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COMBINATION OF ANIONIC SURFACTANTS WITH THERMAL-ACTIVATED PERSULFATE FOR SIMULTANEOUS REMEDIATION OF PHENANTHRENE-CONTAMINATED SOIL

The application of persulfate in in-situ chemical oxidation for remediating hydrophobic organic contaminants is limited by low solubility and the inherent instability of persulfate radicals in contaminated soils. This study demonstrated that the surfactant-enhanced thermally activated persulfate in the aqueous phase effectively addressed these challenges. Specifically, sodium dodecyl diphenyl ether disulfonate-enhanced thermally activated persulfate was successfully constructed and tested on phenanthrene (PHE)--contaminated soil. The rate of PHE oxidation decomposition was positively correlated with increasing water/soil ratio and exhibited enhanced activity under acidic conditions. The presence of coexisting inorganic anions was observed to exert a variable inhibitory effect on the oxidative efficiency of PHE, with the inhibitory potency following the sequence of HCO_3^- > Cl^-. Additionally, significant modifications were observed in key soil physicochemical parameters during the remediation process, marked by decreases in pH, organic matter content, and ion exchange capacity. This study highlights the potential of surfactant-enhanced thermally activated persulfate for remediating contaminated soils, particularly for in-situ chemical oxidation remediation at sites with dense non-aqueous phase liquids.

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), compounds of two or more fused aromatic benzene rings, are prominent pollutants primarily generated through the incomplete combustion and pyrolysis of organic materials such as wood, fossil fuels, and petroleum products, particularly during the rapid industrial advancement [1, 2]. Globally, PAH concentrations vary by orders of magnitude, with reported levels ranging from 30.6 to 35,000 mg/kg in North America, 3.6–11,600 mg/kg in Europe, 889–11,820 mg/kg in Australia, and 0.5–5,453 mg/kg in China [3]. Research by Menone [4] indicates PAHs concentrations within estuarine salt marshes of South America typically range from 50 to 1070 ng/g dry weight in sediments, roots, and leaves. Owing to their hydrophobic nature and stable molecular configuration, PAHs exhibit a high propensity for accumulation in soil or sediments, thereby engendering groundwater contamination [5]. As a subset of persistent organic pollutants, PAHs possess carcinogenic, mutagenic, and teratogenic properties, persisting in the environment, accumulating within biological food chains, and imparting deleterious impacts on both human health and ecosystem integrity [6]. Consequently, driven by these concerns, researchers worldwide have diligently pursued numerous investigations aimed at innovating and advancing technologies for the remediation of PAH-contaminated soil.

Current research demonstrates the availability of various technologies for the removal of PAHs from contaminated soils and groundwater. These include physical methods such as incineration, in-situ thermal desorption, and solvent extraction/soil washing, as well as chemical oxidation, bioremediation, and integrated approaches [7, 8]. Among these, chemical oxidation stands out as a widely employed in-situ treatment modality for organically contaminated sites. This technique involves the injection of oxidizing agents, such as ozone, permanganate, hydrogen peroxide, Fenton's reagent, and persulfate, into the soil and groundwater to facilitate degradation reactions [7, 9]. Persulfate, owing to its affordability, high stability, and ease of storage, emerges as a commonly utilized oxidant for site applications. Upon activation by heat, ultrasound, iron salts, or alkali, persulfate generates sulfate radicals ($^{\bullet}SO_4^-$, $E_0 = 2.6$ V) and hydroxyl radicals ($^{\bullet}OH$, $E_0 = 2.7$ V), thereby facilitating enhanced mineralization in PAHs degradation [10, 11].

Thermally activated persulfate (TAP) is particularly advantageous for remediating complex, site-scale organic-contaminated soils and groundwater, owing to its straightforward temperature control and the environmentally benign nature of its primary active species, sulfate radicals. However, the efficacy of mineralization is contingent upon the direct reaction of free radicals with organic contaminants in the aqueous phase, posing challenges due to the low solubility of PAHs in water and the interactions between free radicals. Surfactants, with their amphiphilic molecular structures, can address this limitation: their hydrophobic moieties interact with both hydrophobic pollutants and soil matrices, while their hydrophilic groups remain dispersed in the aqueous phase, thereby enhancing the water solubility of organic pollutants [12]. Certain surfactants, such as sodium dodecyl

sulfonate, sodium dodecyl benzene sulfonate, and sodium dodecyl diphenyl ether disulfonate (C_{12}-MADS), are compatible with persulfate in aqueous solutions. Their inclusion as additives in chemical oxidation remediation techniques enhances the water solubility of hydrophobic organic pollutants [13]. Furthermore, different surfactant types may either promote or impede persulfate decomposition through mechanisms such as hydrogen extraction with $^{\bullet}SO_4^-$ or attraction or repulsion of sulfate radicals due to Coulombic forces. For instance, alkyl sulfonate and alkylbenzene sulfonate surfactants retard persulfate decomposition [14]. Despite its promise for organic-contaminated site remediation, the effectiveness of surfactant-enhanced TAP (S-TAP) in real soil environments remains uncertain [13]. Site-specific factors-such as soil pH, water/soil ratio, and background ion concentrations-introduce significant variability, challenging the direct application of exploratory S-TAP studies across diverse environmental conditions.

Existing studies have demonstrated that C_{12}-MADS, a divalent anionic alkylbenzene sulfonate surfactant, exhibits notable Coulombic repulsion toward sulfate radicals. This property reduces its reactivity with sulfate radicals, suppresses persulfate decomposition, and thereby enhances oxidant utilization efficiency [14]. Phenanthrene (PHE), a pervasive and notably elevated contaminant found in PAH-contaminated sites, is classified as a hazardous pollutant by the US EPA [6]. In soil environments, PHE oxidation is significantly constrained by its low aqueous solubility, limiting the mass transfer and the inherent instability of sulfate radicals. To address these dual limitations by simultaneously enhancing radical stability and promoting PHE dissolution, the application of C_{12}-MADS enhanced TAP (C_{12}-MADS-TAP) presents a promising remediation strategy. The oxidation of PHE proceeds in two successive stages. The process begins with dissolution and mass transfer of PHE from the soil matrix into the aqueous phase. Following mass transfer, PHE is oxidized in the aqueous phase by sulfate radicals, the primary reactive species in TAP systems, as represented in Eqs. (1)– (3).

$$PHE_{soil} \rightarrow PHE_{aq} \tag{1}$$

$$S_2O_8^{2-} \rightleftarrows 2^{\bullet}SO_4^- \tag{2}$$

$$PHE_{aq}^- + {}^{\bullet}SO_4^- \rightarrow \text{product} + SO_4^{2-} \tag{3}$$

To elucidate the potential of S-TAP for in-situ chemical oxidation (ISCO) of contaminated soils, this study investigated the oxidative degradation performance of a C_{12}-MADS--TAP system under various environmental conditions using PHE-contaminated soil. The primary objectives of this study are as follows: 1) to determine the optimal operational parameters, including activation temperature, surfactant concentration, and persulfate dosage, for the constructing an efficient C_{12}-MADS-TAP remediation system; 2) to analyze the influence of key environmental factors such as pH, water/soil ratio, and ionic concentration on PHE oxidation efficiency, degradation kinetics and underlying mechanisms; 3) to

assess the practical applicability of C_{12}-MADS-TAP for field scale ISCO by examining changes in soil properties before and after treatment, and to provide insights for its implementation at actual contaminated sites.

2. MATERIALS AND METHODS

Materials. All chemicals utilized were of analytical grade or higher purity and were employed as received. Sodium persulfate ($Na_2S_2O_8$, SPS), the predominant persulfate salt used in ISCO, was utilized in the study. Phenanthrene ($C_{14}H_{10}$), chosen as the target compound for this experiment, was procured from J&K Scientific with a purity of 95%, while C_{12}-MADS was obtained from Wengjiang Chemical Reagent. Organic solvents, including acetone, acetonitrile, hexane, and methanol, were acquired from Aladdin and were of high-performance liquid chromatography (HPLC) grade. Additional reagents such as calcium chloride ($CaCl_2$), ferrous sulfate ($FeSO_4$), ammonium ceric sulfate ($(NH_4)_4Ce(SO_4)_4$), sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), and sulfuric acid (H_2SO_4) were sourced from SINOPHARM. All aqueous solutions were prepared using deionized water with a resistivity of approximately 18 $M\Omega \cdot cm^{-1}$. The soil utilized was a typical red lateritic soil collected from an uncontaminated site in southern China at a depth of 10–20 cm, exhibiting a pH of approximately 6.89. The soil was air-dried naturally, cleared of twigs and stones, ground through a 100-mesh sieve, and then stored for subsequent use. The soil samples exhibited an organic matter content of 29.11 g/kg and a cation exchange capacity (CEC) of 24.67 mol/kg. PHE dissolved in acetone was incorporated into the soil and aged for a period exceeding six months to prepare soil contaminated with 100 mg/kg of PHE.

Optimization of C_{12}-MADS-TAP. The experiments were conducted at a water/soil ratio of 20:1. 1 g of PHE-contaminated soil and 20 cm^3 of freshly prepared solution containing C_{12}--MADS (at concentrations of 1, 2, 5, and 10 g/dm^3) and $Na_2S_2O_8$ (at concentrations of 5, 10, 25, and 50 g/dm^3) were combined in a series of 40 cm^3 EPA VOA vials. These vials, sealed with silicone/PTFE septa and equipped with Teflon-lined screw caps, were placed on a shaker shaken at 150 rpm at various temperatures (25, 40, 60, and 80 °C). At predetermined intervals, the samples were centrifuged every 4 h to separate the aqueous solution from the soil. Subsequently, the aqueous phase containing C_{12}-MADS was initially diluted to a final concentration of 0.5 g/dm^3. This resulting solution was then subjected to extraction with hexane (5 cm^3 of aqueous solution with 5 cm^3 of hexane), followed by the addition of 5 cm^3 of 0.1 M $CaCl_2$ solution as an emulsion breaker. It is noteworthy that all sample treatment methods and subsequent tests were performed in triplicate to ensure statistical robustness and reproducibility. These experiments were carried out to investigate the impact of temperature, surfactant concentration, and oxidant dosage on the degradation of PHE. The

results indicate that 60 °C, 5 g/dm^3 of C_{12}-MADS, and 25 g/dm^3 of SPS increase the reactivity of SPS toward PHE most effectively. The optimized synthetic procedures of C_{12}-MADS-TAP were outlined as follows.

Investigation of the effect of soil environmental factors on the application of C_{12}-MADS-TAP. Batch experiments were conducted to explore the impact of soil environmental factors on the oxidative degradation of PHE by C_{12}-MADS-TAP. The investigated factors included initial pH, water/soil ratio, and the presence of coexisting ions. Specifically, 1 g of PHE-contaminated soil was combined with a freshly prepared solution containing 5 g/dm^3 C_{12}-MADS and 25 g/dm^3 SPS in vials maintained at 60 °C. The initial pH of the 20 cm^3 freshly prepared solution was adjusted to 6, 7, and 8 using 0.1 mol/dm^3 phosphate buffer. The water/soil ratio varied at 1:1, 5:1, 10:1, 20:1, and 30:1. Additionally, the influence of various coexisting ions, namely 1 mol/dm^3 sodium bicarbonate (HCO_3^-) and 1 mol/dm^3 sodium chloride (Cl^-), was examined. At predetermined intervals, samples were extracted from the solutions for periodic measurement and analysis.

Investigation of the C_{12}-MADS-TAP application on the soil physicochemical properties. The investigation encompassed an examination of alterations in the physicochemical characteristics of the soil throughout the reaction process. Specifically, 1 g of PHE-contaminated soil was combined with 20 cm^3 freshly prepared solution containing 5 g/dm^3 C_{12}-MADS and 25 g/dm^3 SPS in vials maintained at 60 °C, with a control group established that contained neither C_{12}-MADS nor SPS. Subsequently, the samples were extracted to assess variations in soil pH, total organic matter content, and CEC.

Analytical methods. PHE quantification was conducted utilizing a Shimadzu GCMS-QP2010 instrument equipped with an HP-5MS fused silica capillary column (30 m ×0.25 mm, i.d., 0.25 μm film thickness). Helium served as a carrier gas, with a flow rate of 1.2 cm^3/min. The GC oven temperature was programmed as follows: initially held at 60 °C for 1 min, then ramped at 20 °C/min to 290 °C, with a final hold time of 10 min. Mass spectrometry was performed at 70 eV with electron impact ionization. Sample pH was determined using a pH meter, CEC was assessed employing the barium chloride exchange method, and organic matter content was quantified utilizing the potassium dichromate oxidation colorimetric technique [15, 16].

3. RESULTS AND DISCUSSION

3.1. PRELIMINARY OPTIMIZATION OF REACTION CONDITIONS IN SURFACTANTS ENHANCED DEGRADATION OF PHE

To establish an effective C_{12}-MADS-TAP system, the initial phase of this study involved optimizing the activation temperature, surfactant dosage, and oxidant dosage.

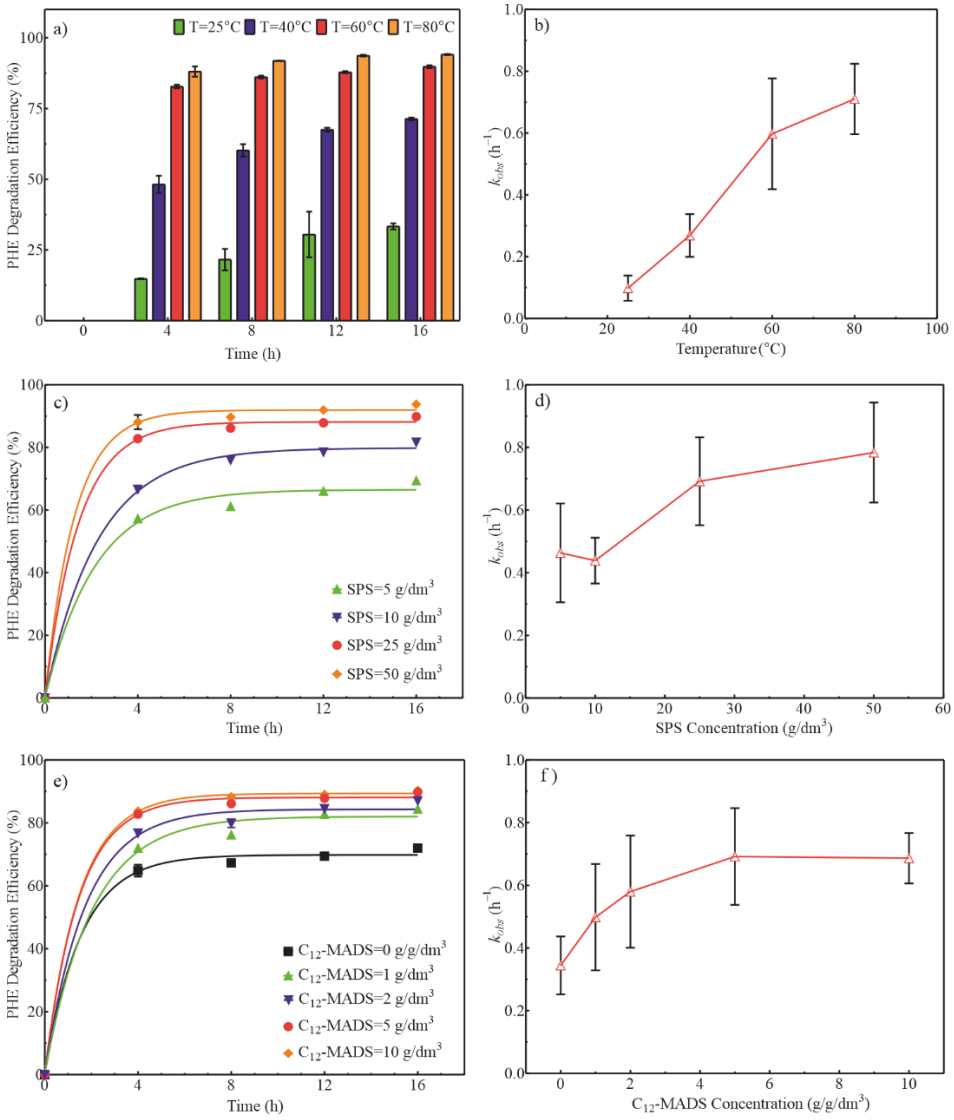

Fig. 1. PHE degradation under various reaction conditions: a, b) effect of thermal-activation temperatures on PHE oxidation and corresponding observed rate constants (k_{obs}), c, d) effect of persulfate concentration, e, f) effect of C_{12}-MADS concentration; $[PHE]_0$ = 100 mg/kg, water/soil ratio = 20:1, $[C_{12}\text{-MADS}]$ = 5 g/dm^3 , and [SPS] = 25 g/dm^3, reaction time = 16 h, no pH adjustment

As shown in Fig. 1a, temperature critically influenced PHE oxidation. At 25 °C, only 14.80% degradation was achieved within 4h. Raising the temperature to 40 and 60 °C significantly enhanced the process, attaining approximately 48.18 and 77.88% degradation, respectively. A further increase to 80 °C yielded only marginal improvement

(88.06%). This trend is attributed to the temperature-dependent acceleration of both persulfate activation (generating more $^{\bullet}SO_4^-$) and PHE dissolution, which collectively improve mass transfer and oxidation kinetics. Notably, while low temperatures suppress radical generation, excessively high temperatures can compromise process efficiency through radical-radical quenching. Moreover, they substantially increase operational costs. Therefore, considering both efficacy and practical feasibility for field application, 60 °C was selected as the optimal activation temperature for subsequent experiments [17].

Research has indicated that certain surfactants exhibit dual functionality, enhancing both the solubilization of organic pollutants and mitigating the decomposition of SPS, thereby augmenting the overall degradation process. As illustrated in Fig. 1e, the addition of C_{12}-MADS (at 1–10 g/dm^3) significantly increased PHE removal from soil by 14% to 18% at 16 h, compared to without C_{12}-MADS. The oxidative degradation of PHE in soil exhibited a gradual increase with escalating surfactant concentrations. Furthermore, the concentration of the surfactant governs its molecular arrangement as either monomers or micelles in aqueous environments. When the concentration surpasses the critical micelle concentration (CMC), surfactant micelles hinder the ingress of oxidants due to charge repulsion, thereby constraining the oxidative degradation of PHE. Consequently, based on this trade-off between solubilization and oxidant accessibility, a C_{12}-MADS concentration of 5 g/dm^3 C_{12}-MADS was selected for subsequent experiments.

As shown in Fig. 1c, increasing the oxidant dosage from 5 to 25 g/dm^3 markedly elicits a consistent and pronounced oxidation of PHE, increasing degradation efficiency from 69.36 to 89.81%. A further increase to 50 g/dm^3, however, resulted in only marginal improvement. This pattern arises from the relatively consistent decomposition of sulfate radicals at the same activation temperature, wherein higher concentrations of SPS engender an augmented generation of sulfate radicals, thereby enhancing the efficiency of PHE oxidative degradation. Given the low aqueous solubility of PHE, sufficient C_{12}-MADS is required to enhance its dissolution. Figure 1e confirms that raising the C_{12}-MADS concentration from 0 to 5 g/dm^3 significantly promotes PHE oxidation, while further escalation to 10 g/dm^3 provides additional benefit. Given the cost implications associated with higher concentrations of SPS and the desire for expedited remediation processes, an oxidant concentration of 25 g/dm^3 SPS was deemed optimal for subsequent experiments.

In summary, preliminary experiments established the following optimal conditions for effective PHE oxidation using the C_{12}-MADS-TAP system: an activation temperature of 60 °C, an initial persulfate concentration ($[Na_2S_2O_8]_0$) of 25.0 g/dm^3, and an initial C_{12}-MADS concentration ($[C_{12}\text{-MADS}]_0$) of 5.0 g/dm^3, balancing efficacy with economic and practical viability.

3.2. OXIDATION KINETICS OF PHE IN THE SOIL

The oxidation of PHE in soil involves a multifaceted reaction process shaped by external conditions and intrinsic soil properties. To gain deeper insights into this oxidation

process and discern the primary factors influencing PHE oxidation efficiency, kinetic modeling and analysis were performed. Nonlinear fitting analysis revealed that the oxidative degradation of soil-contaminated PHE adhered to a pseudo-first-order kinetic model, consistent with prior investigations[17]. The removal of soil-contaminated PHE could be effectively described by Eq. (4), where C_t and C_0 represent the PHE concentration ($mg \cdot kg^{-1}$) at reaction time t and the initial time, respectively, and k_{obs} denotes the pseudo-first-order rate constant (h^{-1}), which directly reflects the pollutant decay rate.

$$\ln \frac{C_t}{C_0} = -k_{obs} t \tag{4}$$

Table 1

Fitting parameters for PHE oxidation in soil under various conditions

Parameter		k_{obs} [h^{-1}]	R^2	$t_{1/2}$ [h]
Temperature, °C	25	0.0981	0.9408	7.0690
	40	0.2685	0.9948	2.5810
	60	0.6919	0.9982	1.0020
	80	0.7103	0.9995	0.9759
SPS, g/dm^3	5	0.4635	0.9927	1.4950
	10	0.4387	0.9983	1.5800
	25	0.6919	0.9990	1.0020
	50	0.7835	0.9983	0.8847
C_{12}-MADS, g/dm^3	0	0.3444	0.9945	2.0120
	1	0.4984	0.9906	1.3910
	2	0.5799	0.9958	1.1950
	5	0.6919	0.9982	1.0020
	10	0.6867	0.9997	1.0090

The pseudo-first-order kinetic fitting results for the C_{12}-MADS-TAP degradation of PHE-contaminated soil are summarized in Figs. 1b, d, f and Table 1. The observed k_{obs} exhibited a substantial increase with increasing temperature, from 0.0981 to 0.7103 h^{-1}, due to the enhanced conversion of SPS to $^{\bullet}SO_4^-$, which accelerated PHE oxidation. Consequently, the corresponding half-life time ($t_{1/2}$) generally decreased with increasing temperature. Similarly, k_{obs} rose with increasing oxidant concentration, reflecting higher oxidation efficiency. The $t_{1/2}$ decreased continuously from 1.4950 h to 0.8847 h, attributed to the abundance of persulfate radicals, facilitating increased reaction sites with PHE. Moreover, increasing the C_{12}-MADS concentration from 0 to 10 g/dm^3 also increased k_{obs} from 0.3444 to 0.6867 h^{-1}, confirming its positive role in promoting oxidation. However, beyond this concentration, a marginal reduction in oxidation efficiency was observed, likely due to excessive micelle formation in the aqueous solution hindering the diffusion of PHE

to sulfate radicals. This trend was also reflected in the $t_{1/2}$ values from the fitting results, as concentrations surpassing the CMC of C_{12}-MADS led to diminished reactivity of sulfate radicals in the solution.

3.3. THE EFFECT OF FIELD FACTORS ON THE PHE DEGRADATION

Figure 2 shows the effect of the water/soil ratio on PHE oxidation efficiency and the corresponding kinetic parameters. The increase of the water/soil ratio from 1:1 to 20:1 led to a more homogeneous dispersion of soil (Fig. 2a) due to the higher aqueous volume, which in turn increased the available oxidant and enhanced PHE degradation from 12.79 to 82.79% after 4 h.

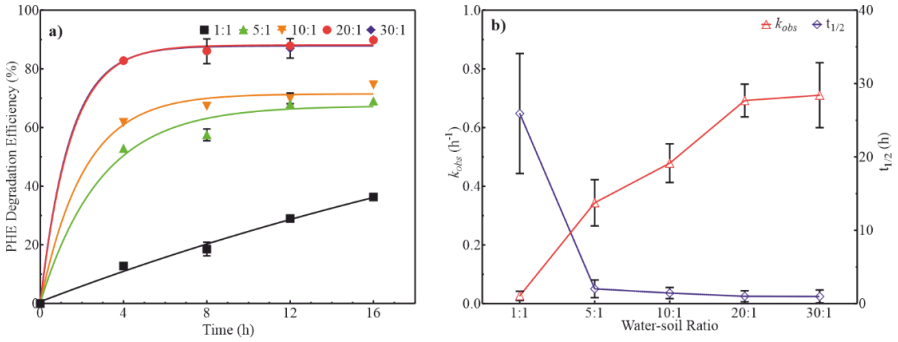

Fig. 2. The effects of water/soil ratios on the degradation of PHE in soil by C_{12}-MADS-TAP:
a) effectiveness of oxidative degradation of PHE and nonlinear fitting curves,
b) k_{obs} and $t_{1/2}$ of PHE degradation under various water/soil ratios;
$[PHE]_0$ = 100 mg/kg, $[C_{12}\text{-MADS}]$ = 5 g/dm^3, [SPS] = 25 g/dm^3, reaction time = 16 h, no pH adjustment

Table 2

Fitting parameters of the PHE oxidation at various conditions

Parameter		k_{obs} [h^{-1}]	R^2	$t_{1/2}$ [h]
Water/soil ratio	1:1	0.0267	0.9915	25.9200
	5:1	0.3439	0.9867	2.0160
	10:1	0.4787	0.9950	1.4480
	20:1	0.6922	0.9991	1.0010
	30:1	0.7104	0.9958	0.9758
pH	6	0.4358	0.9812	1.5910
	7	0.1254	0.9867	5.5300
	8	0.0546	0.9938	12.6900
Coexisting ions[a]	Cl^-	0.5976	0.9964	1.1600
	HCO_3^-	0.2301	0.9940	3.0120
	CK	0.6922	0.9991	1.0010

[a]Concentration of the coexisting ions – 1 mol/dm^3, CK – no ions added.

Consistent with this trend, Fig. 2b and Table 2 illustrate a substantial increase in the k_{obs} value with increasing water/soil ratio, nearly 26-fold, accompanied by a reduction in $t_{1/2}$ from 25.92 to 1.001 h. This improvement arises from the enhanced fluidity of the solution at a higher water/soil ratio, facilitating optimal contact between $^{\bullet}SO_4^-$ and PHE within the soil matrix. However, once the soil was fully dispersed at a water/soil ratio of 20:1, further increases yielded minimal gains: degradation efficiency increased by only 0.21%, k_{obs} and $t_{1/2}$ changed only marginally. Comparable findings were reported by Peng et al. [18] in a study, which observed improved removal efficiency with increasing water/soil ratio during the study of PHE removal from soil via microwave-activated persulfate.

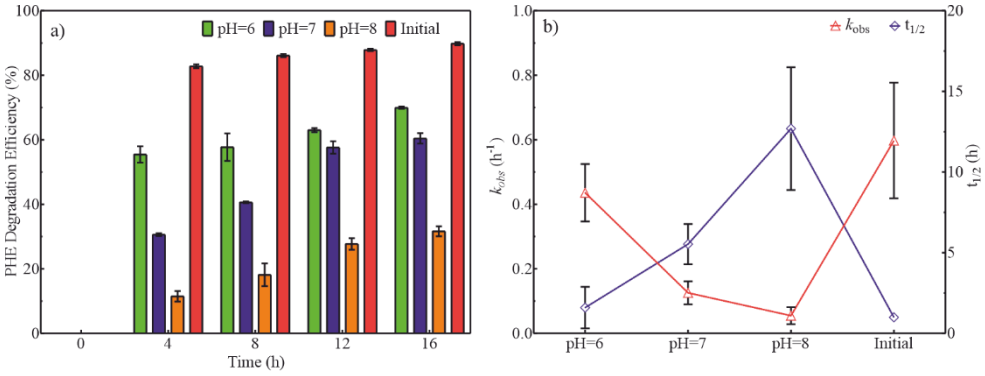

Fig. 3. The effects of pH on the degradation of PHE in soil by C_{12}-MADS-TAP: a) effectiveness of oxidative degradation of PHE, b) k_{obs} and $t_{1/2}$ of PHE degradation under various pH; $[PHE]_0$ = 100 mg/kg, $[C_{12}$-MADS] = 5 g/dm^3, [SPS] = 25 g/dm^3, reaction time = 16 h, water/soil ratio = 20:1

The effect of pH on on PHE oxidation is shown in Fig. 3 and Table 2. As pH increased from 6 to 8, the PHE degradation efficiency over 16 h decreased from 89.80 to 31.64%. Correspondingly, the k_{obs} exhibited a decrease from 0.4358 to 0.0546 h^{-1}, while the resulting $t_{1/2}$ increased from 1.59 to 12.69 h. These results align with previous research on persulfate-based oxidation. For example, Deng et al. [19] reported that the degradation rate constant of carbamazepine (CBZ) also decreased with increasing pH. The k_{obs} value for PHE oxidation at pH 7 in our system (0.1254 h^{-1}) was higher than the corresponding value for CBZ degradation (0.013 min^{-1}), suggesting that the added surfactant helps to stabilize and enhance SPS oxidation. The decrease in efficiency with increasing pH can be explained by two main mechanisms. Acid-catalyzed persulfate radical generation in acidic environments has been reported to accelerate the oxidative degradation of PHE [20, 21]. Therefore, an increase in pH diminishes the effect of acid catalysis, consequently reducing the reaction rate. In comparison to the reaction system without pH adjustment, the removal efficiency, k_{obs}, and $t_{1/2}$ exhibited superior performance at pH values of 6, 7, and 8. This is

attributed to the sulfate radical triggering a series of chain reactions, with free radicals undergoing quenching reactions and ultimately terminating the reaction. Moreover, in weakly alkaline conditions, side reactions such as those described in Eqs. (5)– (8) become dominant: $^{\bullet}SO_4^-$ is consumed by $^{\bullet}OH$ to form HSO_4^- and oxygen, thereby reducing the availability of radicals for PHE degradation

$$^{\bullet}SO_4^- + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \quad (5)$$

$$^{\bullet}SO_4^- + {}^{\bullet}OH \rightarrow HSO_4^- + 1/2O_2 \quad (6)$$

$$^{\bullet}SO_4^- + H_2O \rightarrow SO_4^{2-} + H^+ + {}^{\bullet}OH \quad (7)$$

$$^{\bullet}OH + 2RH \rightarrow 2R^{\bullet} + H_2O + H^+ \quad (8)$$

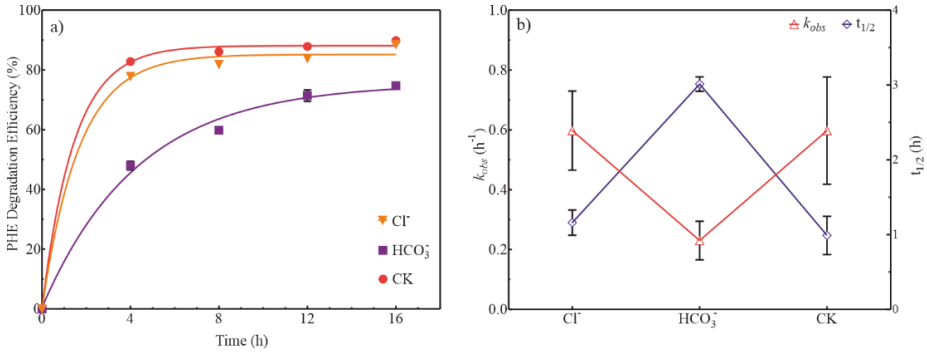

Fig. 4. The effects of coexisting ions on the degradation of PHE in soil by C_{12}-MADS-TAP: a) effectiveness of oxidative degradation of PHE and nonlinear fitting curves, b) c_{obs} and $t_{1/2}$ of PHE degradation under presence of coexisting ions; $[PHE]_0$ = 100 mg/kg, water/soil ratio = 20:1, $[C_{12}\text{-MADS}]$ = 5 g/dm^3, and [SPS] = 25 g/dm^3, $[Cl^-]$ = 1 mol/dm^3, $[HCO_3^-]$ = 1 mol/dm^3, reaction time = 16 h, no pH adjustment

Figure 4 and Table 2 present the influence of inorganic anions on PHE degradation kinetics. Both Cl^- and HCO_3^- inhibited oxidation, with HCO_3^- exhibiting a stronger inhibitory effect than Cl^-. In the absence of added ions, the k_{obs} value was 0.6922 h^{-1}; adding 1 M Cl^- or HCO_3^- reduced k_{obs} to 0.5976 h^{-1} and 0.2301 h^{-1}, respectively. After 4 h of treatment with C_{12}-MADS-TAP, PHE degradation decreased from 82.79 to 77.88% with Cl^- and to 47.98% with HCO_3^-. The stronger inhibition by HCO_3^- is attributed to its efficient scavenging of $^{\bullet}SO_4^-$, generating less reactive carbonate radical ($^{\bullet}HCO_3$) (Eq. (9)) [22, 23]. Additionally, HCO_3^- increased soil pH, promoting the $^{\bullet}SO_4^-$ reaction with OH^- to generate $^{\bullet}OH$ (Eq. (5)), which further reduces oxidation efficiency [24]. Similarly, in PHE-contaminated soils with elevated Cl^- levels, the oxidative degradation efficiency of

PHE slightly decreased due to Cl^- consumption of $^{\bullet}SO_4^-$ and the formation of low-activity chlorine radicals such as $^{\bullet}Cl$ and $^{\bullet}Cl_2^-$ (Eqs. (10), (11)) [19, 20]. The redox potentials of Cl^--containing radicals are much lower than the 2.6 V of $^{\bullet}SO_4^-$, and both $^{\bullet}Cl$ and $^{\bullet}Cl_2^-$ can further react with each other to ultimately produce Cl^- and Cl_2 (Eqs. (12), (13)), thereby diminishing overall oxidative capacity [19, 25, 26].

$$^{\bullet}SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + {}^{\bullet}HCO_3 \quad (9)$$

$$^{\bullet}SO_4^- + Cl^- \rightarrow SO_4^{2-} + {}^{\bullet}Cl \quad (10)$$

$$^{\bullet}Cl + Cl^- \rightarrow {}^{\bullet}Cl_2^- \quad (11)$$

$$2{}^{\bullet}Cl_2^- \rightarrow Cl^- + Cl_3^- \quad (12)$$

$$^{\bullet}Cl + {}^{\bullet}Cl \rightarrow Cl_2 \quad (13)$$

3.4. THE EFFECT OF C_{12}-MADS-TAP APPLICATION ON THE SOIL PROPERTIES

Advanced oxidation processes often exert significant impacts on key soil properties during soil remediation [27]. The oxidation process induced by C_{12}-MADS-TAP in soil elicits alterations in soil properties owing to its potent oxidizing nature. As illustrated in Figure 5, the C_{12}-MADS-TAP system induced pronounced changes in soil pH, soil organic matter, and CEC compared to the control group. Soil pH dropped sharply from approximately 6.89 to 3.1, indicating significant acidification and structural alteration. Soil organic matter registers a significant reduction, declining from 2.66 to 1.15 g/kg (a 43.23% decrease) in the blank system and declining from 2.54 to 0.91 g/kg (a 64.17% decrease) in the C_{12}-MADS-TAP remediation system. This accelerated decrease in soil organic matter during C_{12}-MADS-TAP oxidation remediation can be attributed to the depletion caused by the oxidizing effect of SPS. The CEC underwent substantial decreases of 91.91 (blank) and 94.14% (C_{12}-MADS-TAP), decreasing from initial values of 16.82 and 15.69 cmol/kg to 1.36 and 0.92 cmol/kg, respectively, indicating a more pronounced impact of the treatment on soil exchange sites. This reduction is likely due to the oxidative process lowering soil pH, leading to H^+ occupying the soil surface and reducing ion exchange capacity. Analogous effects have been reported by other researchers investigating the SPS system in the remediation of contaminated soils. Tsitonaki et al. [28] demonstrated a significant decrease in initial soil pH proportional to the persulfate dosage. Additionally, Liang et al. [27] observed a decrease in total organic carbon (TOC) in silt following the application of chemical oxidants such as persulfate, peroxide, and permanganate.

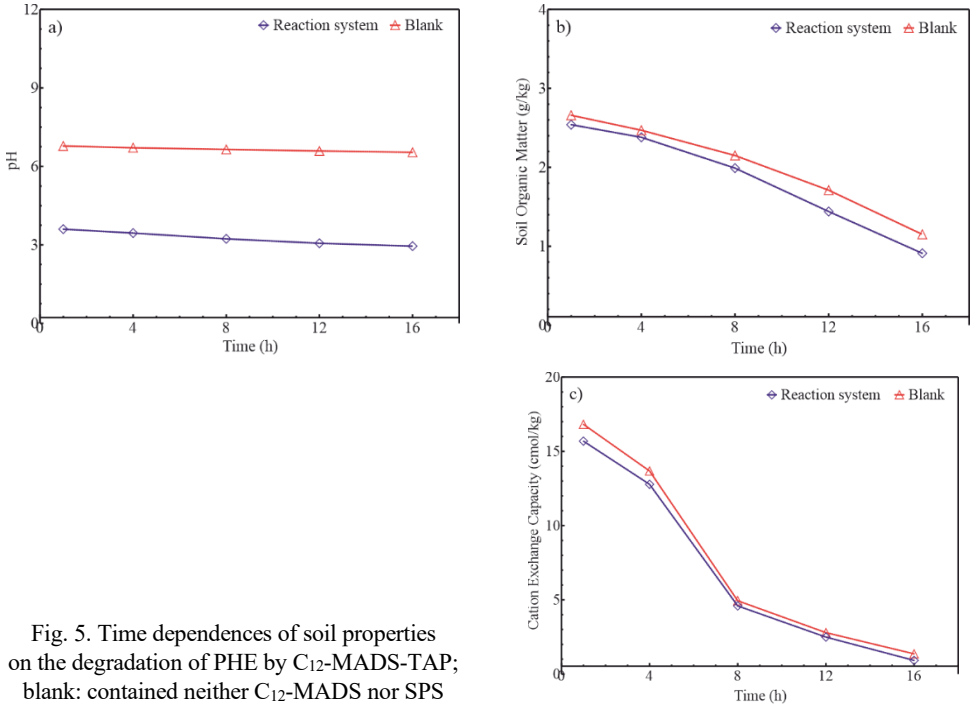

Fig. 5. Time dependences of soil properties on the degradation of PHE by C_{12}-MADS-TAP; blank: contained neither C_{12}-MADS nor SPS

4. CONCLUSIONS

This study systematically established an efficient C_{12}-MADS-TAP system for remediating PHE-contaminated soils by optimizing the activation temperature, surfactant concentrations, and persulfate dosage. The system's performance was further evaluated under varied field-relevant conditions, including pH, water/soil ratio, and coexisting ions, while monitoring associated changes in soil properties. These investigations aimed to assess the applicability of C_{12}-MADS-TAP for ISCO and to provide actionable insights for field implementation. Key operational parameters were identified: a C_{12}-MADS concentration of 5 g/dm^3, and a persulfate dosage of 25 g/dm^3, collectively delivered high degradation and cost-effectiveness. Under these conditions, the degradation kinetics of PHE followed pseudo-first-order kinetics, with the reaction rate constantly increasing by 99% from 0.3444 to 0.6867 h^{-1} upon surfactant addition. Environmental factors significantly influenced treatment outcomes. Elevated soil moisture (water/soil ratio = 20:1) promoted contaminant solubilization and radical contact, achieving a remarkable degradation efficiency of 89.8% with k_{obs} = 20.6922 h^{-1} and $t_{1/2}$ = 1.0010 h. Acidic conditions favored $^{\bullet}SO_4^-$ sta-

bility and activity, whereas near-neutral to alkaline pH reduced oxidation rates. Co-existing anions also modulated efficiency: Cl^- induced mild inhibition, while HCO_3^- caused more pronounced suppression due to radical scavenging and pH elevation. While enhancing the oxidative degradation of phenanthrene, the C_{12}-MADS-TAP system inevitably perturbs the physicochemical properties of the soil. On one hand, the oxidation process disrupts soil aggregate structure, alters pore permeability, and, due to oxidant decomposition, leads to a decline in pH, triggering soil acidification. On the other hand, the non-selective oxidation by reactive radicals depletes soil organic matter, thereby impairing the soil's nutrient retention capacity and biological activity. Therefore, in practical remediation applications, a comprehensive evaluation integrating site-specific geological conditions and intended post-remediation land use is essential to identify the optimal technological solution that balances environmental disturbance with remediation efficacy.

Practical implications for field application include:

- Pre-remediation assessment. Site characterization should prioritize soil moisture, pH, and background ions (especially HCO_3^-) to anticipate and counteract potential inhibition.
- Operational tuning. Adjusting the water/soil ratio (toward 20:1) and maintaining slightly acidic conditions can maximize radical utilization.
- Surfactant-oxidant synergy. The selected C_{12}-MADS concentration (5 g/dm^3) balances solubilization enhancement with oxidant preservation, avoiding micellar hindrance.
- Post-treatment evaluation. Monitoring soil pH and nutrient status is recommended to gauge secondary impacts and guide possible soil restoration.

Given its robust performance under diverse conditions and manageable soil impacts, C_{12}-MADS-TAP represents a promising strategy for field-scale ISCO. Pilot-scale trials are recommended to validate its adaptability across heterogeneous site conditions and to refine implementation protocols for long-term remediation success.

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