Degradation of azo and anthraquinone dyes by a low-cost Fe^0/air process

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ARTICLE INFO

ABSTRACT

Degradation of two different kinds of dyes, anthraquinone Reactive Blue 4 (RB4) and azo Reactive Black 5 (RB5), by low-cost zero valent iron (Fe^0) in a N_2 bubbling system (Fe^0/N_2 process) and air bubbling system (Fe^0/air process) was investigated. The operating parameters, including initial solution pH, dye concentration and Fe^0 dose, were also evaluated. The Fe^0/air process shows a higher decolorization rate compared to the Fe^0/N_2 process. Both RB4 and RB5 solutions at $100\,mg\,L^{-1}$ were rapidly decolorized by Fe^0/air process within 9 and 3 min, respectively, at initial solution pH 3, Fe dose of $50\,g\,L^{-1}$ and air flow rate of $5\,L\,min^{-1}$. The optimal initial solution pH was 3. The Fe^0/N_2 process removed only <17% of COD. However, significant COD removals were achieved for RB 4 (87%) and RB5 (43%) by the Fe^0/air process after 9 min of treatment. Spectra analysis results indicated that the Fe^0/N_2 process destroyed only the anthraquinone group (A_{594}) for the RB4 solution and decreased the azo (A_{596}) and naphthalene group (A_{310}) for the RB5 solution. However, the Fe^0/air process rapidly removed A_{594}, A_{370}, A_{296} (anthraquinone group) and A_{256} (aromatic and dichlorotriazine group) for RB4, and A_{597} and A_{310} (naphthalene group) for RB5. The results indicated that the low-cost Fe^0/air process is a potential technique for rapid degradation of RB4 and RB5 solutions.

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1. Introduction

Textile wastewater is one of the major industrial water pollution sources in developing countries. It contains high concentrations of un-fixed (about 20%) dyes. Dyes are of great concern because of their widespread use, toxic aromatic intermediates, and biorecalcitrance for traditional aerobic wastewater treatment [1]. According to the class of chromophore, the two classes of dyes used mostly are azo and anthraquinone dyes. Several techniques such as GAC adsorption [2], chemical oxidation [3], electrochemical degradation [4], AOPs [5], and combined AOP-biological treatment [6] have been investigated to treat dye wastewater. However, the high costs of the above methods often limit their application.

Zero-valent iron reduction in anoxic condition has received wide attention, because it is low-cost and effective for reductive decolorization of azo dyes [7,8]. However, studies on dye degradation with zero-valent iron reduction focus mostly on decolorizaton and rarely on COD removal. Recently, several studies have reported that zero-valent iron under oxic condition can generate strong oxidants and degrade organic pollutants like EDTA [9,10], herbicides [11,12], chlorinated-phenol [13], aromatic compounds [14], landfill leachate [15], and dyes [16,17]. However, the coating iron oxide

layer on Fe^0 surface decreases the degradation rate of Fe^0 [12,18]. Several efforts have been made to enhance the degradation, including EDTA addition to reduce the iron oxide layer thickness [9,10,14], or the application of nanoscale iron to increase its active surface [11,12,18]. The use of a high Fe^0 dose in a bubbling system may significantly facilitate the dye degradation rate. However, related studies on degradation of azo and anthraquinone dyes by low-cost Fe^0/air process are limited.

In this study, two common dyes, I.C. Reactive Blue 4 (RB4, anthraquinone dye) and I.C. Reactive Black 5 (RB5, azo dye), were selected as the model dyes. The study aims to (1) compare dye removals by the Fe^0/N_2 and Fe^0/air processes, and (2) investigate the effects of initial solution pH and Fe^0 dose on dye removal. The color, UV–vis spectrum, and COD of the solution were monitored in this study.
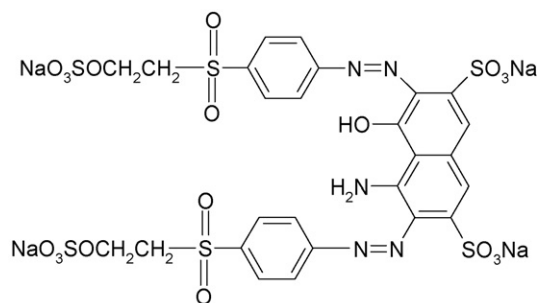
2. Material and methods

I.C. Reactive Blue 4 (RB4, C.I. No. 61205, $C_{23}H_{14}Cl_2N_6O_8S_2$, MW = $637.44\,g\,mol^{-1}$, 35% purity) and I.C. Reactive Black 5 (RB5, C.I. No. 20505; $C_{26}H_{21}Na_4N_5O_{19}S_6$, MW = $991.8\,g\,mol^{-1}$, 55% purity) were purchased from Sigma–Aldrich and were used as received. The molecular structures of the dyes are shown in Fig. 1. The zero-valent iron (analytical grade, 99% purity, 300 mesh) was obtained from Shimakyu Chemical (Osaka, Japan). The dye degradation experiment was conducted in a 275 mL glass reactor (5 cm diameter, 13 cm high)

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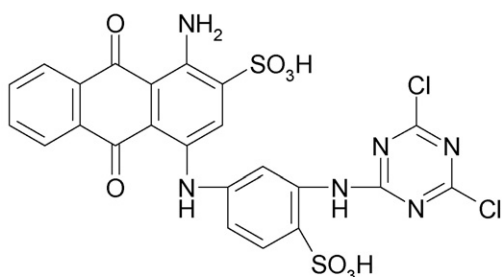
C. I. Reactive Blue 4 (RB4, anthraquinone dye)   C. I. Reactive Black 5 (RB5, azo dye)

Fig. 1. Molecular structure of the dyes studied.

containing 100 mL of dye solution. The initial dye concentration for RB4 and RB5 solution was 100 mg L^{-1}. A flow rate of 5 L min^{-1} of nitrogen (in Fe^0/N$_2$ process) or air (in Fe^0/air process) was used to maintain the suspension of iron powder in the solution. The initial pH of the solution was adjusted with diluted sodium hydroxide or diluted hydrochloric acid and measured by pH meter (Cyberscan 510, Taiwan). In the Fe^0/N$_2$ experiment, the solution was purged with N$_2$ for 2 m before the addition of Fe^0 powder.

All experiments were conducted at room temperature (20 ± 2 °C). The concentration of the treated dye solution was measured based on the constructed calibration curves at absorption wavelength of 594 nm for RB4 and 597 for RB5. The UV–visible spectrum during the dye degradation was measured at 200–800 nm using a UV–visible spectrophotometer (Shimadzu, UV-mini 1240, Japan). The sample was diluted with distilled water when the absorbance exceeded the range of calibration curve. COD was determined according to Standard Methods for Examination of Water and Wastewater [19].

The kinetic expression can be presented as follows:

$$\ln \frac{C}{C_0} = -K_{\text{obs}} t$$

where C is the dye concentration at instant t, C_0 is the initial dye concentration, K_{obs} is the observed pseudo first-order degradation rate constant, and t is the time of reaction.

3. Results and discussion

3.1. Effects of Fe^0/N$_2$ and Fe^0/air on decolorization of RB4 and RB5

The decolorization of RB 4 and RB5 by the Fe^0/N$_2$ and Fe^0/air processes was investigated. The experimental conditions were dye concentration of 100 mg L^{-1}, initial solution pH 3, Fe dose of 50 g L^{-1} and gas flow rate of 5 L min^{-1}.

Fig. 2a and b show that N$_2$ and air without Fe^0 did not obviously degrade RB4 or RB5 (<1% after 21 min of treatment). Less than 5% of RB4 and RB5 sorbed onto iron in the Fe^0 alone set without mixing. When the Fe^0/N$_2$ process was applied, only 36% color was removed in the RB4 solution after 21 min (Fig. 2a). However, the application of Fe^0/air treatment significantly enhanced the RB4 decolorization and 97% color was removed after 9 min of treatment.
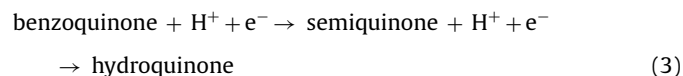
Fig. 2b shows that when the Fe^0/N$_2$ process was used, 72% of RB5 color was rapidly removed in the first 6 min. However, after that, a slow decolorization rate was observed. Eighty-three percent of color removal was obtained until 21 min. In contrast, the Fe^0/air process significantly improved the rate and extent of RB5 degradation. More than 99% of RB5 was rapidly decolorized in the first 3 min. Table 1 indicates that the reaction rates for decolorization of RB4 and RB5 were significantly increased by the Fe^0/air process compared to those by the Fe^0/N$_2$ process. The observed pseudo

first-order rate constants for the degradation of RB4 and RB5 by the Fe^0/N$_2$ was 0.056 and 0.224 min^{-1}, respectively. The application of the Fe^0/air process significantly increased the first-order rate constants to 1.528 and 4.367 min^{-1} for the RB4 and RB5 solution, respectively. Fig. 2c indicates the evolution of solution pH during treatments. The solution pH increased from 3 to 4.5 for RB4 solution and from 3 to 5.7 for RB5 solution.

Fe^0 is a mild reductant ($E^0_{\text{red}} = -0.44$, vs SHE) under the anoxic condition. In the Fe^0/N$_2$ treatment, the oxidation of Fe^0 (Eq. (1)) accompanies the reductive cleavage of the azo bonds of RB5, resulting in the decolorization of RB5 (Eq. (2)) [7,8].

$$\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \tag{1}$$

$$\text{-N} = \text{N-} + 2\text{H}^+ + 2e^- \rightarrow \text{-NH} + \text{HN-} \tag{2}$$

In addition, RB4 can be decolorized by Fe^0 through quinone reduction under redox condition as shown in Eq. (3) [20].

$$\text{benzoquinone} + \text{H}^+ + e^- \rightarrow \text{semiquinone} + \text{H}^+ + e^-$$
$$\rightarrow \text{hydroquinone} \tag{3}$$

In this study, the decolorization rate of RB5 was much higher than that of RB4 in the Fe^0/N$_2$ system. Several studies have reported that the decolorization rates are generally higher for azo dyes than for anthraquinone dyes under anaerobic conditions [20–22].

Most studies on dye decolorization by Fe^0 are conducted under anoxic conditions. However, the present study indicated that decolorization rate and extent of RB4 and RB5 were much quicker by the Fe^0/air process than the Fe^0/N$_2$ process. It is possible that, in addition to the direct reduction (Eqs. (1)–(3)) of dyes on the Fe^0 surface under oxic condition [16], the generation of strong oxidants in the Fe^0/air process was also responsible for the enhancement of dye decolorization. Several studies have indicated that iron corrosion in the presence of air can generate hydrogen peroxide [9,13,16,18]. The hydrogen peroxide can react with the Fe^{2+} (Eq. (6), Fenton reaction) and produce strong oxidants such as hydroxyl radical (OH$^\bullet$) and ferryl (iron (IV) iron species). Azo chromophore and anthraquinone chromophore can be decolorized by OH radical attack [23].

Additionally, Fe^{3+} can be reduced to Fe^{2+} if zero valent iron is present in the solution [16]. The continuous production of Fe^{2+}

Table 1
Reaction kinetic equations for dye decolorization by Fe^0/N$_2$ and Fe^0/air processes. Dye concentrations of 100 mg L^{-1}, initial solution pH 3, and gas flow rate of 5 L min^{-1}. Fe^0 doses were 70 and 50 g L^{-1} for the RB4 and RB5 solution, respectively.

Dye	Treatment	Reaction kinetic equation	K_{obs} (min^{-1})	R^2
RB4	Fe^0/N$_2$	ln(C/C_0) = −0.056t + 4.589	0.056	0.855
RB4	Fe^0/Air	ln(C/C_0) = −1.528t + 6.595	1.528	0.926
RB5	Fe^0/N$_2$	ln(C/C_0) = −0.224t + 4.374	0.224	0.808
RB5	Fe^0/Air	ln(C/C_0) = −4.367t + 8.972	4.367	1
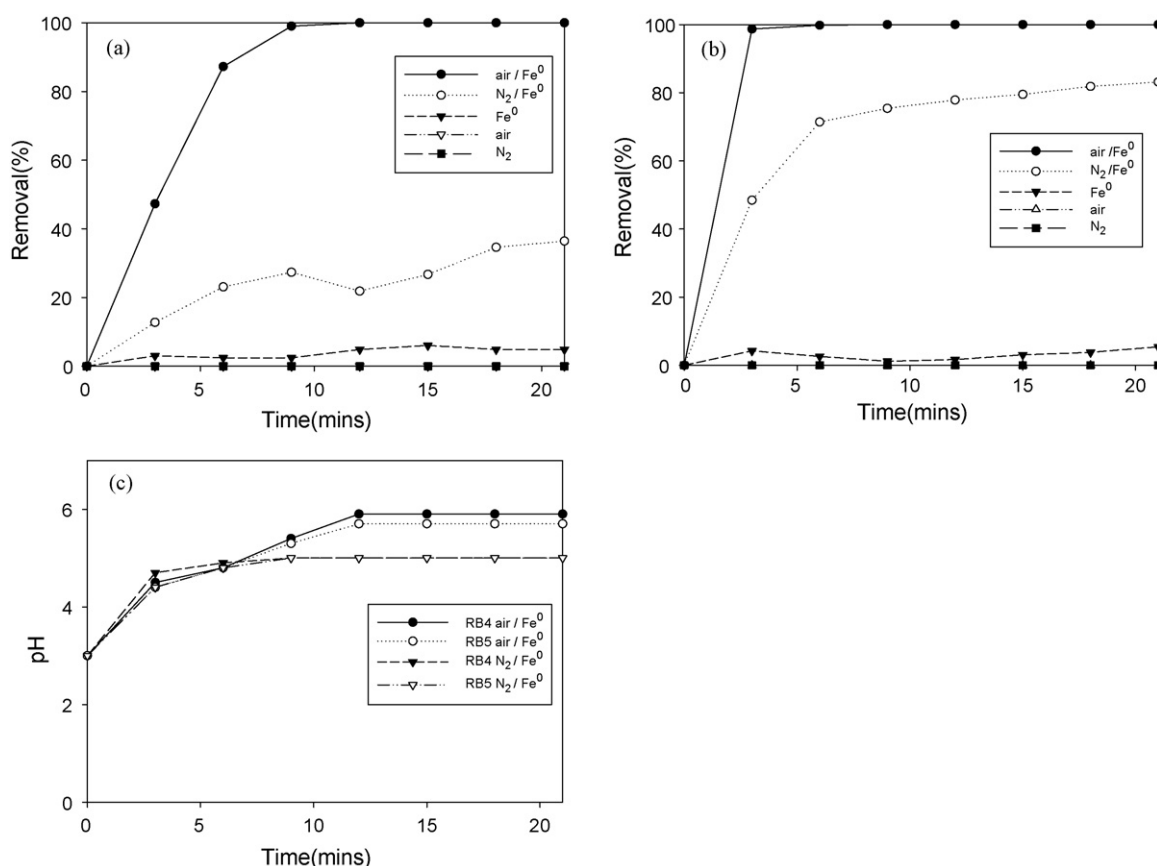
Fig. 2. (a) Effects of different processes on decolorization of RB4 and RB5 solution. Experimental conditions: dye concentration of 100 mg L^{-1}, gas flow rate 5 L min^{-1}, initial solution pH 3, and Fe^0 dose 50 g L^{-1}. (a) RB4, (b) RB5, (c) pH changes during different treatments.

and H$_2$O$_2$ in the Fe^0/air process could generate strong oxidants and facilitate the decolorization of dyes.

$$Fe^0 + O_2 + 2H^+ \rightarrow H_2O_2 + Fe^{2+} \tag{5}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^3 + OH^\bullet + OH^- \tag{6}$$

$$Fe^{3+} + Fe^0 \rightarrow Fe^{2+} \tag{7}$$

Even though the adsorption of dyes onto the iron surface also accounted for dye decolorization in this study, the color removal by sorption was low (<5%) (Fig. 2a and b). Fig. 2b indicates that RB5 decolorization by the Fe^0/air and the Fe^0/N$_2$ processes showed biphasic kinetics phenomena (rapid removal rate followed by slow reaction rate). The coating of an iron oxides/hydroxides layer on the Fe^0 surface might be response for these phenomena. Joo et al. [18] indicate that the iron corrosion forms a passive film of γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ oxides on the Fe^0 surface, leading to the reduction of the active surface area and decolorization efficiency. Besides, the increase of the solution pH during the experiment (Fig. 2c) may also decrease the decolorization rate. The influences of solution pH on dye decolorization are discussed in the following section.

3.2. Influences of Fe^0 dose on dye decolorization

The effect of Fe^0 doses (30, 50 and 70 g L^{-1}) on dye decolorization by the Fe^0/air process was investigated. The experimental conditions were dye concentrations of 100 mg L^{-1}, initial solution pH of 3, and air flow rate of 5 L min^{-1}. The color removal efficiency significantly increased with the Fe^0 doses in the RB4 solution (Fig. 3a). When 30 g L^{-1} of Fe^0 was used, 97% of RB4 color removal was achieved after 21 min. As the Fe^0 dose was increased to 70 g L^{-1}, it only took 9 min to decolorize 99% of RB4. Fig. 3b shows that

RB5 color removal was also sensitive to the applied Fe^0 doses and the color removal of RB5 increased with the Fe^0 doses. When the Fe^0 dose was 30 g L^{-1}, 95% of color removal was obtained at 9 min of treatment. As Fe^0 dose increased to 50 g L^{-1}, more than 99% of RB5 was removed within 3 min. To investigate the influences of initial solution pH on color removal of the dyes, Fe^0 doses of 70 and 50 g L^{-1} were selected for the RB4 and RB5 solutions, respectively, in the sequential experiments.

3.3. Effects of initial solution pH on color removal of dyes

Effects of initial solution pH (3, 4, and 5) on color removal were investigated. Initial solution pH remarkably influenced color removal efficiency in both the Fe^0/N$_2$ process and the Fe^0/air process for RB4 solution (Figs. 3c–f). The color removal rate was much higher at initial solution pH of 3 compared to pH of 4 and 5.

When the Fe^0/N$_2$ process was used, dye decolorization was through direct reductive reaction on Fe^0 surface (Eqs. (2) and (3)). The thickness of the iron oxide/hydroxide layer might greatly influence the decolorization rate. Mielczarski et al. [24] indicated that the iron oxide/hydroxide layer covering the Fe^0 surface is thin and that most iron oxides exist in the solution at solution pH 3. However, when solution pH increases to 4, most iron oxides accumulate on the iron surfaces and inhibit the dye decolorization rates.

When the Fe^0/air process was applied in this study, the indirect oxidation of dye by strong oxidants generated by iron (Eqs. (5) and (6)) was also responsible for dye decolorization besides the direct reductive decolorization on iron surface (Eqs. (2) and (3)). Joo et al. [18] indicates that the H$_2$O$_2$ generation rate (Eq. (5)) is related to the thickness of the iron oxide/hydroxides layer covering the Fe^0 surface. The biphasic kinetics phenomena of RB5 decolorization in

the Fe^0/air and the Fe^0/N$_2$ processes can possibly also be attributed to the formation of the iron oxide/hydroxide layer on the Fe^0 surface when solution pH increased during the experiment (Fig. 2c).

3.4. Effects of initial dye concentrations

Initial concentration of dyes is an important parameter in practical application. The effects of initial dye concentrations (50, 100

and 200 mg L^{-1}) on decolorization efficiencies of RB4 and RB5 solutions by the Fe^0/air process were evaluated. Fig. 3g indicates that an increase in RB4 concentrations decreases the decolorization efficiencies. For example, more than 99% of color was rapidly removed after 3 min of treatment when the initial RB4 concentration was 50 mg L^{-1}. In contrast, when the initial RB4 concentration increased to 100 mg L^{-1}, it took 9 min to remove 98% of color. Fig. 3h indicates that >99% of color was rapidly removed at RB5 concentrations
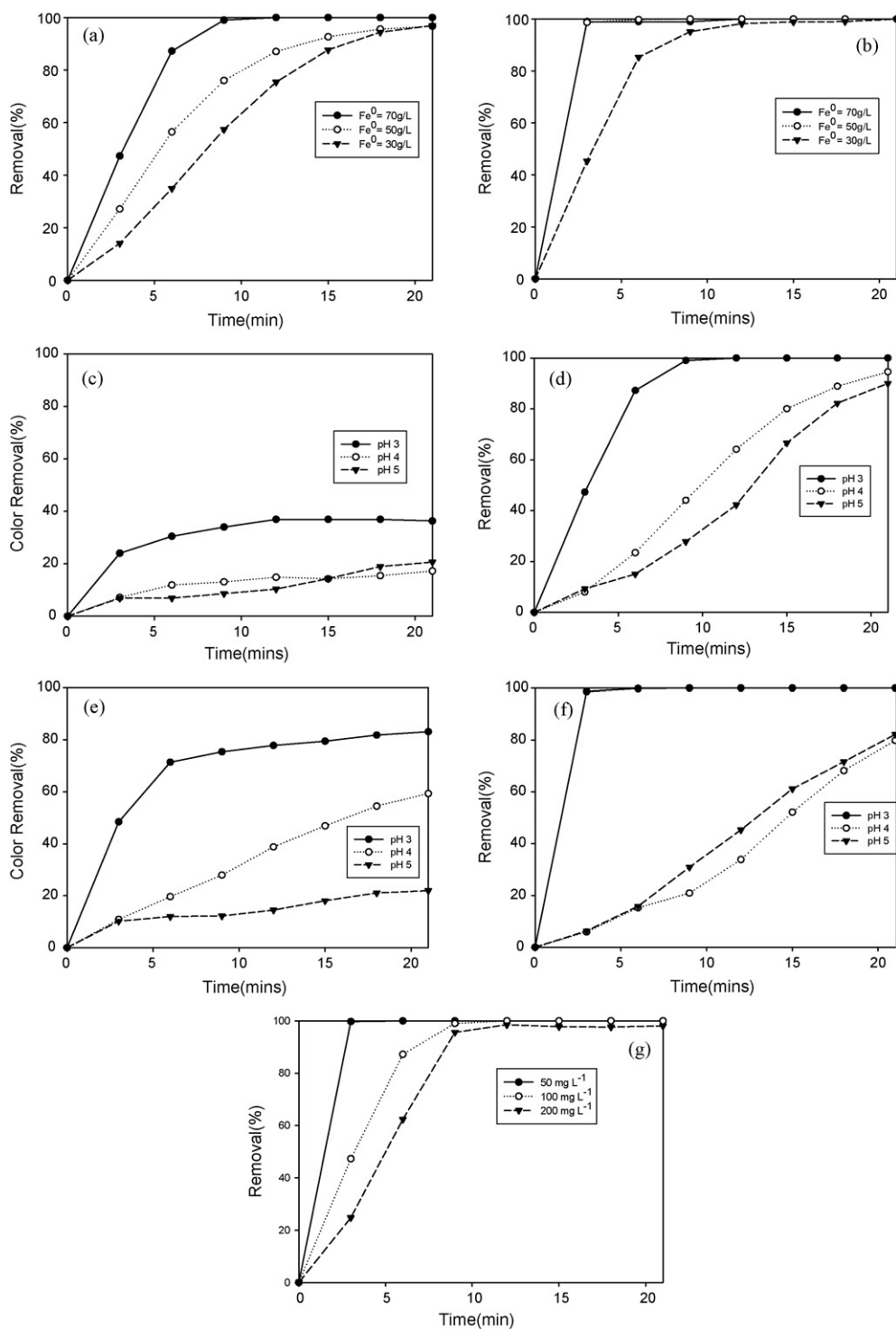
Fig. 3. Effects of operating parameters on RB4 and RB5 decolorization. (I) Effects of Fe^0 doses; (a) RB4 and (b) RB5 by Fe^0/air process, pH 3; (II) effects of pH on RB4 by (c) Fe^0/N$_2$ and (d) Fe^0/air process and on RB5 by (e) Fe^0/N$_2$ and (f) Fe^0/air process; (III) effects of initial dye concentrations (g) RB4 and (h) RB5 by Fe^0/air process; (IV) effects of recycled Fe^0 on RB5 solution (i). If not mentioned otherwise, the experimental conditions were dye concentrations of 100 mg L^{-1}, gas flow rate of 5 L min^{-1}, Fe^0 doses 70 and 50 g L^{-1} for RB4 and RB5 solution, respectively.
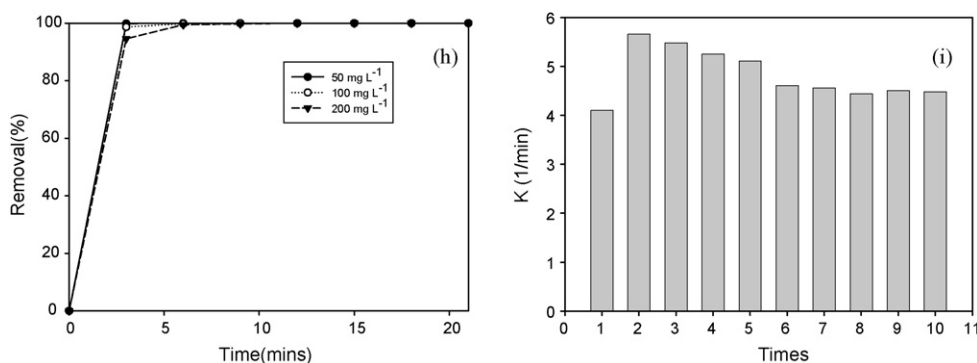
Fig. 3. (*Continued*).

of 50 and 100 mg L^{-1}. When the RB5 concentration increased to 200 mg L^{-1}, the decolorization efficiency slightly decreased and 98% of color removal was obtained after 3 min of treatment.

3.5. Effects of recycled Fe^0 on decolorization

Since 50 g L^{-1} of Fe^0 doses were used in the Fe^0/air process, the effectiveness of recycled Fe^0 on dye decolorization is an important factor influencing the cost of the process. Because the color removal rate was much higher at initial solution pH of 3 compared to pH of 4 and 5 (Fig. 3d and f), the initial solution pH was adjusted each time to pH 3.

Effects of recycled Fe^0 on dye decolorization were evaluated as follows: After the end of each experiment, the solution was settled for 1 min. Supernatant was carefully removed by pipette. One hundred mL of RB5 solution (100 mg L^{-1}) was reinserted into the reactor and adjusted to pH 3. Then aeration was started to begin the experiment. Fig. 3i indicates that after 10 time cycles of the Fe^0/air treatment, Fe^0 still maintained its effectiveness and the reaction rate constants were from 4.1 to 5.7 min^{-1}.

3.6. COD removal by Fe^0/N$_2$ and Fe^0/air treatment

COD removal in RB4 and RB5 solution by Fe^0/N$_2$ and Fe^0/air treatments were investigated. The experimental conditions were initial dye concentrations of 100 mg L^{-1}, gas flow rate of 5 L min^{-1}, initial solution pH 3, and Fe^0 dose of 70 and 50 g L^{-1} for RB4 and RB5, respectively. Fig. 4a and b show that when the Fe^0/N$_2$ process was used, less than 17 and 11% of COD was removed for RB4 solution and RB5 solution, respectively. However, the Fe^0/air process significantly enhanced COD removal for the RB4 and the RB5

solution. Eighty-seven percent of COD was removed for the RB 4 solution at the first 9 min (Fig. 4a), but after that, COD removal did not significantly increase until the end of the experiment (21 min). Similarly, 43% of COD was removed in the first 9 min for the RB5 solution (Fig. 4b). The prolonged treatment time to 21 min also did not significantly increase COD removal.

Even though several studies have reported that the dyes can be decolorized by Fe^0 under anoxic condition, such decolorization occurred only by destruction of the chromophore groups through reductive cleavage of azo bonds [7,8] or by quinone reduction of anthraquinone groups [20]. In the present study, dye decolorization by the Fe^0/N$_2$ process did not remove COD. In contrast, the Fe^0/air process not only rapidly removed color but also COD for both RB4 and RB5 solutions. It is possible that strong oxidants generated through the processes in Eqs. (5) and (6). The difference of COD removal between the RB4 solution (87%) and the RB5 solution (43%) after 21 min treatment could be related to their different chemical structures. The similar trends for COD and color removal at the first 6 min of treatment could be used as an important index for RB4 and RB5 treatment by the Fe^0/air process.

3.7. UV–VIS spectra change during treatment

The changes of the UV–visible spectra of dyes can be used to realize dye degradation and intermediate evolution during treatments. The changes of the UV–visible spectrum of RB4 and RB5 solutions by the Fe^0/N$_2$ and Fe^0/air processes are shown in Fig. 5. The experimental conditions were initial dye concentration of 100 mg L^{-1} and pH 3. Fe^0 doses were 70 and 50 g L^{-1} for RB4 and RB5, respectively. For the RB4 solution, the characteristic absorption peaks at wavelength 595, 370 and 296 nm are attributed to the anthraquinone group, and
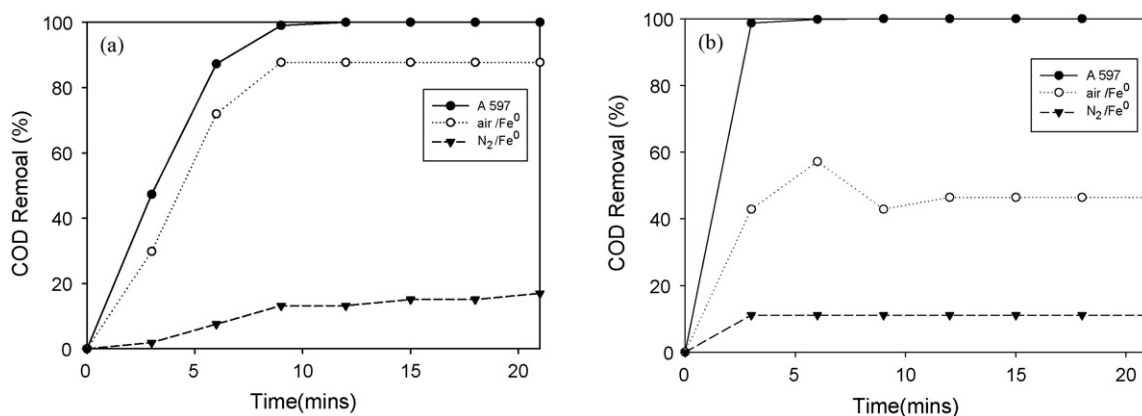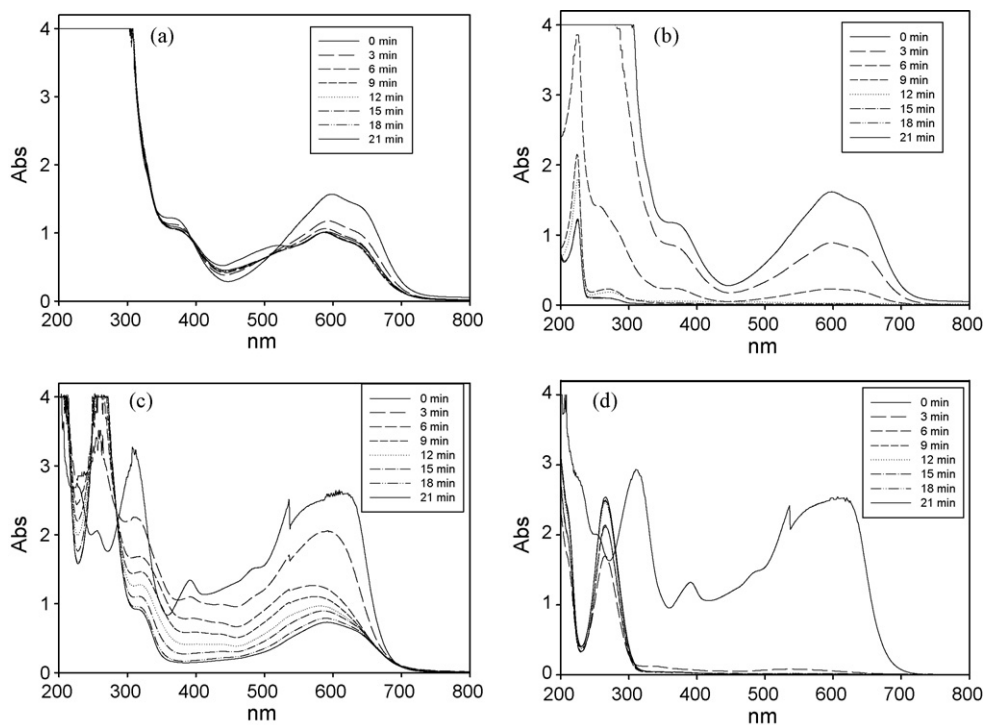

Fig. 4. COD removal by Fe^0/N$_2$ and Fe^0/air process in (a) RB4 solution and (b) RB5 solution. Experimental conditions were dye concentrations of 100 mg L^{-1}, pH 3 and gas flow rate of 5 L min^{-1}. Fe^0 doses were 70 and 50 g L^{-1} for RB4 and RB5 solution, respectively.

Fig. 5. UV–visible absorption spectral changes of RB4 and RB5 solution during Fe^0/N_2 and Fe^0/air treatments. (a) RB4 by Fe^0/N_2 process, (b) RB4 by Fe^0/air process, (c) RB5 by Fe^0/N_2 process, (d) RB5 by Fe^0/air process. Experimental conditions: dye concentrations of $100\,mg\,L^{-1}$, gas flow rate of $5\,L\,min^{-1}$, pH 3. Fe^0 dose 70 and $50\,g\,L^{-1}$ for RB4 and RB5 solution, respectively.

the absorption peak at wavelength 256 is related to the aromatic and reactive dichlorotriazine groups [25]. For the RB5 solution, the absorption peaks at wavelength 597, 310 and 254 nm are attributed to azo bond, naphthalene and benzene components, respectively [26].

Fig. 5a and b show the changes of the UV-spectrum of the RB4 solution by the Fe^0/N_2 and the Fe^0/air processes. When the Fe^0/N_2 treatment was used, only the absorption peak at 594 nm decreased from 1.6 to 1.0 after 21 min. In contrast, the A_{296} and A_{370} did not significantly change. This indicated that the quinone reduction was the only major reaction in the Fe^0/N_2 treatment. However, when the Fe^0/air process was applied, not only A_{594} but also A_{370} and A_{296} significantly and rapidly decreased. This implies that besides the direct reduction reaction (Eq. (2)), the Fe^0/air process might generate strong oxidants that could destroy the anthraquinone, aromatic, and dichlorotriazine groups of RB4.

For the RB5 solution, the Fe^0/N_2 process could destroy azo bond (A_{597}) and naphthalene groups (A_{310}) (Fig. 5c). After 21 min of treatment, A_{594} decreased from 2.6 ($t = 0\,min$) to 0.7, and A_{310} decreased from 3.2 ($t = 0\,min$) to 1. However, the destruction of the naphthalene groups (A_{310}) occurred with the accumulation of a high amount of benzene components (A_{254}). The A_{254} increased from 2 ($t = 0\,min$) to 4 after 21 min treatment. Fig. 5d shows that when the Fe^0/air process was applied, A_{594} and A_{310} rapidly decreased to less than 0.15 in the first 3 min. The accumulation of benzene components (A_{254}) was also observed. However, the accumulation of benzene components in the Fe^0/air treatment ($A_{254} = 2$ at 21 min) was much lower than that in the Fe^0/N_2 treatment ($A_{254} = 4$ at 21 min). Additionally, because benzene components accumulated in the Fe^0/N_2 process after 21 min treatment, it seems that the evaporation of benzene components might not be the major mechanism for COD removal during the Fe^0/air process.

To conclude, the low-cost Fe^0/air process could effectively degrade RB4 and RB5. It could remove not only the color but also COD of dye solutions. Thus, the Fe^0/air process is a poten-

tial technique for rapid treatment of RB4 and RB5 solutions at $100\,mg\,L^{-1}$.

4. Conclusions

The rate and extent of dye degradation were much higher by the Fe^0/air process than by the Fe^0/N_2 process at dye concentrations of $100\,mg\,L^{-1}$, gas flow rate of $5\,L\,min^{-1}$, and initial solution pH 3. The optimal initial solution pH was 3. Both RB4 and RB5 solutions at $100\,mg\,L^{-1}$ were rapidly decolorized by Fe^0/air process within 9 and 3 min, respectively, at initial solution pH 3, Fe dose of $50\,g\,L^{-1}$ and air flow rate of $5\,L\,min^{-1}$. Less than 5% of dyes sorbed onto Fe^0 in the Fe^0 alone set.

For both RB4 and RB5, less than 17% of COD was removed by the Fe^0/N_2 process after 21 min of treatment. However, 87% and 43% COD removal was achieved for RB4 and RB5, respectively, within 9 min by the Fe^0/air treatment. Spectra analysis indicated that application of the Fe^0/N_2 process decreased only A_{594} (chromophore) for RB4 and decreased A_{597} (chromophore) and A_{310} (naphthalene group) for RB5. The Fe^0/air process rapidly decreased A_{594}, A_{370}, A_{296} (anthraquinone group) and A_{256} (aromatic and dichlorotriazine group) for RB4 and A_{597} and A_{254} (naphthalene group) for RB5. The results indicated that the low-cost Fe^0/air process is a potential technique for rapid degradation of RB4 and RB5.

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