Degradation of organic dye using zero-valent iron prepared from by-product of pickling line

ABSTRACT
In this study, zero-valent iron (ZVI) was produced using iron oxide that is a by-product of a pickling line at a steel works. The reaction activity of the produced ZVI was evaluated through a series of decomposition experiments of Orange II aqueous solution. The size of ZVI particles increased with reduction temperature due to coalescence. Correspondingly, the specific surface area of ZVI decreased with increasing reduction temperature. The decomposition efficiency of synthesized ZVI particles was higher at a lower pH. In particular, no significant decomposition reaction was observed at pH of 4 and higher. The rate of the ZVI-assisted decomposition of Orange II was increased by addition of H2O2 at pH of 3, whereas it was reduced by addition of H2O2 at a higher pH of 6. Nevertheless, simultaneous use of ZVI, UV and H2O2 led to a considerable increase in the decomposition rate even at a high pH condition (pH = 6).

Key words | azo dye, H2O2, pH, UV, zero-valent iron

INTRODUCTION
Azo dye is the most widely used synthesized organic dye, whose market share is about 50% of the whole dye market. The high market share of azo dye stems from its relatively low production cost and easy supply of raw materials. When discharged, however, it causes an unpleasant deep color and is reduced to toxic amines. Therefore, wastewater treatment is necessary after use of azo dye.

Generally, adsorption using activated carbon (Bayer & Finkel 2005) and biological treatment using microorganisms (Pagga & Brown 1986) are used to remove organic pollutants such as dyes contained in wastewater. However, these methods do not easily remove the complex aromatic compounds with various substitutions contained in dye wastewater. In addition, they cause the generation of a large amount of sludge and solid waste leading to high treatment cost. Oxidation has been widely used to convert toxic non-biodegradable materials into biodegradable forms. Conventional oxidation processes using ozone or hydrogen peroxide (H2O2), however, have limits in treating a number of different kinds of pollutants, calling for a more efficient oxidation process (Šuláková et al. 2007; Song et al. 2008).

Recently, several studies on advanced oxidation processes (AOP) have been conducted (Glaze et al. 1987, 1988). AOP is an advanced water treatment process, in which highly oxidative species such as OH• are produced as an intermediate product and are used for oxidizing organic water pollutants. Zero-valent iron (ZVI) is attracting a great deal of attention as a material for pollutant treatment due to its strong reduction potential, environment-friendly...
characteristics, and low cost. Since ZVI has a high potential as a reduction agent and catalyst, its applications as an environmental material especially for the restoration of polluted soil and underground water are reported to be promising (Nam & Tratnyek 2000; Bigg & Judd 2001).

Waste acid is produced in pickling lines of steel works where the surface of cold rolled sheets is descaled with hydrochloric acid. This waste acid is refined in the regeneration process and the regenerated acid is recycled into the pickling line. A by-product of the regeneration process is iron oxide, which is used as a raw material for electronic parts and pigments. The recent mass production of iron oxide in China, however, caused an oversupply of iron oxide. Therefore, a technology converting iron oxide into ZVI can be economically competitive.

In this study, ZVI was produced from iron oxide obtained from a pickling line. The physical and chemical characteristics of the ZVI produced in this way were examined by instrumental analyses. A series of experiments of decomposition of an azo dye, Orange II, were performed to evaluate the reaction activity of the ZVI. To enhance the decomposition efficiency of the ZVI, UV and H$_2$O$_2$ were added and their effects were investigated.

**EXPERIMENTAL**

In this study, the iron oxide recovered from the waste acid generated in a pickling line at a steel works in Kwangyang, Korea was used to produce ZVI (D-ZVI hereafter). Table 1 shows the chemical composition of the iron oxide recovered from waste acid.

Figure 1 shows the experimental setup to reduce iron oxide into D-ZVI using hydrogen gas. Iron oxide 5 g was put in a quartz pot installed in a quartz reactor tube (47φID × 50φOD, length 400 mm). It was reduced into D-ZVI using hydrogen gas. Before the temperature reached a target reaction temperature, only 100 sccm of Ar gas was supplied. Once the reduction reaction temperature (773–973 K) was reached, 500 sccm of Ar gas and 500 standard cubic centimetres per minute (sccm) of H$_2$ gas were supplied simultaneously for 2 h. When the reaction was completed, H$_2$ gas supply was stopped and the temperature was decreased to the room temperature with a supply of Ar gas only. The D-ZVI produced in this way was then put in an oxygen-free container filled with nitrogen gas and was stored at room temperature until it was used for the experiments.

A commercial ZVI (C-ZVI hereafter) purchased for comparison with the synthesized D-ZVI was also used. Table 2 shows the characteristics of C-ZVI used in this study. The diameter of C-ZVI particles was measured using Testing Sieve (Chungyesang Gongsa, Korea).

Orange II (Aldrich Co. Ltd.), an azo dye, was used in this study as the target organic pollutant. The characteristics of Orange II used in this study are shown in Table 3. Experiments were conducted in two different ways. First, batch experiments were conducted in 250 mL glass bottles. Each bottle was filled with ZVI particles and 100 mL of 0.2 mM Orange II solution. These bottles were rotated for an adequate time for Orange II reduction at about 200 rpm to ensure complete mixing. Second, aqueous solution of Orange II mixed with 1 g of ZVI particles was re-circulated at a constant flow rate.

**Table 1 | Chemical composition of iron oxide recovered from waste acid**

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Cl</th>
<th>Al$_2$O$_3$</th>
<th>MnO</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>0.0118</td>
<td>0.0084</td>
<td>0.2033</td>
<td>0.0023</td>
<td>0.2185</td>
<td>99.27</td>
</tr>
</tbody>
</table>

**Table 2 | The characteristics of C-ZVI used in the experiment**

<table>
<thead>
<tr>
<th>Name</th>
<th>Iron, Electrolytic, Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>55.85</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>Min. 98.0%</td>
</tr>
<tr>
<td>Particle diameter (µm)</td>
<td>120–150</td>
</tr>
<tr>
<td>Company</td>
<td>Kanto Chemical Co., Inc.</td>
</tr>
</tbody>
</table>

**Table 3 | Characteristics of Orange II used in this study**

<table>
<thead>
<tr>
<th>Formula</th>
<th>C$<em>{16}$H$</em>{11}$N$_2$NaO$_4$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ (nm)</td>
<td>484</td>
</tr>
<tr>
<td>Formula weight</td>
<td>350.33</td>
</tr>
<tr>
<td>Solubility in water (mg/mL)</td>
<td>50</td>
</tr>
<tr>
<td>Initial concentration (mM)</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 2 shows a schematic diagram of the experimental apparatus using the annular tube type photo-reactor. A 6-W UV-C lamp (Sankyo denki, G6T5, the most intensive wavelength; 240 nm) was used as a light source. To conduct re-circulating flow experiments, 1 L of Orange II solution was prepared and circulated with a flow rate of 450 mL/min using a roller pump (RP-1000, Eyela). The decomposition rate was calculated from the change in Orange II concentration obtained by measuring the absorbance at 484 nm using a spectrophotometer (UV-1601, Shimadzu). The effect of pH was investigated by adjusting pH in the range of 2–8 by the addition of NaOH or H₂SO₄.

Field emission microscopy (Hitachi, S-4800) and transmission electron microscopy (FEI, Tecnai20) were used to observe the size and morphology of the iron oxide and the D-ZVI used in the experiments. The crystal structure was observed using X-ray diffraction (Panalytical, 2500V/PC). The physical and chemical properties were examined using ICP (Varian, Vista 710-ES), Sub-Sieve Sizer (Fisher, M95), and BET surface area analyser (Micromeritics, Flowsorb III).

RESULTS AND DISCUSSION

Characterization of the synthesized D-ZVI

Figure 3 shows the FESEM images of the iron oxide particles and the D-ZVI particles produced at different reduction temperatures. The reduced D-ZVI particles (b) showed an irregular shape similar to that of iron oxide (a). When the particle surface was observed with high resolution, it was noticed that the particles had been generated by coagulation of smaller particles. The grain size increased with the reduction temperature due to coalescence (c–f). In particular, significant melting was observed for D-ZVI produced at 973 K (f).

Figure 4 shows the normalized and accumulated particle size distributions of the iron oxide particles and the D-ZVI particles produced at 873 K. The mean diameter of iron oxide particles before reduction was 3.77 μm, whereas the mean particle diameter of ZVI produced at 873 K was 20.44 μm. The mean particle diameters of D-ZVI produced at 773 and 973 K were 16.56 and 23.78 μm, respectively. This result indicates that higher reduction temperature leads to larger particle size due to the effect of coalescence as is shown in the micrograph images.

The BET measurements of D-ZVI particles produced at different temperatures were plotted in Figure 5. The specific
surface areas of D-ZVI particles deduced from these BET plots were 11.90, 7.41, and 3.42 m²/g for the reduction temperature of 773, 873, and 973 K, respectively. The larger specific surface area of D-ZVI particles produced at a lower reduction temperature corresponds with the smaller particle size shown in Figure 3.

Figure 6 shows the X-ray diffraction spectra of the iron oxide and the D-ZVIs produced at different temperatures. The apparent peaks appearing at the 2θ of 44.9° indicate the presence of crystalline-phase D-ZVI (α-Fe). Two Fe₂O₃ peaks were observed from the spectrum of iron oxide.

Evaluation of decomposition reaction activity of D-ZVI

Figure 7 shows the results of decomposition experiments of Orange II obtained at three different D-ZVI dosages. Addition of a larger amount of D-ZVI resulted in a higher decomposition rate. The plots for the three cases were all fitted well by linear lines, which indicates that decomposition of Orange II in the presence of D-ZVI can be approximated by a pseudo first order reaction model:

\[ \frac{C}{C_0} = \exp(-Kt) \]  

where \( C \) is the Orange II concentration at time \( t \), \( C_0 \) the initial concentration, and \( K \) the overall reaction rate constant.
The overall reaction rate constant $K$ is determined from the slopes of the lines in Figure 7 using a regression analysis. The values of $K$ obtained in this way for different kinds of ZVI's used and for different amounts of ZVI dosage are shown in Figure 8. The decomposition efficiency of D-ZVI was higher than that of C-ZVI, which showed low performance for the ZVI dosage range tested. The particle sizes of D-ZVI and C-ZVI used in the experiments were 20.44 and 120–150 μm, respectively. Therefore, it is believed that a smaller particle size, hence a larger specific surface area, led to a higher decomposition rate.

The effect of pH on the decomposition of Orange II using synthesized D-ZVI is shown in Figure 9. The D-ZVI showed a higher decomposition rate at a lower pH. Virtually no decomposition reaction was observed at pH of 4 and higher. ZVI is oxidized easily when it is exposed to the air or to water. Equations (2) and (3) show the oxidation reactions of ZVI. Oxidation usually occurs through the mechanism of Equation (2) under an anaerobic condition.

At a lower pH, the concentration of H$^+$ is higher, leading to higher reaction rates of Equations (2) and (3). A higher corrosion rate of ZVI results in a higher reduction rate of H$^+$, a higher production rate of hydrogen gas, and a higher decomposition rate of dyes.

$$\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$$ (2)

$$2\text{Fe}^0 + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$$ (3)

On the other hand, a high pH makes the reaction of Equation (4) dominant. Oxidation of ZVI results from reduction of water molecules because the concentration of H$^+$ is too low. The reduction rate of water molecules is lower than that of H$^+$, which is believed to be the reason why the decomposition rate of Orange II using synthesized ZVI is higher at a lower pH.

$$2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^-$$ (4)

**Decomposition reaction activity of ZVI including UV and H$_2$O$_2$**

It is required to enhance the decomposition efficiency of the D-ZVI to use it in non-acidic conditions. Addition of UV and H$_2$O$_2$ was tested in this study to see if it can increase the rate of the ZVI-assisted decomposition reaction. The experimental apparatus shown in Figure 2 was used. Figure 10 shows the results obtained with different amounts of H$_2$O$_2$ added at different initial pH levels. The initial concentration of Orange II was 0.1 mM and the D-ZVI dosage was 1 g. At the initial Orange II solution pH of 3, addition of 6 mM of H$_2$O$_2$ increased the decomposition rate considerably. When 60 mM of H$_2$O$_2$ was added, however, the increase in the decomposition rate was smaller. At the initial Orange II solution pH of 6, the decomposition rate was decreased by addition of H$_2$O$_2$.

Equation (5) shows the standard reduction potential of Fe$^{2+}$ at 25 °C, whose negative potential indicates that the reaction is not spontaneous. This means that external energy must be provided to oxidize Fe$^{2+}$. The Fe$^{2+}$/H$_2$O$_2$ reaction (Fenton reaction) shown in Equation (6) is believed to have provided the energy required to induce the oxidation reaction of Equation (5) in this study.

$$\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + \text{e}^- \quad -0.77 \text{ V}$$ (5)
As is shown in Equation (6), OH radicals are produced by the reaction between Fe^{2+} and H_{2}O_{2}. The increase in the Orange II removal rate by H_{2}O_{2} addition at a low pH shown in Figure 10(a) suggests that the Orange II decomposition by OH radicals plays an important role in the removal of Orange II. Addition of excessive H_{2}O_{2}, however, was shown to reduce the decomposition rate.

Fe^{3+}, a product of Equation (6), reacts with H_{2}O_{2} to produce HO_{2} radical (peroxyl radical) and is reduced back into Fe^{2+} (Equation (7)). It was observed that sedimentation sludge was formed during the Fenton reaction, which is a result of the reaction between Fe^{3+} and OH^{-} as is shown in Equation (8). Being a spontaneous reaction with the Gibbs free energy of −166.0 kcal/mol, this reaction occurs at a pH higher than about 5.0, terminating the cycle of Fe^{2+} and Fe^{3+} (Equations (6) and (7)) and hence hindering the catalytic function of Fe^{2+}. The reduction of the decomposition rate by addition of H_{2}O_{2} at pH 6 (Figure 10(b)) can be explained by this phenomenon.

Figure 11 shows the results obtained with the addition of UV and H_{2}O_{2} to the D-ZVI-assisted decomposition of Orange II at the initial pH of 6. The decomposition reaction did not occur when only UV or only H_{2}O_{2} was applied in the absence of ZVI. When ZVI was used, addition of either UV or H_{2}O_{2} alone decreased the reaction rate. When UV and H_{2}O_{2} were added together, the decomposition rate was high even without using ZVI. It has been reported that the electromagnetic energy of UV-C can decompose H_{2}O_{2} into two OH radicals (Equation (9)) ([Malik & Sanyal 2004]), to which the high decomposition rate obtained with the simultaneous use of UV and H_{2}O_{2} can be attributed.

\[ \text{H}_{2}\text{O}_{2} + \text{UV} \rightarrow 2\text{OH} \]  

The decomposition rate was highest when ZVI, UV and H_{2}O_{2} were all used simultaneously. It is believed that UV and H_{2}O_{2} were used as the energy source for the oxidation of Fe^{2+} (Equation (5)), on top of the above-mentioned effect of the H_{2}O_{2} decomposition by UV-C, leading to a further increase in the rate of the decomposition of Orange II. Based on this result, it is concluded that the photo-Fenton reaction (UV/Fe^{2+}/H_{2}O_{2}) increased the Orange II decomposition rate to a large extent when both the energy sources, UV and H_{2}O_{2}, were added to ZVI.

**CONCLUSIONS**

In this study, ZVI was produced using iron oxide generated in a pickling line at a steel works (D-ZVI) and its reaction
activity was evaluated experimentally. The conclusions deduced from this study are as follows.

1. The size of D-ZVI particles increased with reduction temperature due to coalescence. Correspondingly, the specific surface area of D-ZVI decreased with increasing reduction temperature.

2. The decomposition efficiency of D-ZVI particles was higher at a lower pH. No significant decomposition reaction was observed at pH of 4 and higher.

3. The addition of H$_2$O$_2$ promoted the ZVI-assisted decomposition of Orange II at a low initial pH of 3, whereas it decreased the decomposition rate at a higher initial pH of 6.

4. Even at a high pH condition (pH = 6), simultaneous use of ZVI, UV and H$_2$O$_2$ led to a considerable increase in the decomposition rate.

ACKNOWLEDGEMENT

This research was supported by the Program for the Construction of Eco Industrial Park (EIP) which was conducted by the Korea Industrial Complex Corporation (KICOX) and the Ministry of Knowledge Economy (MKE).

REFERENCES


