

Fenton Oxidation of TCE Vapors in a Foam Reactor

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Oxidation of dilute TCE vapors in a foam reactor using Fenton's reagent was investigated. The new process relies on rapid mass transfer from the gas undergoing treatment to a fine aqueous foam and oxidation by Fenton's reagents. Laboratory investigations demonstrated that TCE elimination capacity was as high as 56–61 g TCE m⁻³ reactor h⁻¹ with a removal efficiency of 62% and TCE mineralization of 83% at gas retention time of 30 s and TCE inlet concentration of 0.6 g m⁻³. Compared to oxidation in wet scrubbers packed with commercially available plastic packings and using the same composition of Fenton's reagents, the foam reactor configuration provided a higher rate absorption and greater elimination capacity of TCE vapors. The treatment performance far exceeded those of current bioreactors and was comparable to those of advanced oxidation techniques such as TiO₂/UV and ozone/UV, suggesting that Fenton oxidation in foam reactors may be a promising technique for treating TCE and other recalcitrant vapors. © 2007 American Institute of Chemical Engineers Environ Prog, 26: 226–232, 2007

Keywords: chemical oxidation, trichloroethylene, vapor phase reactor, air pollution control, advanced oxidation

INTRODUCTION

Trichloroethylene (TCE) has been one of the most widely detected contaminants in soil and groundwater for the past decades [1, 2]. Since TCE is volatile, site remediation often results in contaminated air streams that require treatment. TCE is also extensively used as a solvent, degreasing agent and in dry cleaning resulting in widespread air emissions. Since TCE is toxic and carcinogenic, treatment of gaseous emissions is required. Treatment of TCE vapors can be

conducted by a variety of physical, chemical, and biological methods [3–6]. Although biological treatment is economical for many hydrocarbons, it is difficult for most chlorinated solvents. Biological treatment using cometabolic degradation was found to be effective only for low concentrations of TCE under well-controlled conditions due to the toxicity of TCE biodegradation intermediates [7, 8]. On the other hand, advanced oxidation processes provide an effective nonselective oxidation of biorefractory compounds such as TCE [9, 10]. For removal of TCE vapors, direct photolysis by UV, TiO₂/UV, and ozone/UV have demonstrated excellent efficiency [11–13]. However, the high capital and maintenance costs, sensitivity to gas moisture, and difficulty in scale-up may offset the advantages of these technologies [13, 14]. Fenton oxidation could be a suitable solution for degrading TCE vapors. Fenton oxidation uses a mixture of hydrogen peroxide and iron catalysts [15]. It has gained popularity over the past decade because of its strong oxidation capability, low environmental impacts, and relatively low costs. The mechanism of Fenton oxidation involves oxidation of Fe²⁺ to Fe³⁺ by hydrogen peroxide (H₂O₂) yielding hydroxyl radicals (HO·, hereafter), one of the strongest and least specific oxidants known [15]. Because of its strong oxidation capacity, Fenton oxidation has been used for degrading a variety of organic contaminants in soil and water [9, 16]. In the case of Fenton oxidation of TCE, the reactivity of hydroxyl radicals with TCE ($k = 3.3\text{--}4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is higher than the reactivity with other competing chemicals [17]. Also, laboratory and field studies have shown that Fenton oxidation is quite effective in oxidizing several chlorinated compounds including TCE in the aqueous phase [18, 19].

However, few studies report treatment using Fenton oxidation of TCE vapors. To be successful, vapor treatment requires a high rate of gas–liquid mass

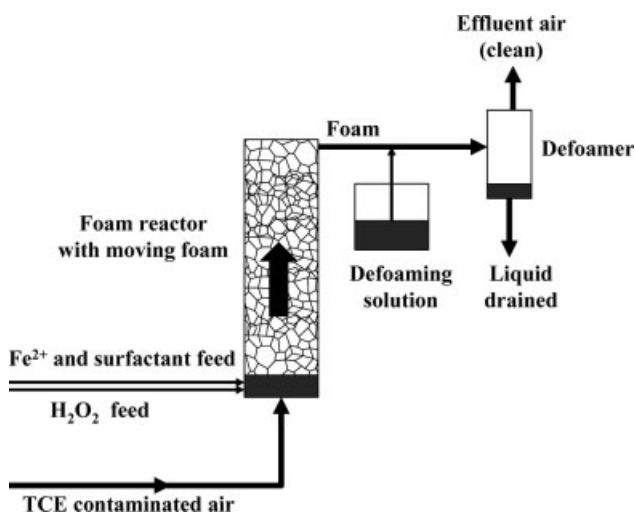


Figure 1. Configuration of the foam reactor (not to scale). See methods section for details.

transfer followed by rapid oxidation. Here, we demonstrate implementation of Fenton oxidation in a foam reactor. The foam reactor relies on fine aqueous foam bubbles made with entrapped gas containing TCE vapor, a surfactant and Fenton's reagents in the aqueous phase. The large interfacial area of the foam allows rapid mass transfer of TCE vapors to the aqueous phase where Fenton reactions take place. The objective of the present study was to prove the concept of Fenton oxidation in a foam reactor for the treatment of recalcitrant vapors.

MATERIALS AND METHODS

Reactor Setup and Operating Conditions

The foam reactor system consisted of the actual foam column, separate vessels for hydrogen peroxide solution and an aqueous solution containing a surfactant and ferrous sulfate, a defoamer vessel, and a drain tank for liquid drainage/settling (Figure 1). The prototype was modified from the foamed emulsion bioreactor used for toluene and TCE biotreatment [20, 21]. The foam column (4.04 cm ID, 40 cm height, volume of 0.51 L) had a fine gas sparger at the bottom of the foam reactor. The aqueous solution was prepared by adding a surfactant (0.2% (w/v), DC-193 silicone, Sigma Co.) and ferrous sulfate (8 g L^{-1} of $\text{FeS-O}_4 \cdot 7\text{H}_2\text{O}$, Sigma Co.), followed by addition of several drops of 1 N sulfuric acid to adjust pH at 3, while 3% (w/v) of hydrogen peroxide solution was prepared from 30% (w/v) hydrogen peroxide (Sigma Co.). A metered stream of TCE contaminated air (0.6 g m^{-3} at various air flow rates) was introduced through the gas sparger while the hydrogen peroxide solution and the iron salt/surfactant solution ($1.4\text{--}4.8 \text{ mL min}^{-1}$ and 27 mL min^{-1} , respectively) were separately introduced at the bottom of the foam reactor. This produced a fine foam (individual bubbles had a diameter of 2–2.5 mm) in which Fenton oxidation took place as the foam was rising in the foam reactor. After ris-

ing through the foam reactor, the foam leaving through a side port was mixed with a 0.02% (v/v) aqueous emulsion of antifoam agent (A-5758, Sigma Co.) and defoamed in a defoamer consisting of a 0.5 L flask. After defoaming, the gas and liquid were analyzed separately. Control experiments showed that the removal of TCE in the defoamer was not significant. Defoaming was not optimized and other defoaming techniques exist. Also, the volume of the vessels for chemicals, the defoamer and the drain tank were not optimized at this stage of the research.

For determining the optimum ratio of the initial concentration of hydrogen peroxide to ferrous sulfate ($[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$, hereafter), a 3% (w/v) hydrogen peroxide solution was metered ($1.4\text{--}4.8 \text{ mL min}^{-1}$) together with a solution containing 8 g L^{-1} of $\text{FeS-O}_4 \cdot 7\text{H}_2\text{O}$ (1.6 g L^{-1} of Fe^{2+}) supplied at a rate of 27 mL min^{-1} to the bottom of the foam reactor. These flows corresponded to $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$ of 0.5–3.3 (gram of hydrogen peroxide per gram of ferrous ion). An air stream ($0.12 \text{ m}^3 \text{ h}^{-1}$, i.e., gas retention time of 15 s) containing 0.6 g m^{-3} of TCE vapor was introduced through the gas sparger. The effect of gas retention time on TCE vapor removal in the foam reactor was investigated by varying the gas flow rate within a range corresponding to gas retention times of 10–60 s.

To compare Fenton oxidation in the foam reactor to scrubbing and chemical oxidation in conventional wet scrubbers, selected experiments were conducted in traditional packed bed scrubbers. The same reactor vessel was used and packing consisted of porous ceramic beads (PorceliteTM, 4 mm diameter, surface area of $1600 \text{ m}^2 \text{ m}^{-3}$, Aisin Takaoka, Japan), plastic rings (nominal size of 8 mm, surface area of $1100 \text{ m}^2 \text{ m}^{-3}$), and crushed pall rings (average size of 8 mm, surface area of $1250 \text{ m}^2 \text{ m}^{-3}$, Jaeger, Houston, Texas). The scrubbers were operated counter currently.

For all the experiments, the pH of Fenton's reagents was 3.0 because acidic conditions have been found to be effective for Fenton oxidation [22]. TCE inlet and outlet concentration, concentrations of hydrogen peroxide, total iron, ferrous ion, and chloride ion were monitored in order to calculate removal efficiency and elimination capacity (EC) of TCE as well as TCE mineralization. TCE mineralization was calculated by dividing the measured chloride ion production by the theoretical chloride ions expected from the TCE removed assuming that 3 moles of chloride are liberated from each mole of TCE degraded. The temperature for all the experiments was $(20 \pm 2)^\circ\text{C}$. Note that all aqueous samples were collected before the addition of the defoaming agent to avoid diluting the samples.

Analytical Methods

Gaseous TCE concentrations were measured by injecting grab samples in a HP 5890 gas chromatograph fitted with a 30 m HP-5 column (0.32 mm ID and $0.25 \mu\text{m}$ film), a 10-port gas injection valve, and a FID detector. The GC was operated isothermally at 80°C and the TCE lower detection limit was about

0.005 g m⁻³. Chloride ions were measured by a colorimetric assay [23]. The foam stability was assessed using the 50% drain time according to the method described by Ripley *et al.* [24]. H₂O₂ was measured using a modified peroxytitanic acid colorimetric procedure [25]. The detection limit was 2.9 μM using titanium sulfate (TiSO₄, Pfaltz and Bauer). Total iron and ferrous ion concentrations were measured using Environmental Protection Agency (EPA) Method No. 3500-Fe D, Phenanthroline method.

RESULTS AND DISCUSSION

The main parameters influencing the performance of Fenton oxidation in a foam reactor are foam stabil-

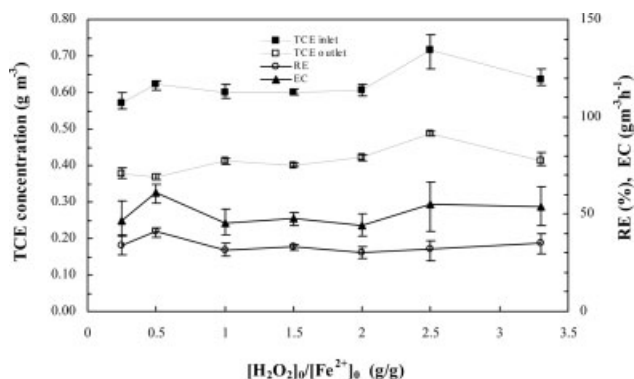


Figure 2. Effect of initial ratio of H₂O₂ to Fe²⁺ concentration on TCE vapor removal efficiency (RE) and elimination capacity [EC = (concentration in-out) × air flow/foam bed volume] in the foam reactor. Conditions: TCE inlet concentration, 0.62 ± 0.05 g m⁻³; gas retention time in the foam reactor, 15 s.

ity, ratio of initial concentration of hydrogen peroxide to ferrous ion ([H₂O₂]₀/[Fe²⁺]₀), and gas retention time. Foam stability is directly related to mass transfer rate of TCE in the reactor because a stable foam implies a large interfacial area while unstable foam results in short circuiting of air and dead volumes [21, 24]. In all the experiments, very good foam stability was observed while foam formation and foam size was a function of the air velocity in the sparger (results not shown). The 50% drain time of foam [24] ranged from 12 to 18 min which is much longer than the retention time of foam in the system (10–30 s).

Since H₂O₂ and Fe²⁺ are scavengers as well as producers of HO· [26], the initial experiments focused on determining the effect of [H₂O₂]₀/[Fe²⁺]₀ on TCE vapor removal (Figure 2). The removal efficiencies of TCE vapors at a ratio of 0.25–3.3 (gram H₂O₂ per gram Fe²⁺) were 30–40% with TCE elimination capacities between 44 and 61 g TCE m⁻³ reactor h⁻¹. As summarized in Table 1, the EC obtained from the present study was much higher than those in biological treatment and very comparable to current chemical treatment such as UV, TiO₂/UV, and ozone/UV. Considering the high capital cost, high maintenance, impact of humidity, and difficulties in scaling-up UV, TiO₂/UV, and ozone/UV, Fenton oxidation in the foam reactor may be a worthwhile alternative to current biological and chemical treatments.

Figure 3 shows TCE mineralization, H₂O₂ utilization efficiency, consumption of Fe²⁺ and H₂O₂ at various [H₂O₂]₀/[Fe²⁺]₀ ratios during the treatment. TCE mineralization increased when increasing [H₂O₂]₀/[Fe²⁺]₀, reaching up to 73–77% at [H₂O₂]₀/[Fe²⁺]₀ of 2.5–3.3 (Figure 3a). Although mineralization was not complete, no volatile metabolites (e.g., vinyl chloride or partially chlorinated compounds) were detected in

Table 1. Performance of various gas-phase reactors for treating TCE vapors.

Treatment method	TCE inlet concentration (g m ⁻³)	TCE removal (%)	TCE elimination capacity (g _{TCE} m ⁻³ h ⁻¹)
Parallel BTF, <i>B. cepacia</i> G4 [27]	5–36	50–100	0.3–0.7
Bubble column, <i>B. cepacia</i> G4 [28]	0.07–0.4	60–80	0.3–1.5
CSTR, Unidentified actinomycetes [29]	0.18–0.46	55–75	1.6–2.1
HFMB, <i>M. trichosporium</i> [30]	0.14–0.19	54–86	1.4–3.9
BTF, <i>B. cepacia</i> PR1 ₂₃ [31]	0.04–2.4	79–100	0.4–16
FEBR, <i>B. cepacia</i> G4 [21]	0.06–0.12	82–96	6.5–28
*Direct photolysis by UV light [11]	0.77–1.55	90	146–348
**TiO ₂ /UV in a packed bed reactor [12]	0.79	45–98	39–90
†TiO ₂ /UV in a plug flow reactor [13]	0.17–1.92	80–100	6–57
††TiO ₂ /O ₃ /UV in a plug flow reactor [13]	0.46–0.54	48–82	10–20
‡Fenton oxidation in a foam reactor	0.6	22–67	17–61

BTF, biological trickling filter; CSTR, continuously stirred tank reactor; HFMB, hollow fiber membrane bioreactor; FEBR, foamed emulsion bioreactor.

*Four xenon UV lamps (3.7 kW, 200–300 nm), operating temperature of 25–65°C.

**UV lamp (0.45 W m⁻² at 365 nm), operating temperature of 50°C, TiO₂ loading of 81.4 mg.

†UV (20–55 W m⁻² at 254, 365 nm), operating temperature of 40°C.

††UV (20–55 W m⁻² at 254, 365 nm), operating temperature of 40°C, ozone dosage of 150–1000 ppm.

‡From the present study.

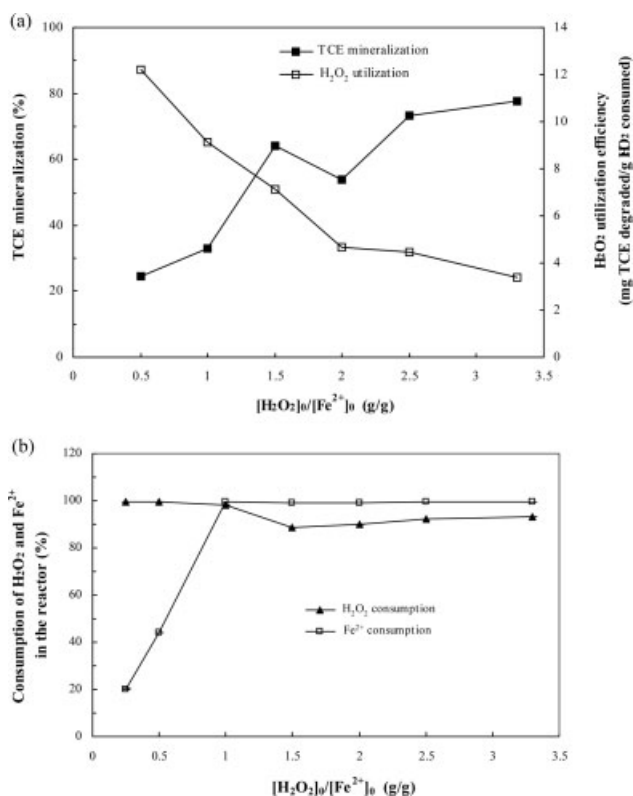
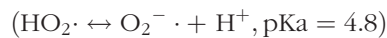
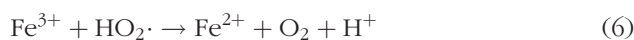
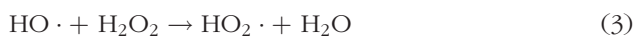
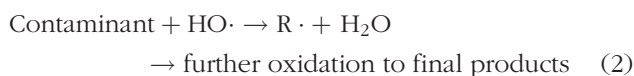


Figure 3. (a) TCE mineralization and H₂O₂ utilization efficiency, (b) Consumption of H₂O₂ and Fe²⁺ in the foam reactor at various initial ratios of H₂O₂ and Fe²⁺. Conditions: TCE inlet concentration, $0.62 \pm 0.05 \text{ g m}^{-3}$; gas retention time in the foam reactor, 15 s.

the effluent gas. To better understand the effect of the Fenton reagents, the consumption of H₂O₂ and Fe²⁺ during oxidation in the foam reactor was monitored (Figure 3b). The results showed that H₂O₂ was completely consumed below [H₂O₂]₀/[Fe²⁺]₀ of 1 (H₂O₂-limited process) while Fe²⁺ was totally consumed above the ratio of 1 (Fe²⁺-limited process). This can be explained by a detailed examination of the mechanism of Fenton reaction (Eqs. 1–7, [15]) that reveals that the excessive H₂O₂ would result in reduction of Fe³⁺ to Fe²⁺ by the H₂O₂ and HO₂/O₂^{•-} being generated by reaction of H₂O₂ and HO[•]. The Fe²⁺, which is reduced from Fe³⁺, generates more HO[•] for further degradation of TCE intermediates.



The high TCE mineralization obtained here is consistent with the fact that Fenton oxidation provides rapid and complete or near complete destruction of contaminants to harmless compounds such as CO₂, water, and chloride ions [17, 26]. Also, excessive H₂O₂ at [H₂O₂]₀/[Fe²⁺]₀ > 1 would have less scavenging effect of HO[•] than excessive Fe²⁺ found at [H₂O₂]₀/[Fe²⁺]₀ < 1 due to a lower reactivity of H₂O₂ with HO[•]. Below is the cursory calculation of relative reactivity of Fe²⁺ and H₂O₂ with HO[•] for the experiments, based on the initial rates of each reaction with assumption of steady state (ss) concentration of HO[•].

$$\begin{aligned} \text{Relative reactivity} &= \frac{\text{Initial rate for Fe}^{2+} - \text{HO}^\bullet}{\text{Initial rate for H}_2\text{O}_2 - \text{HO}^\bullet} \\ &= \frac{k_{\text{Fe}^{2+} - \text{HO}^\bullet} [\text{HO}^\bullet]_{\text{ss}} [\text{Fe}^{2+}]_0}{k_{\text{H}_2\text{O}_2 - \text{HO}^\bullet} [\text{HO}^\bullet]_{\text{ss}} [\text{H}_2\text{O}_2]_0} = 2.9 - 21 \end{aligned}$$

where $k_{\text{Fe}^{2+} - \text{HO}^\bullet} = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{H}_2\text{O}_2 - \text{HO}^\bullet} = 3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C [15].

The calculation illustrates that excessive Fe²⁺ at [H₂O₂]₀/[Fe²⁺]₀ < 1 had a 3–21 times higher scavenging effect of HO[•] than excessive H₂O₂ at [H₂O₂]₀/[Fe²⁺]₀ < 1, which indicates a relatively efficient utilization of HO[•] at [H₂O₂]₀/[Fe²⁺]₀ > 1. H₂O₂ utilization efficiency (milligram TCE degraded per gram H₂O₂ consumed) was calculated from the experiments in Figures 2 and 3. The H₂O₂ utilization efficiency decreased from 12.2 to 3.4 as [H₂O₂]₀/[Fe²⁺]₀ increased from 0.5 to 3.3. Treatment costs are directly linked to H₂O₂ utilization, as the cost of H₂O₂ is the main cost for Fenton oxidation because Fe salts are much cheaper than H₂O₂. It should be noted that the H₂O₂ consumption for the experiments of Figures 2 and 3 includes consumption by other HO[•] scavengers such as the silicone surfactant used for the present study, and the released chloride ions although the extent of scavenging by these chemicals was not determined [32].

Gas retention time in the foam reactor influences the treatment performance, and effective TCE degradation can only be achieved if the gas retention time is greater than the time required for oxidation of TCE by HO[•]. Figures 4a and 4b present the effect of gas retention time and [H₂O₂]₀/[Fe²⁺]₀ ratio on TCE treatment. As expected, both the removal efficiency and the mineralization of TCE vapors markedly increased as the gas retention time was increased from 10 to 30 s. The TCE elimination capacity at [H₂O₂]₀/[Fe²⁺]₀ of 2.5 was as high as 49–56 TCE m⁻³ reactor h⁻¹. H₂O₂ utilization efficiency was relatively constant (3.7–4.2 mg TCE degraded per gram H₂O₂ consumed) at [H₂O₂]₀/[Fe²⁺]₀ of 2.5 (Figure 4b). This indicates that TCE removal in the foam reactor was proportional to gas retention time (10–30 s) at constant H₂O₂ utilization

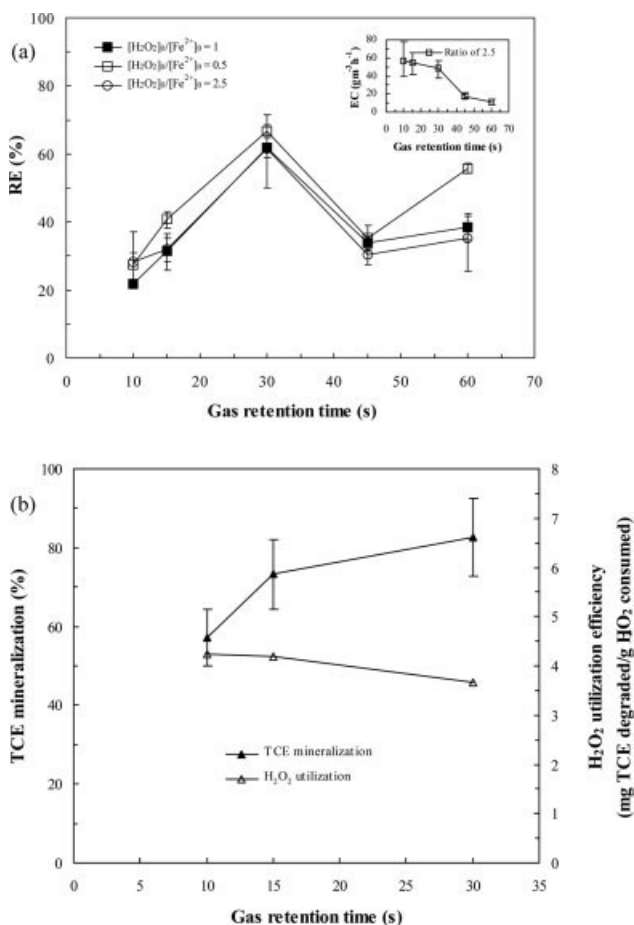


Figure 4. Effect of gas retention time (a) on TCE vapor removal efficiency and elimination capacity at $[H_2O_2]_0/[Fe^{2+}]_0 = 2.5$ (inset), (b) TCE mineralization and H_2O_2 utilization efficiency in a foamed reactor at $[H_2O_2]_0/[Fe^{2+}]_0$ of 2.5. TCE inlet concentration, $0.63 \pm 0.03 \text{ g m}^{-3}$.

efficiency. For the experiments in Figure 3, a more complete degradation of TCE was observed in the presence of an excess of H_2O_2 because of the greater concentration of $HO\cdot$ radicals resulting from such conditions. Surprisingly, TCE removal efficiency was drastically reduced at a gas retention time of 40 s and 60 s. The most likely explanation is that our reactor prototype required a certain minimum air velocity in order to produce a fine and uniform foam. At gas retention times of 40 and 60 s, coarse foam with a low interfacial area was observed, leading to poor performance for TCE removal. These observations emphasize the fact that size and stability of foam are key factors in enhancing mass transfer in foam reactors. Thus, careful design of the foam generation system is warranted.

Finally, TCE removal in the foam-Fenton reactor was compared to oxidation using identical concentrations of Fenton reagent in conventional wet scrubbers packed with three different random inert packings. Figure 5 shows a comparison of TCE removal and

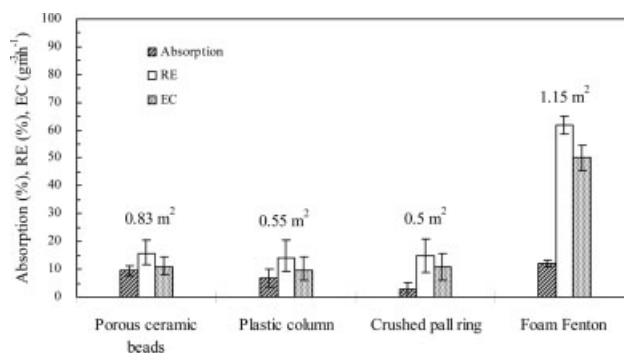


Figure 5. Comparison of Fenton oxidation in a foam reactor to wet scrubbers packed with various solid packings. For all the experiments, TCE inlet concentrations were $0.58 \pm 0.018 \text{ g m}^{-3}$. The numbers above each packing indicate total surface area provided by each packing. See the details in the text.

elimination capacities. As mentioned in the Methods section, the ceramic beads had the largest surface area and the crushed Pall rings had the lowest surface area. Earlier studies have also shown that ceramic beads had a very high gas and liquid film mass transfer coefficients [33].

Absorption of TCE was measured first using deionized water. As shown in Figure 5, the absorption of TCE was proportional to the total surface area of packing materials. Gas absorption primarily depends on gas-liquid interfacial area and on gas to liquid flow ratio [34, 35]. TCE removal by Fenton oxidation showed a marginal improvement over simple absorption in all three conventional scrubbers while a major increase in TCE removal was observed for the foam reactor when Fenton's reagent was introduced. Besides the large area for mass transfer, another explanation for the effective reaction in the foam reactor is the short diffusion length in the thin (130–160 μm) liquid films that make up the foam. Because the Fenton reaction is a fast reaction [36], if diffusion limitations exist in the liquid, unused hydroxyl radical will react to form superoxide radicals ($HO_2\cdot$), which are not reactive towards TCE. Thus, the marginal improvement of TCE removal using Fenton's reagent in the conventional scrubbers indicates that there were significant mass transfer limitations in these systems.

CONCLUSIONS

Fenton oxidation of TCE vapors was conducted in a prototype foam reactor. Laboratory-scale experiments demonstrated rapid mass transfer and high elimination capacity (up to $60 \text{ g TCE m}^{-3}_{\text{reactor}} \text{ h}^{-1}$) of TCE vapors at short gas retention times. TCE mineralization depended on the $[H_2O_2]_0/[Fe^{2+}]_0$ and was highest when H_2O_2 was provided in excess. Overall, this study demonstrates the potential utilization of a foam reactor for advanced chemical oxidation of polluted gases or vapors.

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