Degradation of C.I. Acid Orange 7 by ultrasound enhanced heterogeneous Fenton-like process

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ABSTRACT

The effect of ultrasonic power density, goethite addition, hydrogen peroxide concentration, initial pH, hydroxyl radical scavenger, and initial dye concentration on the decolorization of C.I. Acid Orange 7 by ultrasound/goethite/H_2O_2 process was investigated. The results showed that the decolorization rate increased with power density, goethite addition, and hydrogen peroxide concentration, but decreased with the increase of initial dye concentration. The ultrasonic power density, goethite addition, and initial dye concentration have little effect on decolorization efficiency after 30 min reaction, while the increase of hydrogen peroxide concentration results in the increase of decolorization efficiency. There existed an optimal initial pH to achieve the highest decololrization rate and decolorization efficiency. The presence of hydroxyl radical scavenger would inhibit the decolorization reaction. Only less than half of total organic carbon (TOC) was removed after 90 min reaction, indicating more aggressive conditions are required to achieve the complete mineralization than those employed to simply break the chromophore group.

1. Introduction

Recently, more and more attention has been paid to the use of ultrasonic irradiation in the treatment of dye wastewater [1]. During ultrasonic irradiation, the collapse of cavitation bubbles leads to localized high temperatures and pressures, which allows the formation of oxidizing species such as hydroxyl radicals ($^{\bullet}OH$), hydrogen radicals ($H^{\bullet}$), hydroperoxyl radicals ($HO_2^{\bullet}$) and hydrogen peroxide [1–3]. As a result, organic pollutants can be degraded in the cavitation bubbles, at the bubble/water interface, or in the bulk solution that depends strongly on the nature of the organics [2]. Hydrophilic compounds with a low vapor pressure such as azo dyes are destroyed by oxidative degradation in the bulk liquid [1,2]. Although several studies have reported the beneficial use of ultrasonic irradiation for the decolorization of various textile dyes, the total mineralization of these complex compounds is difficult to obtain with ultrasound alone [1]. In addition, the cost of sonochemical oxidation is comparable to incineration based on economic analysis [4]. For these reasons the combination of ultrasound with advanced oxidation processes is a more convenient approach in the degradation of textile dyes [1,4]. The promising results have been reported when the coupling of Fenton's reagent with ultrasonic irradiation (named sono-Fenton process) was used to the decomposition of chlorinated aromatic hydrocarbons [5], endocrine disruptors [6,7], anionic surfactants [8], 2,4-dinitrophenol [9], EDTA [10], MTBE [11], and dyes [12,13]. Like classical Fenton process, the use of homogeneous iron catalysts leads to the ferric hydroxide sludge during neutralization stage of sono-Fenton process, which requires additional separation and disposal [3]. To overcome this drawback, heterogeneous catalysts were used as an alternative to conventional homogeneous catalysts [14]. When heterogeneous Fenton process is combined with ultrasound, the active catalyst surface area would increase, and cavitation bubble formation would be promoted [15]. Therefore, ultrasound enhanced heterogeneous Fenton-like process was proposed recently where CuO [2,15], Cu/Al_2O_3 [15], $CuO \cdot ZnO/Al_2O_3$ [15], iron powder [16–19], Fe_2O_3/SBA-15 [3,20], a mixed (Al–Fe) pillared clay (FAZA) [21] and goethite [3,4,22] was employed as heterogeneous catalysts. Among these catalysts, goethite is the most abundant crystalline iron oxide mineral in nature [23], which can be used repeatedly without losing its catalytic activity [22]. To our knowledge, only Muruganandham et al. [4] studied the decolorization of azo dye by ultrasound/goethite/H_2O_2 process with focus on the effect of ultrasonic irradiation on the catalytic activity and stability of goethite powder. Therefore, in this study, C.I. Acid Orange 7, as a model azo dye, was treated by ultrasound enhanced Fenton-like process using goethite as catalyst. The effects of operating conditions such as ultrasonic power density, goethite addition, hydrogen peroxide concentration, initial pH, hydroxyl radical scavenger, and initial dye concentration on color removal were investigated. The mineralization of C.I. Acid Orange 7 in terms of total organic carbon (TOC) removal was also explored.

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2. Materials and methods

2.1. Materials

C.I. Acid Orange 7 (sodium 4-(2-hydroxy-1-naphthylazo) benzenesulfonate) was purchased from Shanghai No. 3 Reagent Factory (China) and used as received. Hydrogen peroxide (analytical grade, 30%, w/w) was obtained from Shanghai Shiyi Chemicals Reagent Co. Ltd. (China). Goethite was prepared by dissolving 50 g $FeSO_4 \cdot 7H_2O$ into 600 ml distilled water. The solution was adjusted to pH 9–10 by adding about 200 ml NaOH solution (2 mol l^{-1}) and the stirring was provide during the addition. After $Fe(OH)_2$ precipitate was produced, it was settled down for 24 h. Then the supernatant was removed and 50 g $FeSO_4 \cdot 7H_2O$ was applied again. Distilled water was added till the whole volume reached 800 ml. The mixture was adjusted to pH 4–5 by adding H_2SO_4, and then placed in water bath with the temperature of around 40 °C for 2.5–3 h. The air was bubbled into the mixture and 20 ml H_2O_2 soultion (10%) was dripped to shorten the ageing step. The formed orange precipitate was goethite, which was dried around 100 °C after vacuum filtering.

2.2. Methods

The experimental set-up (Fig. 1) was similar to that in our previous study [24]. A stock solution of C.I. Acid Orange 7 was prepared fresh with de-ionized water before each run. Sulphuric acid or sodium hydroxide was used to adjust the initial pH (pH_0) of the dye solution. After 250 ml stock solution was fed into a 300 ml reactor, a given amount of hydrogen peroxide and goethite was added into the reactor. A magnetic stirrer provided complete mixing of the solution in the reactor. Sonication was performed with a KS-250 ultrasonic generator (250 W, 20 kHz, Ninbo Kesheng Instrument Co., China) equipped with a titanium probe transducer. The tip of the probe was 1 cm in diameter and was placed 3 cm into the liquid layer. The sonication was administered in a pulse mode of 2.5 s on and 2.1 s off. The acoustic power (P) was determined calorimetrically [25]. The reactor was immersed into a water bath to keep the temperature around 20 °C. At different time intervals, samples were removed by syringe and filtered through 0.45 μm membranes. The dye's maximum absorption wavelength was measured at 485 nm using a Shimadzu UV-1700 spectrophotometer. Total organic carbon was determined using an Analytik Jena AG multi N/C® 2100 TOC analyzer. The concentration of hydrogen peroxide was analyzed using a titanium sulfate spectrophotometric method [26]. Ferrous iron was determined using a 1,10-phenanthroline colorimetric method [27].
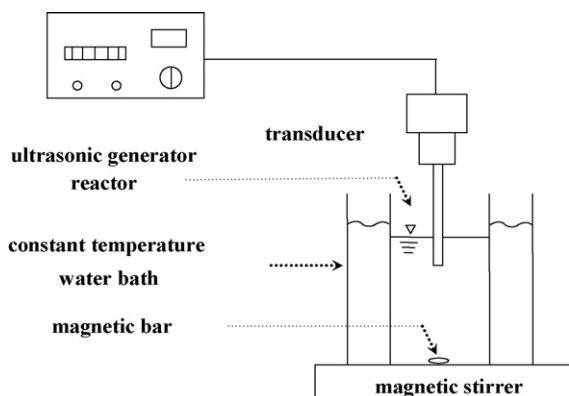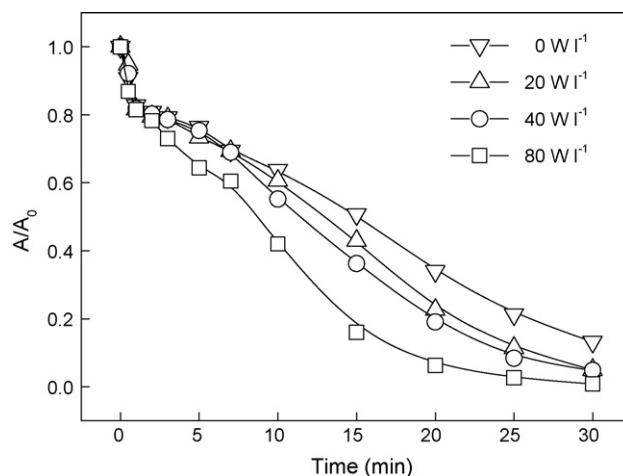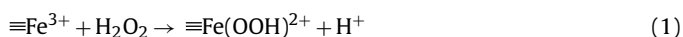

Fig. 1. Experimental set-up.

Fig. 2. The effect of power density on the decolorization ($C_0 = 79.5$ mg l^{-1}, [FeOOH] = 0.2 g l^{-1}, [H_2O_2] = 7.77 mmol l^{-1}, pH_0 3).
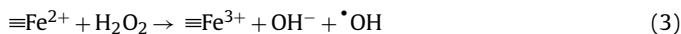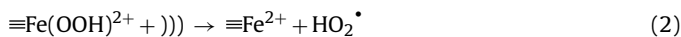
3. Results and discussion

3.1. The effect of power density on the decolorization of C.I. Acid Orange 7

Blank experiments were first conducted to observe ultrasound, hydrogen peroxide, and goethite effects on the decolorization independently. Color removal was negligible in the presence of 80 W l^{-1} ultrasound, 7.77 mmol l^{-1} hydrogen peroxide, or 0.2 g l^{-1} goethite alone (data not shown). Due to the non-volatile and hydrophilic nature of the azo dyes, decolorization would occur mainly at the interface of cavitation bubbles or in the bulk solution via a radical reaction rather than inside of the bubbles via a pyrolytic reaction. While at 20 kHz frequency, the production of hydroxyl radicals in the bulk liquid was too low to affect the decolorization of C.I. Acid Orange 7 [28]. Also, the limit oxidizing power of hydrogen peroxide ($E^0 = 1.78$ V) means that no significant color removal could be achieved by hydrogen peroxide alone. Although C.I. Acid Orange 7 was observed to be adsorbed by goethite when mixed overnight [29], color removal was not pronounced in this study. This may result from the low goethite addition, the short contact time, and the different properties of goethite used. Further blank experiments indicated that the decolorization was not significant after 30 min reaction even if ultrasound was combined with hydrogen peroxide or goethite (data not shown). As a result of the high water solubility and low volatility, hydrogen peroxide may be mainly present not inside the cavitation bubbles but in the bulk solution. The sonolytic decomposition of hydrogen peroxide, therefore, would be too slow, although the dissociation energy of the O–O bond (213 kJ mol^{-1}) in hydrogen peroxide is less than that of the O–H bond (418 kJ mol^{-1}) in water [2–4]. The combination of ultrasound and goethite could not lead to the significant color removal, indicating the enhancement was not strong enough to affect the decolorization though the presence of solid catalyst provided addition nuclei for the cavitation phenomena [3].

The heterogeneous Fenton-like process with or without ultrasonic irradiation could achieve fast color removal, and the presence of ultrasonic irradiation could improve the decolorization rate (Fig. 2). The oxidation of azo dyes would take place on the surface of goethite [4], where the symbol ≡ represents the iron species bound to the surface of the catalyst and))) indicates ultrasonic irradiation.

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe(OOH)^{2+} + H^+ \qquad (1)$$

$$\equiv Fe(OOH)^{2+} +))) \rightarrow \equiv Fe^{2+} + HO_2^{\bullet} \tag{2}$$

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

In the meantime, decolorization may result from homogeneous Fenton oxidation in the bulk solution via the reaction of hydrogen peroxide and the dissolved ferrous ion [30]. To investigate the contribution of homogeneous oxidation to the decolorization, a separate experiment was conducted using ferrous ion as catalyst. Ferrous ion concentration was selected as $0.86\,mg\,l^{-1}$ which was detected in the aqueous medium after 30 min sonication under the identical conditions of decolorization at $0.3\,g\,l^{-1}$ of goethite addition. The rest of reaction conditions were kept constant to those used in the heterogeneous Fenton process. Color removal after 30 min reaction was only 11.6% compared with >99% of total decolorization efficiency, indicating the low contribution of dissolved iron on the decolorization in this oxidation system and under the specified reaction conditions. Melero et al. [3] also observed the total phenol removal was over 99.5% by a heterogeneous ultrasound/Fe-SBA-15/H_2O_2 process whereas the contribution of homogeneous catalytic process was as low as 5%.

Since the decolorization was mainly through the heterogeneous Fenton reaction in this study, and the limiting step in Fenton reactions is the low kinetic rate of $\equiv Fe^{3+}$ reduction to $\equiv Fe^{2+}$ mediated by the formation of $\equiv Fe(OOH)^{2+}$ complex, the dissociation of this complex to reduced $\equiv Fe^{2+}$ and $HO_2^{\bullet}$ radicals can be improved by sonication (Reaction (2)) [20]. This is one reason that the efficiency of this heterogeneous Fenton-like process system for decolorization of C.I. Acid Orange 7 was enhanced by ultrasound as compared with the silent process. The monitoring of residual hydrogen peroxide illustrated that hydrogen peroxide decomposed faster in the presence of ultrasonic irradiation than in the absence of ultrasonic irradiation (data not shown). This is in agreement with the result observed by Neppolian et al. [22]. In the meantime time, the heterogeneous reaction between hydrogen peroxide and goethite would be influenced by the reactive surface of catalyst and mass transfer of solute reagents to and from the solid particles. When cavitation bubble implodes symmetrically, microstreaming was formed [31]. This phenomenon resulted in the enhanced mixing in the case of metal–liquid interfaces [17] and the continuous cleaning of iron powder for further surface reactions [22].

The increase in ultrasonic power would increase the mixing intensity due to the turbulence generated by cavitational bubble collapse [22] as well as microstreaming. Since the heterogeneous reaction would be enhanced with the increasing ultrasonic power, the decolorization rate would increase in consequence, as can be seen in Fig. 2. However, the final decolorization efficiency under three power densities was higher than 95%. This indicated that ultrasonic irradiation would only affect the generation rate of hydroxyl radicals. The amount of hydroxyl radicals generated was only dependent on hydrogen peroxide concentration. At the same hydrogen peroxide concentration, decolorization efficiency was almost the same despite that the decolorization rate increased with the increasing power density.

3.2. The effect of goethite addition on the decolorization of C.I. Acid Orange 7

Fig. 3 displays decolorization of C.I. Acid Orange 7 at different goethite additions when initial dye concentration is $79.5\,mg\,l^{-1}$, hydrogen peroxide concentration is $7.77\,mmol\,l^{-1}$, ultrasonic power density is $80\,W\,l^{-1}$, and the initial pH value is 3. It can be seen that the decolorization rate increased with goethite addition. The oxidation of azo dyes was mainly through heterogeneous Fenton reaction, which depends on the specific area of the catalyst. The increase of goethite addition corresponds to the higher
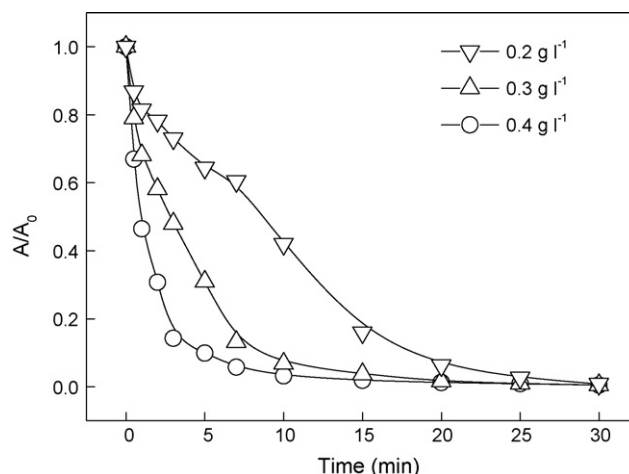

Fig. 3. The effect of goethite addition on the decolorization ($C_0 = 79.5\,mg\,l^{-1}$, $[H_2O_2] = 7.77\,mmol\,l^{-1}$, $P = 80\,W\,l^{-1}$, pH_0 3).

total area. This would result in the faster decomposition of hydrogen peroxide to generate hydroxyl radicals [22]. The monitoring of residual hydrogen peroxide illustrated that the decomposition rate of hydrogen peroxide increased with goethite addition (data not shown). This is in agreement with the result observed by Neppolian et al. when *para*-chlorobenzoic acid was degraded by ultrasound/goethite/H_2O_2 process [22]. Although the increase of goethite addition led to the increase of decolorization rate, the decolorization efficiency after 30 min reaction was nearly the same at the fixed hydrogen peroxide concentration, which was higher than 99% (Fig. 3). This is due to the fact that the amount of hydroxyl radicals generated was only dependent on hydrogen peroxide concentration, and $7.77\,mmol\,l^{-1}$ of hydrogen peroxide was sufficient to generate hydroxyl radicals when only decolorization was concerned.

3.3. The effect of hydrogen peroxide concentration on the decolorization of C.I. Acid Orange 7

Fig. 4 illustrates decolorization of C.I. Acid Orange 7 at different hydrogen peroxide concentrations when initial dye concentration is $79.5\,mg\,l^{-1}$, goethite addition is $0.3\,g\,l^{-1}$, ultrasonic power density is $80\,W\,l^{-1}$, and the initial pH value is 3. It can be seen that both of the decolorization rate and decolorization efficiency increased
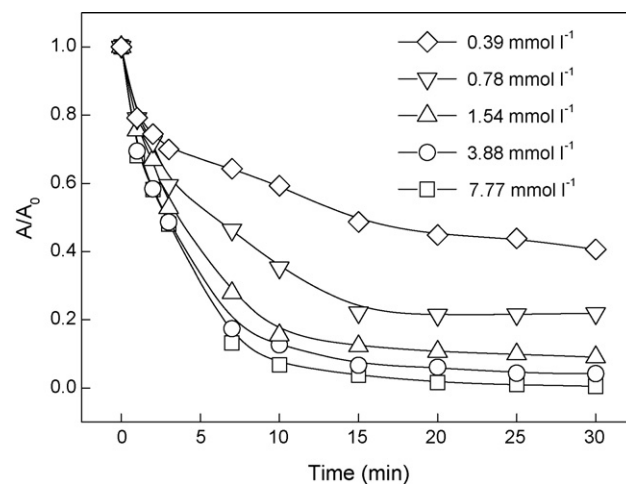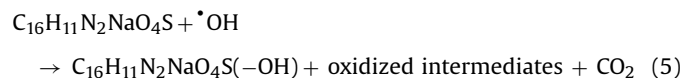

Fig. 4. The effect of hydrogen peroxide concentration on the decolorization ($C_0 = 79.5\,mg\,l^{-1}$, $[FeOOH] = 0.3\,g\,l^{-1}$, $P = 80\,W\,l^{-1}$, pH_0 3).

with hydrogen peroxide concentration. As discussed above, hydrogen peroxide was decomposed at the surface of goethite to generate hydroxyl radicals. The increase of hydrogen peroxide concentration would lead to more hydroxyl radicals produced. However, decolorization efficiency did not increase as much as hydrogen peroxide was applied. When hydrogen peroxide increased from 0.39 to 0.78 mmol l^{-1}, decolorization efficiency increased from 59.4% to 78.1%. Decolorization efficiency would rose to 90.9% when hydrogen peroxide reached to 1.54 mmol l^{-1}. Bur further increase in hydrogen peroxide resulted in an insignificant increase of color removal. Decolorization efficiencies were 95.8% and 99.5%, respectively when hydrogen peroxide concentrations were 3.88 and 7.77 mmol l^{-1}.

Feng et al. [32] proposed that the complete mineralization of C.I. Acid Orange 7 could be described by equation below,

$$C_{16}H_{11}N_2NaO_4S + 42H_2O_2$$
$$\rightarrow 16CO_2 + 46H_2O + 2HNO_3 + NaHSO_4 \quad (4)$$
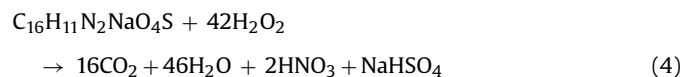
On the basis of this equation, 9.54 mmol l^{-1} of H$_2$O$_2$ are theoretically needed to completely degrade 79.5 mg l^{-1} of C.I. Acid Orange 7. But when only decolorization was concerned, the following mechanism could be suggested for the decomposition of C.I. Acid Orange 7, taking into account Eqs. (1)–(3) [33],

$$C_{16}H_{11}N_2NaO_4S + {}^{\bullet}OH$$
$$\rightarrow C_{16}H_{11}N_2NaO_4S(-OH) + \text{oxidized intermediates} + CO_2 \quad (5)$$

Then the amount of oxidants needs to decompose C.I. Acid Orange 7 (decolorization only) would be much less than that needed to complete mineralize C.I. Acid Orange 7. Over 90% decolorization efficiency was achieved when hydrogen peroxide concentration was only 1.54 mmol l^{-1}, compared with 9.54 mmol l^{-1} of hydrogen peroxide needed to total mineralization theoretically. However, the increase of hydrogen peroxide concentration would not lead to the increase of generated hydroxyl radicals to the same extent. For example, 68.1% of hydrogen peroxide (corresponding to 2.64 mmol l^{-1} of hydrogen peroxide) was decomposed after 30 min reaction at 3.88 mmol l^{-1} of hydrogen peroxide dosage, while only 37.1% of hydrogen peroxide (corresponding to 2.88 mmol l^{-1} of hydrogen peroxide) was decomposed when hydrogen peroxide dosage rose to 7.77 mmol l^{-1}. This means the amount of hydrogen peroxide decomposed to generate hydroxyl radicals increased only a little even if H$_2$O$_2$ dosage was doubled. Moreover, the undecomposed hydrogen peroxide may act as a hydroxyl radical scavenger resulting in the generation of hydroperoxy radicals that are less active than the hydroxyl radicals [20],

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2{}^{\bullet} + H_2O \quad (6)$$

Therefore, the decolorization efficiency increased insignificantly after hydrogen peroxide concentration reached 1.54 mmol l^{-1}.

3.4. The effect of initial pH on the decolorization of C.I. Acid Orange 7

The initial pH values investigated are 2, 3, 5, and 7, respectively when initial dye concentration is 79.5 mg l^{-1}, hydrogen peroxide concentration is 7.77 mmol l^{-1}, goethite addition is 0.3 g l^{-1}, and ultrasonic power density is 80 W l^{-1}. As can be seen in Fig. 5, both the decolorization rate and decolorization efficiency increased with the decrease of initial pH and reached the highest at pH$_0$ 3. This is in agreement with the classical Fenton reaction. However, color removal became worst when initial pH dropped to 2. The concentration of hydrogen ions would become very high at lower pH (<2.5), which may slow down the formation of ≡Fe(OOH)$^{2+}$ based on Reaction (1). The production rate of ≡Fe^{2+} and hydroxyl radicals would
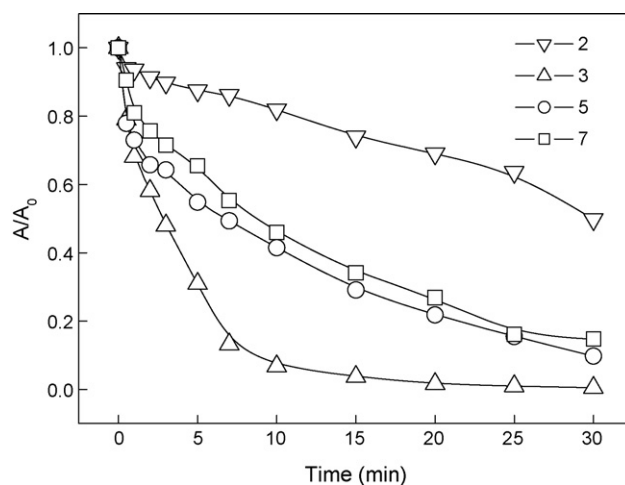

Fig. 5. The effect of initial pH on the decolorization ($C_0 = 79.5$ mg l^{-1}, [FeOOH] $= 0.3$ g l^{-1}, [H$_2$O$_2$] $= 7.77$ mmol l^{-1}, $P = 80$ W l^{-1}).

consecutively decrease as well [34]. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH [35],

$${}^{\bullet}OH + H^+ + e^- \rightarrow H_2O \quad (7)$$

where electrons may be gained from ferrous ions. Therefore the Fenton reaction would be retarded.

Unlike the conventional Fenton process, 85.3% of color removal was still obtained after 30 min reaction even if initial pH was as high as 7. He et al. also reported that azo dye Mordant Yellow 10 and aromatic compounds could be degraded in aqueous dispersions of goethite/H$_2$O$_2$ at neutral pH under UV irradiation [36,37], and dimethyl sulphoxide (DMSO) would also be oxidized by goethite/H$_2$O$_2$ at neutral pH [38].

In this study, the effect of pH on the decolorization was investigated without adding any buffer solution. He et al. observed that the carboxyl acids such as acetic acid were generated during photooxidation of azo dye in aqueous dispersions of goethite/H$_2$O$_2$ [36]. Therefore, it is expected that pH values would drop during the reaction in the absence of buffer solution. The final pH value decreased to 4.1 after 30 min reaction when initial pH was 7, and this value dropped to 3.9 at pH$_0$ 5. Drijvers et al. also observed that the solution became already slightly acidic after 15 min phenol was degraded by ultrasound/H$_2$O$_2$/CuO [2]. When initial pH decreased to 3 or less, the production of intermediates including carboxyl acids may not affect pH in the solution, and pH changed insignificantly during the reaction. The final pH values were 2.1 and 2.9, respectively when the initial pH values were 2 and 3.

3.5. The effect of hydroxyl radical scavenger on the decolorization of C.I. Acid Orange 7

The decolorization of C.I. Acid Orange 7 mainly occurs by goethite-catalyzed hydrogen peroxide decomposition resulting in the generation of hydroxyl radical, which would attack on the azo bond of C.I. Acid Orange 7. To investigate the dependence of the decolorization of C.I. Acid Orange 7 on hydroxyl radicals, the decolorization was carried out in the presence of carbonate, a widely known hydroxyl radical scavenger. Fig. 6 illustrated that the presence of carbonate decreased the decolorization rate and color removal was negligible when carbonate concentration reached 240.7 mg l^{-1}. This indicated that the main reactive species in this process are hydroxyl radicals. Muruganandham et al. [4] also observed t-butanol addition decreases the removal rate of Direct Orange 39 appreciably in the ultrasound/goethite/H$_2$O$_2$ system.
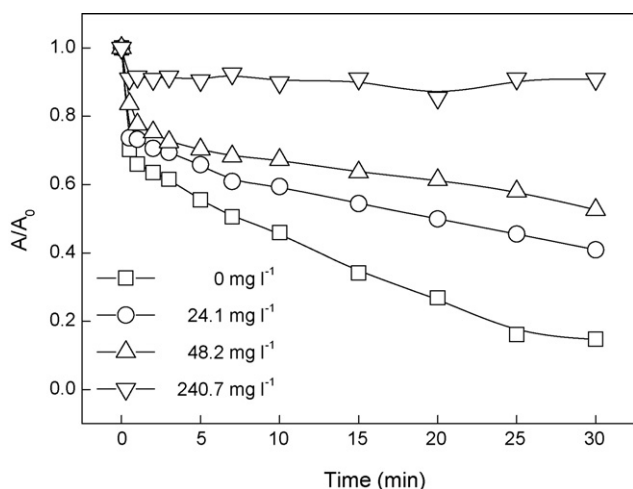
Fig. 6. The effect of hydroxyl radical scavenger on the decolorization ($C_0 = 79.5\,\mathrm{mg\,l^{-1}}$, $[\mathrm{FeOOH}] = 0.3\,\mathrm{g\,l^{-1}}$, $[\mathrm{H_2O_2}] = 7.77\,\mathrm{mmol\,l^{-1}}$, $P = 80\,\mathrm{W\,l^{-1}}$, $\mathrm{pH_0}$ 7).

3.6. The effect of initial dye concentration on the decolorization of C.I. Acid Orange 7

Fig. 7 depicts decolorization of C.I. Acid Orange 7 at different initial dye concentrations when hydrogen peroxide concentration is $7.77\,\mathrm{mmol\,l^{-1}}$, goethite addition is $0.3\,\mathrm{g\,l^{-1}}$, ultrasonic power density is $80\,\mathrm{W\,l^{-1}}$, and the initial pH value is 3. It can be seen that the decolorization rate decreased with the increase of the initial dye concentration. This behavior is one of the characteristics of advanced oxidation processes [39]. In the constant conditions of oxidation system such as hydrogen peroxide concentration, amount of goethite, etc., the hydroxyl radical formed in this process is also constant [22]. The increase of initial dye concentration would decrease the probability of reaction between azo dye molecules and the hydroxyl radicals [40]. In addition, the unspecific oxidation of all molecules especially major intermediates with hydroxyl radicals may lead to the side reactions and the competitive consumption of hydroxyl radicals [41]. Despite of the parallel consumption of hydroxyl radicals, color was nearly removed completely at different initial dye concentration, indicating hydroxyl radicals generated from goethite-catalyzed hydrogen peroxide decomposition was sufficient enough to oxidize C.I. Acid Orange 7 completely after 30 min reaction.
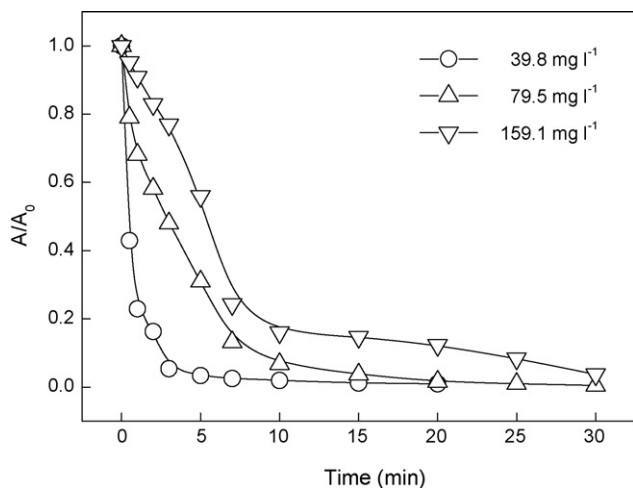

Fig. 7. The effect of initial dye concentration on the decolorization ($[\mathrm{FeOOH}] = 0.3\,\mathrm{g\,l^{-1}}$, $[\mathrm{H_2O_2}] = 7.77\,\mathrm{mmol\,l^{-1}}$, $P = 80\,\mathrm{W\,l^{-1}}$, $\mathrm{pH_0}$ 3).
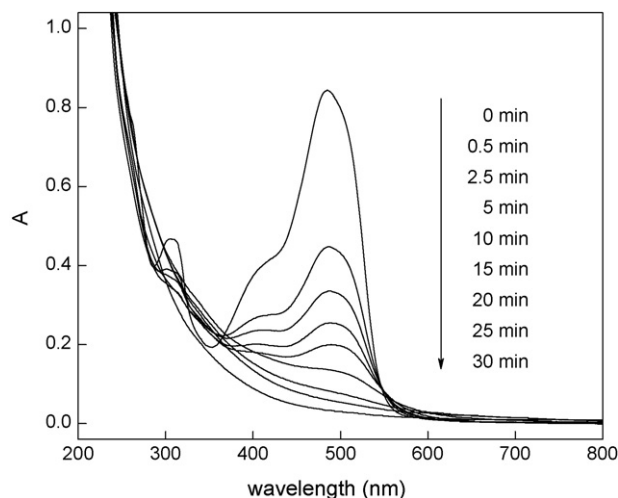
Fig. 8. UV–vis spectra changes with reaction time ($C_0 = 79.5\,\mathrm{mg\,l^{-1}}$, $[\mathrm{FeOOH}] = 0.3\,\mathrm{g\,l^{-1}}$, $[\mathrm{H_2O_2}] = 7.77\,\mathrm{mmol\,l^{-1}}$, $P = 80\,\mathrm{W\,l^{-1}}$, $\mathrm{pH_0}$ 3).

3.7. UV–visible spectra changes during the reaction

To clarify the changes in molecular and structural characteristics of C.I. Acid Orange 7 as a result of oxidation via ultrasound enhanced heterogeneous Fenton-like process, representative UV–visible (vis) spectra changes in the dye solution as a function of reaction time were observed and the corresponding spectra are shown in Fig. 8. As can be observed from these spectra, before the oxidation, the absorption spectrum of C.I. Acid Orange 7 in water was characterized by one main band in the visible region, with its maximum absorption at 484 nm and by the other band in the ultraviolet region located at 310 nm, respectively. The peaks at 310 nm were associated with "benzene-like" structures in the molecule, and that at 484 nm originated from an extended chromophore, comprising both aromatic rings, connected through the azo bond. The disappearance of the visible band with the time was due to the fragmentation of the azo links by oxidation [13]. In addition to this rapid decolorization effect, the decay of the absorbance at 310 nm was considered as evidence of aromatic fragment degradation in the dye molecule and its intermediates.

3.8. Mineralization of C.I. Acid Orange 7

It is known that complete decolorization of C.I. Acid Orange 7 does not mean that the dye is completely oxidized [33], and so the mineralization of C.I. Acid Orange 7 in terms of TOC removal was investigated. As can be seen in Fig. 9, the mineralization of C.I. Acid Orange 7 by ultrasound/goethite/$\mathrm{H_2O_2}$ process follows zero-order kinetics. This is in agreement with the result reported by He et al. when salicylic acid was mineralized by heterogeneous photo-Fenton process using goethite as catalyst [37]. However, only 42% TOC was removed even if the reaction time was as long as 90 min when initial dye concentration was $79.5\,\mathrm{mg\,l^{-1}}$, hydrogen peroxide concentration was $7.77\,\mathrm{mmol\,l^{-1}}$, goethite addition was $0.3\,\mathrm{g\,l^{-1}}$, ultrasonic power density was $80\,\mathrm{W\,l^{-1}}$, and the initial pH value was 3, while over 90% decolorization efficiency was achieved within 10 min reaction under the same conditions (Fig. 3). This is due to the fact that the intermediate products such as carboxyl acids are more difficult to oxidize than their parent compound (azo dye in this case), and complete oxidation proceeds at a much slower reaction rate [33]. Melero et al. observed a complete degradation of phenol and only 25.2% TOC removal in a ultrasound enhanced heterogeneous Fenton process when $\mathrm{Fe_2O_3/SBA}$-15 was use as catalyst and $\mathrm{H_2O_2}$ concentration was equivalent to two times of the
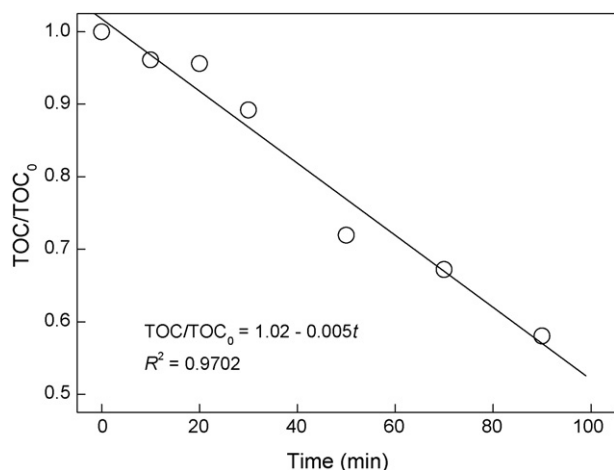
Fig. 9. The variation of TOC with reaction time ($C_0 = 79.5$ mg l^{-1}, [FeOOH] $= 0.3$ g l^{-1}, [H$_2$O$_2$] $= 7.77$ mmol l^{-1}, $P = 80$ W l^{-1}, pH$_0$ 3).

stoichiometric amount for a theoretical complete mineralization of phenol [3]. Molina et al. also reported the TOC removal ranged from 30% to 40% at the optimal hydrogen peroxide concentration of twice the stoichiometric amount for a theoretical complete mineralization of phenol, which represents a low oxidant dosage as compared with similar studies reported in the literature [20]. Therefore it could be expected that more aggressive conditions are required to achieve higher TOC removal than those employed to simply break the chromophore group [33].

4. Conclusion

This study shows that the combination of ultrasound and heterogeneous Fenton process can decolorize C.I. Acid Orange 7 effectively. The decolorization reaction mainly takes place on the surface of goethite, and homogeneous Fenton oxidation in the bulk solution via the reaction of hydrogen peroxide and the dissolved ferrous ion from goethite could be neglected. The decrease of initial dye concentration and the increase of ultrasonic power density, goethite addition, and hydrogen peroxide concentration favor the increase of decolorization rate. The ultrasonic power density, goethite addition, and initial dye concentration have little effect on decolorization efficiency after 30 min reaction. The increase of hydrogen peroxide concentration leads to the increase of decolorization efficiency. Both the decolorization rate and decolorization efficiency reaches highest at the optimal initial pH of 3. The presence of hydroxyl radical scavenger would hinder the decolorization reaction. More aggressive conditions are required to achieve higher TOC removal than those employed to simply break the chromophore group.

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