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Research Article

Potential risks of organic contaminated soil after persulfate remediation: Harmful gaseous sulfur release

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ABSTRACT

Persulfate is considered a convenient and efficient remediation agent for organic contaminated soil. However, the potential risk of sulfur into the soil remediation by persulfate remains ignored. In this study, glass bottles with different persulfate dosages and groundwater tables were set up to simulate persulfate remediation of organic pollutants (aniline). The results found sulfate to be the main end-product (83.0%–99.5%) of persulfate remediation after 10 days. Moreover, H₂S accounted for 93.4%–99.4% of sulfur reduction end-products, suggesting that H₂S was the final fate of sulfur. H₂S was released rapidly after one to three days at a maximum concentration of 33.0 ppm, which is sufficient to make a person uncomfortable. According to the fitted curve results, H₂S concentration decreased to a safe concentration (0.15 ppm) after 20–85 days. Meanwhile, the maximum concentration of methanethiol reached 0.6 ppm. These results indicated that secondary pollution from persulfate remediation could release harmful gases over a long time. Therefore, persulfate should be used more carefully as a remediation agent for soil contamination.

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Introduction

Soil contamination is a global environmental problem occurring in most countries (Li, 2018; Mandal et al., 2022; Nguyen et al., 2021; Tapia-Gatica et al., 2022; Tiankao and

Chotpantarat, 2018). In China, contaminated soil covers more than 5.6 million km² (Li, 2018; Tiankao and Chotpantarat, 2018). The main types of soil contamination are organic contamination and heavy metal contamination. Organic contamination mainly includes polycyclic aromatic hydrocarbons, organic chloride, and pesticide pollutants among others. These contaminants are highly toxic, difficult to biodegrade, and greatly impede soil remediation (Gao et al., 2019; Raschitor et al., 2019). Overall, soil organic contamination has

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become an important problem restricting social and economic development.

Of the current technologies for organic contaminated soil remediation, in-situ chemical oxidation is widely used (Angkaew et al., 2019; Liao et al., 2014; Peng et al., 2015). Persulfate is the most popular agent for in-situ chemical oxidation remediation due to its high redox potential, low cost, and relatively low environmental toxicity (Angkaew et al., 2019; Peng et al., 2015). After activation (Hu et al., 2020), persulfate generates sulfate and hydroxyl radicals with high redox potentials (Liu et al., 2019; Zhou et al., 2018), which subsequently completely degrades most organic pollutants (Zhou et al., 2019). Several studies have explored the use of persulfate for the remediation of organic contaminated soils, with dosages ranging from 40%–80% (converted by mass to ratio of persulfate to soil) (Wei et al., 2022; Xue et al., 2022). These are substantial amounts of persulfate added to the soil for better remediation effects. However, such large dosages rarely exist in everyday engineering, which carries visible costs and consequences. In true engineering, the amount of persulfate rarely exceeds 3% (Li et al., 2021). Studies looking at these low levels of persulfate usually introduce microbes to achieve better remediation effects. For example, Li et al. (2021) used persulfate coupled microbial fortification to remediate phenanthrene-contaminated soil, at a maximum dosage of 2.38% and a maximum removal rate of 84%. However, even at 2.38%, a very large amount of persulfate still enters the soil during the remediation process.

When the target pollutant concentration falls below the limit, the soil remediation program is often declared finished. However, little attention is paid to the abundant persulfate left in the soil after remediation. It has been reported that the physical and chemical properties of the soil, and the landscape, may be permanently altered because of the added sulfate (produced by persulfate reaction) (Amina et al., 2022; Vithana et al., 2021), which introduces certain potential risks (Ji et al., 2017). For example, it dramatically changes the properties of the soil and its microbial communities (Fortunato et al., 2021). Xue et al. (2022) pointed out that after the addition of 23.8% persulfate, the pH of the soil decreased from 7.6 to 3.6, thereby creating a highly acidic environment. It is bound to affect the properties and functions of the soil itself. Concurrently, the conductivity and cation exchange capacity of the soil changes dramatically. Li et al. (2021) found that after the addition of 2.38% persulfate, the microbial structure in the soil significantly changed. Here, 43 species at an abundance of > 1% were reduced to only a dozen species, suggesting that persulfate addition reduces soil microbial diversity. Moreover, persulfate will continue to seep through the soil and into the groundwater (Xue et al., 2022), further expanding the range of potential risks. Unfortunately, these issues have not received enough attention.

Sulfate, as the main product of persulfate activation, will remain in the soil for a long time (Cao et al., 2022). Relevant studies have shown that the soil environment contains a large amount of sulfate, which, when used by anaerobic sulfur-reducing bacteria, may produce reductive and harmful hydrogen sulfide gas (Olivera et al., 2022). This has been demonstrated in the landfill field (Liu et al., 2018; Ying et al., 2019). In these anaerobic environments of soil and ground-

water, the accumulated sulfate is likely treated as an electron acceptor and undergoes reduction by sulfate-reducing bacteria (SRB). Moreover, the soil is rich in organic materials, which serve as electron donors. These conditions create an environment for sulfate reduction, leading to the release of H₂S (Olivera et al., 2022). H₂S is problematic because of its low odor threshold (around 0.5 ppm) and high toxicity (Ying et al., 2019). An odor concentration and human health risk assessment showed that the non-carcinogenic risk of H₂S reached 2.3, which exceeded the acceptable level and posed a risk to human health (Ying et al., 2019). A multitude of similar reports has been released over the years (Jin et al., 2020; Liu et al., 2018; Liu et al., 2019; Ying et al., 2019). In all of these studies, the H₂S concentration exceeded the low odor threshold, with the highest concentration reaching about 4500 ppm. Meanwhile, H₂S is always produced, even without anaerobic conditions (Ying et al., 2019). In addition to sulfur-rich landfills, H₂S release can pose a problem in other environments. For example, Kryger and Lee (1995) showed that a large amount of H₂S is released in subtropical forest soils in southern China. Forests tend to have a lot of rainfall, and consequently possess wet soil, creating an anaerobic environment. Subtropical forests can produce 28 ppm of H₂S when the sulfur content in the soil is much lower than that in landfills. This indicates that hydrologic conditions can also intensify the generation and release of H₂S. However, organic contaminated soil after persulfate remediation contains very high sulfate levels and anaerobic hydrologic conditions (Cao et al., 2022). It can therefore be predicted that H₂S will be released in a large amount and cause harm to the soil after persulfate remediation. Moreover, the gaseous sulfur produced by SRB may also contain organic sulfur such as methanethiol, which has a lower odor threshold (7e-5 ppm). A small amount of methanethiol can cause great harm. This further increases the potential risk of contaminated soil (Jin et al., 2020) and is a cause for concern.

Currently, no research is being conducted on the possible H₂S emission caused by accumulated sulfate following soil remediation by persulfate. This study simulated organic contaminated soil remediation by persulfate and investigated the transformation and location of the persulfate entering the soil. Moreover, the release behaviors of H₂S and organic sulfur were recorded in different remediation scenarios. The results obtained in this study will help to assess the potential risk of sulfur in organic contaminated soil after persulfate remediation and provide guidance for the determination of persulfate dosage in practical soil remediation processes.

1. Materials and methods

1.1. Organic contaminated soil simulation

Natural soil was collected from the campus of Zhejiang Gongshang University, Hangzhou, China. Thirty kilograms of soil was screened using a 2.36 mm sieve to remove inert fractions such as gravel and grass leaves. The basic properties of screened soils are as follows: soil bulk density 1.42 ± 0.17 g/cm³, soil porosity $45.4\% \pm 6.6\%$, pH 6.78 ± 0.05 , conductivity 26.8 ± 2.3 μS/cm, SOM 23.6 ± 8.1 g/kg, ammonia nitrogen 5.15 ± 1.19 mg/kg, and sulfate 42.1 ± 4.6 mg/kg. An aniline aqueous solu-

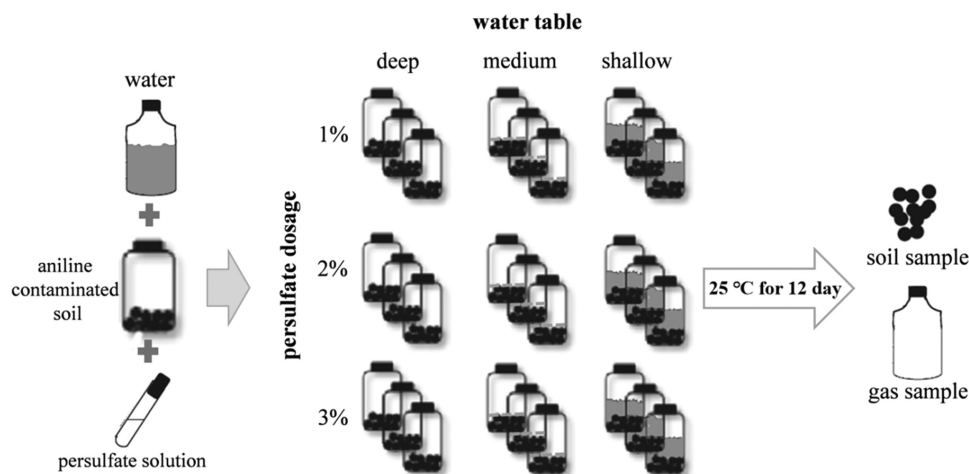


Fig. 1 – Experimental flow chart.

tion was added to the screened soil at a concentration of 5,588 mg/kg (60 mmol/kg), which was approximately 8.5 times the maximum limit of the Chinese standard (GB36600-2018). The soil was stirred evenly to simulate the organic contaminated soil.

1.2. Soil remediation experiment design

Two variables at three levels were simulated, namely persulfate dosage (1% (1), 2% (2), and 3% (3) (by mass ratio of persulfate to soil)) and groundwater table (deep (D), middle (M), and shallow (S)), yielding nine experimental groups (1D, 1M, 1S, 2D, 2M, 2S, 3D, 3M, and 3S). The experimental process is outlined in Fig. 1. Each group comprised a glass bottle (5 cm diameter, 250 mL volume) containing 210 g of contaminated soil and 10 mL of persulfate. For the high water table, no water was added. For the middle water table, water was added to reach 50% of the soil layer. For the shallow water table, enough water was added to flood the soil. Contaminated soil, persulfate solution, and water were added in turn. The glass bottles were maintained at room temperature (25 °C) away from direct sunlight. Additional glass bottles were used to collect gas samples to prevent damaging the air tightness of the glass bottles during sample collection. Two grams of soil samples were collected every 5 days, and 1 mL of gas samples were collected every day for analysis. For each group, beakers with the same experimental conditions were set to determine aniline after 60 min. All group protocols were repeated thrice.

1.3. Sample measurements

Ethanol was added for aniline determination or distilled water for other indexes to the soil samples at the ratio of 1:10 (solid: liquid). The solution was shaken at 200 r/min for 6 hr (25 °C) and filtered. Aniline, ammonium, and nitrite were measured using spectrophotometry and the following chromogenic reagents: naphthalene ethylenediamine hydrochloride (aniline) (Li et al., 2022), alkaline sodium hypochlorite solution (ammonium) (Xiong et al., 2021), and sulfanilamide and naphthalene ethylenediamine hydrochloride (ni-

trite) (Xiong et al., 2021). Sulfate content was determined using water quality monitor (ZY-360, Luheng Company, Hangzhou, China). Sulfite, thiosulfate, and nitrate were measured using methodologies from our previously published papers (Jin et al., 2020; Ying et al., 2019). Gas samples were used for gas chromatography to measure H₂S, methanethiol, CO₂ and CH₄. H₂S and methanethiol were measured using the GC-FPD instrument (7890A, Agilent Technologies, Santa Clara, CA, USA) and CO₂ and CH₄ were measured using a GC 7890II instrument (Tianmei Company, Shanghai, China) (Jin et al., 2020; Ying et al., 2019).

1.4. Statistical analyses

Statistical analyses were performed in SPSS 22.0, and standard deviations (SDs) were obtained using descriptive statistics. An H₂S concentration curve was fitted using a first-order kinetic curve (Eq. (1)) and a methanethiol concentration curve using a unary linear curve (Eq. (2)).

$$C = C_m e^{-k_1(x-t)} \quad (1)$$

where C (ppm) is the H₂S concentration; C_m (ppm) is the maximum H₂S concentration; t (day) is the date of maximum concentration; x (day) is the date; and k_1 is the H₂S reaction rate constant.

$$y = k_2 x + b \quad (2)$$

where y (ppm) is the methanethiol concentration; k_2 (ppm/day) is the methanethiol reaction rate constant; x (day) is the date; and b (ppm) is the intercept.

2. Results and discussion

2.1. Conversion of persulfate in soil after remediation

After persulfate addition, the aniline in the soil degraded within 10 min (Appendix A Fig. S1), and a large amount of

CO₂ was generated within one day of incubation (Appendix A Fig. S2), confirming the decomposition of organic pollutants. These results indicated that the remediation effect of persulfate was excellent.

Only 0.042 g/kg sulfate were detected in non-treated soil samples, which is negligible compared to the sulfate produced from persulfate added to the soil (5.8~17.7 g/kg soil). Thus, added persulfate was almost the only source of sulfur. Persulfate was rapidly converted to sulfate during the aniline oxidation process. The sulfate concentration converted by all the added persulfate was considered as the theoretical maximum concentration (Liu et al., 2022) and the ratios of actual sulfate concentration to the theoretical maximum concentration (calculated according to Appendix A Eq. (S1)) are showed in Fig. 2. After 1 day, the sulfate ratio ranged from 48.2% to 98.4%. The sulfate ratio slowly increased during further incubations. It increased to 70.4% and 94.4% after 5 days and 82.9% and 99.5% after 10 days. However, aniline was almost completely degraded as early as 60 min following persulfate addition (Appendix A Fig. S1). Hence, the subsequent sulfate increase may result from the reaction of persulfate with natural organic matter in the soil or from natural decay. For the deep water table groups, the sulfate ratio increased from 84.6% after 1 day to 98.5% after 10 days at a 1% persulfate dose (1D) (Fig. 2a). When the dose was increased to 2% (2D), the sulfate ratio range decreased from 86.0% to 78.2%, and when it was increased to 3% (3D), the sulfate ratio range decreased from 84.1% to 73.8%. Thus, increasing the persulfate dosage reduced the sulfate produced rate. It may be that a higher persulfate dosage requires more time to convert. For middle water table groups, the sulfate ratios after the 1st day were lower than those of the deep water table groups (2D and 3D) and ranged from 63.3% to 69.1%. The only exception was for the 1% persulfate dosage group (Fig. 2b). After 10 days, however, the ratio increased to 94.6%–95.6%, which was higher than the deep water table groups. The same phenomenon was observed for the shallow water table groups (Fig. 2c). The sulfate ratios increased from 48.2%–64.6% to 96.9%–99.5%. These results indicated that increasing the water table slowed down sulfate production during the initial stages of the reaction (1 day) but increased it during the subsequent stages (10 days). The results in this study are in keeping with the results of other studies. For example, Li et al. (2021) used persulfate to repair phenanthrene-contaminated soil. Three days after adding 2.38% persulfate, the persulfate consumption rate of each group was above 53%. After 14 days, the persulfate consumption rate of each group ranged from 92%–97%. Overall, the increase in persulfate dosage always reduced the rate of sulfate production. The groundwater table will reduce the early production rate and increase the late production rate. These results indicate that sulfate may be the primary destination of persulfate after entering the soil. While persulfate dosage and the water table may influence this conversion rate, it does not prevent the process from happening.

Although sulfate converted from persulfate is not considered harmful, it still poses a potential risk. Moreover, resident SRB in the soil can convert sulfate into other products. This phenomenon occurs more frequently in high sulfate concentration environments, like landfills (Ying et al., 2019). Hence,

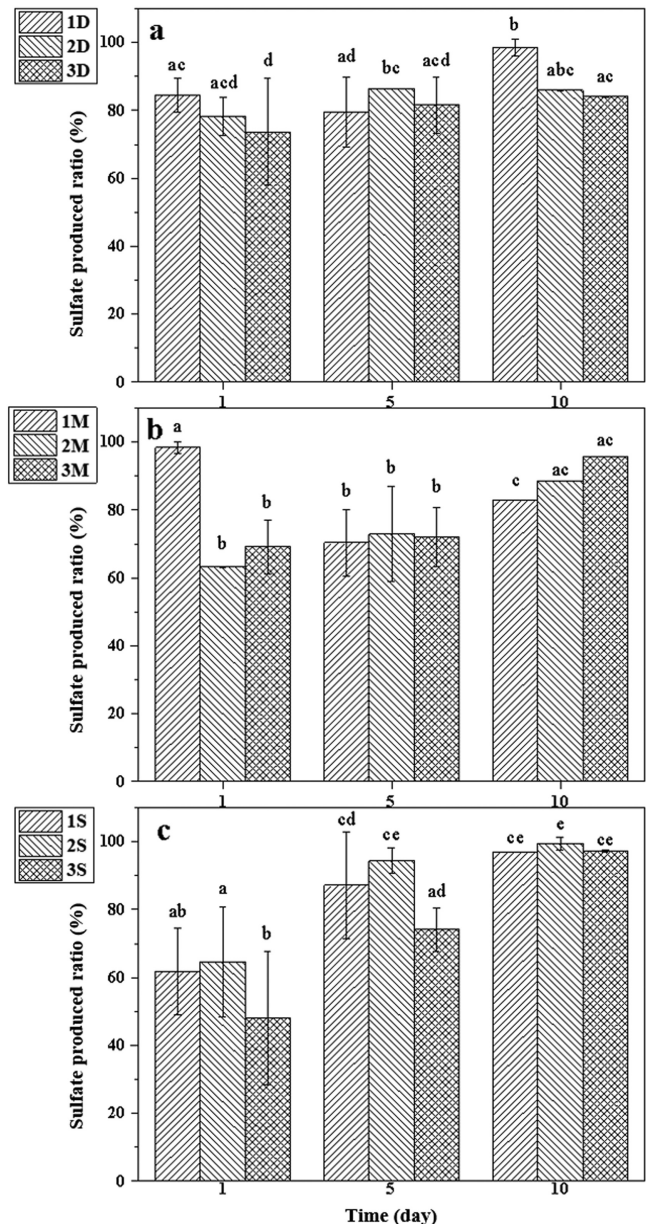


Fig. 2 – The ratios of sulfate produced to the theoretical maximum in the different experimental groups. a: Deep water table; b: Middle water table; c: Shallow water table. The lowercase letters above the columns present significant differences.

the potential risks of sulfate reduction by SRB cannot be ignored.

2.2. Inorganic gaseous sulfur production in the soil after persulfate remediation

In this study, some gases were produced during the incubation, the volume of which is shown in (Appendix A Fig. S3). The average gas production was 46.5 mL when 3% persulfate was added, and decreased remarkably when the dose of persulfate is reduced. Among them, H₂S was detected in high concentration, suggesting that sulfate was not the fate of per-

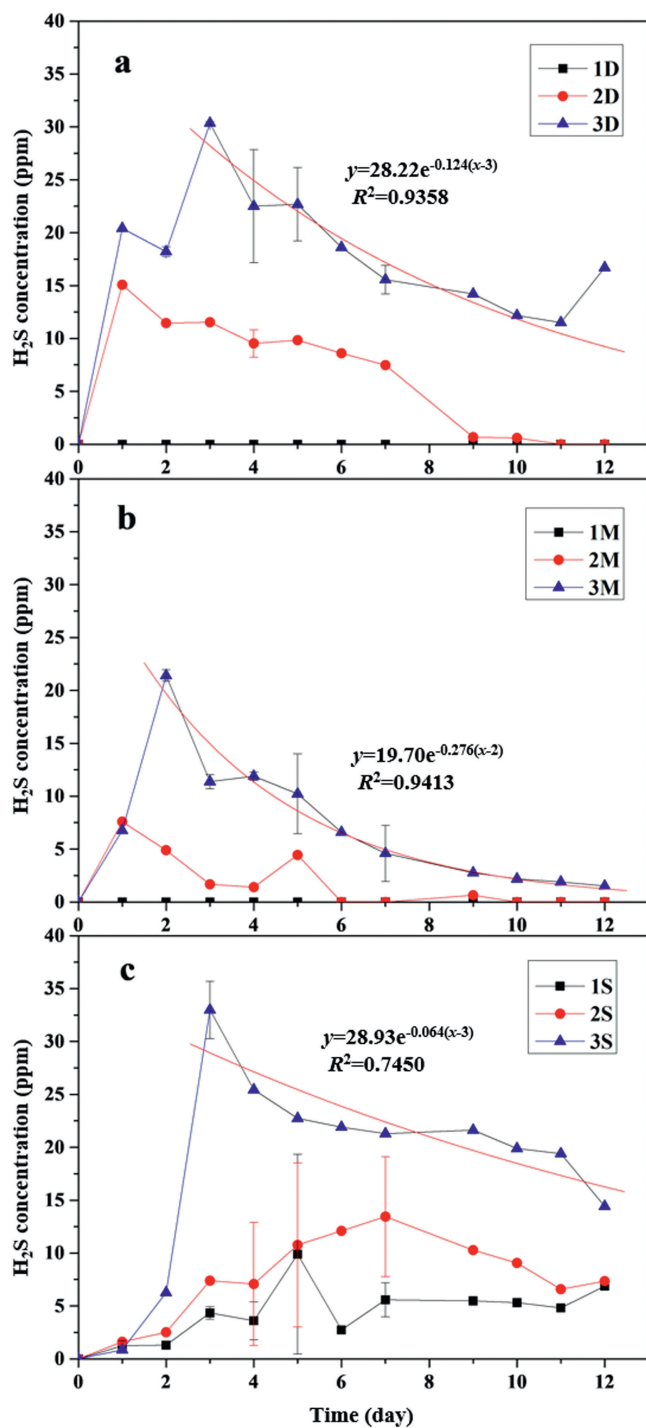


Fig. 3 – H₂S production for all groups and the fitted curves for the 3% (W/W) dosage groups. **a:** Deep water table; **b:** Middle water table; **c:** Shallow water table.

sulfate; however, the gaseous sulfur generated by SRB was. The highest concentration observed for H₂S was 33.0 ppm (Fig. 3c), which is an extremely dangerous level for human beings (Ying et al., 2019; Yu et al., 2018). This demonstrates that persulfate is not completely harmless.

H₂S is the inorganic form of gaseous sulfur released from soil. H₂S was not detected in the 1D and 1M groups; there-

fore it will not be discussed. The results of H₂S production in the other groups and their fitted curves for the 3% dosage groups, are shown in Fig. 3. Except for the 1S and 2S groups, all the groups released H₂S of different concentrations within 1 day and reached the maximum concentration within three days. After three days, the H₂S concentrations started to decrease. After the addition of persulfate into the soil, a large amount of sulfate substrate could stimulate the activity of SRB, resulting in the rapid generation of H₂S after 1–3 days. With the consumption of electron donors (e.g., organic carbon sources, including the organic pollutant), the SRB activity decreased, and consequently, H₂S concentrations dropped. As the main end-product of pollutant oxidation, CO₂ production sharply increased in the first 5 days and then leveled off, indicating variations in microbial activity (Appendix A Fig. S2). Therefore, in these groups, a large amount of H₂S was produced when the sulfate and carbon sources were sufficient at the beginning of the oxidation process. When these substrates became depleted, the production rate of H₂S decreased significantly, and the H₂S concentrations began to decline. As for 1S and 2S groups, less H₂S and CO₂ were produced after 3 days compared to the other groups. However, in the subsequent process, H₂S concentrations continued to increase after 3–7 days and subsequently declined more slowly. Meanwhile, the concentrations of CO₂ increased with time (Appendix A Fig. S2). This may be because the higher water table dissolved some of the H₂S and inhibited the release of the gasses. Owing to increased gas production, the inhibition of the water table showed no significant effect on gaseous sulfur release in the 3S group. Therefore, the above phenomenon was not significant in the 3S group. In short, the H₂S release concentration increased with the increase in persulfate dosage, and the production of H₂S by sulfate reduction was a rapid process. The maximum H₂S concentration was achieved within three days, reaching dangerous levels for human beings. Moreover, high water tables can prevent H₂S release, delaying the occurrence of the maximum H₂S concentration appeared.

Although the short-term release of H₂S is concerning, it should also be noted that H₂S will continue to be released in the long-term, therefore posing a long term risk. The decrease in H₂S in the 3% dosage groups after reaching the maximum concentration showed obvious regularities. To further clarify the release process of H₂S and its long-term potential risks, the fitted curves were calculated using Eq. (1) (Fig. 3). The C_m values in descending order were 28.93 (3S), 28.22 (3D), and 19.70 (3M), indicating that H₂S production was highest in the 3S group. The k_2 absolute values in descending order were 0.276 (3M), 0.124 (3D), and 0.064 (3S), indicating that H₂S decayed the fastest in the 3M group. The order of the reaction rate constant (k) was opposite to that of C_m . This is consistent with the fact that groups with faster decay rates H₂S tend to have lower maximum concentrations. It can be observed that both persulfate dosage and the water table have a great influence on sulfate production and H₂S release. A high sulfate dosage will increase the sulfur content in the soil, which will inevitably increase soil potential risk. The water table increases the potential risk in soil by creating an anaerobic environment. These results are in keeping with previously published studies. Kryger and Lee (1995) found that high levels of H₂S release in mangrove soils are caused by

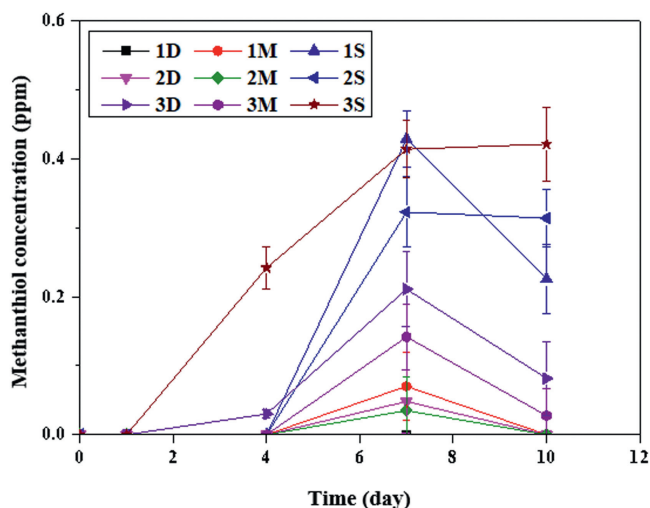


Fig. 4 – Methanethiol concentration produced in all groups. D: Deep water table. M: Middle water table. S: Shallow water table.

the anaerobic environment created by frequent soil flooding. Jin et al. (2020) studied the release of H_2S in the saturated zone of landfill leachate (high sulfur content and a shallow water table), with findings similar to our study. When the addition ratio of sulfate was 0.41% (ca. 0.68% persulfate), a maximum H_2S of ca. 4,500 ppm was produced, much higher than that reported in this paper. This is because the research environment they reported is closer to a completely anaerobic environment. Moreover, the concentration of H_2S reached its peak after four days under all conditions, and then decreased rapidly, which is consistent with our findings. Overall, persulfate dosage and the water table influenced the release concentration and behavior of H_2S by changing soil substrates and oxygen conditions.

It was generally believed that when the H_2S concentration was lower than 0.15 ppm, the “rotten egg smell” would not be detectable and was therefore considered a safe concentration (Long et al., 2017). According to the fitting results (Fig. 3), the H_2S concentration would drop to below 0.15 ppm after 46, 20, and 85 days for the 3D, 3M, and 3S groups respectively. This indicated that the H_2S released from soil maintained a hazardous concentration for a long period after the remediation process. Hence, the contaminated soil remediated by persulfate had obvious secondary pollution characteristics. However, when the persulfate dosage decreased, its harmfulness greatly reduced, which has guiding significance for the selection of dosage in the actual remediation process and must be considered when using persulfate as a remediation reagent.

2.3. Gaseous sulfur production process in the soil after persulfate remediation

SRB-dependent sulfate reduction also produces organic gaseous sulfur, dominated by methanethiol, which poses another risk (Fig. 4). A certain amount of methanethiol was generated in all groups except for 1D. Although no H_2S was detected in the 1M group (Fig. 3b), methanethiol was detected.

Table 1 – Linear fitting analysis results of methanethiol for the eight groups.

Treatments	k_2 (slope)	b (intercept)
1M	-0.0071	0.0904
1S	-0.0573	0.7714
2D	-0.0272	0.2590
2M	-0.0130	0.1181
2S	-0.0081	0.3808
3D	-0.0333	0.4043
3M	-0.0298	0.3159
3S	0.0108	0.3337

For these eight groups, methanethiol was gradually generated over 3–5 days, which roughly corresponds to the same time as the peak concentration of H_2S appeared. The overall concentration of methanethiol showed a fluctuating trend and remained below 0.6 ppm.

The concentration of methanethiol fluctuated greatly and the rule was not obvious. Therefore, a linear model was used to conduct a fitting analysis (Eq. (2)) after methanethiol reached the maximum concentration (ca. 5 days) for most groups (Table 1). The k_2 of all the groups, except for 3S, was negative, indicating that their methanethiol concentration showed a general downward trend after 5 days. The k_2 of the 3S group was 0.0108, indicating an upward trend. These results indicate that persulfate may be converted into methanethiol after entering the soil. Moreover, the release concentration may be gradually increased in some scenarios, which introduces potential risks that cannot be ignored. The water table had a significant effect on the variation trend of methanethiol. The k_2 in the shallow water table groups (2S and 3S) was always much higher than that of the middle water (2M and 3M) and deep water (2D and 3D) table groups. Moreover, the k_2 in the deep water group was smaller. The changes in methanethiol concentrations will be exacerbated with the increase in persulfate dosage, and the mean k_2 absolute value of 3% dosage groups was greater (53%) than of 2% dosage groups. In a similar study, Long et al. (2017) simulated a landfill methanethiol release experiment. At a 1.50% sulfate concentration (ca. 2.51% persulfate input), the methanethiol concentration released could reach ca.12 ppm, which was much higher than the detected concentration in this study. Moreover, dimethyl sulfide was also detected in the landfill, another compound not detected in this study. These results indicated that the concentration of organic sulfur gas generated from the contaminated soil after persulfate remediation was less than that inside of a landfill. However, the harm cannot be ignored, as methanethiol not only continues to be produced at a shallow water table and high persulfate dosage, but its concentration also keeps increasing.

An average concentration analysis was performed on the two gaseous sulfur products, and the ratio of H_2S to all gaseous sulfur was calculated (Fig. 5). For inorganic sulfur, an increase in persulfate dosage could significantly increase the production of H_2S . For the 1% dosage groups, the average daily H_2S concentration was only 1.55 ppm. When the dosage increased to 2% and 3%, it rapidly increased to 5.57 and 14.9 ppm, re-

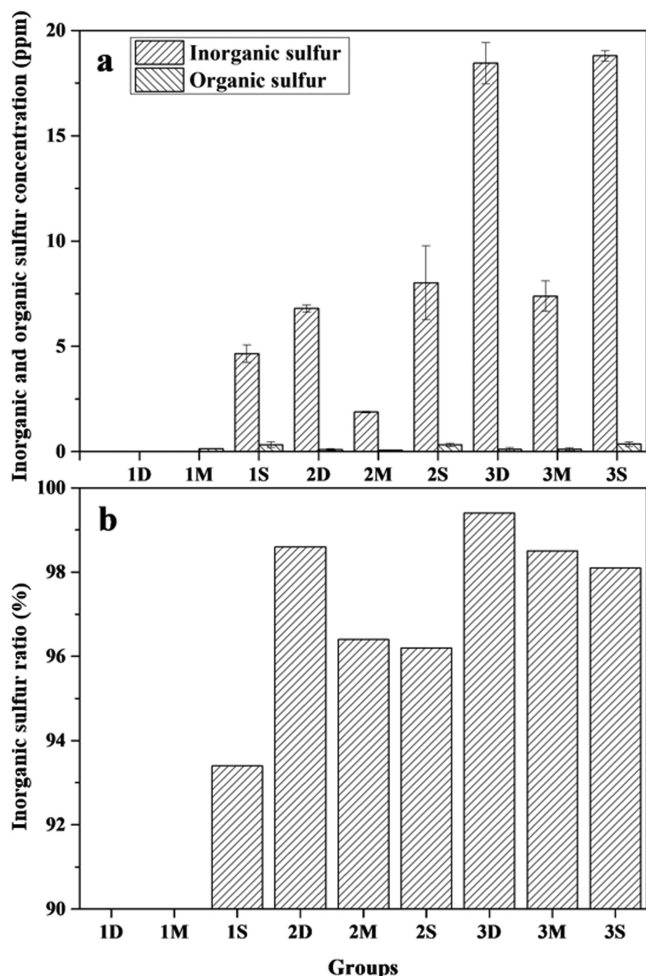


Fig. 5 – Results of inorganic and organic sulfur in the gas phase. a: Mean daily concentration; b: Ratio of inorganic sulfur in the gaseous sulfur produced.

spectively, increases of 2.6 and 8.6 times, respectively. This is because gaseous sulfur is the end-product of sulfur reduction by SRB in the soil. The addition of persulfate could have provided more electron receptors for SRB, thereby promoting the sulfur reduction reaction. Olivera et al. (2022) set up an anaerobic bioreactor experiment. When the sulfate loads were 2.78, 7.77, 12.8, 17.8, and 25.3 g/mL/day, the maximum H_2S concentrations were approximately 5,000, 10,000, 21,500, 32,500, and 44,500 ppm, respectively. This indicates that H_2S production increases with an increase in sulfate dosage, which is consistent with the results of this study.

The water table also had a significant effect on H_2S production. For the deep and shallow water table groups, more H_2S were produced, with average daily concentrations of 8.42 and 10.5 ppm, respectively. However, for the middle water table groups, the H_2S produced was only 3.09 ppm. This may be because a shallow water table created an anaerobic environment that promoted a reduction reaction. Regarding the middle water table, H_2S concentration was reduced because of its poor effect on creating an anaerobic environment, and a certain water table blocked the release of gas. For methanethiol, the effect of persulfate dosage and water table on its pro-

duction was similar to that of H_2S . The only difference was that methanethiol production was lower in the deep water table groups (average 0.068 ppm), specifically 36.9% and 79.7% lower than that of the middle and shallow water table groups, respectively. Overall, the highest daily concentration of methanethiol was only 0.36 ppm, which was much lower than that of inorganic sulfur. Therefore, the ratio of H_2S to all gaseous sulfur was calculated. When the persulfate dosage was 3%, the ratios of H_2S reached 98.1%–99.4%, which was higher than that of 96.2%–98.6% when the dosage was 2% (Fig. 5b). The persulfate dosage increased the ratio of H_2S , which was opposite to the effects of the water table. The ratio of H_2S decreased from 98.6%–99.4% in the deep water table to 96.4%–98.1% in the shallow water table. Overall, the ratio of H_2S in each group was between 93.4%–99.4%. This indicated that H_2S was the main form of sulfur in the gas phase. Jin et al. (2020) monitored the gaseous sulfur in a simulated landfill experiment and found that H_2S accounted for more than 77.6% of gaseous sulfur, which was lower than that reported in this study. In the anaerobic bioreactor experiment conducted by Olivera et al. (2022), the ratio of H_2S (when only considering H_2S and methanethiol) ranged from 86.4%–91.3%, which was also lower than that reported in this study. These results suggest that contaminated soil remediated by persulfate may not be suitable for methanethiol production.

To summarize, inorganic sulfur was the dominant form of gaseous sulfur released following soil remediation. Even though H_2S had been released from the soil, a considerable amount of sulfur remained in the soil in the form of sulfate, making its long-term release possible. Therefore, persulfate poses a risk in the long-term. The organic contaminated soil after persulfate remediation is characterized by a high sulfur content and an anaerobic environment. Therefore, it is likely to pose greater potential risks than rainforest soil or other regions.

3. Conclusions

Persulfate is a convenient and efficient remediation agent for organic contaminated soil. After persulfate addition, aniline concentration decreased rapidly. Most of the sulfur was converted to sulfate after 10 days, with no other sulfur detected in the soil. Persulfate dosage and the water table have a certain effect on this conversion. However, sulfate is not the final fate of sulfur. Based on the average concentration, H_2S accounts for 93.4%–99.4% of gaseous sulfur, which represents the most important sulfur reduction end-product and the final fate of sulfur. Increasing the dosage of persulfate will ultimately increase the production of H_2S . Moreover, a shallow water table will promote the production of H_2S by creating an anaerobic environment, whereas a middle water table will inhibit the production and release of H_2S . The maximum concentration of H_2S reached 33.0 ppm, a concentration that is toxic to human health. A fitted curve analysis was used to determine that it takes 20–85 days for H_2S to decay to a safe concentration. Another harmful gas released is methanethiol, with the maximum detected concentration of 0.6 ppm also posing a risk. To conclude, persulfate may seem green and environmentally friendly; however, it continues to release harmful gases for a

long period after remediation is finished. This is a key problem to be focused on in the process of soil remediation by persulfate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2023.01.008.

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