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Effect of various chemical oxidation reagents on soil indigenous microbial diversity in remediation of soil contaminated by PAHs

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Abstract

Chemical oxidation is a promising pretreatment step coupled with bioremediation for removal of polycyclic aromatic hydrocarbons (PAHs). The effectiveness of Fenton, modified Fenton, potassium permanganate and activated persulfate oxidation treatments on the real contaminated soils collected from a coal gas plant ($263.6 \pm 73.3 \text{ mg kg}^{-1}$ of the $\Sigma 16$ PAHs) and a coking plant ($385.2 \pm 39.6 \text{ mg kg}^{-1}$ of the $\Sigma 16$ PAHs) were evaluated. Microbial analyses showed only a slight impact on indigenous microbial diversity by Fenton treatment, but showed the inhibition of microbial diversity and delayed population recovery by potassium permanganate reagent. After potassium permanganate treatment, the microorganism mainly existed in the soil was *Pseudomonas* or *Pseudomonadaceae*. The results showed that total organic carbon (TOC) content in soil was significantly increased by adding modified Fenton reagent (1.4%–2.3%), while decreased by adding potassium permanganate (0.2%–1%), owing to the nonspecific and different oxidative properties of chemical oxidant. The results also demonstrated that the removal efficiency of total PAHs was ordered: permanganate (90.0%–92.4%) > activated persulfate (81.5%–86.54%) > modified Fenton (81.5%–85.4%) > Fenton (54.1%–60.0%). Furthermore, the PAHs removal efficiency was slightly increased on the 7th day after Fenton and modified Fenton treatments, about 14.6%, and 14.4% respectively, and the PAHs removal efficiency only enhanced 4.1% and 1.3% respectively from 1st to 15th day after potassium permanganate and activated persulfate treatments. The oxidants greatly affect the growth of soil indigenous microbes, which cause further influence for PAHs degradation by bioremediation.

Graphical Abstract

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.126>.

Keywords

Chemical oxidation; Diversity; Microorganism; PAHs

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a wide range pollutants in environment, which pose a great threat to human health through the bioaccumulation in the food chain (Moscoso et al., 2012; Liu et al., 2017). Due to the strong persistence, many researches has been devoted to creating methods to remove PAHs from the contaminated soil. The chemical oxidation has emerged as a viable remediation to remove PAHs in contaminated soils (Cheng et al., 2016).

In general, the oxidative stress increase in persulfate treatment or decrease in Fenton's reagent with increasing pH, and changes in redox conditions caused by chemical oxidation significantly alter subsurface conditions and are toxic to microbial populations (Kakosová et al., 2017). Although microbial activity can be reduced temporarily by chemical oxidation, the populations of microorganism could recover for contaminant degradation in laboratory experiments (Xu et al., 2016) and in some industrial field (Sutton et al., 2013). It has been proved that chemical oxidation treatments significantly decrease original pollutant concentrations (Silva-Castro et al., 2013; Chen et al., 2016), improve pollutant bioavailability and biodegradability (Sutton et al., 2014), reduce toxicity (Gong, 2012), and provide oxygen for aerobic biological transformation of contaminants (Kulik et al., 2006).

Although the effects of conventional oxidants including hydrogen peroxide, permanganate, persulfate and ozone on microorganisms have been reviewed (Sahl and Munakata-Marr, 2006; Sutton et al., 2011; Chen et al., 2016), critical research is lacking on the effects of these oxidants on indigenous soil microbial diversity. A recent study has shown changes in intrinsic microbial community in diesel-contaminated soil after oxidants (persulfate, permanganate and hydrogen peroxide) were applied (Chen et al., 2016). Another study has demonstrated changes in bacterial genetic diversity in the phenanthrene-contaminated soil as a function of persulfate concentrations, where the composition of microbial communities may influenced by salinity, because the genotypes of microorganisms differ in their tolerance to osmotic pressure. (Mora et al., 2014).

Therefore, the purpose of our study is to find out the effect of various chemical oxidation reagents on indigenous soil microbial diversity and to evaluate the impact of indigenous soil microorganisms for PAHs contaminated soil remediation after various chemical oxidations.

The results reveal the variation of indigenous soil microbiology after persulfate, permanganate, Fenton and modified Fenton oxidation and propose the feasible remediation of residual PAHs using chemical oxidation followed by indigenous soil microbial degradation.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (H_2O_2 , 30%), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >99%), and potassium permanganate (KMnO_4 , >99%) were used as the oxidants. Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, >99.8%) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, >99.8%) were used as the activated reagents. Acetone (HPLC), dichloromethane (HPLC) and n-hexane (HPLC), purchased from Duksan Pure Chemicals Co., Ltd, were used for GC-MS analysis. Milli-Q water was used in the experiment.

2.2. Experimental design

Soil samples collected from a coking plant field (abbreviated C) in Shijiazhuang City and a coal gas plant field (abbreviated G) in Nanjing City (Table 1). According to the content of PAHs in the soil, 4 optimal oxidant with the highest removal efficiency was selected from 18 different doses of chemical oxidants (Ranc et al., 2016; Zhao et al., 2011). The optimal oxidant dosage of Fenton reagent (Fenton), modified Fenton reagent (M-Fenton), potassium permanganate (KMnO_4) and activated persulfate (Active-PS) were used to oxidize the contaminated soils (Table 2), which selected Use water instead of chemical oxidant as control.

Sixty experiments were conducted to investigate the role of chemical oxidant stress on indigenous soil microbiology. For each oxidant, 50 g contaminated soil was weighted into a 250-mL Erlenmeyer flask. Milli-Q water was first added into the flask according to Table 1 (the final volume of the Milli-Q water and oxidant was 100 mL), and the flask was sealed to form a slurry by magnetic stirrer at 150 rpm. Then the chemical oxidant was added slowly to the set amount. To make the oxidant in contact fully with the contaminated soil, the Erlenmeyer flasks were placed on the magnetic stirrer at 150 rpm for about 2 h. After standing for 22 h, the flasks were covered with a sterile breathable film, and the microbes in soil suspensions were cultured in a sterile dark room at room temperature. Soil suspension samples (10 mL of each one) were collected using a pipette on 0, 0.5, 1, 3, 5, 7, 10, 15 d for further analysis. All experiments in this study were performed in triplicates.

2.3. Total organic carbon (TOC) and pH analysis

A 5 g soil samples were freeze-dried and 50 mg freeze-dried soil samples were analyzed for TOC (Elementar TOC analyzer, Germany) by using the solid model. TOC was quantified as a difference between total carbon (TC) and total inorganic carbon (TIC). Soil suspension ($V_{\text{soil}}:V_{\text{water}} = 1:2$) pH were measured by using a pH meter (PB-10, Sartorius, Germany).

2.4. PAHs concentration analysis

Freeze-dried soil (2.0 g) were extracted by ultra-sonication with acetone and dichloromethane mixture. The extracts were concentrated and then transferred to a silica gel column for cleanup by washing with hexane and dichloromethane (v:v = 1:1) mixture. The eluate was concentrated and analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) (Agilent 7890A GC coupled with a 5975C MS, USA). The average recoveries of PAHs were 95–110% (n = 6, relative standard deviation < 2.61%). The detection limit for PAHs was 1 ng g⁻¹ (Sun et al., 2014).

2.5. Microbial counts and diversity analyses

The microbial counts refer to the ISO 6222, 1999, in briefly, blending and shaking the soil with physiological saline according to the ratio of 1:2, than Diluting the supernatant by a series of times, inoculating on plate count agar at 22 °C for 4 days. The samples were counted for the colony forming unit (CFU).

Sequencing was completed on Illumina Miseqplatform in Shanghai Majorbio Co. Ltd. E.Z.N.A. Soil DNA Kit was used to extract DNA of soil bacteria. 16S rRNA genes were amplified using primers with the barcode for high-throughput sequencing. Primers were 338F (5'-ACTCCTACGGGAGGCAGCA-3') and 806R (5'-GGACTACHVGGGTWTCTAAT-3') targeting the V3–V4 region of the 16S rRNA gene (Yu et al., 2017).

2.6. Statistical analysis

The mean and standard deviations of triplicate independent experiments were calculated. The mean values were compared by a parametric one-way ANOVA test. $P < 0.01$ indicates the significant difference. Parts of the statistical analyses and graphing were performed using the Origin 2016 software program (OriginLab Corporation, USA).

3. Results and discussion

3.1. Effect of oxidants on soil TOC content and pH

Soil TOC content and pH value were stabilized after three days of reaction. Therefore only the data of three days were given. As shown in Fig. 1A, the effects of different oxidants on soil TOC content of the two soils collected from different sources (coal gas plant and coking plant) were significantly different. Compared to CK(which is Blank, replace the oxidants with Milli-Q water), there was no significant effect on soil TOC by Fenton reagent ($P > 0.01$), potassium permanganate had the greatest effect on TOC ($P < 0.01$), and the soil TOC content in the soil collected from the coking plant decreased by about 50%. However, M-Fenton contains a large amount of citric acid, resulting in a large increase in soil TOC content.

Oxidation is non-specific. Thus, oxidant is consumed not only by the targeted pollutants but also by organic matter (Haselow et al., 2003). The TOC consumption is significantly related to the H₂O₂ doses and Fe²⁺/C ratios. The TOC decreased slowly with H₂O₂ only, while mineralization increases with increasing iron concentration (Chamarro et al., 2001). Bogan

and Trbovic (2003) used Fenton's reagent on six soils spiked with 1000 mg kg^{-1} of coal tar and found that PAH removal rate increased when TOC increased up to 5.8% but seemed to decrease subsequently. In this experiment, the TOC content by KMnO_4 and A-PS treatment in coking plant soil was significantly reduced (about 50%) than Fenton treatment, owing to the higher oxidation performance of KMnO_4 and persulfate. Tirol-Padre and Ladha, (2004) reported that organic C was oxidized by KMnO_4 to the greatest extent, 45% C in 1 h and 100% in 24 h. In addition, the TOC content could decrease 80% at pH 3.1 in soil slurries by sodium persulfate, owing to the strong oxidizing property (Wang et al., 2014). Furthermore, high levels of TOC in the soil are not conducive to chemical oxidation remediation. The effect of chemical oxidant on TOC content was significant in the coking plant soil due to the higher TOC background value, which consumes a certain amount of oxidant. However, the background value of TOC content in the coal gas plant soil was lower, more oxidant could be used to oxidize PAHs.

The oxidant not only had a significant effect on soil TOC but also had a significant effect on soil pH. The presence of citric acid in oxidant of modified Fenton and activated persulfate resulted in a minimum soil pH reduction of 2.85 ± 0.21 and 2.19 ± 0.15 , respectively. However, potassium permanganate significantly increased the pH values of the two soils to 8.07 ± 0.11 (G) and 8.13 ± 0.13 (C) (Fig. 1B). Lemaire et al. (2013) analyzed the effects of potassium permanganate and activated persulfate on soil pH. The result was similar to our experiment; the pH value of the soil treated with potassium permanganate was close to 8, while the soil pH treated by activated persulfate was reduced to 4 approximately.

Studies have shown that soil pH has a significant effect on the removal efficiency of soil organic pollutants. Goi et al. (2006) indicated that Fenton-like treatment of contaminated soil under the same H_2O_2 /contaminant weight ratio and at pH 3.0 led to a higher removal efficiency (63%) of the contaminant than at the pH 6.4 (22% removal efficiency). In this experiment, the use of citric acid is to stabilize iron species and to decrease the pH of the soil suspension, which made the oxidation more efficient in Fenton-based and persulfate-based oxidation treatments. However, sudden changes in soil pH can have a harmful effect on the soil microbial community, resulting in subsequent biodegradation of residual contaminant or their oxidation byproducts.

3.2. Effect of oxidants on indigenous soil microbial population

The number of indigenous microbes in the soil decreased first and then increased with the addition of chemical oxidants. Then indigenous microorganisms began to grow exponentially at the 7 d after activated persulfate and Fenton reagent treatment; while the indigenous microbes treated with M-Fenton and potassium permanganate began to grow slowly after 10 d (Fig. 2). This result was similar with Chen et al. (2016) that the total bacteria from 10^4 CFU g^{-1} soil to 10^3 CFU g^{-1} soil by hydrogen 5% peroxide treatment and 10^4 CFU g^{-1} soil to 10^2 CFU g^{-1} soil by 5% persulfate treatment in 5 d, then began to grow slowly after 10 d.

There are two different points on the effects of chemical oxidants on microbes. One is that chemical oxidation can produce adverse environmental conditions (pH and oxidation potential), which inhibiting the growth and function of normal microbes. Moreover, the pH

value plays a vital role in biodegradation including PAHs. Usually, microorganisms are pH-sensitive and near neutral conditions (6.5–7.5) are favored by most of them for their normal activity. Low pH value may limit the survival and activity of soil microorganisms (Mora et al., 2014). Laurent et al. (2012) used a high dose of Fenton reagent to treat with PAHs-contaminated soil, result in a low soil pH value and significantly reduction of soil microorganism quantity. Research in oil-contaminated soil revealed that microbial cellular membranes were disrupted by Fenton's treatment (Palmroth et al., 2006). Sutton et al. (2014) indicated that no significant biological activity was measured in permanganate and persulfate-treated microcosms. On the other hand, although chemical oxidation can temporarily reduce microbial activity, bacterial populations do regenerate contaminant degradation ability in the soil (Medina et al., 2018). The oxidants which involving H_2O_2 and citric acid can significantly increase microbe respiration, accompanied by an increase in microbial population. It is one of the reason for increasing microbes in soil by Fenton and A-PS treatments. Kakosová et al. (2017) indicates utilization of citric acid as a better growth substrate for the more active part of the microbial community. Sutton et al. (2011) figured that microorganisms were killed by permanganate oxidation, but the microbial populations were increased following the oxidation. Our findings are consistent with the second point of view. The microbial activity could be recovered over time in our studies. These results indicate that chemical oxidant application coupled with intrinsic biodegradation is a feasible approach for PAH site remediation.

3.3. Effect of oxidants on indigenous soil microbial diversity

The Rank-Abundance curve can be used to explain the two aspects of diversity, species abundance, and species uniformity. It can be seen from Fig. 3 that the abundance order of microorganisms in the coal gas plant soil is modified Fenton > activated persulfate > CK > Fenton treatment > permanganate. Similarly, the abundance of microorganisms in the coking plant soil followed the order modified Fenton > Fenton treatment > CK > activated persulfate > permanganate. The results showed that M-Fenton significantly increased the diversity of microbial in both coal gas plant soils and coking plant soils, permanganate showed negative effect to microbial diversity. While Fenton and persulfate revealed different effect between two types of soil.

The heat-map can be used to reflect the color changes in the two-dimensional matrix or table of data information and it can visually show the size of the data value to the definition of the color depth. Classification of the total abundance of the top 30 species is shown in Fig. 4. The results of our experiment indicated that the microbial community compositions were similar between Fenton treatment and CK in the two different soils. This demonstrated that Fenton treatment has negligible impact on the microbial community compositions of indigenous microbes. While the microbial community compositions changed dramatically in the soil treated by activated persulfate and permanganate. This kind of behavior has been reported that the hydrogen peroxide had less effect on microbial community but persulfate get worse (Chen et al., 2016).

According to the results of taxonomy, we can know the classification of one or more samples at each level of classification. Fig. 5 shows the microbial community structure at the

family level for each sample. The microbial species in the soil of coking plant were more abundant than that of coal gas plant soil, and the activation of persulfate and potassium permanganate treatment could significantly reduce the soil biodiversity. Interestingly, the soil microbial diversity was increased by the M-Fenton treatment. In the soil of coal gas plant, *Xanthomonadaceae* was the predominant family of CK soil. After the treatment with potassium permanganate, the main microorganism existed in the soil was *Pseudomonas*, which accounted for about 70% of total population. After the activated sodium persulfate treatment, the main microorganism present in the soil was *Burkholderiaceae*. In the CK soil of coking plant, *Alcaligenaceae* and *Anaerolineaceae* accounted for 8% each of them. After the treatment with potassium permanganate, the microorganism mainly existed in the soil was *Pseudomonadaceae*, which accounted for 90%.

Although some bacteria in native soil were affected, the addition of modified Fenton reagent caused increased microbial diversity. This may be because more biodegradable byproducts were produced after the PAHs were exposed to the modified Fenton oxidants. Some initially non-dominant microbes may use the PAH oxidizing byproducts, leading to increased microbial diversity (Medina et al., 2018). Sutton et al. (2014) also indicated that bacterial diversity temporarily increased after the addition of modified Fenton reagent. The microbial community was observed more serious destruction in the permanganate solution due to the high residue (Tirol-Padre and Ladha, 2004). Sutton et al. (2014) revealed that although a gene related to diesel degradation capacity was tested in permanganate treated microcosms, no biotic activity was observed, and speculated that microbial DNA was potentially damaged during chemical oxidation. The destruction of the microbial community was observed in the persulfate solution might due to low pH values. Richardson et al. (2011) introduced six pore volumes of 20 g L⁻¹ (approximately 2% w/w) persulfate into a soil column, following persulfate injection, the diversity of the soil microbial community was immediately reduced.

Organisms belonging to genera *Cellulomonas*, *Pseudomonas*, *Mycobacterium*, *Micrococcus*, *Gordonia*, *Rhodococcus*, *Paenibacillus*, *Bacillus*, *Burkholderia*, *Xanthomonas*, *Arthrobacter*, *Acinetobacter* and *Corynebacterium* have been documented to effectively degrade PAH compounds (Wu et al., 2013). Medina et al. (2018) indicated that the microorganism mainly existed in PAHs-contaminated soil was *Actinomycetales* after one month of chemical oxidation, while the *Pseudomonadaceae* become the dominant after five month. Our results demonstrated that the predominant microbes, *Xanthomonadaceae*, *Burkholderiaceae*, *Alcaligenaceae* and *Pseudomonadaceae*, were presented in the two soils. Among them, *Alcaligenes*, *Pseudomonas*, *Xanthomonas*, and *Burkholderia* can utilize naphthalene as a sole source of carbon and energy (Seo et al., 2009). *Burkholderia* and *Pseudomonas* can completely mineralize anthracene (Mrozek et al., 2003). The characteristics of other types of microbes that existed after chemical oxidation remain to be further studied.

3.4. Effects of oxidants on total PAHs and the effects of indigenous microorganisms on the degradation of residual PAHs

In this study, several common and efficient chemical oxidants were tested. The soils of two different sources were studied according to the optimum dose of the previous study. The

results demonstrated that the removal efficiency of total PAHs was ordered: permanganate > activated persulfate > modified Fenton > Fenton. The highest PAHs removal efficiency (92.40%) was for the potassium permanganate in coal gas plant soil, and the lowest (54.10%) was for the Fenton treatment in the same soil. Furthermore, the removal efficiency of PAHs achieved the highest level of treatment with each chemical oxidant for 24 h. It is noted that the PAHs removal efficiency was slightly increased at 7 d after Fenton and modified Fenton treatments, about 14.56%, and 14.37% respectively from 1 to 15 d (Fig. 6 and Appendix A).

In the combined systems, in situ bacteria may use PAHs and their oxidation byproducts as carbon sources for their growth, resulting in further reduction of PAHs concentrations in the soil (Lee and Hosomi, 2001). It has been reported in the literature that the priority by-product was oxy-PAHs included furan, xanthene and thiophene by chemical oxidation (Li et al., 2019). The transformation of PAHs to more biodegradable substrates in oxidation systems has been reported in previous studies. Sahl and Munakata-Marr (2006) indicated that chemical oxidation could enhance subsequent biotransformation, and it can also enhance biological activity by oxidizing humic acids and fulvic acid in the natural organic matter as substrates. On the other hand, some oxidants will accelerate the delivery of the soil nutrients. Xu et al. (2016) indicated that a huge of soil NH_4^+N released after Fenton oxidation, resulted in a high activity of microbiological and improved the biodegradation of oil-contaminated soil. The indigenous microbial population after chemical oxidant treatments was presented. Consistent with the removal efficiency of PAHs, the number of microbes began to recover exponentially on 7th d. However, the PAHs removal efficiency was only enhanced 4.08% and 1.32% respectively from 1 to 15 d after potassium permanganate and activated persulfate treatments, respectively. We can speculate that this may be due to the reduction of indigenous microbial diversity after potassium permanganate and activated persulfate treatments (Fig. 5) owing to the oxidative stress on microorganisms by chemical oxidants. Although the number of microbes recovered gradually, the decrease of microbial diversity led to the deficiency of PAHs degradation.

Focus on reducing the lower concentrations of PAHs in soil after chemical oxidation by microbial methods, we could speculate that chemical oxidation combined with microbial remediation is feasible, and is carried out under suitable conditions of soil environment (organic matter and water content). The combined remediation can be faster, more efficient, and less costly than chemical oxidation or microbial remediation alone.

4. Conclusions

Effects of Fenton, modified Fenton, potassium permanganate and activated persulfate treatments on PAHs degradation and soil microbial community in coking and gas coal field soils were tested. The results of this study demonstrated that the soil TOC content and pH value showed the difference after various oxidations, i.e., higher TOC content was accompanied by lower pH value by modified Fenton treatment, while lower TOC content was accompanied by higher pH value by potassium permanganate treatment. Fenton treatment had positive impact on indigenous microbial diversity. Oppositely, potassium

permanganate treatment reduced the microbial diversity, given the seriously impact of microbial community structure. In addition, a threshold of the PAHs removal efficiency was shown in 3 d by chemical oxidation. However, the removal efficiency of PAHs was improved with the increase of the number of indigenous microorganisms after 7–15 d of chemical oxidant treatment. The results indicate that use the chemical oxidant alone (such as potassium permanganate) could be an effective method. In addition, although microbial communities may potentially be adversely affected by chemical oxidation in the short term, a rebound of microbial biomass and bioremediation activity can be expected after inefficient chemical oxidation treatment.

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Appendix A

Table 1

The PAHs contents of different treatments ($\text{mg}\cdot\text{kg}^{-1}$)

Time	Treatments							
	Fenton		M-Fenton		KMnO ₄		A-PS	
	G	C	G	C	G	C	G	C
0d	263.57±73.25	385.16±39.54	274.71±43.08	411.10±31.57	301.24±47.32	409.46±57.94	298.13±12.28	427.16±62.15
0.5h	182.01±13.74	276.43±32.25	122.31±38.26	235.61±32.11	145.00±16.42	163.00±12.37	102±8.72	143.00±22.81
1d	121.24±12.35	154.01±72.16	83.49±12.38	134.82±21.57	22.89±4.42	40.94±2.22	40.13±2.58	79.30±12.43
3d	116.83±24.61	149.82±13.24	79.72±2.41	126.91±12.57	21.95±1.37	42.35±10.10	37.78±12.82	41.25±22.09
5d	109.27±23.10	143.84±59.73	76.34±4.26	124.56±17.67	25.27±8.24	38.53±7.63	35.27±18.46	39.00±17.73
7d	98.46±56.24	139.82±20.18	63.91±6.57	113.00±14.24	24.18±6.34	32.23±6.58	36.48±20.42	32.82±10.39
10d	81.86±34.24	128.02±11.34	55.31±14.64	102.32±11.49	20.34±3.23	30.13±3.63	30.72±4.94	35.03±13.94
15d	79.31±13.68	114.65±34.28	51.37±8.60	96.58±32.12	19.17±3.65	28.57±4.82	29.17±6.68	37.85±4.37

Note: "G" denotes soil sample of coal gas plant field, "C" denotes soil sample of coking plant field conditions.

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HIGHLIGHTS

- A promising combined technology for PAHs contaminated soil was put forward.
- Indigenous microbes reduced first and increased exponentially after chemical oxidation.
- Modified Fenton oxidation had slightly impact on indigenous microbial diversity.

Fig. 1. Impacts of various chemical oxidant treatments on TOC (A) and pH (B) after 3 days. Note: “G” denotes soil sample of coal gas plant field, “C” denotes soil sample of coking plant field. “CK” means treated with sterile water. The lowercase letters indicate significant differences between treatments.

Fig. 2. Changes of microbe counts in soil G and C under different treatment. Note: “G” denotes soil sample of coal gas plant field, “C” denotes soil sample of coking plant field conditions.

Fig. 3.
The Rank-Abundance curve of microorganism in coal gas plant soil (G) and coking plant soil (C) treated by different chemical oxidants.

Fig. 4.
The community heat map of microorganism in coal gas plant soil (G) and coking plant soil (C) treated by different chemical oxidants.

Fig. 5.
The microbial community structure in coal gas plant soil (G) and coking plant soil (C) treated by different chemical oxidants.

Fig. 6. Removal efficiencies of total PAHs in coal gas plant soil (G) and coking plant soil (C) treated by different chemical oxidants.

Table 1.

Physical and chemical characteristics of soils used in this study (n = 3).

Parameters	Coal gas plant soil	Coal plant soil
pH	7.41 ± 0.13	7.57 ± 0.16
TOC/%	0.27 ± 0.05	2.29 ± 0.56
Depth of soil	20–25 cm	20–25 cm
Texture classification	Loam	Sandy loam
Naphthalene (NAP)/mg·kg ⁻¹	16.9 ± 9.6	16.4 ± 3.96
Acenaphthylene (ANY)/mg·kg ⁻¹	15.2 ± 2.1	14.69 ± 8.8
Acenaphthene (ANE)/mg·kg ⁻¹	39.6 ± 5.5	101.98 ± 6.8
Fluorene (FLE)/mg·kg ⁻¹	26.3 ± 5.5	75.2 ± 6.49
Phenanthrene (PHE)/mg·kg ⁻¹	28.1 ± 5.4	51.1 ± 16.7
Anthracene (ANT)/mg·kg ⁻¹	18.2 ± 6.0	29.18 ± 7.76
Fluoranthene (FLA)/mg·kg ⁻¹	18.5 ± 6.9	34.29 ± 12.6
Pyrene (PYR)/mg·kg ⁻¹	15.3 ± 3.6	17.29 ± 3.7
Benzo(a)anthracene (BaA)/mg·kg ⁻¹	12.7 ± 5.5	11.1 ± 1.58
Chrysene (CHR)/mg·kg ⁻¹	15.0 ± 6.6	9.2 ± 1.1
Benzo(b)fluoranthene (BbF)/mg·kg ⁻¹	10.8 ± 4.0	9.37 ± 1.1
Benzo(k)fluoranthene (BkF)/mg·kg ⁻¹	9.7 ± 2.6	6.4 ± 3.1
Benzo(a)pyrene (BaP)/mg·kg ⁻¹	12.0 ± 3.0	5.8 ± 2.9
Benzo(a)pyrene (I (cd)P)/mg·kg ⁻¹	7.7 ± 4.0	1.3 ± 0.3
Dibenzo (a,h)anthracene (D (ah)A)/mg·kg ⁻¹	7.5 ± 3.1	1.0 ± 0.3
Benzo (g,h)perylene (B (gh)P)/mg·kg ⁻¹	10.1 ± 8.8	0.9 ± 0.1
Σ16 PAHs/mg·kg ⁻¹	263.6 ± 73.3	385.2 ± 39.6

Table 2

The dosage of chemical oxidants.

Chemical oxidants	Abbreviation	Reagents (concentration)	Dose/ $\text{mmol}\cdot\text{g}^{-1}$	solid-to-liquid ratio
Fenton reagent	Fenton	H_2O_2 (30%)	1	1:2
modified Fenton reagent	M-Fenton	FeSO_4 (0.5 mol L^{-1})	0.2	50 g soil:100 mL (water + oxidants)
		H_2O_2 (30%)	2	
		FeSO_4 (0.5 mol L^{-1})	0.4	
		Citric acid	0.4	
potassium permanganate	KMnO_4	KMnO_4 (0.4 mol L^{-1})	1.5	
activated persulfate	A-PS	Sodium persulfate (1 mol L^{-1})	2	
		FeSO_4 (0.5 mol L^{-1})	0.2	
		Citric acid	0.04	