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Environmental Engineering Science

Treating Methyl Orange in a Two-Dimensional Flow Tank by *In Situ* Chemical Oxidation Using Slow-Release Persulfate Activated with Zero-Valent Iron

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Abstract

Slow-release oxidant candles are an emerging technology being used to deliver chemical oxidants for groundwater remediation. The objective of this study was to quantify the efficacy of slow-release persulfate (PS) candles to treat an organic contaminant in a long-term and controlled manner. Release characteristics of slow-release PS candles (1:3, wt/wt, paraffin:$Na_2S_2O_8$) with and without zero-valent iron (ZVI) candles (1:4.7, wt/wt, paraffin:Fe^0) under batch conditions were quantified. Batch results showed that PS + ZVI candles initially released a large mass of PS with concentrations reaching 5,000 mg/L, which would be sufficient to treat most prominent organic contaminants. This passive *in situ* technology was able to completely degrade an aqueous solution of methyl orange (MO, 100 mg/L), which served as an organic contaminant surrogate, in 50 h. Using a stacked array of PS + ZVI candles in a saturated sand tank ($70 \times 30 \times 3$ cm) with 2 mL/min flow rate and spatial sampling throughout the tank with time, the PS distribution pattern and zone of influence were determined. Results showed the uneven PS distribution toward the bottom of the tank and MO concentration decreased by 90% in 36 h from both the sampling array and the effluent ports from the two-dimensional tank. A longevity study projected that using this PS + ZVI formula to create candles will negate the need for oxidant replenishment. Results support the use of the slow-release PS + ZVI candles as a practical approach for long-term *in situ* remediation of contaminated aquifers.
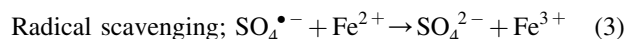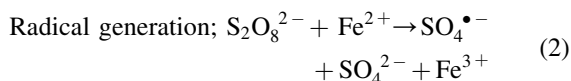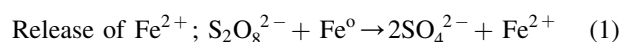
Key words: dye decolorization; *in situ* chemical oxidation; persulfate; slow-release oxidant; zero-valent iron activation

Introduction

PERSULFATE (PS; $S_2O_8{}^{2-}$), A STRONG oxidizing agent ($E^o = +2.01$ V), has been frequently chosen to remediate contaminated groundwater and has proven to have an oxidizing potential to mineralize many organic pollutants (Krembs *et al.*, 2010). Despite its ability to directly accept electrons, $S_2O_8{}^{2-}$ is usually induced to form sulfate radicals ($SO_4{}^{\bullet-}$), which have a higher redox potential of +2.6 V (Eberson, 1982). Activated PS, therefore, can be used to treat threats to groundwater quality such as leaking petroleum from underground storage tanks, primarily (i.e., benzene, toluene, ethylene, and xylene) BTEX, chlorinated benzenes, polycyclic aromatic hydrocarbons (PAHs), and chlorinated solvents. The PS radical ($SO_4{}^{\bullet-}$) has several advantages over other oxidizing agents. For example, $SO_4{}^{\bullet-}$ is more stable than other oxidizing species in the subsurface (Gomathi Devi *et al.*, 2009; Deng *et al.*, 2014); and, unlike permanganate, $SO_4{}^{\bullet-}$ does not leave undesirable precipitates (i.e., MnO_2), which can cause plugging and flow diversion and possibly lead to plume bifurcation or plume fingering (Crimi and Siegrist, 2004). Common activators used to produce $SO_4{}^{\bullet-}$ formation include heat, (Huang *et al.*, 2005; Waldemer *et al.*, 2007; Ghauch *et al.*, 2012), UV (Wang and Liang, 2014), and transition metals (Anipsitakis and Dionysiou, 2003; Teel *et al.*, 2011; Rodriguez *et al.*, 2014). Among these activation methods, using zero-valent iron (Fe^o or ZVI) as the source of ferrous iron (Fe^{2+}) to activate PS [Eqs. (1)–(3)] is widely used since it is relatively economical, environmentally friendly, easy to implement, and effective (Gomathi Devi *et al.*, 2009; Yang *et al.*, 2010; Hussain *et al.*, 2012; Li *et al.*, 2014; Rodriguez *et al.*, 2014).

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Release of Fe^{2+}; $S_2O_8^{2-} + Fe^o \rightarrow 2SO_4^{2-} + Fe^{2+}$ (1)

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

Radical scavenging; $SO_4^{\bullet-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+}$ (3)

A challenge to successfully implementing *in situ* chemical oxidation (ISCO) in aquifers is when the contaminants of interest are present in low permeable zones (LPZ). This obstacle may be overcome by adopting a passive approach where a slow-release oxidant is created in the form of reactive solids and inserted into the well assembly to serve as an oxidant source by providing a slow but sustained release of an oxidant (Dhananjeyan *et al.*, 2000; Ross *et al.*, 2005; Lee and Schwartz 2007a, 2007b; Lee *et al.*, 2008; Liang *et al.*, 2011a, 2011b; Christenson *et al.*, 2012; Kambhu *et al.*, 2012; Rauscher *et al.*, 2012; Liang *et al.*, 2014).

Dhananjeyan *et al.* (2000) was one of the first to create the use of a long-term polymer release device to treat an azo dye under visible light irradiation. The release system included the composition of the copolymer ethylene vinyl acetate and bovine serum, which acts as a carrier for PS. However, this system still requires specialized equipment for the application process (mixing trailer, pumps, hoses, etc.). Liang *et al.* (2011a, 2011b) developed slow-release PS in the form of a PS cement cube (4×6×7 cm) and a PS barrier to evaluate the PS-releasing behavior in column experiments, to quantify their efficacy in removing petroleum hydrocarbons. Their results showed that ∼95–99% of the benzene and 86–92% of methyl tert-butyl ether were removed during the initial stage of the column experiment. Recently, paraffin wax has been used as the releasing material for oxidants such as permanganate (Christenson *et al.*, 2012; Rauscher *et al.*, 2012) and PS (Kambhu *et al.*, 2012; Eyerdom, 2014). Christenson *et al.* (2012) was one of the first researchers to field test the use of slow-release oxidant by inserting it into a trichloroethylene (TCE)-contaminated aquifer at an unregulated landfill. They achieved 67–85% TCE reduction in the first 15 months. Kambhu *et al.* (2012) successfully treated BTEX using ZVI-activated PS-releasing candles.

In this study, an azo dye methyl orange (MO) was selected as a representative organic pollutant in the subsurface. Although ∼15% of dye is lost to the wastewater during dyeing processes (Daneshvar *et al.*, 2006; Inoue *et al.*, 2006; Gomare *et al.*, 2008), dyeing waste deposited in landfills has also built-up and can cause a possible contamination route to groundwater and drinking water supplies (Riu *et al.*, 1998; Sureshvarr *et al.*, 2010). The removal of this contaminant group is of great interest due to its carcinogenic potential, toxicity, and perturbation in aquatic life, as well as recalcitrance in the biodegradation process (Coughlin *et al.*, 1999; Guettai and Ait, 2005; Puvaneswari *et al.*, 2006; Peng *et al.*, 2008). Therefore, the need to oxidize the azo dye into smaller molecules is necessary before the biodegradation process can be employed (Gayathri *et al.*, 2010; Pi *et al.*, 2014). Furthermore, the use of dyes allows visualization of the hydrodynamic behavior plus the radius of influence of the PS + ZVI candles during the transport experiment.

To the best of our knowledge, the degradation of an azo dye using PS + ZVI slow-release candles in a laboratory scale

has not been studied; little effort has been made to demonstrate the PS-releasing pattern and MO decolorization with advection in a two-dimensional tank (2D tank); and there is no report on the longevity of the PS + ZVI candles. Therefore, this research attempts to close these knowledge gaps and to expand on the works reported by Kambhu *et al.* (2012).

Materials and Methods

Chemicals

MO (Ajax Finechem; CAS 547-58-0) was selected as a target compound; it has several synonyms such as *p*(*p*-dimethyl amino phenyl azo)-benzene sulfonate of sodium, orange III, and gold orange (Supplementary Table S1). Sodium persulfate ($Na_2S_2O_8$, reagent grade ≥98%; Panreac) and paraffin (Suksapanpanit) were used to make a slow-release candle. Iron powder (Ajax Finechem) was used as the activator iron species. Sodium hydrogen carbonate ($NaHCO_3$), potassium iodide (KI), and potassium chloride (KCl) were purchased from Carlo Erba. Ottawa sand (Humboldt) was used as a packing material in transport experiments. All stock solutions were prepared in deionized water.

Slow-release PS + ZVI candles

Slow-release PS candles were manufactured for laboratory experiments and produced in batches by mixing solid paraffin with $Na_2S_2O_8$ (Supplementary Fig. S1). The paraffin wax of 5 g was placed into a ceramic bowl on a hot plate adjusted to 65°C. Once the wax had melted, various amounts of $Na_2S_2O_8$ ranging from 8.75 to 17.5 g were quickly added to the wax. Each mixture was slowly stirred by a glass rod until all PS particles had blended with the wax and the mixture texture had reached a milkshake-like consistency. The mixture was then poured into a cylindrical mold and tapped gently to eliminate air pockets. The candles were allowed to cool in their molds for 5 min and then removed. Candles shaped as cylinders were 1.0 cm in diameter and 3.0 cm in length. The final ratio by mass of paraffin to PS ranged from 1:1.75 to 1:3.5 (wt/wt). Individual PS candles were weighed for each experiment and maintained at ∼5 g.

A slow-release ZVI candle was made in the same manner as the PS candles by mixing melted paraffin and ZVI in a 1:4.7 ratio (23.5 g ZVI and 5 g paraffin wax) (Supplementary Fig. S1). ZVI candles were trimmed to a weight of either 1.25 or 2.5 g. ZVI candles were smaller and of lighter weight (i.e., 1.25 and 2.5 g) compared to the PS candles (i.e., 5 g). When control candles were needed, the candles were made in the same mold, using the same proportions, where KCl replaced the PS (Rauscher *et al.*, 2012) and the procedures used to make the PS candles were followed. Individual control candle weights were also maintained at ∼5 g.

Batch experiments

The first experiment was to determine the optimum ratio of PS, paraffin, and the ZVI. The criteria used to select the most suitable mixture are that the slow-release oxidant should provide a continuous supply of PS and maintain its cylindrical shape in the wells. The second experiment was designed to determine the candle lifetime. The final batch test was conducted to compare
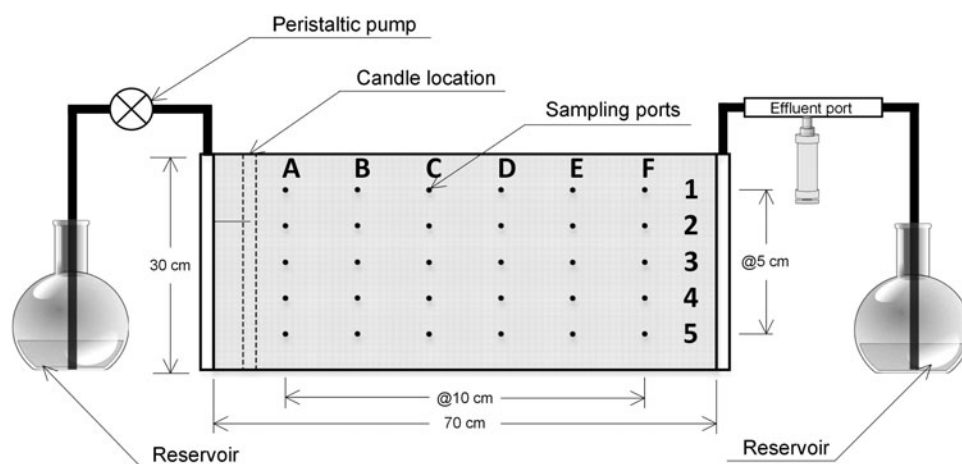
FIG. 1. Schematic diagram of two-dimensional (2D) sand dimensions.

the kinetics of MO destruction from the pairing of PS candles with different lengths of ZVI candles.

Chemical release rates from PS + ZVI candles. To quantify the PS release rates, batch experiments were conducted with 3.0 cm lengths of different proportions of candles. Each candle was placed in a separate Erlenmeyer flask filled with 500 mL distilled water, which was maintained at room temperature. Candles were adjusted so that they were completely immersed in the water. Each treatment mixture of candle was replicated thrice. Immediately before sampling, candles were removed and the solutions were gently mixed by swirling. Aliquots were withdrawn at selected times, and the PS concentration was measured colorimetrically using iodine at a wavelength of 450 nm (Kambhu *et al.*, 2012) with a Spectronic 21 spectrophotometer (Milton Roy). Samples were diluted when necessary to fall within the linear range of the PS standard curve.

The effect of the ZVI candles on PS dissolution rates was also quantified to represent the two candle system (PS and activator). Before placing the PS and ZVI candles in the Erlenmeyer flask filled with 500 mL distilled water, they were joined together with a layer of pure wax. Temporal samples were taken to measure PS release rates.

PS + ZVI candle longevity study. To quantify PS release rates and predict the candle lifetime, a PS + ZVI candle that was 1.7 cm in length and 4.7 cm in diameter was created. This joined candle was sealed on the flat top and bottom with a layer of pure paraffin to ensure the radial diffusion direction of PS. The proportions of PS, ZVI, and paraffin in the candles were chosen from the results based on previous experiments. Candles were placed in 25 L polyethylene carboy containing 20 L deionized water. Solution samples were periodically collected to quantify the PS concentration over 10 weeks. An empirical function used to calculate the concentration ratio (C_r) to characterize release of PS was as follows:

$$C_r = \frac{CV}{M} \quad (4)$$

where C and V are concentration and volume at predicted time; M is the initial mass of PS in the candle. C_r was plotted and fitted using nonlinear regression to a two-parameter power function using the SigmaPlot scientific analysis and

graphing software. The fitted equation was used to characterize and predict the release of PS from the candles (Christenson *et al.*, 2012).

MO degradation kinetics. To determine the kinetic degradation of MO by ZVI-activated PS, an aqueous solution of 500 mL of 100 mg/L MO was treated with a selected mixture of PS candle and ZVI candle. Batch experiments were run in triplicate. Samples were periodically collected through a pipette every hour for the first 6 h and approximately every 6 h for the remainder of the experiment. Candles were removed, and the solutions were gently swirled before each sampling. When needed, samples were diluted with distilled water before analysis at the isosbestic wavelength of MO at 464 nm (Parthasarathy and Sanghi, 1958; Al-Qaradawi and Salman, 2002).

Transport experiments

Construction of 2D tank. Transport experiments were conducted to investigate the effectiveness of selected PS + ZVI candles for contaminant removal in the specifically designed rectangular acrylic tank (2D tank) consisting of three chambers.
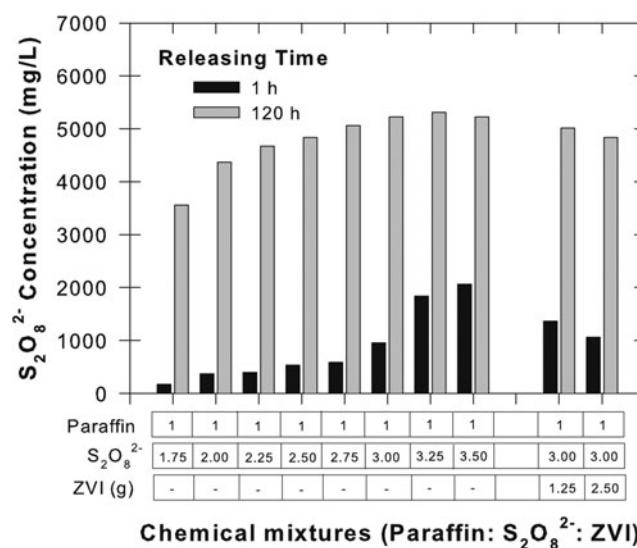

FIG. 2. Persulfate (PS) release characteristics from PS candles and PS + zero-valent iron (ZVI) candles at 1 and 120 h.

The main chamber housed the transmissive zone, which was packed with Ottawa sand, and had internal dimensions of $70 \times 30 \times 3$ cm (Fig. 1). The other two chambers were upgradient and downgradient of the main chamber. Titanium mesh was used in the inlet and main chambers to prevent clogging of the array of tank openings between chambers and to contain the sand. The 2D tank was equipped with a grid of 30 septa-sealed sampling ports on the front, spaced 10 cm vertically and 5 cm horizontally, and arranged in a 5 by 6 array (Fig. 1). The packed systems had a total pore volume (PV) of ~ 2.5 L. Liquid flow was controlled using a peristaltic pump that provided a constant flow rate of 2 mL/min from the 5 L Erlenmeyer flask as a solution reservoir. The effluent connection was constructed with the separate sampling port before the solution was flooded to the final reservoir (Fig. 1).

The remediation experiment. To determine the radius of influence of the PS + ZVI candles when the hydraulic gradient was present, a well assembly was placed 5 cm upgradient from the first sampling column (Fig. 1). A well was fabricated using a 1.6 cm id polypropylene tube slotted along the length of the tube. Slow-released candles were slowly inserted into the well assembly before the start of the experiments. Seven pairs of PS + ZVI candles were aligned vertically by attaching each one with a thin layer of paraffin to hold each candle, such that the PS could only diffuse by radial influence. Two transport experiments, which differed in the initial flooding solution, were performed separately. The experiments were either flooded with deionized water water or MO solution (100 mg/L) with a consistent flow rate for at least 2 PV to confirm the flow consistency. One mL samples were collected periodically at each sampling point array using a 3 mL syringe connected with a 21G needle. Samples from the first experiment were measured colorimetrically for PS, while when MO was used, samples were measured for MO concentration. At the same sampling time, samples were also taken at the effluent outlet to quantify total removal (%).

Results and Discussion

Chemical release rates from PS + ZVI candles

The release of the PS concentration from a series of tests with varied mass ratios of $Na_2S_2O_8$ and paraffin was carried out in an attempt to select the most suitable mixture for the entire study. We tested the release rate for 120 h and reported results as short-term release (i.e., 0–1 h) and long-term release (i.e., 24–120 h) (Fig. 2; Supplementary Fig. S2; Supplementary Table S2). In the initial phase, only three mixtures (Paraffin:PS: 1:3.00, 1:3.25, and 1:3.50) showed distinct differences in PS release rates. By doubling the mass of PS in the formulation (1:3.50 vs. 1:1.75), we observed approximately a 10-fold higher PS concentration (Fig. 2; Supplementary Fig. S2A). In this study, a large flux of oxidant released from the candles was initially observed and similar results have been reported by other researchers (Dhananjeyan *et al.*, 2000; Kang *et al.*, 2004; Lee and Schwartz, 2007a, 2007b). After this initial release, the PS concentrations were much more consistent ($\sim t > 48$ h). This finding was similar to Liang *et al.* (2011a) who found that the release rate of PS dropped rapidly within the first 6 days (i.e., 144 h) and then declined for the remainder of their experiment (i.e., 50 days). While the initial PS concentration varied
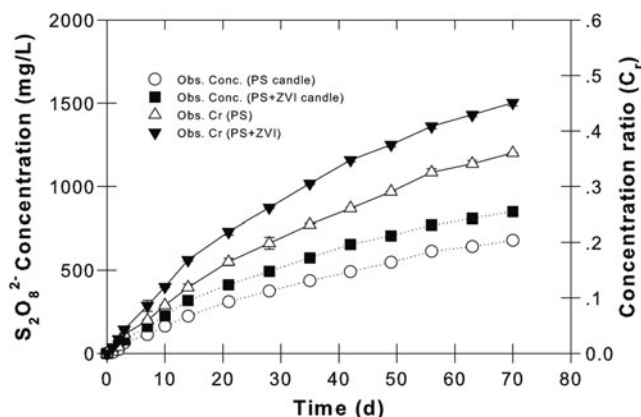

FIG. 3. Observed PS concentrations and concentration ratio (C_r) in water.

depending on the amount of $Na_2S_2O_8$, apart from the lowest mixture of PS (i.e., 1:175), all mixtures were in the range of 4,000–5,000 mg/L at 120 h (Fig. 2). Several researchers have demonstrated that these concentrations would be sufficient to remove most prominent organic contaminants in the aqueous solution (Huang *et al.*, 2005; Tsitonaki *et al.*, 2010; Petri *et al.*, 2011; Xu *et al.*, 2012).

To successfully create a reactive barrier to treat contaminated groundwater, the slow-release oxidant should provide a continuous supply of PS and maintain its cylindrical shape in the wells. Although the highest mixture of 1:3.50 was able to release sufficient concentration, due to higher PS mass, the candle lost its shape after releasing PS. This could impede removal of the spent candles from wells. By contrast, the higher paraffin composition encapsulated the $Na_2S_2O_8$ granules and prevented complete release of PS (Fig. 2). Therefore, we selected the 1:3.0 mixtures for further study.

Once the mixture of paraffin and PS was finalized, we further evaluated the suitable mixture of the activator candle (i.e., ZVI) with PS candles. As PS was released from the top candle in the perpendicular-to-the-axis direction, it slowly reacted with the released ZVI from the bottom candle. Since
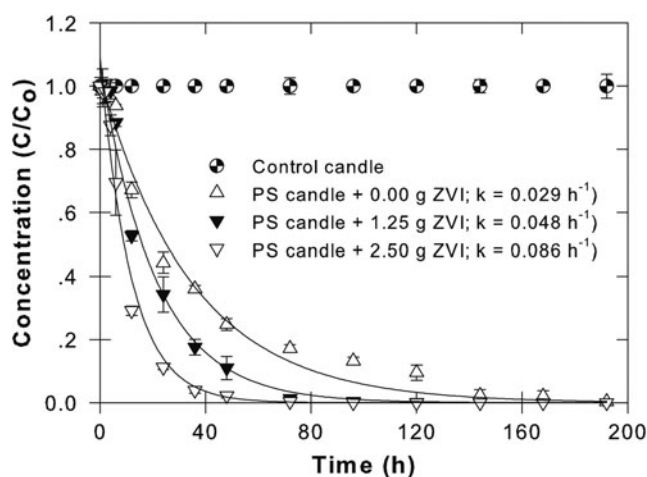

FIG. 4. Temporal changes in methyl orange (MO) concentration (100 mg/L) when treated with PS and varying mass of ZVI candles.

the iron activation process involves both sulfate radical generation [Eq. (2)] and radical scavenging [Eq. (3)], the optimum amount of ZVI is important to avoid excess scavenging (Tsitonaki *et al.*, 2010; Liang *et al.*, 2011; Li *et al.*, 2014). To produce $SO_4^{\bullet-}$, an equal amount of PS and ZVI for one candle is unnecessary. Previous research has found that an excess amount of Fe^{2+} could reduce $SO_4^{\bullet-}$ from the solution as it acts as an intrinsic scavenger (Kolthoff and Miller, 1951; Anipsitakis and Dionysiou, 2003; Teel *et al.*, 2011). In addition, the concentration of Fe^{2+} of <250 mg/L was sufficient for the PS activation; otherwise it would compete with $SO_4^{\bullet-}$ for target contaminants (Block *et al.*, 2004; Chen *et al.*, 2009).

To determine the appropriate mass of ZVI candle to use, a PS candle of 1:3.0 mixtures was paired with two different ZVI candle weights (1.25, 2.50 g). This ZVI mass reflects 25% and 50% of the PS candle weight (i.e., 5 g). Results showed that the 2.50 g ZVI+PS candle pairing released a twofold increase in PS concentration over the PS only candle at 0.25 h (Supplementary Fig. S2B). This is likely due to the fact that ZVI not only activated PS in the solution but also activated PS at the candle surface to generate $SO_4^{\bullet-}$. When PS is released from the candles, it leaves tiny voids, which later serve as activating sites for subsequent PS particles, causing PS embedded in the nearby surface of the wax to be released rapidly into solution. While the initial release rate of PS was affected by ZVI, the concentration of PS observed at 120 h was similar between the 2.5 and 0 g ZVI candle (Fig. 2). Thus, we confirmed that the ZVI candle had no effect on the PS release at 120 h after initiation.

Longevity of PS candles

To take advantage of the merits of the slow-release candles for field application, the performance of the PS+ZVI candles must first be characterized. The results from the longevity experiment showed that the PS concentration reached 850 mg/L within 70 days (Fig. 3). This longer timeframe, compared to the earlier batch experiment, was due to the larger experimental setup (~ 20 L). We used C_r data from our longevity experiment and fit the dissolution data to a power function to extrapolate data from the 70-day experiment (Kang *et al.*, 2004). Results showed that, with our candle size and formulation, the PS+ZVI candles would possibly release most PS to the subsurface (i.e., $C_r = 1.0$) at 210, and 270 days for the PS candle (Supplementary Fig. S3). Comparing our longevity study of PS with that of slow-release permanganate (Christenson *et al.*, 2012), we found a similar pattern of oxidant release. However, the release ratios in both results are not proportional because both the candle system and oxidant mass differ. Besides solid paraffin wax, a mixture of cement/sand/water (Liang *et al.*, 2011a) and stearic acid (Yuan *et al.*, 2013) had also been used to bind these oxidant granules. Although different materials were selected, all results indicated that these release materials would be able to release oxidant for a long time.

Treatment of MO by PS+ZVI candles

Two questions regarding using the selected PS candle (1:3.0) for treating contaminant are as follows: what ratio of PS and ZVI should be used and will this dual candle

TABLE 1. TEMPORAL CHANGES IN pH OF TREATMENT SOLUTIONS UNDER BATCH CONDITIONS

| | pH | pH following treatment of methyl orange | | | | | | | | | |
| | 0 min | Time (min) | | | | | | | | | |
Treatment		15	30	45	60	90	120	180	270	360	360
PS slow-release experiment											
Control (KCl)	6.70	7.48 (0.03)	7.03 (0.06)	7.12 (0.07)	6.92 (0.11)	7.12 (0.08)	7.10 (0.07)	7.08 (0.06)	6.93 (0.05)	6.54 (0.03)	6.11 (0.03)
MO+PS	6.70	3.55 (0.09)	3.42 (0.10)	3.34 (0.09)	3.30 (0.11)	3.26 (0.11)	3.21 (0.09)	3.16 (0.10)	3.09 (0.09)	3.03 (0.11)	2.83 (0.10)
MO+ZVI	6.70	5.92 (0.02)	5.98 (0.01)	6.09 (0.05)	5.76 (0.11)	5.97 (0.02)	5.94 (0.03)	5.89 (0.02)	5.96 (0.15)	5.80 (0.13)	5.77 (0.19)
MO+PS+ZVI	6.70	3.37 (0.05)	3.28 (0.09)	3.17 (0.08)	3.12 (0.03)	3.05 (0.01)	2.94 (0.03)	2.86 (0.05)	2.70 (0.02)	2.55 (0.05)	2.33 (0.04)

Values in parenthesis are standard deviation.
KCl, potassium chloride; PS, persulfate; ZVI, zero-valent iron; MO, methyl orange.

effectively treat MO-contaminated solution? In an attempt to answer these questions, MO degradation by a PS candle with a varied mass of ZVI was tested. The results showed an increase in first-order degradation with increasing mass of ZVI ($k = 0.029 \, h^{-1}$, 0 g ZVI; $k = 0.048 \, h^{-1}$, 1.25 g ZVI; $k = 0.086 \, h^{-1}$, 2.50 g ZVI) (Fig. 4). PS alone reduced the MO concentration from 100 mg/L to nearly zero in 200 h (Fig. 4), while with PS + ZVI candles, MO degradation was completed within 50 h for 2.50 g ZVI and within 90 h for 1.25 g ZVI. These results confirmed that if PS candles with 2.50 g ZVI candles generate and sustain PS concentration $\geq 4,000$ mg/L at 50 h (Supplementary Fig. S2B), most organic contaminant degradation would be possible within the chemically active zone (Huang *et al.*, 2005; Tsitonaki *et al.*, 2010; Petri *et al.*, 2011; Xu *et al.*, 2012).

Given that the PS + ZVI candles released a large pulse of PS immediately after placing the candles in the solution (Supplementary Fig. S2B), the MO concentration did not dramatically decrease as expected. Rather, the MO concentration slowly decreased and followed a first-order degradation rate after 3 h (Fig. 4). We first suspected that the adsorption of MO on the paraffin may have been responsible, so we conducted a parallel experiment using a control candle with KCl instead of PS. The result showed no reduction in the MO concentration (Fig. 4). Similar work by Rauscher *et al.* (2012) and Kambhu *et al.* (2012) using paraffin as the mixture media reported mixed results on chemical adsorption. Neither adsorption of PS nor benzene by paraffin was observed by Kambhu *et al.* (2012). In contrast, Rauscher *et al.* (2012) found that paraffin was responsible for the adsorption of phenanthrene onto the permanganate candle surface, which later desorbed as a degradation product.

Temporal changes in pH were monitored for 360 h (Table 1). The results showed that the pH measurements dropped from 6.7 to 2.8 for the treatment of MO with PS candles and to pH 2.3 for the treatment of MO with PS + ZVI candles. This reduction in pH likely resulted from the production of sulfate and, subsequently, sulfuric acid (House, 1962; Petri

et al., 2011). In contrast, an increase in the pH from 6.7 to 7.1 was observed when PS and ZVI became limited (data not shown). The differences here were from the continual supply of PS ions and ZVI, which is the main advantage of using slow-release candles. The solution, therefore, received an excess amount of $SO_4^{\bullet-}$, thereby continually reducing the solution pH. This is attributed to the continued generation of HSO_4^- with the progress of the reaction (Liang and Lai, 2008). Given that a pH decrease usually occurs following PS + ZVI treatment, the intrinsic groundwater buffering system and dilution capacity would eventually adjust the overall pH to normal (ITRC, 2005).

In the MO and PS + ZVI candle system, MO decolorization was observed during the degradation experiment. It was proposed that the MO decolorization was a direct result of the destruction of the azo bond ($-N=N-$) in the chromophore of the azo dyes by $SO_4^{\bullet-}$ (Gomathi Devi *et al.*, 2009; Li *et al.*, 2014; Rodriguez *et al.*, 2014). Another possible mechanism is from the $SO_4^{\bullet-}$ induction of the formation of other active species, that is, hydroxyl radicals ($OH^\bullet$) as shown in Equation (5) (Waldemer *et al.*, 2007):

$$OH^\bullet \text{ generation; } SO_4^{\bullet-} + H_2O \rightarrow OH^\bullet + SO_4^{2-} + H^+ \quad (5)$$
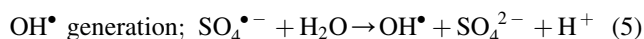
The $OH^\bullet$ generation would also cause a decrease in solution pH during treatment (Table 1). Although this reaction is slow, past research has shown that the MO azo bond started to break 25 min after starting the experiment (Naderpour *et al.*, 2013). Therefore, we proposed the breakage of $-N=N-$ in MO molecules by ZVI-activated PS as similar to the breakage of the $-N=N-$ bond of orange G, one of the prominent azo dyes (Rodriguez *et al.*, 2014).

The 2D tank experiment

In the second part of this study, 2D tank experiments were conducted to investigate the following: (1) the PS release pattern in the 2D tank with advection, and (2) the removal

FIG. 5. Changes in spatial MO concentration in 2D tank when treated with PS + ZVI candles at $T = 2$, 6, 12, 24, and 36 h.
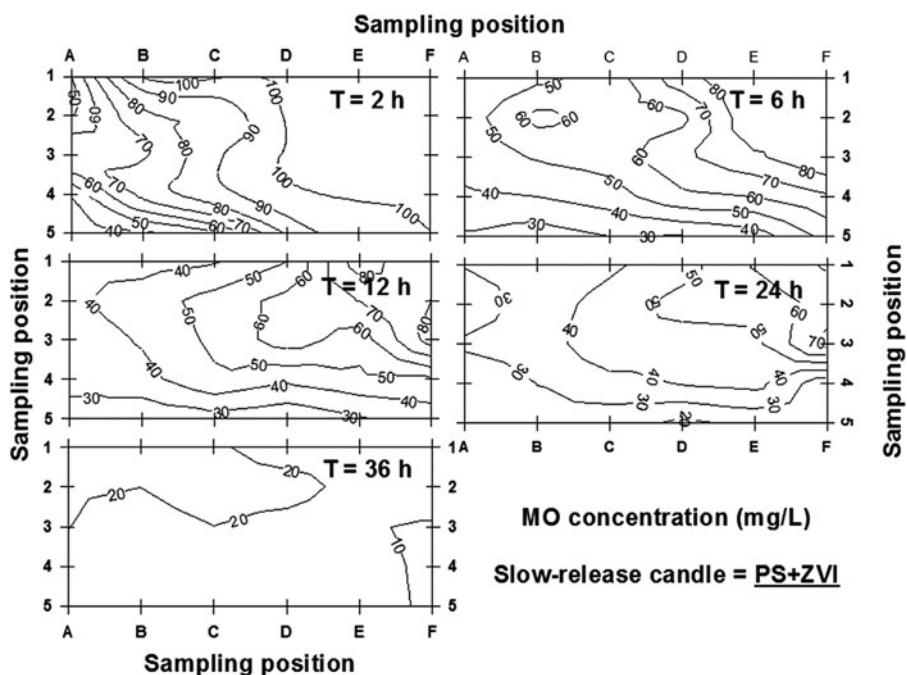
percentage of MO and the delineation of MO degradation in the tank. PS and ZVI candles were sealed on top of each other, which imitated how they would be inserted into an aquifer (Supplementary Fig. S4). PS concentrations from any sampling points in the 2D tank (i.e., A1 to F5, Supplementary Fig. S4) were representative of the PS plume at the time of collection. The PS concentration observed from the tank was highest at 8,000 mg/L in the first 2 h and slowly decreased as the fresh water came in. These large initial amounts of PS in the initial phase were in agreement with the PS release in the batch experiment (Supplementary Fig. S2B). At 72 h, PS concentration from 2,000 to 7,000 mg/L was observed throughout the 2D tank. The uneven PS distribution can be explained by the gaps between the well casting and the outer surface of the candles and that the oxidant releases only downward in the tank through density-driven advection. These release patterns also manifested that the contaminant embedded under the candle location would likely be first affected and the treatment zone increased vertically.

To qualitatively visualize the MO decolorizing pattern, we saturated a 2D tank with MO and analyzed the temporal changes in color disappearance following treatment with the PS + ZVI candles. Using a spatial array of sampling ports, in 2 h, MO adjacent to the candle location had decreased ∼45%, and in 24 h, ∼75% of MO had been removed at the bottom of the tank (Fig. 5). By 36 h, >85% had been removed from most of the tank, except the top two rows of the tank where between 70% and 80% removal was recorded (Fig. 5). Since we did not apply any agitation and had less control on the preferential flow compared to the batch experiment, an uneven pattern of hydrodynamic behavior in the 2D tank was expected.

To quantify the overall removal percentage, the effluent samples were collected from the effluent port (Fig. 1). We only recovered ∼50% after 36 h of flushing (data not shown). The MO concentration in the outflow water was higher than in the water samples collected from the sampling ports alongside the 2D tank, suggesting that MO was not completely degraded from the slow release in the tank. This is not uncommon as it is often difficult to quantify treatment differences in short finite-length tanks (Lee and Schwartz, 2007a; Chokejaroenrat *et al.*, 2013). MO is pushed out while the $SO_4^{\bullet-}$ is dissolved in, and the area for interaction between the $SO_4^{\bullet-}$ and MO is generally confined to the interface between the oxidant and the contaminant plume. To evaluate the efficacy of using PS + ZVI candle, we selectively collected samples from the effluent reservoir. Approximately 90% of MO removal was observed within 120 h, suggesting a beneficial use of PS + ZVI in the form of a slow-release oxidant. This reveals that the release of PS from the PS + ZVI candles was able to oxidize MO effectively in the downgradient area. Therefore, the candles can also be used as a containment of organic contaminant plume.

Our experimental conditions included a flow rate of 2 mL/min, while the others had no flow rate (Kambhu *et al.*, 2012). In addition, in our case, the density-driven flow was minor compared with advection. Given that natural groundwater flow is slower than under our experimental conditions, chemical oxidants may bypass the contaminated zone resided in LPZ during treatment. Once the porous zones surrounding a LPZ are treated, contaminants diffuse out of the LPZ and contaminate flowing water (Bass *et al.*, 2000; McGuire *et al.*,

2006). To overcome both a density-driven oxidant and to ensure uniformity of oxidant throughout the treatment zone, the PS concentration should remain high and continuously be released. Therefore, with time, the PS + ZVI candles would be capable of creating larger treatment zones in the aquifer. However, the efficiency of ZVI-activated PS toward other organic contaminants depends on the competition kinetic between contaminants and reactive species that may be resided in the soil and groundwater system. To effectively use PS + ZVI candles in the subsurface, the candles were needed to be optimized for the hydrologic and environmental conditions of the target treatment zone before extrapolate batch treatability studies for practical application.

Conclusion

Slow-release PS + ZVI candles were encapsulated in paraffin and tested under batch and transport conditions to evaluate the sustainable release of activated PS and its ability to degrade the test pollutant, MO, in solution. The composition ratio of release material and PS was selected at 1:3.0 by weight in our study and can be adjusted depending on the designed PS release rate and field conditions. Differing amounts of ZVI as an activator were also tested. Early in the experiment, the initial release rate was high and then it slowed, but was sustained with time. The degradation results showed that the activated PS was able to degrade ∼98% of the MO in 48 h under the batch condition, while 90% removal was observed within 120 h in the 2D tank. Although a number of factors associated with the subsurface hydrogeology of the contaminated site must first be considered before using slow-release PS + ZVI candles under field conditions, our laboratory-scale results supported that slow-release PS + ZVI candles could be used as an alternative means for long-term *in situ* remediation of contaminated aquifers.

Author Disclosure Statement

No competing financial interests exist.

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