Treatment of Pharmaceutical Wastewaters by Hydrogen Peroxide and Zerovalent Iron

Byeong-Cheol Jeon, Se-Yong Nam, Young-Kwon Kim†

Department of Civil, Safety & Environmental Engineering, Hankyong National University, Anseong 456-749, Korea

Abstract
Fenton reaction with zerovalent iron (ZVI) and Fe²⁺ ions was studied to treat pharmaceutical wastewaters (PhWW) including antibiotics and non-biodegradable organics. Incremental biodegradability was assessed by monitoring biochemical oxygen demand (BOD) changes during Fenton reaction. Original undiluted wastewater samples were used as collected from the pharmaceutical factory. Experiments were carried out to obtain optimal conditions for Fenton reaction under different H₂O₂ and ion salts (ZVI and Fe²⁺) concentrations. The optimal ratio and dosage of H₂O₂/ZVI were 5 and 25/5 g/L (mass basis), respectively. Also, the optimal ratio and dosage of H₂O₂/Fe²⁺ ions were 5 and 35/7 g/L (mass basis), respectively. Under optimized conditions, the chemical oxygen demand (COD) removal efficiency by ZVI was 23% better than the treatment with Fe²⁺ ion. The reaction time was 45 min for ZVI and shorter than 60 min for Fe²⁺ ion. The COD and total organic carbon (TOC) were decreased, but BOD was increased under the optimal conditions of H₂O₂/ZVI = 25/5 g/L, because organic compounds were converted into biodegradable intermediates in the early steps of the reaction. The BOD/TOC ratio was increased, but reverse-wise, the COD/TOC was decreased because of generated intermediates. The biodegradability was increased about 9.8 times (BOD/TOC basis), after treatment with ZVI. The combination of chemical and biological processes seems an interesting combination for treating PhWW.

Keywords: Biodegradability, Fenton's oxidation, Ferrous irons, Pharmaceutical wastewater, Zerovalent iron

1. Introduction

The pharmaceutical industry includes manufacturing, fermentation, chemical synthesis, and extraction and formulating processes [1]. The effluents from manufacturing and formulation processes of pharmaceutical products include diverse contaminants of varying aromaticity, including non-biodegradable and structurally complex organic compounds having low biodegradability. Hence, it is not easy to treat those wastewaters by conventional treatment processes. The range of organic compound concentration in pharmaceutical wastewaters (PhWW) is in general 10,000 to 100,000 mg/L or more on a chemical oxygen demand (COD) basis and lower than 1,000 mg/L on a biochemical oxygen demand (BOD) basis. PhWW includes antibiotics and other organic molecules that cannot be removed completely by biological processes, since they tend to inhibit the activity of microorganisms. Also, microorganisms have acquired resistance to antibiotics, and these bacteria, when discharged into receiving waters systems, may cause extensive damage to human or ecosystems [2]. In recent studies in North America and Europe, a diverse group of antibiotics have been detected in surface waters and their concentrations are rising to several µg/L or even higher in some situations [3-5]. In Korea, antibiotics have become of increasing concern, since high concentrations of antibiotics have been found to increase rapidly in surface waters and soils especially near livestock farms [6, 7]. The occurrence of antibiotics in surface waters has also been shown to be high enough to contribute to antibiotic resistance [8].

Biological processes, such as activated sludge and membrane bioreactor, have been applied for treatment of PhWW [9, 10]. To reduce the toxicity and enhance their biodegradability, PhWW are often diluted before being subjected to a biological treatment. This certainly increases operation costs, because of the higher wastewater volumes needing to be treated. Therefore, it is necessary to combine the chemical processes with biological processes. PhWW cannot be completely eliminated during biological treatment, because it has a high amount of organics as well as antibiotics. Therefore, a coupling process (biological and chemical process combined) has been used after converting non-biodegradable into biodegradable materials and reducing the toxicity of antibiotics [1, 10].

The chemical processes, especially advanced oxidation processes (AOPs), can effectively break down some of the structurally complex organic compounds and bio-inhibitory compounds.

†Corresponding Author
E-mail: ykkim@hknu.ac.kr
Tel: +82-31-670-5173  Fax: +82-31-670-5170

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AOPs are one of the favored techniques to remove refractory pollutants involving hydroxyl radicals, a powerful oxidant. The combinations O₃/UV, O₃/H₂O₂, H₂O₂/UV, and TiO₂/UV are techniques using oxidants like ozone and UV. Their application is nevertheless somewhat restricted depending on the characteristics of the wastewaters, such as pH, total dissolved solids, turbidity, and gas solubility.

During Fenton reaction, Fe²⁺ catalyzes the decomposition of H₂O₂ into hydroxyl radicals, which are then able to convert organic pollutants into more easily biodegradable compounds, such as lower molecular weight fatty acids. Further microbial degradation can then transform these fatty acids into CO₂ and H₂O. Unfortunately, this process generates a large amount of sludge, because Fenton reaction relies on the supply of Fe²⁺ ions and H₂O₂. Fe²⁺ ions are oxidized to Fe³⁺ ions and oxidized Fe³⁺ ions precipitate as hydroxides at neutral or alkaline pH. To prevent the precipitation of Fe hydroxide, the pH should be kept acidic (pH 2–5). Also, untreated iron salts may harm receiving water systems, because iron salts consume oxygen. To overcome the drawback in Fenton reaction, an alternate approach is proposed that reduces the generation of sludge and operating costs. This new approach uses zerovalent iron (ZVI, Fe⁰) as the catalyst in Fenton process instead of Fe²⁺. The oxidized Fe³⁺ ions form hydroxyl complexes at high pH, and those complexes do not dissolve readily and do not participate in the reduction steps of the classic Fenton reaction [11]. The oxidation of ZVI at acidic conditions involves producing Fe²⁺, which promote the generation of hydroxyl radicals (Eqs. (1) and (2)). A fast recycling of Fe²⁺ into Fe³⁺ species at the metal surface can occur following (Eq. (3)). Moreover, ZVI has been used for the degradation of different model pollutants. ZVI oxidation by dissolved oxygen produces H₂O₂ via a two-electron transfer from the metal surface to oxygen (Eq. (4)). The H₂O₂ generated is reduced to water (Eq. (5)) as well as converted to HO⁻ or Fe(IV) by reaction with Fe³⁺ (Eqs. (1) and (6), respectively) [12, 13].

The antibiotics being synthesized and manufactured in Korea are known β-lactam antibiotics, and they account for 50% or more of production [14]. Cephradine is a major representative of β-lactam antibiotics and is usually used to treat inflammations, such as respiratory infection, urinary tract infection, abscess, and ear infection, etc. This investigation was aimed at studying the operating conditions and improvement of its biodegradability by Fenton reaction with ZVI. The efficiency was also compared to Fenton reaction with Fe²⁺ ions. The target was the wastewater of a cephradine manufacturing site. The experiments were carried out under different parameters (H₂O₂/ZVI and Fe²⁺ ion ratios, and reaction time). The improvement of biodegradability was optimized through variations of ratios of BOD/TOC and COD/TOC, and various combinations of chemical and biological processes were tested to improve biodegradability [15, 16].

### 2. Materials and Methods

#### 2.1. Pharmaceutical Wastewater Samples

Samples were collected at ‘A Pharmaceutical Co., Ltd.’ in Gyeonggido, Korea. This factory produces mainly cephradine products from chemical synthesis and formulation processes. The daily generation of wastewater is 250 m³/day from the formulation process and the washing of the equipment. The treatment system uses an extended aeration process and samples were collected from the treatment facility upstream from the water treatment, i.e., raw wastewaters were used for this study. Samples were pretreated to remove solids, by filtration through a 0.45-µm membrane filter (mixed-cellulose ester, ø 47 mm; product #1353001; HACH, Loveland, CO, USA). All samples were kept cold (4°C ± 0.2°C) to prevent substrate decomposition. The sample characteristics and the operation conditions of the extended aeration are given in Table 1.

#### 2.2. Experimental Procedure

Experiments were carried out to determine the optimum ratio of H₂O₂/ZVI and H₂O₂/Fe²⁺ ions. The tests were conducted using a 1,000 mL sample of undiluted wastewaters (initial COD = 15,000 mg/L) in glass jars with magnetic stirrers. The samples were acidified to pH 3 and Fenton reagent was added into the jars. The ratios of H₂O₂/Fe²⁺ in Fenton reagent were 1, 3, 5, and 7 as mass ratio, while Fe²⁺ ions concentration was kept constant at 5 g/L. After determination of the optimum ratio, other parameters were changed. The jars were covered with Parafilm (Whatman, Maidstone, Kent, UK) to prevent evaporation of volatile compounds. The reaction times were 0, 15, 30, 45, 60, and 120 min. The samples were acidified to pH 3, because Fenton reaction is most effective at low pH, and acidic conditions also prevent the auto-decomposition of H₂O₂ [11, 17]. At planned reactions times, the stirring equipment was removed and the pH was raised to 8 to allow settling down of the generated solids for 30 min. The supernatants were then filtered by passing through a 0.45-µm membrane filter (mixed-cellulose ester, ø 47 mm; HACH), and the filtrates were measured for BOD₅, COD, and TOC. The ZVI experiments followed the same experimental procedures as for Fe²⁺ ions. ZVI powder was added into the samples and stirred for 5 min in order to be distributed among ZVI and samples completely. The H₂O₂ was added into the jars according to the different H₂O₂/ZVI ratios.

#### Table 1. Characteristics of samples and operating conditions in extended aeration

<table>
<thead>
<tr>
<th>Samples (average value)</th>
<th>pH</th>
<th>6.8</th>
</tr>
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<tbody>
<tr>
<td>BOD₅ (mg/L)</td>
<td>1,790</td>
<td></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>8,750</td>
<td></td>
</tr>
<tr>
<td>COD₅ (mg/L)</td>
<td>15,000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating conditions in extended aeration</th>
<th>F/M ratio (kg BOD/kg MLVSS)</th>
<th>0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MLSS (mg/L)</td>
<td>4,500</td>
</tr>
<tr>
<td></td>
<td>SRT (day)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>BOD loading rate (kg/m²/day)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Acid and base adjustments were made using 0.1 M H$_2$SO$_4$ and 0.1 M NaOH. The Fe$^2+$ (325 mesh iron powder, 97%) and Fe$^3+$ ions (99% FeSO$_4$$\cdot$7H$_2$O), and H$_2$O$_2$ (35 wt% solution) were the American Chemical Society (ACS) reagent grade from Sigma-Aldrich. COD was determined by the colorimetric method (COD photometer, 610 nm; K-7360S; CHEMetrics Inc., Midland, VA, USA), and TOC was analyzed using a TOC analyzer (TOC-5000A; Shimadzu, Kyoto, Japan). BOD was measured using a BOD meter (PCD-6500; Sechang Instrument, Seoul, Korea). All analytical methods used standard methods [18]. COD was analyzed to determine the optimal condition for Fenton oxidation in terms of H$_2$O$_2$/ZVI and H$_2$O$_2$/Fe$^{2+}$ ratios (mass basis). The values of BOD/TOC and COD/TOC were used to estimate the improvement of biodegradability.

### 3. Results and Discussion

#### 3.1. Determination of the H$_2$O$_2$/ZVI or Fe$^{3+}$/Ratio

Experiments were conducted to determine the optimal ratio of H$_2$O$_2$/iron salts at various dosages of H$_2$O$_2$ while maintaining the dosage of iron salts (ZVI or Fe$^{3+}$) at 5 g/L. When the H$_2$O$_2$/Fe$^{3+}$ ratio was increased from 1 to 5, the COD removal efficiency was increased from 58.7% to 74.3% for a reaction time of 120 min in Fig. 1(a). But COD removal efficiencies were not improved by the increase of H$_2$O$_2$/Fe$^{2+}$ ratio up to 7. It is probable that excess H$_2$O$_2$ becomes oxygen and water by auto-decomposition, or acts as a scavenger, and thus consumes hydroxyl radicals [19-21]. Using ZVI, the maximum COD removal value was again observed using a ratio of 5 giving 91.4% removal efficiency in 120 min reaction. The phenomenon of hydroxyl scavenging by excess H$_2$O$_2$ was also observed with a lower efficiency for higher oxidant ratio. COD removal efficiency was higher for Fenton reaction using ZVI than Fe$^{3+}$ ion with the measured COD removal efficiency improved by roughly 23% through ZVI.

Tests were carried out to elucidate the optimum dosage of Fenton reagents. The iron salts were increased from 1 to 9 g/L and H$_2$O$_2$ dosages were maintained proportional to the iron salt doses. During this test, the ratio of H$_2$O$_2$/iron salts was always kept at 5 (Fig. 2). When the H$_2$O$_2$/Fe$^{3+}$ ratios were increased from 5/1 to 45/9 g/L (as mass ratio), the COD removal efficiencies were increased from 38.2% to 88.3%. However, its increments were insignificant between an H$_2$O$_2$/Fe$^{2+}$ ratio range of 35/7 and 45/9 g/L. Therefore, the optimal dosage of Fenton reagent by Fe$^{3+}$ ions was determined to be H$_2$O$_2$/Fe$^{3+}$ = 35/7 g/L.

In Fenton reaction with ZVI, COD removal efficiencies were rapidly increased from 43.7% to 91.4%, when the ratios of H$_2$O$_2$/ZVI were changed from 5/1 to 25/5 g/L. But further increases from 25/5 to 45/9 g/L did not show any significant improvements. The optimal dosage of Fenton reagents is a ratio of H$_2$O$_2$/ZVI = 25/5 g/L. If ZVI was used to treat the PhWW, a lower mass of reagents is required, relative to Fe$^{3+}$ ions.

#### 3.2. Comparison with the Effectiveness between Fe$^{2+}$ and ZVI in Fenton Reaction

Experiments were carried out to compare the effectiveness of ZVI and Fe$^{2+}$ ions in Fenton reaction. After reaction for 120 min, the remaining concentrations of COD were measured at each ratio of H$_2$O$_2$/iron salts, and the fractions of COD$_{zvi}$/COD$_{Fe^{2+}}$ were compared. As shown in Fig. 3, all of the COD$_{zvi}$/COD$_{Fe^{2+}}$ fraction...
values were higher than 1 within the range of different H$_2$O$_2$/iron salt ratios. Again, this emphasizes that ZVI is more efficient than Fe$^{2+}$ ions to treat PhWW through Fenton reaction. The maximum fraction value was 1.23 at an H$_2$O$_2$/iron salts = 5 ratio, and the resulting COD removal efficiency by ZVI was 1.23 times higher than using Fe$^{2+}$. This increased efficiency is attributed to the ability of ZVI, not only to convert Fe$^{3+}$ ions into Fe$^{2+}$ ions (see Eq. (4)), but regenerated Fe$^{2+}$ ions can also further participate in the activated reaction of H$_2$O$_2$ [12, 13].

### 3.3 Assessment of Biodegradability by BOD/TOC and COD/TOC Ratio

Fig. 4 shows the changes of BOD$_5$, COD, and TOC concentrations during Fenton reaction with ZVI (pH = 3; initial COD = 15,000 mg/L; H$_2$O$_2$/ZVI = 25/5 g/L mass basis). BOD: biochemical oxygen demand, COD: chemical oxygen demand, TOC: total organic carbon, ZVI: zerovalent iron.

Table 2. Pearson correlation coefficients between the COD, BOD, and TOC values

<table>
<thead>
<tr>
<th></th>
<th>COD</th>
<th>BOD$_5$</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>-0.875&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>TOC</td>
<td>+0.983&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.941</td>
<td>1</td>
</tr>
</tbody>
</table>

COD: chemical oxygen demand, BOD: biochemical oxygen demand, TOC: total organic carbon.
<sup>a</sup>Negative or inverse association, <sup>b</sup>positive association.

The enhancement of biodegradability was in general observed for the BOD/TOC and COD/TOC ratios. Table 2 shows the degree of association between two variables of BOD, COD, and TOC by Pearson correlation. The correlation coefficients of BOD/COD, BOD/TOC, and COD/TOC were -0.875, -0.941, and +0.983, respectively. Because the coefficients for BOD/TOC and COD/TOC are higher, they seem better predictors of biodegradability. Khan et al. [22] observed that the BOD/COD ratio had restrictions, such as low sensitivity against low organics or non-biodegradable wastewater. Fig. 5 shows that the...
BOD/TOC values were increased 0.2 to 1.95 during the first 45 min, because the BOD was increased about 77% but the TOC decreased about 54%. It is suggested that organic compounds were effectively decomposed into intermediates by Fenton with ZVI. The increments of BOD/TOC were slightly decreased from 1.95 to 1.91 after 45 min, because the BOD values only increased 3% in the latter stages of the reaction. The COD/TOC ratio decreased to 0.37 during the first 45 min and it was stable afterwards. This suggests that the formation of intermediates progressed rapidly for the initial 45 min period. It has been previously reported that the diminution of the COD/TOC ratio is linked to the generation of intermediates [23-25]. It seemed probable that the biodegradability increased about 9.8 times according to the BOD/TOC ratio after treatment using ZVI. Increasing the biodegradability through Fenton reaction with ZVI seems an opportune possibility to combine chemical and biological processes for PhWW.

4. Conclusions

This paper explains the treatability of PhWW and the enhancement of biodegradability by Fenton reaction with ZVI. The following results can be drawn. 1) In the experiment to determine the optimal ratio of \( \text{H}_2\text{O}_2/\text{iron salts} \), the maximum COD removal value between ZVI and Fe(II) ion was observed using a ratio of 5, giving 91.4% and 76.1% removal efficiency in 120 min reaction, respectively. The COD removal efficiency was improved by 23% using ZVI instead of Fe(II). 2) The optimum dosages of ZVI and Fe(II) ion were 25/5 and 33/7 g/L (mass basis), respectively, and the COD removal efficiencies were 91.4% (at ZVI) and 88.3% (at Fe(II) ion). If ZVI was used to treat the PhWW, it used less reagents than the use of Fe(II) ions. This means that it is more efficient to use ZVI than Fe(II) ions, as it reduces the operating costs and improves the treatment efficiency. 3) A comparison of the effectiveness between ZVI and Fe(II) ions was used for the fractions of COD_{org}/COD_{TOC}. The COD_{ZVI}/COD_{Fe(II)} fraction values were higher than 1 within the whole ratios of \( \text{H}_2\text{O}_2/\text{iron salts} \). It was shown that ZVI was more efficient than Fe(II) ions in treating PhWW by Fenton reaction. The COD removal efficiency by ZVI was enhanced 1.23 times over the use of Fe(II) ions. 4) In \( \text{H}_2\text{O}_2/\text{ZVI} = 25/5 \) g/L, the COD and TOC values decreased, but the BOD increased, because organic molecules were converted into biodegradable intermediates. The BOD/TOC values increased, but in contrast, the COD/TOC ratios decreased in the early steps of the reaction, because of generated intermediates. The biodegradability was enhanced about 9.8 times (BOD/TOC basis) after treatment using ZVI.

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References


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