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Treatment of Pharmaceutical Wastewaters by Hydrogen Peroxide and Zerovalent Iron

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Abstract

Fenton reaction with zerovalent iron (ZVI) and Fe^{2+} 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 H_2O_2 and ion salts (ZVI and Fe^{2+}) concentrations. The optimal ratio and dosage of H_2O_2/ZVI were 5 and 25/5 g/L (mass basis), respectively. Also, the optimal ratio and dosage of H_2O_2/Fe^{2+} 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 Fe^{2+} ion. The reaction time was 45 min for ZVI and shorter than 60 min for Fe^{2+} ion. The COD and total organic carbon (TOC) were decreased, but BOD was increased under the optimal conditions of H_2O_2/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 soils 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.

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AOPs are one of the favored techniques to remove refractory pollutants involving hydroxyl radicals, a powerful oxidant. The combinations O_3/UV, O_3/H_2O_2, H_2O_2/UV, and TiO_2/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, Fe^{2+} catalyzes the decomposition of H_2O_2 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 CO_2 and H_2O. Unfortunately, this process generates a large amount of sludge, because Fenton reaction relies on the supply of Fe^{2+} ions and H_2O_2. Fe^{2+} ions are oxidized to Fe^{3+} ions and oxidized Fe^{3+} 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, Fe^0) as the catalyst in Fenton process instead of Fe^{2+}. The oxidized Fe^{3+} ions form hydroxyl complexes at high pH, and those complexes do not redissolve readily and do not participate in the reduction steps of the classic Fenton reaction [11]. The oxidation of ZVI at acidic conditions involves producing Fe^{2+}, which promote the generation of hydroxyl radicals (Eqs. (1) and (2)). A fast recycling of Fe^{3+} into Fe^{2+} 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 H_2O_2 via a two-electron transfer from the metal surface to oxygen (Eq. (4)). The H_2O_2 generated is reduced to water (Eq. (5)) as well as converted to $HO^·$ or Fe(IV) by reaction with Fe^{2+} (Eqs. (1) and (6), respectively) [12, 13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \quad (1)$$
$$Fe^0 + 2H^+ \rightarrow 2Fe^{2+} + H_2 \quad (2)$$
$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (3)$$
$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (4)$$
$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (5)$$
$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \quad (6)$$

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

Samples (average value)	
pH	6.8
BOD_5 (mg/L)	1.780
TOC (mg/L)	8,750
COD_{Cr} (mg/L)	15,000
Operating conditions in extended aeration	
F/M ratio (kg BOD/kg MLVSS)	0.04
MLSS (mg/L)	4,500
SRT (day)	25
BOD loading rate (kg/m^3/day)	0.2

BOD: biochemical oxygen demand, TOC: total organic carbon, COD: chemical oxygen demand, F/M: food-to-microorganism ratio, MLVSS: mixed liquor volatile suspended solids, MLSS: mixed liquor suspended solids, SRT: solids retention time.

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 Fe^{2+} ions. The target was the wastewater of a cephradine manufacturing site. The experiments were carried out under different parameters (H_2O_2/ZVI and Fe^{2+} 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 process 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 m^3/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 H_2O_2/ZVI and H_2O_2/Fe^{2+} 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 H_2O_2/Fe^{2+} in Fenton reagent were 1, 3, 5, and 7 as mass ratio, while Fe^{2+} 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 H_2O_2 [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 BOD_5, COD, and TOC. The ZVI experiments followed the same experimental procedures as for Fe^{2+} ions. ZVI powder was added into the samples and stirred for 5 min in order to be distributed among ZVI and samples completely. The H_2O_2 was added into the jars according to the different H_2O_2/ZVI ratios.

Acid and base adjustments were made using 0.1 M H_2SO_4 and 0.1 M NaOH. The Fe^0 (325 mesh iron powder, 97%), Fe^{2+} ions (99% $FeSO_4 \cdot 7H_2O$), and H_2O_2 (35 wt% solution) were the American Chemical Society (ACS) or 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_5 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_2O_2/ZVI and H_2O_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_2O_2/(ZVI or Fe^{2+}) Ratio

Experiments were conducted to determine the optimal ratio of H_2O_2/iron salts at various dosages of H_2O_2, while maintaining the dosage of iron salts (ZVI or Fe^{2+}) at 5 g/L. When the H_2O_2/Fe^{2+} 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_2O_2/Fe^{2+} ratio up to 7. It is probable that excess H_2O_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_2O_2 was also observed with a lower efficiency for higher oxidant ratio. COD removal efficiency was higher for Fenton reaction using ZVI than Fe^{2+} 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_2O_2 dosages were maintained proportional to the iron salt doses. During this test, the ratio of H_2O_2/iron salts was always kept at 5 (Fig. 2). When the H_2O_2/Fe^{2+} 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_2O_2/Fe^{2+} ratio range of 35/7 and 45/9 g/L. Therefore, the optimal dosage of Fenton reagent by Fe^{2+} ions was determined to be H_2O_2/Fe^{2+} = 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_2O_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_2O_2/ZVI = 25/5 g/L. If ZVI was used to treat the PhWW, a lower mass of reagents is required, relative to Fe^{2+} 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_2O_2/iron salts, and the fractions of $COD_{ZVI}/COD_{Fe(II)}$ were compared. As shown in Fig. 3, all of the $COD_{ZVI}/COD_{Fe(II)}$ fraction

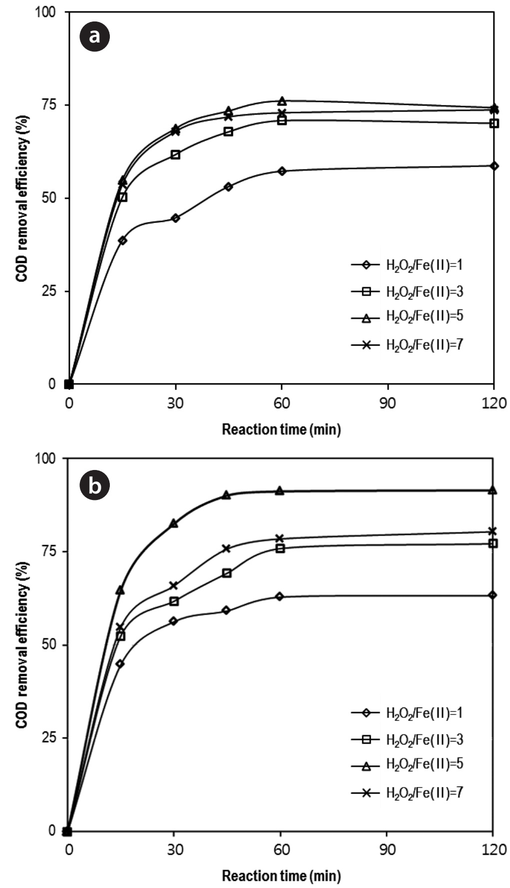

Fig. 1. Determination of optimum H_2O_2/iron salts ratio at various H_2O_2 dosages (pH = 3; initial COD = 15,000 mg/L). (a) Fe(II) = 5 g/L, (b) ZVI[Fe(0)] = 5 g/L. COD: chemical oxygen demand, ZVI: zerovalent iron.

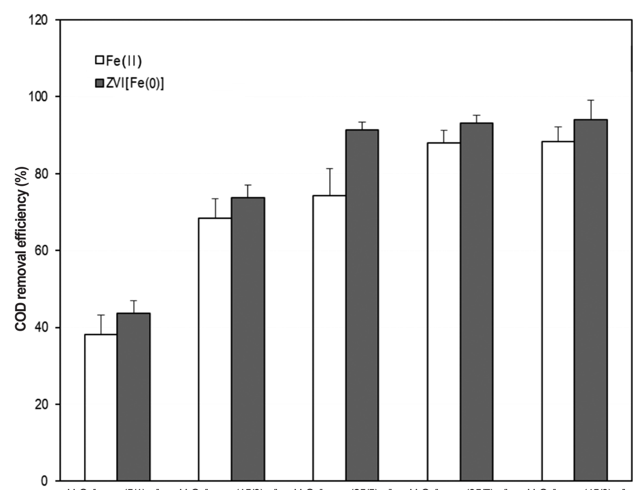

Fig. 2. Effect of dosages with iron salts and H_2O_2 on COD removal efficiencies (pH = 3; initial COD = 15,000 mg/L; dosage of iron salts = 1, 3, 5, and 7 g/L). The error bars represent the standard errors of duplicated experiments. COD: chemical oxygen demand, ZVI: zerovalent iron.

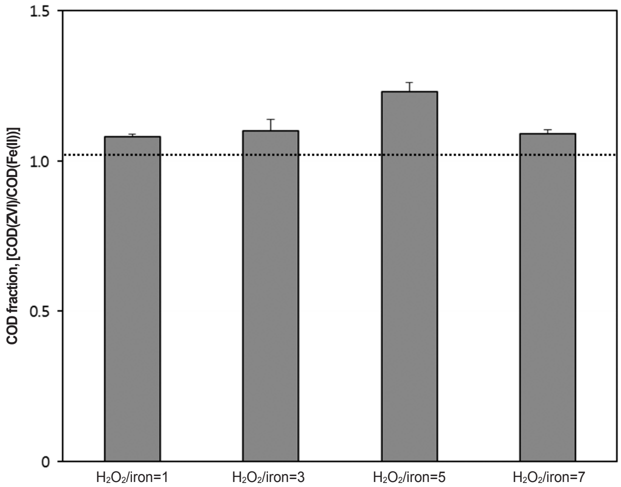

Fig. 3. Estimation of the effectiveness between ZVI and Fe^{2+} ion for different H_2O_2/iron salts ratios (pH = 3; initial COD = 15,000 mg/L; iron salts = 5 g/L; reaction time = 120 min). The error bars represent the standard errors of duplicated experiments. COD: chemical oxygen demand, ZVI: zerovalent iron.

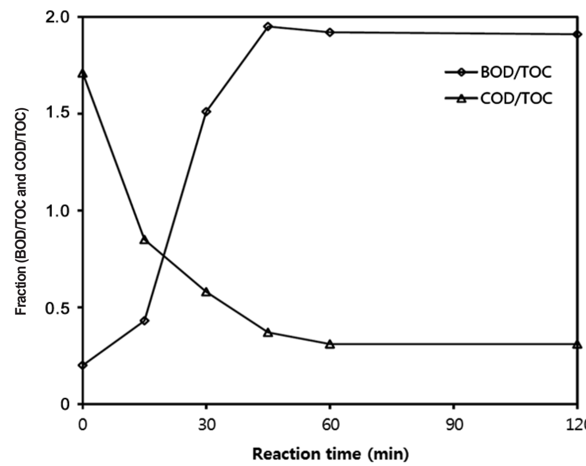

Fig. 5. Change of fraction between BOD/TOC and COD/TOC during Fenton reaction with ZVI (pH = 3; initial COD = 15,000 mg/L; H_2O_2/ZVI = 25/5 g/L mass basis). BOD: biochemical oxygen demand, COD: chemical oxygen demand, TOC: total organic carbon, ZVI: zerovalent iron.

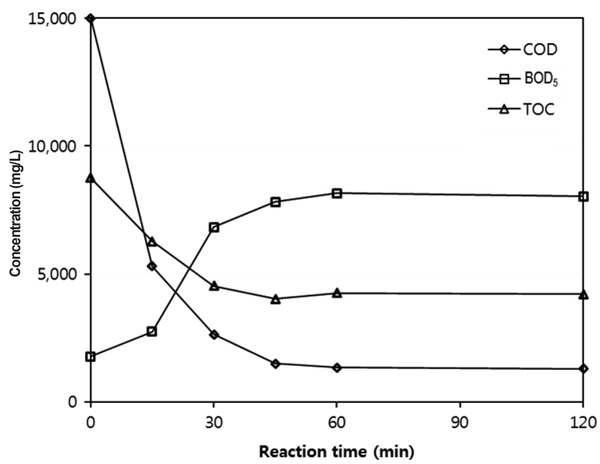

Fig. 4. Changes of BOD_5, COD, and TOC concentrations during Fenton reaction with ZVI (pH = 3; initial COD = 15,000 mg/L; H_2O_2/ZVI = 25/5 g/L mass basis). BOD: biochemical oxygen demand, COD: chemical oxygen demand, TOC: total organic carbon, ZVI: zerovalent iron.

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

	COD	BOD_5	TOC
COD	1	-	-
BOD_5	-0.875[a]	1	-
TOC	0.983[b]	-0.941	1

COD: chemical oxygen demand, BOD: biochemical oxygen demand, TOC: total organic carbon.
[a]Negative or inverse association, [b]positive association.

values were higher than 1 within the range of different H_2O_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_2O_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_2O_2 [12, 13].

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

Fig. 4 shows the changes of BOD, COD, and TOC at H_2O_2/ZVI = 25/5 g/L. The COD values were steeply decreased during the early stages of the reaction, but the BOD values were increased. The TOC values also steadily decreased. The rapid reduction of COD was caused by the elimination of organic carbon and the slow reduction of TOC was the result of converting a part of the organic molecules into intermediates. BOD was increased through the formation of biodegradable low molecular weight fatty acids intermediates in the early stages of reaction. The incremental increase of BOD seemed to stop after a reaction of 45 min, presumably because the intermediates were being oxidized to carbon dioxide and water at the latter stages of reaction.

The enhancement of biodegradability was in general observed for the BOD/TOC, BOD/COD, 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 H_2O_2/iron salts, the maximum COD removal value between ZVI and Fe^{2+} 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^{2+}. 2) The optimum dosages of ZVI and Fe^{2+} ion were 25/5 and 35/7 g/L (mass basis), respectively, and the COD removal efficiencies were 91.4% (at ZVI) and 88.3% (at Fe^{2+} ion). If ZVI was used to treat the PhWW, it used less reagents than the use of Fe^{2+} ions. This means that it is more efficient to use ZVI than Fe^{2+} ions, as it reduces the operating costs and improves the treatment efficiency. 3) A comparison of the effectiveness between ZVI and Fe^{2+} ions was used for the fractions of $COD_{ZVI}/COD_{Fe(II)}$. The $COD_{ZVI}/COD_{Fe(II)}$ fraction values were higher than 1 within the whole ratios of H_2O_2/iron salts. It was shown that ZVI was more efficient than Fe^{2+} ions in treating PhWW by Fenton reaction. The COD removal efficiency by ZVI was enhanced 1.23 times over the use of Fe^{2+} ions. 4) In H_2O_2/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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