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Rapid decolorization and mineralization of simulated textile wastewater in a heterogeneous Fenton like system with/without external energy

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ABSTRACT

A novel Fenton like system, employing Zero Valent Iron (ZVI) and air bubbling, was developed to treat a simulated textile wastewater containing azo dye Reactive Black 5 (RB5) and Ethylenediaminetetraacetic acid (EDTA). By dioxygen activation, H_2O_2 was self-produced continuously in the system through a series of iron-EDTA ligands reactions. After 3 h reaction, the removal rates of RB5, EDTA, Total Organic Carbon (TOC), and Chemical Oxygen Demand (COD) were 100%, 96.5%, 68.6% and 92.2%, respectively. The effects of pH, atmosphere as well as the initial concentration of RB5, EDTA and ZVI were also investigated. Two types of external energy—Ultrasound (US) and Ultraviolet (UV) were introduced into the Fenton like system, respectively. The effect of these external energies on the degradation of the wastewater was assessed. It was demonstrated that US presented significant synergistic effect on the degradation and mineralization of both RB5 and EDTA, while UV could not achieve any improvement.

1. Introduction

In the past decades, wastewater discharged from textile industries has gained greater environmental concern because of high content of dyestuffs, surfactants and additives. It was reported that sixty to seventy percent of dyes used in the textiles industries are azo dyes with one or more azo bonds (—N=N—). Generally, azo dyes are toxic, mutagenic and carcinogenic. The half-life time of most of the azo dyes under sunlight exposure is more than 2000 h, which make them resistant to biological and conventional chemical degradation. As a result, azo dyes are normally hazardous to the environment even if they are present at low concentration [1].

Ethylenediaminetetraacetic acid (EDTA) is a commonly used chelating agent in the manufacture of textiles and for paper pulp bleaching [2]. It is unavoidable that large amount of EDTA contained in the effluent of textile production. Damage from EDTA pollution includes the possible toxic heavy metal mobilization, extended biological availability to aquatic life and further risk on groundwater and drinking water [3]. It has been demonstrated that most of the industrial chelating agents are not degradable in the commonly used wastewater treatment facilities [2,4–6]. Kari and Giger [7] reported that considerable amounts of EDTA pass through wastewater treatment facilities in the form of $Fe^{III}EDTA$.

Since a lot of complex compounds were contained in textile wastewaters, conventional biological treatment such as activated sludge process is not considered as an effective solution. As to traditional physical/chemical treatment technologies applied in textile wastewaters such as chemical coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or activated carbon adsorption [8], only a phase transfer of the pollutants was supplied.

Over the last decade, numerous studies have suggested Advanced Oxidation Processes (AOPs) as good alternatives to treat textile wastewater [9,10]. It is generally accepted that AOPs can produce a highly reactive non-specific oxidant called hydroxyl radicals (•OH), which is capable of destroying a wide range of organic pollutants in water and wastewater [11]. Fenton reagent is a homogeneous catalytic advanced oxidation process which uses a mixture of hydrogen peroxide and ferrous to induce a complex redox reaction in acidic environment [12]. Ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, •OH (Eq. (1)) [13].

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (1)$$

Despite the significant oxidizability of Fenton's reagent, two disadvantages limit its actual application. One is the homogeneous catalyst, usually added as ferrous salt, cannot be retained in the degradation process. In order to achieve complete degradation,

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continuous addition of ferrous salt is necessary. The other drawback lies in the unacceptable high costs from direct addition of H_2O_2 into the industrial scale wastewater treatment facilities.

In the past decade, a so-called Fenton like system has been developed using some heterogeneous iron supported catalysts such as Zero Valent Iron (ZVI) [14,15] or goethite (α-FeOOH) [16] as a substitute for ferrous to catalyze H_2O_2. In these Fenton like system, rapid decomposition of H_2O_2 and degradation of target pollutants were achieved.

Recent studies found that EDTA could activate dissolved oxygen and eventually produce H_2O_2 through a series of complex reactions occurred in a Fe^{2+}/EDTA system (Eqs. (2)–(6)) [17].

$$Fe^{2+} + EDTA + H_2O \xrightarrow{k_1} [Fe^{II}(EDTA)] \rightarrow [Fe^{II}(EDTA)(H_2O)]^{2-} \quad (2)$$

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + O_2 \overset{k_2, k_{-2}}{\rightleftharpoons} [Fe^{II}(EDTA)(O_2)]^{2-} + H_2O \quad (3)$$

$$[Fe^{II}(EDTA)(O_2)]^{2-} \xrightarrow{k_3} [Fe^{III}(EDTA)(O_2{}^-)]^{2-} \quad (4)$$

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + [Fe^{III}(EDTA)(O_2{}^-)]^{2-} \xrightarrow{k_4} [(EDTA)Fe^{III}(O_2{}^{2-})Fe^{III}(EDTA)]^{4-} + H_2O \quad (5)$$

$$[(EDTA)Fe^{III}(O_2{}^{2-})Fe^{III}(EDTA)]^{4-} \overset{k_5, H^+}{\underset{\text{fast}}{\longrightarrow}} 2[Fe^{III}(EDTA)H_2O]^- + H_2O_2 \quad (6)$$

It is supposed that H_2O_2 can be continuously produced in the presence of abundant Fe^{II}EDTA ligand and dissolved oxygen. Based on these findings, a novel Fenton like system, which only employed low-cost materials—Zero Valent Iron with air bubbling, was developed in the present study. A simulated textile wastewater was prepared from a mixture of azo dye Reactive Black 5 (RB5) with chelating agent EDTA. In this system, H_2O_2 was expected to be continuously self-produced, which ensure simultaneous Fenton like reactions occur in the presence of ZVI and EDTA. The objectives of the study were to: (1) investigate the degradation of simulated textile wastewater in the Fenton like system, (2) study the effect of reactants and operating parameters in the Fenton like system, (3) investigate the effect of two external energy–Ultrasound (US) and Ultraviolet (UV) on the degradation of simulated textile wastewater in the Fenton like system.

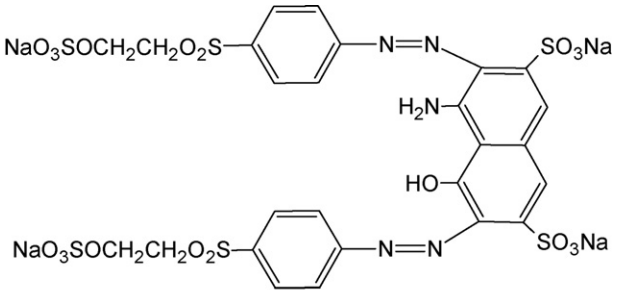
2. Experimental

2.1. Chemicals

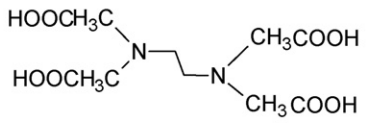
All chemicals were used as received. C.I. Reactive Black 5 of purity 55% was purchased from Sigma–Aldrich Ltd. (Singapore). Ethylenediaminetetraacetic acid disodium dihydrate salt (Na_2EDTA, purity > 99%) was also obtained from Fisher Company. The molecule structures of RB5 and EDTA are shown in Fig. 1. Zero Valent Iron (purified, 325 mesh) was purchased from Fisher Company with a specific surface area of $0.0786 \pm 0.0159\ m^2\ g^{-1}$ determined by BET assay. Ultra pure water, produced from Millipore Milli-Q system, was used to prepare all the solutions in this study.

2.2. Experimental procedures

The heterogeneous Fenton like experiments were conducted in a series of 600 mL Pyrex® borosilicate beakers under dark circumstance. Accurate 500 mL simulated textile wastewater containing certain concentration of RB5 and EDTA was prepared and mixed well in the beakers by magnetic stirring at 600 rpm. The experiments started by adding iron powder. Before the reaction, the wastewater was oxygen saturated through continuous air purging. At the given reaction time intervals, samples was taken out and centrifuged for 10 min (10,000 rpm), the supernatants were then withdrawn for the assay of RB5, TOC and EDTA.



Reactive black 5



Ethylediaminetetraacetic acid (EDTA)

Fig. 1. Molecular structures of azo dye Reactive Black 5 (RB5) and chelating agent Ethylenediaminetetraacetic acid (EDTA).

The US/Fenton like experiment was performed in a 600 mL Pyrex® jacket Reactor. Constant reaction temperature was maintained by cycling water through a Temperature Controller (Polyscience, Singapore). Ultrasound was generated by an XL2020 Sonicator® ultrasonic processor (Misonix Incorporated, New York, USA) equipped with a 20 kHz frequency of probe (5 in. $L \times 1.5$ in. Diameter, 12.7 cm × 3.8 cm) vertically set in the middle of the reactor (2 cm to the bottom). A magnetic stirrer was used to mix the solution continuously at 600 rpm. Purified air (National Oxygen of Singapore Pte Ltd.) was supplied through a glass diffuser at the flow rate of $1.0\ L\ min^{-1}$.

The UV/Fenton like experiment was performed in a 600 mL Pyrex® Beaker. UV irradiation was provided by four 8 W black light fluorescent lamps (NEC FL8 BL-B) suspended in a quartz tube that located in the center of the photoreactor. The photoreactor was also covered by aluminum foils in order to improve utilization of UV light. Initial photonic efficiency of RB5 can be calculated by [18]. Purified air (National Oxygen of Singapore Pte Ltd.) was supplied through a glass diffuser at the flow rate of $1.0\ L\ min^{-1}$.

2.3. Methods of analysis

The simulated textile wastewater in the reaction mixture was quantified through measurement of the absorbance at maximum wavelength (λ_{max} = 595 nm) of RB5 followed by concentration calculation according to predetermined calibration curve. An UV–vis spectrophotometer (Lambda Bio 20, 118 PerkinElmer, USA) was used to analyze the samples.

Quantitative analysis of EDTA was performed with high performance liquid chromatography (WATERS 2695) equipped with a XTerra C18 column and a photodiode array detector (WATERS 2996). Before HPLC analysis, EDTA in samples was converted to Fe(III) complex with the addition of a drop of $FeCl_3$ solution (≥50:1 Fe^{3+}:EDTA molar ratio) and glacial acetic acid. 0.03 M acetate-acetic acid buffer solution (pH 4.0) was used as a mobile phase and the analysis was conducted at flow rate of $1.0\ mL\ min^{-1}$ with absorbance wavelength set at 254 nm.

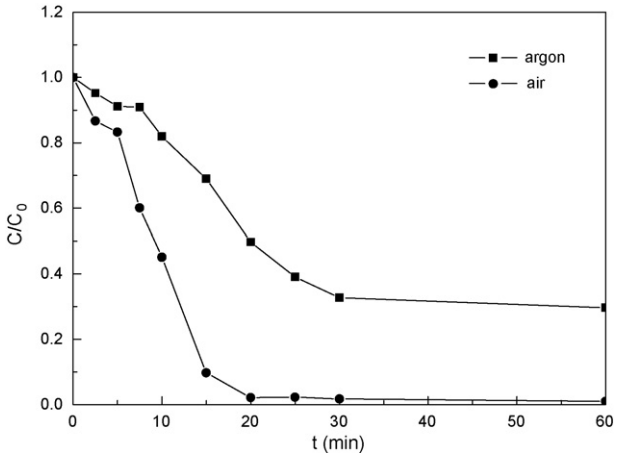


Fig. 2. Decolorization of the simulated RB5 wastewater in the ZVI system under anoxic/air bubbling circumstance. Initial parameters were ZVI 25 g/L, RB5 100 mg/L and gas flow rate 1 L min^{-1}.

The released Nitrate (NO_3^-) was measured by an Ion Chromatography (Shimadzu, Singapore) coupled with a Shim-Pack IC-A3 non-suppressor column (4.6 mm × 150 mm) and a CDD-10A *VP* conductivity detector. An eluent solution, containing 8 mM *p*-hydroxybenzoic acid, 3.2 mM bis–tris and 50 mM boric acid, was pumped at a flow rate of 1.0 mL min^{-1}.

Total Organic Carbon was measured by a TOC analyzer (TOC-500, Shimadzu, Singapore).

Chemical Oxygen Demand (COD) were determined through the Hach test kits with a UV–vis Spectrophotometer (DR 5000, Hach, USA).

A pH meter (Hach Co., Loveland, CO) was calibrated prior to each test and used to track the solution pH.

3. Results and discussion

3.1. Decolorization of simulated RB5 wastewater in a Zero Valent Iron system under anoxic/air bubbling condition

It is well accepted that many reactive dyes could be decolorized by zero-valent iron reducing reaction under anoxic conditions [19]. In order to investigate the decolorization of RB5 in ZVI system, a simulated dye wastewater containing RB5 alone was used as a model pollutant. As shown in Fig. 2, 63% of RB5 was decolorized at 30 min under argon purging atmosphere. Nevertheless, slight further decolorization of RB5 was observed in the succedent 30 min. This indicated that the reductive decolorizaiton reaction of RB5 by ZVI is surface-determined. In order to achieve complete decolorization of RB5 in the anoxic reductive system, more active ZVI surface, i.e. more iron loading is needed.

Compared to the sole reductive ZVI system, a more rapid decolorization rate of RB5 was achieved in a ZVI/air bubbling system where RB5 was almost completely decolorized at 20 min (Fig. 2). Along with the reaction, accumulation of brown iron oxides occurred. It was supposed that RB5 adsorption by the iron oxides could contribute to the decolorization of wastewater. But this possibility was excluded by an acid dissolution test that non-color recovery of the wastewater was observed with the dissolution of iron oxides after addition of hydrogen chloride. It was reported that low-level H_2O_2 could be produced in an iron/aeration system (Eq. (7)) [20] and thus lead to further Fenton reactions (Eq. (1)).

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (7)$$

However, this oxidation effect was proved weak in the ZVI/air aeration system because any mineralization of the wastewater was not achieved at the end of reaction. Therefore, the decolorization of RB5 in the ZVI/air system could be mainly attributed to ZVI reduction. The improvement of decolorization rate may be ascribed to the accelerated release of electron from ZVI surface through the enhancement of iron corrosion.

3.2. Degradation of the simulated textile wastewater containing RB5 and EDTA in the novel Fenton like system

Different from the monocomponent RB5 wastewater, not only rapid decolorization of the azo dye RB5 but also high mineralization of the simulated textile wastewater containing EDTA was achieved in the Fenton like system (Fe/air system). Fig. 3(a) illustrates the profiles of UV/vis spectra versus different reaction time. Quick disappearance of peak 595 nm within the initial 10 min accompanied by gradual increase of absorbance between 200 and 480 nm indicated rapid decolorization of RB5 and formation of intermediates in the initial reaction stage. With the elapse of reaction time, the profiles of the absorbance of the wastewater presented an initial rapid drop followed by subsequent gradual decrease. At 180 min, a very low level of absorbance spectrum was observed. This indicated that most intermediates, which derivated from RB5 and EDTA of the simulated wastewater, could be further oxidized to lower molecule organic compounds or carbon dioxide. The assumption could be validated through the test of the concentration of RB5, EDTA, TOC and COD at different reaction time in the Fenton like system. As shown in Fig. 3(b), rapid decrease of RB5 concentration occurred in the initial 30 min, which indicated almost complete removal of the color of the wastewater. Simultaneously, a slower degradation rate of EDTA was observed with 96.5% of EDTA removed at 180 min. Rapid mineralization of the simulated wastewater was also achieved with 68.6% TOC removed at the end of reaction. In addition, 92.2% of COD removal after 180 min signified good performance of the heterogeneous Fenton like system in treating industrial textile wastewater.

Fig. 3(c) illustrates the variation of pH value and nitrate (NO_3^-) concentration versus reaction time in the Fenton like system. Except for the rapid increase of pH occurred in the initial several minutes, near neutral solution pH was observed throughout the rest of the reaction time, which indicated the excellent self-buffering capacity of this Fenton like system.

Monitoring of the released nitrate concentration could be indicative of the decomposition of RB5 and EDTA due to the fact that nitrogen is one of the constituents in the molecule of the both pollutants. Generally, higher release of nitrate represents more complete decomposition of RB5 and EDTA molecules. Accordingly, nitrate concentration could be partially used to represent the decomposition level of both RB5 and EDTA. Compared to the theoretical nitrate value of 81.7 mg/L that calculated from the total nitrogen molar content in the initial RB5 and EDTA molecules, only 40 mg/L nitrate was released at 180 min (shown in Fig. 3(c)), which indicated the presence of the final organic products with nitrogen in the molecule structure.

3.2.1. Effect of initial dye concentration

As shown in Fig. 4(a), the effect of initial dye concentration on the Fenton like system was investigated. No obvious change of the decolorization rate of RB5 was observed with the increase of initial RB5 concentration from 20 to 100 mg/L. However, a significant reduction of degradation rate occurred at a higher initial RB5 concentration of 200 mg/L. Different from the decolorization of RB5, a gradual decrease of the EDTA degradation rate with the increase of initial RB5 concentration was observed. It seemed that RB5 and its

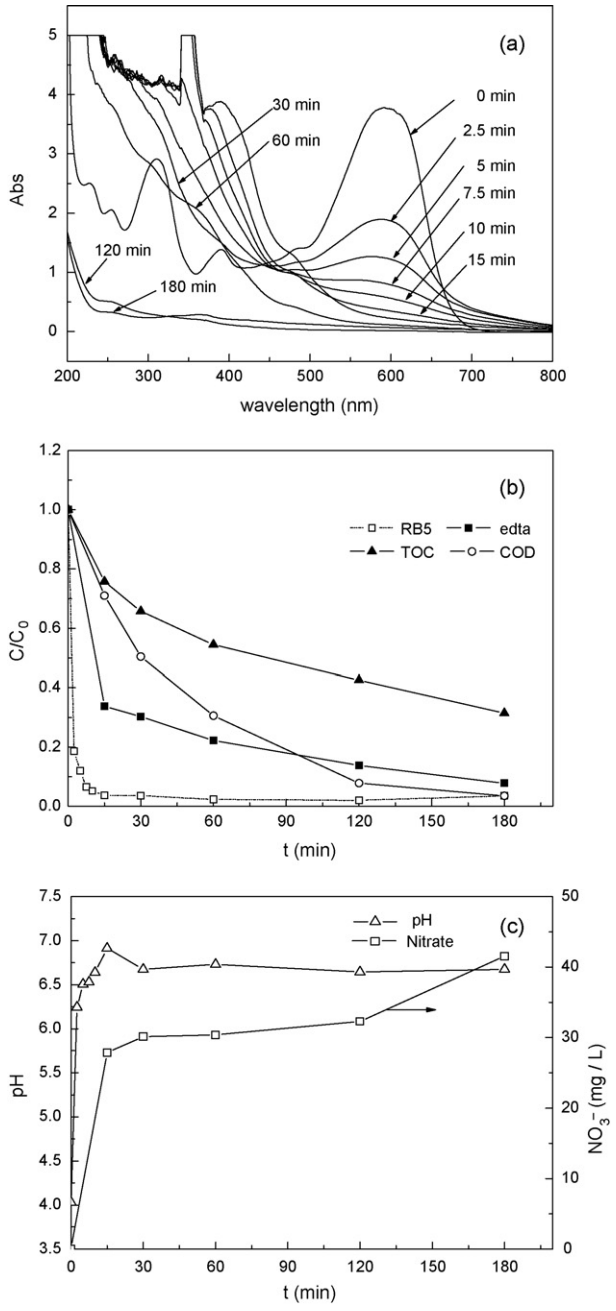


Fig. 3. Degradation of the simulated textile wastewater in the novel Fenton like system (ZVI/air aeration), (a) UV/vis spectra of the wastewater versus reaction time, (b) degradation profiles of RB5, EDTA, TOC and COD, (c) variation profiles of solution pH and Nitrate. Initial parameters were ZVI 25 g/L, RB5 100 mg/L, EDTA 0.4 mM and air 1 L min^{-1}.

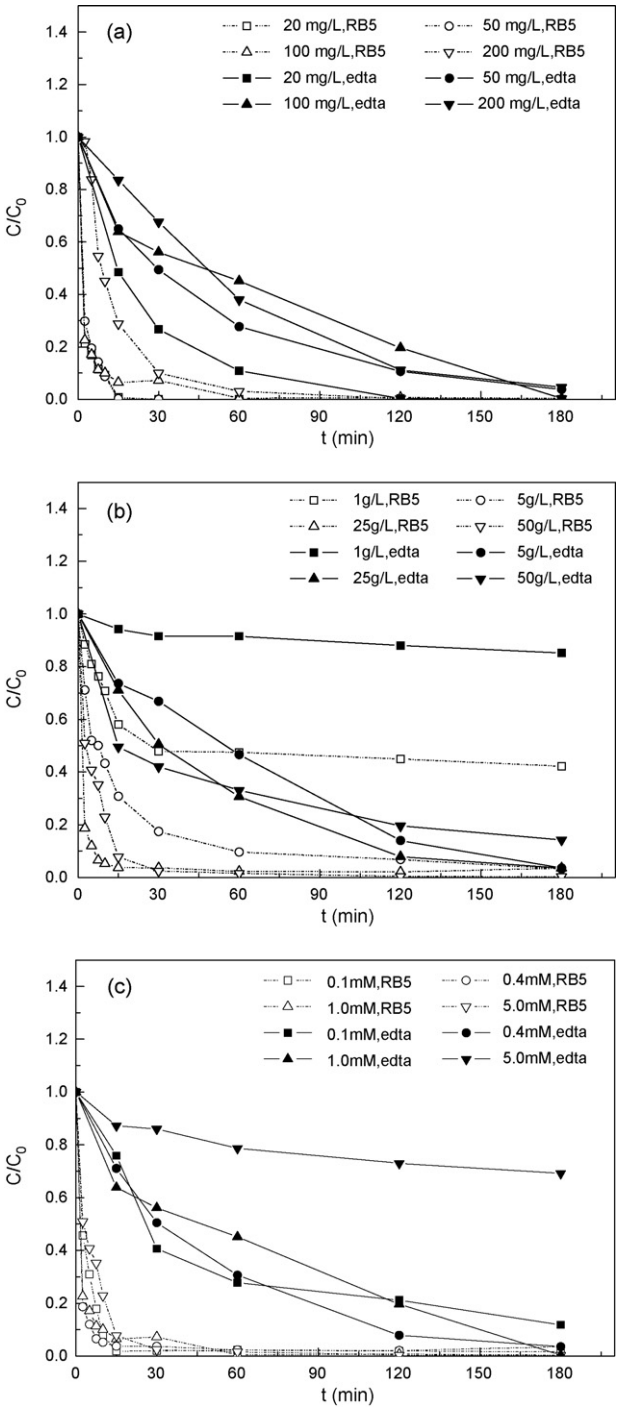


Fig. 4. Effect of (a) initial RB5 concentration, (b) initial EDTA dosage, (c) iron loading on the degradation of RB5 and EDTA in the Fenton like system. Except for the parameters investigated, other initial parameters held on ZVI 25 g/L, RB5 100 mg/L, EDTA 0.4 mM, air flowrate 1 L min^{-1} and original pH.

intermediates are more easily to be degraded prior to EDTA in the Fenton like system. But this competitive relationship might be weak because both RB5 and EDTA were almost degraded completely at the end of reaction at different initial RB5 concentrations. Since H_2O_2 was produced from dioxygen under the reaction involving ZVI and EDTA in the Fenton like system, the effect of increasing initial RB5 concentration on the degradation rate would be very slight if abundant ZVI is present.

3.2.2. *Effect of initial iron loading*

The role of ZVI in the Fenton like system is important. On one hand, RB5 could be decolorized on ZVI surface through reduction reaction. On the other hand, ZVI provided ferrous ion to the bulk solution, which could participate and catalyze the reactions for H_2O_2 production (Eqs. (2)–(6)) and Fenton reaction (Eq. (1)), respectively. Fig. 4(b) illustrates the effect of initial iron loading on the degradation of RB5 and EDTA. Under initial 1 g/L iron loading, 57.8% of RB5 and 14.8% of EDTA was removed, respectively, at the end of reaction. Further increasing iron loading to 5 g/L and 25 g/L could result in a significant increase of RB5 decolorization rate and EDTA degradation rate. Although abundant ZVI loading

could accelerate the production rate of H_2O_2, excessive iron loading (50 g/L) could lead to slight decrease of degradation rate of EDTA since excessive reductive ZVI could accelerate the decomposition of H_2O_2 and the consumption of oxidants generated from Fenton like reactions.

3.2.3. Effect of initial EDTA dosage

EDTA plays two-fold role in the Fenton like system–a target pollutant as well as an essential activated element of H_2O_2 production (Eqs. (2)–(6)). Thus it was expected that higher initial EDTA dosage would bring faster degradation of RB5 and EDTA because of the more rapid H_2O_2 production. However, as shown in Fig. 4(c), this assumption was invalidated by the result of the experiments conducted at different initial EDTA concentrations. The degradation of EDTA was more complex although rapid decolorization of RB5 was all achieved at different initial EDTA dosages. In lower EDTA dosage range (from 0.1 to 1.0 mM), the degradation of EDTA was rapid and high removal rate was achieved at the end of reaction. Whereas remarkable slow degradation rate of EDTA was observed that only 30.8% EDTA was removed after 180 min reaction with an initial 5 mM EDTA dosage.

The above phenomenon could attribute to the fact that high [EDTA]:[$Fe^{II/III}$] ratios could be a kinetic barrier to either O_2 activation or H_2O_2 reduction (Eqs. (2) and (4)), which thus inhibits the subsequent Fenton like reactions. Some studies indicated that the activation of oxygen from iron-EDTA ligands reactions (Eqs. (2)–(6)) is indispensable for the formation of an O_2-Fe^{II}EDTA complex with a coordination number of 7 in the metal center [17,21]. Nevertheless, excessive EDTA, i.e. a molar ratio of [EDTA]:[$Fe^{II/III}$] greater than 1:1, could decrease the coordination number and eventually prevent the formation of O_2^--$Fe^{II/III}$EDTA and/or O_2-$Fe^{II/III}$EDTA ligands which is thought necessary for the activation of O_2 to H_2O_2. Therefore, much lower production of H_2O_2 with a much high initial EDTA dosage could lead to slower degradation of EDTA due to the inhibition of Fenton like reactions.

3.2.4. Effect of pH

Although the Fenton like system showed excellent degradation rate on the simulated textile wastewater at neutral solution pH, effect of solution pH on the degradation of RB5 and EDTA was still investigated since many studies reported that higher degradation kinetic constants in Fenton system were achieved at acidic circumstance [22]. In order to adjust solution pH to certain values, concentrated hydrogen chloride was added per 5 min. Fig. 5(a) shows the results of degradation of RB5 and EDTA at different solution pH. The decolorization of RB5 at pH 4 was similar with the result of the original system (without pH adjustment). However, the decolorization behaviors of RB5 at lower pH (2 and 3) were unique because the color of the simulated wastewater was partially recovered in the latter phase of the reaction. In the process of the experiments conducted at lower pH, accumulation of iron oxides that generally occurred in the original system was not observed. Although the underlying mechanism is still uncertain, enhancement of the absorption of RB5 by modification of the characteristic of ZVI surface at lower pH could be one possible explanation.

The degradation rates of EDTA at different pH were also different. The degradation rate became slower as the solution pH lowered. For instance, the removal of EDTA at the end of reaction was 71.8%, 83.3%, 93.0% and 96.5% for systems of pH 2, 3, 4 and original (about 7), respectively. Seibig, etc. [17] reported that oxygen activation by iron-EDTA ligand could be inhibited at low pH circumstance. At pH below 3, hydrogen ion can combine into Fe^{II}EDTA ligand and Fe^{II}(EDTA H) or Fe^{II}(EDTA H_2) ligand, which has lower ability to activate oxygen, would be produced. As a result, production of H_2O_2 and further Fenton like reactions could be inhibited. It

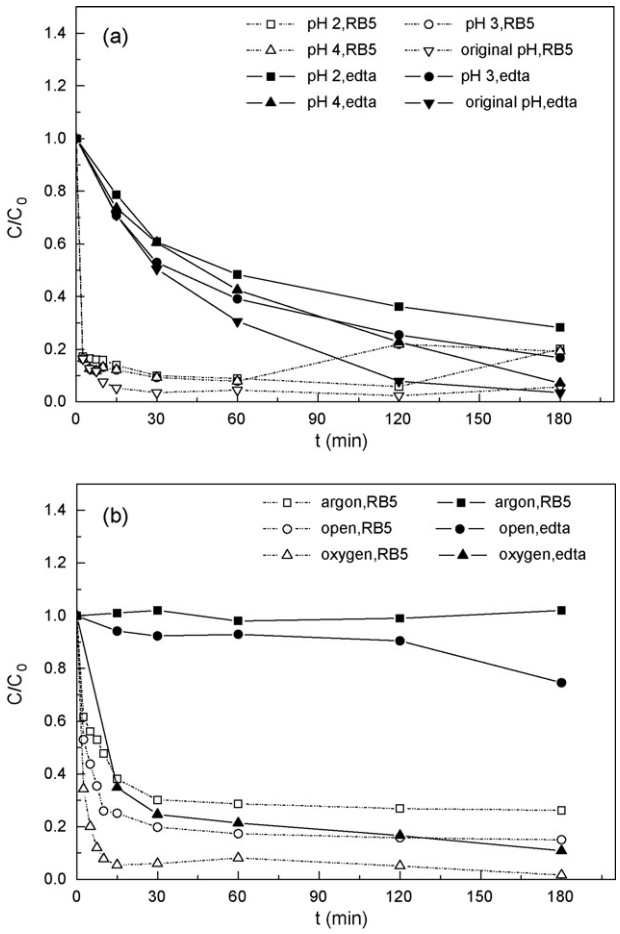


Fig. 5. Effect of (a) different solution pH, (b) different system atmospheres on the degradation of RB5 and EDTA in the Fenton like system. Except for the parameters investigated, other initial parameters held on ZVI 25 g/L, RB5 100 mg/L, EDTA 0.4 mM, air flowrate 1 L min^{-1} and original pH.

was also supported by the result of mineralization degrees in different pH systems in which the removal of TOC was 2.2%, 34.4%, 59.8% and 68.6% for the systems of pH 2, 3, 4 and 7, respectively. Even if a majority of RB5 and EDTA could also be removed in the acidic systems, the low removal rate of TOC meant that further mineralization of the produced organic intermediates was almost inhibited due to the lower H_2O_2 production rate in low pH (<3) system.

3.2.5. Effect of atmospheres

Since H_2O_2 was converted from dissolved dioxygen in the Fenton like system, it was expected that gas atmosphere could have significant effect on the degradation of RB5 and EDTA. Thus the Fenton like systems under three different atmospheres—argon purging, open to air and oxygen purging were investigated. As shown in Fig. 5(b), non-degradation of EDTA and 70% decolorization of RB5 were observed in the system of argon atmosphere at 180 min. Compared to the argon-purging ZVI system of non-EDTA (Fig. 2), slight improvement of RB5 decolorization rate was observed in the initial 30 min. It could be attributed to the reactivation of ZVI surface in the presence of EDTA [23].

In the open-to-air Fenton like system, rapid decolorization of RB5 and slow degradation of EDTA were observed. At 180 min, 80% of RB5 and only 18% of EDTA was removed, respectively. Compared to rapid degradation and mineralization rate of the textile wastewater in the air-aerated Fenton like system (Fig. 3b), the mineralization rate of the simulated wastewater in the open system was only 22%

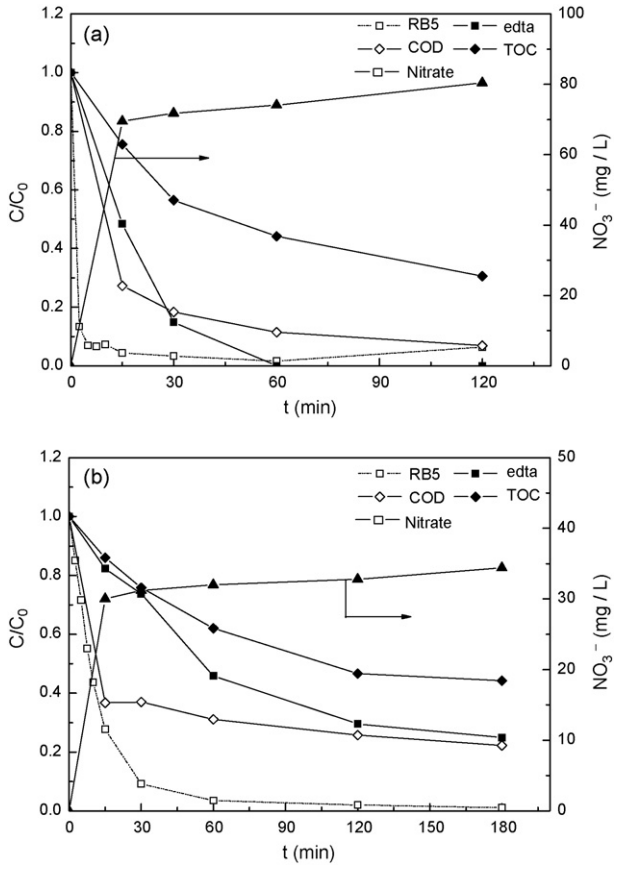


Fig. 6. Degradation of the simulated textile wastewater in two external energy combined Fenton like systems (a) Ultrasound (b) Ultraviolet. Initial parameters were ZVI 25 g/L, RB5 100 mg/L, EDTA 0.4 mM and air 1 L min^{-1}.

at the end of the reaction. The low degradation efficiency suggested much slower production of H_2O_2 as compared with the air purging system, which was caused by much slow recovery of dissolved oxygen (DO) in the open system (without air purging).

The Fenton like system under pure oxygen gas purging was also investigated. Despite the production of more abundant dioxygen, slight inhibition on both decolorization of RB5 and degradation of EDTA was observed in the pure oxygen purging system as compared with the air purging system. Due to rapid accumulation of iron oxides in pure oxygen atmosphere, deactivation of ZVI surface occurred, which may inhibit the release of ferrous into the bulk solution.

3.3. Degradation of the simulated textile wastewater in the Fenton like system with external energy

External energy such as Ultrasound and Ultraviolet could lead to enhancement of degradation efficiency after it was introduced to Fenton system [24,25]. Thus, the system with combination of external energy—US or UV was developed, respectively, to treat the textile wastewater. As shown in Fig. 6(a), US had significant enhancement on the Fenton like system. In the US/Fenton like system, RB5 was decolorized rapidly within the initial 5 min with 86.6% of RB5 removed at 2.5 min. The improvement in EDTA degradation was also significant. After 60 min reaction, EDTA concentration in the wastewater was detected below limit indicating complete removal of EDTA. The mineralization degree of the wastewater was also improved with 93.9% and 70.0% removal of COD and TOC achieved at 120 min, respectively. Besides, the result of released nitrate could also support the synergistic improvement by US irradiation. At the end of the reaction, 80.2 mg/L nitrate, i.e. 98.2% of the initial theoretical nitrogen was released indicating highly efficient treatment of the textile wastewater in the US/Fenton like system. US is thus identified as a useful approach for the enhancement of the Fenton like system in treating textile wastewater.

However, as shown in Fig. 6(b), slight inhibition of degradation of the wastewater was found in a UV combined Fenton like system. The degradation curves of RB5 and EDTA in the UV/Fenton like system were similar to those in the Fenton like system. One of the inhibitions could partially ascribe to the effect of hydraulic condition in the UV/Fenton like system. In the presence of a centered UV light tube, the mixing of ZVI with the solution was not as good as in the Fenton like system. Another inhibition may come from high color of the textile wastewater, which can abate the utilization of UV light. In addition, since H_2O_2 was self-produced in the Fenton like system, the reaction of O_2 activation (Eq. (4)) is rate-limited. Therefore, it can be concluded that UV light could not improve the degradation efficiency of the Fenton like system.

4. Conclusion

In the present study, a novel low-cost heterogeneous Fenton-like system, employing only Zero Valent Iron under air aeration, was developed for degradation of the simulated textile wastewater composed of azo dye – Reactive Black 5 and chelating agent – EDTA. Through a series of iron-EDTA ligands reactions, H_2O_2 was self-produced in this system by dioxygen activation. The main conclusions can be made as follows:

(1) In the Fenton like system, rapid decolorization of the simulated textile wastewater as well as complete degradation of EDTA were achieved after 3 h reaction. Removals of 68.6% TOC and 92.2% COD were also accomplished, indicating good mineralization of the organics in the wastewater. Furthermore, it is interesting to note that the reaction was conducted at a neutral pH circumstance implying the commercialization potential of the system.
(2) The effect of some reactants and operating parameters such as initial concentration of RB5 and EDTA, Zero Valent Iron loading, solution pH and atmosphere of the reaction were investigated. It demonstrated that EDTA and ZVI play important roles in the degradation of the simulated textile wastewater. Compared to the neutral Fenton like system, obvious inhibition of reaction was found in the acidic Fenton like systems. At pH of the system below 2, mineralization of the organics in the wastewater was almost inhibited completely. It was demonstrated that supply of sufficient dioxygen in this system is necessary because automatic recovery of dissolve oxygen from air could not meet the oxygen demand.
(3) Two types of external energy—Ultrasound and Ultraviolet were introduced into the Fenton like system, respectively, and the effect of the external energies on the degradation of the wastewater was assessed. Ultrasound presented significant synergistic improvement on both the decolorization rate of the wastewater and degradation rate of EDTA. Increased mineralization degree of the wastewater and complete release of nitrate further proved the improvement from US on the Fenton like system. In contrast, Ultraviolet light presented slight inhibition on degradation of the wastewater in the Fenton like system.
(4) Fe/EDTA system presents an effective approach to completely break down the recalcitrant macromolecular organics such as the recalcitrant azo dye. The release of nitrate together with high removal of TOC indicates that sufficient degradation of

toxic and recalcitrant azo dye molecule has been achieved. Afterwards, it would become easy and feasible to adopt subsequent conventional treatment process such as biological process for conversion of nitrate and further removal of organics.

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