Article

Remediation of Anthracene-Contaminated Soil with Sophorolipids-SDBS-Na$_2$SiO$_3$ and Treatment of Eluting Wastewater

Wei Li $^{1,2,*}$, Xiaofeng Wang $^{1,2}$, Lixiang Shi $^{1,2}$, Xianyuan Du $^3$ and Zhansheng Wang $^3$

$^1$ State Key Laboratory of Petroleum Pollution Control, Beijing 102206, China; xiaofengwww123@163.com (X.W.); slxlyq0218@163.com (L.S.)
$^2$ College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China
$^3$ CNPC Institute of Safety and Environmental Protection Technology, Beijing 102206, China; duxianyuan@cnpc.com.cn (X.D.); wangzs@cnpc.com.cn (Z.W.)

* Correspondence: li.wei@ncepu.edu.cn

Received: 29 May 2020; Accepted: 6 July 2020; Published: 4 August 2020

Abstract: The soil pollution of polycyclic aromatic hydrocarbons (PAHs) is serious in China, which not only affects the living and growing environment of plants and animals but also has a great impact on people’s health. The use of hydrophobic organic compounds to make use of surfactant ectopic elution processing is more convenient and cheaper as a repair scheme and can effectively wash out the polycyclic aromatic hydrocarbons in the soil. Therefore, we mixed sophorolipids:sodium dodecylbenzene sulfonate (SDBS):Na$_2$SiO$_3$ according to the mass ratio of 1:15:150. We explored the influencing factors of high and low concentrations of PAH-contaminated soil using a single factor test and four factors at a two-level factorial design. Then, the elution wastewater was treated by ultrasonic oxidation technology and the alkali-activated sodium persulfate technology. The results showed that: (1) In the single factor test, when the elution time is 8 h, the concentration of the compounded surfactant is 1200 mg/L, the particle size is 60 mesh, the concentration of NaCl is 100 mmol/L, and the concentration of KCl is 50 mmol/L, and the effect of the PAH-contaminated soil eluted by the composite surfactant is the best. Externally added NaCl and KCl salt ions have a more obvious promotion effect on the polycyclic aromatic hydrocarbon-contaminated soil; (2) in the interaction experiment, single factor B (elution time) and D (NaCl concentration) have a significant main effect. There is also a certain interaction between factor A (concentration agent concentration) and factor D, factor B, and factor C (KCl concentration); (3) the treatment of anthracene in the eluate by ultrasonic completely mineralizes the organic pollutants by the thermal and chemical effects produced by the ultrasonic cavitation phenomenon, so that the organic pollutants in the eluate are oxidized and degraded into simple environmentally friendly small molecular substances. When the optimal ultrasonic time is 60 min and the ratio of oxidant to activator is 1:2, the removal rate of contaminants in the eluent can reach 63.7%. At the same time, the turbidity of the eluent is significantly lower than that of the liquid after centrifugal separation, indicating that oxidants can not only remove the pollutants in elution water but also remove the residual soil particulate matter; and (4) by comparing the infrared spectrum of the eluted waste liquid before and after oxidation, it can be seen that during the oxidation process, the inner part of eluent waste liquid underwent a ring-opening reaction, and the ring-opening reaction also occurred in the part of the cyclic ester group of the surfactant, which changed from a ring to non-ring.

Keywords: combinational surfactant; anthracene; elution wastewater; ultrasonic oxidation
1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic compounds that are ubiquitous in the environment. They consist of two or more fused benzene rings, such as phenanthrene, anthracene, and benzo[α]pyrene, which are potentially carcinogenic and mutagenic in contaminated soil and water bodies [1]. It has the characteristics of low volatility, low water solubility, and low biodegradability [2–5], which makes the accumulation of polycyclic aromatic hydrocarbon in the soil and groundwater environment increase year by year, resulting in non-negligible pollution. They are generated through natural and man-made means, such as the pyrolysis of organic matter and the use of fossil fuels [6,7]. It has toxicity, mutagenicity, and carcinogenicity, and its toxicity increases with the increase of the molecular weight. Surfactant leaching technology has a good effect on eluting PAHs in soil. There are two main mechanisms for surfactant remediation of oil-contaminated soil: (1) When its critical micelle concentration (CMC) is reached [8–13], surfactant molecules will quickly aggregate and arrange to form an ordered polymer with a certain structure, forming a stable micelle, which can be used to increase the concentration of hydrophobic petroleum hydrocarbon pollutants in the liquid phase through micelle solubilization; and (2) by reducing the interfacial tension between the water–soil, oil–soil, and oil–water, surfactants can improve the migration ability of petroleum hydrocarbon pollutants, promote their desorption from the soil, disperse the pollutants in the soil pores, and make them contact with the surfactant solution to elute. Although the surfactant remediation technology has a high efficiency and short cycle, the high cost and ecological risk of the surfactant limit its wide application to some extent. Choosing suitable surfactants, improving repair efficiency, reducing the amount of surfactants, and reducing the pollution and ecological risks of surfactants on the soil are the key issues facing the current technology.

Ji et al. [14] investigated the oxidative remediation performance of activated sodium persulfate (SPS) on polycyclic aromatic hydrocarbon (PAH)-contaminated soil with the aid of solubilization of typical nonionic surfactant Tween 80. Wang et al. [15] selected sodium dodecyl benzene sulfonate, sodium dodecyl sulfate, and sodium dodecyl sulfonate for desorption experiments on contaminated soil, and studied the synergistic solubilizing effect of the anionic surfactant and sodium humate on diesel pollutants in loess. The results showed that sodium humate and three anionic surfactants have a significant solubilization effect on the desorption of diesel in loess. Yang et al. [16] compared the elution effect of SDBS-TX100 and single surfactant on phenanthrene in polluted soil, and found that TX100 and SDBS mixed surfactant with a mass ratio of 1:9 had the best elution effect on phenanthrene in soil, which indicated that the mixed surfactant with an appropriate ratio had higher solubilization and elution efficiency. Wang et al. [17] used the biosurfactants rhamnolipid (Xi’an rege biotechnology Co., Ltd., Xi’an, China) and Tween-80 (Macklin biochemical Co., Ltd., Shanghai, China) to analyze the concentration, leaching time, temperature, and frequency of surfactants for five polycyclic aromatic hydrocarbon (fluoranthene, pyrene, benzo[b]fluoranthene, benzene, and [k] fluoranthene, benzo [α] pyrene)-contaminated soil’s leaching effect.

For the selection of surfactants, the potential impact on the environment, the hydrophilic and oil-wet equilibrium (HLB) values, and the availability of the surfactants should be considered [18]. Sophorolipids is a kind of lactone surfactant, which can be 100% degraded in the natural environment, while HLB ranges from 9 to 12 and can be produced in a large scale [19]. The critical micelle concentration (CMC) of sophorolipids ranges from 40 to 100 mg/L, two orders of magnitude lower than chemically synthesized surfactants [20], and remains stable over a wide range of temperatures and salt concentrations. Sun et al. [21] investigated the effects of indigenous microorganisms, inoculated mixed petroleum hydrocarbon-degrading bacteria, and the addition of sophorolipid biological surfactant. The mechanism of oil-containing sludge remediation enhanced by sophorolipid biological surfactant and inoculating petroleum hydrocarbon-degrading bacteria was discussed. Li et al. [22] investigated the influence of the sophorolipid concentration, electrolyte ion strength, and electrolyte acidity on the effect of chrome-contaminated soil electric remediation with sophorolipids. The results showed that the electric current intensity increased significantly in the electric remediation system with sophorolipids.
added. With the increase of the ionic strength and acidity of the electrolyte, the removal rate of chromium increased gradually.

Sodium dodecylbenzenesulfonate is an anionic surfactant with a high removal rate and low adsorption rate. However, the surfactant exhibits a higher CMC value, which results in a higher concentration of the agent in the washing residues and is more likely to precipitate in the presence of polyvalent cations (Ca$^{2+}$ and Mg$^{2+}$) [23,24]. Someone used sodium dodecylbenzenesulfonate to elute the nitrobenzene and benzoic acid in the soil under laboratory and actual contaminated site conditions, respectively. It was found that the surfactant had a better removal rate under the laboratory conditions for the two pollutants, and the maximum elution efficiency at the contaminated site could also reach more than 90% [25]. Ni et al. [26] took sodium dodecyl benzenesulfonate and Tween-80 as the representatives of nionic and non-ionic surfactants, respectively, and studied the influence of mixed surfactants on the interface behavior between phenanthrene and pyrene in soil, as well as the effect and mechanism of strengthening the remediation of phenanthrene and pyrene-contaminated soil.

Na$_2$SiO$_3$ affects the pH value of the solution and can react with the acidic components in the oil to form salt, increasing the water solubility of the oil [27,28]. Na$_2$SiO$_3$ belongs to an electrolyte, which can enhance the wetting, emulsification, and solubilization of the surfactant in the washing solution after being added into the solution; it can compress the double electric layer of the micelle, and increase the contact between the surfactant molecules, making more ions enter the micelle.

Because cationic surfactant has a low elution efficiency for pollutants, anionic surfactant has a higher CMC, resulting in the higher economic cost, and non-ionic surfactant has a stronger adsorption effect on soil, thus people pay more attention to the solubilization system obtained through compounding. One of the more widely used types of complex is the anionic and non-ionic surfactant complex applications. This may be because the oxygen atoms in the nonionic surfactant molecules are easily combined with the hydrogen ions in the water, so that the nonionic surfactant is positively charged, causing the nonionic surfactant and the anionic surfactant to attract each other to reduce the mixed micelles. Due to the repulsion between the bundles, the critical micelle concentration (CMC) of the system decreases. Anionic surfactants are likely to precipitate in the soil and nonionic surfactants are more likely to adsorb onto the soil fractions [29], which results in a high remediation cost due to the need for more surfactants [30]. It further pollutes the environment. Sorption of nonionic surfactants could be prevented using a combination of nonionic and anionic surfactants [9]. Most of the studies have introduced the solubilization effect of anions and nonionic surfactants. Some studies have shown the effects of soil’s physical and chemical properties and the surfactants themselves on the eluting effect. There is little research on the addition of auxiliaries to anionic and nonionic surfactants. Adding sodium silicate as auxiliaries can prevent surfactants from being adsorbed into the soil solid phase and play an anti-reprecipitation role.

However, surfactants only transfer the pollutant from the soil to the aqueous phase and further treatment of this polluted aqueous solution is required. The chemistry of persulfate as the oxidant has been widely studied [31]. In aqueous solution, persulfate salts dissociate to persulfate anions as shown in Equation (1):

$$S_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$$ (1)

Subsequently, when persulfate anion is activated, sulfate radical ($\text{SO}_4^{2-}$), a non-selective oxidant with a high redox potential ($E_0 = 2.6V$), is produced. This activation can be achieved by the addition of the transition metal, light or heat activation, by the addition of the hydrogen peroxide, or alkaline activation (pH > 10) [18]. Iron activation has the drawback that the pH must be maintained in the acid region to avoid iron precipitation [32], whereas the cost of thermally activated persulfate at the field scale can be unaﬀordable. Therefore, it is of great interest to develop a low-cost high-eﬃciency method for the activation of persulfates for organic pollutant degradation [33]. Alkaline activation has gained attention recently, but only few works have studied the remediation of eluting wastewater with polycyclic aromatic hydrocarbons (PAHs) by using this technology [34].
The eluting effect of sophorolipids-SDBS-Na$_2$SiO$_3$ on anthracene pollutants was studied, and the interaction between exogenous additives and environmental influencing factors was explained. At the same time, alkali-activated sodium persulfate was used to elute anthracene-contaminated soil wastewater with compound surfactants.

2. Materials and Methods

2.1. Materials

Table 1 shows the properties of sophorolipids, SDBS, and Na$_2$SiO$_3$. The surface tension was determined by the hanging sheet method. The minimum concentration of surfactant molecules to form micelles in solvent is critical micelle concentration, and the surface tension of surfactant molecules does not increase at the same time. The CMC of sophorolipids and SDBS was determined as 40 and 100 mg/L, respectively. Anthracene is a polycyclic aromatic hydrocarbon containing three rings, which is obtained in the final stage of distillation of coal tar and can be separated from anthracene oil from coal tar. It is mainly used as luminescent materials, insecticides, fungicides, and gasoline coagulants. It has a non-volatile and special linear molecular structure. Its toxicity can be multiplied under light conditions [35]. Therefore, it is considered as a representative of PAH pollutants. The analysis of polycyclic aromatic hydrocarbon pollution used anthracene. Anthracene was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The standard for GC (chromatographically pure) was $\geq99.5\%$.

| Surfactant     | Purity | Molecular Formula | CMC (mg/L) |
|----------------|--------|-------------------|------------|
| Sophorolipids  | AR     | C$_{34}$H$_{56}$O$_{14}$ | 40         |
| SDBS           | AR     | C$_{18}$H$_{29}$NaO$_2$S | 100        |
| Na$_2$SiO$_3$  | AR     | Na$_2$SiO$_3$      | -          |

The mass concentration of surfactant for sophorolipids-SDBS-Na$_2$SiO$_3$ was 10 g·L$^{-1}$. First, 0.12 g of sophorolipids, 9 g of Na$_2$SiO$_3$, and 0.9 g of SDBS were dissolved in 1 L of pure water solution. After dilution, surfactant solutions of different mass concentrations were prepared.

Soil samples were taken from the 20–40 cm soil layer in the suburbs of Beijing, China. They were air-dried for 7 days, tapped to break aggregated soil, and homogenized before sieving to remove gravel larger than 2 mm. Selected physical and chemical properties of the soil samples are listed in Table 2.

| pH (H$_2$O) | Organic Matter Content (%) | Moisture Content (%) | Cation Exchange Capacity (cmol/kg) | Salinity (%) | Particle Diameter (mm) |
|-------------|---------------------------|----------------------|-----------------------------------|--------------|------------------------|
| 8.59        | 0.75                      | 2.63                 | 7.73                              | 0.35         | 2                      |

High-concentration polluted soil: First, 80 mg of anthracene were weighed, completely dissolved with acetone solution, and the solution mixed with 200 g of spare soil evenly. Then, the mixture was put in at room temperature, and dried in a fume hood until the acetone was completely volatilized to obtain polluted soil with a high pollution concentration of 400 mg·kg$^{-1}$.

Low-concentration polluted soil: First, 40 mg of anthracene was weighed, completely dissolved with acetone solution, and the solution was mixed with 200 g of spare soil evenly. Then, at room temperature, the mixture was dried in a fume hood until the acetone was completely volatilized to obtain a polluted soil with a low pollution concentration of 200 mg·kg$^{-1}$. 
2.2. Soil Washing Using Mixed Surfactants

PAH-contaminated soil was washed in a small stirring reactor with a total loading volume of approximately 20 L. The high-concentration polluted soil was washed with a liquid–soil ratio (L/S) of 6:1 at a speed of 160 rpm for 8 h. The low-concentration polluted soil was washed with a liquid–soil ratio (L/S) of 8:1 at a speed of 160 rpm for 8 h. An ultrasonator (Shenzhen Xingde Trade Co., Ltd., Shenzhen, China) was used to extract PAHs from soil samples. PAH concentrations were determined with an HPLC system (Agilent Technologies 1200 Series).

2.3. Eluant Using Alkali-Activated Sodium Persulfate

Sodium hydroxide, calcium hydroxide, calcium oxide, and potassium hydroxide were selected as the bases to activate sodium persulfate. Aqueous solutions of sophorolipids, SDBS, Na$_2$SiO$_3$, and their mixtures were respectively put in a 150-mL conical glass flask with a stopper. Excess sodium peroxodisulfate and alkali were added to the flasks, which were then centrifuged at 160 rpm for 24 h. PAH concentrations were determined with an HPLC system (Agilent Technologies 1200 Series).

2.4. Removal Effectiveness Evaluation

In order to evaluate the soil eluting efficiency, the anthracene removal ratio was determined as the concentration of residual anthracene in soil divided by the concentration of original anthracene in soil:

$$\text{Elution efficiency (\%) } = \frac{(C_0 - C_e) \times 100}{C_0},$$

where $C_0$ (mg/L) and $C_e$ (mg/L) are the initial and equilibrium soil anthracene concentrations, respectively.

In the present study, a full $2^4$ factorial design was performed to evaluate the interactions of the eluting time, mixed-surfactant concentration, and the concentration of NaCl and KCl, with the response of the anthracene elution efficiency.

2.5. Analytical Methods

PAHs in the aqueous phases were also measured by HPLC (Agilent, mod. 1200) coupled with an Agilent 1290 Infinity Diode Array Detector. The column used was a ZORBAX Eclipse XDB 80Å C18 in 4.6 $\times$ 150 mm and a 5-µm particle size. The column temperature was 35 °C. Analysis was carried out under isocratic mode at a flow rate of 1.0 mL-min$^{-1}$, selecting as the mobile phase a mixture of 60% acetonitrile and 40% water; the selected injection volume was 10 μL. The operation time of the liquid phase was 18 min. The wavelengths chosen were 254 nm for anthracene. The detection limit was less than 50 ppbs.

The calculation formula of anthracene in aqueous solution is as follows:

$$\rho_i = \frac{\rho_{xi} \times V_i}{V},$$

where $\rho_i$ is the mass concentration (mg/L) of component i in the sample, $\rho_{xi}$ is the mass concentration (mg/L) of component i found from the marking line, $V_i$ is the volume (mL) of the concentrated extract, and V is the volume of the water sample (mL).

The calculation formula of anthracene in soil is as follows:

$$\omega_i = \frac{\rho_i \times V}{m \times W_{dm}},$$

where $\omega_i$ is the content of component i in the sample (µg/kg), $\rho_i$ is the concentration of component i calculated from the standard curve (µg/mL), V is the constant volume (mL), m is the sample volume (kg), and $W_{dm}$ is the dry matter content in the soil sample (%).
2.6. Data Analysis

The factorial experimental design and statistical analysis were conducted using Design Expert 8.0.6 (Stat-Ease Inc., Minneapolis, MN, USA). The OriginPro 8.5 software (OriginLab Corporation, Northampton, MA, USA) was used for the elution analysis of the experimental data.

3. Results and Discussion

3.1. Experiment of Single Surfactant Remediation of Anthracene-Contaminated Soil

After configuring different concentration gradients of sophorolipids and SDBS solution to elute and repair petroleum-contaminated soil, the results are shown in Figure 1a,b. As the concentration of surfactant increases, the elution efficiency reaches a certain value and becomes stable. The elution efficiency of sophorolipid solution can reach 67.03%, and the optimal elution efficiency of SDBS can reach 76.96%. The elution ratio of surfactants to PAHs is inversely proportional to the octanol/water partition coefficient of PAHs. Subsequent experiments are based on the combination of these two surfactants, and the additive sodium silicate (Na$_2$SiO$_3$) is added to the system to improve its elution efficiency.

![Figure 1. Elution efficiency of surfactants with different concentrations. (a) Elution efficiency of sophorolipids with different concentrations. (b) Elution efficiency of sodium dodecylbenzene sulfonate (SDBS) with different concentrations.](image)

3.2. Effect of Mixed Surfactants on the Single Factor of Anthracene-Contaminated Soil Eluting

3.2.1. Effect of Eluting Time

If the elution time is too short, the surfactant cannot fully contact with the pollutant, resulting in a weak elution effect. When the elution time reaches a certain value, most of the soluble pollutants will enter the surfactant solution. On the one hand, oil droplets or surfactants that have been desorbed from the surface of soil particles can be re-adsorbed to the surface of particles; on the other hand, the oil-water mixture may form an emulsion, which increases the cost of elution and increases the difficulty of subsequent elution [36,37]. Therefore, the elution time should be selected within a reasonable range. The low- and high-concentration PAH-contaminated soil were repaired with mixed surfactants at different shaking times. It can be seen clearly from Figure 2 that in the PAH-contaminated soil, regardless of the low-concentration contaminated soil or the high-concentration contaminated soil, the eluting rate reached a maximum at 8 h, while the elution efficiency showed a decreasing trend after 8 h. Therefore, it is determined that the optimal elution time of surfactant eluting and eluting PAH-contaminated soil was 8 h.


3.2.2. Mixed Surfactant Concentration

It can be seen from Figure 3 that the elution efficiency of 1200 mg·L\(^{-1}\) surfactant is the highest, 77.49% for low-concentration PAH-contaminated soil, and 85.27% for high-concentration PAH-contaminated soil. As the concentration of surfactant increases, the elution efficiency does not increase but decreases. Similarly, for polycyclic aromatic hydrocarbon-contaminated soils, as the concentration increases, the polycyclic aromatic hydrocarbons adsorbed by the surfactants are excessively depleted, so that they are re-desorbed into the soil solid phase. Therefore, selecting a suitable surfactant concentration can not only improve the elution efficiency and reduce the waste of the surfactant but also reduce the surfactant concentration in the cleaning solution and reduce the subsequent wastewater treatment load. Surfactant can reduce the interfacial tension between oil substances and soil particles, and make oil substances roll away from the soil surface, which can occur when the concentration is lower than the CMC [38]; when the concentration reaches or is higher than the CMC, surfactant forms micelles in the solution, and solubilizes the insoluble diesel substances, which are desorbed from the soil and distributed into the aqueous phase, increasing the diesel removal rate [39,40].

![Figure 3](image3.png)

**Figure 3.** Effect of mixed surfactants on high- and low-concentration anthracene-contaminated soil.

3.2.3. Effect of Ion Concentration

The effect of the NaCl and KCl concentration on the elution experiment was studied. From Figure 4, the elution efficiency of the high-concentration contaminated soil is significantly higher than that of the low-concentration contaminated soil. The results show that, when the concentration of NaCl is 100 mmol/L (Figure 4a), the effect of sophorolipids-SDBS-Na\(_2\)SiO\(_3\) on anthracene is obviously...
increased. For ionic surfactants, when inorganic salts with the same anti ions as surfactants are added (such as Cl\(^-\) and Na\(^+\)), the double electron layer will be effectively compressed and reduce the mutual exclusion of surfactant ions. For ionic surfactants, the surface activity increases and the critical micelle concentration decreases [41]. When the concentration of KCl is 50 mmol/L (Figure 4b), the addition of K\(^+\) can promote the remediation of anthracene in soil to a certain extent but it cannot be over added.

![Graph](image)

**Figure 4.** Effect of ion concentration on high- and low-concentration anthracene-contaminated soil. (a) Effect of NaCl concentration on high- and low-concentration anthracene-contaminated soil; (b) Effect of KCl concentration on high- and low-concentration anthracene-contaminated soil.

3.2.4. Effect of Granularity

The eluting rate of polycyclic aromatic hydrocarbon pollutants in the soil is closely related to the properties of the soil, among which the soil texture is the most affected, followed by the properties of soil minerals and the content of organic matter. The smaller the soil particles, the larger the specific surface area of soil is, and the stronger the adsorption of pollution is, so the eluting efficiency of pollutants will be greatly suppressed [42,43]. As can be seen from Figure 5, as the mesh number increases, the soil particle size is gradually decreasing, and the pollutant of the polycyclic aromatic
hydrocarbon in the soil gradually increases. Regardless of the concentration of pollutants, the decrease of the soil particle size is beneficial to the separation of difficult eluting substances from the surface of soil particles, so as to achieve the purpose of eluting.

3.2.4. Effect of Granularity

The eluting rate of polycyclic aromatic hydrocarbon pollutants in the soil is closely related to the soil particle size. The decrease of the soil particle size is beneficial to the separation of difficult eluting substances from the surface of soil particles, so as to achieve the purpose of eluting.

3.3. Effect of Mixed Surfactants on the Eluting Interaction of PAH-Contaminated Soils

3.3.1. Design Scheme of Mixed Surfactant on Eluting PAH-Contaminated Soil

Factorial design is a multi-factor and multi-level cross-grouping design method for a comprehensive test. It can study the effects of multiple levels of two or more factors, and can provide more experimental information than single factor experiments. It can be used to analyze the main effects of all factors and the interaction between factors at all levels. It is comprehensive and balanced. The effect of the compound reagent concentration, eluting time, KCl concentration, and NaCl concentration on the remediation of anthracene-contaminated soil by the sophorolipids-SDBS-Na2SiO3 mixed-surfactant system was studied by using a four-factor and two-level factor design scheme to explore the interaction between the factors.

The formula of the model function was as follows:

\[
\ln R = b_1 + b_2 \times A + b_3 \times B + b_4 \times D + b_5 \times A \times B + b_6 \times A \times C + b_7 \times A \times D + b_8 \times B \times C + b_9 \times B \times C + b_{10} \times C \times D + b_{11} \times A \times B \times C + b_{12} \times A \times B \times D + b_{13} \times A \times B \times C \times D
\]

In the formula, R represents the response value; A, B, C, D represents the four factors; AB, AC, BC, CD, AD, ABC, ABD, ABCD represents the interaction between the factors; and bi is the constants matching with the single factor and interaction. The factors and their interactions are expressed in the form of code, that is, the high-level code is 1, and the low level is -1. The experimental design and levels of independent variables considered in this study are presented in Table 3.

In this experiment, the dependent variable is the elution efficiency (R) of anthracene. The empirical relationships between anthracene removal (R) and four test variables in coded units (A, mixed surfactants concentration; B, effect of eluting time; C, the concentration of NaCl; D, the concentration of KCl) obtained by the application of factor analysis are given by the following models:

\[
\ln R = -0.14 + 0.011 \times A + 0.028 \times B + 0.029 \times D + 0.015 \times A \times B - 0.045 \times A \times C + 7.063 \times 10^{-0.003} \times A \times D + 0.025 \times B \times C - 0.057 \times B \times C + 0.023 \times C \times D + 0.015 \times A \times B \times C + 0.018 \times A \times B \times D - 0.039 \times A \times B \times C \times D
\]

The Pareto analysis of this model is shown in Figure 6a, with a positive correlation between the significance level of the factor and the length of the column. The red and gray line in the Pareto chart
stand for the “Bonferroni limit” and “t-value limit”, respectively, which are two levels of significance on the Pareto chart of effects. The value of the “Bonferroni limit” is a kind of significance indicator calculated based on the input data into Design Expert software in accordance with the Bonferroni test methodology, which is a type of multiple comparison test used in statistical analysis. The “t-value limit” is another kind of the significance indicator based on t-test methodology. The t-value is a test statistic for t-tests that measures the difference between an observed sample statistic and its hypothesized population parameter in units of standard error. It can be seen from the graph that the interaction effect of the oscillation time with the sodium chloride is the most significant factor, followed by the effect of the concentration of the compound medicament and the concentration of the potassium chloride, and finally the interaction effect of the four factors was selected.

Table 3. Experimental design matrix and dependent variables attributed to the factor analysis design.

| Run | A Coded | A Actual | B Coded | B Actual | C Coded | C Actual | D Coded | D Actual |
|-----|---------|----------|---------|----------|---------|----------|---------|----------|
| 1   | 1       | 1500     | 1       | 12       | 1       | 0.05     | 1       | 0.1      |
| 2   | 1       | 1500     | -1      | 6        | 1       | 0.05     | 1       | 0.1      |
| 3   | 1       | 1500     | -1      | 6        | -1      | 0        | -1      | 0        |
| 4   | 1       | 1500     | 1       | 12       | 1       | 0.05     | -1      | 0        |
| 5   | 1       | 1500     | -1      | 6        | -1      | 0        | 1       | 0.1      |
| 6   | -1      | 500      | 1       | 12       | 1       | 0.05     | -1      | 0        |
| 7   | -1      | 500      | -1      | 6        | 1       | 0.05     | -1      | 0        |
| 8   | -1      | 500      | 1       | 12       | 1       | 0.05     | 1       | 0.1      |
| 9   | -1      | 500      | -1      | 6        | -1      | 0        | 1       | 0.1      |
| 10  | -1      | 500      | 1       | 12       | -1      | 0        | -1      | 0        |
| 11  | -1      | 500      | -1      | 6        | -1      | 0        | -1      | 0        |
| 12  | 1       | 1500     | 1       | 12       | -1      | 0        | 1       | 0.1      |
| 13  | 1       | 1500     | -1      | 6        | 1       | 0.05     | -1      | 0        |
| 14  | 1       | 1500     | 1       | 12       | -1      | 0        | -1      | 0        |
| 15  | -1      | 500      | -1      | 6        | -1      | 0        | -1      | 0        |
| 16  | -1      | 500      | -1      | 6        | 1       | 0.05     | 1       | 0.1      |

Figure 6. Factorial experimental error analysis diagram. (a) Pareto chart, (b) Normal plot of residuals.

In general, the effect of the interaction on the elution rate of polycyclic aromatic hydrocarbons is greater than that of a single factor. The residual graph of the model, as shown in Figure 6b, is evenly distributed on both sides of the straight line, indicating that the residual meets the normal distribution.
The error analysis of the model was used to evaluate the correlation between the equation of the model and the experimental data. The p value of the model is lower than 0.05, which indicates that this factor has a significant effect on the remediation of anthracene-contaminated soil with compound agents [44]. The error analysis of the experimental model is shown in Table 4, and the p value is less than 0.0018, which indicates that the model is significant. The R² is 0.99971, which indicates that the regression model has good reliability. Among them, the interaction between the concentration of the compound reagent and the amount of ion is obvious.

Table 4. ANOVA report for factorial model on anthracene removal.

| Source | Sum of Square | df | Mean Square | F-Value | p-Value |
|--------|--------------|----|-------------|---------|---------|
| model  | 0.167        | 12 | 0.014       | 86.77   | 0.0018  |
| A      | 0.002        | 1  | 0.002       | 12.34   | 0.0391  |
| B      | 0.012        | 1  | 0.012       | 75.67   | 0.0032  |
| D      | 0.013        | 1  | 0.013       | 83.58   | 0.0028  |
| AB     | 0.003        | 1  | 0.003       | 21.13   | 0.0194  |
| AC     | 0.032        | 1  | 0.032       | 200.37  | 0.0008  |
| AD     | 0.001        | 1  | 0.001       | 5.77    | 0.0957  |
| BC     | 0.010        | 1  | 0.010       | 60.90   | 0.0044  |
| BD     | 0.052        | 1  | 0.052       | 324.18  | 0.0004  |
| CD     | 0.008        | 1  | 0.008       | 51.62   | 0.0056  |
| ABC    | 0.003        | 1  | 0.003       | 21.72   | 0.0186  |
| ABD    | 0.005        | 1  | 0.005       | 30.97   | 0.0114  |
| ABCD   | 0.025        | 1  | 0.025       | 152.99  | 0.0011  |
| Cor Total | 0.167    | 15 |             |         |         |

3.3.2. Main Effect Analysis

Through Design-Expert analysis, the main effect results of these factors are shown in the Figure 7. According to ANOVA statistics, the order of significance among the single factors is D > B > A. The effects of the compound agent concentration (Figure 7a), oscillation time (Figure 7b), and NaCl (Figure 7c) concentration on the eluting effect of polycyclic aromatic hydrocarbons (PAHs) have a positive and significant effect, while the effect of the KCl concentration on the eluting effect is insensitive. The slope of the compound reagent concentration is smaller than the other two factors, which indicates that the slope of the compound reagent concentration has little effect on the other two factors.
B > A. The effects of the compound agent concentration (Figure 7a), oscillation time (Figure 7b), and NaCl (Figure 7c) concentration on the eluting effect of polycyclic aromatic hydrocarbons (PAHs) have a positive and significant effect, while the effect of the KCl concentration on the eluting effect is insensitive. The slope of the compound reagent concentration is smaller than the other two factors, which indicates that the slope of the compound reagent concentration has little effect on the other two factors.

**Figure 7.** Analysis of the main effect of the factorial experiment. (a) Relationship between elution efficiency (R) and surfactant concentration; (b) Relationship between R and eluting time; (c) Relationship between R and NaCl concentration.

3.3.3. Interaction Analysis

It can be seen from the graph that the slope of the two straight lines is not the same, which means that there is a certain interaction between the two factors on the response value. According to ANOVA statistics, the influence of interaction is BD > AC > BC > CD > AB. The factor A and the factor B are obtained at the left to the left of Figure 8a, while a high level of the factor B is always higher than the low level of factor B, and when the compound agent concentration changes from a low level to a high level, the linear slope becomes large, which indicates that a high level of factor b is beneficial to the elution of the polycyclic aromatic hydrocarbons.
Figure 8. The interaction between four test variables. (a) The interaction between surfactant concentration and eluting time; (b) The interaction between surfactant concentration and KCl concentration; (c) The interaction between eluting time and KCl concentration; (d) The interaction between eluting time and NaCl concentration; (e) The interaction between KCl concentration and NaCl concentration.
The factor A and the factor C are also taken at the left to the left of Figure 8b and a higher elution rate can be obtained when the factor A is at a low level and C is at a high level. With the increase of the concentration of factor A, the low factor c is gradually occupying the advantage. As can be seen in Figure 8c,d, the intersection of factor B and factor C on the right, and the slope of the two straight lines is positive, and it has a positive significant effect.

However, the slope of the low-level factor D is positive and the slope of the high factor D is negative, indicating that the low level of factor D is dominant after a high level of factor B is reached. The factor C and the factor D can be seen in Figure 8e to have a clear interaction, with the intersection point on the left. The high level of the factor D is always higher than the low level of factor D. When the concentration of factor C changes from a low level to a high level, the linear slope becomes large, indicating that the high level of factor D is beneficial to the elution of the polycyclic aromatic hydrocarbons.

### 3.4. Removal of Anthracene from Eluent by the Base/SPS

#### 3.4.1. The Oxidation Effects of Different Types of Alkali Activation on the Eluent

In the experiment, sodium hydroxide, calcium hydroxide, calcium oxide, and potassium hydroxide were selected as the bases to activate sodium persulfate, and the optimal removal efficiency could reach more than 50%. It can be seen from Figure 9 that the removal rate of PAHs in elution waste liquid from high to low is potassium hydroxide, calcium oxide, sodium hydroxide, and calcium hydroxide, which may be related to the dissociation capacity of the substance. Chengdu Qi et al. [33] studied the effect of alkali-activated peroxic monosulfate on the degradation of organic pollutants, and the results were consistent. Therefore, potassium hydroxide was used as the activator in the subsequent oxidation experiment.

![Figure 9. The oxidation effects of different types of alkali activation.](image)

The efficiency of alkali-activated sodium persulfate has a certain relationship with the concentration of added alkali. Figure 10 shows the analysis of base-activated persulfate decomposition kinetics. The pseudo-first-order loss of persulfate in solutions with a range of base:persulfate molar ratios is shown in Figure 10. As can be seen from Figure 10, after adding different concentrations of sodium persulfate, the degradation rate of persulfate increases with the increase of the potassium hydroxide concentration at different times, indicating that the decomposition rate of persulfate is a function of the alkalinity. OLHA S [37] also reached the same conclusion by measuring the relationship between the ultrasonic time and ln (C/C0), where C is the persulfate ion concentration after adding the oxidizing agent, and C0 is the concentration of persulfate ions before oxidant treatment. These results also indicate
that alkali-catalyzed hydrolysis of persulfate is the first step of persulfate activation under alkaline conditions and the decomposition rate of persulfate increases with an increasing KOH concentration.

3.4.2. Effect of Different Ultrasound Times on the Base of Sodium Persulfate

This mixed surfactant solution only transfers contaminants from the soil to the aqueous phase. From Figure 11, we can conclude that in different ultrasonic time ranges, the removal effect of alkali-activated sodium persulfate on anthracene pollutants in eluent increased from 28.41% to 61.77% in the range of 20–60 min. With the increase of the time, the removal efficiency of anthracene tends to be gentle or even decreases. Due to the action of the ultrasonic wave, anthracene pollutants dissolved in eluent are dissociated from the soil. After 60 min, the eluting efficiency no longer increases, which may be due to the existence of a large number of surfactants in the waste eluent, which has a certain competitive effect on the sulfate radical [45], so it will further affect the removal efficiency of pollutants in the waste eluent.

3.4.3. Effect of Different Activation Ratios on the Base of Sodium Persulfate

Oxidant/pollutant ratios were selected according to previous studies in the literature with alkaline persulfate in diesel and PAHs abatement [46,47]. The molar ratio of activator/oxidant in the literature ranges from 2 to 6 [35]. As shown in Figure 12, it was shown that the ratio of oxidant to activating...
agent is 1:2 when sodium persulfate is activated by alkali, which is consistent with the above research contents and ensures that it can be carried out in an alkaline environment.

3.4.4. Effect of Turbidity of Eluent

After centrifugation, the turbidity value of the soil contaminated by PAHs eluted with complex surfactants was about 200–400 nephelometric turbidity unit (NTU), which was relatively high. This is because of the soil remains in the aqueous solution, or when the centrifugal solution is poured out, some of the fine particle suspensions flow out with the washing solution [48,49]. The solubilization and emulsification of the surfactant during the washing process results in the presence of oil-in-water, dispersed oily substances, and micelles in the liquid phase. In the filtration process, there are different filtration states, small soil particles are intercepted, and the oil substances and macromolecular micelles attached to the particles may also be intercepted. This is an unavoidable problem in the process of operation, so it will have a certain impact on the turbidity of the water. As shown in Figure 13a, after the elution waste solution was treated with alkali-activated oxidant, the turbidity changed significantly and decreased to below 100 NTU. For the results of different activation ratios, as shown in Figure 13b, that is, the turbidity of eluent waste solution before and after alkali addition significantly changed from 346–440 NTU to 39–72 NTU under the condition of different alkali concentrations, indicating that the turbidity of the solution changed significantly under different alkali activations and treatment times.

Figure 12. Effect of different activation ratios on the base of SPS.

Figure 13. Changes in the turbidity of anthracene elution wastewater. (a) Turbidity of anthracene elution wastewater in different ultrasonic times; (b) Turbidity of anthracene elution wastewater in different rations of oxidant and activator.
3.4.5. Results and Analysis of Elution Waste Liquid by Infrared Spectrum

The infrared spectra of eluent without oxidant treatment is shown in Figure 14a. Here, 3183 cm\(^{-1}\) is the C-H stretching vibration absorption peak (-C≡C-H), 1276 cm\(^{-1}\) is the C-O (ester) absorption peak, and 692 cm\(^{-1}\) is the C-H surface bending vibration absorption peak of aromatic hydrocarbon. As shown in Figure 14b, the infrared spectrum after oxidation treatment increased by 1726 cm\(^{-1}\) as ester (non-cyclic), 1037 cm\(^{-1}\) as the absorption peak of bending vibration in the C-H plane, 918 cm\(^{-1}\) as the absorption peak of bending vibration outside the C-H plane, and 724 as the absorption peak of bending vibration outside the C-H plane.

![Infrared spectra](image)

**Figure 14.** Infrared spectra before and after oxidation treatment. (a) The infrared spectra of eluent without oxidant treatment; (b) The infrared spectra of eluent after oxidant treatment.

Anthracene is a thick cyclic aromatic hydrocarbon containing three rings. Through the analysis of infrared spectroscopy, the inner part of eluent waste liquid underwent a ring-opening reaction, and the ring-opening reaction also occurred in the part of the cyclic ester group of the surfactant, which changed from a ring to non-ring. The results show that the oxidant had a significant effect on the removal of the elution waste liquid containing surfactant and anthracene.

4. Conclusions

The use of surfactants to repair PAH-contaminated soil is an economical and efficient method with environmental sustainability. The present study showed that the sophorolipids-SDBS-Na\(_2\)SiO\(_3\) could remove anthracene from soil to a certain extent. Alkali-activated sodium persulfate also has a good effect on the removal of anthracene pollutants from eluting wastewater.

1. In the single factor experiment, the best concentration of sophora and SDBS was 40 and 100 mg/L, respectively, that is to say, the removal efficiency was best at the critical micelle concentration. At the same time, the additive sodium silicate can react with the acidic components of oil to form salt, which increases the water solubility of oil and improves the removal efficiency of the composite surfactant.
(2) When the elution time was 8 h, the concentration of the compounded surfactant was 1200 mg/L, the particle size was 60 mesh, the concentration of NaCl was 100 mmol/L, and the concentration of KCl was 50 mmol/L, thus the effect of the PAH-contaminated soil eluted by the composite surfactant was the best; externally added NaCl and KCl salt ions had a more obvious promotion effect on the polycyclic aromatic hydrocarbon-contaminated soil.

(3) In the factorial design experiment, the residual plot of the regression equation conformed to the normal distribution, and the $p$ value of the error analysis was less than 0.0018, which showed that the regression equation simulation was significant. It can be seen from the Pareto analysis chart that single factor B (elution time) and D (NaCl concentration) have a significant main effect. There is also a certain interaction between factor A (concentration agent concentration) and factor D, factor B, and factor C (KCl concentration).

(4) The ultrasonic oxidation technology was used, combined with alkali-activated sodium persulfate, to explore the influence of the ultrasonic time, activation ratio, turbidity, and other factors on the oxidation effect. When the optimal ultrasonic time was 60 min and the ratio of oxidant to activator was 1:2, the removal rate of contaminants in the eluent could reach 63.7%. At the same time, the turbidity of the eluent was significantly lower than that of the liquid after centrifugal separation, indicating that oxidants can not only remove the pollutants in elution water but also remove the residual soil particulate matter.

(5) By comparing the infrared spectrum of the eluted waste liquid before and after oxidation, it was seen that during the oxidation process, the inner part of eluent waste liquid underwent a ring-opening reaction, and the ring-opening reaction also occurred in the part of the cyclic ester group of the surfactant, which changed from a ring to non-ring.

Through the eluting of soil pollutants and the removal of pollutants from wastewater, organic matter can be mostly removed. This complete removal process is suitable for the field of surfactant eluting soil and polluted wastewater. However, there are still some deficiencies in the current research, such as: (1) The elution effect of the composite surfactant studied in this paper on PAHs in the actual contaminated site was not measured, and the subsequent research should start from the actual contaminated site to determine the elution effect; (2) some basic water quality parameters should be measured after the treatment of the elution wastewater, so that the removal method is more practical; and (3) the removal mechanism of PAH eluting wastewater should be further studied.

**Author Contributions:** Conceptualization, L.S. and X.W.; methodology, X.W.; software, X.W. and L.S.; validation, X.W., and W.L.; formal analysis, X.W.; investigation, X.W.; resources, X.W.; data curation, X.W. and L.S.; writing—Original draft preparation, X.W.; writing—Review and editing, X.W. and L.S.; visualization, X.W.; supervision, W.L.; project administration, X.D. and Z.W.; funding acquisition, W.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This Study was funded by the National Key Research and Development Plan, grant number (2018YFE0196000).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Shi, Z.; Chen, J.; Liu, J.; Wang, N.; Sun, Z.; Wang, X. Anionic-nonionic Mixed-surfactants-enhanced remediation of PAH-contaminated soil. *Environ. Sci. Pollut. Res. Int.* 2015, 22, 12769–12774. [CrossRef] [PubMed]
2. Lane, W.F.; Loehr, R.C. Estimating the equilibrium aqueous concentrations of polynuclear aromatic hydrocarbons in complex mixtures. *Water Environ. Res.* 1995, 67, 169–173. [CrossRef]
3. Paria, S.; Yuet, P.K. Solubilization of Naphthalene by Pure and Mixed Surfactants. *Ind. Eng. Chem. Res.* 2006, 45, 3552–3558. [CrossRef]
4. Lamichhane, S.; Bal Krishna, K.C.; Sarukkalige, R. Surfactant–enhanced remediation of polycyclic aromatic hydrocarbons: A review. *J. Environ. Manag.* 2017, 199, 46–61. [CrossRef]
5. Zhai, M.; Huang, G.; Liu, L.; Zheng, B.; Guan, Y. Inter-regional carbon flows embodied in electricity transmission: Network simulation for energy-carbon nexus. Renew. Sustain. Energy Rev. 2020, 118, 109511. [CrossRef]

6. Gallego, E.; Roca, F.J.; Perales, J.F.; Guardino, X.; Berenguer, M.J. VOCs and PAHs emissions from creosote-treated wood in a field storage area. Sci. Total Environ. 2008, 402, 130–138. [CrossRef]

7. Ravindra, K.; Sokhi, R.; René, V.G. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos. Environ. 2008, 42, 2895–2921. [CrossRef]

8. Lee, P.H.; Ong, S.K.; Golchin, J.; Nelson, G.S. Use of solvents to enhance PAH biodegradation of coal tar-contaminated soils. Water Res. 2001, 35, 3941–3949. [CrossRef]

9. Yu, H.; Zhu, L.; Zhou, W. Enhanced desorption and biodegradation of phenanthrene in soil–water systems with the presence of anionic–nonionic mixed surfactants. J. Hazard. Mater. 2007, 142, 354–361. [CrossRef]

10. Zhou, W.; Zhu, L. Efficiency of surfactant-enhanced desorption for contaminated soils depending on the component characteristics of soil-surfactant–PAHs system. Environ. Pollut. 2007, 147, 73. [CrossRef]

11. Xu, H.; Ho, S.S.H.; Gao, M.; Cao, J.; Guinot, B.; Ho, K.F.; Long, X.; Wang, J.; Shena, Z.; Liu, S.; et al. Microscale spatial distribution and health assessment of PM2.5-bound polycyclic aromatic hydrocarbons (PAHs) at nine communities in Xi’an, China. Environ. Pollut. 2016, 218, 1065–1073. [CrossRef] [PubMed]

12. Yi, X.H.; Jing, D.D.; Wan, J.; Ma, Y.; Wang, Y. Temporal and spatial variations of contaminant removal, enzyme activities, and microbial community structure in a pilot horizontal subsurface flow constructed wetland purifying industrial runoff. Environ. Sci. Pollut. Res. 2016, 23, 8565–8576. [CrossRef] [PubMed]

13. Zhai, M.; Huang, G.; Liu, L.; Liu, H.; He, C.; Liu, Z. Three-perspective energy-carbon nexus analysis for developing China’s policies of CO2-emission mitigation. Sci. Total Environ. 2020, 705, 135877. [CrossRef]

14. Ji, H.J.; Long, T.; Chen, Q.; He, Y.; Lin, Y.S.; Yu, R.; Zhu, X. Tween 80 enhanced activated sodium persulfate oxidation remediation of PAHs contaminated soil. Chem. Eng. J. 2016, 67, 3879–3887. [CrossRef]

15. Wang, H.T.; Zhu, H.; Wei, X.; Liang, Y.; Lu, X.Y. The effect of sodium humate and surfactant on desorption and solubilization of petroleum pollutants in loess. J. Saf. Environ. 2004, 4, 2–55.

16. Yang, K.; Zhu, L.; Xing, B. Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS. Environ. Sci. Technol. 2006, 40, 4274–4280. [CrossRef]

17. Wang, Z.R.; Sun, F.L.; Pu, C.X. The leaching treatment of polycyclic aromatic hydrocarbon contaminated soil by mixed surfactants. China Water Supply Drain. 2019, 35, 92–96.

18. Zhang, L.; Somasundaran, P.; Singh, S.K.; Felse, A.P.; Gross, R. Synthesis and interfacial properties of sophorolipid derivatives. Colloids Surf. A Physicochem. Eng. Asp. 2004, 240, 75–82. [CrossRef]

19. Pekin, G.; Vardar-Sukan, F.; Kosaric, N. Production of Sophorolipids from Candida bombicola ATCC 22214 Using Turkish Corn Oil and Honey. Eng. Life Sci. 2005, 5, 357–362. [CrossRef]

20. Hirata, Y.; Ryu, M.; Oda, Y.; Igarashi, K.; Nagatsu, A.; Furuta, T.; Sugiyama, M. Novel characteristics of sophorolipids, yeast glycolipid biosurfactants, as biodegradable low-foaming surfactants. J. Biosci. Bioeng. 2009, 108, 142–146. [CrossRef]

21. Sun, Y.X.; Yang, Z.L.; Yu, G.H.; Zhan, R.; Liang, S.K. Study on the bioremediation of oil-containing sludge with sophorolipids surfactant and petroleum hydrocarbon degrading bacteria. J. Ocean. Univ. China 2017, 47, 72–80.

22. Li, Z.S.; Liang, S.K.; Li, J.F. Experimental study on electrokinetic remediation of chromium contaminated soil with sophorolipids biosurface. J. Ocean. Univ. China 2019, 49, 33–43.

23. Deshpande, S.; Shiau, B.J.; Wade, D.; Sabatini, D.A.; Harwell, J.H. Surfactant selection for enhancing ex situ soil washing. Water Res. 1999, 33, 351–360. [CrossRef]

24. Fabbri, D.; Prevot, A.B.; Zelano, V.; Ginepro, M.; Pramauro, E. Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis. Chemosphere 2008, 71, 59–65. [CrossRef]

25. Gao, S.X.; Cao, J.S.; Sun, C.; Wang, L.S. Solubilization of 1, 2, 4-trichlorobenzene by different surfactants. Soil Environ. 1999, 184–188.

26. Ni, H.W. Anionic-Non-Ionic Mixed Surfactants Strengthen Plant-Microorganism Joint Remediation of Pahs Contaminated Soil. Master’s Thesis, Zhejiang University, Hangzhou, China, 2014.

27. He, Z.N.; Li, Z.S.; Ji, G.D. Simulation study on oil recovery from oil field contaminated soil. J. Appl. Found. Eng. Sci. 2005, 2, 136–145.
28. Lee, D.H.; Chang, H.W.; Kim, C. Mixing effect of NaCl and surfactant on the remediation of TCB contaminated soil. *Geoences J.* 2008, 12, 63-68. [CrossRef]

29. Tsomides, H.J. Effect of surfactant addition on phenanthrene biodegradation in sediments. *Environ. Toxicol. Chem.* 1994, 6, 953-959. [CrossRef]

30. Kim, I.S.; Park, J.S.; Kim, K.W. Enhanced Biodegradation of Polycyclic Aromatic Hydrocarbons Using Nonionic Surfactants in Soil Slurry. *Appl. Geochem.* 2001, 16, 1419-1428. [CrossRef]

31. Devi, P.; Das, U.; Dalai, A.K. In-situ chemical oxidation: Principle and applications of peroxide and persulfate treatments in wastewater systems. *Sci. Total Environ.* 2016, 571, 643-657. [CrossRef]

32. Lominchar, M.A.; Lorenzo, D.; Romero, A.; Santos, A. Remediation of soil contaminated by PAHs and TPH using alkaline activated persulfate enhanced by surfactant addition at flow conditions. *J. Chem. Technol. Biotechnol.* 2017, 93, 1270-1278. [CrossRef]

33. Qi, C.; Liu, X.; Ma, J.; Lin, C.; Li, X.; Zhang, H. Activation of peroxymonosulfate by base: Implications for the degradation of organic pollutants. *Chemosphere* 2016, 151, 280-288. [CrossRef] [PubMed]

34. San Roman, I.; Galdames, A.; Alonso, M.L.; Bartolome, L.; Vilas, J.L.; Alonso, R.M. Effect of coating on the environmental applications of zero valent iron nanoparticles: The lindane case. *Sci. Total Environ.* 2016, 565, 795-803. [CrossRef]

35. Gilman, D.V.; Ovanes, G.M.; Gerald, T.A.; Daniel, J.C. A QSAR analysis of substituent effects on the photoinduced acute toxicity of PAHs. *Chemosphere* 1995, 30, 2129-2142.

36. Wu, W.; Chen, J.J.; Peng, S. Effect of process parameters on surfactant remediation of PAHs contaminated soil. *J. Environ. Eng.* 2012, 6, 977-982.

37. Furman, O.S.; Teel, A.L.; Watts, R.J. Mechanism of Base Activation of Persulfate. *Environ. Sci. Technol.* 2010, 44, 6423-6428. [CrossRef] [PubMed]

38. Ji, G.D.; Zhou, G.H. Heterotopic chemical leaching to repair petroleum contaminated soil. *J. Peking Univ.* 2007, 43, 863-871.

39. Kile, D.E.; Chiou, C.T. Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environ. Sci. Technol.* 1989, 23, 832-838. [CrossRef]

40. Lee, D.H.; Chang, H.W.; Cody, R.D. Synergism effect of mixed surfactant solutions in remediation of soil contaminated with PCE. *Geoences J.* 2004, 8, 319-323. [CrossRef]

41. Jiang, B. Study on the Solubilization and Elution Mechanism of Mixed Surfactants for Pahs. Master’s Thesis, Lanzhou Jiaotong University, Lanzhou, China, 2007.

42. Li, S. The Washing Remediation of the Contaminated Soil by Pahs with Surfactants. Master’s Thesis, Shenyang University, Shenyang, China, 2017.

43. Ran, D.Q. Heterotopic Leaching Method to Repair Oil Contaminated Soil. Master’s Thesis, Shandong University, Jinan, China, 2012.

44. Chen, G. Remediation of the Oil Contaminated Soil by Surfactants. Master’s Thesis, Shangdong University of Science and Technology, Qingdao, China, 2008.

45. Sen, M.U. Experimental Study on Removal of Phenanthrene from Water by Gemini Surfactant Modified Sepiolite. Master’s Thesis, North China Electric Power University, Beijing, China, 2016.

46. Ma, H. Study on Remediation of Petroleum Hydrocarbon Contaminated Soil by CMC Solubilization Combined with SPS Chemical Oxidation. Master’s Thesis, Chongqing University, Chongqing, China, 2016.

47. Liang, C.; Guo, Y.Y. Remediation of Diesel-Contaminated Soils Using Persulfate Under Alkaline Condition. *Water Air Soil Pollut.* 2012, 223, 4605-4614. [CrossRef]

48. Zhao, D.; Liao, X.; Yan, X.; Huling, S.G.; Chai, T.; Tao, H. Effect and mechanism of persulfate activated by different methods for PAHs removal in soil. *J. Hazard. Mater.* 2013, 254, 228-235. [CrossRef] [PubMed]

49. Lv, P.P. Study and Application of Surfactant Ectopic Washing Oil Contaminated Soil. Master’s Thesis, Dong Hua University, Shanghai, China, 2015.