–persulfate binary system and alkaline activated persulfate were all lower than in the unactivated system. No persulfate was consumed when the hydrogen peroxide/persulfate ratio was above 1/10 and 1/1, and limited differences in persulfate consumption between the alkaline activated and unactivated systems. Overall, thermal and citrate chelated ferrous iron activation yielded more aggressive persulfate reaction and oxidative potential (E_h) than alkaline activation or H₂O₂–persulfate binary systems.

3.2. Oxidation rate of PAHs by different persulfate activation methods

Loss of PAHs (13%) in the soil was measured in the control treatment without persulfate, which presumably represents the result

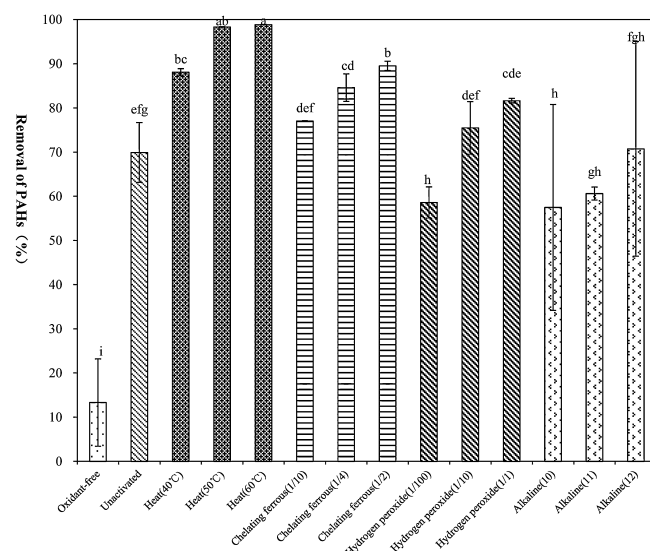


Fig. 2. Removal of PAHs in soil from the coking plant (Beijing, China) by chemical oxidation using activated persulfate. The persulfate was activated and used under a range of conditions including unactivated, thermal activation, citrate chelated ferrous iron activation, H₂O₂–persulfate binary mixture treatment system, and alkaline activation. Letters in lower case indicate statistical significance between treatments, data pairs with the different letter are significantly different ($P \leq 0.05$), and pairs with same letters are not significantly different.

of natural degradation by microbial action or variability in PAH concentration. Significant removal of PAHs was measured in both unactivated and activated persulfate, but varied among the activation methods (Fig. 2). Removal of PAHs from unactivated persulfate treatment may be due to the volatilization, especially for naphthalene. Except that, naturally occurring activation of persulfate may also contributed to the removal [33].

The removal of PAHs in thermal activated persulfate was the highest (87–99%), and increased with activation temperature. PAH removal (73–82%) in citrate chelated ferrous activated persulfate was the second highest, and increased with the ferrous/persulfate ratio. Removal of PAHs in citrate-chelated ferrous iron (1 mol/2 mol) activated persulfate was 17.4% higher than in the unactivated system. H₂O₂–persulfate binary systems was not as effective as thermal or chelated iron activated treatment systems, however, the oxidative treatment of PAHs increased with the H₂O₂–persulfate ratio. The oxidative treatment removal of PAHs was lowest in alkaline activated persulfate, including the unactivated control.

Loss of all 16 PAHs was measured in the oxidant-free control, and relative losses of naphthalene, anthracene, benzo(a)pyrene and benzo(b)fluoranthene were greatest (Fig. 3a). In the unactivated persulfate amended test reactor, the loss of all PAHs increased except for acenaphthylene, especially acenaphthene, pyrene, benzo-anthracene, benzo(k) fluoranthene and benzo(g, h, i) perylene (Fig. 3b). Relative to the control reactors, significant and uniform removal of all 16 PAHs was measured under thermal activation conditions (Fig. 3c) and removal was correlated with temperature. The removal of low molecular weight PAHs (except acenaphthylene) were above 94% in the thermal activated persulfate system at 60 °C, where 85% of high molecular weight PAHs (benzo(b) fluoranthene, indeno(1,2,3-cd) pyrene, the diphenyl and (a, h)anthracene) were oxidized. Relative to the controls, significant PAH removal was measured resulting from citrate chelated ferrous iron activate persulfate, and greater removal of acenaphthylene, fluorene, phenanthrene, fluoranthene, benzo(b) fluoranthene and benzo(k) fluoranthene resulted with increasing ferrous/persulfate ratios. Seventy-five percent of 16 PAHs, except indeno(1,2,3-cd)

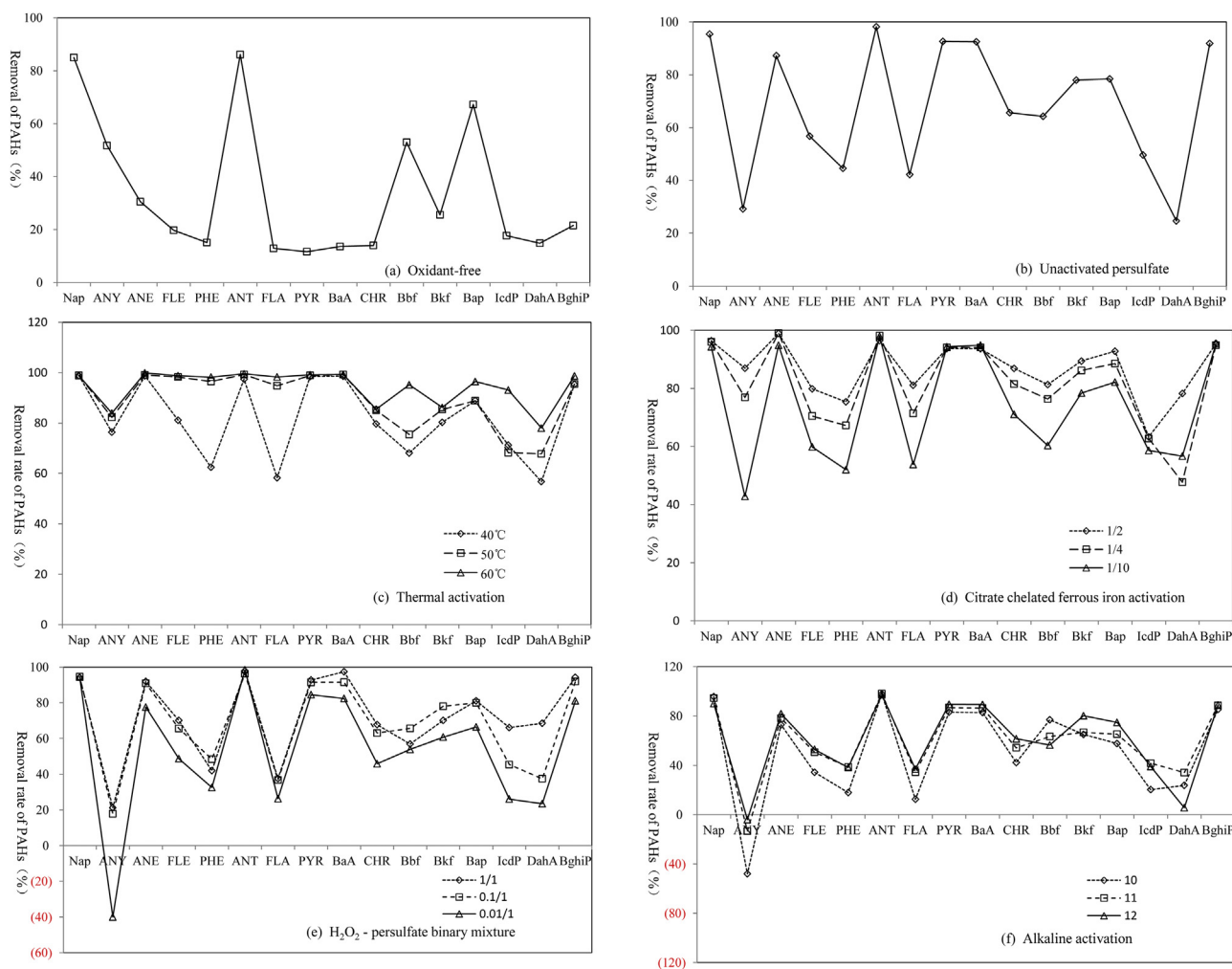


Fig. 3. Removal of PAHs in soil at the coking plant (Beijing, China) under different persulfate oxidative conditions. Persulfate testing and activation conditions included (a) oxidant-free control, (b) unactivated persulfate, (c) thermal activation, (d) citrate chelated ferrous iron activation, (e) H_2O_2 -persulfate binary mixture, and (f) alkaline activation.

pyrene, were removed in the citrate-chelated ferrous (1/2) activated system. Naphthalene, acenaphthene, anthracene, pyrene, benzo-anthracene, and benzo (g, h, i) perylene were removed in the H_2O_2 -persulfate binary system and in the alkaline activated persulfate systems, while oxidation rates of acenaphthylene, phenanthrene, fluoranthene, and dibenzo (a, h) anthracene were relatively low.

3.3. ESR radical detection in persulfate treatment systems

Different radicals and combinations of radicals were measured in the activated persulfate systems and the H_2O_2 -persulfate binary mixture. The ESR spectra illustrating the characteristic spectra for sulfate, hydroxyl, and superoxide radicals produced in the persulfate treatment systems are presented in Fig. 4. Compared with the standard spectra, the hydroxyl radical was the main species generated in the thermal activation of persulfate, while some superoxide radicals and sulfate radicals were also generated (Fig. 4A). It is noteworthy that no radicals were observed in citrate chelated ferrous iron activated persulfate, although it was sampled every 5 min during the first 1 h of reaction (Fig. 4B). Hydroxyl radicals were generated in the H_2O_2 -persulfate binary treatment system, but the spectral intensity was weaker than that in the thermal activation treatment system. Superoxide radicals, hydroxyl radicals, and

sulfate radicals were detected in alkaline activated persulfate, with the superoxide radical being predominant.

4. Discussion

Activated persulfate is a robust and effective oxidant for the purpose of destroying PAHs. After activation, strong and non-specific radicals were detected in these treatment system including the hydroxyl ($E_h = 2.8 \text{ V}$) and sulfate radicals ($E_h = 2.6 \text{ V}$). Despite the short persistence of these radicals under environmental conditions, these radicals are capable of oxidizing a wide range of environmental contaminants in soil and groundwater [9]. Recent findings have documented that E_h values in persulfate systems activated by different methods differ in measured persulfate consumption and removal of PAHs. The removal of PAHs was highest using thermal activation, followed by citrate-chelated ferrous iron activation, whereas the H_2O_2 -persulfate binary system and alkaline activation treatment systems were relatively low. The oxidation rate of PAHs was related to the radicals generated in the persulfate activated by different methods. Further, sulfate radicals reacted very rapidly with aromatic compounds as do hydroxyl radicals and H atoms, but with higher selectivity[34].

E_h values, persulfate consumption, and the removal efficiency of PAHs in thermal activated persulfate all increased with

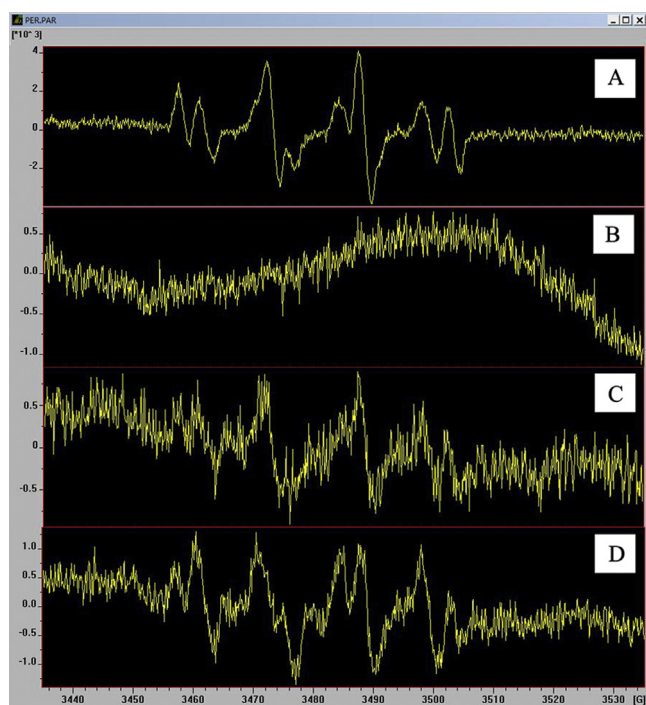


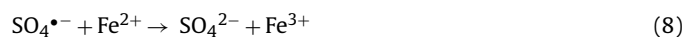
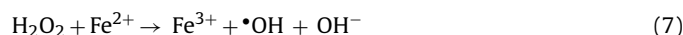
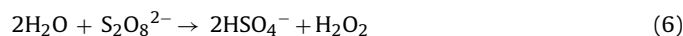
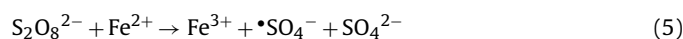
Fig. 4. Electron spin resonance spectra of radicals produced in the persulfate oxidation treatment systems; (A) thermal activation of persulfate (60 °C); (B) citrate-chelated ferrous iron activation of persulfate (1 mol iron/2 mol persulfate); (C) H₂O₂–persulfate binary treatment system (1 mol H₂O₂/1 mol persulfate); and (D) alkaline activation of persulfate systems (pH 12; NaOH).

increasing temperature. The thermal activation temperature for persulfate generally falls in the range 40–99 °C [35]. A temperature rise from 20–40 °C increased the removal efficiency of naphthalene from 50.6% to 98.3% [12], and the removal efficiency of PAHs reached 75% in 3 h involving thermally activated persulfate at 70 °C [17]. For some volatile organic pollutants, the removal efficiency may decrease with increasing temperature [12]. It was shown that thermal activation can improve the oxidative ability of persulfate by producing a large number of oxygen radicals with a more strongly oxidative active. Sulfate radicals were the main radicals generated in a homogeneous liquid persulfate system (pH 2–7), both sulfate radicals and hydroxyl radicals were present at pH 9, while hydroxyl radicals were the main radicals in an alkaline system (pH > 12) (reactions (2)–(4)) [30]. Kolthoff and Miller [36] suggested that under acidic conditions (pH < 2), persulfate may decompose without generating sulfate radicals. In our study, the removal efficiency of PAHs rose from 88% to 99% when the activation temperature increased from 40 °C to 60 °C, which was attributed to the hydroxyl, sulfate radicals and the role of superoxide radicals generated in the thermal activated systems.



Iron activation of persulfate is a common activation method investigated for PAH degradation. EDTA chelated ferrous iron activated persulfate removed 75–100% of PAHs in 24 h [18], and the removal efficiency of PAHs in sediment by catechol chelated ferrous iron activated persulfate was 76–88% [5]. Previous research has demonstrated that the oxidation rate of pollutants in chelated ferrous iron activated systems is influenced by the ratios of oxidant, catalyst and chelating agent. Removal efficiency reached a

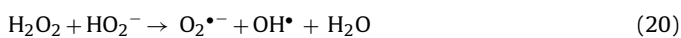
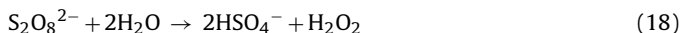
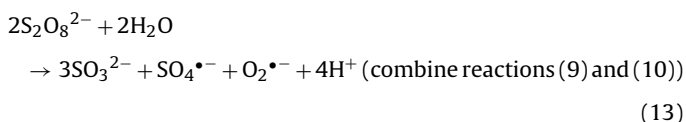
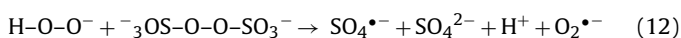
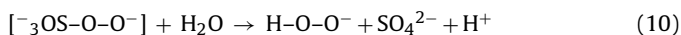
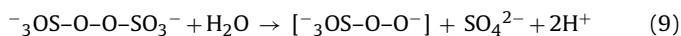
maximum with a persulfate/ferrous iron ratio of 100/1 and an EDTA/ferrous iron ratio of 1/1 [31,37]. Hydroxyl radicals and sulfate radicals are generated in an EDTA chelated ferrous iron activated system (reactions (5)–(7)) [38]. It was found that sulfate radicals and chelating metal sulfate radicals were generated in silver ion activated systems, sulfate radicals and hydroxyl radicals were generated in ferrous ion activated systems, while no radicals were produced in a ferric iron activated system [23]. In our study, no radicals were detected in the citrate chelated ferrous iron activated persulfate system over a 1 h reaction period. It may be possible that the reaction time of chelated ferrous iron and persulfate was sufficiently short and ferrous ion had not yet been released and/or available for reaction preventing radical formation and detection. The time required for the detection of radicals in alkaline and EDTA chelated ferrous iron activated treatment systems was 1 min and 22 h, respectively [38,39]. Except for radical generation (reaction (5)), ferrous iron was also involved in radical scavenging (reaction (8)), which may also contribute to the absence of radicals during ESR detection. This issue required further investigation.



The E_h in the H₂O₂–persulfate binary treatment system was relatively low and limited detection of hydroxyl radicals was measured. Although E_h in the H₂O₂–persulfate binary system was lower than that in the unactivated system, the removal of PAHs in reactors amended with 1/10 and 1/1 (mol H₂O₂/mol persulfate) was higher than in the unactivated system. For the E_h was measured after reaction, it was not exactly related to the removal of PAHs. H₂O₂ and persulfate treatment respectively removed PAHs from soil by up to 53% [24] and 69.93%, while H₂O₂–persulfate binary treatment system increased PAHs removal by 29% and 12% compared to H₂O₂ alone and persulfate alone, which indicated the role of H₂O₂ for persulfate activation. In other studies, the addition of H₂O₂ to persulfate improved the removal efficiency of PAHs by 4% [5]. Persulfate consumption was low in the H₂O₂ amended system, which may be due to the role of H₂O₂ in the system. H₂O₂ amended persulfate systems have been shown to be affected by several factors, including concentration of persulfate, concentration of H₂O₂, pH, and temperature. Hence, the removal efficiency may decrease with increasing H₂O₂/persulfate ratios [40].

Alkaline activated persulfate is capable of treating a variety of pollutants, while it was less effective than other activated persulfate systems [41]. In our study, E_h values, persulfate consumption and removal of PAHs (57.5–70.7%) after 72-h reaction in the alkaline activated systems were relatively low. E_h values and the removal of PAHs increased with increasing pH, while persulfate consumption was variable. The main radicals generated in the alkaline activated persulfate system were superoxide radicals, with small amounts of hydroxyl and sulfate radicals also produced. The mechanism of base activated persulfate involved the base-catalyzed hydrolysis of persulfate to a hydroperoxide anion and sulfate followed by the reduction of another persulfate molecule by hydroperoxide [38]. Reduction persulfate by hydroperoxide decomposes persulfate into sulfate radicals and sulfate anions, while hydroperoxide is oxidized to superoxide, and the sulfate radicals react with hydroxyl ion to produce hydroxyl radicals (reactions (9)–(14)) [38,39]. Another possible mechanism is base-catalyzed hydrolysis of persulfate produces peroxide which then decompose to produce reactive

oxygen (reactions (15)–(20)) [32]. Radical production in base activated persulfate system is related to pH, SOM, oxidant and base dosage. It is reported that the radical production rate increased as the persulfate and base dosage increased, or the pH increased [23,41,42]. As the soil organic matter (SOM) increased, the production rate of hydroxyl radicals decreased, while that of superoxide radicals increased [42]. Superoxide radicals have reducing properties, which may offset the effect of hydroxyl and sulfate radicals, making the oxidizing ability of base activated persulfate systems lower than that of other systems.



5. Conclusions

Among different methods, thermal activation was one of the most effective way for persulfate activation and PAHs removal, followed by citrate chelated ferrous iron activation, and then hydrogen peroxide(H_2O_2)-persulfate binary mixture and alkaline activation. Both E_h and oxidant consumption can be used to predict the oxidative capability of oxidation system, which was closely related to radicals generated in the system. The high redox potential and PAHs removal of thermal activated persulfate was attributed to the hydroxyl radicals generated during activation. While few hydroxyl radicals generated in the hydrogen peroxide-persulfate binary mixture system and superoxide radicals predominated in the alkaline activated systems led to the low pollutant removal.

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