Application of persulfate-releasing barrier to remediate MTBE and benzene contaminated groundwater

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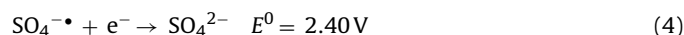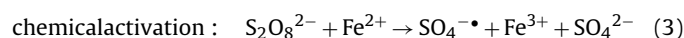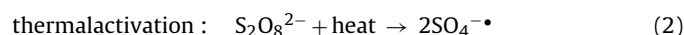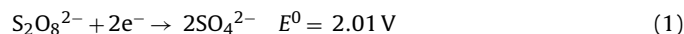
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ABSTRACT

The objective of this study was to assess the potential of using an in situ oxidation barrier system to remediate gasoline-contaminated groundwater. The passive remedial system included a persulfate-releasing barrier containing persulfate-releasing materials to release persulfate for contaminant oxidation. Bench experiments were performed to determine the components and persulfate-releasing rate of the persulfate-releasing materials. Column experiments were conducted to evaluate the effectiveness of the designed persulfate-releasing materials on the control of petroleum-hydrocarbon plume. In this study, methyl tert-butyl ether (MTBE) and benzene were used as the target compounds. The optimal persulfate releasing rate was obtained when the mass ratio of persulfate/cement/sand/water was 1/1/0.16/0.5, and the rate varied from 31 to 8 mg persulfate per day per g of material. Significant amounts of MTBE and benzene were removed through the oxidation process due to the release of persulfate, and the produced tert-butyl formate (TBF) and tert-butyl alcohol (TBA), byproducts of MTBE, were further oxidized in the system. Results suggest that the oxidation rate would be affected by the oxidant reduction potential and concentrations of ferrous iron and persulfate.

1. Introduction

Accidental releases of petroleum products from pipelines and fuel-oil storage tanks are most common causes of groundwater contamination. Petroleum hydrocarbons contain benzene, toluene, ethylbenzene, and xylene isomers (BTEX), which are hazardous substances regulated by many nations [1,2]. Gasoline contains approximately 10–20% of BTEX, and thus, the residual amount of BTEX persists in a pure liquid phase within pore spaces at many gasoline spill sites [3]. The slow dissolution of residual BTEX results in a contaminated plume of groundwater. In addition to BTEX, methyl tertiary-butyl ether (MTBE) is another major chemical of concern, which is also toxic to humans [3]. MTBE is an organic chemical with high water solubility and low adsorption to soil. In addition, MTBE is not readily biodegradable because of the tertiary butyl group and ether linkage on it [4,5]. Among BTEX, benzene is especially toxic and is categorized as a carcinogen by the US National Toxicology Program [6]. For this reason, more active measures may be required to control the movement of MTBE and benzene at gasoline-contaminated sites.

Pump-and-treat technology and in situ air sparging are commonly used groundwater remedial technologies to clean up gasoline spill sites [7,8]. However, both technologies have inherent limitations such as high operation and electricity costs, decreased efficiency after a long period of operation, sensitivity to variations in operating parameters, and possible expansion of the plume [9]. Among the remedial technologies, in situ chemical oxidation (ISCO) is an effective and potent groundwater remedial option, which is capable of breaking down many contaminants in water. Hydrogen peroxide, Fenton's reagent, permanganate, persulfate, and ozone are common oxidants used to oxidize organic pollutants [10–15]. Among these ISCO oxidants, sodium persulfate ($Na_2S_2O_8$) is a relatively new oxidant, which exhibits some potential advantages for hazardous waste site remediation. The persulfate (peroxydisulfate) anion ($S_2O_8{}^{2-}$) with a high redox potential ($E^0 = 2.01\,V$) (Eq. (1)) [16] can be thermally or chemically activated (Eqs. (2) and (3)) [17,18] to form the sulfate radical ($SO_4{}^{-}\bullet$), a stronger oxidant ($E^0 = 2.4\,V$) (Eq. (4)) [19].

$$S_2O_8{}^{2-} + 2e^- \rightarrow 2SO_4{}^{2-} \quad E^0 = 2.01\,V \tag{1}$$

$$\text{thermal activation}: \quad S_2O_8{}^{2-} + \text{heat} \rightarrow 2SO_4{}^{-}\bullet \tag{2}$$

$$\text{chemical activation}: \quad S_2O_8{}^{2-} + Fe^{2+} \rightarrow SO_4{}^{-}\bullet + Fe^{3+} + SO_4{}^{2-} \tag{3}$$

$$SO_4{}^{-}\bullet + e^- \rightarrow SO_4{}^{2-} \quad E^0 = 2.40\,V \tag{4}$$

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Persulfate can exist longer in the environments than other oxidants (such as O_3 and H_2O_2) resulting in a greater transport distance in the subsurface. In addition, persulfate reacts less with natural organic matters (NOM), and thus, it appears to be more appropriate for the remediation of contaminated aquifers containing high NOM [20–22]. Dose demand of persulfate would be less because of its lower affinity to NOM and its longer retention time in the subsurface. As a result, the cost of using persulfate as the oxidant for contaminant oxidation may be lower compared to other oxidants, making it a promising alternative in site remediation [23].

Permeable reactive barriers (PRBs) have received a great deal of attention as an innovative and cost effective method for in situ remediation of contaminated groundwater. A wide variety of reactive materials have been developed and successfully used in PRBs for the removal of contaminants [24–29]. Although the treatment objectives vary between sites, the one of the most important remedial objects for most of the contaminated sites is to prevent the off-site migration of contaminants. In this study, the concept of PRBs and ISCO using persulfate as the oxidant was combined for the development of oxidation barrier system containing persulfate-releasing materials. Applications of persulfate-releasing materials can be used to form the downgradient oxidation PRBs to oxidize groundwater contaminants migrating into the treatment zone. The persulfate-releasing materials would release persulfate slowly and continuously when they contact groundwater. The released persulfate would then oxidizes petroleum hydrocarbons in situ.

In this study, MTBE and benzene were selected as the target compounds. The main objectives were to (1) conduct the batch experiments to determine the components of the persulfate-releasing materials and optimal composition ratio of the applied components; and (2) perform the column study to evaluate the potential of the designed passive in situ oxidation barrier system on the control of MTBE and benzene plume.

2. Materials and methods

2.1. Chemicals

MTBE (99.97%, TEDIA Company Inc., Fairfield, OH), benzene (99.97%, TEDIA Inc., Fairfield, OH), and sodium persulfate ($Na_2S_2O_8$, min. 99%, Riedel-de Haen, Germany) were reagent grade, and sodium persulfate was used as the oxidant. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$, min. 99.5%, Riedel-de Haen, Germany) was used to activate persulfate with an attempt to continuously supply oxidant. The cement (type I) and sands were obtained from Taiwan Cement Corp. Sands were sieved with a 2 mm sieve to remove large sand particles.

2.2. Batch experiments

Batch experiments were conducted to identify appropriate compositions of the mixture. The persulfate-releasing materials were prepared by blending sodium persulfate, cement, sand, and water together. Cement was used as a binder; persulfate was used as oxidant for in situ oxidant supplement. Regular medium filter sand (grain size ranged from 0.4 to 2 mm) was used to increase the permeability of the mixture. In the batch experiments, sodium persulfate, cement, and sand were introduced into a 500-mL beaker, then distilled water was gradually added to the beaker during mixing to ensure all components were distributed in the beaker evenly. The pasty liquid was poured into a mold (4 cm × 6 cm × 7 cm) before it was solidified. The persulfate-releasing material was then air-dried at 25 °C for 24 h till the cube-shaped persulfate-releasing material (density = 1.8 g (cm³)⁻¹) was formed.
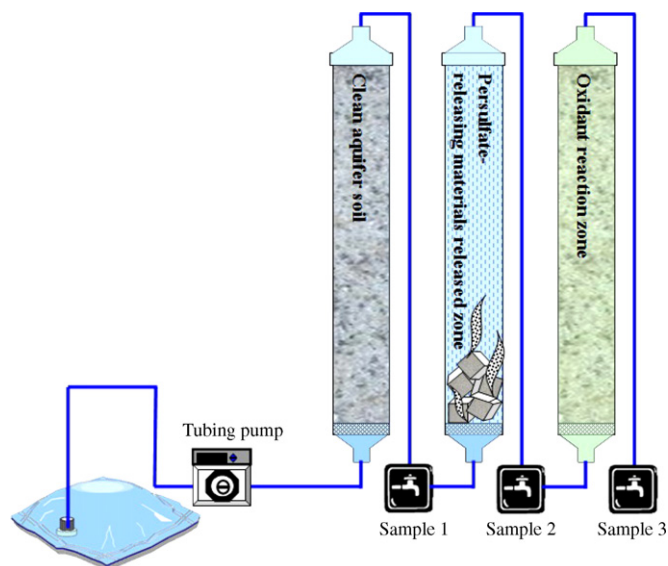

Fig. 1. Schematical diagram of the laboratory persulfate-releasing material barrier system.

Three serum bottles (2 L) were used as batch reactors for the semi-continuous fill-and-draw tests. Each serum bottle containing one persulfate-releasing cube was filled with 1 L distilled water, which was replaced daily. Water samples were collected and analyzed for persulfate concentrations (represented as sodium persulfate concentration equivalent). The averaged persulfate release rate (mg $S_2O_8^{2-}$ per day per g of persulfate-releasing material) from three batch experiments at each time point was then calculated using the results from the tests.

2.3. Column study

The laboratory-scale in situ oxidation barrier system was developed and evaluated using a series of continuous-flow glass columns consisted of the first soil column followed by the persulfate-releasing material column (the second column), and the second soil column (the third glass column). Fig. 1 illustrates the schematic diagram of the laboratory persulfate-releasing barrier system. Each glass column was 30-cm long with an inside diameter of 5 cm. The first column (soil column) was used to represent the upgradient area of the persulfate-releasing material barrier, and it was used to equilibrate the feed solution with the aquifer materials and evaluate the absorbability of MTBE and benzene onto soils without the supplement of oxidant. The second column filled with persulfate-releasing cubes for persulfate supplement was designed to simulate the persulfate-releasing barrier. The third column was used to represent the downgradient area of the persulfate-releasing barrier, and it was applied to evaluate the effectiveness of MTBE and benzene oxidation by the released persulfate. To accelerate the oxidation efficiency, smaller persulfate-releasing cubes (total weight = 432 g, size of each cube = 2 cm × 2 cm × 2 cm) were made and filled in the second column for this column study.

A peristaltic pump (Cole Parmer MasterFlex L/S®) was used to deliver the solution. All tubing materials in contact with solution were made of Teflon. The applied flow rate was approximately 72 mL d⁻¹. Three pore volumes (PVs) of the test solution were flushed though the system at the beginning of the experiment to equilibrate the system. The pH of the feeding solution (site groundwater) was approximately 7.6. Ferrous iron with a concentration of 150 mg/L was added in the filling solution to enhance the persulfate oxidation [21,22]. The MTBE and benzene solution were continuously pumped into the columns with an upflow mode under

Table 1
Characteristics of the tested soils used in the column study.

Parameters	Value	References
pH	7.6	[30] S410.6C
Total chromate oxidizable matter (%)	0.06	[31]
Total organic carbon (%)	0.08	
Cation exchange capacity (mequiv. per 100 g)	3.5	[30] S202.60A
Iron (Fe) (mg kg^{-1})	26.7	[30] S321.63B
Manganese (Mn) (mg kg^{-1})	0.35	[30] S321.63B
Copper (Cu) (mg kg^{-1})	0.02	[30] S321.63B
Cadmium (Cd) (mg kg^{-1})	N.D.	[30] S321.63B
Nickel (Ni) (mg kg^{-1})	0.018	[30] S321.63B
Lead (Pb) (mg kg^{-1})	N.D.	[30] S321.63B
Zinc (Zn) (mg kg^{-1})	0.11	[30] S321.63B
Soil texture	Sandy loam texture	[32]

saturated conditions. The MTBE and benzene concentrations entering the first soil column were approximately 0.5 mg/L and 0.1 mg/L, respectively. The column system was operated for 43.5 PVs in the dark at the ambient temperature of 25 °C. A control experiment was also operated using the three-column system. In this control system, no persulfate-releasing material cubes were placed in the second column. A Student's *t* test statistical analysis method was used to evaluate differences between two contaminant variation curves obtained from different columns. A level of 0.05 was used as the lower bound to determine the significance of the variation.

2.4. Sample analyses

The effluent from each column was analyzed for MTBE, byproducts of MTBE oxidation [tert-butyl formate (TBF) and tert-butyl alcohol (TBA)], benzene, persulfate, sulfate, ferrous, oxidation-reduction potential (ORP), and pH. The soils and groundwater (feed solution) used in this study were collected from a background and uncontaminated area of a petroleum-hydrocarbon spill site. The collected soils were air dried, passed through a 2-mm sieve, and kept refrigerated at 4 °C until analyzed. Tables 1 and 2 present the characteristics of tested soils and groundwater used in the column study.

Water samples were pretreated by a purge and trap system (Tekmer 3000), and analyzed for MTBE, TBF, TBA, and benzene in accordance with US EPA Method 502.2, using a Varian 3800 Gas Chromatograph (GC) equipped with a HP-1 capillary column (30 m × 0.53 mm × 0.5 μm, Agilent Technologies, USA) and flame ionization detector (FID) [30–33]. Sodium persulfate concentration was determined by the colorimetric method [34]. ORP (InLab 501) and pH (InLab 415) were measured using a pH/ORP meter (Metter MP120). Anion ion analysis was performed using an ion chromatography (Dionex 600) equipped with an analytical column (IonPac AS-17, 4 mm × 250 mm, Dionex). Metals were measured using Perkin-Elmer Plasma II Inductively Coupled Plasma-Argon Emission Spectrometer (ICP-AES). The characteristics of soil sam-

Table 2
Groundwater characteristics used in the column study.

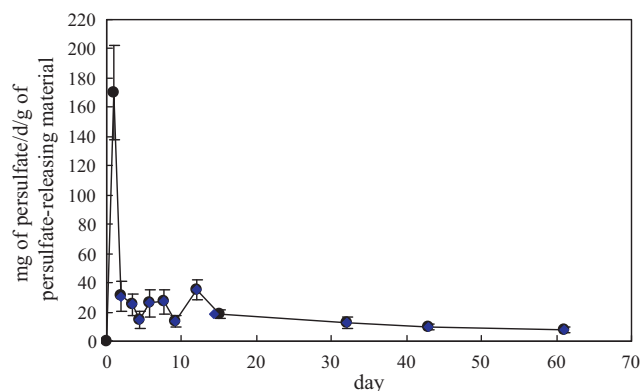| Parameters	Value	References
pH	7.6	[30] W424.52A
Dissolved oxygen (mg O$_2$ L^{-1})	0.48	[30] W455.50C
Alkalinity (mg CaCO$_3$ L^{-1})	113	[30] W449.00B
Chloride (mg Cl$^-$ L^{-1})	194	[30] W415.52B
Nitrite (mg NO$_2^-$ L^{-1})	N.D.	[30] W415.52B
Nitrate (mg NO$_3^-$ L^{-1})	14.6	[30] W415.52B
Phosphate (mg PO$_4^{3-}$ L^{-1})	10.1	[30] W415.52B
Sulfate (mg SO$_4^{2-}$ L^{-1})	26.9	[30] W430.51C
Ferrous (mg Fe^{2+} L^{-1})	0.040	[33] 8146
Total ferric (mg Fe L^{-1})	0.043	[33] 8008

Fig. 2. Variation in persulfate release rate (with error bars) versus release time in the batch experiments. Each measurement (designated as ●) is an average of three persulfate measurements.

ples were analyzed by X-ray powder diffraction (XRD). The XRD analysis was performed with a Siemens D5000 diffractometer using Ni-filtered Cu Kα radiation generated at 30 kV and 10 mA. The XRD patterns were recorded over the range 0–40° (2θ) with a scanning speed of 1.0° (2θ)/min [35].

3. Results and discussions

3.1. Batch experiments

The optimal ratio between sodium persulfate, cement, sand, and water was 1:1:0.16:0.5 by weight was determined in the batch experiments. With this composition ratio, a more stable persulfate release rate was obtained. Fig. 2 presents the variations (with error bar) in persulfate release rate (mg of persulfate per day per g of persulfate-releasing material) versus the operational time in the batch experiments. The calculated persulfate release rate at each time point was the average result from three batch experiments. The composition ratio of the material can be adjusted depending on the designed persulfate release rate and site conditions for future practical application. Significant increase in the persulfate release rate (from 0 to 168.9 mg d^{-1} g^{-1}) was observed during the first operational day, and it dropped rapidly to 31 mg d^{-1} g^{-1} on the second operational day. The persulfate release rate declined slowly for the remainder of the experimental period (from day 2 to day 60) although some flocculation was observed. The persulfate release rate dropped to 19, 10, and 8 mg d^{-1} g^{-1} on day 14, 43, and 60, respectively. The release rate was relatively constant after the significant drop on day 2, and a more stable release rate was observed after 15 days of operation. The designed persulfate-releasing material was able to release persulfate with a steady release rate for a long period of time. Thus, the persulfate-releasing material can be used for the design of in situ oxidation barrier system for practical application.

3.2. Column experiments

In the column experiments, cube-shaped persulfate-releasing materials were placed in the second column. Approximately 43.5 PVs of groundwater solution was pumped into the column system with a flow rate of 72 mL d^{-1}. Influent and effluent samples from each column were collected and analyzed for MTBE, benzene, degradation byproducts, and the third column effluents were collected and analyzed for indicating parameters including persulfate, sulfate, ferrous iron, pH, and ORP.

Fig. 3(a)–(d) presents the variations in ferrous iron, ORP, pH, and concentrations of persulfate and sulfate in water samples col-
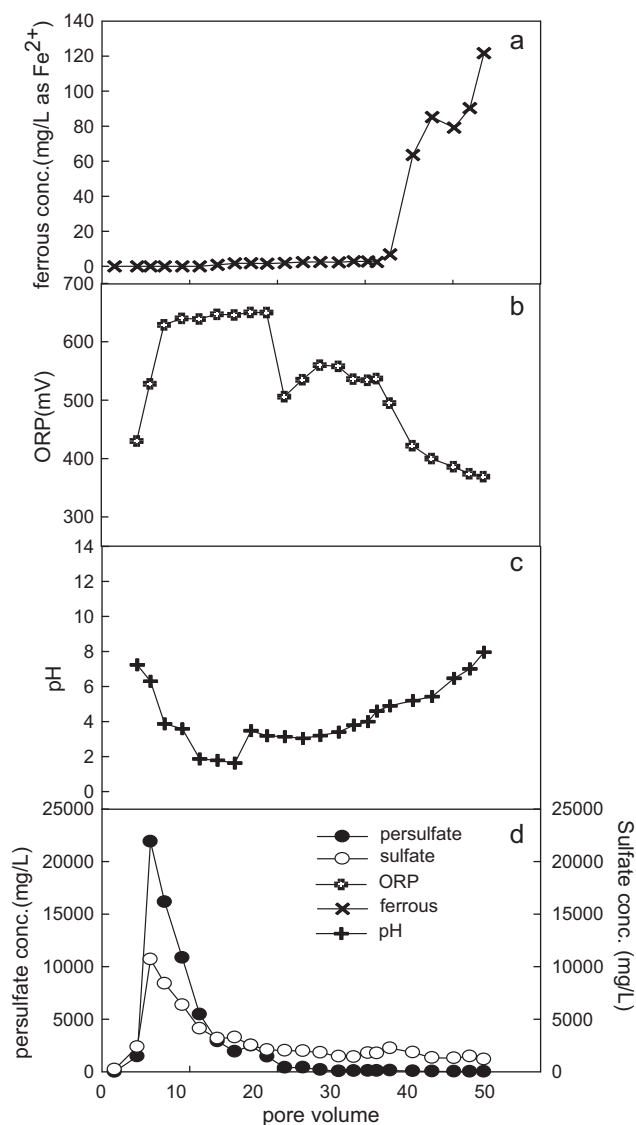
Fig. 3. Variations of in (a) ferrous iron, (b) pH, (c) ORP, and (d) sulfate and persulfate in the effluent from third column.

Fig. 4. Concentrations of MTBE, benzene, and degradation byproducts of MTBE versus PVs in effluents from three columns.

lected from the third column effluents, respectively. Fig. 4 presents the variations in MTBE, benzene, and degradation byproducts of MTBE versus PVs for the effluents collected from all three columns. Results from Fig. 3 show that persulfate and ferrous iron concentrations varied from 0 to 2902 mg/L and 0 to 0.88 mg/L, respectively, when 0–13.2 PVs of groundwater were pumped through the column system. The released persulfate could be activated by ferrous irons, and produce sulfate radicals as reported in Eq. (3) for the oxidation of MTBE and benzene. The decreased ferrous iron concentrations from 150 mg/L to 0.88 mg/L during the groundwater pumping period from 0 to 13.2 PVs indicate that most of the ferrous irons were depleted in the second column. The consumed ferrous irons might be used for the activation of persulfate oxidation process. This can be confirmed by the decrease in MTBE and benzene concentrations within the pumping period from 0 to 13.2 PVs. Because of the low dissolved oxygen (DO) concentration in the influent (0.48 mg/L) (Table 2), decrease in ferrous irons in the first column would not be significant.

Results from Fig. 3 show that the observed persulfate and ferrous concentrations in the third column effluents varied from 2902 to 14 mg/L and 0.88 to 122 mg/L, respectively, when 13.2–43.5 PVs of groundwater were pumped through the column system. Results
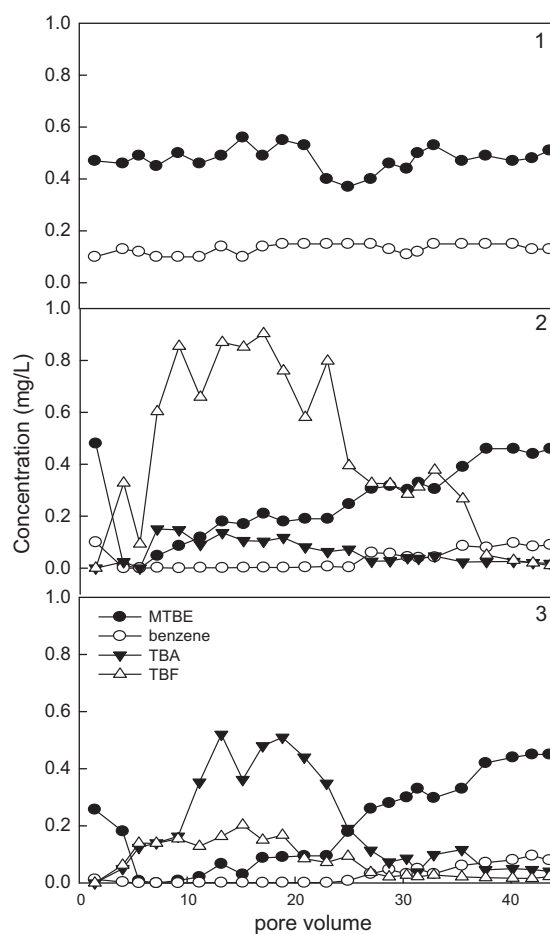
show that the persulfate release pattern reached a stabilized stage after approximately 20 PVs of groundwater pumping. Because of the decreased persulfate concentration, less ferrous irons were required for the activation of persulfate oxidation. Thus, higher ferrous iron concentrations were observed in the third column effluents.

Although ferrous irons are able to activate the persulfate oxidation process, excessive ferrous irons might act as intrinsic scavengers of sulfate radicals (Eq. (5)) [18], and caused the decrease in sulfate radical concentrations. Thus, ferrous iron concentrations should be effectively controlled to minimize the adverse effects of ferrous iron on sulfate radical production [23,36,37]. Researchers also indicate that destruction of sulfate radical might occur in the presence of excess Fe^{2+} due to the rapid conversion of Fe^{2+} to Fe^{3+}, which limited the ultimate oxidizing capability [37,38]. Thus, the decrease in MTBE and benzene oxidation efficiency after 20 PVs of groundwater pumping might be also due to the effects of excess ferrous irons on the limiting of oxidizing capability.

$$Fe^{2+} + SO_4^{-} \bullet \rightarrow Fe^{3+} + SO_4^{2-} \qquad (5)$$

Fig. 3(b) shows the variations in ORP values versus PVs in the third column effluents. Results imply that ORP values increased dramatically from 270 to 650 mV during the pumping period from 1.4 to 18.3 PVs. The increase of the ORP values could be attributed to the production of sulfate radicals, which caused a more oxidized condition [23]. The observed persulfate concentrations and ORP values varied from 1448 to 14 mg/L and 650 to 369 mV, respectively, after 18.8–43.5 PVs of groundwater was pumped through the system. Because of the decreased persulfate production, which caused the

decreased sulfate radical production, decreased ORP value was also observed. Because ORP is an indication of the status of oxidizing environment [22], ORP measurement can be used as an indicator to monitor the fate and transport of persulfate or sulfate radical in the aquifer.

Fig. 3(c) presents the variations in pH measurements versus PVs in the third column effluents. Results show that the pH measurements varied from 7.24 to 1.63 during the pumping period from 1.4 to 15.1 PVs. The results indicate that the application of persulfate oxidation in situ has the potential to lower the groundwater pH owing to the production of sulfate and subsequent sulfuric acid (Eq. (3)). For the field application, pH might not be a serious concern because of the natural soil/groundwater buffer system and dilution capacity [22]. Thus, the increase of observed pH values from 1.63 to 7.96 in the latter part of the operational period (during the pumping period from 15.1 to 43.5 PVs) was attributed to the decreased production of persulfate and subsequent sulfuric acid.

Fig. 3(d) presents the variations in both sulfate and persulfate concentrations versus PVs in the third column effluents. Measurements of persulfate and sulfate concentration varied from 0 to 21,905 mg/L and from 225 to 10,700 mg/L during the pumping period from 1.4 to 5.53 PVs, respectively. In this study, sulfate concentrations were monitored because the variations in sulfate concentrations were affected by persulfate consumption and subsequent decomposition. The observed persulfate and sulfate concentrations varied from 21,950 to 34 mg/L and 10,700 to 1179 mg/L during the pumping period from 5.53 to 43.5 PVs, respectively. The decrease in persulfate and sulfate concentrations indicates the persulfate release rate of the designed persulfate releasing materials reached the latter part of the persulfate release pattern.

Results from Fig. 4 show that insignificant removals of MTBE and benzene were observed in the first column effluents, indicating that the biodegradability of MTBE and benzene was low under anoxic conditions. Results from the second column effluents show that approximately 73% of MTBE and 97% of benzene were removed during the operational periods from 1.4 to 22.9 PVs, and 31% of MTBE and 49% of benzene were removed during the operational periods from 22.9 to 43.5 PVs. This indicates that the released persulfate was able to oxidize significant amount of MTBE and benzene during the persulfate release stage from 1.4 to 22.9 PVs of groundwater pumping. Results from the third column effluents show that approximately 87% of MTBE and 99% of benzene were removed in the third column effluents during the operational periods from 1.4 to 22.9 PVs of groundwater pumping. Moreover, 38% of MTBE and 54% of benzene were removed after 22.9–43.5 PVs of groundwater was pumped through the system. This reveals that the released persulfate from the persulfate-releasing materials had ability to cause the significant oxidation of MTBE and benzene in the following soil column. After the majority of persulfate was released from the persulfate-releasing materials, the oxidation efficiency of MTBE and benzene dropped gradually and a gradual increase in their concentrations was observed. This indicates that MTBE and benzene concentrations corresponded with the amount of released persulfate. Higher persulfate release rate caused higher degradation efficiency of MTBE and benzene. Results from Fig. 4 show that MTBE and benzene dropped from 0.5 and 0.1 mg/L to below 0.01 mg/L, respectively, after 3 PVs of groundwater pumping. Thus, the calculated first-order decay rates for MTBE and benzene were 0.53 and 0.07 d^{-1}, respectively. Higher MTBE decay rate reveals that MTBE is more degradable under the persulfate oxidation process. With sufficient persulfate-releasing materials, MTBE and benzene would be oxidized completely.

Results from other researchers indicate that the increase in persulfate concentrations caused the increased BTEX degradation rates [39,40]. Chen et al. [23] also demonstrated that persulfate

concentration had a linear correlation with MTBE degradation rate. Thus, the persulfate-releasing materials can be designed and applied for the oxidation of petroleum hydrocarbons and control the petroleum-hydrocarbon plume. No significant MTBE and BTEX removal (less than 5%) was observed from the control experiments without the supplement of persulfate-releasing materials (data not shown). This indicates that the released persulfate from the persulfate-releasing materials were able to cause the oxidation of MTBE and benzene in groundwater. Results from the column study show that the replacement of the persulfate-releasing materials is required to maintain desired persulfate release rates and oxidation efficiency. However, the life time of the persulfate-releasing materials can be extended with larger size of cubes. The t-test analysis was performed between two MTBE (or benzene) curves obtained from any two columns. Results from the t-test analysis show that significant variation was observed (at $p < 0.05$) for the two MTBE (or benzene) curves from any two columns. This indicates that the released persulfate caused the oxidation of MTBE and benzene in the second and third columns.

In this study, TBF and TBA, the degradation byproducts of MTBE, were detected in the second and third columns. TBF was first produced after MTBE oxidation followed by the production of TBA (Fig. 4). The observed degradation pathway of MTBE matched with the findings reported by other researchers [23,34,41]. Results show that the production of TBF and TBA corresponded with the depletion of ferrous irons in the second and third columns with ferrous iron concentrations varied from 0 to 0.88 mg/L. This indicates that all of the ferrous irons added in the filling solution had been oxidized, and thus, the observed oxidation efficiencies for MTBE and benzene via the ferrous iron-activated persulfate oxidation reached approximately 83% and 99% in the early stage (0–13.2 PVs) of the oxidation process. The t-test analysis was performed between two TBA (or TBF) curves obtained from the second and third columns. Results from the t-test analysis show that significant variation was
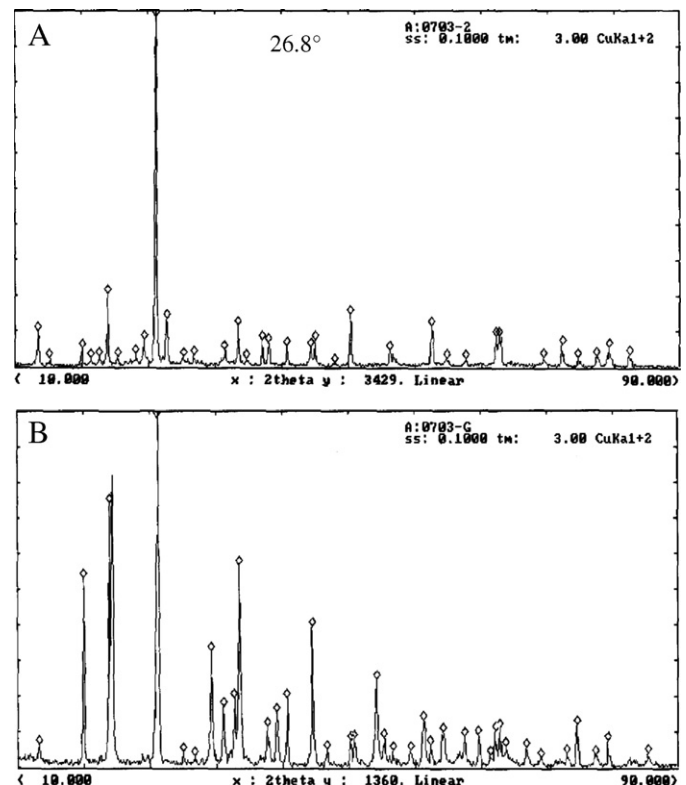

Fig. 5. XRD diffraction patterns of the (a) tested soil and (b) goethite.

observed (at $p < 0.05$) for the two TBA (or TBF) curves from the second and third columns. This indicates that the released persulfate caused the oxidation of MTBE and its byproducts TBA and TBF in the second and third columns.

Fig. 5 shows the XRD diffraction patterns for the test soils and goethite containing Fe. Results from the XRD analysis show that different crystallites in soils were identified in the XRD patterns. The main diffraction peak of the test soils was observed at $2\theta = 26.8$, and thus, soils contained significant amount of goethite. Kong et al. [42] reported that goethite, the naturally occurring iron mineral could be used to catalyze H_2O_2 for organic oxidation. Tsai et al. [43] reported that the basic oxygen furnace slag (BOF slag) contained significant amount of Fe_2O_3 and FeO, and thus, it can be used as the iron supplement continuously. Results from the soil analyses show that the measured amorphous iron was approximately 26.7 mg kg^{-1} of soils. The iron-contained soils might be able to supply iron catalyst to activate the persulfate oxidation process. Thus, in the practical application, other substitutes (e.g., iron-contained intrinsic soils, BOF) can be applied for the supplement of ferrous irons in the field.

4. Conclusions

The passive persulfate-releasing material barrier system was developed in this study to remediate MTBE and benzene-contaminated groundwater. Conclusions of this study are described as follows:

1. Persulfate-releasing material could be prepared from a mixture of sodium persulfate, cement, sand, and water. The composition ratio of the material can be adjusted depending on the designed persulfate release rate and site conditions for future practical application. The designed persulfate-releasing material could release significant amount of persulfate continuously during the operational period.
2. Release of persulfate and occurrence of persulfate oxidation of MTBE and benzene can be verified by the following findings: (1) increased sulfate and persulfate concentrations, (2) decreased MTBE and benzene concentrations in the system, (3) increased MTBE degradation byproducts (TBA and TBF), (4) decreased pH values, and (4) increased ORP measurements. ORP measurement can be used as an indicator to monitor the fate and transport of persulfate or sulfate radical in the aquifer.
3. The proposed persulfate-releasing material barrier has the potential to become a passive and cost-effective remedial alternative to remediate petroleum-hydrocarbon contaminated groundwater in situ.

Acknowledgements

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