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Iron electrolysis-assisted peroxymonosulfate chemical oxidation for the remediation of chlorophenol-contaminated groundwater

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Abstract

BACKGROUND: Electrolysis with an iron anode is a novel way to provide ferrous activators for chemical oxidation. The objective of this study is to evaluate the performance of peroxymonosulfate (PMS) for chlorophenol destruction when compared with H₂O₂ and persulfate (PS), and to see whether the electrolysis mode facilitates the buildup of conditions that favor the activation of PMS and removal of chlorophenols.

RESULTS: Ferrous species can effectively activate the PMS over a wide pH range. In comparison with H₂O₂ and PS, PMS is less sensitive to the solution's pH and possesses stronger oxidation capability at alkaline pHs. The optimal molar ratio of PMS to Fe(II) activator is 1:1 for the destruction of 2,4-dichlorophenol (2,4-DCP). The column experiments show that an acidic zone developed downstream from the anode is favorable to maintain ferrous ions and subsequent activation of PMS. The reactivity of the PMS can be manipulated by varying the electrical currents, and the process demonstrates effectiveness for treating organic contaminants. 2,4-DCP contaminated groundwater shows decreased biotoxicity after the chemical oxidation process without considering the residual PMS.

CONCLUSIONS: Iron electrolysis-assisted peroxymonosulfate chemical oxidation can effectively treat the 2,4-dichlorophenol and mixtures of organic contaminants. This process can be engineered as an *in situ* chemical oxidation method for groundwater remediation.

Keywords

environmental remediation; chemical oxidation; iron electrolysis; peroxymonosulfate; chlorophenol

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INTRODUCTION

Chlorinated phenols (CPs) have been widely used in agriculture and industrial applications since the 1920s. Misuse, accidental spills, and improper disposal of CPs have resulted in extensive soil and groundwater contamination in many countries, posing significant threats to human health.¹ Most CPs are toxic, carcinogenic, and biorefractory, and are designated as priority pollutants by the US EPA.^{1–3} Moreover, due to their aryl structure and the presence of chlorine atom, CPs are recalcitrant towards chemical reactions aiming at their destruction.⁴ This continues to raise a need for efficient methods to eliminate such contaminations from both concentrated industrial effluents and diluted polluted groundwater.

For decades, chemical oxidation has been investigated as a rapid and versatile technology to degrade organic contaminants like CPs in natural systems. Typical treatments include Fenton's reagent with hydrogen peroxide and ferrous iron, permanganate, ozone and persulfate (PS) injection.^{5–7} These chemicals have high redox potentials capable of oxidizing a variety of organic contaminants, but also have their own drawbacks for groundwater remediation. The Fenton reagent, which involves the formation of strong oxidizing hydroxyl radicals (2.8 V redox potential), proved effective in the oxidation of many organic contaminants. However, the short life spans of H₂O₂ and the pH-dependent character of Fenton reaction restrict their extensive use for remediation.^{8,9} Permanganate is an oxidant (1.8 V redox potential) characterized by its comparative stability, ease of handling and relatively low cost. Its selective reactivity toward electron-rich organic moieties and the generated MnO₂ limited wider applicability for water treatment. Ozone is a very strong oxidizing gas that can react with many important environmental pollutants; however, its low water solubility poses a problem when mixed with water.¹⁰ Persulfate oxidizes the organic contaminants via sulfate radicals, which can be generated by different activation processes, such as heat, ultraviolet light, high pH, and transition metals. Studies show that persulfate has been successfully utilized for laboratory or field treatment of a variety of organic pollutants.^{5,11–13} Another type of sulfate radical-based oxidant, peroxymonosulfate (PMS), has a high oxidative capability for organic contaminants destruction.^{14–18} Processes of a typical PMS/Fe(II) oxidation system for organics may include:¹⁹

In comparison with persulfate, the activation condition of peroxymonosulfate is mild, but the oxidation efficiency is enhanced for most of the common organic contaminants. PMS

appears to be more powerful than persulfate for oxidation of 4-chlorophenol with chelated ferrous iron as the activator.¹⁵ The conjunction of PMS/Co(II) shows even better performance than Fenton reagent when applied to mineralize 4-chlorophenol.¹⁷ Studies also show that PMS can be effectively activated by transition metal oxides, such as manganese dioxide and cobalt oxide.^{18,20}

The aim of this study is to evaluate combining iron electrolysis with PMS injection for the remediation of chlorophenols in groundwater. We reported that iron electrolysis was an effective approach for *in situ* delivery of ferrous species for groundwater remediation.²¹ When a positive potential was applied to an iron sheet embedded in a saturated aquifer, ferrous ions were generated, and a series of ferrous species (e.g. ferrous ions and ferrous hydrates) were formed, contributing to transformation of contaminants such as Cr(VI), selenate, and arsenate.^{21,22} Our hypothesis herein is that the *in situ* electro-generated ferrous species can activate the injected PMS for organic oxidation, and the design of the electrolysis mode facilitates the buildup of conditions that favor the activation of PMS and removal of chlorophenols. The electrochemically generated ferrous ions prove to be able to effectively activate the H₂O₂ and persulfate,^{23,24} thereby it is interesting to compare their performances with PMS. Unlike pumping of ferrous chemicals for activating oxidants, *in situ* electrolytic production of ferrous iron is controlled with limited mass loss compared with what is usually encountered in the hydraulic delivery of ferrous species to the subsurface.²⁵ The ferrous amount can be easily regulated by varying the applied current based on the type and level of the contaminants.

EXPERIMENTAL

Reagents and materials

The following analytic grade chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd and used as received: 2,4-dichlorophenol, sodium hydroxide, sodium persulfate, hydrogen peroxide (30wt% H₂O₂), ferrous sulfate, sulfuric acid, methanol, o-phenanthroline, ammonium acetate, hydroxylamine hydrochloride, hydrochloric acid, and acetonitrile. Oxone (KHSO₅ 0.5KHSO₄ 0.5K₂SO₄), a triple salt providing strong oxidant peroxymonosulfate, was purchased from Aladdin Industrial Corporation, and the oxidative ingredient was calibrated using iodometric titration. For a concise expression, PMS was used to denote the Oxone oxidant below. The humic acid (>90% purity, Aladdin Industrial Corporation, CAS 1415–93-6) was treated as follows to remove ash content:²⁶ 1.1 gram humic acid was dissolved with 3 mol L⁻¹ NaOH, and the solution was filtered with 0.45 µm cellulose acetate membrane; the filtrate was further neutralized to pH 7 with H₂SO₄, and deionized (DI) water was added to obtain the stock solution of humic acid. The iron electrodes for the column experiments were machined from commercial cast iron materials (with ~95% iron and 3.5% carbon).

Batch experiments

Stock solutions of all the chemicals used were freshly prepared in deionized water before the experiment. A typical experimental procedure is summarized by the following steps. At the start of each experiment, a known amount of DI water was added in a 150 mL vial capped

with PTFE-lined septa. The vials were placed on the stirrer plate for mixing. A known amount of ferrous sulfate was then added in the reactor, followed by the addition of 2,4-DCP stock to obtain the target concentration (20 mg L^{-1} if not otherwise specified). 1 mol L^{-1} sodium hydroxide or 1 mol L^{-1} sulfuric acid was added to adjust the pH of the solution if needed. Finally, the predetermined volume of oxidant was added to start the reaction, and the total volume of the solution was increased to 100 mL . The reaction time for all batch experiments was 1 h . 10 mL methanol was added in the vial to terminate the oxidation reaction, and the remnant 2,4-DCP was measured. Identical sequences for chemical addition were followed in all the experiments reported in this paper. Experiments were performed in duplicate to assure accurate data acquisition, and error bars in figures represent the standard deviation. The removal efficiency ($\eta_r, \%$) of 2,4-DCP and the apparent specific utilization efficiency ($SUE, \text{ mg mmol}^{-1}$) of PMS were calculated using the following equations:

$$\eta_r = \frac{[DCP]_0 - [DCP]_t}{[DCP]_0} \times 100\% \quad (4)$$

$$SUE = \frac{([DCP]_0 - [DCP]_t) VM}{m} \quad (5)$$

where $[DCP]_0$ and $[DCP]_t$ are the initial 2,4-DCP concentration and the concentration at time t , mg L^{-1} (the inlet concentration is used as $[DCP]_0$ for column experiments); V is the volume of reaction solution, L, m represents the mass of added oxidants, mg, and M is the molar molecule weight of the oxidant.

Column experiments

A 5.5 cm inner diameter column filled with glass beads (2 mm bead diameter) was set up for testing, as shown in Fig. 1. The column reactor, constructed with an acrylic tube, simulates one-dimensional flow through a saturated aquifer. Two perforated cast iron electrodes (with thirty 4.5 mm diameter holes and a working area of 13.6 cm^2) were mounted in the columns, serving as anode and cathode. The pore volume of the beads in the column was 0.2 L . Constant electrical currents, I , ranging from 5 to 20 mA ($0.37\sim 1.47\text{ mA cm}^{-2}$ current densities, i) were applied using a DC power supply (SYK-1002D, Shunyi Electronic, China). Simulated contaminated water was prepared by dissolving sodium sulfate (0.01 mol L^{-1}) and a predetermined amount of 2,4-dichlorophenol ($0\sim 40\text{ mg L}^{-1}$ in this study) in deionized water. The water was pumped into the column from the bottom using a peristaltic pump (3 mL min^{-1} flow rate if not otherwise specified). When oxidant injection was conducted, the solution containing oxone was pumped into the column from the injection port (Port I in Fig. 1) using a precise peristaltic pump. Inside the column, a tube connected at Port I enabled the release of oxidant into a specific location in the column. Water samples were collected from the six sampling ports (see the numbering of the ports in Fig. 1). The volumes collected for measurements of pH, 2,4-DCP and iron concentrations were 1.2 mL , 1.5 mL and 2 mL , respectively. All experiments were conducted at a room temperature of $23(\pm 2)^\circ\text{C}$.

Analytical methods

For quantification of 2,4-DCP degradation, the remaining 2,4-DCP was analyzed by a high performance liquid chromatography (HPLC), consisting of a Shimadzu 15C HPLC pump and a UV/visible detector. Chromatographic separations were performed using a WondaSiL C18 reversed phase column. A mixture of methanol and water in the ratio of 85:15 (v/v) was selected as the mobile phase with a flow rate of 1.0 mL min⁻¹ and an injection volume of 10 µL. The UV/visible detector was set at 289 nm. Total organic carbon (TOC) content was measured using a Jena TOC analyzer. Methanol and sodium thiosulfate were used to terminate the oxidation process for HPLC and TOC measurement, respectively. A digital pH meter (Fondriest Environmental Company) was used to measure the solution pH. The concentration of Fe(II) species was determined by a spectrophotometric method at 510 nm after complexing with 1,10-phenanthroline using a UV-vis spectrophotometer, as described in our previous study.^{21,27} The residual PMS in the solution after activation was measured using an iodometric titration method with starch as the indicator.^{28,29} The degradation intermediates of 2,4-DCP degradation were analyzed by a GC-MS method (Varian 450 GC/320MS, DB-5 MS capillary column). The water samples were collected from the effluents of the column experiments at different times. A solid-phase extraction process using PLS-3 cartridges (Shimadzu, InertSep, 6 mL per 200 mg) was employed to extract the degradation intermediates of 2,4-DCP. The pH of all water samples was adjusted to ~2 prior to the extraction. 5 mL dichloromethane was used as the elution solution.

Assays for the biotoxicities of water samples

The acute biotoxicities of water samples were evaluated using a soil dehydrogenase activity assay. The procedure follows the description in the references but with minor modifications.^{30,31} Fresh clayey soil samples were collected from the campus of Wuhan University at a depth of 5 cm below the soil surface. The soil was homogenized and passed through a 1 mm sieve before use. For each trial, 5.0 g fresh soil was mixed with 3 mL water samples in a 25 mL sealed conical flask, and the mixture was incubated in the dark at 37 °C for 24 h. Afterwards, 2 mL 1% 2,3,5-triphenyltetrazolium chloride was added for an additional 6 h incubation. Finally, each flask received 10 mL methanol and the triphenylformazan (TPF) produced in the methanol-water extract was determined using a spectrophotometric method (wavelength 485). All trials were carried out in duplicate. The dehydrogenase activity was expressed as the TPF content (µg g⁻¹ dry soil). Lower TPF content means the water sample has stronger inhibition of dehydrogenase activity.

RESULTS AND DISCUSSION

Batch experiments

Comparative study of different processes—Because pH affects oxidation, two groups of tests were conducted to evaluate the oxidation efficiency of different oxidants activated by ferrous sulfate: (1) the solution pH was adjusted immediately after the addition of oxidants by adding a known amount of concentrated NaOH solution (the addition of NaOH was based on preliminary experiments, Fig. 2(a)); and (2) the pH of the ferrous sulfate solution was adjusted prior to oxidant addition to a pH of 2.9, 5.1 and 10.5; and the final solution pH after oxidation was recorded (Fig. 2(b)). The results are presented in Fig. 2.

When the pH values were controlled at the same level, different oxidation efficiencies were observed for the three oxidants (Fig. 2(a)). At acidic condition with a pH of 2.9, H₂O₂ plus equimolar Fe²⁺, namely the classic Fenton reagent, produced the best performance for 2,4-DCP removal, followed by PMS and PS. However, at a pH of 6.5, the oxidation efficiency of the Fenton process apparently deteriorated and was less effective than the PMS oxidation. Tang *et al.* also reported that the 2,4-DCP degradation efficiency decreased by more than 50% when the solution pH was increased from 3.5 to 6.³² At a pH of 10.5, the 2,4-DCP removal efficiency by PMS was 31.3%, while the other two oxidants were relatively ineffective under this alkaline condition. The results indicate that increasing solution pH is not favorable for these oxidants due to the change of iron speciation. However, PMS appears to still possess appreciable oxidation capability at alkaline conditions.

Figure 2(b) shows the effect of adding more oxidants to treat 2,4-DCP. For solutions with an initial pH of 2.9 and 5.1, the addition of oxidants further acidified the solution. These conditions result in more than 99% 2,4-DCP removal efficiency for Fenton reagent, even for the solution containing 2,4-DCP and FeSO₄ at an initial pH of 5.1. The performance of PMS and PS also improved under similar conditions. Adding similar molar ratios of oxidants to the solution with an initial pH of 10.5 resulted in different removal efficiencies and final pH values. The PMS unexpectedly exhibited 78.8% removal efficiency, and a final solution pH of 4.88. In contrast, for the other two oxidants, the pH changes were much less compared with initial values, and low removal efficiencies were observed.

According to the results, PMS is a favorable oxidant as it is less sensitive to pH. In this study, Oxone (KHSO₅, 0.5KHSO₄, 0.5K₂SO₄) was applied, and KHSO₄ contributed to the acidification. As a result, a more acidic condition that favors the activation of PMS caused better 2,4-DCP removal efficiency (Fig. 2(b)). In addition, the unique activation process of PMS at alkaline pH appears to contribute to the better performance. PMS ion (HSO₅⁻) is a weak acid with pK_a = 9.4. It exists in the forms of SO₅²⁻ and HSO₅⁻ at alkaline conditions of pH around 10.^{33,34} SO₅²⁻ can oxidize the organics since it has the standard potential of 1.22 V vs. SHE (SO₅²⁻/SO₄²⁻ redox couple).³⁵ Our experiments show that equimolar PMS can decrease the 2,4-DCP by 3% at pH 10.5 in the absence of any iron salt. Moreover, the HSO₅⁻ ions may be activated by the ferrous hydroxide at alkaline condition, as illustrated by:

The generated sulfate radicals, although weak at alkaline condition, further contribute to the oxidation of 2,4-DCP, resulting in 20.8% 2,4-DCP removal efficiency at a pH of 10.3 (Fig. 2(a)).

Effect of the ratio of PMS to activator—Figure 3 displays the 2,4-DCP removal efficiency and specific utilization efficiency of PMS under different [PMS]:[Fe(II)] molar ratios. Increasing the ratio improves the removal efficiency to 88.5% at a molar ratio of 20:5. However, the best *SUEs* of PMS are obtained at ratios of 2:5 and 5:5. In other words, molar ratios within the range of 0.4 to 1 are the most effective for PMS activation for oxidation.

When the ratio is lower than 0.4, the excess Fe(II) may act as a radical scavenger to consume the generated oxidative radicals, causing lower *SUE*. The effect of Fe(II):PMS ratio on Rhodamine B (RhB) degradation was reported.¹⁹ When the molar ratio Fe(II):PMS was higher than 2, a lower overall RhB decay was observed due to the futile-consumption of sulfate radicals by excessive Fe(II), as given by:

On the other hand, when the ratio was higher than 1 (from 10:5 to 20:5 in Fig. 3), the improvement in removal efficiency of 2,4-DCP was limited with respect to the notable increase in PMS concentration. Apparently, the excessive PMS in the solution cannot be fully utilized under these PMS:Fe(II) molar ratios, resulting in a drop in *SUE*. Preliminary experiments show that at a higher 2,4-DCP concentration of 50 mg L⁻¹, a ratio of 2 ([PMS] is fixed at 0.615 mmol L⁻¹) is still not favorable for removing 2,4-DCP or for improving the *SUE* of PMS. Measurements of residual PMS after 1 h show that 52% PMS is not activated for the case of 20:5 PMS/Fe(II) ratio (see values in Fig. 3). As the PMS:Fe(II) ratio decreases, the residual PMS decreases, and only 9.8% PMS remain in the solution for the case of 5:5 molar ratio. It is reported that the regeneration reaction of Fe(II) activator (Equation (2)) is slower than the activation reaction of PMS (Equation (1));¹⁹ therefore a PMS:Fe(II) ratio of more than 1 does not improve the oxidation efficiency within a short reaction time. Our results further support this point, indicating that a molar ratio between 0.4 and 1 results in optimum conditions for *SUE* of PMS. It is noted that the optimal PMS:Fe(II) ratio appears to be different from that of PMS/Co(II). PMS:Co(II) molar ratios greater than 1:1 and up 100:1 were reported to be the most effective for the oxidation of chlorophenol.¹⁷ The difference is probably due to the different activation kinetics of the two systems. The regeneration of Co(II) from Co (III) is likely a faster reaction, thus much less Co(II) was needed for the activation of PMS.¹⁷ Hence, for the effective activation of PMS, it is essential to provide sufficient amounts of Fe(II) species.

Effect of 2,4-DCP concentration and oxidants—To evaluate the effect of 2,4-DCP initial concentration on the removal efficiency of 2,4-DCP after 1 h, changes in the solution TOC and the *SUE* of PMS are illustrated in Fig. 4. For Fig. 4(a), the same amount of PMS and ferrous sulfate were added to treat solutions with different 2,4-DCP concentrations. Lower 2,4-DCP removal efficiency and TOC removal efficiency are observed with increasing 2,4-DCP concentration. Initial concentration of 100 mg L⁻¹ (or the molar ratio of PMS:Fe(II):2,4-DCP = 1:1:1) produced 31.9% 2,4-DCP and 25.4% TOC removal. The *SUE*, however, shows the highest value of 58.3 mg mmol⁻¹ (Fig. 4(c)), suggesting higher substrate concentration improves the *SUE* of PMS.

Figure 4(b) presents the results for the molar ratio of 5:5:1 of PMS:Fe(II):2,4-DCP. As the PMS and Fe(II) were kept at a ratio of 1:1, the 2,4-DCP removal efficiencies are all higher than 64.0%, and the TOC removal efficiencies exceed 35.1%. However, the same molar ratio does not result in the same removal efficiency for 2,4-DCP and solution TOC. The added PMS resulted in a final pH of 3.8 and 3.3 for solutions with initial concentrations of 2 mg L

$^{-1}$ and 10 mg L^{-1} , respectively. In contrast, when the concentrations were higher than 20 mg L^{-1} , the added PMS was sufficient to acidify the solution to a pH less than 2.9 and to maintain the presence of free ferrous ions. Therefore, higher removal efficiency and *SUE* are observed at higher 2,4-DCP concentrations (Fig. 4(c)).

Column experiments

pH profiles and ferrous generation—Column experiments were carried out to quantify PMS activation by *in situ* generated ferrous species. Before the injection of the PMS solution, changes in pH and ferrous generation – both associated with electrolysis – were evaluated under different electric currents. Figure 5(a) depicts the pH profiles as the electrolysis progressed at 0.37 mA cm^{-2} . The pH does not show much difference on the anode side and is stable around 5, which is slightly more acidic than the influent pH of 6. However, downstream from the cathode, the pH increased significantly. Formation of a slightly acidic zone followed by an alkaline zone is noted. Electrolysis of the iron anode generates ferrous ions (Equation (8)), which form a series of ferrous species (Equation (9) and (10)) depending on the pH of the aqueous environment:^{36,37}

In the column, the formation of $\text{Fe}(\text{OH})^+$ can decrease the pH slightly. Meanwhile, hydrogen gas and hydroxyl ions are generated on the iron cathode, causing an increase in the pH after the cathode. The downstream electrode arrangement avoids back-mixing of the electrolytes in the vicinity of the cathode, and enables the formation of a pH zone that is conducive to the existence of dissolved ferrous species. Figure 5(b) further illustrates the effect of current intensity on the pH profile. The pH profiles were similar under different currents. Higher electric currents cause more alkaline conditions near the cathode and more acid conditions close to the anode. For the anode, the electrolysis does not generate protons directly, and the slight acidification at higher electric currents is probably due to the hydrolytic process of ferrous ions (Equations (9), (10)).

Figure 6 shows the generation and distribution of the ferrous species. The concentration of ferrous species increased at all sampling ports over time (Fig. 6(a)). The ferrous species profiles eventually stabilized after 5 h at 0.37 mA cm^{-2} , and the equilibrium concentration at Port-1 was 0.43 mmol L^{-1} . The ferrous species distribution within the column shows a downstream decreasing trend which is affected by the pH profile. As the ferrous ions move towards the cathode, the elevated pH causes formation of ferrous hydroxide, which may

form flocs that precipitate on the surface of the glass beads. The ferrous concentration at Port-5 was lower than 0.1 mmol L^{-1} . Increasing the electric current (Fig. 6(b)) produces more ferrous species. After 1 h of electrolysis, the ferrous concentrations (Fig. 6(b)) at Port-S1 were 0.43 mmol L^{-1} , 0.87 mmol L^{-1} , and 1.68 mmol L^{-1} for 0.37 mA cm^{-2} , 0.74 mA cm^{-2} , and 1.47 mA cm^{-2} current densities, respectively. The concentration shows a linear increasing trend as a function of the current. To evaluate the average current efficiency η_c , the total iron was measured in the effluent and pore fluid remaining in the column (a mixture of the total effluent and pore fluid was thoroughly stirred, sampled and analyzed). The average current efficiency is then calculated by:

$$\eta_c = \frac{2mF}{Mt} \times 100\% \quad (11)$$

where m is the mass of the total iron (ferrous and ferric); M is the molar molecular weight of iron; F is Faraday's constant; I and t represent current and electrolysis time, respectively. The current efficiencies are 105.6%, 99.7%, and 102.1% for 0.37 mA cm^{-2} , 0.74 mA cm^{-2} , and 1.47 mA cm^{-2} current densities, suggesting that the amount of ferrous produced can be controlled by the applied current. Note that the current efficiencies higher than 100% are probably due to chemical corrosion of the iron anode. The generation rate of ferrous ions ($V_{\text{Fe(II)}}$, mM h^{-1}) can be expressed by the followed equation based on the Faradic law:

$$V_{\text{Fe(II)}} = I/2F \quad (12)$$

Degradation of 2,4-DCP—The mass flow rate of the PMS (V_{PMS} , mM h^{-1}) and the loading rate of 2,4-DCP (V_{DCP} , $\text{mmol L}^{-1} \text{ h}^{-1}$) in the column can be expressed as:

$$V_{\text{PMS}} = U_{\text{PMS}} \cdot [\text{PMS}]_{\text{in}} \quad (13)$$

$$V_{\text{DCP}} = U_{\text{DCP}} \cdot [\text{DCP}]_{\text{inlet}} \quad (14)$$

where $[\text{PMS}]_{\text{in}}$ is the concentration of injected PMS solution; $[\text{DCP}]_{\text{inlet}}$ represents the influent 2,4-DCP concentration in the simulated groundwater; U_{PMS} and U_{DCP} are the flow rates of the PMS solution and 2,4-DCP feed solution, respectively. DCP degradation is presented in Fig. 7 under different varied electrical currents, $V_{\text{Fe(II)}}: V_{\text{PMS}}: V_{\text{DCP}}$ ratios and 2,4-DCP concentrations. In comparison with the control experiment (the red line in Fig. 7(a), with only iron electrolysis), there is a decreasing trend in 2,4-DCP profiles from the anode towards the cathode as the PMS was injected. After 6 h, the normalized concentration at the port closest to the anode (Port-S1) is around 80%, followed by a sharp decrease down to 28% at Port-S3. The drop in concentration indicates that the destruction of 2,4-DCP occurred in the zone after the anode, where ferrous ions were continuously produced. Eventually, the 2,4-DCP concentration decreases to less than 20% of the influent

concentration. After 4 h operation, there was no buildup in the equilibrium concentration in the column, and 6 h operation appeared to ensure a steady concentration distribution. The 2,4-DCP concentration shows a rebound close to the cathode (Port-S4), which is due to the attenuation of oxidizing capacity of the PMS at the cathode zone. The pH rise at the cathode can decrease the oxidizing capacity of the PMS, as shown in the batch experiments.

Figure 7(b) presents the concentration profiles at the $V_{\text{Fe(II)}}: V_{\text{PMS}}: V_{\text{DCP}}$ ratio of 5:3:1. The concentrations increased to 30% at Port-S5 because less PMS was injected. The result is in accord with the batch experiments shown in Fig. 3, where less PMS lowers the removal efficiency of 2,4-DCP as the PMS/Fe(II) ratio is less than 1. Meanwhile, the pH at Port-S5 increases to 4.1 due to the decrease of PMS injection. In Fig. 7(c), the 2,4-DCP concentration was elevated to 40mgL^{-1} , and the electrical current and the $[\text{DCP}]_{\text{inlet}}$ were also doubled to keep a $V_{\text{Fe(II)}}: V_{\text{PMS}}: V_{\text{DCP}}$ ratio of 5:5:1. The 2,4-DCP was effectively treated in the column, and a normalized concentration of 15.6% was obtained at Port-S5. This suggests that the oxidation capacity of the system can be adjusted in terms of the amount of target pollutants through regulating the PMS injection rate (or PMS concentration) and the intensity of electric current. It is also noted that the pH of the effluent became acid with the injection of oxone solution. Options to control the pH include setting up an additional electrolysis process which produces alkaline electrolyte to mitigate the acidity.³⁸

Effect of coexisting organics on 2,4-DCP removal—Figure 8 shows the removal efficiency of 2,4-DCP after 6 h operation in the presence of other organic pollutants beyond 2,4-DCP, or natural organic matter like humic acid. The mixture of trichloroethylene (TCE), toluene and 2,4-DCP was treated by the iron electrolysis-assisted PMS oxidation process (Fig. 8(a)). The normalized concentrations were less than 40% for all three pollutants in the effluent. For the 2,4-DCP, the removal efficiency is 74%, which is lower than that in the case of absence of other organics (84.4% 2,4-DCP removal efficiency for Fig. 7(c)). This implies that the presence of TCE and toluene competed for oxidants and reduced removal efficiency for 2,4-DCP. However, if TCE and toluene are considered as target contaminants as well, the utilization efficiency of PMS is actually high, suggesting this oxidation process can be developed for the remediation of a groundwater plume with mixed organic contaminants.

Humic substances are recognized to be the most widespread components of natural organic matter (NOM). It is essential to investigate the effect of humic acid on the removal of 2,4-DCP. The oxidation of 2,4-DCP in the presence of different levels of humic acids is presented in Fig. 8(b). When 10 mg L^{-1} was added, the 2,4-DCP concentration is decreased to 10.1% of the inlet concentration, which is lower than that in the case of no humic substance. The enhanced removal of 2,4-DCP is probably attributed to the complexation of humic substances to the ferrous ions.³⁹ The complexed ferrous ions may be superior to the ferrous hydrates (e.g. $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2$) for the activation of PMS, resulting in higher removal efficiency for 2,4-DCP. Fe(II) – fulvate complexes are reported to react more rapidly with hydrogen peroxide than Fe(II) – aquo complexes, leading to a faster Fenton's reaction at higher fulvic acid concentrations.⁴⁰ At 100 mg L^{-1} humic acid, the 2,4-DCP concentration ratio at Port-S5 increased to 56.9%, implying that the humic substance adversely impacts 2,4-DCP removal. Because humic substance is a reductive organic that

can be oxidized by the persulfate radicals,^{41,42} the presence of higher concentrations of humic substances will compete with 2,4-DCP for the PMS and counteract the enhanced effect caused by ferrous complexation. Presence of about 50 mg L⁻¹ seems to be the threshold value that did not exert a negative impact on the oxidation of 2,4-DCP (Fig. 8(b)). Considering that humic acid is usually in the range of 10 µg ~ 10 mg in natural aquatic systems, it can be inferred that naturally occurring humic acid will not adversely affect ferrous-assisted PMS oxidation process. Instead, the complexation effect of humic acid on nascent ferrous ions can promote the oxidation efficiency to some extent.

Assessment of the biotoxicities of effluents—Numerous bioassays employing bacteria, algae, protozoan and enzyme have been developed to evaluate the biotoxicities of chemicals and effluents. In this study, because the remedial method targets contaminated groundwater, the biotoxicity of effluent is assessed via a soil enzyme assay. Dehydrogenase is an intracellular enzyme, which is supposed to reflect microbial activity.⁴³ The assay based on dehydrogenase enzyme activity inhibition is a rapid method that has been used to evaluate the biotoxicities of various chemicals such as heavy metals and chlorophenols.^{31,43,44} The biotoxicities of the influent and effluent liquids from a column experiment are presented in Fig. 9. It shows that, in comparison with the deionized water sample (Fig. 9(a)) and the influent sample (Fig. 9(b)), the effluent liquid results in lower soil dehydrogenase activity (Fig. 9(c), TPF 52.4 µg g⁻¹). Because the treated effluent is an acidic mixture comprising of the remaining pollutants, the daughter compounds and the residual PMS, the effluent liquid is further treated by a pH neutralizing and/or a residual PMS elimination for enzyme assays. The results indicate that neutralizing pH alone (Fig. 9(d)) or eliminating residual PMS alone (Fig. 9(e)) can improve the TPF content. When the effluent is treated by both pH neutralizing and PMS elimination (Fig. 9(f)), which means that it contains only the remaining 2,4-DCP and daughter compounds, the sample demonstrates a higher dehydrogenase activity than the influent sample. The results suggest that the destruction of 2,4-DCP indeed decreased the biotoxicity when the inhibition effect from acidic oxidant is eliminated. The GC-MS analysis shows that chlorohydroquinone and glycerol are detected as the daughter compounds of 2,4-DCP degradation. The observation suggests that the degradation of 2,4-DCP accords with the reported radical-mediated degradation processes: the aromatic ring is attacked by the electrophilic radicals (SO₄⁻· and OH·), followed by cleavage of the aromatic ring and the generation of glycerol and aliphatic acids (e.g. succinic acid and oxalic acid).^{45–47} In comparison with the 2,4-DCP, the final degradation products of the PMS oxidation process obviously are of low toxicity or non-toxicity. Karci *et al.* also reported that the acute toxicity of the water sample decreased with decreasing 2,4-dichlorophenol in classic Fenton and photo-Fenton treating processes.⁴⁸ However, the acute toxicity of the residual oxidants is no doubt a matter of concern for the application of chemical oxidation remediation.

CONCLUSIONS

Iron electrolysis-assisted PMS chemical oxidation is proposed for the remediation of 2,4-DCP contaminated groundwater. Ferrous species can effectively activate the PMS in a wide pH range, leading to the oxidation of 2,4-DCP. In comparison with persulfate and hydrogen

peroxide, PMS is less sensitive to the solution's pH and possesses stronger oxidation capacity at alkaline pH. Equal molar ratio of PMS to Fe(II) activator is better for the removal efficiency of 2,4-DCP and for the *SUE* of PMS. A column with a built-in iron electrolytic system was designed to simulate the remediation of 2,4-DCP contaminated groundwater. Buildup of the acidic zone downstream from the anode is favorable for the presence of ferrous ions in the column. The ferrous distribution within the column shows a downstream decreasing trend. Varying the electrical intensity can readily regulate the production of total ferrous species. 2,4-DCP is successfully transformed by the iron electrolysis-assisted PMS oxidation where most transformation occurs immediately after the anode. A mixture of organic contaminants can be treated by the PMS oxidation process, and the presence of a low level of humic acid ($\sim 10 \text{ mg L}^{-1}$) promotes the 2,4-DCP removal efficiency. The biotoxicity of the 2,4-DCP contaminated groundwater is decreased after the electrolysis-assisted PMS chemical oxidation process, but the residual PMS oxidant also inhibits the enzyme activity. In summary, iron electrolysis provides a simple and electrically-controlled way for the *in situ* production of Fe(II), which can serve as activator for chemical oxidation of groundwater contaminants by PMS or other oxidants.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Schematic of the setup for the column experiment. The column is filled with inert glassy beads. The anode and cathode are perforated. The unit for all indicated sizes is centimeter.

Figure 2.

Comparison of different oxidants for the treatment of 100 mL 2,4-DCP solutions (20 mg L⁻¹). (a) Solution pHs after the addition of oxidants were controlled. The molar ratio of oxidant to Fe(II) was 1:1([FeSO₄] = [PMS] = 0.615 mmol L⁻¹). (b) Solution pHs prior to the addition of oxidants were controlled, and the pHs after reaction were recorded (see values on the top of columns). The molar ratio of oxidant to Fe(II) was 2:1([PMS] = 1.23 mmol L⁻¹, [FeSO₄] = 0.615 mmol L⁻¹).

Figure 3.

Effect of molar ratio of PMS to Fe(II) on the removal of aqueous 2,4-DCP (column) and specific utilization efficiency (*SUE*) of PMS (blue line). The 2,4-DCP concentration was 20 mg L⁻¹. Concentration of FeSO₄ was fixed at 0.615 mmol L⁻¹ for all trials, and solution pH was not adjusted (solution pH prior to the addition of oxidants was 5.1).

Figure 4.

Effect of the 2,4-DCP initial concentration on the removal efficiency of 2,4-DCP, the removal efficiency of TOC and the *SUE* of PMS. (a) Addition of PMS/Fe(II) (1:1, 0.615 mmol L⁻¹ for both) was same for all trials, and the 2,4-DCP concentrations were from 2 to 100 mg L⁻¹. (b) Constant molar ratio of PMS: Fe(II): 2,4-DCP (5:5:1); [PMS] and [FeSO₄] were both 0.061 mmol L⁻¹, 0.308 mmol L⁻¹, 0.615 mmol L⁻¹, 1.845 mmol L⁻¹ and 3.075 mmol L⁻¹; the corresponding 2,4-DCP was from 2 to 100 mg L⁻¹. (c) The *SUE* of PMS under the aforementioned reaction conditions.

Figure 5. pH changes in the column reactor under different electrical currents. Oxidant was not injected for all trials. (a) 0.37 mA cm^{-2} current density. (b) Average of the pH values. Error bar means the standard deviation of the seven pH values obtained at different times (0.5–6 h). The initial pH values of the liquids were 6.0 ± 0.2 .

Figure 6.

Concentration profile of ferrous species (including ferrous ions and ferrous hydrates capable of passing through the syringe needle) along the column. (a) Concentration change as a function of time at 0.37 mA cm^{-2} . (b) The equilibrium concentration profiles (the average of the concentrations of 5 h and 6 h) at different electrical currents.

Figure 7.

2,4-DCP degradation and pH change in the column under varied conditions. (a) 0.37 mA cm^{-2} current density, $[\text{PMS}]_{\text{in}} = 1.845 \text{ mmol L}^{-1}$, $[\text{DCP}]_{\text{inlet}} = 20 \text{ mg L}^{-1}$. The red solid symbols in (a) represent the control experiment without PMS (only iron electrolysis). (b) 0.37 mA cm^{-2} current density, $[\text{PMS}]_{\text{in}} = 1.107 \text{ mmol L}^{-1}$, $[\text{DCP}]_{\text{inlet}} = 20 \text{ mg L}^{-1}$. (c) 0.74 mA cm^{-2} current density, $[\text{PMS}]_{\text{in}} = 3.69 \text{ mmol L}^{-1}$, $[\text{DCP}]_{\text{inlet}} = 40 \text{ mg L}^{-1}$. U_{PMS} and U_{DCP} were 1 mL min^{-1} and 3 mL min^{-1} respectively for all tests (a)–(c). $V_{\text{Fe(II)}}$ was calculated using a current efficiency of 100% for ferrous generation.

Figure 8.

Effect of coexisting organic matter on the removal of 2,4-DCP. (a) 2,4-DCP concentration profile after 6 h operation in the presence of 20 mg L⁻¹ TCE and 20 mg L⁻¹ toluene. $[\text{PMS}]_{\text{in}} = 3.69 \text{ mmol L}^{-1}$, $[\text{DCP}]_{\text{inlet}} = 20 \text{ mg L}^{-1}$. (b) 2,4-DCP concentration profiles after 6 h operation in the presence of different levels of humic acid, $[\text{PMS}]_{\text{in}} = 1.845 \text{ mmol L}^{-1}$. U_{PMS} and U_{DCP} were 1 mL min⁻¹ and 3 mL min⁻¹, respectively, for all tests.

Figure 9.

Assay of soil dehydrogenase activity for the water samples. (a) Deionized water sample. (b) The influent water of the column experiment, $[DCP]_{inlet} = 20 \text{ mg L}^{-1}$. (c) The effluent water of the column experiment. The treating conditions include 0.37 mA cm^{-2} current density and $1.107 \text{ mmol L}^{-1}$ injected PMS. The water sample was collected after 6 h operation. (d) The effluent water further treated by a pH neutralizing (~ 7) process using NaOH. (e) The effluent water plus excessive Na_2SO_3 (i.e. the residual PMS was eliminated). (f) The effluent water plus PMS elimination and pH neutralizing. The inset photo shows the appearances of the methanol – water extracts for TPF determination.