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Characterization of zero valent iron prepared from by-product of pickling line and its decomposition reaction activity

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Abstract−Zero valent iron (ZVI) was produced by using wasted acid and iron oxide that are by-products of a pickling line at a steel work. The reaction activity of the produced ZVI was evaluated through decomposition experiments of Orange II aqueous solution. The ZVI particles produced directly from wasted acid (A-ZVI) were not easy to handle because they were very small (10-200 nm) and were easily oxidized in the air. The size of ZVI particles produced from the iron oxide recovered from the regeneration process of wasted acid (O-ZVI) increased with reduction temperature due to coalescence. Correspondingly, the specific surface area of O-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 or higher with O-ZVI. The decomposition efficiency of A-ZVI was higher than that of O-ZVI or commercially purchased ZVI, but it is not easy to handle. On the other hand, O-ZVI is easier to handle, but has the drawback of low reaction activity at high pH. Further elaboration is required for practical applications of these synthesized ZVIs.

Key words: Zero Valent Iron, Azo Dye, Iron Oxide, pH, Specific Surface Area

INTRODUCTION

Mass production and use of chemicals in various fields brought by industrial development have caused adverse effects on the environment and ecosystem. Among others, the dye industry is one of the main sources of water pollution by chemicals. About 40,000 kinds of synthesized organic dyes have been developed so far and more than 7×10^6 tons are used annually in the dye industry. Azo dye is the most widely used one of those synthesized organic dyes, whose market share is about 50% of the whole dye market. The high market share of azo dye is due to 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 the use of azo dye [1].

Generally, adsorption using activated carbon [2], biological treatment using microorganisms [3], and photochemical treatment [4] are used to remove organic pollutants such as dyes contained in waste water. However, these methods do not easily remove the complex aromatic compounds with various substitutions contained in dye wastewater and generate 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 (H_2O_2), however, have limits in treating a number of different kinds of pollutants, calling for a more efficient oxidation process [5,6].

Recently, several studies on advanced oxidation processes (AOP) have been conducted [7,8]. AOP is an advanced water treatment process in which highly oxidative species such as OH radicals 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 very applicable pollutant treatment material due to its strong reduction potential [9,10], environment-friendly characteristics, and high cost efficiency [11,12]. Since ZVI has high potential as a reduction agent and catalyst, its applications as an environmental material especially for restoration of polluted soil and underground water are reported to be promising [13,14].

Wasted acid is produced in pickling lines of steel works where the surface of cold rolled sheets is descaled with hydrochloric acid. This wasted 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, calling for development of a technology converting iron oxide into ZVI.

In this study, ZVI was produced using wasted acid and iron oxide generated in a pickling line to examine a new application of oversupplied iron oxide. The physical and chemical characteristics of the produced ZVIs were analyzed by using instruments. Reaction activities of ZVIs were evaluated by decomposition experiments of Orange II, a kind of an azo dye.

EXPERIMENTAL

1. Synthesis of ZVI from Wasted Acid

In this study, ZVI was produced by two different methods. In

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Table 1. Chemical composition of the wasted acid used in this study

Composition	SiO_2	P_2O_5	Al_2O_3	Na_2O	MgO	NiO	CaO	CoO	Cr_2O_3	MnO	HCl	H_2O	Fe
Wt%	0.021	0.021	0.048	0.002	0.002	0.010	0.005	0.001	0.011	0.329	7.670	78.56	13.32

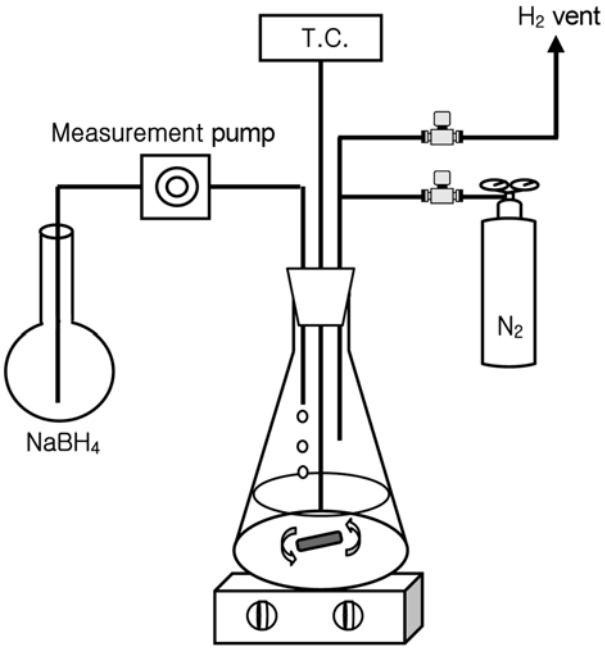

Fig. 1. Schematic of A-ZVI particle synthesis apparatus.

the first method, the wasted acid generated in a pickling line at a steel work in Gwangyang, Korea was used to produce ZVI, which will be referred to as A-ZVI hereafter. Table 1 shows the chemical composition of the wasted acid used in this study. Initial wasted acid consisted of 13% of iron and other oxides. The wasted acid was filtrated with a paper filter (Hyundai Co. Ltd. 1 μm) and then was diluted six times with distilled water.

A-ZVI particles can be prepared from hydrogen reduction of iron oxides. In this study, the sodium borohydride ($NaBH_4$) method was used, in which borohydride was introduced to reduce ferric ion (Fe^{3+}) into ZVI (Fe^0) according to the following reaction.

$$4Fe^{3+}+3BH_4^-+9H_2O \rightarrow 4Fe^0\downarrow+3H_2BO_3^-+12H^++6H_2 \quad (1)$$

Fig. 1 shows the schematic of the A-ZVI particle synthesis apparatus used in this study. The reactor was filled with nitrogen gas to inhibit oxidation of ZVI produced. 1,000 mL of 1.2 M $NaBH_4$ solution was injected by a measurement pump with a flow rate of 0.625 mL/s into 500 mL of wasted acid to produce A-ZVI precipitation. The A-ZVI sediment was washed with a diluted ethanol (≤5%) and was then sampled by using a paper filter (Hyundai Co. Ltd. 1 μm). Sampled A-ZVI was dried under an oxygen-free condition at 343 K using nitrogen gas supply. Dried A-ZVI was then put in an oxygen-free container filled with nitrogen gas and was stored in a refrigerator at 275 K until it was used for the experiments.

2. Synthesis of ZVI from Iron Oxide

In the second method, the iron oxide recovered from the wasted acid generated in the same steel work was used to produce ZVI, which will be referred to as O-ZVI hereafter. Table 2 shows the chemical composition of the iron oxide recovered from wasted acid.

Table 2. Chemical composition of iron oxide recovered from wasted acid

Composition	SiO_2	CaO	Cl	Al_2O_3	MnO	Fe_2O_3
Wt%	0.0118	0.0084	0.2033	0.0023	0.2185	99.27

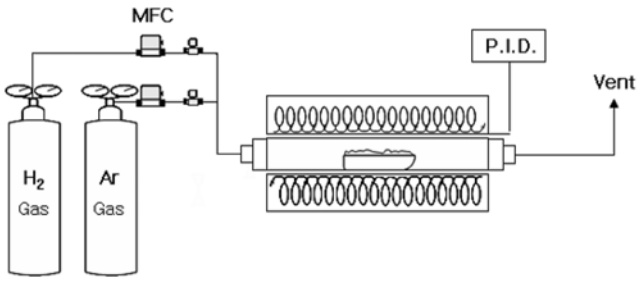

Fig. 2. Experimental setup for O-ZVI particle synthesis using iron oxide.

Table 3. The characteristics of C-ZVI used in the experiment

Name	Iron, Electrolytic, Powder
Formula weight	55.85
Purity (%)	Min. 98.0%
Particle diameter (μm)	120-150
Company	Kanto Chemical Co., Inc

Fig. 2 shows the experimental setup to reduce iron oxide into ZVI using hydrogen gas. Iron oxide 5 g was put in a quartz pot installed in a quartz reactor. It was reduced into 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 sccm of H_2 gas were supplied simultaneously for two hours. 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 O-ZVI produced 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.

3. Evaluation of Decomposition Reaction Activity

In this study, three different kinds of ZVI were used: the A-ZVI produced directly from wasted acid generated in a steel work, the O-ZVI produced by reducing iron oxide recovered from the regeneration process of wasted acid, and a commercial ZVI purchased for comparison with the two synthesized ZVIs, which will be referred to as C-ZVI hereafter. Table 3 shows the characteristics of C-ZVI used in this study. The diameter of C-ZVI particles was measured with a testing sieve (Chunggyesang Gongsa, Korea). Field emission microscopy (Hitachi, S-4800) and transmission electron microscopy (FEI, Tecnai20) were used to observe the size and morphology of iron oxide and ZVIs used in the experiments. The crystal structure

Table 4. The characteristics of Orange II used in this study

Azo dye	Orange II
Formula	$C_{16}H_{11}N_2NaO_4S$
λ (nm)	484
Formula weight	350.33
Solubility in water (mg/ml)	50
Initial concentration (mM)	0.2 mM

was observed using X-ray diffraction (Panalytical, 2500V/PC). The physical and chemical properties were evaluated using ICP (Varian, Vista 710-ES), Sub-Sieve Sizer (Fisher, M95), and BET surface area analyzer (Micromeritics, Flowsorb III).

In this study, Orange II (Aldrich Co. Ltd.), a kind of an azo dye, was used as the target organic pollutant. The characteristics of Orange II used in this study are shown in Table 4. Batch experiments were conducted in 250 mL glass bottles. Each bottle was filled with synthesized and purchased 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. The decomposition rate was evaluated from the change in Orange II concentration. The concentration of Orange II was measured by the absorbance at 484 nm with 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 H_2SO_4.

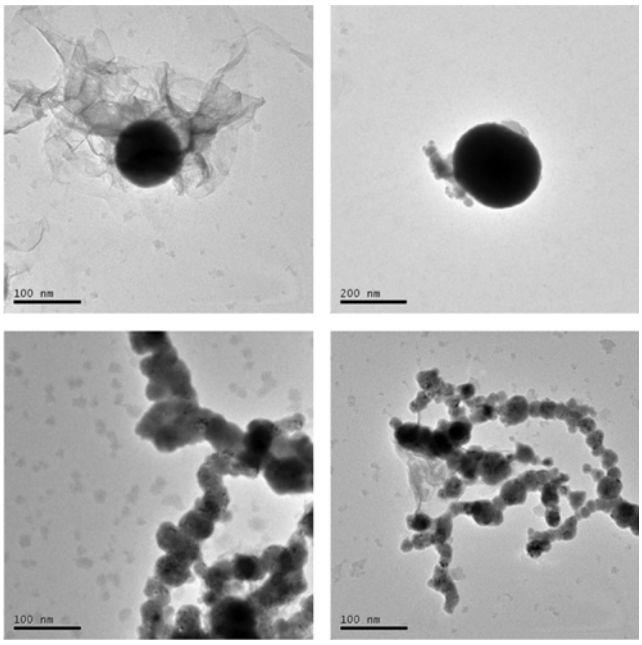

Fig. 3. TEM images of A-ZVI particles produced using the sodium borohydride method.

RESULTS AND DISCUSSION

1. Characterization of A-ZVI

TEM was used to determine ZVI particle size produced from the wasted acid. Fig. 3 shows TEM images of nanoscale A-ZVI particles produced by using the sodium borohydride method. These A-ZVI particles tend to coalesce to become larger particles and exceed the nanoscale range (10-200 nm). As is noticed in Fig. 3, A-ZVI particles are so small that they are oxidized rapidly in the air, which makes it impossible to analyze the crystal structure using XRD or to measure the specific surface area using BET. Therefore, the produced A-ZVI was put in an oxygen-free container filled with nitrogen gas and was stored at a low temperature of 275 K until it was used for the decomposition experiments.

2. Characterization of O-ZVI

Fig. 4 shows the FESEM images of the iron oxide particles and the O-ZVI particles produced at different reduction temperatures. The reduced ZVI particles (b) show 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,

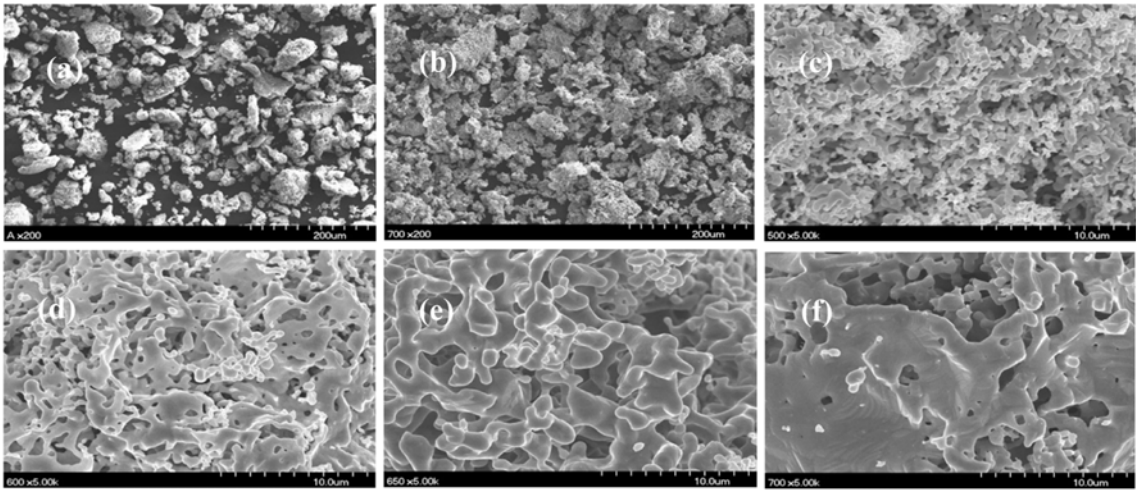

Fig. 4. Scanning electron micrograph images of the iron oxide and O-ZVI particles. (a) iron oxide particles which are by-products of a pickling line at a steel work (20 KeV×200), (b) O-ZVI particles produced from iron oxide at 973 K (20 KeV×200), (c) O-ZVI particles produced at 773 K (20 KeV×5,000), (d) O-ZVI particles produced at 873 K (20 KeV×5,000), (e) O-ZVI particles produced at 923 K (20 KeV×5,000), (f) O-ZVI particles produced at 973 K (20 KeV×5,000).

Table 5. The physical properties of iron particles used in this study

	Iron oxide	O-ZVI		
		773 [K]	873 [K]	973 [K]
Mean diameter [μm]	3.77	16.56	20.44	23.78
Specific surface area [m^2/g]	-	11.90	7.41	3.42

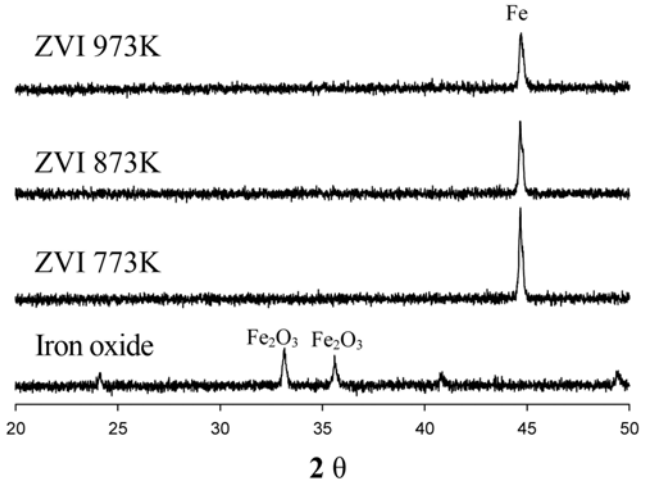

Fig. 5. X-ray diffractogram of the iron oxide and O-ZVI produced at different temperatures.

significant melting was observed for O-ZVI produced at 973 K (f).

Table 5 shows the particle size of the iron oxide particles and the O-ZVI particles produced at different reduction temperatures. The mean diameter of iron oxide particles before reduction was 3.77 μm, whereas the mean particle diameter of O-ZVI produced at 873 K was 20.44 μm. The mean particle diameters of O-ZVI produced at 773 and 973 K were 16.56 and 23.78 μm, respectively. This result indicates that a 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 O-ZVI particles produced at different temperatures are shown in Table 5. The specific surface areas of O-ZVI particles deduced from these BET plots were 11.90, 7.41, and 3.42 m^2/g for the reduction temperature of 773, 873, and 973 K, respectively. The larger specific surface area of O-ZVI particles produced at a lower reduction temperature corresponds with the smaller particle size shown in Fig. 4.

Fig. 5 shows the X-ray diffraction spectra of the iron oxide and O-ZVI produced at different temperatures. The apparent peaks shown at the 2θ of 44.9° indicate the presence of crystalline-phase ZVI (α-Fe). Two Fe_2O_3 peaks were observed from the spectrum of iron oxide.

3. Evaluation of Decomposition Reaction Activity

Fig. 6 shows the results of decomposition experiments of Orange II obtained at three different O-ZVI dosages. Addition of a larger amount of O-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 ZVI can be approximated by a pseudo first order reaction model.

$$C/C_0=\exp(-kt) \quad (2)$$

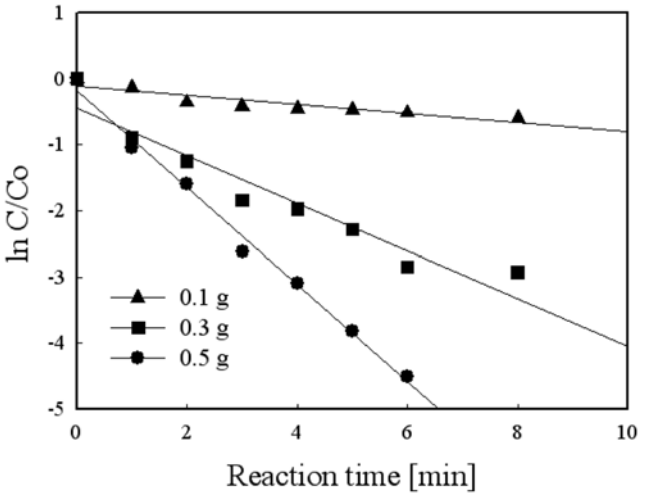

Fig. 6. Decomposition of Orange II at three different amounts of O-ZVI dosage in aqueous solution.

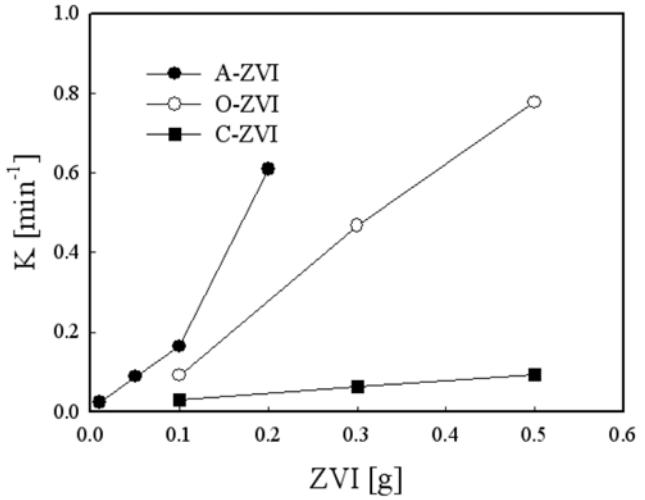

Fig. 7. Effect of ZVI dosage on the observed pseudo first order rate constant K in decomposition reactions of 0.2 mM Orange II aqueous solution.

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 Fig. 6 by a regression analysis. The values of k obtained this way for different kinds of ZVI used and for different amounts of ZVI dosage are shown in Fig. 7. The decomposition efficiency of A-ZVI was highest, whereas C-ZVI showed the lowest performance. The particle size of A-ZVI, O-ZVI, and C-ZVI used in the experiments was 10-200 nm, 20.44 μm, 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 ZVI is shown in Fig. 8. A-ZVI showed higher decomposition efficiencies than O-ZVI at all pH values. Both ZVIs showed a higher decomposition rate at a lower pH. Virtually no decomposition reaction was observed at pH of 4 or higher for O-ZVI.

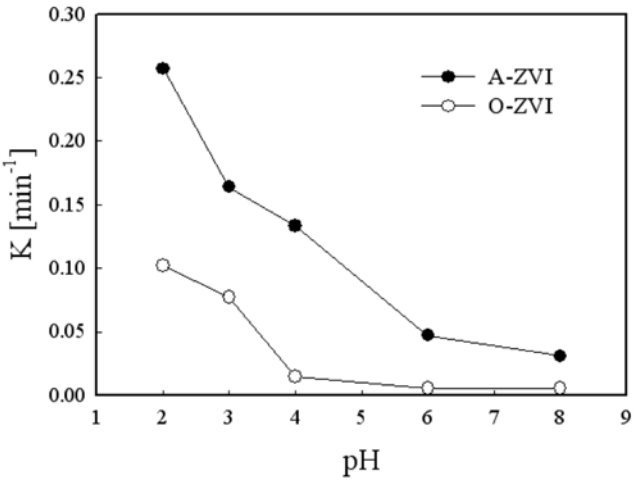

Fig. 8. The pH effect on decomposition of Orange II using ZVI.

ZVI is oxidized easily when it is exposed in the air or in water. Eqs. (3) and (4) show the oxidation reactions of ZVI. Oxidation usually occurs through the mechanism of Eq. (3) under an anaerobic condition, whereas under an aerobic condition the mechanism shown in Eqs. (4) through (6) dominates the oxidation of ZVI into two- or three-valent irons. At a lower pH, the concentration of H^+ is higher leading to higher reaction rates of Eqs. (3) and (4). 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.

$$Fe^0+2H^+ \rightarrow Fe^{2+}+H_2 \quad (3)$$

$$2Fe^0+O_2+4H^+ \rightarrow 2Fe^{2+}+2H_2O \quad (4)$$

$$4Fe^{2+}+O_2+4H^+ \rightarrow 4Fe^{3+}+2H_2O \quad (5)$$

$$Fe^{3+}+3H_2O+ \rightarrow Fe(OH)_3+3H^+ \quad (6)$$

On the other hand, a high pH makes the reaction of Eq. (7) 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.

$$2Fe^0+O_2+2H_2O \rightarrow 2Fe^{2+}+4OH^- \quad (7)$$

CONCLUSION

ZVI was produced by using wasted acid and iron oxide generated in a pickling line at a steel works and its reaction activity was evaluated experimentally. The conclusions from this study are as follows.

(1) The ZVI particles produced directly from wasted acid (A-ZVI) are not easy to handle because they are very small (10-200 nm) and are oxidized easily in the air.

(2) The size of ZVI particles produced from the iron oxide recovered from the regeneration process of wasted acid (O-ZVI) increased with reduction temperature due to coalescence. Correspondingly, the specific surface area of O-ZVI decreased with increasing reduction temperature.

(3) In the decomposition experiments of Orange II aqueous solution, the decomposition efficiency of A-ZVI, which has the smallest mean particle size, was highest, whereas the decomposition efficiency of C-ZVI, which has the largest mean particle size, was lowest.

(4) The decomposition efficiency of synthesized ZVI particles was higher at a lower pH. No significant decomposition reaction was observed at pH of 4 or higher with O-ZVI.

(5) In spite of the high reaction activity of A-ZVI, it is not easy to handle, calling for further elaboration for practical applications. On the other hand, O-ZVI is easier to handle, but has the drawback of low reaction activity especially at high pH. Addition of ozone, UV, and/or H_2O_2 will be considered in the follow-up studies to enhance the activity of O-ZVI.

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