Electrokinetic delivery of persulfate to remediate PCBs polluted soils: effect of different activation methods

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ABSTRACT: Persulfate-based in-situ chemical oxidation (ISCO) for the remediation of organic polluted soils has gained much interest in last decade. However, the transportation of persulfate in low-permeability soil is very low, which limits its efficiency in degrading soil pollutants. Additionally, the oxidation-reduction process of persulfate with organic contaminants takes place slowly, while, the reaction will be greatly accelerated by the production of more powerful radicals once it is activated. Electrokinetic remediation (EK) is a good way for transporting persulfate in low-permeability soil. In this study, different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH and peroxide, were evaluated to enhance the activity of persulfate delivered by EK. All the activators and the persulfate were added in the anolyte. The results indicated that zero-valent iron, alkaline, and peroxide enhanced the transportation of persulfate at the first stage of EK test, and the longest delivery distance reached sections S4 or S5 (near the cathode) on the 6th day. The addition of activators accelerated decomposition of persulfate, which resulted in the decreasing soil pH. The mass of persulfate delivered into the soil declined with the continuous decomposition of persulfate by activation. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation > without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of activator and persulfate.

Key words: Polychlorinated biphenyls (PCBs), soil remediation, electrokinetics, persulfate activation.

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Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that strongly adsorb in soils and sediments. Developing cost-effective and sustainable solutions for the remediation of PCB-contaminated soils is imperative (Gomes et al., 2014). The present technologies include capping, solvent extraction, thermal desorption, Fe-promoted dechlorination, chemical oxidation, biological remediation and many others still in development phase (Gomes et al., 2013).

Among these technologies, in-situ chemical oxidation (ISCO) is an emerging technology for soil and groundwater remediation due to its wide applicability, relatively fast treatment, simplicity of operation and cost effectiveness (ITRC, 2005; Watts and Teel, 2006; Rastogi et al., 2009b; Tsitonaki et al., 2010). ISCO involves the introduction of chemical oxidant into the subsurface to transform organic contaminants into less harmful chemical species. Hydrogen peroxide, permanganate and ozone are widely used oxidants, but their practical applications are hindered due to their low stability (hydrogen peroxide and ozone) or high soil affinity for natural soil organics (permanganate) (Gates-Anderson et al., 2001; Li and Schwartz, 2004; Tsai et al., 2008; Navalon et al., 2010). Persulfate is a strong oxidant with a redox potential (E_0) of 2.01 V and a relatively long life in the subsurface due to its slow reaction kinetics with organics, which can promote more favorable contact time (Tsitonaki et al., 2010). Also, upon activation, persulfate can produce sulfate radicals ($SO_4^{-\bullet}$, E_0=2.6 V) and hydroxyl radicals ($\bullet OH$, E_0=2.7 V) which are more powerful and kinetically faster than persulfate anions (Liang et al., 2004a). There are many methods available for persulfate activation including the use of heat, chelated or unchelated transition metals, hydrogen peroxide, or strong alkaline pH (Eqs. (1)-(4)) (Petri et al., 2011). But the site conditions such as lithology (clay, sand, etc.), hydrogeology and the structure of the target contamination will affect the oxidation effectiveness. Thus, the activation method selected must be dependent on the contaminants to be treated and the subsurface environment (Block et al., 2004).

$$S_2O_8^{2-} \xrightarrow{\text{heat}} 2SO_4^{\bullet -} \qquad (1)$$

$$M^{n+} + S_2O_8^{2-} \rightarrow M^{n+1} + SO_4^{\bullet -} + SO_4^{2-} \qquad (2)$$

$$S_2O_8^{2-} + \bullet OH \rightarrow SO_4^{2-} + SO_4^{\bullet -} + 1/2O_2 + H^+ \qquad (3)$$

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + \bullet OH \qquad (4)$$

Fe(II) was used initially to activate persulfate. However, the activation by Fe^{2+} is not practical because the reaction is almost instantaneously stopped due to the $SO_4^{\bullet -}$ scavenging by excess Fe^{2+}

or to the rapid conversion of Fe^{2+} to Fe^{3+}. As an alternative activator, zero-valent iron (an insoluble form of iron) has been employed to activate persulfate with promising results by directly reacting with persulfate to release Fe^{2+}, or releasing Fe^{2+} through the corrosion of zero-valent iron activation (Eqs. (5)-(7)) (Oh et al., 2009; Liang and Guo, 2010; Oh et al., 2010). On the other hand, aqueous Fe(II) is relatively insoluble at the ambient pH⩾5 of most aquifer systems and Fe(II) chelated by chelating agents (e.g. ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid and citric acid) is effective in activating persulfate by maintaining iron in solution at neutral pH (Liang et al., 2004b; Crimi and Taylor, 2007; Rastogi et al., 2009a).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (5)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -} \quad (6)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (7)$$

A significant difficulty in ISCO is promoting the contact between the oxidant and the contaminant, particularly in low-permeability subsurface. When ISCO is combined with EK, EK has the potential to increase the delivery of oxidant in soil and improve the remediation efficiency (Reddy and Cameselle, 2009). Also, in-situ electrolysis by iron electrodes allows to manipulate the reactivity of persulfate in EK + ISCO system. According to Yuan et al. (2013), Fe^{2+} can be continuously produced in situ by electrochemical corrosion (Eqs. (8) and (6)) and chemical corrosion (Eqs. (9) and (7)) when applying a positive current on an iron anode, and the electrolytic supply of Fe^{2+} will improve the utilization of both Fe^{2+} and persulfate (Yuan et al., 2013).

$$Fe - 2e^- \rightarrow Fe^{2+} \quad (8)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -} \quad (6)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (9)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (7)$$

The effect of different activators on persulfate oxidation has been studied extensively. However, the persulfate activation in EK was rarely referred. Recently, Yukselen-Aksoy et al. (2012) investigated the effect of heat and alkaline activation on the electrokinetically enhanced persulfate oxidation of PCB44 in kaolin and glacial till soils. Persulfate (30%) was injected from a position 3 cm away from the anode and the result showed that both activation methods (heat or heat and high pH) improved the degradation of PCB44 in kaolin, but not in glacial till soil due to its high buffering capacity, nonhomogeneous mineral contents and high organic content (Yukselen-Aksoy and Reddy, 2012). Furthermore, we investigated the transport behaviors of inactivated persulfate under electric field, and found that electroosmotic flow (EOF) was more effective for persulfate delivery than electromigration and the anode was the best injection spot for high dosage of persulfate (Fan et al., 2014a). However, the activity of persulfate in soil is relatively low without activation, so choosing appropriate activators to accelerate the reaction kinetics of persulfate is a key process for the application of EK + persulfate technology.

In this study, different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH, and peroxide, were evaluated to enhance the activity of persulfate delivered by EK. The transport behavior of activated persulfate under electric field and the remediation efficiency of PCBs contaminated soil were also investigated.

2. Experimental

2.1 Chemicals and materials

PCBs standard solution containing 20 PCBs congeners (＞99.4%) were obtained from AccuStandard (New Haven, CT, USA). Sodium persulfate (99.0%) was purchased from Chengdu Kelon Chemical Reagent Factory. Zero-valent iron power (98.0%) was provided by Shanghai Miura Chemical Co. Ltd., China. Sodium hydroxide (＞96%), citric acid (＞99.6%), acetone (analytical reagent) and hexane (analytical reagent) were obtained from Nanjing Chemical Reagent Co. Ltd., China. Hydrogen peroxide (30% solution, 99.0%) and $FeSO_4 \cdot 7H_2O$ (99.0%) were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Deionized water (18 MΩ cm^{-1}) obtained from a Millipore Milli-Q system was used in all experiments.

The PCBs polluted soil was sampled from a place near a capacitor storage site in Zhejiang province, which was diluted with a clean soil sampled from a farmland in Nanjing. The properties of the two soils are shown in Table 1. Both soils belong to yellow brown soil and have similar properties. The soils were air-dried, ground and passed through 20 mesh and 60 mesh sieves, respectively. Approximately 100 g of PCBs polluted soil was mixed with 2200 g of clean soil thoroughly, after that, the mixed soil was stored in the fume hood one week for equilibrium. Also, the properties of the mixed soil were analyzed and shown in Table 1. The initial values of PCBs in the final soil were determined before starting the experiments.

2.2 EK tests

The experimental setup used in this study was reported in our previous studies (Fan et al., 2014a). The setup consisted of a direct-current power supply, a four-channel peristaltic pump, a cylindrical soil column (12 cm L×6.6 cm D), anode and cathode compartments with two titanium electrodes, *in situ* soil solution samplers and a pH auto-control system. About 570 g of the dry soil was loaded into the EK cell in layers and compacted manually using a rammer. During this process, five in-situ soil solution samplers were also vertically embedded at target locations through the soil column. According to our previous results, the anode was selected as the persulfate injection location and 200 g L^{-1} (20%) of persulfate was chosen as the optimum oxidation dosage injection in the anode (Fan et al., 2014a; Fan et al., 2014b). A total of six tests were conducted under different conditions as shown in Table 2. The initial PCBs concentration was 46 mg kg^{-1}. In the control test (Exp-01), only 20% of persulfate was added in the anode to evaluate the performance of transported persulfate by EK without activation. Exp-02 was performed with zero-valent iron activation by adding 1 g of zero-valent iron powder in the anode compartment on 3rd, 6th, 9th and 12th day, and the molar ratio of persulfate and the total zero-valent iron we added was 5.88:1. The discontinuous input of zero-valent iron aimed to avoid the over-consumption of persulfate by the activator. In Exp-03, citric acid was selected as the Fe^{2+} chelator, injecting citric acid chelated Fe^{2+} in the anode at one time under the $Na_2S_2O_8$/ citric acid /Fe^{2+} molar ratio of 20/5/5 (Liang et al., 2004b). In Exp-04, a 14# galvanized iron wire (2.03 mm D × 8 cm L) was used as the iron anode to keep the current continuity. The iron anode was occasionally replaced by a new one after its complete corrosion. Exp-05 was performed with alkaline activation using a pH controller to keep the anode pH at 12.0. In Exp-06, 6 mL of 30% H_2O_2 was injected into the anolyte per day to keep a molar ratio of the total H_2O_2 and $Na_2S_2O_8$ nearly 1:1 (Block et al., 2004). For all the treatments, 0.01 M $NaNO_3$ was used as the supporting electrolyte. Before application of electrical field, the soil was saturated with 0.01 M $NaNO_3$ solution for 24 h. A voltage gradient of 1.0 V cm^{-1} was applied to the EK system by a DC power supply for a period of 15 d (14 d for Exp-03). During EK tests, the electric current and the EOF were recorded and the soil solution and electrolytes were sampled on 3rd, 6th, 9th, 12th and 15th day for persulfate concentration and pH analysis. At the end of the tests, the soil was extruded from the column and divided into five sections, labeled as

S1 to S5 from anode to cathode. For each soil section, pH, EC (electrical conductivity) and residual PCBs concentration were determined.

2.3 Analytical methods

The soil pH and EC were determined with a solid:water ratio of 1:2.5 (Lu, 2000). The soil particle-size distribution was analyzed by laser particle analyzer (LS13320, Beckman Coulter Inc. USA). The TOC (total organic carbon) of soil was measured by potassium dichromate oxidation method at 100 ℃ for 90 min and determined by the UV-Vis spectrophotometer at 590 nm (721-100, Jinghua Science and Technology Instrument Co., Ltd, China). Moreover, the OM (organic matter) of soil was calculated after the soil TOC with a factor of 1.724 (Lu, 2000). The CEC (cationic interchange capacity) of soil was measured by the ammonium acetate extraction method (Lu, 2000). The metal concentration of soil was determined by ICP (Inductively Coupled Plasma, Optima 8000, PerkinElme Inc., USA) after HF-$HClO_4$-HNO_3 digestion. After extracting the soil solution, persulfate concentration was determined in the UV-Vis spectrophotometer according to Liang et al. (Liang et al., 2008). This method was detailed in our previous study (Fan et al., 2014a). For PCBs concentration measurement, the air-dried soil samples were ground and passed through 20-mesh sieve, and then extracted by sonication using hexane:acetone (V/V, 1:1) for three times. Three replicate samples were tested for each analysis to ensure accuracy. PCBs in the supernatant was quantified by gas chromatography (GC-×ECD, Agilent 7890A, USA) coupled with a micro-electron capture detector and a HP-5 (30 m × 0.25 mm × 0.25 μm) fused silica capillary column. The oven temperature was programmed starting at 150 ℃ for 2 min, and then increased to 280 ℃ at a rate of 5 ℃ min^{-1} where it was hold for 2 min. The temperature of the injector and detector was 250 ℃ and 300 ℃, 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.

3. Results and discussion

3.1 Electrical current and EOF

The evolution of electric current and EOF is presented in Fig. 1. In the control test (Exp-01), the current started increasing, reached a peak value of 66 mA at 121 h, and then decreased rapidly and stabilized at around 8 mA at the end of the test (Fig. 1a). In Exp-02, the addition of zero-valent iron activator every three days in the anolyte increased the current drastically with a peak value of 330 mA at 197 h. The periodic addition of zero-valent iron caused the decomposition of persulfate into more ions (e.g. Fe^{2+} and SO_4^{2-}), and the increased ionic strength enhanced the current intensity. When citric acid chelated Fe^{2+} was introduced into the persulfate solution in the anode chamber (Exp-03), the current was relatively low with a small fluctuation (ranged from 10 to 34 mA). The sharp contrast of the ionic concentration in the anodic and the counter compartment increased the electric resistance that resulted in the low current (Yuan et al., 2013). In the presence of Fe^{2+} chelator, once the activator is injected into the persulfate solution, a large amount of chelated Fe^{2+} reacted and exhausted most of the persulfate in the anolyte before it could be transported in the soil by EK. The treatment using an iron anode (Exp-04) yielded the lowest current, with a highest current value about 20 mA at the initial and last stages. This was attributed to the small surface area of the iron electrode as the current intensity is proportional to the electrode surface area. The iron wire anode (d = 2.03 mm) used in Exp-04 had a much small surface area comparing to the other electrodes (4 cm × 4 cm) and needed to be replaced with a new one after it was completely corroded within several hours. The highest current value was obtained in Exp-05 using alkaline activate persulfate, and the current reached its peak value of 700 mA at 164 h. In order to maintain the high pH value (12.0) of the anolyte, large amount of NaOH solution was applied in the anode, which increased the ionic density and current of the system. In Exp-06, the current reached the maximum value of 194 mA due to the addition of H_2O_2 in the anode every day, which can activate persulfate and accelerate its decomposition to produce more acidity. The decreased soil pH may cause more salts dissolving into the soil solution and also enhance the current.

Fig. 1b presents the variation of cumulative EOF during the experiments. EOF was required to deliver persulfate and its derivatives into the soil from the anode to the cathode to interact with PCBs in soil (Yukselen-Aksoy and Reddy, 2012; Fan et al., 2014a). In all treatments, the EOF was directed and followed the order of alkaline activation > zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron electrode activation. In the treatment without activation (Exp-01), a EOF of 299 mL was obtained. Persulfate activated by alkaline (Exp-05) yielded the highest EOF of 370 mL due to its high pH (Saichek and Reddy, 2005). Persulfate activated by zero-valent iron (Exp-02) has the second highest EOF of 327 mL after Exp-05. The EOF was related to its current, and it was proportional to the current strength. In the treatment of citric acid chelated Fe^{2+} activation and peroxide activation (Exp-03 and Exp-06), the EOF was lower than that without activation. This was probably attributed to the exhaustion of persulfate. The activator accelerated the decomposition of persulfate and the acidic by-product (such as H^+ or HSO_4^-) enter into the soil solution, resulting in the decrease of soil pH (Liang and Lai, 2008). As a result of lower pH, the zeta potential of the soil surface will also be reduced and the EOF hampered. The Exp-04, using an iron electrode to activate persulfate obtained the lowest EOF, only 164 mL. The relatively lower electric current was responsible for this weak EOF.

3.2 Soil pH and EC

Fig. 2 shows the pH and EC distribution of soil sections after EK tests. The initial soil pH was 5.7. In the control test without activation (Exp-01), the soil pH ranged from 1.4 to 4.0 in S1-S3 with the transport of persulfate from anode to cathode by electroosmosis, whereas in the pH jumping location, the soil pH drastically increased to above 11.0 in S4 and S5 due to water electrolysis on the cathode. Compared to Exp-01, the addition of zero-valent iron (Exp-02) decreased the soil pH near the anode (SI-S3) to some extent, with pH in the range of 1.3 to 2.2 due to the persulfate decomposition after activation. The pH reduction was also observed in the treatment with citric acid chelated Fe^{2+} (Exp-04) and peroxide (Exp-06), and the pH in the pH jumping location dropped to 2.6 and 3.6, respectively. This result indicated that the acidic by-products after persulfate decomposion were transported to this section by electroosmosis and electromigration and promoted the pH decrease. When persulfate was activated by pH control in the anolyte (Exp-05), the soil pH of all sections was kept at about 12.5 after EK tests. In all the tests, the pH change of persulfate activated by the iron electrode was not significant. This was probably related to the lack of the H^+ producing process in the anode as the water electrolysis was replaced by the iron electrolysis, and also, the lower current inhibited the OH^- production on the cathode.

The initial soil EC was 0.08 mS cm^{-1}. The distribution of EC (as shown in Fig. 2b) decreased from anode to cathode, which follows the same pattern as the soil pH, and the lower pH leads to the higher EC. Besides the iron electrode activation, all of the activation methods enhanced the soil EC compared to the treatment without activation.

3.3 The transport of persulfate and changes of soil solution pH

The spatial and temporal distribution of persulfate concentration and pH in soil solution is plotted in Fig. 3. In the treatment without activation (Exp-01), persulfate can be delivered from the anode toward the cathode by electroosmosis, the maximum transport distance of persulfate reached the S4 section and the maximum average persulfate concentration transported in the soil was 127 g L^{-1} at 9 d. With the consumption of oxidant, the persulfate concentration in S4 and S3 dropped gradually to a minimum value. The pH variation in the soil solution is shown in Fig. 3b. As the acid front resulting from water electrolysis and persulfate decomposition migrated into the soil from anode, a pH decline was observed from the anode towards the cathode. From 12th to 15th day, the pH in anolyte, S1 and S2 was below zero. However, the pH reduction ended in S3 section, the location of which coincides with the location of a high persulfate front. At the pH jumping location (S4), the pH increased to more than 12.0, and the OH^- produced from the cathode migrating toward the anode by electromigration resulted in the alkaline condition. Under strong alkaline conditions, a large amount of precipitates such as metal sulphates, phosphates and hydroxides (especially calcium sulphate) will be produced to decrease the permeability of soil, which in turn prevented the migration of persulfate towards the cathode (Suèr et al., 2003; Isosaari et al., 2007; Fan et al., 2014a).

In Exp-02, 1 g of zero-valent iron was added in the anolyte on 3rd, 6th, 9th and 12th day to activate persulfate (as shown in Fig. 3c). The addition of zero-valent iron significantly enhanced the transport of persulfate towards the cathode. After 6 d, persulfate was detected throughout the whole column length with a persulfate front concentration of 61.9 g L^{-1} in S5 section. All the other sections had a concentration above 140 g L^{-1}. Moreover, at this time, the maximum average persulfate concentraion transported in soil was 144 g L^{-1}, which was higher than that of Exp-01. The higher transfer mass was related to its higher EOF, which confirms that EOF is the main transport mechanism of persulfate and its derivatives. Additionally, the mass of the zero-valent iron added to the anolyte is 1 g, which is lower than the persulfate concentration. Although some persulfate can be decomposed by the activator, most of the persulfate migrated towards the cathode without being affected. As time goes by, the concentration of persulfate delivered into the soil column decreased due to the discontinuous iron addition. Also, the persulfate in S4 and S5 sections was exhausted by activation due to the OH^- production on the cathode and encountering the persulfate. The pH variation of the soil solution is in agreement with the transport of persulfate. As shown in Fig. 3d, when persulfate got through the whole column on 6th day, the pH of soil solution increased from the anode to the cathode with a range of 1.3-4.2. Moreover, after 9 d, the pH in S4 and S5 sections rose to more than 12.0 due to the water electrolysis on the cathode.

When persulfate was activated by citric acid chelated Fe^{2+} (Exp-03), a large amount of activator reacted with the oxidant immediately which resulted in the over consumption of oxidant before it was delivered into the soil column (Fig. 3e). On 3rd day, the residual persulfate concentration in the anolyte was only 42.2 g L^{-1}, and after 6 d, the persulfate was used up completely within. The mass of persulfate transported into the soil was extremely low with a concentration of 2 g L^{-1} in S1 section. Due to the complete decomposition of persulfate, a large amount of acidic byproducts such as HSO_4^- and H^+ entering into soil by electroosmosis and electromigration lead to the decrease in pH (as shown in Fig. 3f). At the end of the test, the soil solution pH ranged from 0.04 to 2.4 in S1-S4 sections, and only S5 section had a pH of above 12.0.

In the treatment with an iron electrode to activate persulfate (Exp-04), the migration of persulfate was inhibited due to the weak EOF, as well as the depletion of persulfate by iron electrolysis. In Fig. 3g, the persulfate was only transported to S1 section with a concentration of 86.8 g L^{-1} on 3rd day. After 6 d, the persulfate migrated to S3 section with a minimum front of 1.3 g L^{-1}, meanwhile, the persulfate in the anolyte decreased to 61.7 g L^{-1} as a result of constant dissolution of the iron electrode. The maximum average persulfate concentration transported in soil was 14.4 g L^{-1}, which occurred on 9th day. The changes of soil solution pH were related to the persulfate transportation. As shown in Fig. 3h, on 3rd day, the pH of anolyte and S1 section reduced to 1.2 and 1.8, respectively, and the pH of other soil sections was above 5.0. At the end of the test, the pH of S1 and S2 sections decreased to about 1.5, and the pH in S3 section was 4.0 due to the lower amount of persulfate transported into the soil. Also, the pH of soil solution near the cathode (S4 and S5) increased to about 6.5 as the result of water electrolysis. The relatively low pH near the cathode was attributed to the weak water electrolysis resulting from the low current intensity.

As alkaline activation was used in Exp-05, the transport of persulfate was enhanced dramatically. Fig. 3i shows that at the early stage (on 3rd day), the persulfate was delivered to S1 section with a high concentration of over 300 g L^{-1} that is much more than the initial value. On 6th day, the persulfate front reached S4 section and every section had an even persulfate concentration of about 180 g L^{-1}. The maxmium average persulfate concentration transported in soil (149 g L^{-1}) was also obtained, which is higher than all the other treatments. The improvement of persulfate transport is highly dependent on the high EOF resulting from the high pH. Nevertheless, at the later stage (on 9th, 12th and 15th day), the soil pH increased with the exhaustion of persulfate by alkaline activation, which decreased the permeability of soil which prevented the soil solution extraction (the blank spots in Fig. 3i). Fig. 3j shows the changes of soil solution pH. Under the pH auto-control system, the pH of anolyte was kept around 12.0. With the transport of persulfate in soil, the pH of soil solution in S1-S4 decreased to about 3.0 due to persulfate decomposition. Then, the soil solution pH of the spots that could be extracted went up to more than 13.0 after the persulfate in soil was exhausted.

In Exp-06, peroxide was used to activate persulfate. As shown in Fig. 3k, on 3rd day, persulfate could be delivered to S1 section with a front of 109 g L^{-1}. After 6 d, the front approached the S4 section and every section (S1-S4) has a concentration of about 65 g L^{-1}. Compared to Exp-01, the addition of peroxide improved the migration distance of persulfate at the same time. However, the continuous addition of peroxide in the anolyte led to persulfate decomposition and on 6th day the persulfate concentration in anolyte was reduced to 102 g L^{-1}. The maxmum average persulfate concentration transported in soil was only 53.2 g L^{-1}. At the end of the test, the persulfate transported in soil dropped gradually to the minimum value. The activator intensified the decomposition of persulfate and thus decreased the soil solution pH. As shown in Fig. 3l, the anolyte pH after 9 d decreased to below zero, and the soil solution pH from S1 to S4 kept dropping. The minimum value was obtained on 12th day with the soil solution pH in S1 to S4 ranging from 0.6 to 2.4. Only the soil solution pH in S5 increased above 12.0 after 9 d due to the water electrolysis on the cathode.

From the above results, we can conclude that comparing to persulfate without activation, zero-valent iron, alkaline and peroxide activation improved the transport of persulfate at the early stage of EK test, and the longest delivery distance reached sections S4 or S5 on 6th day . The transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent activation > without activation > peroxide activation > iron electrode activation > citric acid chelated Fe^{2+} activation.

3.4 Residual PCBs concentration in soil

Table 3 presents the distribution of residual PCBs in different treatments after EK tests. In general, besides the iron electrode, all the other activation methods enhanced the degradation of PCBs in the soil as compared to that without activation. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation > without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. As the persulfate and activators were injected in the anode, the degradation of PCBs in soil was predominant on the section near the anode, followed by the section near the cathode, while the degradation of PCBs in the central part was minor.

In the control test without activation (Exp-01), the distribution of residual PCBs in soil increased from the anode towards the cathode with the degradation of PCBs mainly concentrated on S1 section with a removal rate of 51.7%. In the other sections, the degradation of PCBs was insignificant even with a high persulfate concentration (more than 100 g L^{-1}) in S2 until the end of the test, and most of the PCBs were accumulated in the middle sections. In the location near the cathode (S4 and S5), a relatively higher PCBs degradation efficiency was observed (≈27%), although the persulfate transported to these sections was limited. This can be probably attributed to the alkaline hydrolysis function occurred in the cathode (Jeffers et al., 1989; Waisner et al., 2008).

When zero-valent iron was added to activate persulfate (Exp-02), the removal of PCBs in soil was not remarkably improved even though the transport distance and mass of persulfate was higher than the control test. The residual PCBs in S1 to S3 section followed the same trend as Exp-01, whereas, the removal rates of S4 (35%) and S5 (33%) were higher than that of the control test (26%). This result was due to the lower amount of zero-valent iron added in the anolyte. The molar ratio of persulfate and total iron we added is 5.88:1 and the optimum rate referenced is 1.5:1 (Lang et al., 2010), so, the mass of zero-valent iron added is not enough to break down persulfate completely. When persulfate was delivered to S4 and S5 section, it could be activated by the high pH near the cathode, which enhanced PCBs degradation in these sections.

In Exp-03, the distribution of residual PCBs in soil was uniform, with a removal rate of about 35%. Although the mass of persulfate transported in soil was almost zero, as the result of the abundant of citric acid chelated Fe^{2+} put into the oxidant solution, the activation products such as $SO_4^{-\bullet}$ or $\bullet OH$ radicals generated by persulfate decomposition were transported into soil by EOF, which resulted in the degradation of PCBs in soil. The mass of $SO_4^{-\bullet}$ or $\bullet OH$ transported into the soil could not be measured, but the extremely low pH distribution in this treatment confirmed that the decomposition products had been transported into the soil column. Moreover, the drastic reaction between activator and oxidant released much heat, which could also favored persulfate activation, as well as the PCBs desorption from the soil.

The lowest PCBs degradation percentage was found in the treatment with an iron electrode to activate persulfate (Exp-04). The activated persulfate transported in soil enhanced the degradation of PCBs near the anode, and the degradation percentages of PCBs in S1, S2 and S3 were 44%, 33% and 30%, respectively. However, the degradation of PCBs in S4 and S5 was low, only 21% and 25%. This distribution of residual PCBs in soil was consistent with the delivery of persulfate in the soil. Besides, the low removal of PCBs was probably due to its low EOF, as the low EOF inhibited the transportation of persulfate and its derivatives in the soil.

The treatment of alkaline activation yielded the highest PCBs degradation percentage (Exp-05). In the section near the anode (S1), the removal reached as high as 53% with about 40% degradation in the other sections. The relatively high PCBs degradation was based on the long transport distance and high transfer mass of persulfate as well as the high pH. Also, during the alkaline activation process, •OH was predominent while its oxidizing ability is more powerful than that of $SO_4^{-\bullet}$. Meanwhile, on the condition of pH above 12.0, alkaline hydrolysis also plays an important role in PCBs degradation.

When peroxide was used to activate persulfate (Exp-06), the distribution of residual PCBs in soil increased first and decreased subsequently. The degradation of PCBs in soil was mainly focused on the section near the anode (about 40%) and cathode (about 32%), and most of PCBs were accumulated in the central part of the soil column (28%). Compared to the treatment without activation, peroxide activation facilitated the degradation of PCBs in soil. This result indicated that the radicals resulting from peroxide activating persulfate entered into the soil and led to the degradation of PCBs. The low pH in S1 to S4 also confirms that the decomposition products migrated from the anode towards the cathode, and also that lower pH is conducive to the degradation of PCBs by persulfate (House, 1962; Liang et al., 2007; Fang et al., 2013).

In conclusion, the impact of different persulfate activation methods on the degradation of PCBs is different, and PCBs degradation was related to persulfate transfer distance, transfer mass, and the soil pH. The relationship between the degradation effect and weight factors with different activation methods is summarized in Table 4. In essence, all these factors were based on the ratio of oxidant and activator, which is controlled by the injection quantity and rate. In general, persulfate activation did not enhance the degradation of PCBs significantly, and the highest enhancement only increased by 10% compared with that without activation. The activation parameters should be optimized in future studies. Although alkaline activation (pH control in the anode) reached the highest enhancement, the high pH would damage the soil properties in field remediation. Additionally, iron electrode activation has a good applicability for in-situ remediation, but further research is needed on how to regulate its activation effect.

4. Conclusions

In this study, a series of experiments were undertaken to assess the transport behavior of activated persulfate under electric field and the efficiency of remediation of PCBs polluted soil. The impact of different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH and peroxide on the persulfate migration was evaluated as well as the degradation of PCBs in soil.

Electroosmostic flow was the main transfer mechanism for persulfate and its derivatives, the EOF flowed from anode towards cathode (direct EOF) and followed the order of alkaline activation > zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron electrode activation.

Zero-valent iron, alkaline, and peroxide activation improved the transport of persulfate at the early stage of EK test, and the longest delivery distance reached S4 or S5 section on 6th day. The transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent activation > without activation > peroxide activation > iron electrode activation > citric acid chelated Fe^{2+} activation.

The addition of an activator accelerated the decomposition of persulfate, and the persulfate transported in soil decreased with its degradation. The decomposition of persulfate will decrease the soil pH, and lower pH was beneficial for the degradation of PCBs.

Besides iron electrode activation, all the other activation methods enhanced the removal of PCBs in soil in different extents. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation >

without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of oxidant and activator.

Acknowledgments

This work was financially supported by the Natural Science Foundation of Jiangsu Province of China (BK20141510), the Natural Science Foundation of China (41471261, 41125007) and the Postdoctoral Science Foundation of China (2014M560452).

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Electrokinetic delivery of persulfate to remediate PCBs polluted soils: effect of different activation methods

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ABSTRACT: Persulfate-based in-situ chemical oxidation (ISCO) for the remediation of organic polluted soils has gained much interest in last decade. However, the transportation of persulfate in low-permeability soil is very low, which limits its efficiency in degrading soil pollutants. Additionally, the oxidation-reduction process of persulfate with organic contaminants takes place slowly, while, the reaction will be greatly accelerated by the production of more powerful radicals once it is activated. Electrokinetic remediation (EK) is a good way for transporting persulfate in low-permeability soil. In this study, different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH and peroxide, were evaluated to enhance the activity of persulfate delivered by EK. All the activators and the persulfate were added in the anolyte. The results indicated that zero-valent iron, alkaline, and peroxide enhanced the transportation of persulfate at the first stage of EK test, and the longest delivery distance reached sections S4 or S5 (near the cathode) on the 6th day. The addition of activators accelerated decomposition of persulfate, which resulted in the decreasing soil pH. The mass of persulfate delivered into the soil declined with the continuous decomposition of persulfate by activation. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation > without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of activator and persulfate.

Key words: Polychlorinated biphenyls (PCBs), soil remediation, electrokinetics, persulfate activation.

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Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that strongly adsorb in soils and sediments. Developing cost-effective and sustainable solutions for the remediation of PCB-contaminated soils is imperative (Gomes et al., 2014). The present technologies include capping, solvent extraction, thermal desorption, Fe-promoted dechlorination, chemical oxidation, biological remediation and many others still in development phase (Gomes et al., 2013).

Among these technologies, in-situ chemical oxidation (ISCO) is an emerging technology for soil and groundwater remediation due to its wide applicability, relatively fast treatment, simplicity of operation and cost effectiveness (ITRC, 2005; Watts and Teel, 2006; Rastogi et al., 2009b; Tsitonaki et al., 2010). ISCO involves the introduction of chemical oxidant into the subsurface to transform organic contaminants into less harmful chemical species. Hydrogen peroxide, permanganate and ozone are widely used oxidants, but their practical applications are hindered due to their low stability (hydrogen peroxide and ozone) or high soil affinity for natural soil organics (permanganate) (Gates-Anderson et al., 2001; Li and Schwartz, 2004; Tsai et al., 2008; Navalon et al., 2010). Persulfate is a strong oxidant with a redox potential (E_0) of 2.01 V and a relatively long life in the subsurface due to its slow reaction kinetics with organics, which can promote more favorable contact time (Tsitonaki et al., 2010). Also, upon activation, persulfate can produce sulfate radicals ($SO_4^{-\bullet}$, E_0=2.6 V) and hydroxyl radicals (•OH, E_0=2.7 V) which are more powerful and kinetically faster than persulfate anions (Liang et al., 2004a). There are many methods available for persulfate activation including the use of heat, chelated or unchelated transition metals, hydrogen peroxide, or strong alkaline pH (Eqs. (1)-(4)) (Petri et al., 2011). But the site conditions such as lithology (clay, sand, etc.), hydrogeology and the structure of the target contamination will affect the oxidation effectiveness. Thus, the activation method selected must be dependent on the contaminants to be treated and the subsurface environment (Block et al., 2004).

$$S_2O_8^{2-} \xrightarrow{\text{heat}} 2SO_4^{\bullet-} \quad (1)$$

$$M^{n+} + S_2O_8^{2-} \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-} \quad (2)$$

$$S_2O_8^{2-} + \bullet OH \rightarrow SO_4^{2-} + SO_4^{\bullet-} + 1/2O_2 + H^+ \quad (3)$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + \bullet OH \quad (4)$$

Fe(II) was used initially to activate persulfate. However, the activation by Fe^{2+} is not practical because the reaction is almost instantaneously stopped due to the $SO_4^{\bullet-}$ scavenging by excess Fe^{2+}

or to the rapid conversion of Fe^{2+} to Fe^{3+}. As an alternative activator, zero-valent iron (an insoluble form of iron) has been employed to activate persulfate with promising results by directly reacting with persulfate to release Fe^{2+}, or releasing Fe^{2+} through the corrosion of zero-valent iron activation (Eqs. (5)-(7)) (Oh et al., 2009; Liang and Guo, 2010; Oh et al., 2010). On the other hand, aqueous Fe(II) is relatively insoluble at the ambient pH⩾5 of most aquifer systems and Fe(II) chelated by chelating agents (e.g. ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid and citric acid) is effective in activating persulfate by maintaining iron in solution at neutral pH (Liang et al., 2004b; Crimi and Taylor, 2007; Rastogi et al., 2009a).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (5)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \quad (6)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (7)$$

A significant difficulty in ISCO is promoting the contact between the oxidant and the contaminant, particularly in low-permeability subsurface. When ISCO is combined with EK, EK has the potential to increase the delivery of oxidant in soil and improve the remediation efficiency (Reddy and Cameselle, 2009). Also, in-situ electrolysis by iron electrodes allows to manipulate the reactivity of persulfate in EK + ISCO system. According to Yuan et al. (2013), Fe^{2+} can be continuously produced in situ by electrochemical corrosion (Eqs. (8) and (6)) and chemical corrosion (Eqs. (9) and (7)) when applying a positive current on an iron anode, and the electrolytic supply of Fe^{2+} will improve the utilization of both Fe^{2+} and persulfate (Yuan et al., 2013).

$$Fe - 2e^- \rightarrow Fe^{2+} \quad (8)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-} \quad (6)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (9)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (7)$$

The effect of different activators on persulfate oxidation has been studied extensively. However, the persulfate activation in EK was rarely referred. Recently, Yukselen-Aksoy et al. (2012) investigated the effect of heat and alkaline activation on the electrokinetically enhanced persulfate oxidation of PCB44 in kaolin and glacial till soils. Persulfate (30%) was injected from a position 3 cm away from the anode and the result showed that both activation methods (heat or heat and high pH) improved the degradation of PCB44 in kaolin, but not in glacial till soil due to its high buffering capacity, nonhomogeneous mineral contents and high organic content (Yukselen-Aksoy and Reddy, 2012). Furthermore, we investigated the transport behaviors of inactivated persulfate under electric field, and found that electroosmotic flow (EOF) was more effective for persulfate delivery than electromigration and the anode was the best injection spot for high dosage of persulfate (Fan et al., 2014a). However, the activity of persulfate in soil is relatively low without activation, so choosing appropriate activators to accelerate the reaction kinetics of persulfate is a key process for the application of EK + persulfate technology.

In this study, different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH, and peroxide, were evaluated to enhance the activity of persulfate delivered by EK. The transport behavior of activated persulfate under electric field and the remediation efficiency of PCBs contaminated soil were also investigated.

2. Experimental

2.1 Chemicals and materials

PCBs standard solution containing 20 PCBs congeners (＞99.4%) were obtained from AccuStandard (New Haven, CT, USA). Sodium persulfate (99.0%) was purchased from Chengdu Kelon Chemical Reagent Factory. Zero-valent iron power (98.0%) was provided by Shanghai Miura Chemical Co. Ltd., China. Sodium hydroxide (＞96%), citric acid (＞99.6%), acetone (analytical reagent) and hexane (analytical reagent) were obtained from Nanjing Chemical Reagent Co. Ltd., China. Hydrogen peroxide (30% solution, 99.0%) and $FeSO_4 \cdot 7H_2O$ (99.0%) were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Deionized water (18 MΩ cm^{-1}) obtained from a Millipore Milli-Q system was used in all experiments.

The PCBs polluted soil was sampled from a place near a capacitor storage site in Zhejiang province, which was diluted with a clean soil sampled from a farmland in Nanjing. The properties of the two soils are shown in Table 1. Both soils belong to yellow brown soil and have similar properties. The soils were air-dried, ground and passed through 20 mesh and 60 mesh sieves, respectively. Approximately 100 g of PCBs polluted soil was mixed with 2200 g of clean soil thoroughly, after that, the mixed soil was stored in the fume hood one week for equilibrium. Also, the properties of the mixed soil were analyzed and shown in Table 1. The initial values of PCBs in the final soil were determined before starting the experiments.

2.2 EK tests

The experimental setup used in this study was reported in our previous studies (Fan et al., 2014a). The setup consisted of a direct-current power supply, a four-channel peristaltic pump, a cylindrical soil column (12 cm L×6.6 cm D), anode and cathode compartments with two titanium electrodes, *in situ* soil solution samplers and a pH auto-control system. About 570 g of the dry soil was loaded into the EK cell in layers and compacted manually using a rammer. During this process, five in-situ soil solution samplers were also vertically embedded at target locations through the soil column. According to our previous results, the anode was selected as the persulfate injection location and 200 g L^{-1} (20%) of persulfate was chosen as the optimum oxidation dosage injection in the anode (Fan et al., 2014a; Fan et al., 2014b). A total of six tests were conducted under different conditions as shown in Table 2. The initial PCBs concentration was 46 mg kg^{-1}. In the control test (Exp-01), only 20% of persulfate was added in the anode to evaluate the performance of transported persulfate by EK without activation. Exp-02 was performed with zero-valent iron activation by adding 1 g of zero-valent iron powder in the anode compartment on 3rd, 6th, 9th and 12th day, and the molar ratio of persulfate and the total zero-valent iron we added was 5.88:1. The discontinuous input of zero-valent iron aimed to avoid the over-consumption of persulfate by the activator. In Exp-03, citric acid was selected as the Fe^{2+} chelator, injecting citric acid chelated Fe^{2+} in the anode at one time under the $Na_2S_2O_8$/ citric acid /Fe^{2+} molar ratio of 20/5/5 (Liang et al., 2004b). In Exp-04, a 14# galvanized iron wire (2.03 mm D × 8 cm L) was used as the iron anode to keep the current continuity. The iron anode was occasionally replaced by a new one after its complete corrosion. Exp-05 was performed with alkaline activation using a pH controller to keep the anode pH at 12.0. In Exp-06, 6 mL of 30% H_2O_2 was injected into the anolyte per day to keep a molar ratio of the total H_2O_2 and $Na_2S_2O_8$ nearly 1:1 (Block et al., 2004). For all the treatments, 0.01 M $NaNO_3$ was used as the supporting electrolyte. Before application of electrical field, the soil was saturated with 0.01 M $NaNO_3$ solution for 24 h. A voltage gradient of 1.0 V cm^{-1} was applied to the EK system by a DC power supply for a period of 15 d (14 d for Exp-03). During EK tests, the electric current and the EOF were recorded and the soil solution and electrolytes were sampled on 3rd, 6th, 9th, 12th and 15th day for persulfate concentration and pH analysis. At the end of the tests, the soil was extruded from the column and divided into five sections, labeled as

S1 to S5 from anode to cathode. For each soil section, pH, EC (electrical conductivity) and residual PCBs concentration were determined.

2.3 Analytical methods

The soil pH and EC were determined with a solid:water ratio of 1:2.5 (Lu, 2000). The soil particle-size distribution was analyzed by laser particle analyzer (LS13320, Beckman Coulter Inc. USA). The TOC (total organic carbon) of soil was measured by potassium dichromate oxidation method at 100 ℃ for 90 min and determined by the UV-Vis spectrophotometer at 590 nm (721-100, Jinghua Science and Technology Instrument Co., Ltd, China). Moreover, the OM (organic matter) of soil was calculated after the soil TOC with a factor of 1.724 (Lu, 2000). The CEC (cationic interchange capacity) of soil was measured by the ammonium acetate extraction method (Lu, 2000). The metal concentration of soil was determined by ICP (Inductively Coupled Plasma, Optima 8000, PerkinElme Inc., USA) after HF-$HClO_4$-HNO_3 digestion. After extracting the soil solution, persulfate concentration was determined in the UV-Vis spectrophotometer according to Liang et al. (Liang et al., 2008). This method was detailed in our previous study (Fan et al., 2014a). For PCBs concentration measurement, the air-dried soil samples were ground and passed through 20-mesh sieve, and then extracted by sonication using hexane:acetone (V/V, 1:1) for three times. Three replicate samples were tested for each analysis to ensure accuracy. PCBs in the supernatant was quantified by gas chromatography (GC-×ECD, Agilent 7890A, USA) coupled with a micro-electron capture detector and a HP-5 (30 m × 0.25 mm × 0.25 μm) fused silica capillary column. The oven temperature was programmed starting at 150 ℃ for 2 min, and then increased to 280 ℃ at a rate of 5 ℃ min^{-1} where it was hold for 2 min. The temperature of the injector and detector was 250 ℃ and 300 ℃, 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.

3. Results and discussion

3.1 Electrical current and EOF

The evolution of electric current and EOF is presented in Fig. 1. In the control test (Exp-01), the current started increasing, reached a peak value of 66 mA at 121 h, and then decreased rapidly and stabilized at around 8 mA at the end of the test (Fig. 1a). In Exp-02, the addition of zero-valent iron activator every three days in the anolyte increased the current drastically with a peak value of 330 mA at 197 h. The periodic addition of zero-valent iron caused the decomposition of persulfate into more ions (e.g. Fe^{2+} and SO_4^{2-}), and the increased ionic strength enhanced the current intensity. When citric acid chelated Fe^{2+} was introduced into the persulfate solution in the anode chamber (Exp-03), the current was relatively low with a small fluctuation (ranged from 10 to 34 mA). The sharp contrast of the ionic concentration in the anodic and the counter compartment increased the electric resistance that resulted in the low current (Yuan et al., 2013). In the presence of Fe^{2+} chelator, once the activator is injected into the persulfate solution, a large amount of chelated Fe^{2+} reacted and exhausted most of the persulfate in the anolyte before it could be transported in the soil by EK. The treatment using an iron anode (Exp-04) yielded the lowest current, with a highest current value about 20 mA at the initial and last stages. This was attributed to the small surface area of the iron electrode as the current intensity is proportional to the electrode surface area. The iron wire anode (d = 2.03 mm) used in Exp-04 had a much small surface area comparing to the other electrodes (4 cm × 4 cm) and needed to be replaced with a new one after it was completely corroded within several hours. The highest current value was obtained in Exp-05 using alkaline activate persulfate, and the current reached its peak value of 700 mA at 164 h. In order to maintain the high pH value (12.0) of the anolyte, large amount of NaOH solution was applied in the anode, which increased the ionic density and current of the system. In Exp-06, the current reached the maximum value of 194 mA due to the addition of H_2O_2 in the anode every day, which can activate persulfate and accelerate its decomposition to produce more acidity. The decreased soil pH may cause more salts dissolving into the soil solution and also enhance the current.

Fig. 1b presents the variation of cumulative EOF during the experiments. EOF was required to deliver persulfate and its derivatives into the soil from the anode to the cathode to interact with PCBs in soil (Yukselen-Aksoy and Reddy, 2012; Fan et al., 2014a). In all treatments, the EOF was directed and followed the order of alkaline activation > zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron electrode activation. In the treatment without activation (Exp-01), a EOF of 299 mL was obtained. Persulfate activated by alkaline (Exp-05) yielded the highest EOF of 370 mL due to its high pH (Saichek and Reddy, 2005). Persulfate activated by zero-valent iron (Exp-02) has the second highest EOF of 327 mL after Exp-05. The EOF was related to its current, and it was proportional to the current strength. In the treatment of citric acid chelated Fe^{2+} activation and peroxide activation (Exp-03 and Exp-06), the EOF was lower than that without activation. This was probably attributed to the exhaustion of persulfate. The activator accelerated the decomposition of persulfate and the acidic by-product (such as H^+ or HSO_4^-) enter into the soil solution, resulting in the decrease of soil pH (Liang and Lai, 2008). As a result of lower pH, the zeta potential of the soil surface will also be reduced and the EOF hampered. The Exp-04, using an iron electrode to activate persulfate obtained the lowest EOF, only 164 mL. The relatively lower electric current was responsible for this weak EOF.

3.2 Soil pH and EC

Fig. 2 shows the pH and EC distribution of soil sections after EK tests. The initial soil pH was 5.7. In the control test without activation (Exp-01), the soil pH ranged from 1.4 to 4.0 in S1-S3 with the transport of persulfate from anode to cathode by electroosmosis, whereas in the pH jumping location, the soil pH drastically increased to above 11.0 in S4 and S5 due to water electrolysis on the cathode. Compared to Exp-01, the addition of zero-valent iron (Exp-02) decreased the soil pH near the anode (SI-S3) to some extent, with pH in the range of 1.3 to 2.2 due to the persulfate decomposition after activation. The pH reduction was also observed in the treatment with citric acid chelated Fe^{2+} (Exp-04) and peroxide (Exp-06), and the pH in the pH jumping location dropped to 2.6 and 3.6, respectively. This result indicated that the acidic by-products after persulfate decomposion were transported to this section by electroosmosis and electromigration and promoted the pH decrease. When persulfate was activated by pH control in the anolyte (Exp-05), the soil pH of all sections was kept at about 12.5 after EK tests. In all the tests, the pH change of persulfate activated by the iron electrode was not significant. This was probably related to the lack of the H^+ producing process in the anode as the water electrolysis was replaced by the iron electrolysis, and also, the lower current inhibited the OH^- production on the cathode.

The initial soil EC was 0.08 mS cm^{-1}. The distribution of EC (as shown in Fig. 2b) decreased from anode to cathode, which follows the same pattern as the soil pH, and the lower pH leads to the higher EC. Besides the iron electrode activation, all of the activation methods enhanced the soil EC compared to the treatment without activation.

3.3 The transport of persulfate and changes of soil solution pH

The spatial and temporal distribution of persulfate concentration and pH in soil solution is plotted in Fig. 3. In the treatment without activation (Exp-01), persulfate can be delivered from the anode toward the cathode by electroosmosis, the maximum transport distance of persulfate reached the S4 section and the maximum average persulfate concentration transported in the soil was 127 g L^{-1} at 9 d. With the consumption of oxidant, the persulfate concentration in S4 and S3 dropped gradually to a minimum value. The pH variation in the soil solution is shown in Fig. 3b. As the acid front resulting from water electrolysis and persulfate decomposition migrated into the soil from anode, a pH decline was observed from the anode towards the cathode. From 12th to 15th day, the pH in anolyte, S1 and S2 was below zero. However, the pH reduction ended in S3 section, the location of which coincides with the location of a high persulfate front. At the pH jumping location (S4), the pH increased to more than 12.0, and the OH^- produced from the cathode migrating toward the anode by electromigration resulted in the alkaline condition. Under strong alkaline conditions, a large amount of precipitates such as metal sulphates, phosphates and hydroxides (especially calcium sulphate) will be produced to decrease the permeability of soil, which in turn prevented the migration of persulfate towards the cathode (Suèr et al., 2003; Isosaari et al., 2007; Fan et al., 2014a).

In Exp-02, 1 g of zero-valent iron was added in the anolyte on 3rd, 6th, 9th and 12th day to activate persulfate (as shown in Fig. 3c). The addition of zero-valent iron significantly enhanced the transport of persulfate towards the cathode. After 6 d, persulfate was detected throughout the whole column length with a persulfate front concentration of 61.9 g L^{-1} in S5 section. All the other sections had a concentration above 140 g L^{-1}. Moreover, at this time, the maximum average persulfate concentraion transported in soil was 144 g L^{-1}, which was higher than that of Exp-01. The higher transfer mass was related to its higher EOF, which confirms that EOF is the main transport mechanism of persulfate and its derivatives. Additionally, the mass of the zero-valent iron added to the anolyte is 1 g, which is lower than the persulfate concentration. Although some persulfate can be decomposed by the activator, most of the persulfate migrated towards the cathode without being affected. As time goes by, the concentration of persulfate delivered into the soil column decreased due to the discontinuous iron addition. Also, the persulfate in S4 and S5 sections was exhausted by activation due to the OH^- production on the cathode and encountering the persulfate. The pH variation of the soil solution is in agreement with the transport of persulfate. As shown in Fig. 3d, when persulfate got through the whole column on 6th day, the pH of soil solution increased from the anode to the cathode with a range of 1.3-4.2. Moreover, after 9 d, the pH in S4 and S5 sections rose to more than 12.0 due to the water electrolysis on the cathode.

When persulfate was activated by citric acid chelated Fe^{2+} (Exp-03), a large amount of activator reacted with the oxidant immediately which resulted in the over consumption of oxidant before it was delivered into the soil column (Fig. 3e). On 3rd day, the residual persulfate concentration in the anolyte was only 42.2 g L^{-1}, and after 6 d, the persulfate was used up completely within. The mass of persulfate transported into the soil was extremely low with a concentration of 2 g L^{-1} in S1 section. Due to the complete decomposition of persulfate, a large amount of acidic byproducts such as HSO_4^- and H^+ entering into soil by electroosmosis and electromigration lead to the decrease in pH (as shown in Fig. 3f). At the end of the test, the soil solution pH ranged from 0.04 to 2.4 in S1-S4 sections, and only S5 section had a pH of above 12.0.

In the treatment with an iron electrode to activate persulfate (Exp-04), the migration of persulfate was inhibited due to the weak EOF, as well as the depletion of persulfate by iron electrolysis. In Fig. 3g, the persulfate was only transported to S1 section with a concentration of 86.8 g L^{-1} on 3rd day. After 6 d, the persulfate migrated to S3 section with a minimum front of 1.3 g L^{-1}, meanwhile, the persulfate in the anolyte decreased to 61.7 g L^{-1} as a result of constant dissolution of the iron electrode. The maximum average persulfate concentration transported in soil was 14.4 g L^{-1}, which occurred on 9th day. The changes of soil solution pH were related to the persulfate transportation. As shown in Fig. 3h, on 3rd day, the pH of anolyte and S1 section reduced to 1.2 and 1.8, respectively, and the pH of other soil sections was above 5.0. At the end of the test, the pH of S1 and S2 sections decreased to about 1.5, and the pH in S3 section was 4.0 due to the lower amount of persulfate transported into the soil. Also, the pH of soil solution near the cathode (S4 and S5) increased to about 6.5 as the result of water electrolysis. The relatively low pH near the cathode was attributed to the weak water electrolysis resulting from the low current intensity.

As alkaline activation was used in Exp-05, the transport of persulfate was enhanced dramatically. Fig. 3i shows that at the early stage (on 3rd day), the persulfate was delivered to S1 section with a high concentration of over 300 g L^{-1} that is much more than the initial value. On 6th day, the persulfate front reached S4 section and every section had an even persulfate concentration of about 180 g L^{-1}. The maxmium average persulfate concentration transported in soil (149 g L^{-1}) was also obtained, which is higher than all the other treatments. The improvement of persulfate transport is highly dependent on the high EOF resulting from the high pH. Nevertheless, at the later stage (on 9th, 12th and 15th day), the soil pH increased with the exhaustion of persulfate by alkaline activation, which decreased the permeability of soil which prevented the soil solution extraction (the blank spots in Fig. 3i). Fig. 3j shows the changes of soil solution pH. Under the pH auto-control system, the pH of anolyte was kept around 12.0. With the transport of persulfate in soil, the pH of soil solution in S1-S4 decreased to about 3.0 due to persulfate decomposition. Then, the soil solution pH of the spots that could be extracted went up to more than 13.0 after the persulfate in soil was exhausted.

In Exp-06, peroxide was used to activate persulfate. As shown in Fig. 3k, on 3rd day, persulfate could be delivered to S1 section with a front of 109 g L^{-1}. After 6 d, the front approached the S4 section and every section (S1-S4) has a concentration of about 65 g L^{-1}. Compared to Exp-01, the addition of peroxide improved the migration distance of persulfate at the same time. However, the continuous addition of peroxide in the anolyte led to persulfate decomposition and on 6th day the persulfate concentration in anolyte was reduced to 102 g L^{-1}. The maxmum average persulfate concentration transported in soil was only 53.2 g L^{-1}. At the end of the test, the persulfate transported in soil dropped gradually to the minimum value. The activator intensified the decomposition of persulfate and thus decreased the soil solution pH. As shown in Fig. 3l, the anolyte pH after 9 d decreased to below zero, and the soil solution pH from S1 to S4 kept dropping. The minimum value was obtained on 12th day with the soil solution pH in S1 to S4 ranging from 0.6 to 2.4. Only the soil solution pH in S5 increased above 12.0 after 9 d due to the water electrolysis on the cathode.

From the above results, we can conclude that comparing to persulfate without activation, zero-valent iron, alkaline and peroxide activation improved the transport of persulfate at the early stage of EK test, and the longest delivery distance reached sections S4 or S5 on 6th day . The transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent activation > without activation > peroxide activation > iron electrode activation > citric acid chelated Fe^{2+} activation.

3.4 Residual PCBs concentration in soil

Table 3 presents the distribution of residual PCBs in different treatments after EK tests. In general, besides the iron electrode, all the other activation methods enhanced the degradation of PCBs in the soil as compared to that without activation. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation > without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. As the persulfate and activators were injected in the anode, the degradation of PCBs in soil was predominant on the section near the anode, followed by the section near the cathode, while the degradation of PCBs in the central part was minor.

In the control test without activation (Exp-01), the distribution of residual PCBs in soil increased from the anode towards the cathode with the degradation of PCBs mainly concentrated on S1 section with a removal rate of 51.7%. In the other sections, the degradation of PCBs was insignificant even with a high persulfate concentration (more than 100 g L^{-1}) in S2 until the end of the test, and most of the PCBs were accumulated in the middle sections. In the location near the cathode (S4 and S5), a relatively higher PCBs degradation efficiency was observed (≈27%), although the persulfate transported to these sections was limited. This can be probably attributed to the alkaline hydrolysis function occurred in the cathode (Jeffers et al., 1989; Waisner et al., 2008).

When zero-valent iron was added to activate persulfate (Exp-02), the removal of PCBs in soil was not remarkably improved even though the transport distance and mass of persulfate was higher than the control test. The residual PCBs in S1 to S3 section followed the same trend as Exp-01, whereas, the removal rates of S4 (35%) and S5 (33%) were higher than that of the control test (26%). This result was due to the lower amount of zero-valent iron added in the anolyte. The molar ratio of persulfate and total iron we added is 5.88:1 and the optimum rate referenced is 1.5:1 (Lang et al., 2010), so, the mass of zero-valent iron added is not enough to break down persulfate completely. When persulfate was delivered to S4 and S5 section, it could be activated by the high pH near the cathode, which enhanced PCBs degradation in these sections.

In Exp-03, the distribution of residual PCBs in soil was uniform, with a removal rate of about 35%. Although the mass of persulfate transported in soil was almost zero, as the result of the abundant of citric acid chelated Fe^{2+} put into the oxidant solution, the activation products such as $SO_4^{-\bullet}$ or •OH radicals generated by persulfate decomposition were transported into soil by EOF, which resulted in the degradation of PCBs in soil. The mass of $SO_4^{-\bullet}$ or •OH transported into the soil could not be measured, but the extremely low pH distribution in this treatment confirmed that the decomposition products had been transported into the soil column. Moreover, the drastic reaction between activator and oxidant released much heat, which could also favored persulfate activation, as well as the PCBs desorption from the soil.

The lowest PCBs degradation percentage was found in the treatment with an iron electrode to activate persulfate (Exp-04). The activated persulfate transported in soil enhanced the degradation of PCBs near the anode, and the degradation percentages of PCBs in S1, S2 and S3 were 44%, 33% and 30%, respectively. However, the degradation of PCBs in S4 and S5 was low, only 21% and 25%. This distribution of residual PCBs in soil was consistent with the delivery of persulfate in the soil. Besides, the low removal of PCBs was probably due to its low EOF, as the low EOF inhibited the transportation of persulfate and its derivatives in the soil.

The treatment of alkaline activation yielded the highest PCBs degradation percentage (Exp-05). In the section near the anode (S1), the removal reached as high as 53% with about 40% degradation in the other sections. The relatively high PCBs degradation was based on the long transport distance and high transfer mass of persulfate as well as the high pH. Also, during the alkaline activation process, •OH was predominent while its oxidizing ability is more powerful than that of $SO_4^{-\bullet}$. Meanwhile, on the condition of pH above 12.0, alkaline hydrolysis also plays an important role in PCBs degradation.

When peroxide was used to activate persulfate (Exp-06), the distribution of residual PCBs in soil increased first and decreased subsequently. The degradation of PCBs in soil was mainly focused on the section near the anode (about 40%) and cathode (about 32%), and most of PCBs were accumulated in the central part of the soil column (28%). Compared to the treatment without activation, peroxide activation facilitated the degradation of PCBs in soil. This result indicated that the radicals resulting from peroxide activating persulfate entered into the soil and led to the degradation of PCBs. The low pH in S1 to S4 also confirms that the decomposition products migrated from the anode towards the cathode, and also that lower pH is conducive to the degradation of PCBs by persulfate (House, 1962; Liang et al., 2007; Fang et al., 2013).

In conclusion, the impact of different persulfate activation methods on the degradation of PCBs is different, and PCBs degradation was related to persulfate transfer distance, transfer mass, and the soil pH. The relationship between the degradation effect and weight factors with different activation methods is summarized in Table 4. In essence, all these factors were based on the ratio of oxidant and activator, which is controlled by the injection quantity and rate. In general, persulfate activation did not enhance the degradation of PCBs significantly, and the highest enhancement only increased by 10% compared with that without activation. The activation parameters should be optimized in future studies. Although alkaline activation (pH control in the anode) reached the highest enhancement, the high pH would damage the soil properties in field remediation. Additionally, iron electrode activation has a good applicability for in-situ remediation, but further research is needed on how to regulate its activation effect.

4. Conclusions

In this study, a series of experiments were undertaken to assess the transport behavior of activated persulfate under electric field and the efficiency of remediation of PCBs polluted soil. The impact of different activation methods, using zero-valent iron, citric acid chelated Fe^{2+}, iron electrode, alkaline pH and peroxide on the persulfate migration was evaluated as well as the degradation of PCBs in soil.

Electroosmostic flow was the main transfer mechanism for persulfate and its derivatives, the EOF flowed from anode towards cathode (direct EOF) and followed the order of alkaline activation > zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron electrode activation.

Zero-valent iron, alkaline, and peroxide activation improved the transport of persulfate at the early stage of EK test, and the longest delivery distance reached S4 or S5 section on 6th day. The transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent activation > without activation > peroxide activation > iron electrode activation > citric acid chelated Fe^{2+} activation.

The addition of an activator accelerated the decomposition of persulfate, and the persulfate transported in soil decreased with its degradation. The decomposition of persulfate will decrease the soil pH, and lower pH was beneficial for the degradation of PCBs.

Besides iron electrode activation, all the other activation methods enhanced the removal of PCBs in soil in different extents. The removal efficiency of PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation >

without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of oxidant and activator.

Acknowledgments

This work was financially supported by the Natural Science Foundation of Jiangsu Province of China (BK20141510), the Natural Science Foundation of China (41471261, 41125007) and the Postdoctoral Science Foundation of China (2014M560452).

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Table and figure captions

Table 1 Physical and chemical characteristics of the soils used.

Table 2 Experimental design of the electrokinetic tests.

Table 3 The distribution of residual PCBs in soil (C/C_0).

Table 4 Relationship between degradation effect and weight factors in different treatments.

Figure 1 Change of (a) electric current and (b) electroosmotic flow at different time in various treatments.

Figure 2 Soil (a) pH and (b) electrical conductivity.

Figure 3 Variation of $Na_2S_2O_8$ concentration and pH in soil solution at different time.

Tables

Table 1 Physical and chemical characteristics of the soils used.

Parameters	Clean soil	PCBs polluted soil	Mixed soil
Location	a farmland, Nanjing	a landfill, Taizhou,	_
Sand (%)	12.0	4.2	7.7
Silt (%)	66.9	83.2	50.1
Clay (%)	21.1	12.6	42.2
pH	5.7	6.3	5.74
OM content (g kg^{-1})	7.08	11.0	7.30
CEC (cmol kg^{-1})	20.4	20.1	20.1
Total metal concentration (mg kg^{-1})			
Ca	9848	2259	9760
Mg	7330	3430	7238
Cu	47	89	46
Zn	159	183	160
Fe	33130	86950	34570
Mn	701	867	724

Table 2 The experimental design of the electrokinetic tests.

Treatments	Anolyte	Catholyte	Treatment (in the anolyte)	Voltage /V cm^{-1}	Duration time /d	PCBs concentration /mg kg^{-1}
Exp-01	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	–	1	15	46
Exp-02	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	Add 1g Fe on 3rd,6th,9th,12th day (Mol $Na_2S_2O_8$:Fe=5.88:1)	1	15	46
Exp-03	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	Citric acid/Fe^{2+} (Mol $Na_2S_2O_8$:Citric acid:Fe^{2+}=20:5:5)	1	14	46
Exp-04	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	Iron anode electrode (Mol $Na_2S_2O_8$:Fe≈1:1)	1	15	46
Exp-05	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	Control anode pH at 12.0	1	15	46
Exp-06	200 g L^{-1} $Na_2S_2O_8$	0.01M $NaNO_3$	Add 6 mL of 30% H_2O_2 at anode per day (Mol H_2O_2 :$Na_2S_2O_8$=1:1)	1	15	46

Table 3 The distribution of residual PCBs in soil (C/C_0).

Soil section	Exp-01	Exp-02	Exp-03	Exp-04	Exp-05	Exp-06
S1	46.3±7.0	50.3±6.9	59.0±3.9	55.9±1.6	47.2±0.5	57.8±1.5
S2	72.3±8.3	72.2±6.9	69.5±3.0	67.1±8.8	59.0±2.5	59.8±0.9
S3	80.2±3.6	83.5±4.9	68.5±1.8	70.2±5.8	63.0±1.3	72.1±2.4
S4	73.7±4.7	65.4±6.0	63.9±1.4	79.4±7.0	61.6±3.4	68.6±5.5
S5	73.6±2.7	66.7±2.0	68.8±7.5	74.7±8.0	66.7±5.3	63.9±2.9
Removal rate (%)	30.8	32.4	34.1	30.5	40.5	35.6

Table 4 Relationship between degradation effect and weight factors in different treatments.

Treatments	Removal rate（%）	Transport distance	Transport mass	pH
Without activation	30.8	○	○	○
zero-valent activation	32.4	√	√	○
citric acid chelated Fe^{2+} activation	34.1	×	×	√
iron electrode activation	30.5	×	×	×
alkaline activation	40.5	√	√	√
peroxide activation	35.6	√	○	√

Notes: ○ average, √ above average, × below average.

Figure

Figures

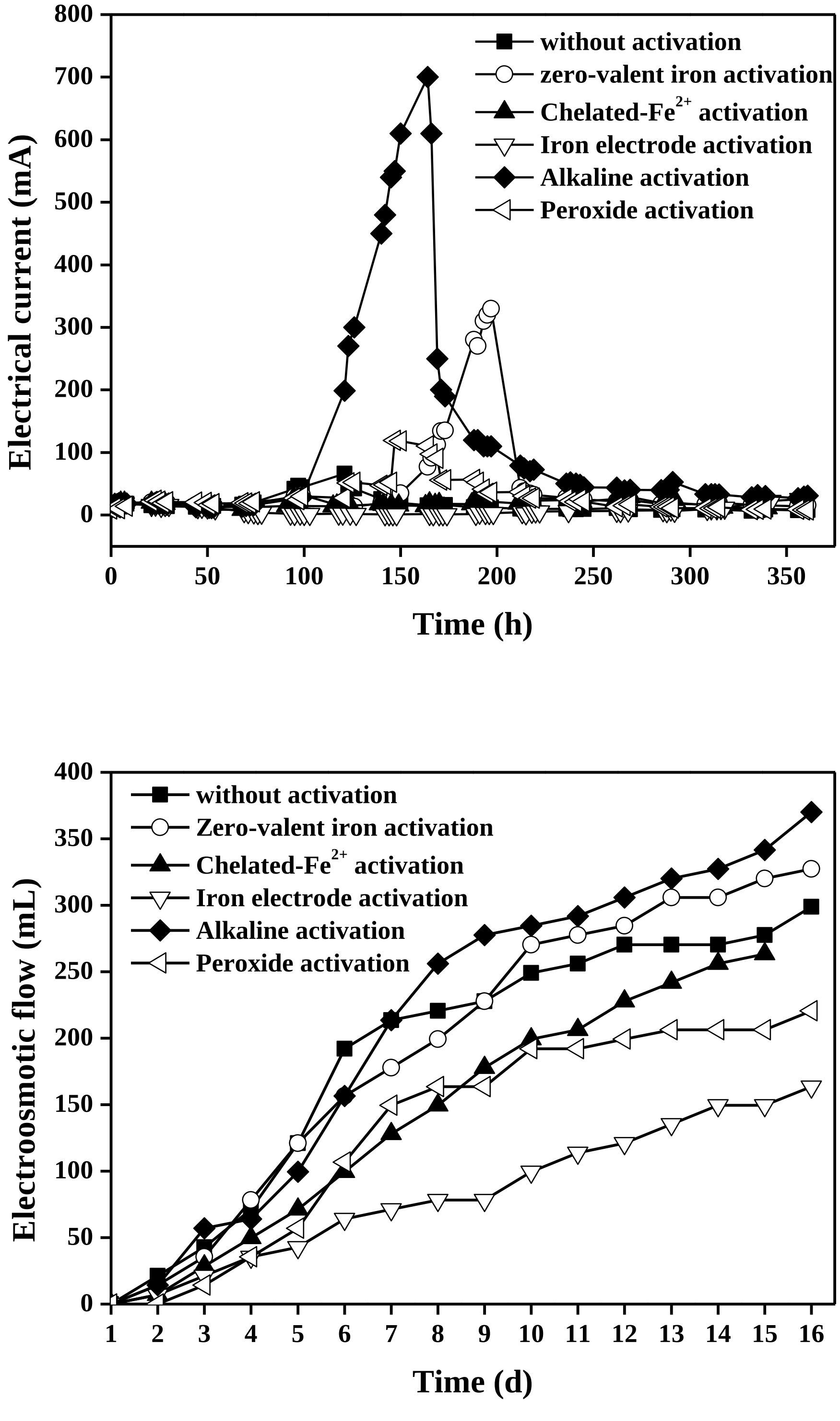


Figure 1 Variation of (a) electric current and (b) electroosmotic flow at different time in various treatments.

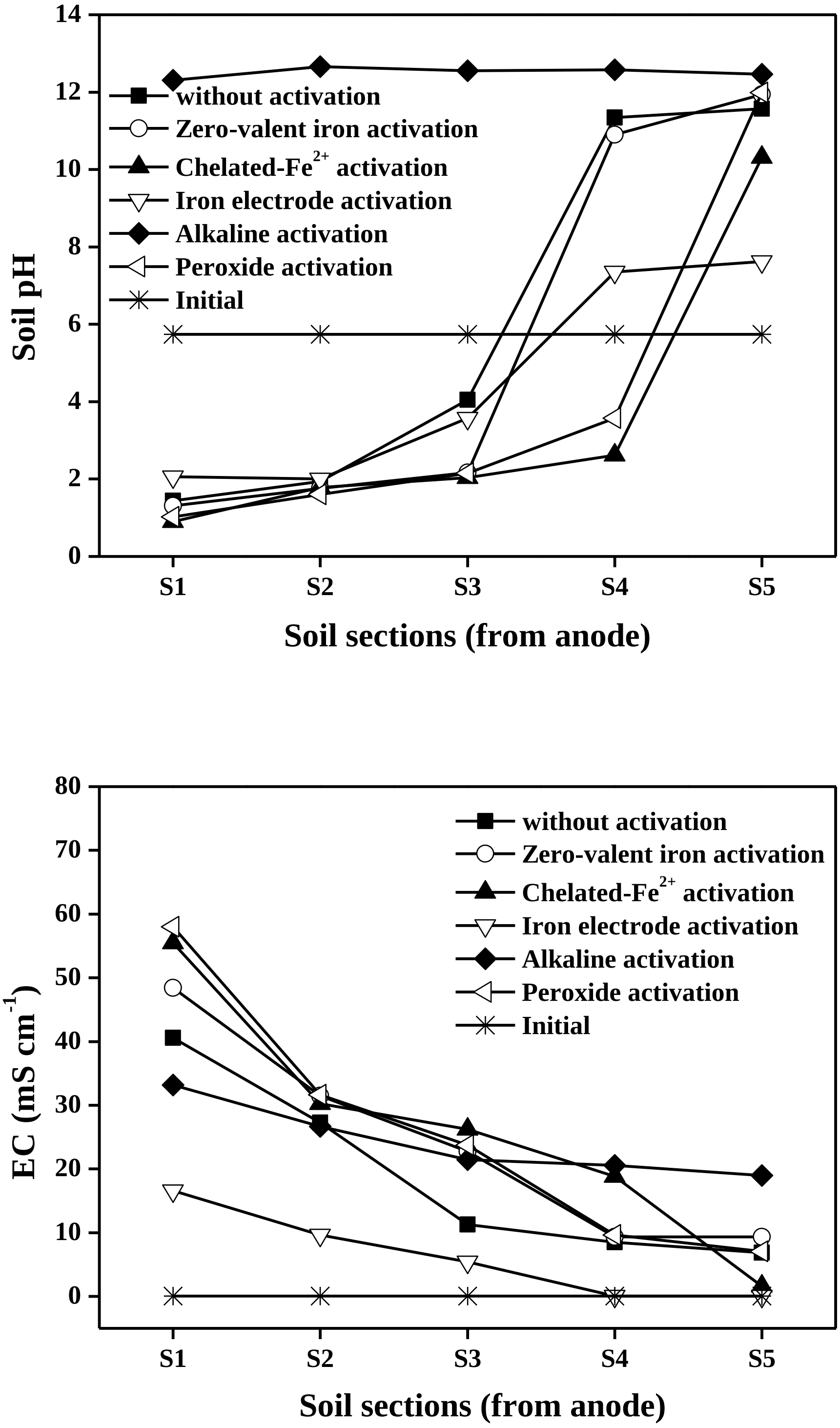
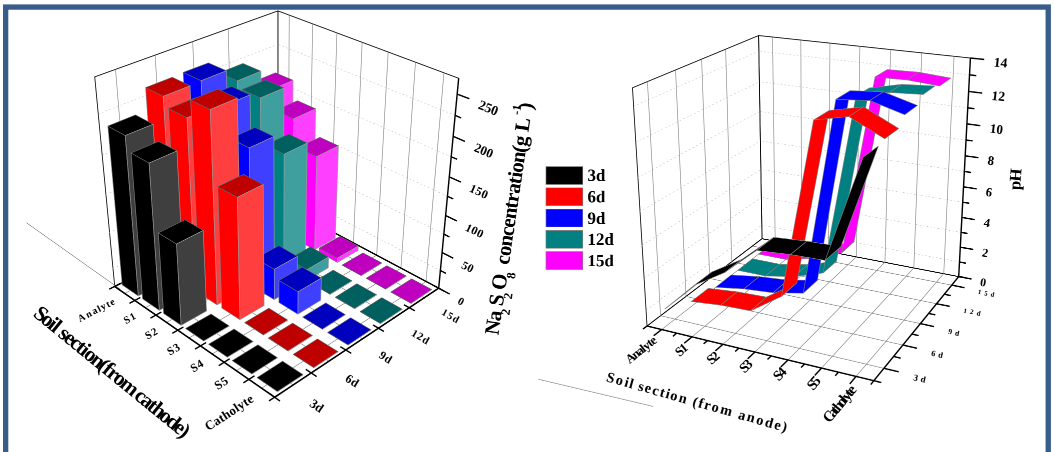
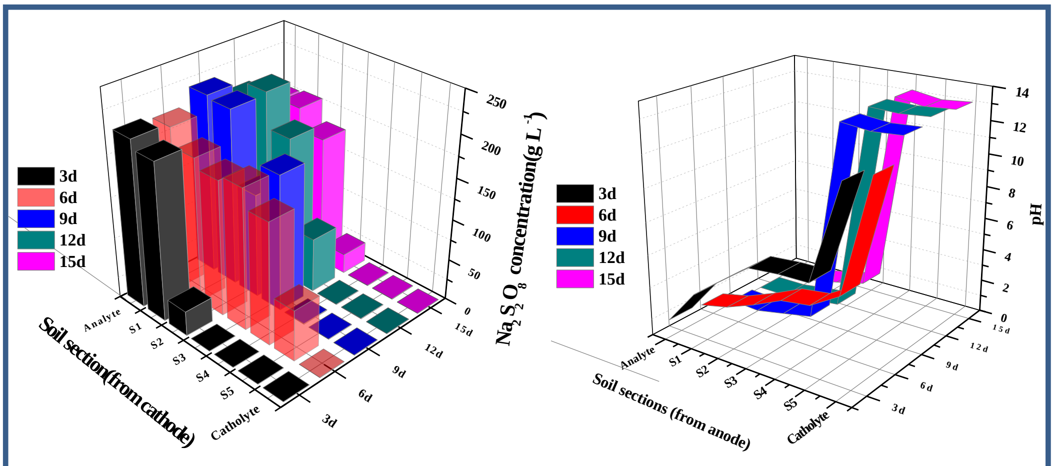


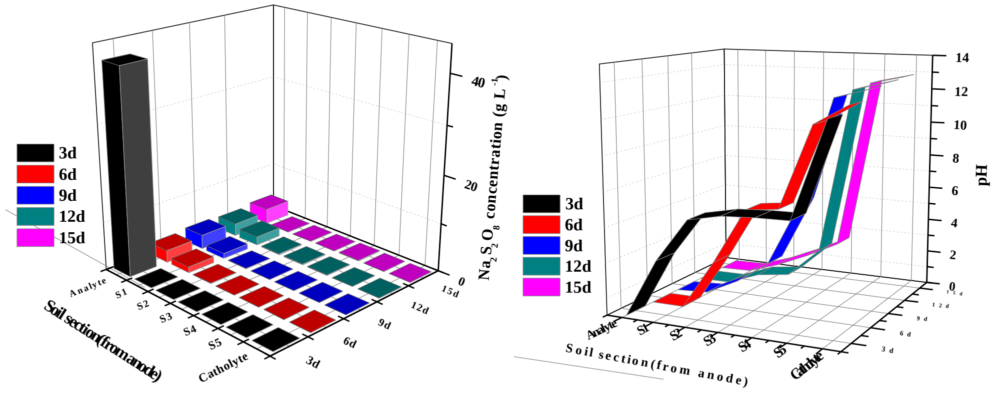
Figure 2 Soil (a) pH and (b) electrical conductivity.



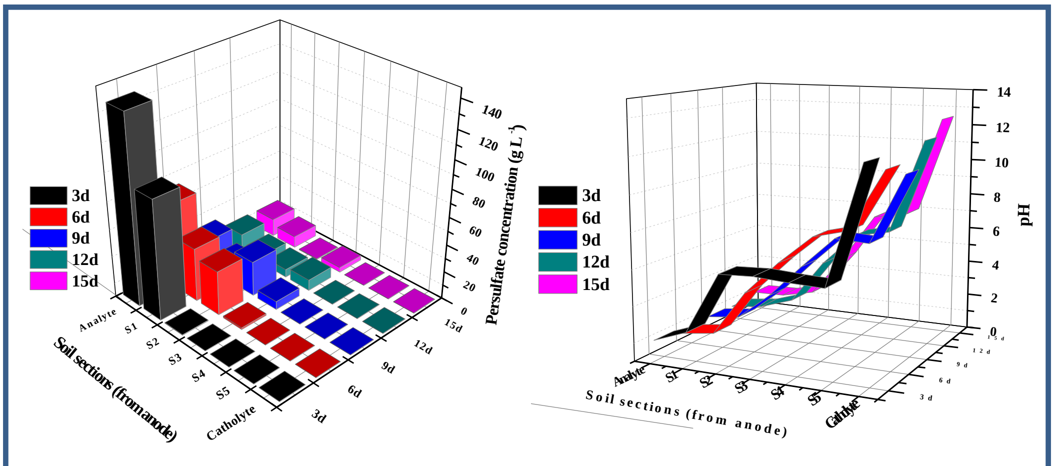
(a) Exp-01 (b)



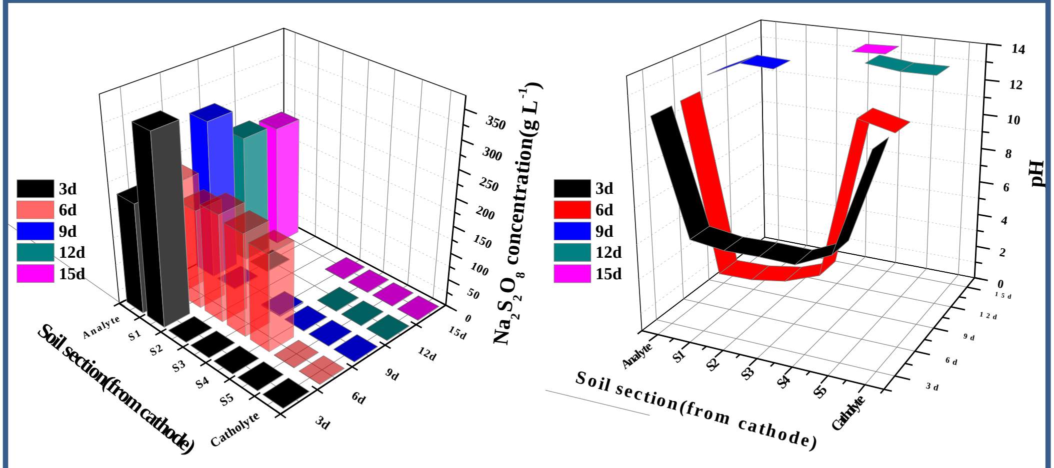
(c) Exp-02 (d)



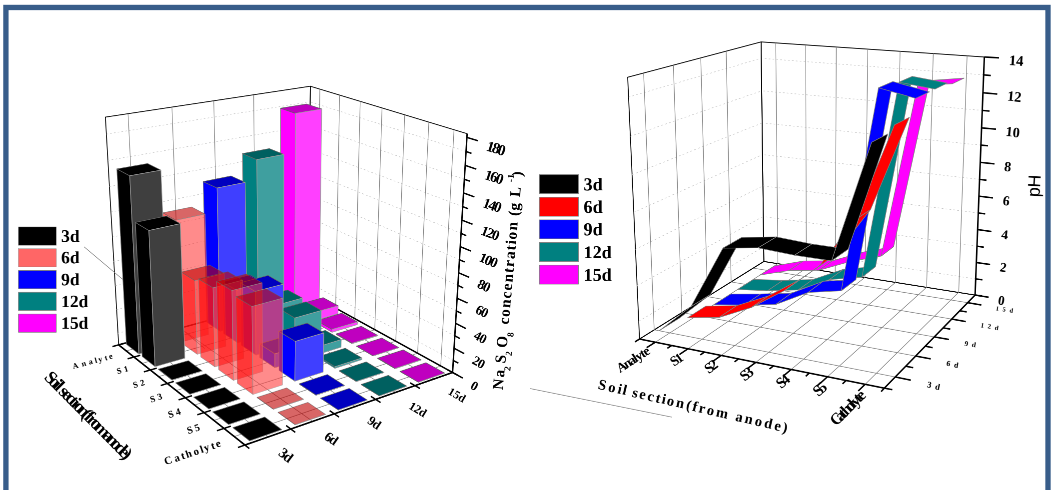
(e) Exp-03 (f)



(g) Exp-04 (h)



(i) Exp-05 (j)



(k) Exp-06 (l)

Figure 3 Variation of $Na_2S_2O_8$ concentration and pH in soil solution at different time.