Degradation of Reactive Yellow 86 with photo-Fenton process driven by solar light

Hideyuki Katsumata1,*, Syunya Koike1, Satoshi Kaneco1, Tohru Suzuki2, Kiyohisa Ohta1,2

1. Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan.
E-mail: hidek@chem.mie-u.ac.jp
2. Environmental Preservation Center, Mie University, Tsu, Mie 514-8507, Japan

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Abstract

The decolorization of Reactive Yellow 86 (RY 86), one of reactive azo dyes, was investigated in the presence of Fenton reagent under solar light irradiation. The decolorization rate was strongly influenced by pH, initial concentrations of H2O2 and Fe(II), and so on. An initial concentration of 40 mg/L was decolored more than 90% after 20 min under optimum conditions. The activation energy of the solar photo-Fenton reaction was 1.50 kJ/mol for RY 86 in the temperature range of 10–60°C. In the kinetic study, the rate constant of RY 86 with OH· radicals could be estimated to be 1.7 × 10^10 L/(mol·sec). The decolorization efficiency of RY 86 under solar light irradiation was comparable to the artificial light irradiation. The decrease of TOC as a result of mineralization of RY 86 was observed during photo-Fenton process. The rate of RY 86 mineralization was about 83% under UV irradiation after 24 hr. The formation of chloride, sulfate, nitrate and ammonium ions as end-products was observed during the photocatalytic process. The decomposition of RY 86 gave two kinds of intermediate products. The degradation mechanism of RY 86 was proposed on the base of the identified intermediates.

Key words: reactive azo dye; photo-Fenton reaction; solar light irradiation; decolorization; mineralization

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Introduction

Wastewaters from textile and dye industries are highly colored with large concentrations of organic matter. Direct discharge of textile industry wastewater into the receiving media causes serious environmental pollution by imparting intensive color and toxicity to aquatic environment (Pierce, 1994). The azo dyes, having an azo group consisting of two nitrogen atoms (N≡N), are the largest class of dyes used in textile industry (Yang and Xu, 1996). Azo dyes have different forms, such as direct, acid, base, reactive, disperse, metal-complex, mordant and sulfur dyes (Yang and Xu, 1996). Azo dyes are the most problematic pollutants of textile wastewaters since more than 15% of the textile dyes enter the wastewater stream (Park and Choi, 2003).

Due to the complex aromatic structure and stability of azo dyes, conventional biological treatment methods are not very effective for dyestuff removal (Dai et al., 1995). A number of physical, chemical and biological methods have been used for the treatment of dyestuff effluents (Kapdan and Kargi, 2002a, 2002b; Kargi and Ozmihiçi, 2005, 2006). Among other methods, advanced oxidation processes are more efficient and capable of mineralizing a wide range of organic pollutants. Recent reports indicate that a combination of H2O2 and UV irradiation with Fe(II), so-called photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds. Fenton reagent can completely decolorize and partially mineralize textile dyes rather rapidly (Neamtu et al., 2001; Meric et al., 2004). Most of literature studies on Fenton treatment of dyestuffs are on color removal rather than mineralization or TOC removal.

The acceleration of photo-Fenton process for the decomposition of organic compounds is believed to have the capacity of photolysis of iron aquacomplex, Fe(H2O)6(OH)2+ (to be Fe(OH)2+ in the succedent form), to provide a new important source of OH· radicals (Brand et al., 1998; Mailhot et al., 1998). Further, the photolysis of Fe(OH)2+ regenerates Fe(II) (Eqs. (1) and (2)), this means that photo-Fenton reaction would need low Fe(II) concentration compared with the Fenton process.

Fe2+ + H2O2 → Fe(OH)2+ + OH· (1)
Fe(OH)2+ + hv → Fe2+ + OH· (2)

Furthermore, Fe(OH)2+ can absorb light at wavelengths up to 410 nm, while TiO2 photocatalysis can use photon
with wavelength close to 380 nm (Hoffmann et al., 1995). In other words, photo-Fenton reaction can be driven with low energy photons in visible spectrum. Therefore, photo-Fenton process is a potential low cost treatment that can be run under solar light irradiation (Safarzadeh-Amiri et al., 1996).

In the present study, we used the solar photo-Fenton process to decolorize Reactive Yellow 86 (RY 86), which is one of Reactive azo dyes in water. Many factors affecting decolorization, such as pH value, initial concentrations of Fe(II) and H₂O₂, were evaluated. The progress of mineralization of RY 86 was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the intermediate products of RY 86 during this photocatalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). The degradation pathway was proposed on the basis of intermediates formed.

1 Experimental

1.1 Reagents

RY 86 was purchased from Wako Pure Chemical Industries (Japan) and was used as received. Analytical grade hydrogen peroxide solution (30%, W/W) was obtained from Wako Pure Chemical Industries (Japan). Ferrous sulfate heptahydrate (FeSO₄·7H₂O) and ferrous chloride tetrahydrate (FeCl₂·4H₂O) were purchased from Nacalai Tesque (Japan). All other chemicals and solvents were of the purest grade commercially available and were used without further purification. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Japan) resulting in a resistivity of > 18 MΩ/cm.

1.2 Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell of 30 mL capacity. The reaction mixture inside the cell, consisting of 20 mL of RY 86 solution and a precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with H₂SO₄ and NaOH solution. The initial concentration of RY 86 in all experiments was 40 mg/L, except for the experiment for initial concentration effect (40–200 mg/L). Dye concentrations of 10 mg/L up to 250 mg/L have been cited as being present in dyehouse effluents (O’Neill et al., 1999). In most experiments, temperature was kept at (20 ± 1)°C with a water bath. The sample solution was irradiated under solar light. In the case of an artificial light, a Xe lamp (990W, Ushio Electronics Co., Japan) was used as a light source. The beam was parallel and the length between lamp and the reactor wall was 10 cm. The lamp was warmed up for 10 min to reach constant output. In this case, the short UV radiation (λ < 300 nm) was filtered out by the vessel wall. The intensity of the light was measured by a UV radio meter (UVR-400, Iuchi Co., Japan) with a sensor of 320 to 410 nm wavelength. The radio meter was set up at the same position as the reactor.

1.3 Analyses

After illumination, the sample solution was filtered through a 0.45 μm-membrane filter. The absorbance of sample solutions containing RY 86 was monitored at 410 nm with a spectrophotometer (Model UV-1650PC, Shimadzu Co., Japan).

The progress of mineralization of fenitrothion was monitored by measuring TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-VE) based on CO₂ quantification by non-dispersive infrared analysis after high-temperature catalytic combustion. Anions and cations formed in reaction were analyzed by ionic chromatography using a Metrohm Compact IC 7611 equipped with a Shodex anionic column (IC SI-90 4E) and a Shodex cationic one (IC YK-421), respectively.

The intermediate products during photodegradation of RY 86 were extracted by the solid phase extraction (C18 disk, 3M Empore). A mixture of dichloromethane and ethyl acetate (1/1, V/V) was used to elute intermediate products. This solution was concentrated under nitrogen flow for the analysis of byproducts. A GC/MS (Shimadzu GC-MS 5050A, Japan) was used for separation and detection of intermediate products. The GC was equipped with a CP-Sil 8 CB Low Bleed capillary column (30 m × 0.25 mm i.d.) in helium carrier gas (1.0 mL/min) and with splitless injection system. The GC oven temperature was programmed to hold 50°C for initial 3 min, to increase from 50 to 280°C at a rate of 15°C/min and to hold at 280°C for 5 min. The injector and interface temperatures were kept at 280°C. Mass spectra were obtained by electron-impact (EI) mode at 70 eV using the full scan mode.

2 Results and discussion

2.1 Effect of variables on the decolorization of RY 86

The time courses of UV absorption spectra of RY 86 solution in photocatalytic decolorization by solar photo-Fenton reaction were observed in a range of 0–10 min. UV spectrum of RY 86 solution before irradiation presented absorption maximum at 410 nm. The disappearance of 410 nm absorption band was observed with increasing reaction time. Consequently, it was confirmed that Fenton reagent was effective photocatalyst for the decolorization of RY 86 under solar light irradiation.

Effect of pH on the decolorization of RY 86 in the solar photo-Fenton process was investigated over a pH range of 2.0–5.0 because much precipitation of Fe(OH)₃ occurred during the process above pH 5.0. These results are shown in Fig. 1. The decolorization percentage of RY 86 rapidly increased with increasing pH value up to 3.0, decreasing at pH above 3.0. Therefore, photo-Fenton reaction is strongly affected by pH. Generally, optimal pH of photo-Fenton reaction is around 3 (Pignatello et al., 1999) because the main species at pH 2–3, Fe(OH)₂⁺, is the one with the largest light absorption coefficient and quantum yield for OH· radical production, along with Fe(II) regeneration (Benkelberg and Warneck, 1995).
Further, the decolorization and reaction rate are limited at low pH (pH < 3) because OH· radicals are consumed by excess H⁺ (Muruganandham and Swaminathan, 2004; Lucas and Peres, 2006).

To obtain optimal initial Fe(II) concentration, the experiment was carried out in Fe(II) concentration range of 0–5.0 × 10⁻³ mol/L (Fig. 2). As it can be seen from Fig. 2, the decolorization rate of RY 86 increased with increasing initial Fe(II) concentration up to 5.0 × 10⁻⁴ mol/L, and then decreasing at higher concentration. This low activity might be due to the direct reduction of OH· radicals by metal ions (Joseph et al., 2000). When Fe(II) concentration was 5.0 × 10⁻⁴ mol/L, the decolorization of RY 86 was 96 % after 20 min. Figure 3 shows the effect of initial H₂O₂ concentration on the decolorization of RY 86 by photo-Fenton process. As expected, the decolorization rate of RY 86 increased with increasing the concentration of H₂O₂. This can be explained by the effect of additionally produced OH· radicals. When H₂O₂ concentration was below 5.0 × 10⁻² mol/L, RY 86 did not achieve 90% decolorization within 20 min.

The influence of solar light intensity on the photocatalytic decolorization of RY 86 was carried out in the range of 0–2.0 mW/cm². The decolorization percentage of RY 86 rapidly increased with increasing light intensity. The enhancement of decolorization rate is due to increase in hydroxyl radical production. Light intensity determines the amount of photons absorbed by the catalyst. With the increase in the solar power the catalyst absorbs more photons and this produces more hydroxyl radicals. In solar/Fe(II)/H₂O₂ process, the photoreduction of Fe³⁺ depends directly on the incident light intensity. At low intensity, the photoreduction is limited. It appears that the solar power tested in our study lies in the linear range and hence all photons produced were effectively used. Therefore, all subsequent decolorization of RY 86 was carried out under light intensity of 2.0 mW/cm².

Effect of temperature on the decolorization of RY 86 by the solar photo-Fenton system was examined in the range of 10–60°C. Although the decolorization efficiency of RY 86 gradually increased as the temperature increased, the appreciable change was not observed in the temperature range. This effect is due to an increase in the rate constant of the decolorization reaction. The thermal enhancement of the decolorization can be explained by the increase of Fe(III) concentration and the temperature dependence of quantum yield of photochemical reduction of Fe(III) (Lee and Yoon, 2004). According to Arrhenius formula, the decolorization reaction rate constant (kₚ) can be
expressed as:

$$k_{ap} = A \exp \left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (3)

where, $A$ is frequency factor, $E_a$ (kJ/mol) is apparent activation energy, $R$ (8.314 J/(mol·K)) is universal gas constant and $T$ (K) is temperature. From the dependence of $\ln k_{ap}$ on $-1/T$, the activation energy of the solar photo-Fenton reaction was found to be 1.50 kJ/mol for RY 86. This $E_a$ value was very similar to the reported values, which were 1.26 kJ/mol for Procion Red H-E7B and 1.09 kJ/mol for Cibacron Red FN-R (Núñez et al., 2007). All subsequent experiments were performed at 20°C, considering practical application and the operating cost for the decolorization system.

To study the influence of initial RY 86 concentration on the decolorization, the initial concentration is controlled between 40 and 200 mg/L. The decolorization efficiency of RY 86 was lower with increasing the initial concentration. The higher RY 86 concentrations in aqueous solution increase the number of RY 86 molecules in the solution but hydroxyl radicals, therefore, the decolorization efficiency decreases. It has been reported that the plot of $C_{H_2O_2}^0/k_{ap}$ vs. $C_{ap}^0$ showed the linear relationship (Xu et al., 2008). The intrinsic rate constant of dye with OH· radicals in aqueous solution could be calculated from the intercept of the plot. The experimental results in this study are shown in Fig. 4. The rate constant of RY 86 with OH· radicals could be estimated to be $1.7 \times 10^{10}$ L/(mol·sec) from this figure.

The photocatalytic decolorization of RY 86 was carried out under artificial light irradiation. The results are compared with solar light irradiation in Fig. 5. The Fe(II)/H$_2$O$_2$ system in the dark (Fenton reaction) was also evaluated for the decolorization of RY 86. For this case, about 80% of RY 86 was decolored after 20 min. On the other hand, the decolorization efficiency of RY 86 under solar light irradiation was comparable to the artificial light irradiation.

$$C_{H_2O_2}^0 \times k_{ap}$$

Fig. 4 Relationship between $C_{RY 86}$ and $C_{H_2O_2}^0/k_{ap}$. Conditions: $C_{H_2O_2}^0$ $5 \times 10^{-2}$ mol/L; $C_{Fe(II)}^0$ $5 \times 10^{-4}$ mol/L; pH 3.0; light intensity 2.0 mW/cm$^2$.

Fig. 5 Decolorization characteristics of RY 86 under dark and light conditions. Conditions: $C_{H_2O_2}^0$ $5 \times 10^{-2}$ mol/L; $C_{Fe(II)}^0$ $5 \times 10^{-4}$ mol/L; pH 3.0; light intensity 2.0 mW/cm$^2$.

The decolorization of RY 86 was more than 90% after 20 min under solar light or artificial one irradiation. If the process is carried out with concentrated sunlight using reflectors then solar process will be more efficient.

2.2 Mineralization

When the total mineralization of RY 86 proceeds stoichiometrically using oxygen as oxidizing agent, the mineralization reaction can be estimated as follows:

$$C_{18}H_{16}Cl_2N_6O_2S_2 + 30O_2 \rightarrow 2HCl + 8HNO_3 + 2H_2SO_4 + 18CO_2 + H_2O$$  \hspace{1cm} (4)

It should be remarked that nitrogen released has been measured as a combination of ammonia and nitrate, but ammonia can be oxidized to nitrate after long irradiation time (Pramauro et al., 1993; Bonsen et al., 1997).

In the mineralization experiments, the photocatalytic degradation of RY 86 was conducted under the Xe lamp irradiation. The formation of sulfate ion from RY 86 degradation was investigated. The concentration of sulfate ion quickly increased with increasing the reaction time, suggesting a very fast degradation/desulfurization stage (Fig. 6a). After a reaction time of 20 min, about 100% of element sulfur in RY 86 was transformed to sulfate ion. The formation of chloride ion showed a similar trend to the sulfate ion formation as shown in Fig. 6a. Therefore, the dechlorination was also early stage of RY 86 degradation. The concentrations of chloride and sulfate ions were higher than the maximum theoretical values, which may be due to impurities in RY 86.

The formations of ammonium and nitrate ions during the photo-Fenton process as a function of reaction time are presented in Fig. 6b. Both ammonium and nitrate ions were detected in different relative concentrations. Only 15% of the initial N was detected as ammonium and nitrate ions after 24 hr of irradiation time. Therefore, a
part of nitrogen atoms from RY 86 could be mineralized by this photocatalytic system. This incomplete nitrogen mass balance has frequently been observed in similar process (Song et al., 2008). This might be the reason that some of the nitrogen was transformed to N\textsubscript{2}, NO and NO\textsubscript{2}, and some might exist in undetected byproducts (Hsing et al., 2006; G"ul et al., 2007).

The progress of mineralization of RY 86 solution was monitored by measuring TOC. As shown in Fig. 6c, the complete mineralization of RY 86 was not achieved after 20 min, although RY 86 was not almost present in the solution after irradiation. This difference indicates that intermediate products were produced during the photo-Fenton process. The generated photoproducts are attacked in their turn by hydroxyl radicals which are formed in a continuous manner via a homogeneous photocatalytic process involving Fe(III, II) (Brand et al., 1998; Mailhot et al., 1998). TOC rapidly decreased with increasing the reaction time up to 4 hr, and then decreased gradually. TOC remained about 1.5 mg/L (83% mineralization) after 24 hr irradiation. Therefore, this result indicates the formation of persistent intermediate compounds which are difficult to be degraded by this photocatalytic system. It is expected that triazine ring remained in the aqueous solution treated after 24 hr as described later.

2.3 Identification of intermediate products and degradation mechanism

The intermediate products formed in this photocatalytic degradation of RY 86 in the aqueous solution for 5 min were investigated by GC/MS analysis. Phenol was identified by the molecular ion and mass fragment ions, and also through comparison with NIST library data. For the identification of cyaniuric acid, the sample solution was evaporated to dryness. The solid residual was dissolved in 0.1 mL of N,N-bis (trimethylsilyl)-acetamide (BSA) before GC/MS analysis. As a result, triazine ring was converted to cyanuric acid and the compound was detected as a final product. Other degradation products still possibly exist in the photo-Fenton system but were not detected because of their low concentration, extraction efficiency and limited sensitivity in GC/MS.

Based on the intermediate products and the results obtained by other researchers (Hu et al., 2003; Song et al., 2008), the possible degradation pathway for RY 86 is proposed in Fig. 7. The C–S and C–N bonds were considered to be easily cleaved by photo-Fenton process. In the first step, ring B could be transformed into phenol, that is, the C–N bond linked to the benzene ring and the C–S bond of sulfonate group linked to the benzene ring were cleaved to form organic acids with or without hydroxyl group, and sulfate, ammonium and nitrate ions. It was considered that ring C was also in a similar degradation pathway. Ring A was replaced by hydroxyl group to yield cyaniuric acid as the final product, and chloride, ammonium, and nitrate ions together were produced. In the second step, the aromatic acids produced from the above pathway were subsequently hydroxylated and led to the cleavage of aromatic ring to form aliphatic acids. The third step involved the further oxidation of the aliphatic acids produced from the second step to produce carbon dioxide and water.

3 Conclusions

The decolorization of RY 86 by solar photo-Fenton treatment in aqueous solution was investigated. The decolorization was strongly affected by many factors. The rate of RY 86 decolorization is more than 90% after 20 min under the optimum conditions. The activation energy of the solar photo-Fenton reaction was 1.50 kJ/mol for RY 86 in the temperature range of 10–60°C. In the kinetic study, the rate constant of RY 86 with OH· radicals could be estimated to be $1.7 \times 10^{10}$ L/(mol·sec). The decolorization efficiency of RY 86 under solar light irradiation was comparable to the artificial light irradiation. These results indicate that the solar photo-Fenton reaction is useful for the treatment of wastewater containing dyes.

The disappearance of TOC was observed during the photo-Fenton process and the remaining TOC achieved 1.5 mg/L after 24 hr (83% mineralization). The formations of chloride, sulfate, nitrate and ammonium ions were also observed. Therefore, we could reach the complete mineralization of the starting compound. Furthermore, we identified two kinds of intermediate products of RY 86 during the photo-Fenton process. The degradation pathway of RY 86 was proposed based on the identified byproducts under a given set of reaction conditions.
The advantages of the photo-Fenton process as an oxidative treatment are rapid decolorization and simple handling. Therefore, the photo-Fenton reaction would be applied to wastewater treatment works as a new developing methodology for reducing levels of other dyes.

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References


