Characterization of effects of selected organic substances on decomposition of hydrogen peroxide during Fenton reaction

K.C. Namkung*, A. Aris** and P.N. Sharratt**

* Conservation and Environmental Chemistry Group, School of Contemporary Sciences, University of Abertay Dundee, Bell Street, Dundee DD1 1HG, UK (E-mail: k.namkung@abertay.ac.uk)
** Environmental Technology Centre, Department of Chemical Engineering, UMIST, PO Box 88, Manchester M60 1QD, UK (E-mail: a.aris@stud.umist.ac.uk; paul.sharratt@umist.ac.uk)

Abstract This study aims to investigate the effects of selected organic substances on the degradation of hydrogen peroxide during the Fenton reaction. Since the presence of organic substances can strongly affect the mechanism of the Fenton reaction, the information on effects of organic substances on the reaction would be a vital guide to the success of its application to the destruction of organics in wastewater. Several organic compounds having different structures were selected as model pollutants: 4-chlorophenol, 1,4-dioxane, chloroform, a dye (reactive black-5), and EDTA. Oxidation of 4-chlorophenol and reactive black-5 resulted in enormously fast degradation of hydrogen peroxide, while others such as 1,4-dioxane and chloroform showed much slower degradation. These experimental data were compared to simulation results from a computational model based on a simple ·OH-driven oxidation model. Modelling results for chloroform and 1,4-dioxane were in relatively good agreement with the experimental data, while those for 4-chlorophenol and reactive black-5 were very different from the experimental data. The results for EDTA showed a different trend to those for other compounds. From these results, classification of organic substances into several sub-groups was tried.

Keywords Fenton reaction; hydrogen peroxide; intermediates; modelling; organic substances

Introduction

There has been a plethora of investigations into the applicability of Fenton or modified Fenton oxidation processes to wastewater treatment in the last two decades (Barbeni et al., 1987; Huang et al., 1993; Kim et al., 1997). However, since they are relatively costly for practical applications and are affected by many factors some of which may be unknown, fundamental research to support the design of cheaper processes is still required. In particular, since the design of Fenton oxidation processes is normally very heuristic, a general approach should be developed. In this context, this work employed a modelling approach based on intrinsic pathways of the Fenton reaction, with consideration of development of simulation tools to support process designs.

It has been known that among process parameters affecting the efficiency of the Fenton oxidation are pH, dosage and ratio of Fenton’s reagent, concentration of scavengers of hydroxyl radicals, concentration of inorganic materials forming complexes with iron species, temperature, mixing, concentration of dissolved oxygen, characteristics and concentration of organic pollutants etc. (Huang et al., 1993; Kim et al., 1997; Yoon et al., 2001; Namkung, 2002; Neyens and Baeyens, 2003). Among these, this work focused on the effects of organic pollutants on the Fenton oxidation. In particular, the effects of organic substances having different chemical structures were compared.

In order to characterize the effects of different organic substances on the Fenton reaction, the concentration of parent compounds against reaction time may be investigated. Very often, since the reactions between OH radicals and organic compounds are very fast
close to diffusion-controlled rate constants, the concentration of parent compounds decreases very rapidly. For these cases, modelling results of concentration of parent compounds against reaction time tends to match the experimental results well. However, these results do not provide enough information to elucidate effects of organic compounds on Fenton reaction due to the similarity of rapid degradation of parent compounds. Alternatively, iron species or hydrogen peroxide concentration profile against reaction time may be selected as an indicator for characterization of Fenton oxidation of different organic substances. This work used hydrogen peroxide concentration profile against reaction time as the indicator because it can be a more reliable indicator in simulating a Fenton reaction system, especially at a high ratio of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]_o (>1)$ (Namkung, 2002). Also, to further clarify the effects of organic substances, an additional input of hydrogen peroxide was made during the Fenton reaction.

**Methods**

**Experimental methods**
The chemicals used were supplied either by BDH (Merck) or by Aldrich. All were reagent grade or better and used without further purification.

$\text{H}_2\text{O}_2$ assay. The concentration of hydrogen peroxide stock solution (about 30%) purchased from BDH was determined with the iodometric method (Mendham et al., 2000). During the Fenton reactions, hydrogen peroxide samples were analyzed with the titanium-complex method using a UV/vis spectrophotometer (Lambda 10, Perkin Elmer) (Pobiner, 1961). In order to consider interference due to color of the solution, iodometric method or catalase was used if necessary.

**Reactor and reaction conditions.** All reactions were conducted at room temperature (21–25°C) in the presence of nitrogen purging. 1L beakers were used as the reactor. Ferrous iron and sodium sulfate or sodium nitrate were dissolved into deionised water, being followed by addition of organic compounds. pH was adjusted to 3 using 1:2 (conc. sulfuric acid:water) sulfuric acid. Fenton reactions were started with addition of hydrogen peroxide. Samples were taken at various times depending on the experimental conditions and were analysed immediately.

**Modelling methods**
The computational model (Namkung and Sharratt, 2001) based on reaction equations used by De Laat and Gallard (1999) was verified with that Gallard et al. data (1998) and Namkung data (2002). The reaction rate equations were built for each chemical species of $\text{Fe}^{2+}$, $\text{H}_2\text{O}_2$, $\text{Fe}^{3+}$, $\text{HO}_2^-$, $\text{O}_2^-$, $\cdot\text{OH}$. For the radical species $\text{HO}_2^-$, $\text{O}_2^-$, and $\cdot\text{OH}$, pseudo steady-state concentrations were assumed. In this work, the effects of sulfate ions from $\text{Na}_2\text{SO}_4$ used to adjust ionic strength were ignored because they are insignificant compared to those of the organic substances.

The differential equations were solved by the 4th-order Runge–Kutta method with a step size of 0.001(sec). The C language compiler on the Linux system or the Microsoft™ Visual C++ compiler (v. 6.0) on the Windows system (WIN NT) was used to develop the computational model.

A simple model (Eqs (1)–(3)), which has been used by many researchers (Andreozzi et al. 2000; Gallard and De Laat, 2000), based on a stepwise oxidation by hydroxyl radicals was employed for modelling Fenton’s reagent/organic compound systems.

\[\text{P} + \cdot\text{OH} \rightarrow I_1\]  

(1)
\[ \text{I}_1 + \cdot \text{OH} \rightarrow \text{I}_2 \]  
(2)

\[ \text{I}_2 + \cdot \text{OH} \rightarrow \text{I}_3 \]  
(3)

where, \( P \) = a parent compound, \( \text{I}_i \) = an intermediate.

The same rate constant for each chemical in Table 1 was used for reactions (1) to (3).

Results and discussion

Comparison of experimental data with modelling results

Figure 1 shows hydrogen peroxide decomposition during the Fenton oxidation of selected organic substances. The modelling results, which were generated using reaction equations without consideration of organic compounds, are also shown in Figure 1 to emphasize the effects of organic substances on the Fenton reaction. The decomposition of hydrogen peroxide against reaction time varied significantly with chemical compounds having different structures. The presence of 4-CP or RB5 resulted in enormously rapid degradation of hydrogen peroxide. However, the decomposition of hydrogen peroxide in the presence of 1,4-dioxane, CHCl3 or EDTA was relatively slow. In particular, the results after the additional input of hydrogen peroxide at 30 min further clarified such differences.

Interestingly, both 4-CP and RB5 contain aromatic groups. It is suggested that such a rapid consumption of hydrogen peroxide is ascribed to occurrence of Hamilton-like systems during Fenton oxidation (Hamilton et al., 1966; Mentasti and Pelizzetti, 1973; Mentasti et al., 1973; Tamagaki et al., 1989; Chen and Pignatello, 1997; Rodriguez et al., 2001; Namkung and Sharratt, 2001). Additionally, the results of our experiments with 4-hydroxybenzoic acid (not presented here) were very similar to those with 4-chlorophenol and supported the view of the presence of a Hamilton-like system.

The modelling results from the computational model including Eqs (1)–(3) are shown in Figure 2. The modelling results for 1,4-dioxane and chloroform are in relatively good agreement with experimental results. However, the modelling results for 4-CP and RB5 totally fail to simulate the reaction systems. As the simple model employed fails to simulate the system suitably, it can be thought that there are strong interactions between iron species or hydrogen peroxide and organic intermediates. In this context, the difference between 4-CP or RB5 and 1-4-dioxane or chloroform could be explained.

As compared to others, the experimental data of EDTA showed a fairly similar trend to the modelling results in Figure 1. However, the modelling results in Figure 2 clearly deviated from the experimental data. From these results, it should be noted that the trend of hydrogen peroxide decomposition in the Fe(II)/H2O2/EDTA system is very similar to that in the Fe(II)/H2O2 system.

Categorization of Fenton oxidation of organic substances

As shown in the results of 4-CP and RB5, our results showed that the additional input of hydrogen peroxide at 30 min could be useful for characterizing Fenton oxidation of various

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kinetic rate constant (M⁻¹s⁻¹)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>4-CP</td>
<td>( 2.45 \times 10^{10} )</td>
<td>Kochany and Bolton, 1991</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>( 2.5 \times 10^{9} )</td>
<td>Thomas, 1965</td>
</tr>
<tr>
<td>Reactive black-5</td>
<td>Unknown</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>( 5 \times 10^{7} )</td>
<td>Haag and Yao, 1992</td>
</tr>
<tr>
<td>EDTA</td>
<td>( 4.0 \times 10^{8} )</td>
<td>Lati and Meyerstein, 1978</td>
</tr>
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organic compounds. From the results, the following classification would be possible in relation to the modelling approach:

- Simple model (for example, Eqs (1)–(3))
  - 1,4-dioxane (cyclohexane or ethers?)
  - chlorinated hydrocarbons such as chloroform, tetrachlorocarbon

- Special model
  - phenolic compounds such as phenol, chlorinated phenols, catechol, and hydroxybenzoic acid: i.e., Hamilton or Hamilton-like system (catechol or catechol-like intermediates/Fe(III)/H₂O₂)
  - EDTA (direct formation of complexes with iron species)

It is thought that the formation of complexes between parent compounds or organic intermediates and iron species plays a key role for special models. This may be important to overcome a Fenton oxidation’s drawback that there is a limit on the oxidation performance because the reduction of Fe(III) to Fe(II) is much slower compared with the oxidation of Fe(II) to Fe(III). In this context, it seems that the role of EDTA in the redox process of Fe(III) to Fe(II) is less significant as compared to the Hamilton or Hamilton-like systems.

Figure 1 The experimental results of H₂O₂ decomposition during Fenton oxidation of several organic compounds and modelling results without consideration of organic substances. (Ionic strength: 0.1 M for all: Na₂SO₄ for (a) and (b), NaNO₃ for others. Fenton’s reagent: [Fe²⁺]₀ = 1 mM and [H₂O₂]₀ = 1 mM for (a) and (b), [Fe²⁺]₀ = 0.5 mM and [H₂O₂]₀ = 1 mM for others. Temperature: 21°C for (a) and (b), 25°C for (c), 23°C for (d) and (e))
The design of catalysts containing enediols such as catechol could be favorably considered to enhance the performance of Fenton oxidation.

Conclusions
In various modified Fenton oxidation processes, the effects of organic compounds investigated in this work would be similar. Additionally, the idea of classification of organic compounds into several groups could be applied for other oxidation processes. In particular, if the modelling approach used in this study can be applied for other AOPs such as UV/TiO₂, H₂O₂/O₃, and ultrasound/O₃, it could provide an insight into selecting AOPs suitable for treatment of wastewaters containing a specific type of organic pollutant. However, since this approach is useful only for the early stages of oxidation, more methods should be developed to characterize the oxidation of various compounds, such as classification of TOC removal trends.

References


