Evaluation of persulfate oxidative wet scrubber for removing BTEX gases

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ABSTRACT

Soil vapor extraction (SVE) coupled with air sparging of groundwater is a method commonly used to remediate soil and groundwater contaminated with volatile organic petroleum contaminants such as gasoline. These hazardous contaminants are mainly attributable to the compounds—benzene, toluene, ethylbenzene, and xylenes (known collectively as BTEX). Exhaust gas from SVE may contain BTEX, and therefore must be treated before being discharged. This study evaluated the use of iron-activated persulfate chemical oxidation in conjunction with a wet scrubbing system, i.e., a persulfate oxidative scrubber (POS) system, to destroy BTEX gases. The persulfate anions can be activated by citric acid (CA) chelated Fe^{2+} to generate sulfate radicals ($SO_4^{\bullet-}$, $E^\circ = 2.4\,V$), which may rapidly degrade BTEX in the aqueous phase and result in continuous destruction of the BTEX gases. The results show that persulfate activation occurred as a result of continuous addition of the citric acid chelated Fe^{2+} activator, which readily oxidized the dissolved BTEX. Based on initial results from the aqueous phase, a suitable Fe^{2+}/CA molar ratio of 5/3 was determined and used to initiate activation in the subsequent POS system tests. In the POS system, using persulfate as a scrubber solution and with activation by injecting Fe^{2+}/CA activators under two testing conditions, varying iron concentrations and pumping rates, resulted in an approximate 50% removal of BTEX gases. During the course of the tests which in corporate activation, a complete destruction of BTEX was achieved in the aqueous phase. It is noted that no removal of BTEX occurred in the control tests which did not include activation. The results of this study would serve as a reference for future studies into the practical chemical oxidation of waste gas streams.

1. Introduction

Leaks have commonly occurred at the underground storage tanks, which contain petroleum products such as gasoline. The hazards associated with gasoline are mainly attributable to the BTEX compounds—benzene, toluene, ethylbenzene, and xylenes (BTEX). Exposure to the BTEX compounds can cause neurological damage [1]. Benzene is especially toxic and is categorized as a carcinogen by the US National Toxicology Program. Ethylbenzene is also possibly carcinogenic to humans [1]. Techniques such as soil vapor extraction (SVE) [2] and in-situ air sparging (IAS) are commonly used to remediate BTEX contamination [3]. The SVE process primarily addresses unsaturated zones, while IAS is used on saturated zones. Due to the specific characteristics of BTEX such as low water solubilities (1780, 515, 152, 170 ppm, respectively)

and high vapor pressures (76, 22, 7, 7 mmHg, respectively) [4], the SVE/IAS air flow results in desorption of BTEX from the surface of the soil particles and volatilization from the dissolved or pure phases of BTEX. Therefore, BTEX is removed as vapors that typically require additional exhaust gas treatment before being discharged into the atmosphere. Traditional methods capable of treating BTEX exhaust gases using SVE remediation systems such as activated carbon adsorption, thermal oxidation, biofiltration and internal combustion engineering, have inherent limitations such as high costs for energy and operation, sensitivity to variations in operating parameters and secondary pollution [5]. Therefore, selection of appropriate exhaust gas treatment technologies for specific site conditions necessitates identifying the principles of the various technologies and their limitations based on site-specific waste-gas attributes, treatment goals and costs.

A wet scrubber, also referred to as a gas absorption process, is one of the most widespread air pollutant control devices used to clean exhaust contaminant vapors by dissolving and/or mixing the contaminant into a liquid medium. Additionally, chemical oxida-

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tion of the waste gas stream through any combination of one or more types of gas–gas, gas–liquid, or gas–solid contacts in a wet scrubber is usually a preferred technique [6]. Due to the fact that most volatile organic compounds (VOCs) of interest (e.g., BTEX) have low water solubility characteristics, the wet scrubber method is rarely used as the primary treatment method for site remediation of exhaust gases at a contaminated site [5]. However, when using this wet scrubber technology, chemical oxidizing agents such as hydrogen peroxide [7] and chlorine dioxide [8] have been used as absorbent solutions to promote rapid oxidation of contaminants in the aqueous phase, which then increases absorption and destruction efficiency in the scrubber. The dissolution of contaminants such as BTEX into the oxidant solution can be illustrated by the conventional mass transfer concept:
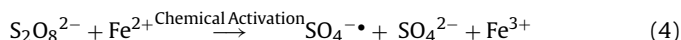
$$\frac{dC}{dt} = K(C_s - C) \tag{1}$$

where dC/dt is the rate of contaminant dissolution ($mg\,L^{-1}\,min^{-1}$), K is the mass transfer coefficient (min^{-1}), C_s is the contaminant water solubility ($mg\,L^{-1}$) and C is the steady-state contaminant concentration in water ($mg\,L^{-1}$).

Through oxidation in the aqueous phase, C is maintained at a minimum (e.g., zero concentration, once the contaminants have been dissolved and then rapidly oxidized) and therefore, the concentration gradient ($C_s - C$) is kept at a maximum. As a result, contaminants can be continuously dissolved into the solution. It should be noted that the mass transfer coefficient (K) is associated with gas and liquid phases transfer and the liquid phase transfer is a limiting process due to natural characteristics of low water solubilities and high vapor pressures of VOCs. Lawson and Adams [7] indicated that chemical oxidation in the scrubbing liquid would chemically remove the absorbed compound, thus maintaining the driving force for absorption. This would also lead to the subsequent destruction of contaminants by oxidation.

Sodium persulfate ($Na_2S_2O_8$) is a promising oxidant for in-situ chemical oxidation (ISCO) remediation of soil and groundwater contamination by chlorinated solvents such as trichloroethylene (TCE) and perchloroethylene [9–11], and by gasoline hydrocarbons such as BTEX [12–14]. The persulfate anion (PS) has a redox potential of 2.01 V (Eq. (2)) and when it is activated by heat or a transition metal (e.g., ferrous ion) can be converted into an even stronger oxidant, i.e., a sulfate radical ($SO_4^{\bullet-}$) with a redox potential of 2.4 V [15] (see Eqs. (3) and (4), respectively).

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \tag{2}$$

$$S_2O_8^{2-} \xrightarrow{Thermal\ activation} 2SO_4^{-\bullet} \tag{3}$$

$k = 1.0 \times 10^{-7}\,s^{-1}$ (25 °C) [16]

$$S_2O_8^{2-} + Fe^{2+} \xrightarrow{Chemical\,Activation} SO_4^{-\bullet} + SO_4^{2-} + Fe^{3+} \tag{4}$$

$k = 2.0 \times 10^1\,M^{-1}\,s^{-1}$ (22 °C) [17].

The rapid destruction of organic contaminants by $SO_4^{\bullet-}$ at a near diffusion-controlled rate ($\sim 10^9\,M^{-1}\,s^{-1}$) has gained great interest among practitioners as a potential method for on-site hazardous waste remediation. Also, one of the important characteristics of $Na_2S_2O_8$, which makes it an attractive oxidant, is that persulfate is far more chemically stable in the presence of impurities such as (bi)carbonates in the aqueous phase, compared to the widely used oxidant hydrogen peroxide (a.k.a. Fenton's reagent). Both persulfate and peroxide can be activated by Fe^{2+} to generate mainly sulfate radicals and hydroxyl radicals, respectively, which are extremely reactive and can readily destroy organic contaminants. Due to the stable nature of persulfate, persulfate may potentially stay active longer when it is used to oxidize contaminants in a natural environment. However, the sulfate radicals formed would also oxidize

the Fe^{2+} to produce the Fe^{3+} form of iron through Eq. (5). Furthermore, if Fe^{2+} is present in large amounts, Fe^{2+} would significantly scavenge $SO_4^{\bullet-}$ and inhibit radical oxidation of the contaminants [9].

$$SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{5}$$

$k = 4.6 \times 10^9\,M^{-1}\,s^{-1}$ [18].

The following equation combines Eqs. (4) and (5) to show the overall stoichiometric reaction between the persulfate anion and the Fe^{2+} cation.

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \tag{6}$$
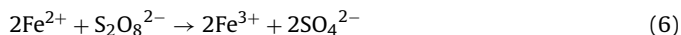
For this study, a preliminary persulfate oxidative scrubber (POS) system with iron activation was designed to evaluate the absorption and destruction of BTEX gases using $SO_4^{\bullet-}$ generated via Eq. (4). Since $SO_4^{\bullet-}$ generation is controlled by quantities of Fe^{2+} in the solution, Liang et al. [10] have reported that citric acid (CA) can act as an effective complexing agent to maintain Fe^{2+} levels in solution for activating the persulfate. Furthermore, a lowest acceptable CA/Fe^{2+} molar ratio of 1/5 under a fixed amount of persulfate was recommended for complete TCE destruction within a short time period (min). The availability of ferrous ions can be controlled by adjusting the molar ratio of CA/Fe^{2+}. However, the optimum ratios of $Na_2S_2O_8$, Fe^{2+} and CA depend upon the targeted contaminants and the specific oxidation environment. In order to determine the optimum operational parameters to be applied in the POS system, batch aqueous oxidation reaction experiments were initially conducted using a CA chelated molar ratio recommended by Liang et al. [10] (i.e., Fe^{2+}/CA molar ratio of 5/1) to investigate the influence of Fe^{2+} concentration on BTEX destruction and also to further explore an optimum Fe^{2+}/CA ratio. Secondly, a preliminarily designed POS system was tested based on the results obtained from the initial oxidation experiments. Two technical parameters were examined in the POS system: activator addition rates and activator concentrations.

2. Materials and methods

2.1. Chemicals

The materials used were purchased from the following sources: benzene (C_6H_6, min. 99.7%) and sodium thiosulfate ($Na_2S_2O_3\cdot5H_2O$, min. 99.5%), Riedel-deHaën; toluene ($C_6H_5CH_3$, ACS) and potassium iodide (KI, min. 99.5%), UNION Taiwan; acetic acid (CH_3CO_2H, min. 99.8%), ethyl benzene ($C_6H_5C_2H_5$, min. 98%) and *m*-xylene ($C_6H_4(CH_3)_2$, min. 98%), Fluka; sodium persulfate ($Na_2S_2O_8$, min. 99.0%) and citric acid ($HOC(COOH)(CH_2COOH)_2$, >99.5%), Merck; ferrous sulfate ($FeSO_4\cdot7H_2O$, 100.8%), J.T. Baker. Water used in the aqueous phase oxidation experiments was purified using a Millipore reverse osmosis (RO) purification system. Tap water was used in the POS system experiments.

2.2. Experimental setup

Batch reaction experiments were conducted in a 1.3-L heavy wall plain pressure reaction flask (ACE glass) and the top of the flask was covered with a flat Teflon reaction head sealed with a stainless steel clamp. The BTEX mixing contaminant solution was prepared by purging BTEX gases with concentrations near their saturated gas phase concentrations of B: $\sim$400 mg/L, T: $\sim$143 mg/L, E: $\sim$570 mg/L and X: $\sim$570 mg/L with variations of $\pm$10%, which were produced by the setup shown in Fig. 1. An approximate 150-mL head space was maintained to allow for injection of the activator liquid. The equilibrium aqueous phase BTEX concentrations were
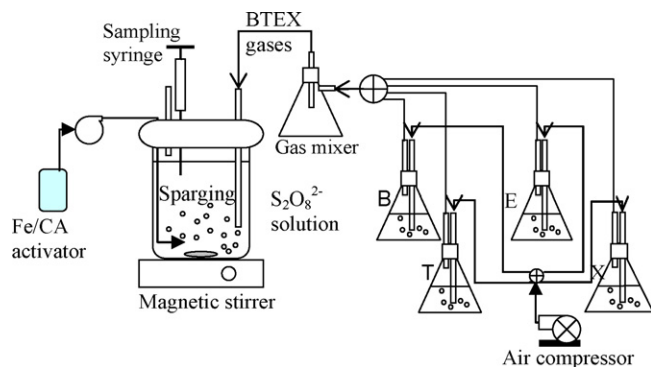
Fig. 1. Schematic diagram of the batch experiment and equipment for the production of BTEX gases.

quickly reached for about 10 min of purging. The concentrations were 6.55, 1.37, 0.48 and 0.73 mM, respectively. However, the overall purging process continued for 60 min to ensure stable aqueous BTEX concentrations. The variations in aqueous BTEX concentrations, which occurred are possibly due to the different aqueous solubilities of the BTEX compounds (i.e., B: 22.79, T: 5.59, E: 1.43, X: 1.88 mM) [4] and variations in the concentrations of the inlet gases. Thereafter, predetermined sodium persulfate was added and mixed for a few minutes (e.g., 1–2 min) before activators (i.e., Fe^{2+}/CA) were pumped into solution at 1.4 mL min^{-1}. Control tests were conducted in the presence of persulfate and water was injected into the reactor. Experimental conditions evaluated are presented in Table 1.

The schematics of the POS system are illustrated in Fig. 2 and the inserted table shows the design parameters. A PS scrubbing solution was circulated from two sucking ports, located at the bottom of the scrubbing tank and near the top of the solution surface to allow better mixing. The solution was sprayed from the top of the tank. The first liquid spraying layer is located 30 cm above the liquid surface and consists of 7 full cone spray nozzles (1/4HH-KY, Spraying Systems Co.). Each spray nozzle has a spray angle of approximately 75°. The second spraying layer consists of eight spray nozzles and is located 20 cm above the first spray layer. It should be noted that the POS system design conditions used in this study do not represent optimized scrubbing conditions, instead, they serve as a preliminary test of the POS system. The activator Fe^{2+}/CA solution, prepared based on predetermined ratios (see Table 1 for experimental conditions), was injected into the middle of the solution at various flow rates. In all experiments, the parameters of interest measured included gaseous phase BTEX concentrations entering and leaving the POS system, aqueous phase BTEX concentrations, persulfate concentration and pH. The removal percentages of BTEX

gases were calculated using the following equation:

$$\text{Removal of BTEX (\%)} = \frac{[\text{BTEX}]_{\text{inlet}} - [\text{BTEX}]_{\text{outlet}}}{[\text{BTEX}]_{\text{inlet}}} \times 100 \qquad (7)$$

2.3. Analytical methods

The BTEX gas and liquid concentrations were measured using a gas chromatography-flame ionization detector (GC-FID) and high-performance liquid chromatography (HPLC) using a UV detector, respectively. The Agilent 6890N GC equipped with a Agilent HP-5 fused silica capillary column (30 mm × 0.32 mm × 0.25 μm) was used. The temperature program used was: 4 min at 40 °C, raised to 150 °C at 30 °C/min and kept finally at 150 °C for 2 min. The detector temperature was set at 250 °C. The HPLC (Agilent 1100) equipped with a reversed-phase ZORBAX Eclipse XDB-C18 (4.6 mm × 150 mm × 5 μm) was used. Acetonitrile–water (70:30, v/v) was used for the mobile phase with a flowrate at 1.00 mL/min and the effluent was monitored at 254 nm. Persulfate ion was determined using iodometric titration with sodium thiosulfate [19]. The pH was measured using a SUNTEX TS-100 pH meter.

3. Results and discussion

3.1. Batch aqueous phase BTEX degradations

After pumping of Fe^{2+}/CA into the persulfate/BTEX mixing solution was started, BTEX was gradually degraded as seen in Fig. 3. The higher Fe^{2+} stock concentrations resulted in increased rates of BTEX degradation. Persulfate oxidation activated by continuous addition of Fe^{2+}/CA appears an effective method for destroying BTEX. An Fe^{2+}/CA molar ratio for 5/1 seems to be a suitable ratio for maintaining available Fe^{2+} in the activating persulfate for the destruction of BTEX. Crimi and Taylor [12] used Fe^{2+}/CA molar ratios of 5/1 and also 1/2 for persulfate activation in degrading BTEX contaminated groundwater. They achieved complete destruction under both molar ratios, in tests conducted using a 3-week reaction time period. Furthermore, the research results indicate that effective Fe^{2+}/CA activated persulfate oxidation may be dependent on specific determination of the most effective ratios of oxidant, activator and the resulting free radicals.

It can also be seen that among the four BTEX compounds, ethylbenzene and xylene were completely degraded within 10 min, when the Fe^{2+} stock concentration was greater than 0.04 M. Benzene degradation was the slowest of all the mixed compounds. A possible reason for this could be a relatively higher initial aqueous phase benzene concentration that occurred as a result of the characteristic higher aqueous solubility of benzene. More-

Table 1

Experimental matrix describing (a) batch aqueous phase BTEX degradation tests and (b) POS system tests

Exp. objectives	$S_2O_8{}^{2-}$ (M)	Fe^{2+} stock (M)	CA (M)	Fe^{2+} Pumping rate (mL/min)
(a) Aqueous phase BTEX degradation				
Influence of Fe^{2+} [a]	0.1	0.04–1.00	0.008–0.2	1.4
Influence of Fe^{2+}/CA M.R.[b]	0.1	0.4	0.08, 0.24, 0.40	1.4

Exp. objectives	$S_2O_8{}^{2-}$ (M)	Fe^{2+} stock (mM)[c]	Fe^{2+} pumping rate (L/min)	BTEX conc. (ppm$_v$)
(b) POS system				
Influence of Fe^{2+} pump rate	0.1	13.6	0.04, 0.16, 0.45	400
Influence of Fe^{2+} conc.	0.1	3.2, 13.6, 38.4	0.16	400

Note: M.R.: molar ratio.

[a] The CA concentration was determined based on a fixed Fe^{2+}/CA molar ratio of 5/1 for each Fe^{2+} concentration tested.

[b] Various Fe^{2+}/CA molar ratios of 5/1, 5/3 and 1/1 were used.

[c] The CA concentration, which was determined based on a fixed Fe^{2+}/CA molar ratio of 5/3 obtained from the experimental matrix (a), was prepared in the Fe^{2+} solution.

Items	Specification
Wet scrubber tank	$\Phi 810 \times$ (H)123 cm (635 L)
Liquid volume	360 L
Activator tank	$\Phi 50 \times$ (H)60 cm (100 L)
Air blower	500 W; 280 L/min
Peristaltic pump	0.04~0.45 L/min
Circulation pump	260 W; 110 L/min

1. Control panel
2. Air blower
3. Flow meter
4. Circulation pump
5. Wet scrubber
6. Activator pump
7. Fe^{2+}/CA solution
8. $S_2O_8^{2-}$ sampling port
9. Over flow port
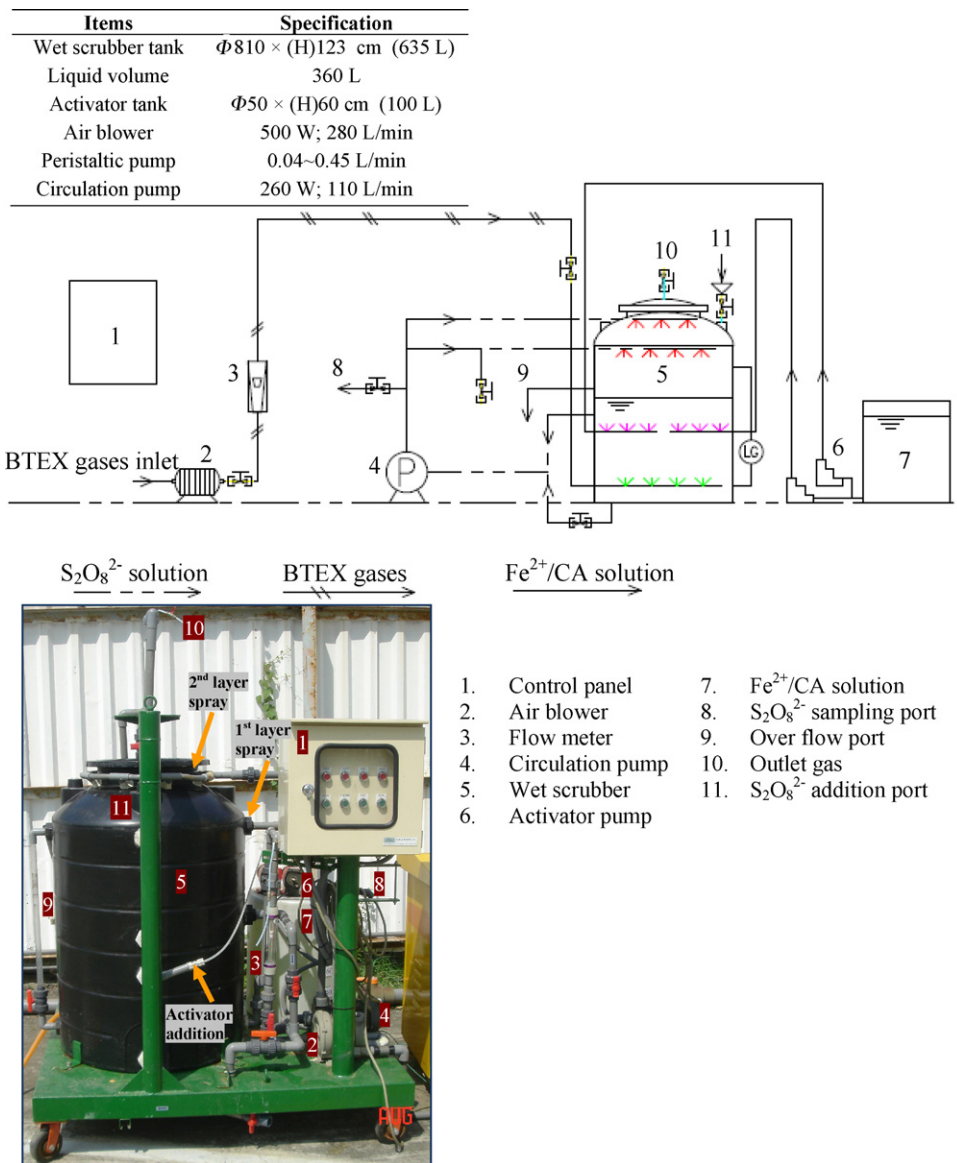10. Outlet gas
11. $S_2O_8^{2-}$ addition port

Fig. 2. Schematic diagram of the apparatus used in the POS system and a picture of the built POS system.

over, Huang et al. [14] studied the thermally activated persulfate oxidation (5 g $Na_2S_2O_8 \, l^{-1}$) of 59 mixed VOCs including BTEX, at 20, 30 and 40 °C and discovered that degradation of benzene is slower than that of others (i.e., TEX). Their study shows that the compounds with carbon-carbon double bonds or with a benzene ring bonded to reactive functional groups are less resistant to oxidation mechanisms, due to the low oxidation state of the carbon structure. Sekiguchi et al. [20] studied the hydroxylation behavior of benzene and toluene in a plasma system containing electrons, ions and radicals. They suggested that, in competing reactions between the two compounds (benzene and toluene), toluene is more reactive because toluene has an additional methyl group (–CH_3). Results from these studies are in agreement with the observations here. Table 2 summarizes the observed BTEX and persulfate pseudo-first order degradation rates (k_{obs}). The observed persulfate degradation characteristics, i.e., faster degradation rates resulting from increasing Fe^{2+} stock concentrations, are consistent with the associated contaminant degradation rates, i.e., faster $k_{obs, PS}$ resulted in faster $k_{obs, BTEX}$. Note that for all experimental conditions evaluated, the pH decreased from ini-

tially 5.6 (RO water) to around 2.0–1.6 at the end of the reaction period.

It has been shown that an Fe^{2+}/CA molar ratio of 5/1 is an acceptable ratio for persulfate activation to degrade BTEX. However, researchers have used iron chelates at various ratios as catalysts in Fenton and persulfate reactions to control the rate of radical formation and therefore, enhance the efficiency of contaminant destruction [10,11,21,22]. The maintenance of Fe^{2+} can be controlled by adjusting the appropriate chelating agent (i.e., CA) concentrations. Therefore, further evaluations were conducted by increasing the concentration of citric acid (i.e., higher ratios of Fe^{2+}/CA of 5/3 and 1/1) and Fig. 4 shows the effect of Fe^{2+}/CA molar ratio on the BTEX destruction. It can be seen that the higher concentration of citric acid (i.e., Fe^{2+}/CA ratio of 5/1 increased to 5/3 or 1/1) also resulted in faster benzene and toluene degradations rates (data summarized in Table 2) and ethylbenzene and xylene were completely degraded (i.e., within the first sampling period, 10 min) by all three ratios evaluated. However, higher ratios of 5/3 and 1/1 resulted in similar benzene and toluene degradation rates. The additional citric acid used (i.e., a Fe^{2+}/CA ratio of 1/1) beyond a
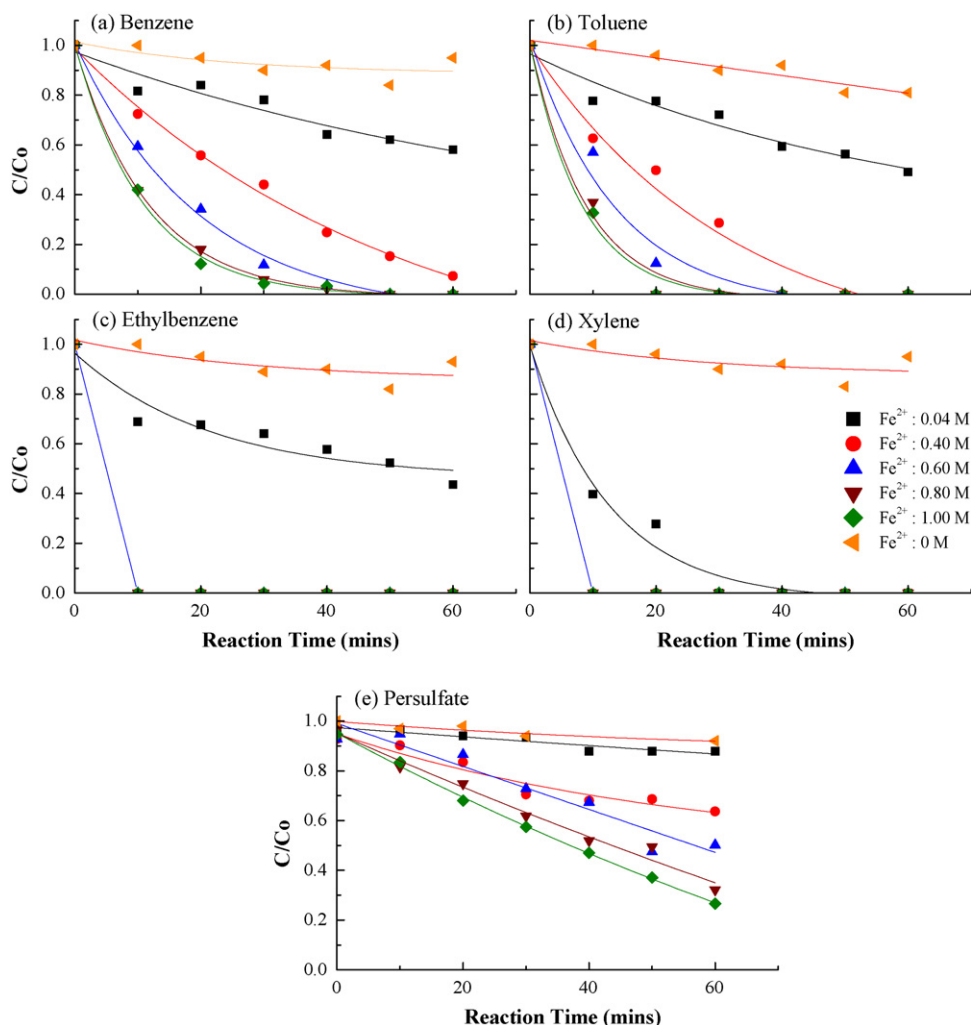
Fig. 3. (a–e) The effect of Fe^{2+} concentration on BTEX and persulfate degradations in the aqueous phase under experimental conditions: Fe^{2+} pumping rate = 1.4 mL min^{-1}; Fe^{2+}/CA molar ratio = 5/1; $[S_2O_8^{2-}]$ = 0.1 M.

Fe^{2+}/CA ratio of 5/3 did not result in a further increase in the degradation rate. It appears likely that stronger CA concentrations (i.e., Fe^{2+}/CA molar ratio of 1/1) limited available Fe^{2+} for persulfate activation [10]. It should be noted that the fate of citric acid was not explored in this study. It is possible that competing reactions due to various citric acid contents occurred and this requires further investigation. Nevertheless, when the Fe^{2+}/CA molar ratio of 5/1 was increased to 5/3, elevated citric acid resulted in accelerated degradation rates for both persulfate and the contaminant. Hence, it is evident that more sulfate radicals are generated in the presence of higher citric acid concentration. However, persulfate degradation rates for Fe^{2+}/CA ratios of 5/3 and 1/1 exhibit similar k_{obs} values (i.e., 11.6 and 11.9 min^{-1}, respectively) and provide no further increase in contaminant degradation. Based on these observed results, a Fe^{2+} stock concentration of 0.4 M supplied at a rate of 1.4 mL/min and a Fe^{2+}/CA molar ratio of 5/3 were used in the subsequent POS system.

3.2. Persulfate oxidative scrubber system

Results of initial wet scrubber analysis by passing BTEX gases ($\sim$100 ppm$_v$ for each compound) into the POS system with scrubber solutions of water and persulfate are presented in Fig. 5(a) and (b), respectively. These control tests indicated that the removal efficiency of the POS system when degrading BTEX with low water solubilities is extremely low, as expected, generally resulting in a less than 10% variations in concentrations. Aqueous BTEX concentrations rapidly reached maximum levels within 10 min (average 1.1, 1.0, 0.8, and 0.8 mg/L for BTEX, respectively) in both water and persulfate solutions. Scrubber efficiency is highly dependent on effective mass transfer of the VOCs to the liquid phase. However, since persulfate oxidation of BTEX without additional activation is relatively slow [14], the usage of persulfate as a scrubbing liquid did not actually result in any significant differences in BTEX removal rates, when compared to the scrubbing system which used water. It should be noted that persulfate concentration remained nearly unchanged during a 2-h operation.

It has been shown above that BTEX degradation rates were dependent upon the available quantities of iron activator added in the persulfate solution. Furthermore, faster BTEX degradation requires aggressive persulfate activation, which would be associated with more persulfate degradation. The variation of the Fe^{2+}/CA molar ratio governs the amount of Fe^{2+} available for persulfate activation and affects the consumption of persulfate. Therefore, in order to minimize sodium persulfate usage, which is a major operating cost, it is necessary to carefully control the quantities of activators (e.g., Fe^{2+}/CA). Based on the results presented in Fig. 4, it can
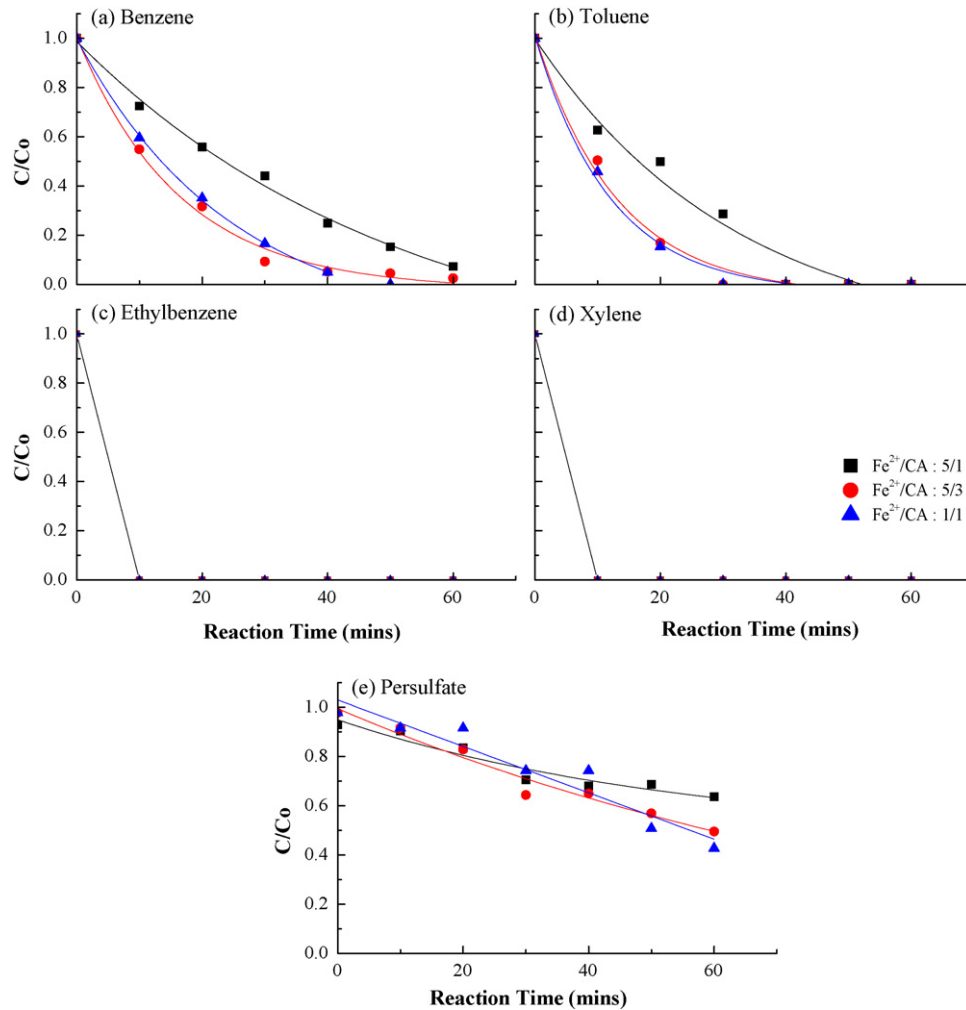
Fig. 4. (a–e) The effect of Fe^{2+}/CA molar ratio on BTEX and persulfate degradations in the aqueous phase under experimental conditions: Fe^{2+} pumping rate = 1.4 mL min^{-1}; $[Fe^{2+}]$ = 0.4 M; [CA] = 0.08, 0.24, 0.40; $[S_2O_8^{2-}]$ = 0.1 M.

be seen that within 10 min, both ethylbenzene and xylene were completed degraded, while benzene and toluene were degraded to 40% and 50%, respectively, under the Fe^{2+}/CA molar ratio of 5/3. Furthermore, removals of benzene and toluene at 20-min intervals readily reached concentrations of 70% and 80%, respectively. Following this, the degradation of contaminants slows down and eventually tails off. Molar ratios of $\Delta Fe^{2+}/\Delta PS$ were recorded after 20 min and indicated values less than the theoretical stoichiometric ratio of 2 (see Eq. (6)) (data presented in Table 2). The low ratio observed (i.e., $\Delta Fe^{2+}/\Delta PS$) suggests less consumption/scavenging of sulfate radicals by Fe^{2+} and this may result in higher contaminant degradation efficiency [9], which is due to the more efficient usage of sulfate radicals generated (Eq. (4)) for the destruction of contaminants and less consumption by excess Fe^{2+} (Eq. (5)). Liang et al. [9] reported a $\Delta Fe^{2+}/\Delta PS$ molar ratio closer to 2 when Fe^{2+} reacted with $S_2O_8^{2-}$ in the absence of citric acid. Based on the analysis of benzene destruction data, an average iron usage per unit mass of benzene destructed (i.e., $\Delta Fe^{2+}/\Delta B$) was determined to be 2.61 mg Fe^{2+} per mg of benzene (see Table 2). This amount is sufficient to generate sulfate radicals for complete destruction of ethylbenzene and xylene, and partial destruction of benzene (~80%). Therefore, in order to determine the trial iron activator stock concentration for initiating rapid destructions of dissolved BTEX in the POS system and to maintain a maximum concentration gradient (i.e., zero contaminant concentration in solution) an empirical formula was used:

Fe^{2+} stock solution (mg/L)

$$= \frac{C_{\text{contam.}} \times V_{\text{sol}} \times (\Delta Fe^{2+}/\Delta \text{Contam.})}{R_{\text{Fe}} \times RT} \quad (8)$$

where $C_{\text{contam.}}$ is the aqueous contaminant concentration (benzene, mg L^{-1}), $V_{\text{sol.}}$ is the solution volume (360 L), $\Delta Fe^{2+}/\Delta \text{Contam.}$ is mg iron used per mg contaminant destructed (2.61 mg Fe^{2+} mg^{-1} Benzene), R_{Fe} is Fe^{2+}/CA injection rate (L min^{-1}), and RT is the retention time (min). The numerator portion presents the total amount of iron required for destruction of the contaminants (i.e., BTEX). These amounts are then to be injected at a fixed pumping rate (R_{Fe} = 0.6 L/min) and allowed to react for a period of time (i.e., retention time, RT = (636 L tank)/(280 L min^{-1}) = 2.27 min). Therefore, a trial iron stock solution concentration can be determined as follows: (average aqueous 1.1 mg benzene L^{-1} × 360 L × 2.61 mg Fe^{2+} mg^{-1} benzene)/(0.6 L min^{-1} × 2.27 min) = 758.9 mg Fe^{2+} L^{-1} (13.6 mM). When preparing the iron activator solution, required contents of citric acid were added at a fixed Fe^{2+}/CA molar ratio of 5/3.

Fig. 6(a) and (b) shows the results of BTEX removals and persulfate degradations in the POS system with a fixed 13.6-mM iron activation added at three different pumping rates. Fig. 6(c) and (d) shows observations of BTEX removal and persulfate degrada-
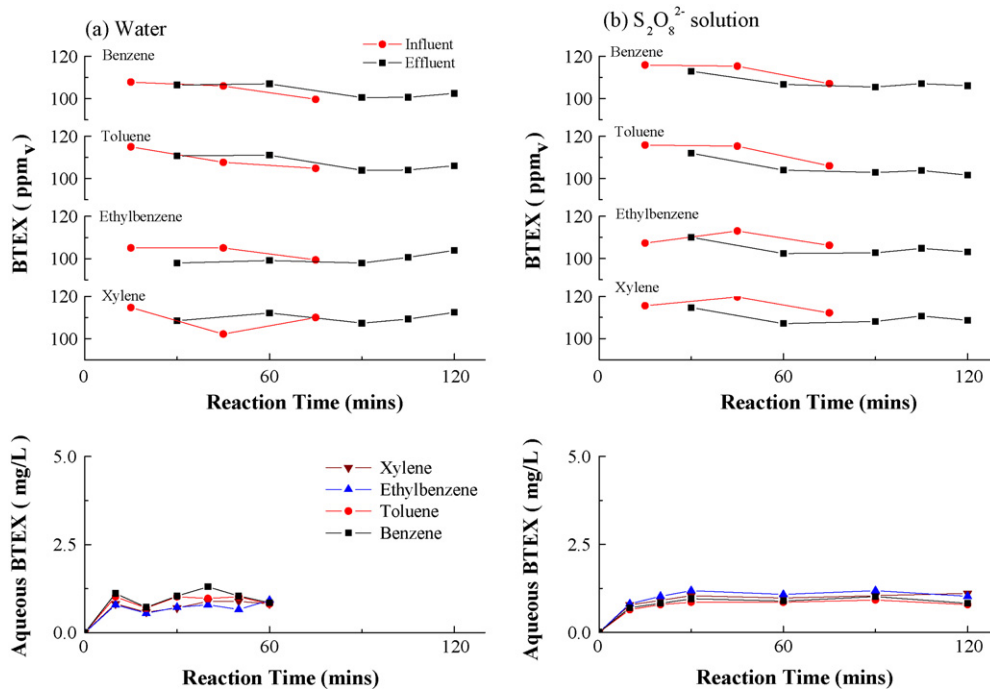
Fig. 5. Concentration variations of influent and effluent BTEX and the resulting aqueous BTEX concentrations in the POS system using (a) water and (b) persulfate as scrubbing solutions without addition of Fe^{2+}. $[S_2O_8^{2-}] = 0.1$ M.
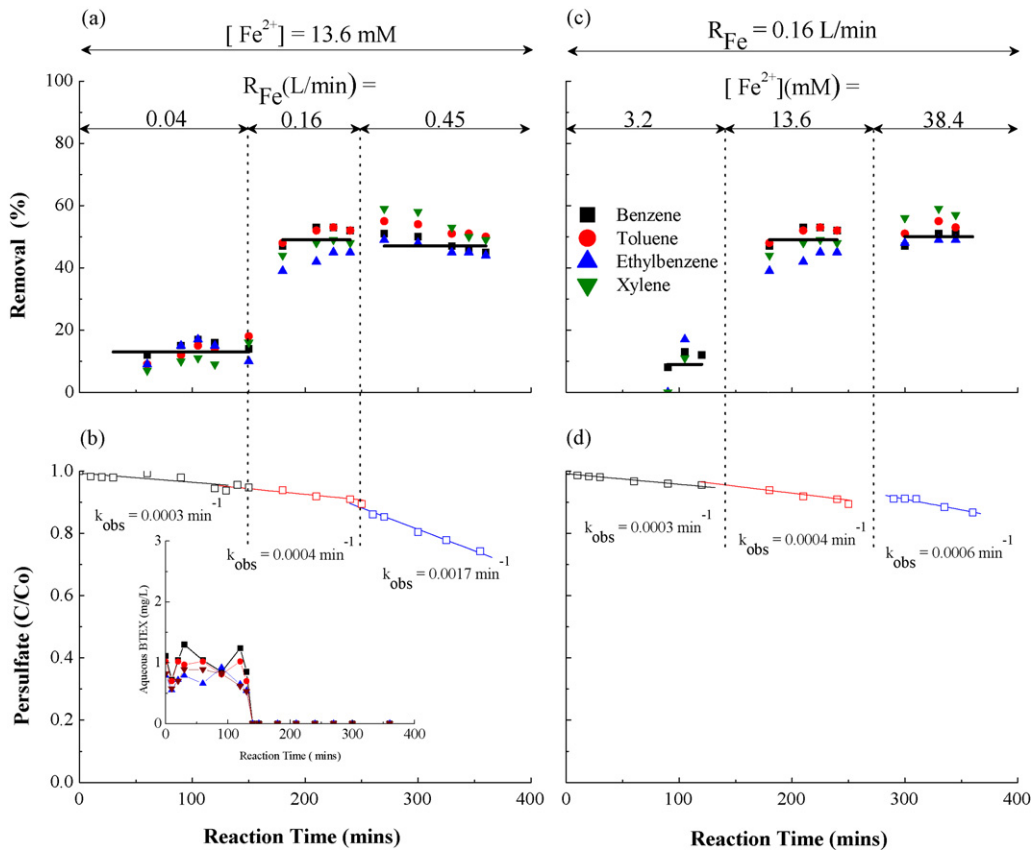

Fig. 6. The effects of (a and b) iron-pumping rate and (c and d) concentration on the removal of BTEX gases and persulfate degradations in the POS system. $[S_2O_8^{2-}] = 0.1$ M.

Table 2
Pseudo–first-order degradation rate constants of BTEX and persulfate with various Fe^{2+} activator concentrations under a fixed $S_2O_8^{2-}$ concentration of 0.1 M

Fe^{2+} (M)	Fe^{2+}/CA M.R.	k_{obs} ($\times 10^{-3}$ min^{-1}) (R^2)					Analysis of benzene destruction data[a]				
		B	E	T	X	PS	ΔB (mM)	ΔFe^{2+} (mM)	ΔPS (mM)	$\Delta Fe^{2+}/\Delta$PS M.R.	$\Delta Fe^{2+}/\Delta$B (mg/mg)
0	–	2.1 (0.45)	2.5 (0.53)	3.4 (0.87)	2.2 (0.46)	1.5 (0.79)	–	–	–	–	–
0.04	5/1	9.6 (0.92)	14.2 (0.83)	12.0 (0.94)	69.7 (0.93)	2.5 (0.75)	–	–	–	–	–
0.4		38.1 (0.95)	–	40.1 (0.98)	–	8.4 (0.83)	3.3	11.2	9.3	1.2	2.4
0.6		94.3 (0.97)	–	94.7 (0.92)	–	11.8 (0.90)	4.7	16.8	18.6	0.9	2.6
0.8		93.0 (0.99)	–	–	–	16.7 (0.95)	6.4	22.4	21.6	1.0	2.6
1.0		75.3 (0.95)	–	–	–	20.4 (0.98)	6.8	28.0	26.6	1.1	3.0
0.4	5/3	65.6 (0.97)	–	84.9 (0.98)	–	11.6 (0.97)	3.1	11.2	14.8	0.8	2.6
0.4	1/1	67.1 (0.95)	–	90.8 (0.99)	–	11.9 (0.86)	4.0	11.2	20.5	0.5	2.0

Note: M.R.: molar ratio. All data points observed in all experiments were used for calculating pseudo-first-order degradation rate constants.

[a] Δ indicates the difference in a component consumed or degraded between 0 and 20 min.
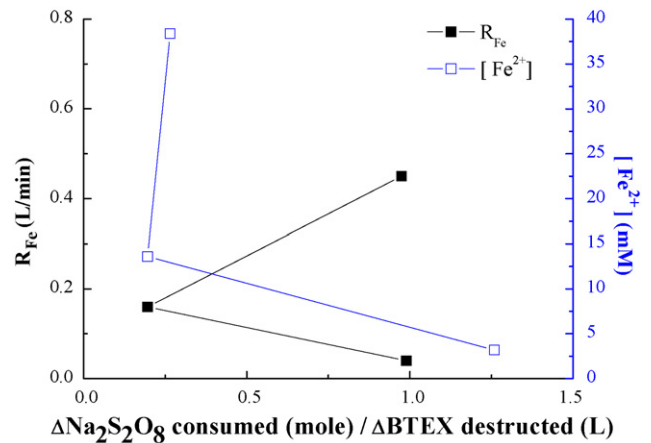

Fig. 7. The effects of iron-addition rate and concentration on the BTEX removal efficiency as a function of the persulfate consumed per liter of BTEX gases destructed.

tion with a fixed iron-pumping rate of 0.16 L/min at three different Fe^{2+}/CA concentration levels. Higher removal percentages were observed for both faster pumping rates and elevated iron activation conditions. When organic compounds such as BTEX are not highly water soluble, in order to achieve high removal efficiencies, extremely fast oxidation reactions must be coupled with mass transfer in the wet scrubber [8]. Therefore, it can be seen that aggressive persulfate activation by quickly injecting iron resulted in relatively high removal efficiencies of approximately 50%, while low pumping rates (0.04 L/min) and low iron concentrations (3.2 mM) resulted in removal efficiencies of only ∼10%. Although no specific kinetic data (i.e., reaction rate constant) on BTEX was recorded in this study, an absolute rate constant of 3.6×10^9 M^{-1} s^{-1} was reported for reaction of $SO_4^{\bullet -}$ with benzene by pulse radiolysis of the persulfate solution [23]. Due to the fast reactions between $SO_4^{\bullet -}$ and BTEX, it was observed that no BTEX in the persulfate scrubbing solution was detected during the course of the experimental runs under two higher iron-pumping rate conditions (see inset figure in Fig. 6(b)). Similar results were also observed for experiments which involved varying Fe^{2+} concentrations (data not shown), where no BTEX remained in the persulfate solutions using Fe^{2+} = 13.6 and 38.4 mM. Note that for all experimental conditions evaluated, the pH decreased from initially 6.5 (tap water) to around 2–2.5 at the end of reaction period.

As previously stated, high contaminant removal efficiencies result from high persulfate consumption. When iron-pumping rates were increased from 0.16 to 0.45 L min^{-1}, the persulfate pseudo-first-order degradation rate constant increased from 0.0004 to 0.0017 min^{-1}; nearly a four-fold increase (see Fig. 6(b)). In comparison, when iron concentration was increased under a fixed pumping rate (i.e., 0.16 L min^{-1}), only a small increase in the persulfate degradation rate was observed (i.e., from 0.0004 to 0.0006 min^{-1}) (see Fig. 6(d)). It should be noted that a maximum designed activator pumping rate of 0.6 L min^{-1} was previously used for determining a trial iron concentration, but the actual measured rate was 0.45 L min^{-1}. When comparing these two activation adjustment methods (i.e., Fe^{2+} pumping rate vs. Fe^{2+} concentration level), it can be seen that the same quantities of iron (13.6 mmoles Fe^{2+} L$^{-1} \times$ 0.45 L min^{-1} equal to 38.4 mmoles Fe^{2+} L$^{-1} \times$ 0.16 L min^{-1} = 6.1 mM min^{-1}) were supplied for the experimental conditions of [Fe^{2+}] = 13.6 mM and R_{Fe} = 0.45 L min^{-1} (see Fig. 6(a)) versus [Fe^{2+}] = 38.4 mM and R_{Fe} = 0.16 L min^{-1} (see Fig. 6(c)). However, the latter conditions resulted in a much slower persulfate degradation rate and both sets of conditions resulted in almost the same BTEX removal efficiency. Moreover, Fig. 7 shows

the effects of iron addition rate and stock concentration on the BTEX removal efficiency as a function of the required persulfate consumption per liter of BTEX gases destructed. It can be seen that persulfate consumption ($\Delta Na_2S_2O_8/\Delta BTEX$) decreased when the iron concentration and pumping rates were initially increased. However, further increases in the iron-pumping rate resulted in increases in persulfate consumption, whereas increases in iron concentration did not. These observations suggest that an increase in iron concentration at a fixed iron-pumping rate to activate persulfate can be more efficient than only increasing the iron-pumping rate. These results are in agreement with the findings of Liang et al. [9] who reported that more efficient contaminant destruction can be obtained in the persulfate system by gradually adding Fe^{2+} at a slower rate to slowly generate sulfate radicals, which can then attack contaminants preferentially, as opposed to adding all the iron at once. It appears that slow and steady persulfate activation is the most suitable method for controlling the destruction of BTEX.

4. Conclusion

The results of the iron-activated persulfate oxidation process combined wet scrubber demonstrated a potential method for treating BTEX exhaust gases. In the batch aqueous phase BTEX degradation experiments, it was observed that, with continuous addition of Fe^{2+}/CA, BTEX was rapidly degraded and the higher iron concentrations used resulted in increased rates of BTEX degradation. The results of the POS system experiments show that the iron activated persulfate system resulted in a BTEX removal efficiency of around 50%, which is superior to using either water or only persulfate as a scrubber solution. The BTEX removal efficiency in the POS system relies on fast oxidation reactions coupled with mass transfer (i.e., BTEX gases dissolved into the solution). As soon as BTEX is dissolved, fast destructions of BTEX can be achieved by adjusting the addition rate and concentration of the iron activator. However, a limitation on contaminant removal efficiency (i.e., incomplete BTEX exhaust removal) was encountered in this preliminarily designed POS system. All scrubbing solutions for gas absorption essentially depend on a large gas–liquid contact surface. Therefore, improvements in the physical configuration of the POS system should be made through the use of a variety of mechanical methods such as sparging the gases over some types of media (packing, meshes, grids, etc.) to create a high gas–liquid surface area in as small a volumetric space as possible. This preliminary POS system may serve as an alternative method and as a reference for destroying SVE exhaust gases.

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