

# An integrated technique using zero-valent iron and UV/H<sub>2</sub>O<sub>2</sub> sequential process for complete decolorization and mineralization of C.I. Acid Black 24 wastewater

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## Abstract

The zero-valent iron (ZVI) reduction succeeds for decolorization, while UV/H<sub>2</sub>O<sub>2</sub> oxidation process results into mineralization, so that this study proposed an integrated technique by reduction coupling with oxidation process in order to acquire simultaneously complete both decolorization and mineralization of C.I. Acid Black 24. From the experimental data, the zero-valent iron addition alone can decolorize the dye wastewater yet it demanded longer time than ZVI coupled with UV/H<sub>2</sub>O<sub>2</sub> processes (Red–Ox). Moreover, it resulted into only about 30% removal of the total organic carbon (TOC), which was capable to be effectively mineralized by UV/H<sub>2</sub>O<sub>2</sub> process. The proposed sequential ZVI–UV/H<sub>2</sub>O<sub>2</sub> integration system cannot only effectively remove color and TOC in AB 24 wastewater simultaneously but also save irradiation power and time demand. Furthermore, the decolorization rate constants were about 3.77–4.0 times magnitude comparing with that by UV/H<sub>2</sub>O<sub>2</sub> process alone. © 2006 Elsevier B.V. All rights reserved.

*Keywords:* Advanced oxidation processes (AOPs); Zero-valent iron; Acid Black 24; Decolorization; Mineralization; UV/H<sub>2</sub>O<sub>2</sub>

## 1. Introduction

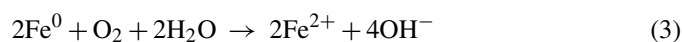
Effluents discharged from textile dyeing and finishing industries containing high organic contents, strong color, surfactants and additives, are difficult to be disposed by traditional biological technologies. Therefore, textile wastewater discharges result into regulatory non-compliance and seriously threaten to the environment. Of increasing importance, the effective decolorization and mineralization technologies for textile wastewater become major challenges. Some researchers observed that the textile effluents were refractory to biological process under aerobic conditions [1,2] due to low BOD/COD ratio. Although the conventional treatment such as coagulation, activated carbon adsorption, and membrane filtration [3–6] can decolorize the dye wastewater, they mainly transfer the pollutants from aqueous to solid phase or concentrate liquid solution. These technologies cannot destruct organics in dye wastewater and demanding further disposals, which increase total treatment cost.

Advanced oxidation processes (AOPs), such as ozonation, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> are widely utilized to successfully degrade organics in industrial wastewater and groundwater. Venkatadri and Peters [7] have reviewed the extensive literatures of these technologies, which were potentially capable to oxidize most of the organic contaminants into carbon dioxide and water. Some researchers found effectively decolorization of textile plant effluents and laboratory synthesized dye solution by AOPs such as significant decolorization of C.I. Acid Orange 7 in UV/H<sub>2</sub>O<sub>2</sub> process with an optimum molar ratio of H<sub>2</sub>O<sub>2</sub>/dye about 1754 by Galindo and Kalt [8]. In addition, UV/H<sub>2</sub>O<sub>2</sub> processes can efficiently enhance color removal of various dyes by several investigators [9–13]. Azbar et al. [14] demonstrated COD and color removal of dyeing effluent by ozonation, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes, that the most efficient decolorization and mineralization of textile effluents was obtained by UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. Thus, AOPs indeed demonstrated their potential and feasibility for decolorizing textile effluents.

In this decade, few investigators successfully applied the zero-valent iron (ZVI) for color removal of dye wastewater. Cao et al. [15] found efficient decolorization for five azo dyes by ZVI

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under anaerobic conditions resulting from the azo link cleavage in the dye molecule. The similar color removal of azo dyes at pH 7.0 was obtained while the decolorization rate constant of Orange II by ZVI was determined [16]. Using ZVI, Chen et al. [17] emphasized the decolorization rates were affected by the pH especially it decelerated by raising pH to alkaline region resulting the precipitation of ferrous hydroxide on the iron surface to occupy the reactive sites rapidly further to terminate the reaction due to the following equations:



Besides, the advanced investigations of decolorization by ZVI need to identify the optimal operating conditions in order to realize the reaction kinetics and decolorization capability of ZVI for dye solutions. Several merits and highly potential site application by ZVI for color removal are easy operation as a pretreatment process, easy recycling the spent iron powder by magnetism, low iron concentration in effluent and no further treatment demand. Although the ZVI reduction technology was proved to be very effective on decolorization, it is very limited to mineralize the organic compounds residues. UV/H<sub>2</sub>O<sub>2</sub> process for textile effluents performed simultaneously excellent efficacy both on decolorization and mineralization, however, it not only consumed high electrical power but also resulting lower UV light efficiency due to high absorbance by dye wastewater. Thus, considering integration of two processes using the initial ZVI for high color removal followed by UV/H<sub>2</sub>O<sub>2</sub> oxidation process for full mineralization was proposed to obtain not only complete decolorization and mineralization but also saving time and energy. The proposed technology employs reductive decolorization by ZVI and sequentially connected to oxidative UV/H<sub>2</sub>O<sub>2</sub> process for mineralization of organics. The operating parameters such as, iron dosage, initial concentrations of dye and hydrogen peroxide were evaluated while color and TOC removal ratios were identified to indicate the optimal conditions. Additionally, the pseudo-first order rate constants and the 90% color removal retention time were obtained to select the optimal treatment process for textile dyeing effluents.

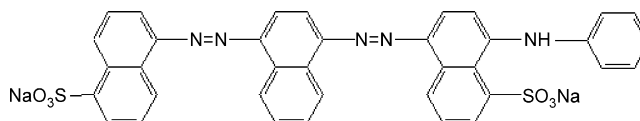
## 2. Experimental

The target dye employed in this study was di-azo dye, C.I. Acid Black 24 (C.I. 26370, AB 24) purchased from Aldrich without further purification that Table 1 summarizes its main characteristics [18]. Hydrogen peroxide was bought from Fluka chemical (35%, w/w). The zero-valent iron (ZVI, 10 μm) powder obtained from Merck was analyzed for characteristics such as diameter and surface area. The morphology was identified by a JEOL 6330CF field emission scanning electron microscope (FESEM) to result the diameter less than 10 μm. The surface area of iron powders may be occupied by unwanted oxides or organic pollutants, therefore, pretreatment of Fe<sup>0</sup> was conducted by washing with 0.1 M HCl acid solution couples of

Table 1  
The characteristics of C.I. Acid Black 24 (AB 24)

Azo dye	C.I. Acid Black 24
Formula	C <sub>36</sub> H <sub>23</sub> N <sub>5</sub> Na <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
λ <sub>max</sub> (nm)	572
MW (g mol <sup>-1</sup> )	731.72
Solubility in water (25 °C) (mg ml <sup>-1</sup> )	20

Chemical structure:



times resulting insoluble oxides deposited on iron surface to be easily flushed. Afterward, the acid-washed iron was rinsed by distilled water several times as long as pH was raised to neutral. Latter, water was exchanged with methanol in order to evaporate easily by vacuum while the iron was dried and stored in a desiccator filled with nitrogen. The 0.290 m<sup>2</sup>/g of BET surface area was obtained by a Beckman Coulter SA3100 surface area and pore size analyzer.

For ZVI reduction decolorization, AB 24 solution (20 cm<sup>3</sup>) was placed in the 40 cm<sup>3</sup> borosilicate glass vials, placing the accurately weighted iron powders to the vials, then mixing at 60 rpm by SeouLin Bioscience Rotamix SLRM-1 rotary mixer. The experimental variables such as reaction time, iron particle dose, and initial dye concentration were evaluated. At defined time intervals, water samples were withdrawn to measure the color at 572 nm of maximum absorbance wavelength by Hitachi U-2000 spectrophotometer while the total organic carbon (TOC) was measured by TOC analyzer made by IO Analytical 1030W total organic carbon (TOC) analyzer. All experimental tests were conducted in triplicate while blank samples were carried out without iron addition. For experiments integrating zero-valent iron coupled with UV/H<sub>2</sub>O<sub>2</sub> process, the ZVI reduction experiments were scaled-up to 1 l and mixing with larger rotary mixer. After ZVI decolorization, the treated dye wastewater was withdrawn and separated with ZVI particles by a filter then transfer to the UV/H<sub>2</sub>O<sub>2</sub> process for further treatment.

In the UV/H<sub>2</sub>O<sub>2</sub> process, a thin gap annular photo-oxidation reactor with plug flow fitted with a Sterilight<sup>®</sup> low pressure mercury arc UV lamp (wavelength 253.7 nm, input power of 14 W) in the inner quartz tube of reactor was conducted. Dye water with AB 24 flowed through the thin gap between quartz tube and outer stainless steel shell where the oxidation process was produced. The detail description of reactor configuration can be confirmed from the author's previous paper [19]. Samples were withdrawn at time intervals and analyzed by methods the same as the above for UV-vis absorbance (wavelength at 572 nm) and TOC. Moreover, the standard color detection procedure developed by the American Dye Manufacturers Institute (ADMI) was employed to express the color strength of dye wastewater in this study. The calculation of ADMI color index by applying the Adams-Nickerson color difference formula, which substituted transmittance data by 30 wavelengths identified by spectrophotometer (every 10 nm interval during 400–700 nm)

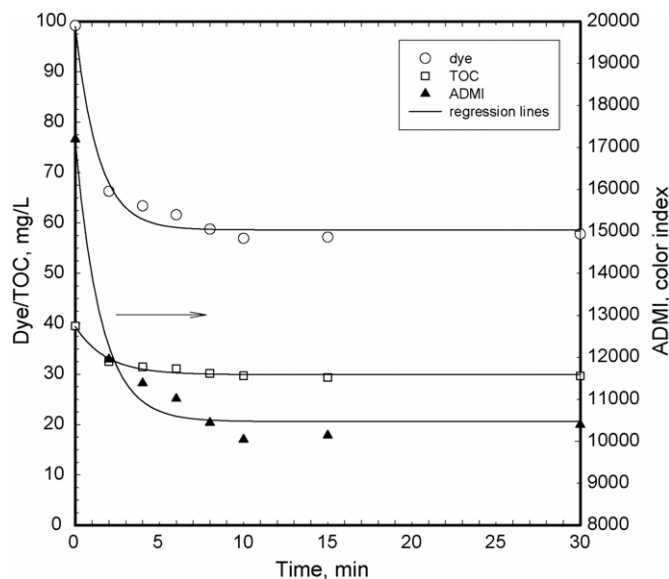


Fig. 1. The dye concentration, TOC, and ADMI color index of C.I. Acid Black 24 wastewater vs. time by zero-valent iron reductive decolorization. Operating conditions: initial dye concentration = 100.0 mg l<sup>-1</sup>; iron dosage = 100.0 g l<sup>-1</sup>.

was described in 2120E of Standard Methods (1995) [20]. The concentration of hydrogen peroxide was determined by spectrophotometer method [21].

### 3. Results and discussion

#### 3.1. Reductive decolorization of Acid Black 24 by zero-valent iron

##### 3.1.1. Effect of reaction time

Adding zero-valent iron (ZVI) in aqueous phase has proved to be a fairly fast process to reduce various organic compounds from previous work according to the dissolution of ferrous ions and electrons transfer to react with the organic molecules on the iron surface [15–17]. In this study of reduction, ZVI addition declined the concentration, TOC and ADMI of AB 24 with time courses shown in Fig. 1 that about 43% color removal within the first dozen minutes while 100.0 g l<sup>-1</sup> of ZVI addition. The color removal efficiencies incremented promptly to the first 10 min; then barely increasing to 20 min, after which it was no change while pH gradually swelled from 6.6 to 7.0. Thus, this scenario proved that reductive decolorization occurred within the first 15 min while nearly effective color removal after 15 min. Moreover, similar removal trend for TOC reduction from 40 to 30 mg l<sup>-1</sup> in first 15 min while ADMI color index decreased sharply from 17,196 down to less than 10,044 in 10 min. Decolorization certainly occurs on the iron surface, which was consumed by time and occupied by dissolved oxygen and oxidative species from the reactions resulting into loss of reactivity. Thus, stoichiometric excess amounts of ZVI addition in order to avoid variation of iron concentration by corrosion during reaction. Color removal is generally assumed to be a first order reaction with respect to dye concentration. By ignoring

iron concentration effect, it converts to the pseudo-first order reaction.

$$\frac{C_{AB\ 24}}{C_{AB\ 24_0}} = e^{-kt} \quad (4)$$

where  $k$  denotes the observed first-order reaction rate constant,  $t$  the reaction time,  $C_{AB\ 24_0}$  the initial concentration of AB 24, and  $C_{AB\ 24}$  is the concentration of AB 24 at time  $t$ .

The removal efficiency hardly reaches complete 100% because reaction occurs in the water–iron limit interphase while the ultimate residual concentration ( $C_{res}$ ) is dependant on iron dosage. Thus, the rate expression can be written as Eq. (5):

$$\frac{C_{AB\ 24}}{C_{AB\ 24_0}} = \frac{C_{AB\ 24_0} - C_{res}}{C_{AB\ 24_0}} e^{-kt} + \frac{C_{res}}{C_{AB\ 24_0}} \quad (5)$$

where  $C_{res}$  is the ultimate residual concentration by certain ZVI dose.  $C_{res}$  and  $k$  were obtained by non-linear regression from Fig. 1. Thus, the higher iron dosage produced significantly lower ultimate residual concentration. While iron doses of 100.0 and 50.0 g l<sup>-1</sup>, the ultimate residual concentration  $C_{res} = 58.63$  and 71.04 mg l<sup>-1</sup>, rate constants  $k = 0.7377$  and 1.0808 min<sup>-1</sup> were obtained, respectively. The rate constants were relatively higher compared with the results of Nam and Trantyeck [22]. They demonstrated an observed color removal rate constant of 0.530 min<sup>-1</sup> for 60 μM Crocein Orange G and an observed rate constant of 0.023 min<sup>-1</sup> for 300 μM Naphthol Blue Black G while adding the same iron dosage of 200 g l<sup>-1</sup>. Similarly, Mu et al. [16] reported the color removal rate constants between 0.017 and 0.022 min<sup>-1</sup> for 0.14–0.71 mM of Orange II by adding 66.6 g l<sup>-1</sup> of iron that may result from more surface area provided by specific iron powder they used.

##### 3.1.2. Effect of iron dosage on unit iron color removal capacity

The iron dosage effect on color removal by each unit weight of Fe<sup>0</sup> is shown in Fig. 2. From our previous work [23], it presented that one can improve color removal efficiencies by increasing dosage of iron particles. It is because that more ZVI provides substantially more surface active sites to accelerate the initial reaction resulting in more iron ions collided with azo dye molecules to remove color. The decolorization was limited by the iron surface area and diffusion of dye molecule to the iron surface. In Fig. 2, the results of unit Fe<sup>0</sup> color removal capacities for initial AB 24 concentrations of 25–100 mg l<sup>-1</sup> were the function of iron dosages (20.0–200.0 g l<sup>-1</sup>) at 60 rpm and 30 min. Over the course of 30 min, the unit color removal capacities were 0.6375, 0.4505, and 0.32422 mg AB 24/g iron by iron doses of 20.0, 120.0, and 200.0 g l<sup>-1</sup> while 100 mg l<sup>-1</sup> of initial AB 24 concentration. Although, more iron dose obtained higher removal efficiencies, less iron dose provided reversely higher unit color removal capacity at the same initial AB 24 concentration. Thus, reductive decolorization under higher initial AB 24 concentration performed higher unit color removal capacity of zero-valent iron in most of cases. In order to gain the unit color removal capacity for considering both economic and technical efficiency simultaneously, the effects of initial dye concentration and iron dosage generated a contour diagram shown

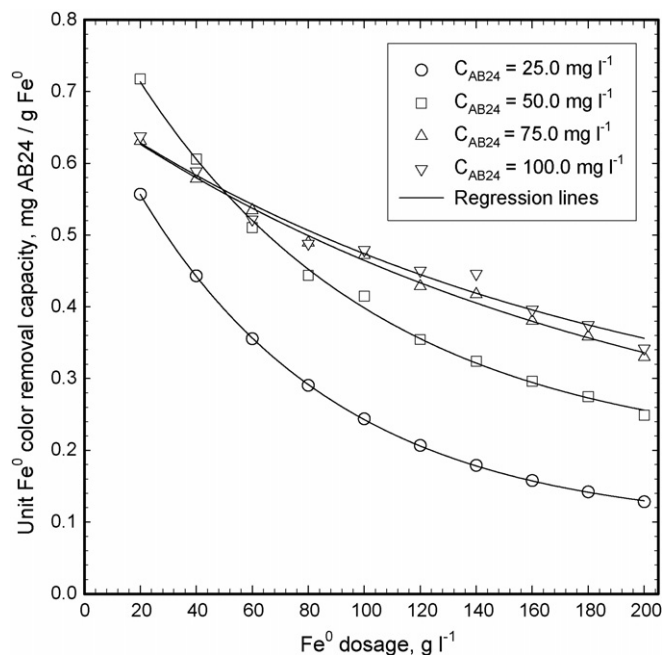


Fig. 2. Unit iron color removal efficiency curves vs. iron dosage for decolorization of AB 24 by ZVI. The retention time was fixed at 30.0 min.

in Fig. 3. The iso-concentration lines represent the unit color removal capacity, which can provide a beneficial reference of experimental conditions for future research. From this figure, the best economical operating region is significantly located within the region of lower iron dosage and higher initial dye concentration.

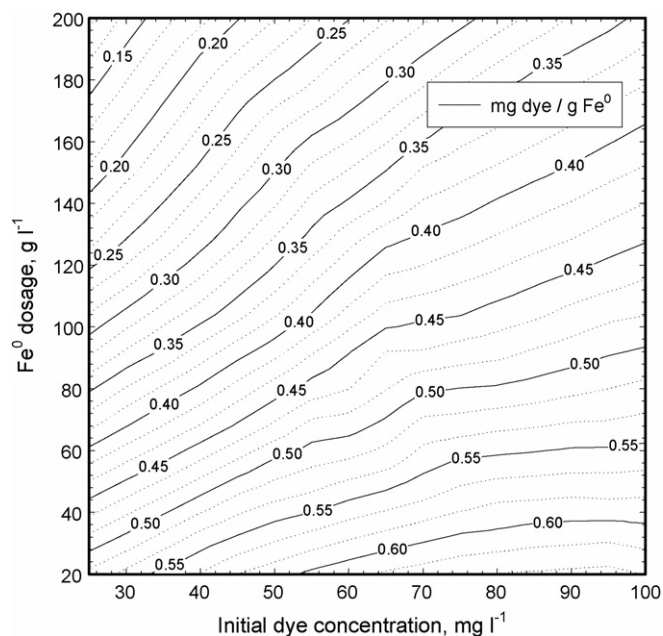


Fig. 3. The contour plot of unit iron color removal capacities with various initial dye concentrations and iron dosages. The unit iron color removal capacity (mg AB 24/g Fe<sup>0</sup>) is presented as a function of iron dosage and initial dye concentration. The retention time was fixed at 30.0 min.

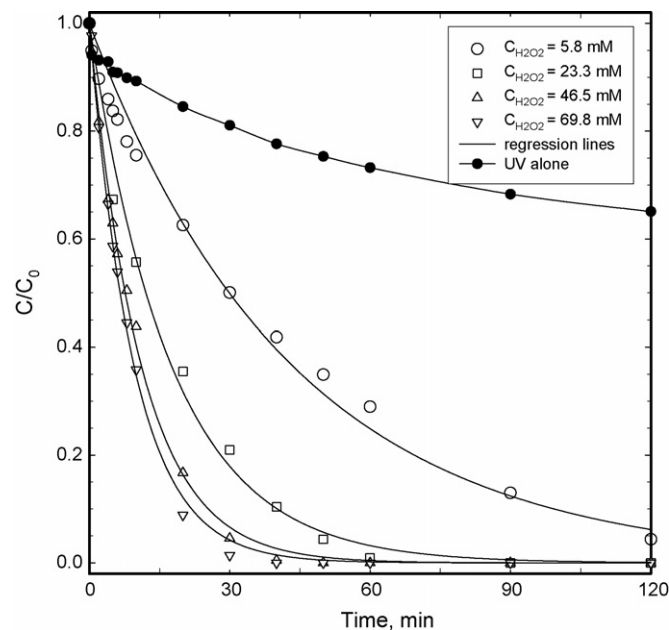


Fig. 4. The normalized dye concentrations ( $C/C_0$ ) of Acid Black 24 wastewater as functions of time in UV/H<sub>2</sub>O<sub>2</sub> process. Initial dye concentration was 100.0 mg l<sup>-1</sup> and UV light power was 14 W.

### 3.2. Decolorization of Acid Black 24 wastewater by UV/H<sub>2</sub>O<sub>2</sub> process

Many researches have evaluated successful decolorization of dye in aqueous solutions by UV/H<sub>2</sub>O<sub>2</sub> process [8–13] that an important parameter for color removal by hydroxyl radicals generated by the initial H<sub>2</sub>O<sub>2</sub> concentration. Thus, the color removal efficiencies of AB 24 with time under various initial H<sub>2</sub>O<sub>2</sub> concentrations were shown in Fig. 4, from which the observed pseudo-first order rate constants were calculated by linear regression of the rate expression, Eq. (4). First of all, the decolorization effect of direct UV irradiation alone (without hydrogen peroxide) was less significant resulting 34.9% of color removal efficiency and 0.008 min<sup>-1</sup> of the observed first order rate constant over 120 min of irradiation time that it was extremely enhanced combining UV irradiation with hydrogen peroxide addition. The decolorization rates linearly increased from 0.0232, 0.0573 to 0.0905 by incrementing the H<sub>2</sub>O<sub>2</sub> concentrations from 5.82, 23.3 to 46.5 mM, however, passing through 46.5 till 69.8 mM, the rates increased insignificantly from 0.0905 to 0.1054. It implies the optimum dosage of H<sub>2</sub>O<sub>2</sub> has to be identified, otherwise the hydroxyl radicals reacts directly not only dye molecules but also excess dosage of H<sub>2</sub>O<sub>2</sub> at the same time resulting no or lower color removal due to radicals competition. Thus, the suitable H<sub>2</sub>O<sub>2</sub> concentration observed for the decolorization of AB 24 was 69.8 mM while the pseudo-first order rate constants are about the same order of magnitude than that of the azo dye C.I. Acid Blue 113 (AB 113) with the same UV/H<sub>2</sub>O<sub>2</sub> process from our previous work [19]. Consequently, the higher rate constants of AB 24 were obtained by 46.5–69.8 mM of the best initial concentrations of H<sub>2</sub>O<sub>2</sub>.



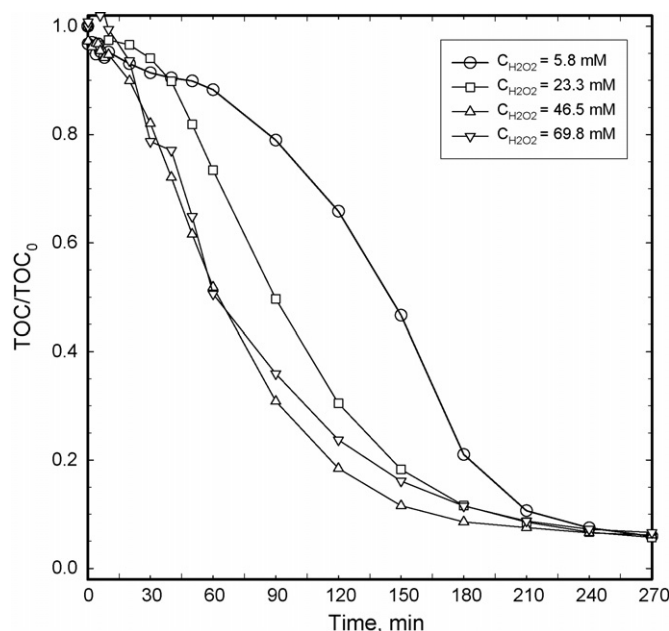


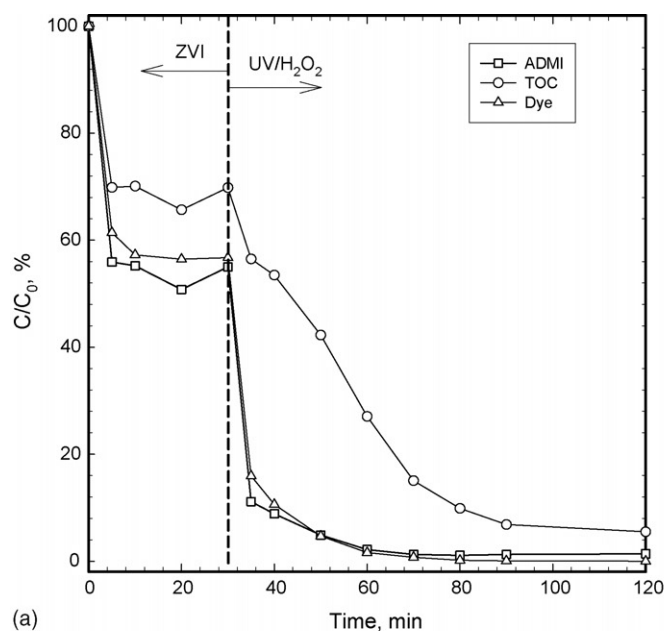
Fig. 5. The normalized TOC concentrations (TOC/TOC<sub>0</sub>) of Acid Black 24 wastewater as functions of time in UV/H<sub>2</sub>O<sub>2</sub> process. The operating conditions were same as those given in Fig. 4. Initial TOC concentration was 39.7 mg l<sup>-1</sup>.

### 3.3. Mineralization of Acid Black 24 by UV/H<sub>2</sub>O<sub>2</sub> process

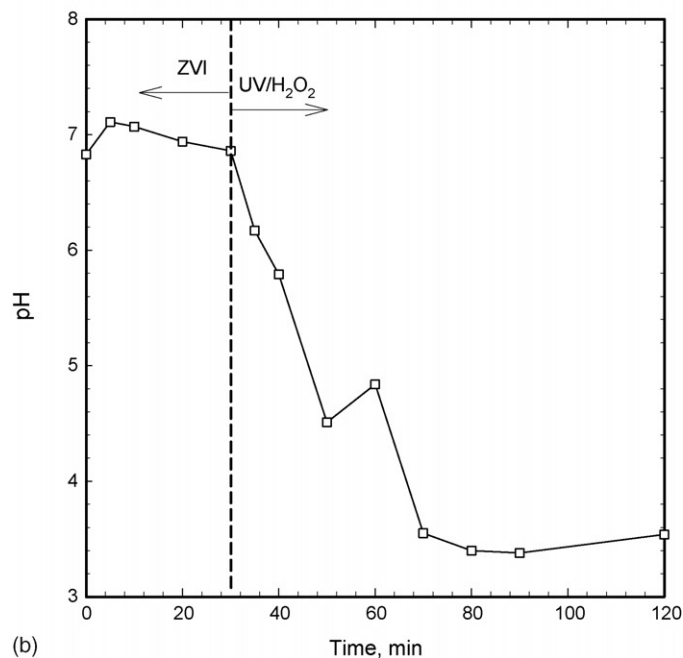
The UV/H<sub>2</sub>O<sub>2</sub> oxidation process produces very strong oxidants, hydroxyl radicals, to non-selectively attack the hydrocarbons resulting bond cleavage into some smaller molecules till further mineralization to carbon dioxide while total organic carbon (TOC) was employed to indicate mineralization effectiveness of AB 24 wastewater as shown in Fig. 5. Utilizing the same dosages of UV and H<sub>2</sub>O<sub>2</sub> with 40 mg l<sup>-1</sup> of the initial TOC of AB 24 wastewater, for 46.5 mM of the best initial H<sub>2</sub>O<sub>2</sub> concentration, the longer time demanded for high mineralization efficiency such as 95% removal of TOC spending 270 min, which was two-fold longer than that of decolorization.

### 3.4. Integration of zero-valent iron coupled with UV/H<sub>2</sub>O<sub>2</sub> process for complete decolorization and mineralization of Acid Black 24 wastewater

From the above results, we knew the UV/H<sub>2</sub>O<sub>2</sub> process performed effectively for not only color removal but also TOC removal, although the latter demanded longer time. On the other hand, the high decolorization efficiencies were obtained but low TOC removal in zero-valent iron reduction process so that connecting zero-valent iron reduction with UV/H<sub>2</sub>O<sub>2</sub> oxidation process was proposed in order to conduct complete color removal and promptly mineralization. From the experimental data, initial zero-valent iron reduction obtained about 40% color removal over 30 min, followed by UV/H<sub>2</sub>O<sub>2</sub> process (46.5 mM of H<sub>2</sub>O<sub>2</sub>) with time as shown in Fig. 6a, whereas more than 95% dye and ADMI color removal and 90% TOC removal within 50 and 80 min of the total reaction time, respectively.



(a)



(b)

Fig. 6. (a) The normalized dye concentration, TOC, and ADMI color index and (b) pH vs. time for C.I. Acid Black 24 wastewater in zero-valent iron reduction coupled with UV/H<sub>2</sub>O<sub>2</sub> processes. The iron reduction time was 30.0 min. Initial color intensity was 17196 ADMI units, initial dye concentration was 100.0 mg l<sup>-1</sup> and TOC was 39.7 mg l<sup>-1</sup>. Reaction conditions were the same as those given in Figs. 1 and 4 for zero-valent iron reduction and UV/H<sub>2</sub>O<sub>2</sub>, respectively. The H<sub>2</sub>O<sub>2</sub> concentration was 46.5 mM.

#### 3.4.1. The pH effect on decolorization by ZVI, UV/H<sub>2</sub>O<sub>2</sub> and integration of zero-valent iron couple with UV/H<sub>2</sub>O<sub>2</sub>

pH is very important operating parameter which affects color and TOC removal efficiency in both ZVI reduction and UV/H<sub>2</sub>O<sub>2</sub> oxidation process. The decrease of zero-valent iron decolorization rate by raising pH to the alkaline region is mentioned by Chen et al. [17]. Fe<sup>2+</sup> ions, from the iron surface and hydroxyl ions in the alkaline solution precipitate ferrous

hydroxide on the surface of iron occupying the reactive sites thus hindering the reaction. Similarly, from our previous study [23], elevating the pH to 9.0, 10.2, and 10.9 by addition of sodium hydroxide solution ( $1.0 \text{ mol l}^{-1}$ ) to dye wastewater with original pH of 6.4 and  $100.0 \text{ g l}^{-1}$  iron addition, results in lower decolorization efficiency. Whereas reducing the pH to 2.1, 3.0, and 4.0 by addition of hydrochloric acid ( $1.0 \text{ mol l}^{-1}$ ) results in the significant elevation of decolorization to more than 46.5% of the original pH. As for the pH effect on UV/ $\text{H}_2\text{O}_2$  process decolorization was also reported in another previous work [24]. By raising pH, decolorization rates of dye decrease under the UV/ $\text{H}_2\text{O}_2$  process because that hydrogen peroxide generally decomposes into water and oxygen rather than hydroxyl radicals in alkaline condition. The pH value in the narrow window of 3.0–5.15 was observed to be best operation range for decolorizing azo dye, Acid Black 1, in a UV/ $\text{H}_2\text{O}_2$  process. Therefore in both ZVI reduction and UV/ $\text{H}_2\text{O}_2$  oxidation processes the acidic pH from 3.0 to 5.5 showed better color removal efficiency. Thus, for combination of ZVI and UV/ $\text{H}_2\text{O}_2$  it is obvious that acidic pH from 3.0 to 5.5 will perform better color removal and mineralization. In this work, since the pH for AB 24 wastewater was about 6.83 that the pH is not controlled during the experiments to reach the high decolorization rate and less chemical added to adjust pH. Fig. 6b showed pH changes versus time through ZVI and UV/ $\text{H}_2\text{O}_2$  reaction. The pH of dye wastewater increased slightly after adding ZVI, and decreased sharply during UV/ $\text{H}_2\text{O}_2$  reaction to pH 3.5.

#### 3.4.2. The ZVI dosage effect on decolorization and mineralization by integration of zero-valent iron couple with UV/ $\text{H}_2\text{O}_2$

Although the integration process demonstrated the improving removal efficiencies of both color and TOC, there existed the best operating parameters to gain both the highest color and TOC removal efficiencies by considering the effect of zero-valent iron dosage shown in Fig. 7(a) and (b). For color removal, one benefit from integration process can be obtained to compare the integration process with UV/ $\text{H}_2\text{O}_2$  alone, the initially zero-valent iron addition reduced color saving the following electrical power consumption of UV light shown in Fig. 7(a) with adjusted iron doses. To obtain 95% color removal, it demanded UV irradiation time of 50, 40 and 20 min by UV/ $\text{H}_2\text{O}_2$  processes alone, UV/ $\text{H}_2\text{O}_2$  with 50 and  $100 \text{ g l}^{-1}$  zero-valent iron, respectively. The residual normalized dye concentrations were declined to 72.5 and 56.7% by adding iron of 50 and  $100 \text{ g l}^{-1}$ , respectively, in the first 10 min that slightly changed till 30 min. Afterwards the dye wastewater flowed into the UV/ $\text{H}_2\text{O}_2$  process substantially achieved the completion of color removal over 50 min so that ZVI addition connected to UV/ $\text{H}_2\text{O}_2$  process resulted the full decolorization of dye wastewater within summation time of 80 min. Alternatively, the mineralization efficiencies were ineffectively declined to 90 and 70% by adding iron of 50 and  $100 \text{ g l}^{-1}$ , respectively, over 30 min by iron reduction, which were enhanced dramatically afterwards connecting to UV/ $\text{H}_2\text{O}_2$  oxidation process shown in Fig. 7(b). Using TOC as an indicator of mineralization and applying 60 min of UV irradiation time, the TOC removal efficiencies of 26.6% by

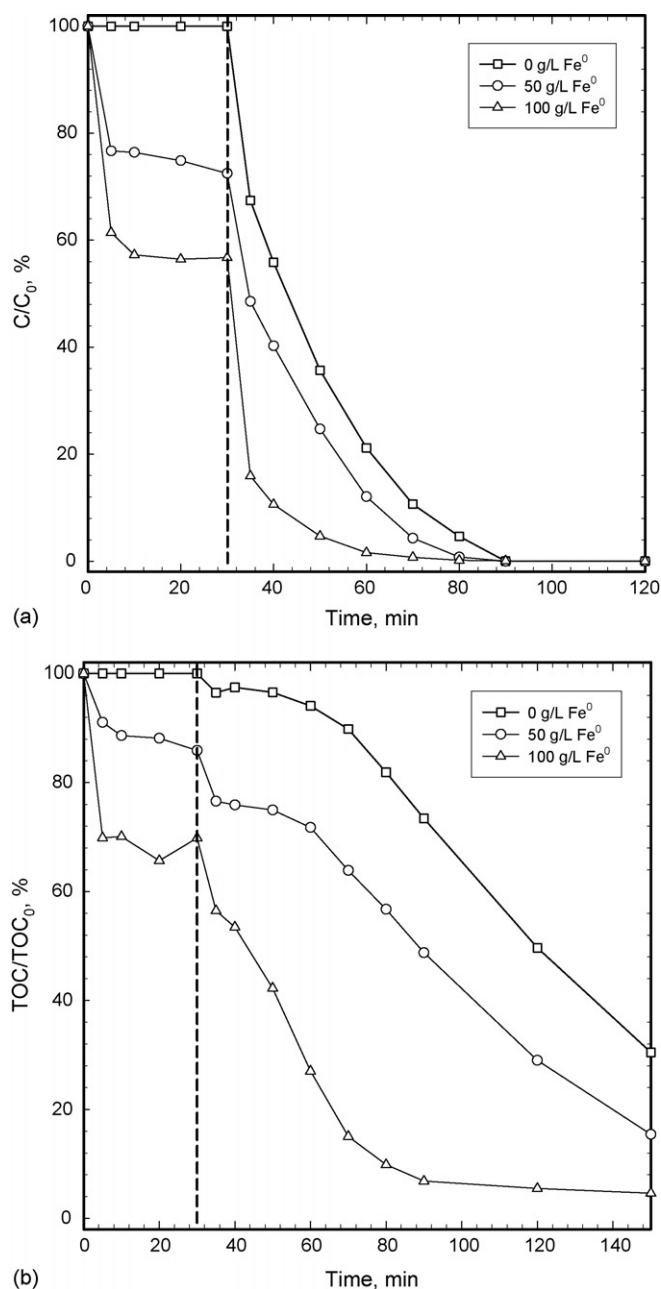


Fig. 7. (a) The normalized dye concentrations vs. time and (b) The normalized TOC concentrations vs. time, for C.I. Acid Black 24 wastewater in zero-valent iron reduction (with various iron dosages) coupled with UV/ $\text{H}_2\text{O}_2$  processes. Reaction conditions were the same as those given in Fig. 6.

UV/ $\text{H}_2\text{O}_2$  process alone without iron addition or 51.2 and 93.2% by UV/ $\text{H}_2\text{O}_2$  process with 50 and  $100 \text{ g l}^{-1}$  iron addition can be reached, respectively. The 90% TOC removal was obtained by integration technique while  $100 \text{ g l}^{-1}$  iron addition in initial 30 min demanding the other 50 min of UV irradiation time, which was only about 20% TOC removal by UV/ $\text{H}_2\text{O}_2$  process alone during the same time period of 80 min. That expressed 145 min more was demanded to reach 90% TOC removal by UV/ $\text{H}_2\text{O}_2$  process alone so that the integration technique can save lots of time and energy turning to be a very feasible attempt.

Table 2  
Rate constants and irradiation time demands for 50% color and TOC removal of Acid Black 24 wastewater in various processes

Processes	Color, first order rate constants ( $\text{min}^{-1}$ )	$R^2$	TOC, first order rate constants ( $\text{min}^{-1}$ )	$R^2$	Irradiation time for 50% color removal (min)	Irradiation time for 50% TOC removal (min)
UV/H <sub>2</sub> O <sub>2</sub> alone	0.05706	0.994	0.0082	0.954	13	90
Zero-valent iron reduction (50 g l <sup>-1</sup> ) + UV/H <sub>2</sub> O <sub>2</sub>	0.06188	0.992	0.0100	0.930	5	60
Zero-valent iron reduction (100 g l <sup>-1</sup> ) + UV/H <sub>2</sub> O <sub>2</sub>	0.2152	0.984	0.0328	0.981	2	12

In UV/H<sub>2</sub>O<sub>2</sub> process without iron reduction, the 100% color removal was obtained by irradiating 60 min of UV light though slower decelerated rate was observed, that UV/H<sub>2</sub>O<sub>2</sub> process with iron addition demanded the same time for 100% color removal. Consequently, initial 30.0 min of zero-valent iron connected to UV/H<sub>2</sub>O<sub>2</sub> process to be an efficient integration of reduction–oxidation processes can effectively remove color and TOC in AB 24 wastewater simultaneously while saving the irradiation time demand. Table 2 summarized the first order rate constants and time demand for 50% color and TOC removal ( $t_{1/2}$ ) in various processes that the pseudo-first order rate constants of Acid Black 24 wastewater were acquired to be 0.2152 and 0.0328  $\text{min}^{-1}$ , respectively, while 100 g l<sup>-1</sup> zero-valent iron addition. The rates were about magnitude of 3.77–4.0 times comparing with that by UV/H<sub>2</sub>O<sub>2</sub> process alone. On the other hand, the irradiation time spent 13 and 60 min to obtain 50% of color and TOC removal, respectively, by UV/H<sub>2</sub>O<sub>2</sub> process alone, that were 2 and 12 min more than that of integration with 100 g l<sup>-1</sup> zero-valent iron addition.

#### 4. Conclusions

The Acid Black 24 wastewater was feasible to be decolorized by either zero-valent iron reduction or UV/H<sub>2</sub>O<sub>2</sub> oxidation process. The reduction of dye solution by zero-valent iron reached better decolorization efficiency than that of mineralization. On the other hand, UV/H<sub>2</sub>O<sub>2</sub> process cannot only remove color but also totally mineralize the organic compounds. For TOC removal, a longer reaction time of 270 min was needed to obtain less than 5% of the residual TOC. The reason for TOC removal by zero-valent iron reduction was extremely limited by the adsorption surface resulting only about 30% TOC removal. In 30 min of reaction time, zero-valent iron reduced color very fast in reaching 56.7% color removal but only about 30% TOC removal was achieved. However, once 100 g l<sup>-1</sup> of zero-valent iron connected to UV/H<sub>2</sub>O<sub>2</sub> process can solve the above problem for eliminating TOC thoroughly to complete color reduction and 98% TOC removal. Consequently, 90% of decolorization and mineralization of dye wastewater can be achieved by integration of zero-valent iron for 30 min coupling with UV/H<sub>2</sub>O<sub>2</sub> process within 11 and 50 min of UV irradiation time, respectively. Reaching full mineralization, the integration process saves 145 min irradiation time than that of UV/H<sub>2</sub>O<sub>2</sub> process alone to be saving energy demand as well. Thus, the integration technique proved to be an innovative and advanced application.

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