Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe^{2+}, and zero-valent iron

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ABSTRACT

The oxidation of polyvinyl alcohol (PVA) by persulfate ($S_2O_8{}^{2-}$) activated with heat, Fe^{2+}, and zero-valent iron (Fe(0)) was investigated via batch experiments. It was hypothesized that elevated temperature and the addition of Fe^{2+} or Fe(0) into a persulfate-water system could enhance the oxidation of PVA by activated persulfate. Increasing the temperature from 20 to 60 °C or 80 °C accelerated the oxidation rate of PVA, which achieved complete oxidation in 30 and 10 min, respectively. At 20 °C, the addition of Fe^{2+} or Fe(0) to the persulfate-water system significantly enhanced the oxidation of PVA. The optimal persulfate-to-Fe^{2+} or Fe(0) molar ratio was found to be 1:1. Complete oxidation of PVA was obtained by Fe(0)-activated persulfate in 2 h. Synergistic activation of persulfate by heat and Fe^{2+} or Fe(0) was also shown to enhance the oxidation of PVA in the persulfate-water system. By using GC–MS analysis, an oxidation product of PVA was identified as vinyl acetic acid ($C_4H_6O_2$), which is readily biodegradable. Our results suggest that the oxidative treatment of PVA by activated persulfate is a viable option for the pretreatment of PVA-laden wastewater to enhance its biodegradability.
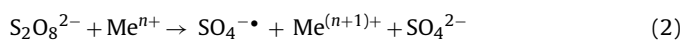
1. Introduction

Polyvinyl alcohol (PVA), a well known recalcitrant compound, is commonly used in the textile industry as a sizing agent and in the pharmaceutical industry as an ophthalmic lubricant [1]. PVA is also used in adhesives, paper-coating, emulsion paints, and detergent-based industries [2]. It has been shown that it is difficult to convert PVA-laden wastewaters to innocuous end products like carbon dioxide and water, which is detrimental to the ecosystem and can lead to accumulation in the human body through the food chain [2,3]. PVA can also cause additional environmental problems due to its potential to mobilize heavy metals from sediments in water streams and lakes [4]. Unfortunately, conventional biological systems (e.g. activated sludge) do not efficiently degrade PVA because the PVA degrading capacity of most microbial species is very specific and limited [5]. It was reported that after 48 days of incubation, mixed cultures acclimated to a PVA solution showed only a 40% mineralization of PVA [6]. In addition, the generation of foam in biological reactors during PVA wastewater treatment makes the operation difficult and the treatment inefficient [7]. Therefore, it is imperative to develop more effective methods to treat PVA in natural and engineered systems.

In the last decades, chemical oxidation of contaminants in the natural environment by oxidants has been increasingly studied to develop novel in situ/ex situ remediation technologies. The oxidants H_2O_2, $KMnO_4$, and O_3 have been widely tested in laboratory work and field applications [8–13]. H_2O_2 has a strong oxidation potential ($E^0 = 1.78$ V) and non-selective reactivity for most organic contaminants. Specifically in soil, Fe^{2+}-bearing minerals could activate H_2O_2 to produce hydroxyl radicals (OH•) ($E^0 = 2.70$ V) which could enhance the oxidative transformation of contaminants [9]. However, H_2O_2 is too reactive to effectively handle the oxidants in subsurface environments [8,9]. Most of the H_2O_2 would be rapidly consumed during transportation through the soil and aquifer before reaching the contaminants due to its high reactivity [8]. O_3 is a strong oxidant ($E^0 = 2.07$ V) and somewhat selectively reactive to electron-rich compounds [10]. Besides, it has the limitation of being soluble in water [8,10]. For this reason, it is difficult to supply enough O_3 to contaminants in subsurface environments. Compared to H_2O_2 and O_3, $KMnO_4$ ($E^0 = 1.68$ V) is relatively stable, which could make its use attractive [13]. However, in contrast to H_2O_2 and O_3, the oxidation of contaminants by $KMnO_4$ is limited because it is selectively reactive to unsaturated chlorinated compounds [13].
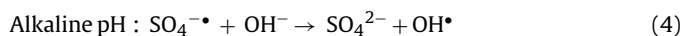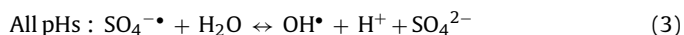
Persulfate ($S_2O_8{}^{2-}$) has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants [14–26]. The use of persulfate has several advantages. It is a strong oxidizing agent ($E^0 = 2.01$ V), non-selectively reactive, and relatively stable at room temperature. Also, heat, transition metal ions (Me^{n+}) such as Fe^{2+}, and UV light can excite persulfate to form sulfate radical

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$(SO_4^{-\bullet})$, a stronger oxidant ($E^0 = 2.60$ V) than persulfate, to significantly enhance the oxidation of contaminants [25,26].

$$S_2O_8^{2-} + heat/UV \rightarrow 2SO_4^{-\bullet} \qquad (1)$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{-\bullet} + Me^{(n+1)+} + SO_4^{2-} \qquad (2)$$

In a persulfate-water system, hydroxyl radicals can be formed via following reactions, and may participate in the oxidation of contaminants [17].
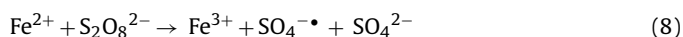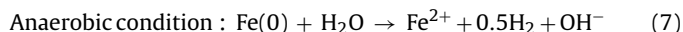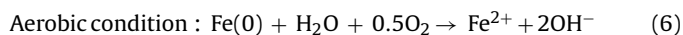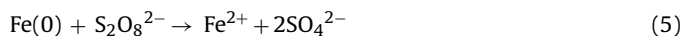
$$\text{All pHs}: SO_4^{-\bullet} + H_2O \leftrightarrow OH^{\bullet} + H^+ + SO_4^{2-} \qquad (3)$$

$$\text{Alkaline pH}: SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \qquad (4)$$

The heat activation of $S_2O_8^{2-}$ has been intensively studied to oxidize recalcitrant toxic contaminants. Huang et al. [14] found that methyl *tert*-butyl ether (MTBE) was degraded in a pseudo-first-order manner and that, as temperature was increased from 20 to 50 °C, the pseudo-first-order rate constant increased accordingly. They observed that an increase in pH and ionic strength resulted in a decrease in the rate constant. Huang et al. [15] also reported that the heat-activated persulfate could effectively oxidize 59 volatile organic compounds, including benzene, toluene, ethyl benzene, xylene, and chlorinated solvents, and that the oxidation of unsaturated compounds by heat-activated persulfate is much faster than saturated hydrocarbons due to the electron density of double/triple bonding and the stability of the compounds. Liang et al. [16] showed that the oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane were enhanced by thermally activated persulfate in aqueous systems and soil slurries, showing activation energies of 97.74 ± 3.04 and 163.86 ± 1.38 kJ/mol, respectively. In soil slurries, the oxidation was inhibited by increasing the amount of organic carbon contents in the soil. They also showed that the sulfate radical was dominant in the oxidation of TCE in a persulfate system under acidic conditions, and that the hydroxyl radical predominated under basic conditions [17]. Waldemer et al. [18] also showed that elevating the temperature from 30 to 70 °C could enhance the oxidation of chlorinated ethenes including tetrachloroethylene (PCE), TCE, cis-dichloroethylene (DCE), and trans-DCE. The activation energies of PCE, TCE, cis-DCE, and trans-DCE were shown to be 101 ± 4, 108 ± 3, 144 ± 5, and 141 ± 2 kJ/mol, respectively.

Aside from heat activation, transition metal ions including Ag^+ and Fe^{2+} have also been studied in the activation of persulfate to enhance the oxidation of recalcitrant compounds. Anipsitakis and Dionysiou [19,20] showed that Ag^+ could activate persulfate to generate sulfate radicals, which could more effectively oxidize 2,4-DCP under acidic conditions. Liang et al. [21] also reported that addition of Fe^{2+} into a persulfate-water system could significantly enhance the oxidative degradation of TCE when sequential addition of Fe^{2+} in small increment was applied. Besides, thiosulfate ($S_2O_3^-$) addition to the Fe^{2+}-persulfate system could also improve the oxidation of TCE by converting Fe^{3+} to Fe^{2+} [21]. They also found that a chelating agent such as citric acid could enhance the activation of persulfate by Fe^{2+} to increase the rate of TCE oxidation under the optimal chelate-to-Fe^{2+} ratio [22]. Currently, Dionysiou and co-workers [23] showed that sulfate radicals generated from activation of persulfate with ferrous ion effectively destruct 2-chlorobiphenyl and chlorophenols and that Fe^{2+}/citrate is a universal chelating agent system to activate oxidants including $S_2O_8^{2-}$, HSO_5^-, and H_2O_2 [24].

So far, several attempts have been made to use chemical oxidation processes for the treatment of PVA in aqueous solution. Lei et al. [27] showed that photochemical Fenton oxidation could significantly enhance the oxidative degradation of PVA. Bossman et al. [28] showed that PVA was mineralized via super macromolecules ($1-5 \times 10^6$ g/mol) in the oxidation by Fenton's reagent. In contrast, PVA was degraded via small molecules such as oxalic acid in the heterogeneous Fenton system (Fe^{3+}-exchanged zeolite + H_2O_2 + UV).

Giroto et al. [1] also showed that photo-Fenton degradation could mineralize PVA up to 90% under optimal conditions. However, to our knowledge, no attempt has been made to apply persulfate oxidation activated by heat and Fe^{2+}. In this study, we also used zero-valent iron ($Fe(0)$) to activate persulfate for the generation of sulfate radicals. We hypothesized that in the presence of persulfate, $Fe(0)$ might be a good Fe^{2+} provider for the activation of persulfate to sulfate radicals under aerobic or anaerobic conditions.

$$Fe(0) + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \qquad (5)$$

$$\text{Aerobic condition}: Fe(0) + H_2O + 0.5O_2 \rightarrow Fe^{2+} + 2OH^- \qquad (6)$$

$$\text{Anaerobic condition}: Fe(0) + H_2O \rightarrow Fe^{2+} + 0.5H_2 + OH^- \qquad (7)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \qquad (8)$$

In the present study, the oxidation of PVA by persulfate activated with heat, Fe^{2+} and $Fe(0)$ was investigated via batch experiments. The effect of elevated temperatures on the kinetics of PVA oxidation was examined and the activation energy was estimated. The optimal ratio of persulfate-to-Fe^{2+} or $Fe(0)$ was determined in the Fe^{2+} or $Fe(0)$-persulfate system. The products of oxidation were determined using gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Chemicals

PVA with a degree of polymerization of 1500 and a degree of hydrolysis value of 86–90% was obtained from Yakuri Pure Chemicals Co. Ltd, Japan. Boric acid and potassium iodide were supplied by DC Chemical Co. Ltd., Japan, and iodine (99.5% pure) was obtained from Acros Organics, USA. $FeSO_4 \cdot 7H_2O$ (98%) was purchased from Daejung Chemicals Co. Ltd., Korea, and $K_2S_2O_8$ (95%) was obtained from Dong Yang Chemical Co. Ltd., Korea. The zero-valent iron used in this study was obtained from Peerless Metal Powders Inc. (Detroit, MI, USA). The specific surface area of the Peerless iron was 1.67 m^2/g [29]. The iron was used as received without pretreatment. The chemicals were of reagent grade and were used without further purification. All of the samples were prepared in double distilled water.

2.2. Batch oxidation experiments

Stock solutions of PVA (100 mg/L) and persulfate (500 mg/L, corresponding to ∼2.6 mM) were prepared in deionized water prior to every batch experiment using a magnetic stirrer (PC-420, Corning, USA). Five hundred millilitres of the prepared PVA and persulfate solutions were immediately added to a 2-L Erlenmeyer flask, which was shaken at 50 rpm using a shaking water bath (HB-2053SW, Hanbaek, Korea) at adjusted temperatures. Accordingly, the initial concentrations of PVA and persulfate were 50 and 250 mg/L, respectively. Duplicate flasks were set up to allow us to determine reproducibility. To investigate the effect of temperature on the oxidation of PVA in the persulfate-water system, the temperature was maintained at 20, 40, 60, and 80 °C. Control experiment in the absence of persulfate at each temperature showed that disappearance of PVA was due to reaction with activated persulfate and not volatilization. To examine the effect of Fe^{2+} and $Fe(0)$ on the persulfate oxidation of PVA, pre-determined amounts of $FeSO_4 \cdot 7H_2O$ and $Fe(0)$ were added to the PVA solution before being completely mixed with the persulfate solution in the flask. Preliminary tests showed that the addition of $FeSO_4 \cdot 7H_2O$ or $Fe(0)$ into the PVA solution did not affect the concentration of PVA. To obtain the optimal Fe^{2+} or $Fe(0)$ to persulfate ratio, the oxidation of PVA was investigated under various Fe^{2+} or $Fe(0)$ to persulfate molar ratios, including 5:1, 2:1, 1:1, 0.5:1, and 0.25:1. The synergistic effect of

elevated temperature on the oxidation of PVA in the persulfate-Fe^{2+} or Fe(0)-water system was also investigated under optimal conditions. At selected time intervals (2, 5, 10, 30, 60, 120 min), 20 mL sample collected from each duplicate flask was immediately filtered through a 0.22 μm membrane filter (Millipore, MA, USA) for PVA determination. Under identical conditions, control experiments were also performed without either Fe^{2+} (or Fe(0)) or persulfate. We checked out quenching in preliminary experiments by addition of concentrated KI to the filtered solutions [21]. However, no difference between quenched and unquenched samples was observed when PVA was analyzed immediately. Therefore, we analyzed samples immediately following each sampling interval.

2.3. Chemical analysis

PVA measurements were performed at a λ_{max} of 690 nm using a UV–vis spectrophotometer (Shimadzu, model UVmini-1240, Japan). The method is based on the blue color produced by reaction of PVA with iodine in the presence of boric acid [30]. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, model TOC-V CPN, Japan). Persulfate concentration was determined by the UV–vis spectrophotometer according to Liang et al.'s modified method [31]. To determine the oxidation products formed in the PVA oxidation by the activated persulfate, qualitative mass spectrometry analysis was performed using a gas chromatography–mass spectrometry (GC–MS, Claus 600, PerkinElmer, Waltham, MA, USA) equipped with an Elite-Wax column (PerkinElmer, Waltham, MA, USA). The electron impact (EI) mode was used and the mass range was set to 30–600 amu.

3. Results and discussion

3.1. Oxidation of PVA by heat-activated persulfate

PVA oxidation by persulfate at various temperatures is shown in Fig. 1a. At 20 °C, only 30% of the PVA was oxidized by persulfate in 120 min. In contrast, under identical conditions, the PVA concentration was constant without the addition of persulfate. As the temperature increased, the rate of PVA oxidation by persulfate significantly increased. Approximately 92% of the PVA was removed by persulfate oxidation in 60 min at 40 °C. Complete oxidation of PVA by persulfate was observed in 30 and 10 min at 60 and 80 °C, respectively. These results indicate that persulfate can be activated to sulfate radicals by heat energy, which is responsible for the increase of PVA oxidation at elevated temperatures. Pseudo-first-order rate constants for PVA oxidation by persulfate at 20, 40, 60, and 80 °C were calculated to be 0.0048 ± 0.0007 ($R^2 = 0.926$), 0.0234 ± 0.0043 ($R^2 = 0.928$), 0.0846 ± 0.0114 ($R^2 = 0.992$), and $0.4238 \pm 0.0120 \, min^{-1}$ ($R^2 = 0.986$), respectively. Based on the pseudo-first-order rate constants, the activation energy for PVA oxidation by persulfate was calculated to be 64.1 ± 1.9 kJ/mol ($R^2 = 0.997$). During the oxidation of PVA by heat-activated persulfate, persulfate consumption was increased with the increase in temperature (Fig. 1b). At each temperature, persulfate concentration was gradually decreased as the oxidation of PVA proceeded. In 120 min, final persulfate consumption at 20, 40, 60, and 80 °C were 34%, 52%, 75%, and 95%, respectively.

3.2. Oxidation of PVA by Fe^{2+}-activated persulfate

Similar to elevated temperature, addition of Fe^{2+} was shown to enhance the oxidation of PVA by persulfate at 20 °C (Fig. 2a). When the persulfate-to-Fe^{2+} molar ratio was 5:1, 23% of the PVA was oxidized by persulfate in 120 min. In contrast, the addition of Fe^{2+} (~1.3 mM) without persulfate did not transform the PVA in water. The rate of PVA oxidation by persulfate increased when the
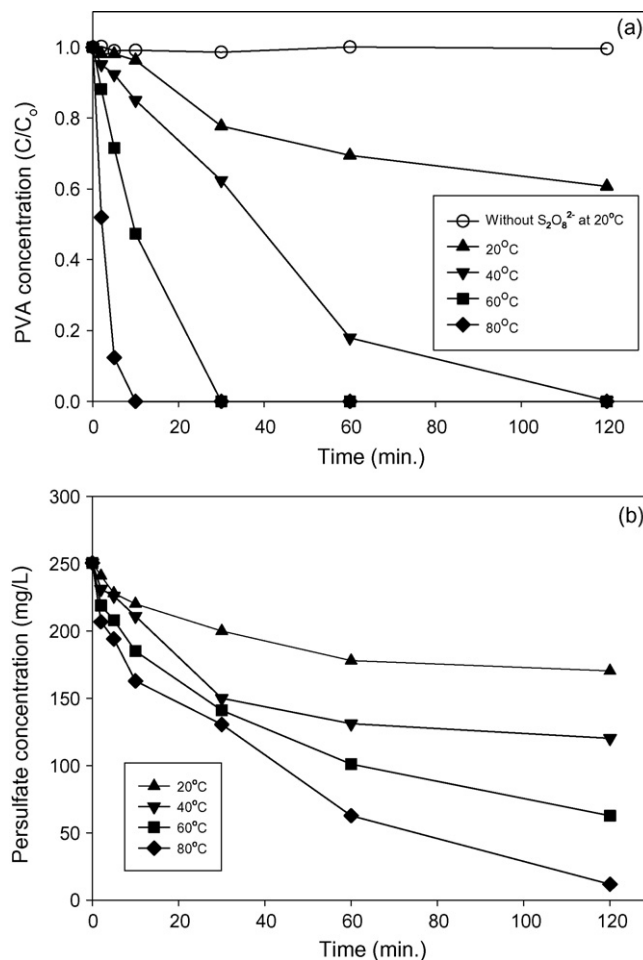

Fig. 1. Change in PVA (a) and persulfate (b) concentrations during oxidation by heat-activated persulfate. Input persulfate concentration is 250 mg/L and initial concentration of PVA is 46.6–60.0 mg/L. Data points represent averages of two samples from duplicate reactors.

amount of Fe^{2+} increased, indicating that Fe^{2+} can activate persulfate into sulfate radicals as previously reported [25,26]. When the persulfate-to-Fe^{2+} molar ratio was 1:1, approximately 70% of the PVA was oxidized. However, as the amount of Fe^{2+} was further increased, the rate of PVA oxidation did not increase. The rate of PVA oxidation by persulfate was shown to be somewhat slower when the persulfate to Fe^{2+} molar ratio was 1:2 or 1:5. It appears that the rate of PVA oxidation was maximized when the persulfate to Fe^{2+} molar ratio was 1:1. Interestingly, this optimal ratio is in agreement with Fe^{2+} to oxidant ratio in other modified Fenton-type advanced oxidation processes. Dionysiou and co-workers [23,32] showed that molar ratio of Fe^{2+} to the oxidant was 1:1 in the oxidation of 2-chlorobiphenyl and MTBE by peroxymonosulfate and hydrogen peroxide, respectively.

Unlike heat-activated persulfate, Fe^{2+}-activated persulfate did not completely oxidize the PVA. An excessive amount of Fe^{2+} might be working as an intrinsic scavenger of sulfate radicals (Eq. (9)) [25], accounting for the decrease in the rate of PVA oxidation in the persulfate-Fe^{2+} system.

$$Fe^{2+} + SO_4^{-\bullet} \rightarrow Fe^{3+} + SO_4^{2-} \tag{9}$$

Besides, under optimal condition where the persulfate to Fe^{2+} molar ratio was 1:1, persulfate consumption was less than those at elevated temperatures (Fig. 2b). Persulfate concentration was gradually decreased as PVA was oxidized by Fe^{2+}-activated persulfate, showing 22% of consumption in 120 min.
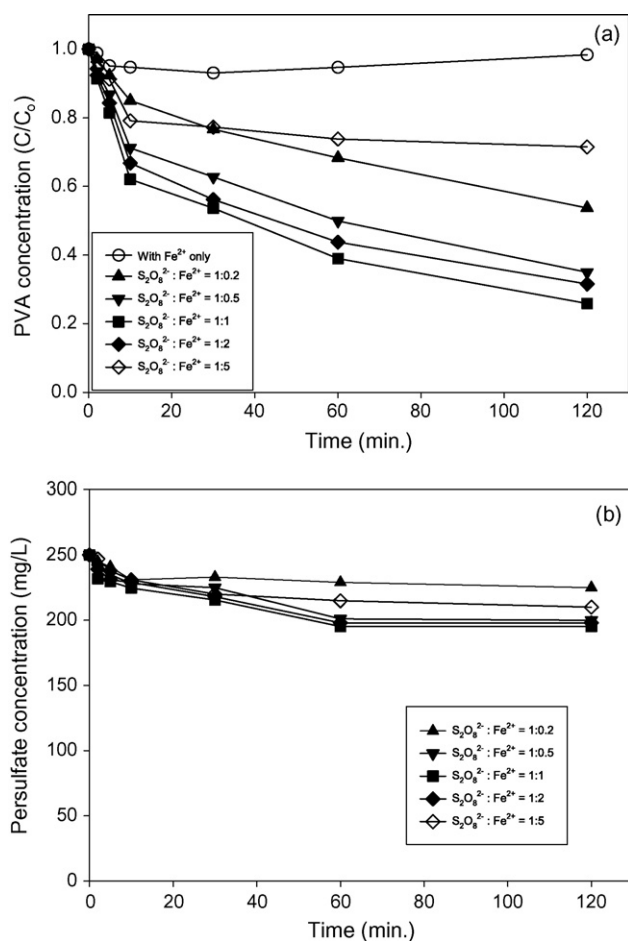
Fig. 2. Change in PVA (a) and persulfate (b) concentrations during oxidation by Fe^{2+}-activated persulfate at 20 °C. Input persulfate concentration is 250 mg/L and initial concentration of PVA is 47.1–50.2 mg/L. Data points represent averages of two samples from duplicate reactors.
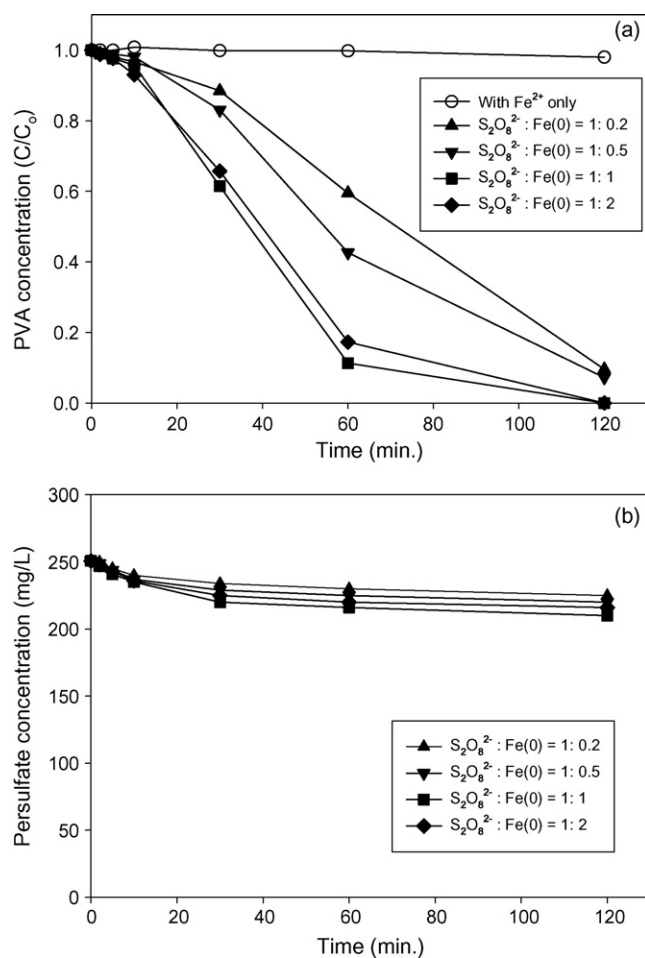

Fig. 3. Change in PVA (a) and persulfate (b) concentrations during oxidation by Fe(0)-activated persulfate at 20 °C. Input persulfate concentration is 250 mg/L and initial concentration of PVA is 47.1–50.2 mg/L. Data points represent averages of two samples from duplicate reactors.

3.3. Oxidation of PVA by Fe(0)-activated persulfate

Similar to the addition of Fe^{2+}, the addition of Fe(0) could enhance the oxidation of PVA in the persulfate system. In the presence of 0.325 mM of Fe(0) in the persulfate solution (the persulfate to Fe^{2+} molar ratio = 5:1), approximately 90% of the PVA was oxidized in 120 min (Fig. 3a). As the amount of Fe(0) increased, the rate of PVA oxidation by persulfate increased accordingly. In contrast to the Fe^{2+}-persulfate system, complete oxidation of PVA was achieved by Fe(0)-activated persulfate when the persulfate-to-Fe(0) molar ratio was 1:1. Further addition of Fe(0) did not enhance the PVA oxidation significantly, indicating that a 1:1 molar ratio of persulfate to Fe(0) is the optimal condition for the effective activation of persulfate. Though complete oxidation of PVA was obtained by Fe(0)-activated persulfate, the TOC concentration did not change significantly, indicating that mineralization of PVA was not achieved. Under optimal condition, persulfate consumption in 120 min was 16%, less than in Fe^{2+}-persulfate systems (Fig. 3b).

The activation of persulfate by Fe(0) is due to the release of Fe^{2+} from Fe(0) in the persulfate-Fe(0) system. By way of the oxidation of Fe(0) by persulfate, Fe^{2+} could be continuously supplied to the persulfate system, which might activate persulfate to sulfate radicals more effectively than a one-time dose of Fe^{2+}. Therefore, compared to the oxidation of PVA by Fe^{2+}-activated persulfate (Fig. 2), the rate and extent of PVA oxi-

dation by Fe(0)- activated persulfate were greatly improved under identical conditions. These results indicated that instead of Fe^{2+}, addition of Fe(0) could more effectively enhance the oxidation of PVA by persulfate.
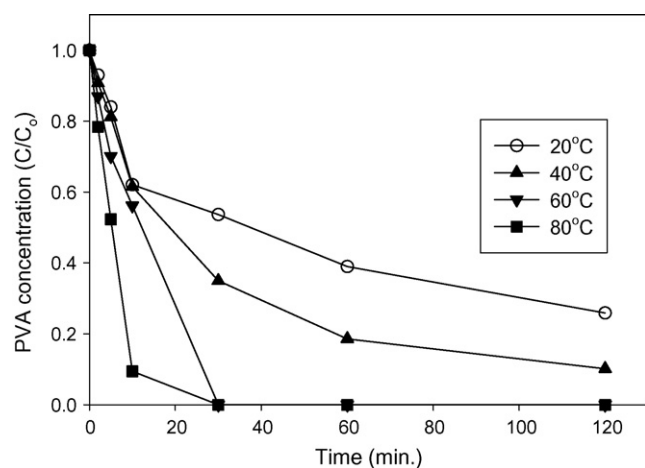

Fig. 4. The effect of temperature on the oxidation of PVA by Fe^{2+}-activated persulfate at the optimal Fe^{2+}-to-$S_2O_8^{2-}$ ratio (1:1). Input persulfate concentration is 250 mg/L and initial concentration of PVA is 46.5–51.9 mg/L. Data points represent averages of two samples from duplicate reactors.

Fig. 5. The effect of temperature on the oxidation of PVA by Fe(0)-activated persulfate at the optimal Fe(0)-to-$S_2O_8^{2-}$ ratio (1:1). Input persulfate concentration is 250 mg/L and initial concentration of PVA is 46.5–51.9 mg/L. Data points represent averages of two samples from duplicate reactors.
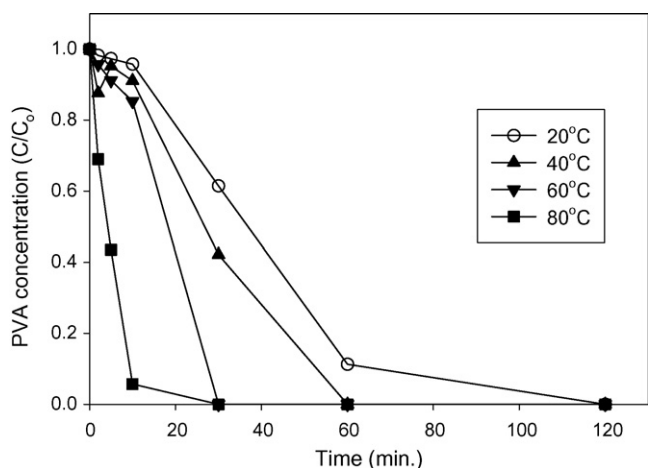
3.4. Oxidation of PVA by persulfate activated by heat in the presence of Fe^{2+} or $Fe(0)$

Under optimal conditions (Fe^{2+} or $Fe(0)$ to persulfate molar ratio = 1:1), the oxidation of PVA by persulfate was further enhanced by temperature elevation. As shown in Figs. 4 and 5, the oxidation of PVA was significantly enhanced in the Fe^{2+} or $Fe(0)$-persulfate system as temperature increased. However, compared to the oxidation of PVA by heat-activated persulfate (Fig. 1), the enhancement of PVA oxidation was mostly due to heat-activated persulfate even under optimal conditions (Figs. 4 and 5), indicating that heat energy can activate persulfate to sulfate radicals more effectively. However, it should be noted that elevating the temperature requires additional cost. Therefore, a cost-effective heating method should be included to apply heat-activated persulfate to the treatment of PVA. It should also be noted that, in view of an in situ remediation technology, elevating the temperature to activate persulfate might not be a promising method because it is very difficult to heat up soil or an aquifer in a cost-effective way. It is likely that the addition of Fe^{2+} or $Fe(0)$ is a better method to activate persulfate in subsurface environments as long as transportation of the Fe^{2+} or $Fe(0)$ to the persulfate is effectively controlled. Field-scale tests might be necessary to use Fe^{2+} or $Fe(0)$-activated persulfate to
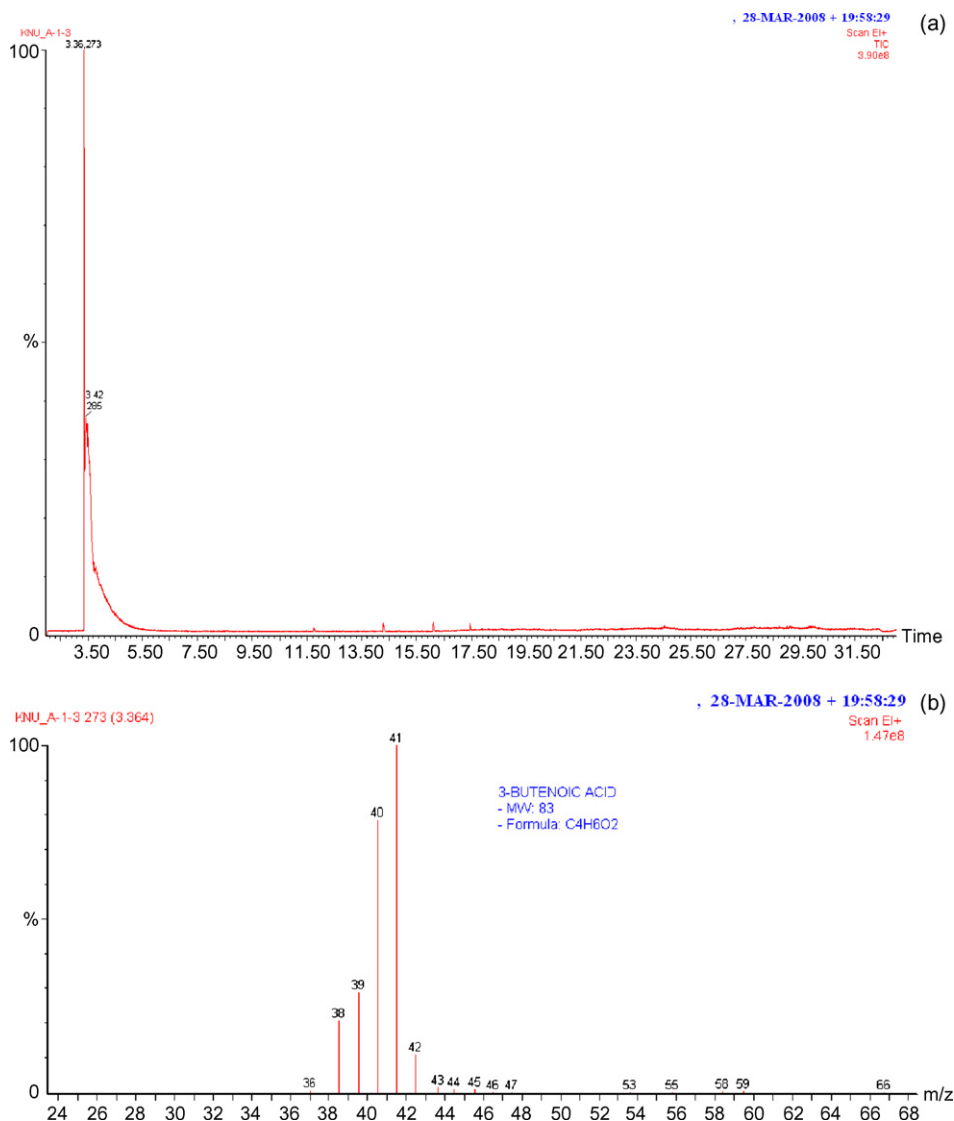

Fig. 6. GC chromatogram (a) and mass spectrum (RT = 3.364) (b) of PVA solution oxidized by Fe(0)-activated persulfate for 120 min.

remediate soil and aquifers contaminated with recalcitrant organic compounds.

3.5. Enhanced biodegradability and product identification

After the complete oxidation of PVA was achieved in the persulfate-Fe(0) system, the solutions were analyzed by GC–MS to identify the oxidation products. As shown in Fig. 6a, the GC chromatogram showed two large peaks. Based on the mass spectrum, these two peaks represent the same compound, identified as vinylacetic acid ($C_4H_6O_2$) (Fig. 6b). The long tail of the second peak is due to a high concentration of the compound. Vinylacetic acid, an unsaturated carboxyl acid, is an acid with a small molecular-weight and is far more biodegradable than PVA. These results suggest that the oxidation of PVA by Fe(0)-activated persulfate may be an effective pretreatment option to enhance the biodegradability of PVA in waste and wastewater treatment facilities as well as in the natural environment.

4. Conclusions

In summary, our results show that PVA is effectively oxidized by persulfate activated with heat, Fe^{2+}, and Fe(0). Complete oxidation of PVA by persulfate in the presence of heat energy or Fe(0) was obtained within two hours under optimal conditions. One oxidation product that was identified was vinylacetic acid, which is readily biodegradable. Our results suggest that (pre)treatment of PVA by heat- or Fe(0)-activated persulfate may be an option for improving the biodegradability of PVA in natural and engineered systems.

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