

Mechanism of Photo-Fenton Degradation of Ethanol and PVA*

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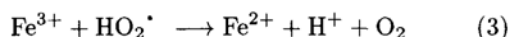
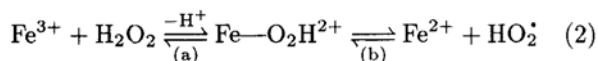
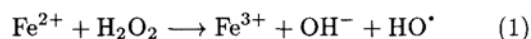
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Abstract Contrast degradation experiments between ethanol and polyvinyl alcohol (PVA) were conducted during H_2O_2 , UV/ H_2O_2 , Fenton, and Photo-Fenton processes in this study. UV/VIS spectra showed that complexes between Fe(III) and organics were easily formed and degraded within reaction time. Compared with the degradation of complex, hydroxyl radicals acted weakly in Fenton or Photo-Fenton process. Hydroxyl radicals involved in Photo-Fenton process were deemed to be generated from the split decomposition of H_2O_2 , photolysis of Fe_{aq}^{3+} , and degradation of hydrated Fe(IV)-complex but not traditional Fenton reaction. Experimental evidence to support this point was presented in this paper.

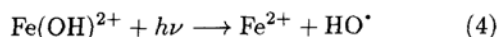
Keywords mechanism, Fenton reaction, oxidation

1 INTRODUCTION

Fenton process has been well studied recently for its prospective applications in unmanageable wastewater treatment^[1-3]. Traditionally, the high efficiency of Fenton process is owed to the generation of hydroxyl radical (HO^\bullet), with a high oxidation potential ($E^0 = 2.80\text{ V}$) and the organic compounds can be mineralized completely to water and carbon dioxide. In acidic media Fenton reaction can be simplified as the following equations according to the free radical mechanism^[4]



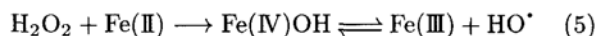
In this ferric system, Fe^{3+} acts as a catalyst. With an excess of H_2O_2 , Fe^{2+} is oxidized to produce hydroxyl radical through Eq. (1). Recently combination of Fenton reaction with UV light, so called Photo-Fenton reaction, has shown to enhance the efficiency of this process. Some previous researchers opined that decomposition of the photo-active $Fe(OH)^{2+}$ would lead to addition of the hydroxyl radicals^[3].



However, the free radical mechanism has been questioned at times because optical absorption measurement during Fenton reaction proves the presence of complexes between Fe(III)/Fe(II) and H_2O_2 ^[5]. Furthermore, recent thermodynamic calculations have demonstrated that an outer-sphere electron transfer

reaction between $Fe(II)_{aq}$ and H_2O_2 [Eq.(1)] cannot take place, because the formation of the intermediate $H_2O_2^-$ is not favored^[6,7]. As a result many alternative mechanisms have been proposed^[8-13].

From recent publications^[10,14,15], it has been well established that complexes of Fe(II)/Fe(III) with organic ligands play an important role in Fenton reaction. These complexes may react with peroxide or other oxidants to form high-valent ferryl moiety, where iron is in +IV or +V valent state. With the degradation of higher-valent hydrated iron-species, hydroxyl radicals appear concurrently, which may confound the interpretation of the experimental results. This process can be simplified as follows



Spin-trapping experiments have demonstrated that free hydroxyl radicals exist in Fenton or Photo-Fenton reactions^[16]. However, spin-trapping experiments are inconclusive because they cannot rule out the existence of nontrapped transient or the conception that the transient gives the same spin trap product as hydroxyl radical.

Ethanol, a simplest linear chain alcohol, and polyvinylalcohol (PVA), a polymeric alcohol, were chosen as the model organic compounds in this work. Experiments were conducted by investigating their decomposition by H_2O_2 , UV/ H_2O_2 , Fenton, and Photo-Fenton processes. Acetic acid, an intermediate that may be generated during the oxidation of ethanol (or PVA) by hydroxyl radicals, was measured in these four processes. The purpose of this study is to provide evidence whether hydroxyl radical oxidation is the key

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reason for the high degradation efficiency of Fenton and Photo-Fenton processes.

2 EXPERIMENTAL SECTION

2.1 Materials

All chemical reagents including PVA were purchased from Merck (ACS grade). Water was of double-distilled quality.

2.2 Photoreactor and photodegradation procedure

All photolysis experiments were carried out in a batch reactor, and the experimental apparatus was shown in Fig. 1. It consists of a reservoir (volume: 0.60 L), a flow-through annular photoreactor (volume: 0.15 L, ID: 10 mm, length: 200 mm, made from quartz glass), equipped with a mercury medium pressure lamp (Heraeus, TQ 150, electrical power consumption: 150 W, the radiant power: 45.6 W) giving a main emission at 365 nm. The solution was recirculated ($250 \text{ ml} \cdot \text{min}^{-1}$) by means of a pump (Bender & Hobein, Masterflex, Easy-load 75-118-00). The ethanol or PVA solution was continuously purged (in the reservoir) by compressed air during the entire reaction time. The photolysis experiments were performed for a duration of 180 min. The temperature of the solutions was kept at 30°C .

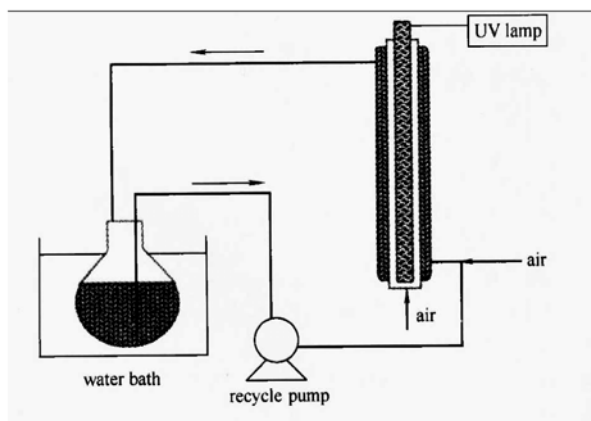
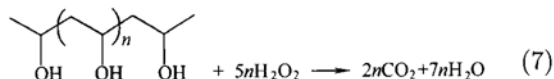


Figure 1 Photochemical batch reactor employed in all irradiation experiments

The total volume of the photolysis solution was 0.50 L. The original concentration of ethanol and PVA solution was $400 \text{ mg} \cdot \text{L}^{-1}$ and $200 \text{ mg} \cdot \text{L}^{-1}$ (carbon content), respectively. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in ethanol or PVA solution before H_2O_2 was added. The molar ratio of Fe(II) to H_2O_2 was 1 : 20. The amount of H_2O_2 added is the stoichiometric amount of H_2O_2 required for the total oxidation of ethanol or PVA as calculated according to Eqs. (6) and (7).



The pH was adjusted using H_2SO_4 to the initial value of 3.0. The analysis was performed immediately after the samples were taken from the batch reactor at various photolysis time intervals. $2.0 \times 10^{-3} \text{ L}$ of "reduction and precipitation agent", composed of $0.10 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_3\text{PO}_4$, $0.10 \text{ mol} \cdot \text{L}^{-1} \text{ KI}$ and $0.10 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_3$, was diluted to a volume of $4.0 \times 10^{-3} \text{ L}$ prior to the DOC (dissolved organic carbon) and HPLC measurements. This procedure led to a complete reduction of the residual H_2O_2 as well as the removal of most of the Fe(II)/Fe(III) by precipitation. The precipitate was removed by filtration using Nylon Luer-Lock membrane filters (Roth, $0.22 \mu\text{m}$).

2.3 Analytical methods

UV/VIS-spectra were recorded using an HP 5800(II) diode-array-spectrophotometer. pH was measured by a Metrohm-pH-analyzer (E 513). H_2O_2 was analyzed by classic KMnO_4 titration^[17].

The analysis of the DOC was carried out using a Dohrmann DC-190 TOC (total organic carbon) analyzer (temperature: 680°C) from Rosemount Analytical.

The detection of intermediates of the ethanol or PVA degradation was performed using an HP Series II Liquid Chromatograph, equipped with a diode-array-detection system (DAD). A LiChrospher-100 RP 18 column (length: 125 mm, diameter: 4 mm, particle size: $5 \mu\text{m}$) and an identical precolumn were employed. The precolumn removed higher molecular weight intermediates ($M_w > 2000$). A mixture of $0.05 \text{ mol} \cdot \text{L}^{-1}$ triethylamine/ H_3PO_4 [pH=7.0, 95% (by volume)] and acetonitrile [5% (by volume), Baker] was chosen as the eluent.

The gel permeation chromatography (GPC) experiments were carried out employing an HP (TSK-AC/40090 SW; $7.5 \text{ mm} \times 300 \text{ mm}$) column to detect the super-macromolecule possibly formed in PVA degradation. Na_2SO_4 ($0.10 \text{ mol} \cdot \text{L}^{-1}$) and Na_2HPO_4 ($0.10 \text{ mol} \cdot \text{L}^{-1}$), dissolved in water were used as eluent. pH was adjusted to 7.0 using diluted H_3PO_4 . The detection of the polymers has been achieved using the wavelength of 220 nm.

3 RESULTS AND DISCUSSION

3.1 Comparison of UV/VIS-absorption spectra

UV/VIS spectra of aqueous ethanol (or PVA), the hydrated Fe(II)/Fe(III) , the complex formed between Fe(II)/Fe(III) and ethanol (or PVA), at a pH of 3.0, are shown in Figs. 2 and 3 respectively. The spectra of these two figures contrast quite well. Linear organics as ethanol or PVA have no obvious absorbance in UV

region, which is greatly different from aromatic organics. Ethanol and PVA were chosen as the model organics for this reason. Both Figs. 2 and 3 demonstrate that under the experimental conditions Fe(III) is the dominant light absorbing species. Furthermore, distinct light scattering can be seen from UV/VIS spectra between Fe(III) and Fe(III) with ethanol (or PVA) added under 200–450 nm. This effect indicates the formation of a complex between Fe(III) and organics. Either ethanol or PVA can serve as a ligand in Fe(III)-complexes and the complexes have a high absorbance in a wider spectral region up to 500 nm. According to their surprisingly high absorbance, the roles linear organics act in degradation are considerable.

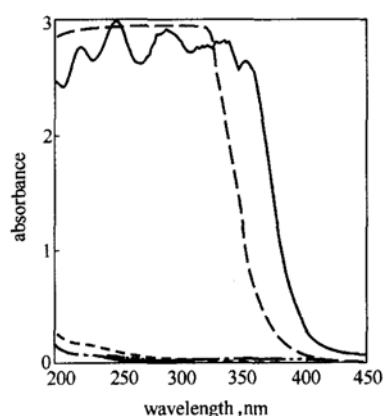


Figure 2 UV spectra of aqueous ethanol, Fe^{2+} , Fe^{3+} solution and their mixtures with ethanol as used in photolysis experiments (ethanol of $400 \mu\text{g}\cdot\text{g}^{-1}$, a ratio of 1 mol of Fe^{2+} or Fe^{3+} to 20 mol of ethanol)
 --- Fe^{3+} solution; — ETOH+ Fe^{3+} ;
 - - - ETOH+ Fe^{2+} ; ··· ETOH;
 — Fe^{2+} solution

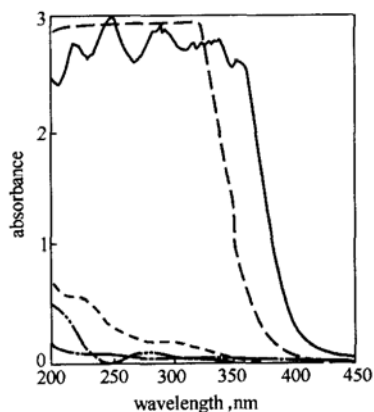


Figure 3 UV spectra of aqueous PVA, Fe^{2+} , Fe^{3+} solution and their mixtures with ethanol as used in photolysis experiments [PVA of $200 \text{mg}\cdot\text{L}^{-1}$ (carbon content), a ratio of 1 mol of Fe^{2+} or Fe^{3+} to 20 mol of PVA units]
 --- Fe^{3+} solution; — PVA with Fe^{3+} ;
 - - - PVA with Fe^{2+} ; ··· PVA;
 — Fe^{2+} solution

Figures 4 and 5 show the UV/VIS spectra of the re-

action mixture during the photochemically enhanced Fenton degradation of PVA and ethanol respectively. As shown in Fig. 4, the UV/VIS spectrum of the initial solution contrasts quite well with that of the PVA- $\text{Fe}(\text{II})$ complexes. When H_2O_2 is added, the spectral characteristics change and become similar to those of the PVA- $\text{Fe}(\text{III})$ complexes. It is evident that $\text{Fe}(\text{III})$ -PVA is formed with the adding of H_2O_2 . With PVA degrading in this process, the amount of $\text{Fe}(\text{III})$ -PVA complexes reduces and consequently absorption in the region of 260 to 400 nm diminishes. However, more mixed absorbance peaks are found in UV/VIS spectra of ethanol reaction mixture than PVA (shown in Fig. 5), arguing that some intermediates other than $\text{Fe}(\text{III})$ -ethanol are formed in Photo-Fenton degradation of ethanol. In order to ensure that these mixed peaks represent some other intermediates other than $\text{Fe}(\text{III})$ -ethanol, HPLC is used in the experiments.

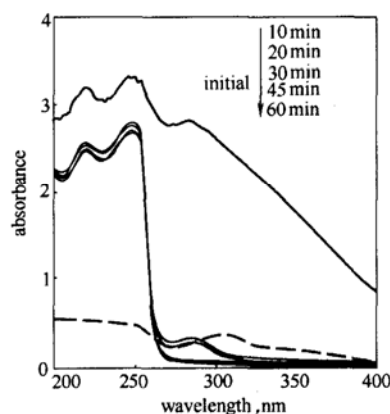


Figure 4 UV-spectra during the Photo-Fenton reaction in the presence of PVA, performed under standard conditions [100% stoichiometric amount of H_2O_2 , PVA of $200 \text{mg}\cdot\text{L}^{-1}$ (carbon content), a ratio of 1 mol of Fe^{2+} to 20 mol of PVA units]

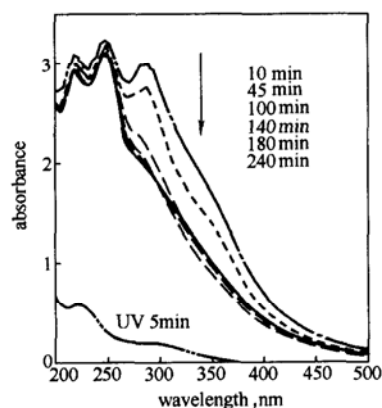
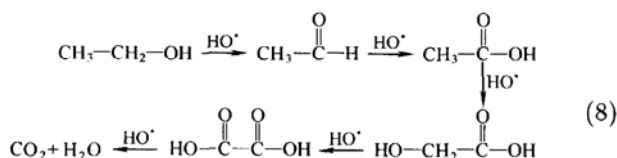


Figure 5 UV-spectra during the Photo-Fenton reaction in the presence of ethanol, performed under standard conditions (100% stoichiometric amount of H_2O_2 , ethanol of $400 \mu\text{L}\cdot\text{L}^{-1}$, a ratio of 1 mol of Fe^{2+} to 20 mol of ethanol)

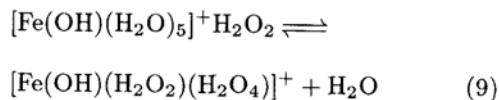
3.2 HPLC results of reaction mixture during Photo-Fenton degradation of ethanol and PVA

HPLC results show that in ethanol reaction mixture, acetic acid acetaldehyde and oxalic acid are detected, which certificates that hydroxyl radicals exist in the Photo-Fenton process and under their attack ethanol is oxidized to acetaldehyde, acetic acid and then to oxalic acid.

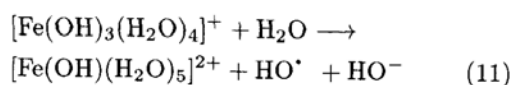
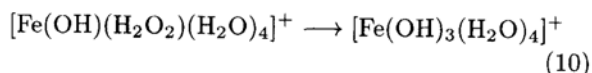


However, low or medium molecular weight intermediates such as acetaldehyde or organic acids have not been found by HPLC (0 to 180 min) in the whole efficient degradation of PVA. Moreover, the gel permeation chromatography (GPC) results show that with the addition of Fe(III), PVA polymers are immediately transformed into one super-macromolecule possessing a distinctly higher macromolecular mass than former PVA polymers. The macromolecule possesses a molecular mass higher than 2×10^6 . Since DOC diminishes with reaction time, polymers must degrade within the macromolecule through electronic transfer. Electron spin resonance (ESR) experiments have demonstrated that hydroxyl radicals do exist in Fenton process^[16]. But the hydroxyl radicals formed in the Photo-Fenton process are too few to break the chemical bond of PVA molecule. The hydroxyl radicals are deemed not to be generated from the classic mechanism reaction for its high reaction rate constant ($k = 76 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)^[18,19].

However, H_2O_2 can serve as a ligand in hydrated Fe(II)/Fe(III)-complex and this kind of formation is thermodynamically favored. So a ligand exchange reaction (H_2O_2 vs. H_2O) will occur in the ligand sphere of the Fe(II) cation firstly.



In agreement with the Fenton-type oxidation mechanisms developed by Bossmann *et al.*^[13], further reaction can be shown as the following equations



In this complex mechanism, Eq.(9) is the rate-determining step. Fe(IV) becomes the key reactive in-

termediates and hydroxyl radicals are just the byproduct. Fe(IV) can also serve as a central ion in Fe(IV)-PVA complex, through the inner electron transfer PVA degrades.

3.3 Degradation process of ethanol and PVA

As discussed in preceding paragraph, hydroxyl radicals will not be generated from classical Fenton reaction. In order to confirm the generating way of the few hydroxyl radicals involved in Photo-Fenton reaction, degradation processes of ethanol and PVA are investigated in detail.

Figures 6 and 7 show the removal of DOC and ethanol during H_2O_2 , UV/ H_2O_2 , Fenton and Photo-Fenton degradation of ethanol respectively. According to radical reaction, acetic acid is one of the prevailing intermediates during the oxidation of ethanol by hydroxyl radicals. Fig. 8 shows the acetic acid concentration changes during H_2O_2 , UV/ H_2O_2 , Fenton, and Photo-Fenton degradation of ethanol. It is found that acetic acid appears after adding H_2O_2 in the ethanol solution for 10 min, indicating that hydroxyl radicals are present in the solution. That the hydroxyl radicals can only be formed in H_2O_2 process in considered to be the splitting decomposition of H_2O_2 . The amount of formed hydroxyl radicals is very small, due to the very high rate constant ($k = 5.2 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) of Eq. (12)^[20].

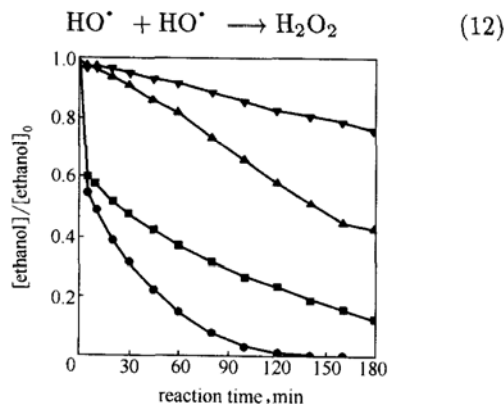
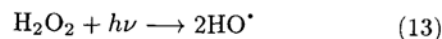


Figure 6 Ethanol degradation in H_2O_2 , UV/ H_2O_2 , Fenton and Photo-Fenton processes, under standard conditions

—▼— H_2O_2 ; —▲— UV/ H_2O_2 ;
—■— Fenton; —●— Photo-Fenton

As for UV/ H_2O_2 process, acetic acid is detected after 5 min. The introduction of UV accelerates the splitting decomposition of H_2O_2 and generates more hydroxyl radicals in a shorter time, which can be explained by the following well-established equation



In Fig. 8, acetic acid is generated immediately in Fenton process. The initial generating rate of acetic

acid is $0.23 \text{ mg}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$. Obviously more hydroxyl radicals are formed after iron ions are introduced, which can be explained by hydrated Fe(IV) -complex degradation [Eq. (11)].

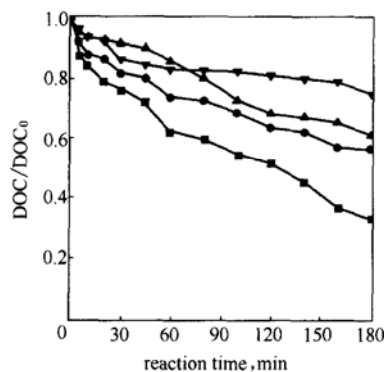


Figure 7 DOC removal in the degradation of ethanol during H_2O_2 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and Photo-Fenton processes, under standard conditions

—■— Photo-Fenton; —●— Fenton;
—▲— $\text{UV}/\text{H}_2\text{O}_2$; —▼— H_2O_2

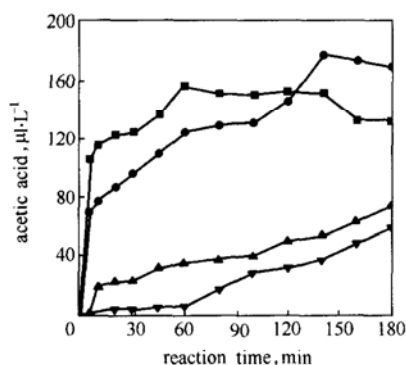
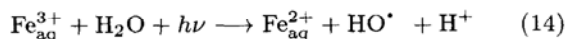


Figure 8 Acetic acid concentration generated in the degradation of ethanol during H_2O_2 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and Photo-Fenton processes, under standard conditions

—■— Photo-Fenton; —●— Fenton;
—▲— $\text{UV}/\text{H}_2\text{O}_2$; —▼— H_2O_2 only

In Photo-Fenton process, the initial generating rate of acetic acid is $0.35 \text{ mg}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ higher than Fenton process. This may result from two factors. One is the introduction of UV that accelerates the decomposition of H_2O_2 [Eq. (12)], the other is that $\text{Fe(III)}_{\text{aq}}$ can generate hydroxyl radicals under the radiation of UV through the following reaction



Hydroxyl radicals involved in Photo-Fenton process may come from splitting decomposition of H_2O_2 [Eq. (13)], photolysis of $\text{Fe}_{\text{aq}}^{3+}$ [Eq. (14)], and degradation of hydrated Fe(IV) -complex [Eq. (11)].

Figure 9 shows the removal of DOC in the treatment of PVA in H_2O_2 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and Photo-Fenton process. Contrasting with the degradation of

ethanol, the DOC does not change during 120 min in H_2O_2 and $\text{UV}/\text{H}_2\text{O}_2$ processes, which means no low molecular weight intermediates, whose mineralization leads to the removal of DOC, can be formed in these two processes. Hydroxyl radicals generated from the decomposition of H_2O_2 during H_2O_2 and $\text{UV}/\text{H}_2\text{O}_2$ process are insufficient to break the refractory chemical bond of PVA.

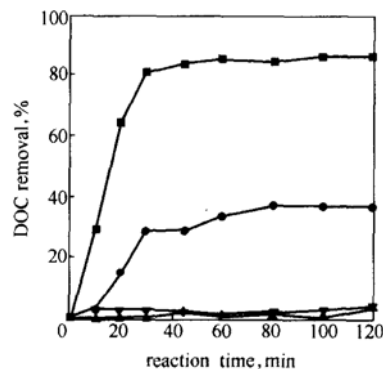


Figure 9 DOC removal in the degradation of PVA during H_2O_2 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and Photo-Fenton processes, under standard conditions

—■— Photo-Fenton; —●— Fenton;
—▲— $\text{UV}/\text{H}_2\text{O}_2$; —▼— H_2O_2 only

However, the removal of DOC appears obviously in Fenton and Photo-Fenton degradation of PVA. Since analytical results of HPLC indicate that no low molecular weight intermediates are found in the whole Fenton process, the introduction of Fe(II) does not catalyze the generation of enough hydroxyl radicals to break the chain of PVA. CO_2 may be released directly from the macromolecule complex formed between Fe(III) and PVA leading to the removal of DOC.

4 CONCLUSIONS

From this study it is found that PVA and ethanol degraded along with the removal of complex formed between Fe(III) [or Fe(IV)] and organics. UV/VIS spectra show the formation of this complex fairly. Though HPLC results support the formation of hydroxyl radicals in the Photo-Fenton process, they are deemed to be generated not from radical mechanism reaction but from the splitting decomposition of H_2O_2 , degradation of hydrated Fe(IV) -complex and photolysis of $\text{Fe}_{\text{aq}}^{3+}$. With these, another reasonable explanation for the traditional radical reaction in Fenton process is suggested.

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