Surfactants-enhanced electrokinetic transport of xanthan gum stabilized nanPd/Fe for the remediation of PCBs contaminated soils

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A B S T R A C T
Polychlorinated biphenyls (PCBs) in the environment pose long-term risk to public health because of their persistence and toxicity. In this study, a novel technology called EK + nano (electrokinetic technology combined with engineered nanoparticles) was used to remediate polychlorinated biphenyls (PCBs) contaminated soil. Three different surfactants (anionic surfactant – SDBS, nonionic surfactant – Brij35 and biosurfactant – rhamnolipid) for enhancing the solubilization of soil PCBs were applied separately with xanthan gum stabilized nanPd/Fe. The stabilized nanPd/Fe was injected in the compartment located 3 cm from the anode chamber daily in EK tests. The results indicated that the surfactants addition enhanced the solubilization capacity of PCB28 significantly but did not affect the stability of xanthan gum–nanPd/Fe suspension. The nanoparticles were successfully transported along with the soil column by EK, and apparent increase of Fe content was found toward the cathode. Higher electroosmotic flow favored the migration of nanoparticles, but the degradation was limited without addition of surfactant. Brij35–xanthan gum stabilized nanPd/Fe gave the highest removal efficiency of PCBs, both in batch experiments and EK tests, in which the removal rates of approximately 50% and 20% were achieved, respectively. The functions of SDBS and rhamnolipid in soil PCBs removal were not significant in all tests.

1. Introduction
Polychlorinated biphenyls (PCBs) are one group of persistent organic pollutants and widely used as dielectric and coolant fluids between 1929 and early 1970s. The widespread distribution of PCBs pose a serious environmental problem due to their persistence and toxicity [1]. Their low water solubility and strong sorption to soil particles are the major challenges in the remediation of PCBs polluted soil.

The traditional methods for remediating PCBs contaminated soils include incineration, thermal desorption, chemical oxidation, solvent extraction, soil washing, solidification/stabilization and vitrification [2]. However, they all have disadvantages, such as high costs and secondary pollution. Recently, nanozero-valent iron (nanoFe0) has attracted growing attentions for remediation of groundwater and soil due to their high reactivity and easy availability. Several studies demonstrated that nanoFe0 was very effective for the transformation and reductive dechlorination of chlorinated organic solvents, organochlorine pesticides and PCBs [3–6]. Furthermore, various inorganic compounds such as nitrate and heavy metals can also be restored in soils by nanoFe0 [7].

However, the easy aggregation of nanoparticles due to their strong van der Waals forces and magnetic attraction limited their delivery in soil and subsequent application in soil remediation [8,9]. Thus, many researchers tried to overcome this limitation by using various modifiers or dispersants to coat the nanoparticles to increase steric and electrostatic hindrance among the particles what results in the stability of the nanoparticles suspension. Different chemicals were used to modify the particle surface such as polyacrylic acid, guar gum and carboxymethyl cellulose, but some of these chemicals are not environmentally friendly [10–12]. Comba and Sethi [13] used the biopolymer xanthan gum to disperse nanoFe0 and found that highly concentrated nanoFe0 slurries (15 g/L) could be stabilized for more than 10 d after adding 6 g/L of xanthan gum. The following sand-packed column experiment also proved that xanthan gum is an excellent stabilizing agent and delivery vehicle of nanoFe0 particles with high potential for use in real scale remediation interventions [13,14]. Although the stabilized nanoFe0 can get through porous media, such as sand, it is still a challenging issue when comes to a low permeability soil.

To solve this problem, a novel technology called EK + nano was adopted for transporting nanomaterials in low permeability soil by electrokinetics. As we know, electrokinetic remediation is a promising technology for remediating soils, sediments and groundwater contaminated with heavy metals, organics or mixed contaminants,
especially in low permeability subsurface [15]. The main migration mechanism of nanoparticle under electric field is electroosmotic flow [16]. Many researchers have worked on EK + nano technology. Reddy and Karri [17] studied the delivery of nanoFe\(^0\) modified with surfactant (Igepal CA720) or organic solvent (ethanol) by EK for the remediation of pentachlorophenol (PCP) spiked kaolin soil. They added nanoFe\(^0\) in the anode compartment, and the results showed that their aggregation, settlement and partial oxidation within the anode limited the transportation of nanoFe\(^0\). Yang et al. [18] also reported that polyacrylic acid modified nanoPd/Fe could be transported by EK to remediate nitrate contaminated soils. In these studies, nanoparticles were injected into the anodic chamber, the production of O\(_2\) and H\(^+\) therein consumed nanoFe\(^0\) and destroyed its stability. More recently, Reddy et al. [19] injected aluminum lactate modified nanoFe\(^0\) into a position 3 cm away from the anode in kaolin, and achieved high removal efficiency for dinitrotoluene (TNT) attributed to both nanoFe\(^0\) and EK. Yuan et al. [20] also achieved obvious nanoPd/Fe transportation and high PCP degradation efficiency in soil by injecting 10 g/L of CMC-stabilized nanoPd/Fe into the central reservoir. In the above studies, the researchers focused more on the transport of stabilized nanoFe\(^0\) without considering the hydrophobicity of organic compounds, which was essential for the reductive dechlorination with nanoFe\(^0\), because the reductive dechlorination reaction by ZVI is a surface-mediated reaction, the strong hydrophobicity of PCB will result in its strong absorption in the soil and lead to the unavailability of surface active site and the low degradation rate. Moreover, according to the latest research developments, although EK remediation has been studied extensively, the EK remediation of PCB polluted soils has seldom been reported [21]. And more recently, Yukselen-Aksoy and Reddy [22] reported electrokinetically enhanced persulfate oxidation of polychlorobiphenyls.

In our study, we attempted to use electrokinetics coupled with nanoPd/Fe to remediate PCBs contaminated soils. For enhancing the solubilization of the absorbed PCBs, we chose three different surfactants (anionic surfactant – SDBS, nonionic surfactant – Brij35, and biosurfactant – rhamnolipid), mixed them with xanthan gum to stabilize nanoPd/Fe. The objectives of this study are (1) to test the effect of different surfactants on the stabilization and reactivity of xanthan gum–dispersed nanopd/Fe, (2) to investigate the transportation of stabilized nanoPd/Fe and degradation of PCBs under electric field, and (3) to study the feasibility of EK + nano technology to remediate practical PCBs polluted soils.

### 2. Experimental

#### 2.1. Chemicals

2,4,4’-Trichlorobiphenyl (PCB28) and PCBs standard solution including 20 PCBs congeners (purity > 99.4%) were obtained from AccuStandard (New Haven, CT, USA). Nanoiron particles used in this study were purchased from Nanjing Emperor Nano Material Co., Ltd., China with a size of 30–100 nm and stored in an anaerobic glove box (nitrogen protect system, YQX-II, Shanghai CIMO Medical Instrument Manufacturing Co. Ltd., China). Palladium acetate (Pd\(^{46.0\%}\)) and sodium nitrate (analytical pure) were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Xanthan gum (with viscosity of 800–1200 cps) and sodium dodecyl benzene sulfonate (SDBS) were provided by Sigma Aldrich. Polyethylene glycol lauryl ether (Brij35) was obtained from Alfa Aesar, and rhamnolipid (4% coarse solution, include mono-rhamnolipids and di-rhamnolipids) was supplied by Zhejiang University. Table 1 provides relevant properties of these surfactants. Hexane [high-performance liquid chromatography (HPLC) grade] was obtained from CNW Technologies GmbH, Germany. Acetone, hexane (analytical reagent), hydrochloric acid (guaranteed reagent) and ethanol (guaranteed reagent) were obtained from Nanjing Chemical Reagent Co. Ltd., China. The water used in the experiments was oxygen free, obtained by sonication for 20 min through milli-Q water (resistivity 18 M\(\Omega\) cm\(^{-1}\)).

#### 2.2. Soils

Two soils were used in this study: a clean soil collected from a farmland, at Nanjing, China and a PCBs polluted soil sampled from a capacitor landfill, in Zhejiang, China. The two soils were air-dried,
quantified amount of nanoFe PCBs concentration in contaminated soils. 

Physical and chemical characteristics of the soils used.

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Clean soil</th>
<th>PCBs polluted soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (%)</td>
<td>12.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>66.9</td>
<td>83.2</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>21.1</td>
<td>12.6</td>
</tr>
<tr>
<td>pH</td>
<td>5.7</td>
<td>6.3</td>
</tr>
<tr>
<td>DOM content (mg kg$^{-1}$)</td>
<td>46.2</td>
<td>166</td>
</tr>
<tr>
<td>Metal ions (mg kg$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>9848</td>
<td>2259</td>
</tr>
<tr>
<td>Mg</td>
<td>7330</td>
<td>3430</td>
</tr>
<tr>
<td>Cu</td>
<td>47</td>
<td>89</td>
</tr>
<tr>
<td>Zn</td>
<td>159</td>
<td>183</td>
</tr>
<tr>
<td>Fe</td>
<td>33,130</td>
<td>86,950</td>
</tr>
<tr>
<td>Mn</td>
<td>701</td>
<td>867</td>
</tr>
</tbody>
</table>

The clean soil ground and passed through 20 mesh and 60 mesh sieves, respectively. The properties of soils are shown in Table 2. The clean soil was spiked with PCB28 and used to dilute the real PCBs polluted soil. For the synthesis of nanoPd/Fe, a modified method using palladium acetate deposited on nanofe$^\circ$ particles in an ethanol solution was used [23]. The synthesis was carried out in 40 mL glass vials. A quantitative amount of nanofe$^\circ$ was added into an ethanol solution containing palladium acetate in the anaerobic glove box to obtain a target Pd loading of 1 wt.% Fe. Then the vials were placed on a reciprocal shaker and shaken at 200 rpm for 2 h for complete deposition of Pd. Finally, the nanoPd/Fe particles were washed four times with oxygen-free water and ethanol solution. After washing, the nanoPd/Fe particles were stored in the anaerobic glove box and dried by nitrogen gas. The synthesized nanoPd/Fe was also characterized by X-ray diffraction (XRD, D/max-III C, Rigaku company, Japan) and transmission electron microscope (TEM, JEOL TEM-2100). The size is consistent with the product introduction, and the composition is also proved. The graph was shown in appendix (Fig. 8).

2.4. Stability tests

The stability of xanthan gum-stabilized nanoPd/Fe was firstly examined. Xanthan gum-nanoPd/Fe slurry was prepared by adding 10 mL of different concentration of xanthan gum solution to the same volume of 2 g/L nanoPd/Fe slurry to achieve a 1 g/L of nanoPd/Fe. The xanthan gum concentration of 0, 0.25, 0.5, 1.0, 1.5, 2.0 g/L were also obtained. The mixture was then shaken with a vortex mixture for 2 min, followed by sonication for 1 min. Regarding the effects of different surfactants on the stability of xanthan gum dispersed nanoparticles, the same volume of surfactant–xanthan gum stabilized nanoPd/Fe (1 g/L) at different surfactant concentrations (0%, 2%, 3%, 4% and 5% for SDBS and Brij35; 0, 1.0, 2.0, 3.0, and 4.0 g/L for rhamnolipid) were added. The stability of the nanoparticle suspension was evaluated by taking photographs of undisturbed suspensions at 0, 1, 12 and 60 h.

2.5. Solubilization tests

Three different surfactants SDBS (anionic surfactant), Brij35 (nonionic surfactant) and rhamnolipid (biosurfactant) were selected as the typical surfactants. Their solubilization for soil PCB28 as spiked was tested. SDBS and Brij35 were investigated at concentrations of 1%, 2%, 3%, 4%, and 5%, respectively; for rhamnolipid, the concentration gradients of 0.5, 1, 2, 3, and 4 g/L were adopted. The batch extraction experiments were conducted in 40 mL glass vials at a soil to solution ratio of 1:10. Thus, 20 mL of surfactant solution was added to 2 g of spiked soil. Then the vials were shaken in a reciprocal shaker at 180 rpm for 2 h. After shaking, the soil–solution mixture was centrifuged at 4000 rpm for 10 min to separate the solution from the soil. The supernatant solution was removed, and the concentration of PCB28 in the solution was determined by liquid–liquid extraction using hexane followed by gas chromatography chemical analysis. Batch extractions were performed in duplicate, and the DI water and xanthan gum (1 g/L) were set as the control tests.

2.6. Reactivity tests

After the solubilization tests and determination of the optimum concentrations of surfactants, batch experiments were conducted to test the reactivity of the nanoPd/Fe for the degradation of PCB28 in spiked soil. Different nanoPd/Fe dosages (2, 5, 10, 20, and 40 g/L) were applied to evaluate its effect on PCB28 degradation. The tests were conducted in 40 mL glass vials at a soil to solution ratio of 1:10. Two grams of spiked soil was added into 20 mL of the surfactant–xanthan gum stabilized nanoPd/Fe solution, and then the vials were shaken in a reciprocal shaker at 180 rpm for 24 h. After shaking, the soil–nanoPd/Fe mixture was centrifuged at 4000 rpm for 10 min to separate the solution from the soil. The supernatant solution and the soil were analyzed for PCB28. For supernatant, 1.0 mL of supernatant was acidified with 1.0 mL of 6 M HCl, and then the vials were shaken in a reciprocal shaker at 180 rpm for 2 h. After shaking, the soil–solution mixture was centrifuged at 4000 rpm for 10 min to separate the solution from the soil. The supernatant solution and the soil were analyzed for PCB28. For supernatant, 1.0 mL of supernatant was acidified with 1.0 mL of concentrated HCl to end the reaction, before extraction with 5.0 mL of hexane for 1 h. All experiments were carried out in duplicate.

2.7. EK tests

The experimental setup used in this study is shown in Fig. 1. The setup is a rectangular translucent box with a lid made of
Plexiglass plate and comprises a reactor cell to hold the soil sample (12.5 cm x 8 cm x 6 cm), two electrolyte compartments at both ends (2.5 cm x 8 cm x 6 cm), and an injection compartment (2.5 cm x 8 cm x 6 cm) which was located about 3 cm from the anode compartment. The experimental set-up also includes a power supply, a multimeter, a four-channel peristaltic pump and a pH control system. Two square mesh titanium alloy electrodes (2.5 cm x 2.5 cm) were used as the anode and cathode. Rapid quantitative filter paper (80–120 µm pore size) and nylon cloth (100 mesh, 150 µm pore size) were used to avoid the leakage of soil particles, and gas vents were set on the chamber cover and located on the top of the electrolysis compartments to allow gases resulting from the electrolyte reactions to escape.

To testify the feasibility of the electrokinetics in a field site, a field PCBs polluted soil was used in the EK tests, which was diluted with a clean yellow–brown soil with the same soil type. About 590 g of the dry soil was loaded into the electrokinetic cell in layers before drying, and then were extracted by 1.0 M HNO₃ for 30 min at 120 rpm. After centrifugation at 4000 rpm for 30 min, the Fe concentration in supernatant was determined by [20], thus 0.5 g of dry soil was digested by 10 mL of 1 M HNO₃ for 30 min at 120 rpm. After centrifugation at 4000 rpm for 10 min, the Fe concentration in supernatant was determined by

### Table 4
Experimental design of electrokinetic treatments.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Dispersants</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Anolyte/catholyte</th>
<th>Soil weight (g)</th>
<th>Voltage gradient (V/cm)</th>
<th>During time (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp-01</td>
<td>1 g/L Xanthan gum</td>
<td>6.9</td>
<td>39.5</td>
<td>0.01 M NaNO₃</td>
<td>590</td>
<td>1 → 2</td>
<td>14</td>
</tr>
<tr>
<td>Exp-02</td>
<td>1 g/L Xanthan gum + 3% SDBS</td>
<td>7.1</td>
<td>4218</td>
<td>0.01 M NaNO₃</td>
<td>588</td>
<td>1 → 2</td>
<td>14</td>
</tr>
<tr>
<td>Exp-03</td>
<td>1 g/L Xanthan gum + 3%Brij35</td>
<td>5.1</td>
<td>900</td>
<td>0.01 M NaNO₃</td>
<td>589</td>
<td>1 → 2</td>
<td>14</td>
</tr>
<tr>
<td>Exp-04</td>
<td>1 g/L Xanthan gum + 3 g/L Rhamnolipid</td>
<td>7.5</td>
<td>2112</td>
<td>0.01 M NaNO₃</td>
<td>590</td>
<td>1 → 2</td>
<td>14</td>
</tr>
</tbody>
</table>

Note: increase the voltage gradient from 1 V/cm to 2 V/cm at 8th day (172 h). Add dispersed nanoPd/Fe (10 g/L, 20 mL) from about 3 cm distance from anode per day.

### 2.8. Analytical methods

The concentration of PCB28 was analyzed by using gas chromatography (GC × ECD, Agilent 7890A, USA) coupled with a micro-electron capture detector and a HP-5 (30 m x 0.25 mm x 0.25 µm) fused silica capillary column. The oven procedure was as follows: the oven temperature was held at 150 °C for 2 min, increased to 280 °C with a gradient of 15 °C min⁻¹ and then held for 2 min. The temperatures of the injector and detector were 250 °C and 300 °C, respectively. High pure nitrogen was used as the carrier gas and the ECD makeup gas with a constant of 1.0 mL min⁻¹ and 30 mL min⁻¹, respectively. For PCBs analysis, the oven temperature was programmed starting at 150 °C for 2 min, and then increased to 280 °C at a rate of 5 °C min⁻¹ where it was hold for 2 min.

Before preparation of stabilized nanoPd/Fe, the pH (Shanghai REX Instrument Factory, model pHS-3B) and EC (Shanghai REX Instrument Factory, model DDS-11A) of the dispersants were measured. For the pH and EC measurement, soil was mixed with DI water at a solid–liquid ratio of 1:2.5. Soil samples were air-dried, ground and passed through 20-mesh sieve. For PCBs measurement, the soil was extracted by sonication. To determine the content of Fe, two methods were adopted to analyze the sectional soils and sampled soils. For the sectional soils, soil samples were air-dried, ground and passed through 100-mesh sieve for 10 min. The Fe concentration in supernatant was determined by...
3. Results and discussion

3.1. Stability of nanoPd/Fe under different conditions

The settlement processes of nanoPd/Fe slurry were shown in Fig. 2. At the same iron content, the stability of nanoPd/Fe increased with increasing xanthan gum concentration. Bare nanoPd/Fe settled immediately, while higher xanthan gum concentration led to a stronger stability due to the increased viscosity which prevented particle aggregation and sedimentation [13]. The addition of 1.0 g/L of xanthan gum yielded stable nanoPd/Fe suspensions at least for 60 h. Similar sedimentation phenomenon was observed when nanoPd/Fe was stabilized with three different surfactants only. As shown in Fig. 2b–d, the nanoparticles settled within 1 h, while, the stable time could last for more than 60 h with addition of 1.0 g/L xanthan gum. This indicates that the addition of surfactant has no negative effect on the stability of xanthan gum–nanoPd/Fe. Moreover, the stability of xanthan gum stabilized nanoPd/Fe in the presence of SDBS was better than that with Brij35, which was due to the net negative charge of SDBS resulting in electrostatic hindrance between particles. Rhamnolipid also presented a little enhancement of the stability of xanthan gum–nanoPd/Fe because of the longer duration (data not shown), which was probably related to its intrinsic dispersive ability at high concentration [24]. The surfactant concentration gradient has no distinct effect on the stability.

3.2. The solubilization of PCB28 by different surfactants

Three different surfactants at series concentration gradients were tested for their abilities to extract PCB28 from soil. Fig. 3 indicates that Brij35 was most effective for solubilization of PCB28 than other surfactants, and approximately 60% of PCB28 was extracted from spiked soil. SDBS had the lowest solubilization of PCB28 with an extract rate of approximately 25%. The capacity of solubilization by rhamnolipid increased with the increased concentration, ranging from 15.1% to 41.7%. Similar results were also reported by Liu et al. [25]. The use of Brij35 to enhance PCB solubilization was also reported by Zhu et al. [26], who found that a high concentration of 100× critical micelle concentration (CMC) obtained near 98% removal rate of PCB3 by nanoTiO2 photocatalytic degradation. This higher solubilization ability of Brij35 was ascribed to its surface charge, compared to anionic surfactant SDBS and rhamnolipid. Brij35 can be favorably adsorbed to soil due to the electrostatic attraction, which can create a sink for retaining more PCB in the soil. The uniform extraction efficiency of SDBS and Brij35 was related to the concentration gradient that was far above the CMC. The CMCs of SDBS and Brij35 were 523 and 51.5 mg/L, respectively [27,28]. Xanthan gum (1 g/L) and DI water almost did not solubilize PCB28 from spiked soil, and the extract rates were 6.6% and 2.5%, respectively. Considering these results, 3% SDBS, 3% Brij35 and 3 g/L rhamnolipid were selected for the

Fig. 2. Pictures of nanoPd/Fe stabilized with different chemicals at different time. Fe loading is 1 g/L with Pd 1 wt.% of Fe. (a) different concentration of xanthan gum (XG) (0 h, 12 h, 36 h); (b) different concentration of SDBS (0 h, 1 h) and combined with 1 g/L XG (80 h); (c) different concentration of Brij35 (0 h, 1 h) and combined with 1 g/L XG (60 h); (d) different concentration of rhamnolipid (RL) (0 h, 1 h) and combined with 1 g/L XG (60 h).

Fig. 3. Extraction efficiency of PCB28 with different surfactants at different concentration gradients (1, 2, 3, 4, and 5 represent 1%, 2%, 3%, 4% and 5% (w/w) for SDBS and Brij35 respectively, and 0.5, 1.0, 2.0, 3.0, and 4.0 g/L for rhamnolipid, the concentration of xanthan gum is 1.0 g/L).
next steps. These concentrations are almost the optimum concentrations.

3.3. Degradation of PCB28 as a function of nanoPd/Fe dosage under different dispersants

The degradation of PCB28 as a function of nanoPd/Fe dosage under different modifiers was evaluated in Fig. 4. These results show that only Brij35–xanthan gum stabilized nanoPd/Fe exhibited higher reactivity when compared to other surfactants. After 24 h reaction, approximately 50% removal rate was obtained. Besides the higher solubilization capacity of Brij35, the acidic pH of Brij35–xanthan gum solution (5.08 as shown in Table 4) also is preferred to enhance the reductive dechlorination activity of nanoPd/Fe [23]. Moreover, the linear chain structure of Brij35 makes the PCB28 associated with Brij35 to be more flexible to contact to the nanoparticles. While using SDBS, the residual concentration of PCB28 was extracted, but the degradation was hindered. This may be due to SDBS acting as a PCB28 carrier, likely subject to greater mass transfer resistance due to the benzene ring, which hinders the delivery of PCB28 to the nanoparticle surface [27]. The PCB28 degradation with bare nanoPd/Fe was also minimal, probably due to its adsorption to the soil particles. This limited the availability of PCB28 in bulk solution making unfeasible of contact with the iron surface activity sites. And also the aggregation of non-stabilized nanoparticles retarded the dechlorination efficiency. Compared to bare nanoPd/Fe, xanthan gum stabilized nanoPd/Fe did not enhance the activity of nanoparticles, which was consistent with the results obtained by other researchers [11,29,30], who found that the adsorbed polyelectrolyte decreased the reactivity of nanoparticles. However, the highest pH of rhamnolipid–xanthan gum solution (pH = 7.49), in the treatment with xanthan gum that reached a value exceeding the initial one. The slight increase of the electrical current at the initial stage was attributed to the H\(^+\) and OH\(^-\) ions generated at anode and cathode, respectively, due to the electrolysis of water. Higher current was ascribed that more ions entered into the pore water as a result of the dissolution of salts present in the soil. Then many ions went into the opposite electrode chamber and/or precipitation of ions at the cathode resulted in the decrease of the electrical current. The current fluctuation at the injection time was ascribed to the production of Fe\(^{3+}\) ions from nanoFe\(^{0}\) dissolution.

3.4. Variation of electrical current and cumulative electroosmotic flow during the EK tests

Fig. 5a displays the profile of electrical current intensity versus time during the EK tests. The current increased slightly at the beginning and then decreased gradually dropping to a comparable stabilized range with regular fluctuations at the injection time. The electrical current in Exp-01 was higher than the other treatments. The lowest current was observed in Exp-04. When the voltage gradient was doubled at 8th day (172 h), a peak was observed, especially in the treatment with xanthan gum that reached a value exceeding the initial one. The slight increase of the electrical current at the initial stage was attributed to the H\(^+\) and OH\(^-\) ions generated at anode and cathode, respectively, due to the electrolysis of water. Higher current was ascribed that more ions entered into the pore water as a result of the dissolution of salts present in the soil. Then many ions went into the opposite electrode chamber and/or precipitation of ions at the cathode resulted in the decrease of the electrical current. The current fluctuation at the injection time was ascribed to the production of Fe\(^{3+}\) ions from nanoFe\(^{0}\) dissolution.

3.5. Soil pH and EC distribution in different treatments after EK tests

As shown in Fig. 5b, the cumulative electroosmotic flow (EOF) in all tests continuously increased with time. Doubling voltage...
3.6. The iron distribution in different treatments during and after EK tests

To avoid the error resulting from the small addition of nanoPd/Fe versus to the very high Fe content of the soil background, 1.0 M HNO₃ was used to extract iron from the sampled soils followed by the modified method of Yuan et al. [20]. All Fe⁰ and exchangeable Fe, partial carbonate, Fe–Mn oxide and organics bound Fe can be extracted. The transportation performances of iron were listed in Table 5. The initial concentration of iron in soil was 2.15 g/kg. The results showed that the migration of the Fe⁰ was very slow at the first 7 d, with no apparent increase of iron concentration in various sampled soils. At the end of experiment (14th d), a dramatic increase of soil iron content was observed in all tests except Exp-04. In the S2 sections, the nearest to the injection points, the iron contents were almost two times of the initial value, and a gradually decreased iron concentration was found in S3 and S4, the positions far from the injection position, which indicated that EK enhanced the migration of nanoPd/Fe. Higher iron contents in S1 section, near the anode, may be attributed to the negative surface charge of modified nanoPd/Fe driven by electrophoresis or diffusion. The highest iron migration was obtained in Exp-01 especially in S2 section, in accordance to its higher electroosmotic flow versus the lowest in Exp-04. In the treatment using Brij35, the iron content in S3 and S4 sections was higher than the other treatments, which reinforces the advantage of using Brij35. In the two treatments the electroosmotic flow was also very high, what indicates that electroosmotic flow played an important role in transportation of nanoPd/Fe-higher electroosmotic flow favored the delivery of nanoparticles. Compared to Yuan’s report, the iron migration rate attained in the present study was much lower, because the mass of iron added was different. In Yuan’s study, 10 g/L of nanoPd/Fe was injected three times at 3, 7 and 10 d, respectively, which amounted to 350 mL, thus 3.5 g total Fe was added, what is higher than our 2.8 g. Then the nanoparticles used were also different, they used freshly synthesized nanoFe⁰ and coated the dispersant CMC before synthesis, so they got smaller nanoPd/Fe (diameter range of 10–20 nm) which guaranteed the feasibility of transport and degradation. He and Zhao [12,33] also found that pre-synthesis addition of stabilizers appears to yield nanoFe⁰ suspensions with enhanced stability and reactivity compared to post-synthesis addition of stabilizers The distribution of iron content at different layer of the sampled soil was uniform, which indicated that the part of nanoPd/Fe transported through the soil pores kept the stability.

3.7. PCBs concentration in soil after EK tests

After completion of the EK tests, the soil was divided into four sections. The total iron concentration was determined in each section. Fig. 7a shows the concentration of total iron in the different sections after the end of the experiments. Because the mass of nanoPd/Fe added into the injection port was 2.8 g, which could be neglected when compared to the background of the soil iron...
(35.5 g/kg), there was no obvious regular pattern in the total iron
distribution. However, in S2 section, the part near the injection
point, the iron content was higher than in the other sections, which
indicate the nanoPd/Fe moved from the injection port to S2 section
by electroosmotic flow.

The distribution of residual PCBs in soils at the end of experi-
ments is shown in Fig. 7b. The initial concentration of PCBs in the soil
was 46.3 mg/kg for all the tests. After EK + nano tests, the removal
efficiencies were 17.1%, 11.0%, 20.4%, and 11.7%, respectively. The
uniform distribution of PCBs in Exp-01, Exp-02 and Exp-04 indicated
that there was no obvious migration and degradation of PCBs in
these treatments, and the surfactant SDBS and rhamnolipid did
not enhance the migration of PCBs by electrokinetics. This was re-
lated to their insignificant function of the reactivity of xanthan
gum stabilized nanoPd/Fe. The slightly decreased concentration
near the cathode may be due to the electrochemical reduction.
When SDBS–xanthan gum stabilized nanoPd/Fe was added into
the injection point, the color of slurry turned to be white immedi-
ately, which indicated SDBS reacted with some matter dissolved
from the soil, maybe calcium. Some researchers found that the anion-
ic surfactant SDS exhibited a solubility limit in the presence of dis-
solved Ca²⁺ ions – when this limit is exceeded, the surfactant falls out
as a SDS–Ca precipitate [34,35]. The slight acid surroundings near
the anode allow the calcium dissolution. This can be used to inter-
pret the ineffectiveness of SDBS under electric field even if the EOF
is high. In the treatment using rhamnolipid, the migration of PCBs
was also limited, probably due to the low EOF. Additionally, the absorp-
tion of rhamnolipid to the soil induced its loss since the elu-
tion of PCBs from aged soils is more difficult and need more surfac-
tant than from spiked soils [36,37]. The migration and degradation
of PCBs was highest when Brij35–xanthan gum stabilized
nanoPd/Fe was used. In S2 and S3 sections, the removal rates
reached 74.1% and 39.1%, respectively. In S4 section, the remained
PCBs increased to 147.1%, indicating that Brij35 enhanced the trans-
port of PCBs and dispersion of nanoparticles in the soil under electric
field. The high accumulation of PCBs in S4 may be related to the high
pH of the soil near the catholyte which passivated the reactivity of
nanoPd/Fe. In Exp-01, the higher rate of iron migration did not lead
to the higher PCBs degradation that was mainly due to the hydro-
phobicity of PCBs resulting in the nanoPd/Fe surface contact avail-
ability. Because this study did not investigate the reaction products,
we could not make sure the degree of the function of nanoPd/Fe in
the EK + nano tests, but from the results reported by other authors
and the reactivity tests we obtained it is possible to obtain the trans-
portation and degradation of organic chlorinated pollutants by this
technology [19,20].

Based on the results, surfactant is necessary to enhance EK + na-
no for remediating hydrophobic organic compound contaminated
soils. However, the removal efficiency is still too low for field appli-
cation. In the future study, enhancing the activity of nanoPd/Fe in
soil such as screening more effective polymer which has both high
dispersity and little negative effect on the activity of nanoPd/Fe
should be considered. Moreover, the background iron content in
the soil is usually high and until now, there is no effective method
to discern soil background Fe and nanoFe⁰. Further research should
be carried out to deeply explore the underlying mechanism.

4. Conclusions

In this study, we combined surfactant with xanthan gum to sta-
bilize nanoPd/Fe and investigated the EK transport of stabilized na-
noPd/Fe for the remediation of PCBs contaminated soil. The effects
of different surfactants on the stabilization and reactivity of xan-
than gum stabilized nanoPd/Fe were also studied. The conclusions
can be summarized as follows.
(1) Xanthan gum well dispersed nanoPd/Fe, while different surfactants SDSB, Brij35 and rhamnolipid did not increase the stabilization of nanoPd/Fe. The addition of surfactant had no negative effect on xanthan gum–stabilized nanoPd/Fe.

(2) All surfactants increased the solubility of PCB28 in the PCBs contaminated soil. Brij35 enhanced the degradation of PCB28 by stabilized nanoPd/Fe, but increasing the dosages of nanoPd/Fe was inefficient. SDSB and rhamnolipid had no improvement of the reactivity of stabilized nanoPd/Fe.

(3) It is feasible to transport the stabilized nanoPd/Fe by EK. Higher electroosmotic flow facilitated nanoPd/Fe transport, but the degradation was low without the solubilization of PCBs strongly adsorbed in soils. SDSB and rhamnolipid did not increase the PCBs migration by EK. Brij35–xanthan gum stabilized nanoPd/Fe obtained the highest removal efficiency. It is necessary to combine surfactant with dispersant to enhance the degradation of organic pollutants in soil by EK + nano technology. In the other hand, a method to enhance the activity of stabilized nanoPd/Fe in soil should be considered more extensively.

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References


