EPA Public Access

Author manuscript

Sci Total Environ. Author manuscript; available in PMC 2020 June 10.

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Published in final edited form as:

Sci Total Environ. 2019 January 10; 647: 1106–1112. doi:10.1016/j.scitotenv.2018.07.420.

The combined effects of surfactant solubilization and chemical oxidation on the removal of polycyclic aromatic hydrocarbon from so

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Abstract

A method for the remediation of polycyclic aromatic hydrocarbons (PAHs) contaminated soils was proposed involving a combination of surfactant-aided soil washing and chemical oxidation by activated persulfate (SP). In this study, Triton X-100 (TX-100) and SP was applied to the soil, either concurrently or sequentially. Results indicated that surfactant followed by amendment with a solution of SP, TX-100 + SP(I), was most effective in decreasing PAHs concentrations in a sandy loam soil (SS) and a silty clay soil (NS) from 1220 mg/kg and 2730 mg·kg⁻¹ to 414 mg·kg⁻¹ and 180 mg·kg⁻¹, respectively. Compared with extraction alone and oxidation alone, TX-100 + SP(I) increased the removal of PAHs by 10–20%. TX-100 improved the degradation of 3–4 ring PAHs (M-PAHs) and 5–6 ring PAHs (H-PAHs) in SS, by approximately 8%–11%. The oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) including furans and xanthene exhibited greater reductions in soil when amended with the TX-100 and SP, than under TX-100 extraction or SP oxidation alone. Overall, increased removal of PAHs in contaminated soil can occur through simultaneous application of TX-100 and SP, relative to the sole use of TX-100 or SP. The sequential combination of surfactant and oxidant was most effective for the elimination of PAHs, especially for M-PAHs and H-PAHs in sandy loam contaminated soil.

Keywords

Surfactant; Chemical oxidation; PAHs; Soil pollution; Oxidation product

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are pollutants found in soil and groundwater that are of major concern due to human and ecological toxicity impacts. PAHs may be generated

by the incomplete combustion or pyrolysis of fossil fuel products including crude oil, tars, and coal materials (Jonsson et al., 2007; EEA, 2008). Due to industrial processes over the last 150 years involving fossil fuel raw materials, soil and groundwater contamination with PAHs has been widely reported. There are at least 600 PAHs contaminated sites among the 1408 hazardous waste sites on the U.S. National Priority List (Duan et al., 2015). Concentrations of PAHs in industrial contaminated soils has been reported to be in the hundreds of thousands of $\text{mg}\cdot\text{kg}^{-1}$ (Gong et al., 2006; Usman et al., 2012). In China, PAHs-contaminated soils are widely distributed in big cities including Beijing, Guangzhou, Nanjing, etc. For example, the concentration of PAHs in soils collected and analyzed from the Beijing coking plant ranged from $342 \text{ mg}\cdot\text{kg}^{-1}$ to $1194 \text{ mg}\cdot\text{kg}^{-1}$ (Liao et al., 2013). While due to the hydrophobicity, PAHs are difficult to degrade in soils and more likely to adsorb on soil surfaces. In addition, the toxicity of PAHs usually increases with the increase of the number of benzene rings. Specifically, the 4–6 ring PAHs are toxic and carcinogenic to humans, which are recalcitrant to biodegradation by indigenous microorganism (Moon et al., 2006; Mousset et al., 2014; Biache et al., 2015). Consequently, there is significant emphases placed on remediation technologies that can effectively degrade PAHs in soils (Hahladakis et al., 2016; Bezza and Chirwa, 2016; Ranc et al., 2016).

Chemical oxidation is a promising and viable technology for the remediation of hydrophobic organic contaminants (HOCs), including PAHs. Potentially, it has the advantages of high efficiency, relatively short time for remediation, low cost, and application to a range of contaminant concentrations (Lemaire et al., 2013). A wide range of organic chemicals are susceptible to oxidative degradation through chemical reactions with oxidants, such as potassium permanganate (KMnO_4), catalyzed hydrogen peroxide (CHP) or modified Fenton's reagent, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), and ozone (Cheng et al., 2016; Kuppusamy et al., 2016). Activated persulfate oxidation is a technology that potentially exhibits low soil oxidant demand (SOD), good stability (i.e. persistence in the subsurface), along with a moderate process of generating hydroxyl radicals ($\bullet\text{OH}$) and sulfate radical ($\text{SO}_4\bullet^-$) (Liang et al., 2007). The mechanism of persulfate oxidation includes —O—O— bond cleavage using chelated ferrous iron as a catalyst. Through this process, $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ are formed that can degrade a wide range of targeted contaminants (Zhao et al., 2013). It is often reported that the oxidation reaction takes place in aqueous phase. It indicates that contaminants adsorbed to soil particles are less vulnerable to this oxidation treatment mechanism. PAHs compounds exhibit both high octanol-water coefficients (K_{OW}) and organic carbon partition coefficients (K_{OC}), indicating high hydrophobicity and a relatively strong affinity to adsorb to the soil organic matter. Consequently, the slow rate of mass transfer of PAHs between the aqueous and solid phases usually limits the reaction between free radicals and adsorbed PAHs (Flottron et al., 2005; Haapea and Tuhkanen, 2006; Bi et al., 2007). In this study, it is proposed to enhance the rate of mass transfer of PAHs from the solid phase into the aqueous phase prior to oxidation. Another concern for chemical oxidation is that some undesirable by-products or residues may emerge during the reaction (Stroo et al., 2012).

Surfactant enhanced chemical oxidation has been studied in the recent years, especially for HOCs that are associated with non-aqueous phase liquids (NAPLs) and chlorinated solvents (EthicalChem, 2016a, EthicalChem, 2016b; Dahal et al., 2016). Surfactants are amphiphilic molecules that can increase the solubility and mobility of HOCs in the soil. They may

reduce aqueous surface tension, promoting the diffusion and emulsification of PAHs from soil phase to aqueous phase (Lundstedt et al., 2006; Yap et al., 2015). Ideally, through this process, surfactants can increase the reaction time and kinetics, leading to higher contaminant removal efficiency (Mao et al., 2015). In one study, the combination of nonionic surfactant TX-100 and Fenton's reagent could remove 98% DDT in soils (Villa et al., 2010). In another study, the degradation efficiency of 5–6 rings PAHs by Fenton's reagent could be significantly improved in the presence of surfactant (Gryzenia et al., 2009). Similarly, the removal of anthracene and pyrene reached 80–85%, which was 2–4 times the average removal achieved through chemical oxidation alone (Nadarajah et al., 2002). Generally, surfactant appears to have the potential to be used in conjunction with chemical oxidation to enhance the treatment of refractory organic contaminants (Besha et al., 2018).

The objectives of this study were to (1) screen the effectiveness of different surfactants to remove PAHs, and different oxidants to oxidize PAHs, (2) to utilize different combinations of the surfactant and oxidant selected from the screening study, (3) and to identify the major decomposition products.

2. Materials and methods

2.1. Chemicals/reagents

PAHs standards were purchased from the national standard substances center (Beijing, China). Biosurfactant Accell was supplied by Advanced BioCatalytics Corporation (Irvine, CA, USA). Rhamnolipid (>99%) (99% RL) was purchased from HongMa Biotechnology Ltd. Co. (Huaian, China) and Rhamnolipid (25%) (25% RL) was provided by Institute of Microbiology Chinese Academy of Sciences (Beijing, China). Analytical reagents including surfactants (TX-100, Tween 80), KMnO_4 , hydrogen peroxide (H_2O_2), SP, citric acid, heptahydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), anhydrous sodium sulfate (Na_2SO_4), copper powder, diatomite, silicone and chromatographically pure solvents including *n*-hexane and dichloromethane were from Sinopharm Chemical Reagent Beijing Ltd. Co. (Beijing, China).

2.2. Soil samples and soil contamination

Soil samples were collected from a coking plant (114°34'4.00"E, 38°3'58.69"N) in Shijiazhuang and a coal gas plant (118°50'47.59"E, 32°6'57.73"N) in Nanjing, respectively. The depth of soil samples was about 100 cm, because the contaminated sites both contained 60–80 cm backfill soil on the surface. Testing proved that Shijiazhuang soil (SS) was a sandy loam soil, and Nanjing soil (NS) was a silty clay. Before experiment, the coarse debris and visible plant materials were removed, then the soil was air-dried and sieved (particle size <2 mm). Preliminary testing of the SS and NS soils indicated the following: density, 1.89 $\text{g} \cdot \text{cm}^{-3}$ and 1.76 $\text{g} \cdot \text{cm}^{-3}$; porosity, 61.5% and 48.1%; permeability, $4.3 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ and $8.1 \times 10^{-7} \text{ cm} \cdot \text{s}^{-1}$, total organic carbon (TOC) in soil, 2.10% and 0.44%, respectively.

2.3. Batch solubilization and oxidation experiments

Batch solubilization experiments were performed by mixing 2 g soil and 20 mL surfactant solutions in 100 mL Erlenmeyer flasks (Chong et al., 2014). Four surfactants were tested

including Accell (6%), 25% RL, 99% RL, TX-100 (8000 mg·L⁻¹) or Tween 80 (6000 mg·L⁻¹). The concentration of each surfactant was above the critical micelle concentration (CMC). All the aqueous solutions for the solubilization tests contained 0.01 mol·L⁻¹ NaCl to keep a constant ionic strength and 0.5 g·L⁻¹ HgCl₂ to inhibit microbial growth. Triplicate test reactors comprised of Erlenmeyer flasks (triplicates) were used in all experiments and then mixed in a constant temperature bath (25 ± 2 °C; 150 rpm; 24 h). The supernatant was separated from the slurry by centrifugation (3000 rpm, 20 min).

In the batch oxidation experiments, contaminated soils (10 g) were loaded into Erlenmeyer flasks (250 mL), and amended with an oxidant solution including KMnO₄ (0.2 mol·L⁻¹), H₂O₂ (0.1 mol·L⁻¹), or Na₂S₂O₈ (0.2 mol·L⁻¹) activated by chelated iron. The total volume (100 mL) was adjusted with de-ionized water (DIW). The soil slurry was mixed in a horizontal shaker (120 rpm; 24 h). After treatment, mixtures were centrifuged (3000 rpm, 20 min) and all experiments were performed in triplicate.

2.4. Sequence of solubilization and oxidation

The removal of PAHs from soils was evaluated according to various sequences and forms of application of solubilization and oxidation after the most suitable chemicals determined. Soil (20 g) was added into Erlenmeyer flasks (250 mL), and five treatments were set up: (i) Control group (100 mL DIW, 4 h); (ii) SP (100 mL SP(0.2 M), 4 h); (iii) TX-100 (100 mL, 8000 mg·L⁻¹, 4 h); (iv) TX-100 + SP(s) (100 mL 8000 mg·L⁻¹ TX-100 extraction, 2 h, solid persulfate (4.8 g) for 2 h); (v) TX-100 + SP(l) (100 mL 8000 mg·L⁻¹ TX-100 extraction, 2 h, then centrifuge and filter, add 100 mL persulfate (0.2 M) to soil for 2 h); (vi) TX-100 + SP(mix) (a mixture of 50 mL 16,000 mg·L⁻¹ TX-100 and 50 mL 0.4 M persulfate, 4 h). The procedures of mixing and centrifuging were similar under all testing conditions. The residual soil and supernatant were analyzed to measure the concentration of PAHs and TOC. All measurements were made in duplicate and average values were reported.

2.5. Analytical methods and procedures

The analytical methods used to measure PAHs and degradation products are described by Zhao et al. (2013). The sieved soils (2 g, <2 mm) were extracted using a stainless steel extraction system (34 mL), with two cellulose membranes (Φ30 mm), anhydrous sodium sulfate (2 g), a spoon of copper powder, diatomite (~4 g). PAHs and degradation products were extracted from the soils by an accelerated solvent extraction system (ASE 350, USA) using *n*-hexane and *n*-hexane/dichloromethane (1:1), respectively. The extraction conditions were as follows: static extraction time 5 min; heating time 5 min; 1500 psi, 100 °C; two static extraction cycles (5 min each); including one volume for rinsing; and a purging time of 90 s.

The concentration of PAHs in the supernatant was measured using a liquid-liquid extraction method. A mixture of the supernatant (5 mL) and *N*-hexane (5 mL) were placed in a glass centrifuge tube, and shaken at 250 rpm for 1 h (Zhao et al., 2013).

The extracts were concentrated by a rotary evaporator (RE-52AA, Shanghai) to 0.5 mL and adjusted to constant volume (1 mL) with *n*-hexane. The internal standard (125 µL) was added to the diluted samples prior to gas chromatography–mass spectrometry (GC–MS,

Agilent 7890A) for quantitative analysis. The instrument parameters were: HP-5MS 30 m × 0.25 mm capillary column; helium as carrier gas; inlet pressure 4.35 psi; linear velocity 37 cm/s; inlet temperature 300 °C; start temperature 60 °C; programmed to 300 °C at a rate of 5 °C·min⁻¹; retained for 20 min until complete elution of all species. The qualitative analysis of oxidative product was measured by GC–MS (full scan) and then identified using the ChemStation library. A selected ion scan was used for a semi-quantitative analysis according to their relative response area compared to the internal standard.

TOC of soil samples and liquid effluent were analyzed with a TOC analyzer (Elementar vario TOC, Germany). First, calibration curves of total carbon (TC) and inorganic carbon (IC) were established with corresponding standards (glucose for TC and Na₂CO₃ for IC). Then, soil samples were ground and sieved with a 140 mesh wire screen. The measurements of TC and IC were conducted according to the manufacturer specifications TOC was calculated as follows: TOC = TC – IC.

3. Results and discussion

3.1. Screening for efficient chemicals on batch experiment

The concentrations of 16 PAHs varied between the two soils (Table 1). The SS soil contained a greater fraction of medium to high molecular weight compounds, whereas the NS soil contained a greater fraction of low molecular weight compounds (Table 1). TX-100 was the most suitable reagent among the five surfactants, removing 66.5% and 31.5% of the total PAHs (TPAHs) from SS and NS, respectively (Fig. 1). Removals of TPAHs in SS are in the following order: Fenton > SP > KMnO₄ > Control (Fig. 2). Fenton and SP removed 98.4% and 97.6% TPAHs, respectively. And, more remarkable, the removal rates of TPAHs of control group close to 80%. Based on the results, we guessed that a larger portion of 2–4 ring PAHs in SS soil might escape into the air. In addition, there was also a minority of low molecular weight PAHs dissolving in water. The degradation of TPAHs in NS from highest to lowest were SP, KMnO₄, Fenton and Control group, with the data of 77.2%, 69.1%, 48.2% and 36.1%.

In general, SS achieved a better effect on both extraction and oxidation than those of NS. The chemical surfactants exhibited greater removal than the biosurfactants in terms of elution effectiveness (Fig. 1), and is consistent with the findings of prior research (Chong et al., 2014). Fenton and SP treatment of the soil exhibited the greatest PAHs removal in the SS soil. However, in the NS soil, SP and KMnO₄ exhibited the greatest removal. But the difficulty in Fenton reaction was rapid dissociation of H₂O₂ with Fe²⁺, which hindered effective oxidation. Between the increased temperature, rapid reaction and evolution of O₂ (g), these mechanisms may contribute to the release of toxic gases and vapors. SP, by contrast, is a strong oxidant where S₂O₈²⁻ in water has a standard redox potential (E) of +2.01 V. Activation of persulfate through of base (>pH 10.5), thermal, ultraviolet light, or transition metal ions (i.e., Fe²⁺, Ag⁺, Ce²⁺, Co²⁺), yields the more powerful oxidants including SO₄•⁻ (E = +2.6 V) and •OH (E = +2.8 V). Due to longer persistence of Na₂S₂O₈ than H₂O₂ in soils, it may remain active for weeks to months (Zhao et al., 2013; Floris et al., 2017). In conclusion, SP activated by citric acid chelated iron was selected for further testing.

3.2. Sequence of extraction and oxidation

3.2.1. The removal of TPAHs from the soils and effluents—Concentrations of TPAHs were measured in the solid phase and liquid phase under various chemical conditions (Table 2). The residual concentrations of TPAHs in both soils were in the general increasing order of: TX-100 + SP(l) < SP < TX-100 + SP(s) = TX-100 + SP(mix) < TX-100 < Control group. In both soils, TX-100 + SP(l) resulted in the lowest TPAHs concentration, with a concentration of 414 mg·kg⁻¹ and 180 mg·kg⁻¹, respectively. But they were not significantly lower than the SP oxidation. TX-100 + SP(l) had a better enhancement in the SS soil which reduced an additional 54 mg·kg⁻¹ TPAHs in comparison with SP oxidation alone. After 4 h treatment, the highest concentration of TPAHs in liquid was by TX-100 extraction, followed by SP oxidation. The other three combinations of TX-100 and SP exhibited lower PAHs concentration in solution. In the NS soil slurry, TPAHs were transferred from the solid phase to the aqueous phase by SP oxidation alone. Overall, the TPAHs residues of TX-100 extraction alone and SP oxidation alone were greater than the treatment by TX-100 + SP(l).

The results indicated that all forms of surfactant combined with oxidation resulted in enhanced removal of TPAHs relative to any single technique in SS (Fig. 3). Among them, the highest removal (82.5%) was achieved by TX-100 + SP(l), followed by TX-100 + SP(s) and TX-100 + SP(mix) with a total removal of 74.8% and 72.3%, respectively. SP oxidation and TX-100 extraction exhibited 71.8% TPAHs removal and 62.9% TPAHs extraction, respectively. Compare to SP oxidation alone, TX-100 + SP(l) could further increase the removal of TPAHs by approximately 11%. But in the NS soil, it had little differences in any of the treatments, ranging between 72.3% and 82.0%. The greatest removal was also measured in TX-100 + SP(l) (82.0%), but closely followed by SP oxidation (81.5%) and TX-100 + SP(mix) (80.4%). Control group was the least effective at removing TPAHs from the soils (11.5%). Overall, any oxidative or surfactant treatment exhibited greater removal than DIW alone (i.e., the control group).

The compatibility between surfactants and oxidants is critical to the potential implementation of this coupled process (Wang et al., 2017). In this study, sequential application of surfactant and oxidant was the most effective way for TPAHs solubilization and destruction. Greater enhancement was observed in SS than NS indicating that soil quality and/or PAHs composition are factors that play a role.

3.2.2. The removal effect of L-PAHs, M-PAHs and H-PAHs—Assessment of the PAH molecular weight dependency of the treatment process (i.e., different number of benzene rings), the 16 PAHs were grouped into three categories: L-PAHs (2 rings), M-PAHs (3–4 rings) and H-PAHs (5–6 rings).

SP achieved the highest removal of L-PAHs in both soils, followed by TX-100 + SP(l) (Fig. 4). After SP oxidation, the L-PAH removal rate was relatively high, 87.0% and 98.4% L-PAHs in SS and NS, respectively. The removal of H-PAHs by SP treatment was significantly lower in the SS and NS soils, 59.3% and 80.5%, respectively. Desorption of PAHs appeared to play a key role to oxidative treatment, and was likely the limiting factor in the oxidation of M-PAHs and H-PAHs. Previously, it was reported that the Fenton oxidation could remove about 80% of the 2–3 ring PAHs and 20–40% of the 4–5 ring PAHs (Nam et al., 2001),

which was consistent with the results in this study. Similarly, Quan et al. (2003) also achieved high removal of anthracene and phenanthrene (i.e., 3 ring PAHs), but the lowest effect on Indene(1,2,3-*cd*) pyrene (6 ring PAHs). The 2 ring PAH (i.e. naphthalene) has a relatively higher water solubility and mass transfer was more rapid to the water phase where it could react with $\cdot\text{OH}$ or $\text{SO}_4^{\bullet-}$.

TX-100 + SP(l) had a synergistic effect on the destruction of M-PAHs and H-PAHs compare with SP oxidation alone, but with a similar result in L-PAHs removal (Fig. 4). Compare to SP oxidation, the removal of M-PAHs in SS increased from 70.9% to 78.8%, and the elimination of H-PAHs improved from 59.3% to 70.2%. NS had the same general trend as SS, and the removal of M-PAHs and H-PAHs increased by 6.3% and 4.4%, respectively. Based on these results, TX-100 had a positive impact on the degradation of M-PAHs and H-PAHs, with a maximum enhancement of ~11%. It was assumed that the amphiphilic characteristic of TX-100 lowered interfacial tension, changed the oil-water interface property and enhanced the mobility of PAHs (Mousset et al., 2014). Through these processes, contaminants desorbed from the soil organic matter and soil surfaces, being more vulnerable to oxidative treatment. TX-100 + SP(s) and TX-100 + SP (mix) exhibited lower PAHs removal in this study. Under these conditions, it was proposed that this was due to simultaneous solubilization and oxidation, and possibly reaction between the TX-100 and the oxidant. The reaction rate of $\text{SO}_4^{\bullet-}$ was 3–5 orders of magnitude faster than the consumption of persulfate, even far more quickly than the release rate of PAHs from the soil. Further, the oxidation mechanism might occur in the micelle structure during the transport process (Wang et al., 2013).

3.2.3. The influences on the TOC content—The TOC contents in soil and extraction liquids were studied to better assess the feasibility of oxidizing the PAHs in soil and to identify potential oxidative mechanisms. The variation of TOC in SS was basically the same as those of NS (Fig. 5). Results indicated that the lowest TOC in soils and the highest TOC in liquid both occurred under SP oxidation with SS soil. Compared to the TOC contents in SS (2.10%) and NS (0.44%), the TOC decreased to 1.70% and 0.37%, respectively. Soil organic matter will likely compete with the PAHs for free radicals during persulfate oxidation, thus serving as a source of oxidation inefficiency (Crimi and Taylor, 2007; Romero et al., 2011). Cuypers et al. (2000) reported that persulfate tended to react with the soil organic matter that is readily biodegradable (Cuypers et al., 2000). However, changes in TOC in soil were different between SS and NS when TX-100 was added into the system. In the SS soil, TX-100 + SP(l) had a similar TOC value to the control group, which was a little lower than the control group. The TOC content increased slightly under the treatments of TX-100 + SP(s) and TX-100 + SP(mix). For NS, the TOC contents increased 2.0–2.2% in all forms of combined treatment. Although a firm explanation is not currently possible, this was partially attributed to the addition of the surfactant, in addition to the differences in background TOC between SS and NS.

In SS and NS reactors where SP was amended, the aqueous phase TOC concentration increased relative to the DIW amended system (i.e. Control group). It is proposed that this is the result of partial oxidation of PAHs and natural organic matter (NOM) in soil, and a reduction in the hydrophobicity of the decomposition products relative to the parent

material. Collectively, incomplete oxidation of PAHs and NOM, and lower hydrophobicity will result in smaller organic molecules that are less inclined to be adsorbed, and are more likely to be in solution.

3.3. Oxidation products identification and mechanism investigation

PAHs degradation intermediates/products were identified by full scan and summarized in Schedule 1 (see Appendix A). There are 46 substances, the contents of which increase after reaction based on the analyses. In addition, there are 28 substances, the contents of which decreased after reaction. Among the increased products, the organic substances containing chlorine, cyclohexyloxane and binapacryl were the main products of concern. Based on the results obtained, oxy-PAHs included furan (i.e., dibenzofuran, naphtho[2,1-*b*] furan, 1,2-dimethyl- and dinaphtho[1,2-*b*:1',2'-difuran), xanthene (i.e., benzo[*k*]xanthene, 9h-Xanthene and naphtho[2,1,8,7-*k**lmn*]xanthene) and thiophene (i.e., dibenzothiophene and nbenzothiophene, 3-methyl-) appeared as a result of the treatment. Some researchers pointed that oxy-PAHs (i.e., ketones, quinones, aldehydes and furans) emerged in the oxidation system had the toxic function of mutagenicity and carcinogenicity, requiring a focus on the variation of their amount (Bergknut et al., 2004; Xue and Warshawsky, 2005; Bandowe et al., 2011). Thus, they must be taken into account to confirm the environment impact. The concentrations of the oxy-PAHs were measured in the post-treatment solutions to assess the relative amounts of oxy-PAHs before and after oxidative treatment (Fig. 6). Relative to the original soil, oxidation combined with surfactants extraction resulted in an overall decline of the oxy-PAHs. Consequently, it is projected that the toxicity and mutagenicity of the treated soils would decline through these treatment processes. TX-100 + SP(l) and TX-100 + SP(s) were the test conditions that resulted in the least concentrations of oxy-PAHs relative to treatment type and reductions in oxy-PAHs, are TX-100 + SP(mix), TX-100 + SP(l) and SP. Therefore, one advantage of treatments using TX-100 is a reduction in toxicity of the reaction byproducts.

Based on reaction process and the analysis of products, the possible mechanism of surfactant enhanced SP oxidation was proposed (Fig. 7). First, surfactant monomers accumulate at the soil-contaminant and soil-water interfaces. When the concentration was above the CMC, the adsorbed layer was formed to reduce interfacial tension, changing the wettability of the system and promoting the separation of the contaminants from the soil particles. Then the core layer structure of surfactant micelles carried hydrophobic organic compounds (i.e., PAHs) into liquid phase, with a higher mobility, increasing the reaction probability of contaminants and oxidants. SP could be activated through one-electron transfer by ferrous iron (Fe^{2+}), which in turn release highly reactive free radicals (such as sulfate radical), oxidizing the target contaminants (i.e., PAHs) desorbing from soil. But too much Fe^{2+} may result in the iron scavenging of $\bullet\text{SO}_4^-$, reducing its effectiveness for degradation (Vicente et al., 2011).

4. Conclusions

Five surfactants (Biosurfactant Accell, Rhamnolipid (>99%), Rhamnolipid (25%), Tween80, TX-100) were tested to assess PAHs removal from the two soil types, and TX-100 was the

most effective. Of the three oxidants tested (KMnO_4 , $\text{H}_2\text{O}_2 + \text{Fe}^{+2}$ (Fenton), SP), SP was most effective in oxidizing PAHs in soil. Greater removal or oxidation of PAHs were measured in the SS sandy loam soil which were attribute to a high proportion of L-PAHs and H-PAHs and the higher permeability and porosity than that of NS, a silty clay soil.

The oxidant and surfactant were amended to the soil separately, and under various combined conditions (solid, liquid, simultaneously mixed). Removal and degradative losses of PAHs from soil were found to be significant, and there were differences between the various testing conditions in the two soils. Specifically, greater removal of 2-ring PAHs (i.e., naphthalene) was measured than 3–4 ring and 5–6 ring classes of PAHs. This was generally correlated to the hydrophobicity and adsorption of these compound classes, and reactivity with $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$. The most effective combination was TX-100 + SP(l), where the SP was added as a liquid (100 mL; 0.2 M) which could significantly improve the degradation efficiency of PAHs, particularly for M-PAHs and H-PAHs with low solubility and reactivity.

Oxy-PAHs are known for greater toxicity. Based on measurements of the decomposition products under the various test conditions, oxy-PAHs were measured in both the original soil and the treated soil. However, the concentrations of oxy-PAHs, especially for furans and xanthenes, were consistently lower when oxidant and surfactant were mixed (i.e. TX-100 + SP(s) and TX-100+ SP(l)), than oxidant alone.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was financially supported by the Key Research Program of the Chinese Academy of Sciences (ZDRW-ZS-2016-5-5) and the Key Research Program of the Chinese Academy of Sciences (KFZD-SW-303).

References

- Bandowe et al., 2011 Bandowe BAM, Sobocka J, Wilcke W Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in urban soils of Bratislava, Slovakia: patterns, relation to PAHs and vertical distribution Environ. Pollut, 159 (2011), pp. 539–549 [PubMed: 21095050]
- Bergknut et al., 2004 Bergknut M, Kittl A, Lundstedt S, Tysklind M, Haglund P Assessment of the availability of polycyclic aromatic hydrocarbons from gasworks soil using different extraction solvents and techniques Environ. Toxicol. Chem, 23 (2004), pp. 1861–1866 [PubMed: 15352473]
- Besha et al., 2018 Besha AT, Bekele DN, Naidu R, Chadavada S Recent advances in surfactant-enhanced In-Situ Chemical Oxidation for the remediation of non-aqueous phase liquid contaminated soils and aquifers Environ. Technol. Innov, 9 (2018), pp. 303–322
- Bezza and Chirwa, 2016 Bezza FA, Chirwa EMN Biosurfactant-enhanced bioremediation of aged polycyclic aromatic hydrocarbons (PAHs) in creosote contaminated soil Chemosphere, 144 (2016), pp. 635–644 [PubMed: 26408261]
- Bi et al., 2007 Bi E, Schmidt TC, Haderlein SB Environmental factors influencing sorption of heterocyclic aromatic compounds to soil Environ. Sci. Technol, 41 (2007), pp. 3172–3178 [PubMed: 17539522]
- Biache et al., 2015 Biache C, Lorgeoux C, Andriatsihoarana S, Colombano S, Faure P Effect of pre-heating on the chemical oxidation efficiency: implications for the PAH availability measurement in contaminated soils J. Hazard. Mater, 286 (2015), pp. 55–63 [PubMed: 25557939]

- Cheng et al., 2016 Cheng M, Zeng G, Huang D, Lai C, Xu P, Zhang C, Liu Y Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review Chem. Eng. J, 284 (2016), pp. 582–598
- Chong et al., 2014 Chong ZY, Liao XY, Yan XL, Sun L, Zhao D, Liang T Enhanced desorption of PAHs from manufactured gas plant soils using different types of surfactants Pedosphere, 24 (2014), pp. 209–219
- Crimi and Taylor, 2007 Crimi ML, Taylor J Experimental evaluation of catalyzed hydrogen peroxide and sodium persulfate for destruction of BTEX contaminants Soil Sediment Contam, 16 (2007), pp. 29–45
- Cuyper et al., 2000 Cuyper C, Grotenhuis T, Joiasse J, Rulkens W Rapid persulfate oxidation predicts PAH bioavailability in soils and sediments Environ. Sci. Technol, 34 (2000), pp. 2057–2063
- Dahal et al., 2016 Dahal G, Holcomb J, Socci D Surfactant-oxidant co-application for soil and groundwater remediation Remediat. J, 26 (2016), pp. 101–108
- Duan et al., 2015 Duan L, Naidu R, Thavamani P, Meaklim J, Megharaj M Managing long-term polycyclic aromatic hydrocarbon contaminated soils: a risk-based approach Environ. Sci. Pollut. R, 22 (2015), pp. 8927–8941
- EEA, 2008 EEA Contamination from Local Sources European Environment Agency (2008) <http://www.eea.europa.eu/themes/soil/soil-threats>, Accessed 5th Jul 2017
- EthicalChem, 2016a EthicalChem SEPR and S-ISCO Remediation of MGP Gasworks, Sydney Australia http://media.wix.com/ugd/9b5eec_1cc453253d8d48149bc96f2ab39f0894.pdf (2016), Accessed 18th Dec 2017
- EthicalChem, 2016b EthicalChem SEPR and S-ISCO Remediation of Creosote Bridgeville Delaware, New York (2016) http://media.wix.com/ugd/9b5eec_3b8b10eb81f84e2bbb9f88775d626d4.pdf, Accessed 18th Dec 2017
- Floris et al., 2017 Floris B, Galloni P, Sabuzi F, Conte V Metal systems as tools for soil remediation Inorg. Chim. Acta, 455 (2017), pp. 429–445
- Flotron et al., 2005 Flotron V, Delteil C, Padellec Y, Camel V Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process Chemosphere, 59 (2005), pp. 1427–1437 [PubMed: 15876386]
- Gong et al., 2006 Gong Z, Wilke BM, Alef K, Li P, Zhou Q Removal of polycyclic aromatic hydrocarbons from manufactured gas plant-contaminated soils using sunflower oil: laboratory column experiments Chemosphere, 62 (2006), pp. 780–787 [PubMed: 15982705]
- Gryzenia et al., 2009 Gryzenia J, Cassidy D, Hampton D Production and accumulation of surfactants during the chemical oxidation of PAH in soil Chemosphere, 77 (2009), pp. 540–545 [PubMed: 19695666]
- Haapea and Tuhkanen, 2006 Haapea P, Tuhkanen T Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment J. Hazard. Mater, 136 (2006), pp. 244–250 [PubMed: 16455197]
- Hahladakis et al., 2016 Hahladakis JN, Latsos A, Gidarakos E Performance of electroremediation in real contaminated sediments using a big cell, periodic voltage and innovative surfactants J. Hazard. Mater, 320 (2016), pp. 376–385 [PubMed: 27585269]
- Jonsson et al., 2007 Jonsson S, Persson Y, Frankki S, van Bavel B, Lundstedt S, Haglund P, Tysklind M Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent: a multivariate evaluation of the importance of soil characteristics and PAH properties J. Hazard. Mater, 149 (2007), pp. 86–96 [PubMed: 17513044]
- Kuppusamy et al., 2016 Kuppusamy S, Palanisami T, Megharaj M, Venkateswarlu K, Naidu R In-situ remediation approaches for the management of contaminated sites: a comprehensive overview Rev. Environ. Contam. Toxicol, 236 (2016), pp. 1–115 [PubMed: 26423073]
- Lemaire et al., 2013 Lemaire J, Buès M, Kabeche T, Hanna K, Simonnot MO Oxidant selection to treat an aged PAH contaminated soil by in situ chemical oxidation J. Environ. Chem. Eng, 1 (2013), pp. 1261–1268
- Liang et al., 2007 Liang C, Wang ZS, Bruell CJ Influence of pH on persulfate oxidation of TCE at ambient temperatures Chemosphere, 66 (2007), pp. 106–113 [PubMed: 16814844]

- Liao et al., 2013 Liao XY, Ma D, Yan XL, Yang LS Distribution pattern of polycyclic aromatic hydrocarbons in particle-size fractions of coking plant soils from different depth *Environ. Geochem. Health*, 35 (2013), pp. 271–282 [PubMed: 22975988]
- Lundstedt et al., 2006 Lundstedt S, Persson Y, Öberg L Transformation of PAHs during ethanol-Fenton treatment of an aged gasworks' soil *Chemosphere*, 65 (2006), pp. 1288–1294 [PubMed: 16735053]
- Mao et al., 2015 Mao X, Jiang R, Xiao W, Yu J Use of surfactants for the remediation of contaminated soils: a review *J. Hazard. Mater*, 285 (2015), pp. 419–435 [PubMed: 25528485]
- Moon et al., 2006 Moon HS, Kahng HY, Kim JY, Kukor JJ, Nam K Determination of biodegradation potential by two culture-independent methods in PAH-contaminated soils *Environ. Pollut*, 140 (2006), pp. 536–545 [PubMed: 16490294]
- Mousset et al., 2014 Mousset E, Oturan MA, Van Hullebusch ED, Guibaud G, Esposito G Soil washing/flushing treatments of organic pollutants enhanced by cyclodextrins and integrated treatments: state of the art *Crit. Rev. Environ. Sci. Technol*, 44 (2014), pp. 705–795
- Nadarajah et al., 2002 Nadarajah N, Van Hamme J, Pannu J, Singh A, Ward O Enhanced transformation of polycyclic aromatic hydrocarbons using a combined Fenton's reagent, microbial treatment and surfactants *Appl. Microbiol. Biotechnol*, 59 (2002), pp. 540–544 [PubMed: 12172623]
- Nam et al., 2001 Nam K, Rodriguez W, Kukor JJ Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction *Chemosphere*, 45 (2001), pp. 11–20 [PubMed: 11572585]
- Quan et al., 2003 Quan HN, Teel AL, Watts RJ Effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in the Fenton-like treatment of soils *J. Hazard. Mater*, 102 (2003), pp. 277–289 [PubMed: 12972243]
- Ranc et al., 2016 Ranc B, Faure P, Croze V, Simonnot MO Selection of oxidant doses for in situ chemical oxidation of soils contaminated by polycyclic aromatic hydrocarbons (PAHs): a review *J. Hazard. Mater*, 312 (2016), pp. 280–297 [PubMed: 27043880]
- Romero et al., 2011 Romero A, Santos A, Cordero T, Rodríguez-Mirasol J, Rosas JM, Vicente F Soil remediation by Fenton-like process: phenol removal and soil organic matter modification *Chem. Eng. J*, 170 (2011), pp. 36–43
- Stroo et al., 2012 Stroo HF, Leeson A, Marqusee JA, Johnson PC, Ward CH, Kavanaugh MC, Sale TC, Newell CJ, Pennell KD, Lebrón CA Chlorinated ethane source remediation: lessons learned *Environ. Sci. Technol*, 46 (2012), pp. 6438–6447 [PubMed: 22558915]
- Usman et al., 2012 Usman M, Faure P, Ruby C, Hanna K Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation *Appl. Catal. B Environ*, 117–118 (2012), pp. 10–17
- Vicente et al., 2011 Vicente F, Santos A, Romero A, Rodriguez S Kinetic study of diuron oxidation and mineralization by persulphate: effects of temperature, oxidant concentration and iron dosage method *Chem. Eng. J*, 170 (2011), pp. 127–135
- Villa et al., 2010 Villa RD, Trovó AG, Nogueira RFP Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation *J. Hazard. Mater*, 174 (2010), pp. 770–775 [PubMed: 19853992]
- Wang et al., 2013 Wang WH, Hoag GE, Collins JB, Naidu R Evaluation of surfactant-enhanced in situ chemical oxidation (S-ISCO) in contaminated soil *Water Air Soil Pollut*, 224 (2013), p. 1713
- Wang et al., 2017 Wang L, Peng L, Xie L, Deng P, Deng D Compatibility of surfactants and thermally activated persulfate for enhanced subsurface remediation *Environ. Sci. Technol*, 51 (2017), pp. 7055–7064 [PubMed: 28548832]
- Xue and Warshawsky, 2005 Xue W, Warshawsky D Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: a review *Toxicol. Appl. Pharmacol*, 206 (2005), pp. 73–93 [PubMed: 15963346]
- Yap et al., 2015 Yap CL, Gan S, Ng HK Feasibility of treating aged polycyclic aromatic hydrocarbons (PAHs)-contaminated soils using ethyl lactate-based Fenton treatment via parametric and kinetic studies *Environ. Sci. Pollut. Res*, 22 (2015), pp. 329–342

Zhao et al., 2013 Zhao D, Liao X, Yan X, Huling SG, Chai T, Tao H Effect and mechanism of persulfate activated by different methods for PAHs removal in soil J. Hazard. Mater, 254 (2013), pp. 228–235 [PubMed: 23618659]

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Highlights

- A combined remediation method with TX-100 and persulfate was proposed.
- Sequential application of TX-100 and persulfate could enhance the elimination of 3–6 ring PAHs.
- The combined method dramatically reduced the amount of oxy-PAHs in contaminated soil.

Fig. 1.
Comparison of TPAH extraction from soils using different surfactants.

Fig. 2.
Oxidative treatment and removal of TPAHs of the two soils.

Fig. 3.

TPAHs removal as the application sequence. (Removal = $1 - (m_s + m_l) / m_t$; m_s : the mass of TPAHs in treated soil; m_l : the mass of TPAHs in solution; m_t : the mass of TPAHs in untreated soil). Different letters above bars indicate significant difference under various application sequences in the same soil at $P < 0.05$.

Fig. 4. Removal of different ring PAHs as the application sequence in SS and NS. Different letters above bars indicate significant difference under various application sequences in the same ring PAHs at $P < 0.05$.

Fig. 5.
The TOC contents in soils and extraction liquids.

Fig. 6.
Concentration of priority products by different treatments.

Fig. 7.

The mechanism of surfactant enhanced persulfate oxidation.

Table 1.

Characteristics and concentrations of 16 PAHs in the soils (N = 3).

Contaminant	Abbreviation	Rings	SS (mg·kg ⁻¹)	NS (mg·kg ⁻¹)
Naphthalene	Nap	2	10.0 ± 3.2	453.3 ± 76.2
Acenaphthylene	ANY	3	13.0 ± 0.1	23.2 ± 3.1
Acenaphthene	ANE	3	167.8 ± 8.1	4.2 ± 0.5
Fluorine	FLE	3	229.1 ± 4.9	19.5 ± 2.5
Phenanthrene	PHE	3	382.2 ± 50.8	152.7 ± 19.7
Anthracene	ANT	3	173.5 ± 10.9	16.7 ± 3.3
Fluoranthene	FLT	4	478.5 ± 28.4	11.2 ± 1.5
Pyrene	PYR	4	343.6 ± 19.1	150.5 ± 18.8
Benzo(a)anthracene	BaA	4	130.1 ± 7.3	43.4 ± 6.2
Chrysene	CHR	4	132.1 ± 0.6	53.4 ± 7.9
Benzo(b)fluoranthene	Bbf	5	354.1 ± 20.3	35.2 ± 6.0
Benzo(k)fluoranthene	Bkf	5	33.0 ± 1.8	68.6 ± 14.1
Benzo(a)pyrene	BaP	5	118.4 ± 6.6	66.7 ± 13.7
Indene(1,2,3- <i>cd</i>)pyrene	I(<i>cd</i>)P	6	20.6 ± 6.0	12.7 ± 1.7
Dibenzo(a,h)anthracene	D(<i>ch</i>)A	5	87.0 ± 4.1	46.0 ± 12.1
Benzoperylene	B(<i>ghi</i>)P	6	60.2 ± 2.5	58.0 ± 12.9
Low molecular weight PAHs	L-PAHs	2	10.0 ± 3.2	453.3 ± 16.8
Middle molecular weight PAHs	M-PAHs	3–4	1917.8 ± 6.2	421.3 ± 51.1
High molecular weight PAHs	H-PAHs	5–6	805.4 ± 28.6	340.6 ± 20.8
Total PAHs	T-PAHs	2–6	2733.2 ± 31.6	1215.2 ± 21.1

Table 2.Distribution of TPAHs in the soils and effluents^a.

	SS			NS		
	Treated soil (mg·kg ⁻¹)	Extract-2 h (mg·L ⁻¹)	Extract-4 h (mg·L ⁻¹)	Treated soil (mg·kg ⁻¹)	Extract-2 h (mg·L ⁻¹)	Extract-4 h (mg·L ⁻¹)
Control group	2135	2.0	1.8	1072	5.7	1.8
SP	468	2.1	152.8	183	6.3	21.1
TX-100	655	4.9	179.8	249	1.9	44.4
TX-100 + SP(s)	651	2.4	19.2	259	4.8	11.2
TX-100 + SP(l)	414	3.3	31.9	180	11.8	15.5
TX-100 + SP(mix)	640	1.2	4.9	210	25.5	13.6

^aTreated soil: concentration of TPAHs in soils after the treatment; Extract-2 h: concentration of TPAHs in liquid after 2 h treatment; Extract-4 h: concentration of TPAHs in liquid after 4 h treatment.