Decoloration of Acid Red 88 Using Synthetic-Zeolite-Based Iron as a Heterogeneous Photo-Fenton Catalyst

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Abstract

Decoloration and mineralization of an azo dye, Acid Red 88, were conducted using synthetic-zeolite-based Fe as a heterogeneous photo-Fenton catalyst in the presence of ultraviolet (UV) rays and H_2O_2. Under the optimal conditions (pH = 5.5, 17.6 mM H_2O_2, and 4 W m^{-2} UVC), 100% decoloration and 90% total organic carbon removal of 0.12 mM Acid Red 88 were achieved in 120 min. The effects of initial pH with time, as well as oxidation, were studied in a batch reactor. It was found that high decoloration was achieved using a heterogeneous Fenton method at pH 7 and lower. The catalyst also had the advantages of low leaching of Fe^{3+} ions and maintenance of a high decoloration in consecutive catalytic treatments. Zeolite-based Fe was successfully used repeatedly (up to three consecutive cycles) for decoloration. A high rate of decoloration was also achieved in the case of continuous operation, although $\leqslant 0.4$ mg L^{-1} of Fe were leached into the treated water.

Keywords: photo-Fenton, synthetic zeolite, dye, heterogeneous catalyst

1. Introduction

In the textile industry, dyeing consists of three processes: preparation, dyeing, and finishing. Large quantities of dyes and other organic matter are therefore present in effluents from the textile industry, resulting in contamination of water. There are currently environmental standards for chemical oxygen demand (COD) and biochemical oxygen demand (BOD), but chromaticity is regulated to a lesser degree. However, when color remains in the effluent, even if COD and BOD meet the environmental standards, there is still a strong impression that the discharge is contaminated. Active-carbon adsorption and biodegradation are usually used as the treatments for effluent coloration, but these treatment methods have problems with respect to running costs and efficiency (Asgher, Azim, & Bhatti, 2009; Nillson et al., 2006; Sirianuntapiboon, Sadahiro, & Salee, 2007).

For environmental protection, there are a number of methods (chemical, physical, and biological) for treating discolored azo dye effluents from various industries. Biological and physical treatment methods are not satisfactory because they simply transfer the pollutants from one phase to another, and the equipment involved in these processes is expensive. In recent years, treatments using advanced oxidation processes, i.e., chemical methods, have attracted much attention. Advanced oxidation processes such as homogeneous photo-Fenton reactions can produce hydroxyl radicals, which are powerful oxidants for organic degradation (Arslan-Alaton, 2007; Selcuk, 2005; Papadopoulos et al., 2007).

Although the homogeneous photo-Fenton reaction is very powerful in the degradation of organic compounds, it has significant disadvantages such as the need for recovery of the Fe sludge after treatment and the narrow pH range in which the reaction proceeds. To overcome these drawbacks, much effort has been made to develop heterogeneous catalysts for the reactions; these catalysts contain Fe clusters or Fe oxides (Feng et al., 2005; 2009; Tekbas, Yatmaz, & Bektas, 2008; Lucas & Peres, 2006).

These catalysts basically consist of Fe supported on clay minerals. There have been reports of the use of natural zeolites as carriers (Kasiri et al., 2008; Rodriguez et al., 2010). Artificial zeolites are also available; these are produced by converting wastes such as coal ash to useful zeolite-type materials, and have attracted much attention because of their low cost. There have been reports on the use of clay minerals such as bentonite (Feng et al., 2005) or montmorillonite (Daud, 2010) as carriers for Fe, but few reports of zeolite-based Fe catalysts. Functionality evaluations of catalysts have also been reported but there have been few on catalyst durability (Feng et al., 2005). In this study the dye was decomposed in a heterogeneous photo-Fenton reaction using an Fe-zeolite. As well as the effect of pH, repeated and continuous treatments using the catalyst were examined to evaluate its durability.

2. Experimental

2.1 Raw Materials

The chemical constituents of the zeolite are shown in Table 1. The zeolite was supplied by Tosoh Ltd., (Shunan-shi, Japan), and acid Red 88, $Fe(NO_3)_3 \cdot 9H_2O$, and 30% H_2O_2 were purchased from Kanto Chemicals Ltd., Japan.

Table 1. Chemical constituents of zeolite

Components and other properties	Values
SiO_2 (%)	72.1
Al_2O_3 (%)	12.9
Fe_2O_3 (%)	0.7
CaO (%)	2.6
Na_2O (%)	1.8
H_2O (%)	7.0
CEC (meq/100g)	120–150
Diameter (Å)	5.5–8
Surface area (m^2/g)	200–300

In this study, an artificial zeolite was used as a carrier, and the catalyst was used repeatedly. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures, and contain Al, Si, and O atoms in a regular framework. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra joined together in various regular arrangements through shared O atoms to form an open crystal-lattice containing pores. Some Si^{4+} are replaced by Al^{3+} in the SiO_2 frame, leading to a positive ion deficit. This can result in interactions leading to exchange with Fe^{3+}. The structure of the Fe-zeolite and a schematic diagram of the heterogeneous Fenton method are shown in Figures 1 and 2, respectively.
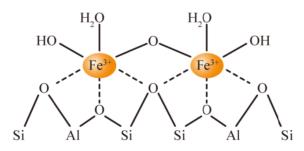

Figure 1. Structural framework of Fe^{3+}-zeolite

Figure 2. Heterogeneous Fenton method

The heterogeneous Fenton method can be described by the following three equations (Feng et al., 2003):

$$Fe^{3+} \text{ on zeolite surface} + h\nu \ \ (UV \text{ energy}) \rightarrow Fe^{2+} \text{ on zeolite surface} \tag{1}$$

$$Fe^{2+} \text{ on zeolite surface} + H_2O_2 \rightarrow Fe^{3+} \text{ on zeolite surface} + \bullet OH \text{ (radical)} + OH^- \tag{2}$$

$$\text{Zeolite-Acid RED 88} + \bullet OH \rightarrow \text{reaction intermediates} \rightarrow CO_2 + H_2O \tag{3}$$

The reaction is initiated by the photoreduction of Fe^{3+} on the zeolite surface to Fe^{2+} under ultraviolet (UV) irradiation. Oxidation with H_2O_2 of the Fe^{2+} formed then generates a hydroxyl radical and Fe^{3+}. The hydroxyl radical attacks Acid Red 88 (Figure 3), giving rise to reaction intermediates such as adjacent ring structures.

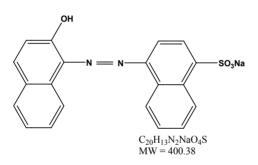$C_{20}H_{13}N_2NaO_4S$
$MW = 400.38$

Figure 3. Acid Red 88

The absorption spectrum of Acid Red 88 is shown in Figure 4; the spectrum exhibits a wide range of absorption bands, with an absorption maximum at 514 nm.
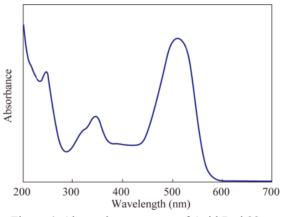

Figure 4. Absorption spectrum of Acid Red 88

In the decoloration experiments, the degree of color removal was calculated as follows:

$$\text{Color removal (\%)} \ = \ 100[(A_i - A_t)/A_i] \tag{4}$$

where A_i is the initial absorbance of the sample and A_t is the absorbance at time t.

The total organic carbon (TOC) removal rate was calculated as follows:

$$TOC\ removal\ rate = 100[(TOC_i - TOC_t)/TOC_i]$$ (5)

where TOC_i is the initial absorbance of the sample and TOC_t is the absorbance at time t.

2.2 Fe Catalyst

A 0.02 M ferric solution was prepared by dissolving ferric nitrate in distilled water. Zeolite (5.0 g) was added to 50 mL of freshly prepared 0.02 M ferric solution, followed by shaking for 6 h at 160 rpm in a water bath at 60 °C. After shaking, the mixture was filtered using a 0.45-μm membrane filter and dried at 30 °C. The whole procedure was repeated four times, and finally Fe^3-zeolite was collected as a brown powder 4.3 g). The Fe^{3+} attachment was determined to be 0.60 mmol g^{-1}.

The XRD patterns of H-zeolite and Fe-zeolite are shown in Figure 5. Diffraction lines for iron oxide are not observed in the XRD pattern of Fe-zeolite. This is not unusual as the diffraction lines of iron oxide are expected to broaden and be buried in the background noise of the XRD pattern (Chen et al., 2000).

2.3 Decoloration Experiments

Fe^{3+}-zeolite (0.298 g) and Acid Red 88 (0.100 g) were added to 1 L of distilled water adjusted to pH 3.0 using H_2SO_4. Then 1 mL of H_2O_2 was added to the solution, and the liquid was irradiated with UV light (4.0 Wm^{-2}). The intensity of the UV lamp is shown in Figure 6. The intensity is strong at 283 nm. Mixing was performed at room temperature at 120 rpm. At each sampling, 30 mL of solution were removed and 1 mL of 0.2 M NaOH solution was added. The solution was then filtered and the TOC and absorbance were measured using a total carbon analyzer (TOC-V, Shimadzu, Japan) and spectrophotometer (V-630Bio, Jasco, Japan), respectively. The pH-dependence tests were performed using 0.1 M H_2SO_4 and 0.1 M NaOH. After decoloration, the Fe-zeolite was separated using a 0.45-μm membrane filter and dried at 30 °C for further use. For comparison, a Fenton reaction was performed as a control experiment, as follows. Ferric sulfate (0.05 g) and Acid Red 88 (0.100 g) were added to 1 L of distilled water, and the pH was adjusted to 3 by adding H_2SO_4, followed by addition of 1 mL of 30% H_2O_2 solution. Mixing was performed at room temperature and 120 rpm. At each sampling, 30 mL of solution were removed and 1.0 mL of 0.2 M NaOH solution was added.
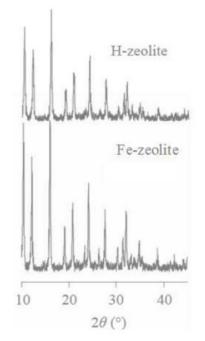

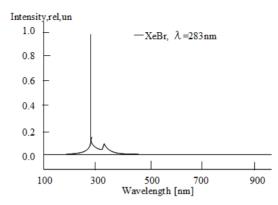Figure 5. XRD patterns of H-zeolite and Fe-zeolite

Figure 6. UV lamp intensity

2.4 Continuous Decoloration

Figure 7 shows the experimental setup for conducting continuous decoloration tests; the experimental conditions are shown in Table 2. The test was carried out in a transparent glass fluidized-bed reactor of inner diameter (ID) 2 cm and a Plexiglass tube of length 10 cm, which was fused to a 6-cm ID and 5-cm long tube to form a 150-mL reactor body. Approximately 0.8 g of the Fe^{3+}-zeolite were soaked in deionized water to facilitate swelling, and then packed into the reactor. The dye solution (0.12 mM Acid Red 88 and 17.6 mM H_2O_2 at pH 5.5) was fed through the bottom of the column at a desired flow rate using an Iwaki PST-100N peristaltic pump. Two small UV lamps were placed in parallel at a position 50 mm from the bottom of the wall, giving irradiation of 0.5 W m^{-2}. A cross-flow membrane filter was installed so that the Fe^{3+}-zeolite could not flow out. At set time intervals, samples were collected using a Biorad Model 2110 Fraction Collector in 8 mL plastic tubes and analyzed for absorbance at 514 nm and Fe^{2+} ions.
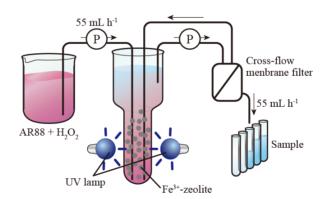

Figure 7. Experimental setup

Table 2. Experimental conditions

Fe^{3+}-zeolite	400 mg	Vol. of reactor	200 mL
H_2O_2	17.6 mM	Flow rate	55 mLh^{-1}
Acid Red 88	0.12 mM	Residence time	3.6 h
pH	5.5	Intensity of UV	4.0 Wm^{-2}

3. Results and Discussion

3.1 Evaluation of Fe^{3+}-Zeolite (Batch Test)

The decoloration rates and TOC values for the Fenton and heterogeneous Fenton reactions are shown in Figures 8 and 9, respectively. As shown in Figure 8, the rate of decoloration was quite high for both methods, but total decoloration was not achieved using the Fenton method, whereas 100% decoloration was attained in the case of the heterogeneous Fenton method; complete decomposition was achieved in 60 min. As can be seen from Figure 9, the TOC decreased faster in the heterogeneous Fenton method than in the Fenton method, and reached less than 5 mg L^{-1} within 120 min. These results show that the decoloration efficiency of the heterogeneous Fenton method was higher than that of the Fenton method.
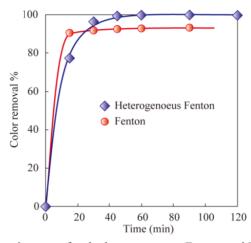

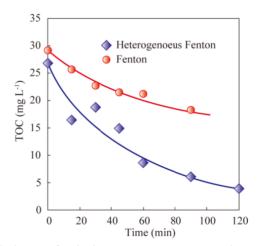Figure 8. Decoloration rates for the heterogeneous Fenton and Fenton methods

Figure 9. TOC changes for the heterogeneous Fenton and Fenton methods

Figure 10 shows changes in the UV-Vis spectra of dye with UV irradiation time. The absorbance at 514 nm is from the azo group in the dye, and the absorbance at 200–300 nm corresponds to the phenyl group of the dye. As shown in Figure 10, the peak for the azo group disappeared earlier and consequently decoloration occurred immediately. At the same time the absorption at 200–300 nm decreases, which is the result of phenyl group decomposition by heterogeneous Fenton oxidation.
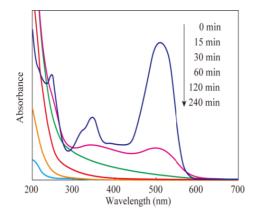
Figure 10. UV spectral changes with time

The percentages of color removal with time at different pH values are shown in Figures 11 and 12 for the heterogeneous Fenton and Fenton reactions, respectively. High decoloration was achieved using the heterogeneous Fenton method at pH 7. This is because Fe^{3+} forms a hydroxide at pH 5 or higher and does not take part in the reaction in the Fenton method. In contrast, in the heterogeneous Fenton method, the catalyst is stable at high pH values because Fe^{3+} is attached to the zeolite.
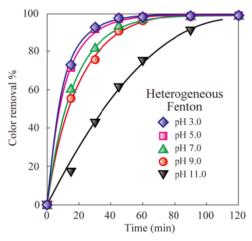

Figure 11. pH dependence of color removal for the heterogeneous Fenton method
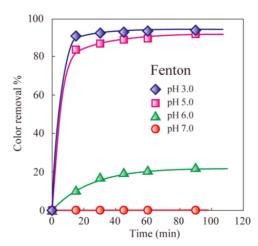

Figure 12. pH dependence of color removal for the Fenton method

Decomposition of dye with respect to time is shown in Figure 13. As decomposition proceeds, the pH changes. This is because low molecular organic acids such as formic acid, acetic acid, oxalic acid, and succinic acid, or nitric acid, are generated as the dye decomposes (Feng, Hu, & Yue, 2006). After decoloration was complete, the Fe^{3+}-zeolite was separated using a membrane filter, and dried at 30 °C for reuse.

3.2 Reuse of Fe^{3+}-Zeolite

To investigate the reusability of the Fe^{3+}-zeolite, cycling tests were carried out using the catalyst three times. The extent of decoloration with time is shown in Figure 14. It is clear that the extent of decoloration is almost the same in each cycle. TOC removal was also performed and no changes were observed. So, it can be concluded that the Fe-zeolite can be reused in decoloration processes.
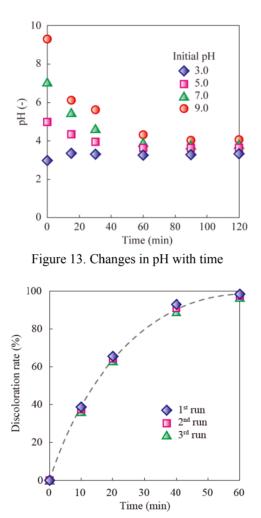

Figure 13. Changes in pH with time

Figure 14. Changes in decoloration rate with repeated use of Fe-zeolite

3.3 Continuous Treatment

Continuous decoloration treatment and TOC removal tests were performed, and the results are shown in Figures 15 and 16, respectively. The percentage decoloration increased with increasing bed volume (BV), and 90% color removal was achieved at a BV of 1200. The BV represents the volume ratio of the solution passed through the column to that of the packed material. Release of Fe into the treated water was insignificant (≤ 0.4 mg L^{-1}).
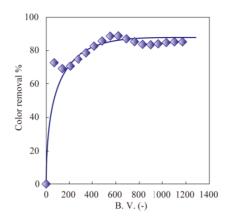
Figure 15. Percentage color removal with outflow

As can be seen from Figure 14, a TOC removal rate of only approximately 50% was maintained. This can be attributed to insufficient mineralization of the dye. This problem could be overcome by using high-strength UV rays and/or increasing the amount of Fe^{3+}-zeolite.
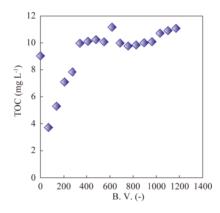

Figure 16. Changes in TOC removal rate with outflow (TOC inflow = 28 mg L^{-1})

4. Conclusions

The effect of initial solution pH on the decoloration and mineralization of 0.12 mM Acid RED 88 using a synthetic-zeolite-based Fe^{3+} heterogeneous photo-Fenton catalyst, and the catalyst durability were studied. The initial pH of the solution did not influence the photocatalytic activity of the Fe^{3+}-zeolite at 60 min. Under optimal conditions, 100% decoloration and 90% mineralization of 0.12 mM Acid Red 88 were achieved in 120 min when the Fe-zeolite was used as the catalyst. In continuous operation, the catalyst displayed reasonably good photocatalytic activity.

In this research, it turned out that heterogenous Fenton oxidization using zeolite is effective for decomposition of azo-dye. The study of application to drainage of an actual textile factory is supposed to perform as further study.

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