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Photodegradation of acid red 114 dissolved using a photo-Fenton process with TiO_2

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Abstract

A dye acid red 114 (C.I. 23635) was photochemically removed by adding ferric ion (Fe^{3+}), TiO_2 particles, and H_2O_2 in the presence of the UV radiation. The removal rates of the acid red 114 (C.I. 23635) dye were 0.183, 0.210, and 0.233 mg/l/min when the concentrations of Fe^{3+} were 50, 100, and 130 mg/l. The removal rate of the dye increased from 0.173, through 0.200, 0.210 to 0.260 mg/l/min when the H_2O_2 concentrations were 10, 50, 100, and 150 mg/l, respectively. The removal rates were 0.200, 0.207, 0.210, 0.273, and 0.293 mg/l/min when the concentrations of TiO_2 were 40, 60, 100, 500, and 1000 mg/l, respectively. The removal rate at pH 2.5 was higher than any other; pH 3.5, 5.5, and 8.5 and the photodegradation efficiency increased with the flow rate of air in the range from 1 to 10 l/min. From these results, relationships between the removal rate and the concentration of added Fe^{3+}, H_2O_2, and TiO_2 could be expressed as the following second-order equations, respectively, $R_{\mathrm{removal}} = 3 \times 10^{-6} \times (C_{\mathrm{Fe}^{3+}})^2 + 5 \times 10^{-5} \times (C_{\mathrm{Fe}^{3+}}) + 0.1729$; $R_{\mathrm{removal}} = 2 \times 10^{-6} \times (C_{\mathrm{H_2O_2}})^2 + 2 \times 10^{-3} \times (C_{\mathrm{H_2O_2}}) + 0.1759$; and $R_{\mathrm{removal}} = -1 \times 10^{-7} \times (C_{\mathrm{TiO_2}})^2 + 2 \times 10^{-4} \times (C_{\mathrm{TiO_2}}) + 0.1867$.

Keywords: Photodegradation; Acid red 114 (C.I. 23635); TiO_2 particles; Ferric ion

1. Introduction

Like many other industrial effluents, wastewaters in a textile industry have been recently also increased significantly in quantity and has been problematic in biodegradability and toxicity. Textile wastewater is strongly colored which creates environmental and aesthetic problems [1], so that contaminations of a water stream have become an issue of a worldwide concern. The decomposition of a dye wastewater using titanium dioxide (TiO_2) as a photocatalyst has been attracted as an alternative wastewater treatment due to its easy handling and high efficiency [2,3].

The photodegradation of organic compounds using TiO_2 particles in the presence of the UV radiation has been known to have many advantages. Firstly, a large number of organic compounds dissolved or dispersed in water can be

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mineralized. Secondly TiO_2 is relatively inexpensive and can be recycled. Thirdly, UV lamps for the photocatalytic oxidation are easily available in various sizes, shapes, and peak wavelengths.

The principle of photooxidation is well known as the UV illumination onto a photocatalyst excites to produce electron and hole pair (e^-/h^+) with high-energy state, which migrate to the particle surface and initiate a wide range of chemical redox reactions [4]. The valence band potential is positive enough to generate hydroxyl radicals at the surface and the conduction band potential is negative to reduce molecular oxygen.

Dye degradation using hydrogen peroxide has been widely performed in the presence of the UV radiation. Alaton et al. [1] reported that the removal rate increased with an increasing initial concentration of H_2O_2 in the degradation of reactive-dye wastewater in a double-skin-sheet reactor, where the spectrum range of the UV radiation was from 315 to 395 nm. Georgiou et al. [5] found the color of azo-reactive dyes was completely removed in less than 1 h in a reactor with UV/H_2O_2 in the absence of TiO_2.

In the photo-Fenton process with Fe^{3+} under the UV radiation, Cermenati et al. [6] reported that the superoxide dismutase and pH had effects on the quinoline activation, followed by superoxide addition in the degradation of quinoline (benzo-pyridine) with Fe^{3+} ions. The degradation rate of organic compounds such as phenol and nitrobenzene in the reactor with added Fe^{3+} followed the first-order kinetics [7]. The degradation rate constant of hydrogen peroxide by ferric ion under pH 3 was estimated as 2.7×10^{-3}/s [8].

Photodegradation studies on various kinds of acid dyes have been extensively done in the textile industry. Photocatalytic removal rates of an acid red 3B with TiO_2 particles prepared at four kinds of calcination temperature were compared, where the dye photo-removal reaction followed a zero order kinetics and the removal rate could be obtained at high pH value and at low calcination temperature [9]. Galindo et al. [2] showed that the degradation by the UV/TiO_2 system was pH dependent and hydroxyl radical was the main oxidative agent in neutral and alkaline solutions in the photodegradation of a dye acid orange 52.

This work has been done to enhance the photo-removal efficiency of a dye acid red 114 (C.I. 23635) using TiO_2 particles as the photocatalyst. Effects of the added concentrations of the Fe^{3+}, TiO_2 particles, and H_2O_2 as well as pH dependency on the dye removal rate have been investigated with/without aeration.

2. Experimental methods

An acid red 114 (C.I. 23635, Aldrich Chem. Co., USA) shown in Fig. 1 as a target dye and TiO_2 particles (P-25, Degussa GmbH, Honau, Germany) as the photocatalyst were used in the experiment. Average diameter, BET surface area, and density of TiO_2 particles were 20 ± 5 nm, 50 ± 15 m^2 /g, and 3.89 g cm^{-3} at 20 °C, respectively [10]. Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, Junsei Chemical Co. Ltd., Japan) was used as a ferric ion source.

The volume and the ratio of surface area to volume of the photoreactor were one litter and 0.94/m, respectively. Experiments were performed in an immersion-type reactor equipped with an external water-jacket to keep the constant temperature. A metal halide lamp of 400 W (Osram Co., Germany) was used as the external UV light source. The UV light was collected and then transmitted by an optical-fiber bundle into the glass tubes in the reactor. The optical fiber (CK-40, Mitsubishi, Co., Japan) with outside diameter of 1 mm, inserted in a glass tube, was composed of two parts; core of PMMA (polymethylmethacrylate) and clad of fluoro-resin. The clad surface was removed by scratching in order to diffuse the UV light laterally from the core through the glass tubes into the solution of the reactor. The quartz fibers were placed in the former section of the PMMA fibers to prevent the melting-down of optical fibers by the high temperature due to the UV irradiation. Air was supplied at the flow rate of 1–10 l/min by using an air diffuser to enhance photooxidation rates [11].

The energy spectrum of the UV light irradiated from a lamp was measured with a monochromator

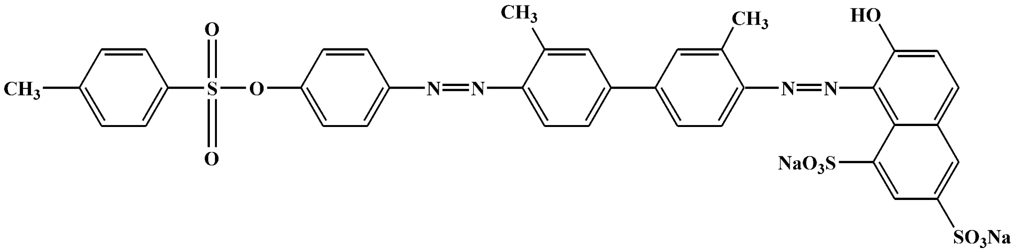

Fig. 1. Chemical structure of a dye acid red 114 (C.I. 23635).

(404VM, Acton Research Co., USA). The major peak of spectrum wavelength occurred at 254 nm and the intensity of UV light irradiated from the lamp is 0.93 μ einstein/m^2. The concentration of an acid red 114 (C.I. 23635) dye dissolved was measured at 365 nm using a UV spectrophotometer (UV-160A, Shimadzu Co., Japan). The removal efficiency of an acid red 114 (C.I. 23635) was estimated by measuring the difference of concentrations in the samples from the reactor before and after photoreactions.

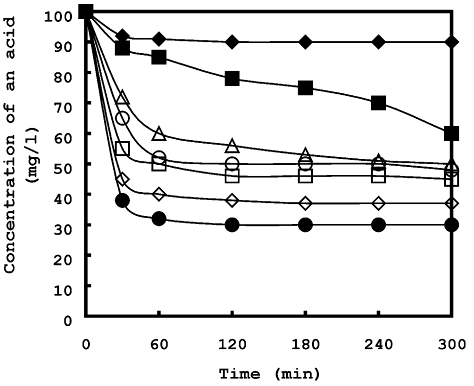

Fig. 2. Effect of add Fe^{3+} on the photodegradation of the acid red 114 (C.I. 23635) dye (at the initial concentration dye of 100 mg/l, pH 3.5, and 30 °C. ◆: Only 100 mg TiO_2/l, ■: both 100 mg TiO_2/l and the UV radiation, △: only 100 mg H_2O_2/l, ○: 100 mg TiO_2/l, 100 mg H_2O_2/l, and the UV radiation, □: 100 mg TiO_2/l, 100 mg H_2O_2/l, 50 mg Fe^{3+}/l, and the UV radiation, ◇: 100 mg TiO_2/l, 100 mg H_2O_2/l, 100 mg Fe^{3+}/l, and UV radiation and ●: 100 mg TiO_2/l, 100 mg H_2O_2/l, 130 mg Fe^{3+}/l, and the UV radiation).

3. Results and discussion

3.1. Effect of added ferric ion (Fe^{3+}) on the photodegradation of an acid red 114 (C.I. 23635) dye in the presence of H_2O_2

The photodegradation of an acid red 114 (C.I. 23635) was performed in the presence of 100 mg TiO_2/l, 100 mg H_2O_2/l and the UV radiation with a peak wavelength of 254 nm to investigate the effect of added Fe^{3+} concentration (Fig. 2).

The dye concentration with added 50 mg Fe^{3+}/l decreased from 100 to 45 mg/l as time elapse of 300 min, where the average removal rate was 0.183 mg/l/min. When Fe^{3+} was not added, the removal rate was 0.173 mg/l/min with both TiO_2 and H_2O_2 in the presence of the UV radiation. When the Fe^{3+} concentration increased to 100 mg/l, the dye concentration changed from 100, through 40 and 38, to 37 mg/l in 60, 120, and 300 min, respectively, where the average removal rate was 0.210 mg/l/min. And then with added 130 mg Fe^{3+}/l, the dye concentration decreased from 100, through 32, to 30 mg/l in 60 and 120 min. However, the concentration was constantly kept at 30 mg/l over 120 min, where the average removal rate was 0.233 mg/l/min. The average removal rate of the dye by the adsorption on the TiO_2 particle surface was merely 0.033 mg/l/ min with only 100 TiO_2/l. When the UV radiation was given, the average removal rate was 0.133 mg/l/min with only 100 mg TiO_2/l. When H_2O_2 was added with 100 mg/l, the average removal rate was 0.166 mg/l/min in the presence of both TiO_2 and the UV radiation.

The Fe^{3+} ion undergoes a photoredox process with the UV light to result in the formation of Fe^{2+} and OH·. The removal efficiency of the dye increased with an increasing Fe^{3+} concentration as co-catalyst and mediator [12,13], which was shown in Fig. 3.

The relationship between the Fe^{3+} concentration and the removal rate could be described as the following second-order equation, where the correlation coefficient (R^2) was 0.9999.

$$R_{\mathrm{removal}} = 3 \times 10^{-6} \times (C_{\mathrm{Fe}^{3+}})^2 + 5 \times 10^{-5} \times (C_{\mathrm{Fe}^{3+}}) + 0.1729 \tag{1}$$

R_{removal} (mg/l/min) is the removal rate of the dye acid-red 114 (C.I. 23635) during the photodegradation and $C_{\mathrm{Fe}^{3+}}$ (mg/l) is the concentration of added Fe^{3+} in the reactor.

3.2. Effect of added H_2O_2 on the photodegradation of an acid red 114 (C.I. 23635) dye in the presence of Fe^{3+}, TiO_2 and the UV radiation

The role of added H_2O_2 is different depending on its concentration [14]. At a low concentration, H_2O_2 increases the formation rate of hydroxyl radical through three ways.

Firstly, it acts as an electron donor. Secondly, the reduction of H_2O_2 at the conduction band would produce hydroxyl radicals. Thirdly, the self-decomposition by illumination would also produce hydroxyl radicals. However, at a high concentration, H_2O_2 adsorbed on the TiO_2 particle surface could effectively scavenge not only the photocatalyst surface-formed hydroxyl radicals but also the photo-generated hole, which can inhibit the major pathway for heterogeneous generation of hydroxyl radicals.

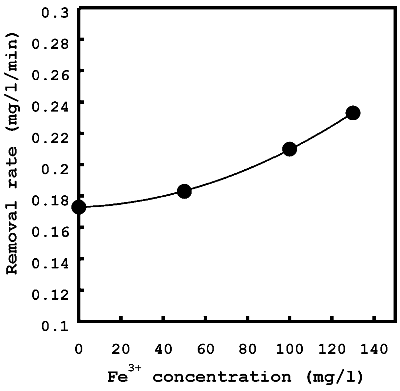

Fig. 3. The relationship of the Fe^{3+} concentration vs. the removal rate of the acid red 114 (C.I. 23635) dye, in the presence of 100 mg TiO_2/l, 100 mg H_2O_2/l, and the UV radiation (at the initial dye concentration of 100 mg /l, pH 3.5, and 30 °C).

Fig. 4 shows the effect of added H_2O_2 concentration on the photo-removal of a dye acid red 114 (C.I. 23635) in the system of UV/TiO_2/Fe^{3+}. In the degradation with only H_2O_2, in the absence of TiO_2, Fe^{3+} and the UV radiation, the average removal rate was merely 0.167 mg/l/min and the removal efficiency increased with an increasing the concentration of H_2O_2. In the TiO_2/Fe^{3+}/UV system with added 10 mg H_2O_2/l, the dye concentration decreased from 100, through 55, 53, and 50, to 48 mg/l in 60, 120, 180, and 300 min, respectively where the average removal rate was 0.173 mg/l/min. In case of adding 50 mg H_2O_2/l, the dye concentration decreased from 100, through 45, 42, and 41, to 40 mg/l in 60,120, 240, and 300 min, respectively where the average removal rate increased to 0.200 mg/l/min. When H_2O_2 concentration was given as 100 mg/l, the dye concentration decreased from 100, through 42, 40, and 38, to 37 mg/l in 60, 120, 180, and 300 min, respectively where the average removal rate was 0.21 mg/l/min. With 150 mg H_2O_2/l, the dye concentration decreased from 100, through 34, 27, 25, and 23, to 22 mg/l in 60, 120, 180, 240, and 300 min, respectively where the average removal rate was 0.260 mg/l/min.

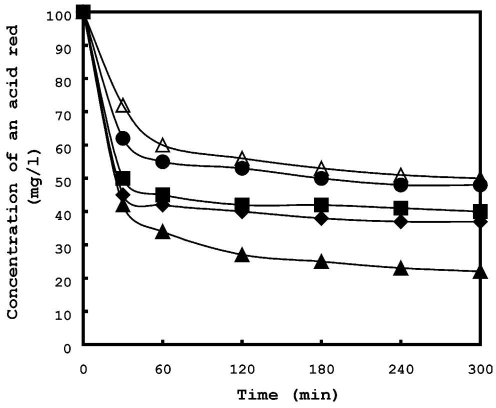

Fig. 4. Effect of H_2O_2 concentration on the photodegradation of the acid red 114 (C.I. 23635) dye in the presence of 130 mg Fe^{3+} /l, 100 mg TiO_2 /l, and the UV radiation (at the initial dye concentration of 100 mg/l, pH 3.5, and 30 °C. △: Only 100 mg H_2O_2/l without Fe^{3+}, TiO_2, and the UV radiation; ●: 10 mg H_2O_2 /l, ■: 50 mg H_2O_2 /l, ◆: 100 mg H_2O_2 /l, and ▲: 150 mg H_2O_2 /l, together with Fe^{3+}, TiO_2, and the UV radiation).

In the range between 10 and 150 mg H_2O_2 /l, the removal rate with the concentration of H_2O_2 was shown in Fig. 5. The relationship between the H_2O_2 concentration and the removal rate could be described as the following second-order equation, where the correlation coefficient (R^2) was 0.9513.

$$R_{\text{removal}} = 2 \times 10^{-6} \times \left(C_{H_2O_2}\right)^2 + 2 \times 10^{-3} \times \left(C_{H_2O_2}\right) + 0.1759 \qquad (2)$$

R_{removal} (mg/ l/ min) is the removal rate of the dye acid-red 114 (C.I. 23635) and $C_{H_2O_2}$ (mg/ l) is the concentration of H_2O_2.

3.3. *Effect of pH on the photodegradation of an acid red 114 (C.I. 23635) dye in the presence of Fe^{3+}, H_2O_2, TiO_2 and the UV radiation*

The effect of pH on the removal rate of the dissolved dye in the batch system is a complicated factor, which is shown in Fig. 6 [15,16]. At pH 8.5, the dye concentration decreased from 100, through 68, 65, 62, and 60, to 59 mg/l as time was in 60, 120, 180, 240, and 300 min, respectively where the average removal rate was 0.137 mg/l/min. At pH 5.5, the dye concentration decreased from 100, through 49, 45, and 44, to 42 mg/l in 60, 120, 180, and 300 min, respectively where the average removal rate was 0.193 mg/l/min. In the acidic region of pH 3.5 and pH 2.5, the dye concentration decreased rapidly during the photodegradation. At pH 3.5, the acid red 114 (C.I. 23635) concentration decreased from 100, through 40 and 38, to 37 mg/l in 60, 120, and 300 min, respectively where the average removal rate was 0.210 mg/l/min. And at pH 2.5, the dye concentration decreased from 100, through 32, 27, 25, and 23, to 20 mg/l in 60, 120, 180, 240, and 300 min, respectively where the removal rate was 0.267 mg/l/min. The removal rate at pH 2.5 was higher than any other; pH 3.5, 5.5, and 8.5.

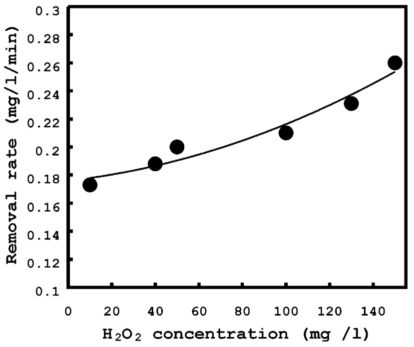

Fig. 5. The relationship of the H_2O_2 concentration vs. the removal rate of the acid red 114 (C.I. 23635) dye, in the presence of 130 mg Fe^{3+}/l, 100 mg TiO_2/l, and the UV radiation (at the initial dye concentration of 100 mg /l, pH 3.5, and 30 °C).

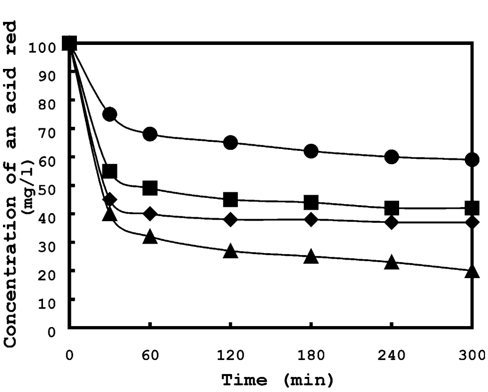

Fig. 6. Effect of pH on the photodegradation of the acid red 114 (C.I. 23635) dye in the presence of 130 mg Fe^{3+}/l, 100 mg TiO_2/l, 100 mg H_2O_2 /l and the UV radiation (at the initial dye concentration of 100 mg /l and 30 °C. ●: pH 8.5, ■: pH 5.5, ◆: pH 3.5, and ▲: pH 2.5).

An apparent removal of the dye, not by the photodegradation but by the adsorption was investigated as the amount of an acid red 114 (C.I. 23635) dye adsorbed on the TiO_2 surface for 15 min in the absence of the UV radiation. Fig. 7 shows the relationship between the pH value and the dye adsorption amount in the range from pH 2 to 8.

At pH 2, the dye concentration was 40 mg/l and it decreased due to adsorption from 34, through 33, 26, 17, and 15, to 14 mg/l, at the pH values of 3, 4, 5, 6, 7, and 8, respectively. The dissolved dye existed as anion, and the adsorption of the dye on the TiO_2 surface occurred by the ion exchange between hydroxyl ions on the surface and an ionized dye in the acidic region [15]. Therefore, the adsorption rate of the dyes increases as the concentration of hydrogen ion increases in the solution.

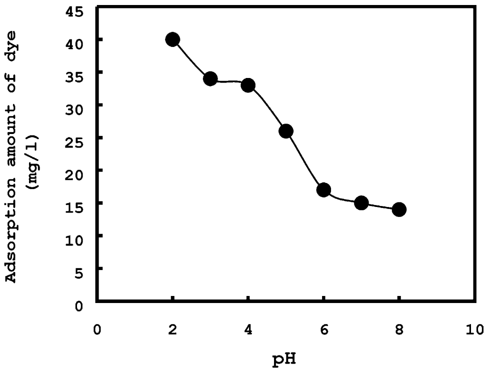

Fig. 7. Effect of pH on the adsorption of the acid red 114 (C.I. 23635) dye on the TiO_2 particle in the presence of 100 mg TiO_2/l (at the initial dye concentration of 100 mg /l, 30 °C, in 15 min).

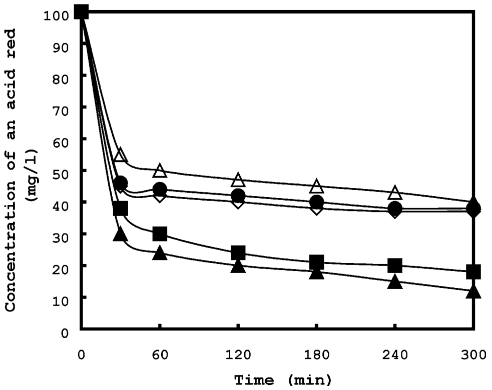

Fig. 8. Effect of TiO_2 concentration on the photodegradation of the acid red 114 (C.I. 23635) dye in the presence of 130 mg Fe^{3+}/l, 100 mg H_2O_2/l, and the UV radiation (at the initial dye concentration of 100 mg/l, pH 3.5, and 30 °C. △: 40 mg TiO_2/l, ●: 60 mg TiO_2/l ▽: 100 mg TiO_2/l, ■: 500 mg TiO_2/l, and ▲: 1,000 mg/l).

However, in the neutral and basic regions over pH 8, the dye concentration decreased rapidly due to their agglomeration and precipitation rather than the adsorption mechanism [17].

3.4. Effect of the TiO_2 concentration on the photodegradation of an acid red 114 (C.I. 23635) in the presence of Fe^{3+}, H_2O_2 and the UV radiation

Since the concentration of added TiO_2 as a photocatalyst was an important parameter to increase the removal rate, the effect of the TiO_2 concentration on the photodegradation was investigated in Fig. 8. The dye concentration decreased from 100, through 50, 47, 45, and 43, to 40 mg/l in 60, 120, 180, 240, and 300 min, respectively, in the presence of 40 mg TiO_2/l where the average removal rate was 0.200 mg/l/min. With a 60 mg TiO_2/l, the concentration of the acid red 114 (C.I. 23635) dye decreased from 100, through 44, 42, and 40, to 38 mg/l/min, in 60, 120, 180, and 300 min, respectively, where the average removal rate was 0.207 mg/l/min. In case of 100 mg TiO_2/l, the dye concentration decreased from 100, through 42, 40, and 38, to 37 mg/l in 60, 120, 180, and 300 min, respectively, where the average removal rate was 0.210 mg/l/min. With 500 mg TiO_2/l, the dye concentration decreased from 100, through 30, 24, 21, and 20, to 18 mg/l in 60, 120, 180, 240, and 300 min, respectively, where the average removal rate was 0.273 mg/l/min. With TiO_2 concentration of 1000 mg/l, the dye concentration decreased from 100, through 24, 20, 18, and 15, to 12 mg/l in 60, 120, 180, 240, and 300 min, respectively, where the removal rate was 0.293 mg/l/min.

The relationship between the TiO_2 concentration and the removal rate in the presence of Fe^{3+}/H_2O_2/UV could be described as the following second-order equation, where the correlation coefficient (R^2) was 0.9877 (Fig. 9).

$$R_{\text{removal}} = -1 \times 10^{-7} \times \left(C_{\text{TiO}_2}\right)^2 + 2 \times 10^{-4} \times \left(C_{\text{TiO}_2}\right) + 0.1867 \qquad (3)$$

R_{removal} (mg/l/min) is the removal rate of a dye acid-red 114 (C.I. 23635) and C_{TiO_2} (mg/l) is the concentration of TiO_2. However, above certain TiO_2 concentrations (e.g. 2 g/l in the oxidation of sodium benzoate), it was reported that the rate of oxidation did not increase since there was a stochiometric TiO_2 loading that was sufficient to use all available photons emitted at a given intensity [18]. In addition the light absorbance from the photocatalysts themselves may result in the decrease of the photooxidation rate [11].

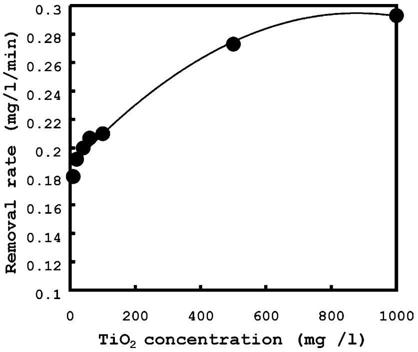

Fig. 9. The relationship of TiO_2 concentration vs. the removal rate of the acid red 114 (C.I. 23635) dye in the presence of 130 mg Fe^{3+}/l, 100 mg H_2O_2 /l and the UV radiation (at the initial dye concentration of 100 mg /l, pH 3.5, and 30 °C).

3.5. *Effect of aeration rate on the photodegradation of an acid red 114 (C.I. 23635) dye in the presence of Fe^{3+}, H_2O_2, TiO_2 and the UV radiation*

The UV radiation onto the photocatalyst surface made the photocatalytic oxidation of a dye acid red 114 (C.I. 23635) with O_2 be mineralized into CO_2, where the photo-excited OH· species as well as O_2^- and O_3^- play a significant role in the complete photocatalytic oxidation of a dye [19,20]. The existence of dissolved O_2 is an important parameter to enhance the photodegradation of a dye. Fig. 10 shows the variation of the removal rate with the aeration rate from 1 to 10 l/min. In the absence of O_2 supply, the dye concentration decreased from 100, through 42, 40, and 38, to 37 mg/l in 60, 120, 180, and 300 min, respectively, where the average removal rate was 0.210 mg/l/min. At an air-flow rate of 1 l/min, the dye concentration decreased from 100, through 35, 30,and 28, to 27 mg/l in 60, 120, 180, and 300 min, respectively, where the average removal rate was 0.240 mg/l/min. At the flow rate of 5 l/min, the concentration of the acid red 114 (C.I. 23635) dye decreased from 100, through 25, 24, 20, and 13, to 12 mg/l in 60, 120, 180, 240, and 300 min, respectively, where the removal rate 0.293 mg/l/min. At the flow rate of 10 l/min, the dye concentration decreased from 100, through 16, 14, 11, and 9, to 8 mg/l in 60, 120, 180, 240, and 300 min, respectively, where the average removal rate was 0.307 mg/l/min. From these results, it was shown that the photodgradation efficiency of the dye acid-red 114 (C.I. 23635) increased as the O_2 supply increased.

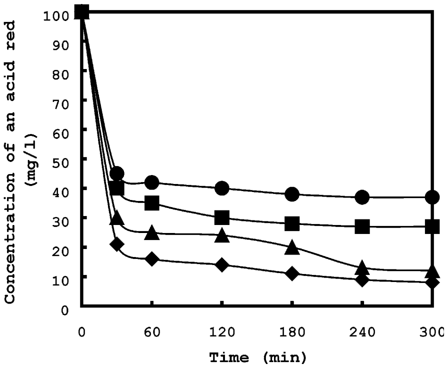

Fig. 10. Effect of aeration rate on the removal rate of the acid red 114 (C.I. 23635) dye in the presence of 130 mg Fe^{3+}/l, 100 mg H_2O_2 /l and the UV radiation (at the initial dye concentration of 100 mg /l, pH 3.5, and 30 °C. ●: no supply, ■: 1 l/ min, ▲: 5 l/min, and ◆: 10 l/ min).

3.6. *Change of UV–Vis spectra of the acid red 114 (C.I. 23635) dye during the photodegradation in the presence of TiO_2, H_2O_2, Fe^{3+} and the UV radiation*

The change of absorption spectra of the dye acid red 114 (C.I. 23635) during the photodegradation in the reactor solution was shown in Fig. 11. The spectra of the initial dye solution of 100 mg/l have different three kinds of the absorbance peaks at 245, 325, and 540 nm as in Fig. 11(a) and their conjugated structures include an azo linkage, benzene ring, and naphthalene

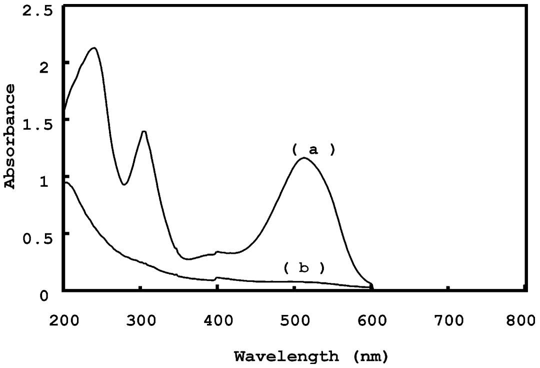

Fig. 11. Change of UV–vis spectra of the acid red 114 (C.I. 23635) dye with photoreaction time, at a start (a) and in 1 h (b) (at the dye initial concentration of 100 mg/l, pH 3.5, and 30 °C).

ring, respectively [21]. With time elapse of 1 h as in Fig. 11(b), the spectral height in 540 nm shown in Fig. 11(a) decreased rapidly, which wavelength indicates the $-N=N-$ bond of the dyes, the most active sites for oxidative attack [22,23]. The absorbance in 325 and 245 nm decreased from 1.2 to 0.1 and from 2.1 to 0.5, respectively, as the time elapse of 1 h.

4. Conclusions

The photodegradation of a dye acid red 114 (C.I. 23635) was done with different concentrations of Fe^{3+}, TiO_2, and H_2O_2. The average removal rate of an acid red 114 (C.I. 23635) dye without adding Fe^{3+} in the existence of 100 mg TiO_2/l, 100 mg H_2O_2/l, and the UV radiation was 0.173 mg/l/min, which increased up to 0.233 mg/l/min with added Fe^{3+} of 130 mg/l. More OH production by the added Fe^{3+} could enhance the photocatalytic degradation of the dye by the TiO_2.

The average removal rate without adding H_2O_2 in the presence of 100 mg TiO_2/l, 130 mg Fe^{3+}/l, and the UV radiation increased from 0.167 to 0.260 mg dye/l/min with 150 mg H_2O_2/l.

As the pH decreased from 8.5, through 5.5 and 3.5, to 2.5, the average removal rate of the dye in the presence of 130 mg Fe^{3+}/l, 100 mg TiO_2/l, and 100 mg H_2O_2/l increased from 0.137, through 0.193 and 0.210 to 0.267 mg/l/min.

The average removal rate of the dye increased from 0.200, through 0.207, 0.210, and 0.273 to 0.293 mg/l/min, respectively, with added TiO_2 concentrations of 40, 60, 100, 500 and 100 mg/l. However, above about 2000 mg/l, the TiO_2 photocatalysts themselves may result in the degradation of the dye.

As the oxygen supply was given as air-flow rates from 0, through 1 and 5 to 10 l/min, the average removal rate increased from 0.210, through 0.240, 0.293 to 0.307 mg/l/min.

From these results, relationships between the removal rate and the concentration of added Fe^{3+}, H_2O_2, and TiO_2 could be described in the concentration range of each added chemical applied in this study, respectively, as the following second-order equations,

$$R_{\text{removal}} = 3 \times 10^{-6} \times (C_{\text{Fe}^{3+}})^2 + 5 \times 10^{-5} \times (C_{\text{Fe}^{3+}}) + 0.1729$$

$$R_{\text{removal}} = 2 \times 10^{-6} \times \left(C_{\text{H}_2\text{O}_2}\right)^2 + 2 \times 10^{-3} \times \left(C_{\text{H}_2\text{O}_2}\right) + 0.1759,$$

and

$$R_{\text{removal}} = -1 \times 10^{-7} \times \left(C_{\text{TiO}_2}\right)^2 + 2 \times 10^{-4} \times \left(C_{\text{TiO}_2}\right) + 0.1867$$

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