Journal of Molecular Catalysis A: Chemical 325 (2010) 79–83

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Photo-oxidation of Mordant Yellow 10 in aqueous dispersions of ferrihydrite and H_2O_2

Yan Wang, Yuchao Zhao, Yan Ma, Hui Liu*, Yu Wei*

School of Chemistry and Material Science, Key Laboratory of Inorganic Nanomaterial of Hebei Province, Hebei Normal University, Shijiazhuang 050016, China

ARTICLE INFO

Article history:
Received 10 February 2010
Accepted 31 March 2010
Available online 8 April 2010

Keywords:
Ferrihydrite
Hydrogen peroxide
Photo-oxidation
Azo dye

ABSTRACT

To investigate the effect of ferrihydrite on the degradation of azo dyes, Mordant Yellow 10 (MY10) was selected as a model azo dye. The photodegradation of MY10 was studied in the presence of both ferrihydrite and hydrogen peroxide under UV irradiation. The results showed that no degradation of MY10 was detected in the H_2O_2/UV system without ferrihydrite. When a small amount of ferrihydrite ($0.5\,g\,L^{-1}$) was introduced into the reaction system, it was found that the degradation of MY10 with H_2O_2 occurred even in the dark, and UV irradiation could significantly accelerate the degradation rate. Hydroxyl radicals ($^{\bullet}OH$) generated through the catalytic decomposition of H_2O_2 by ferrihydrite play a major role in the oxidation of MY10. In addition, the effect of key operating parameters such as initial pH of the solutions, initial concentration of H_2O_2 and temperature was studied on the photo-oxidation of the dye. The results indicated that the degradation rates increase with decreasing initial pH values (from 9 to 3) and increasing concentration of H_2O_2 (from 1 to 5 mM) and temperature (from 288 to 318 K).

1. Introduction

Azo compounds account for over 60% of the total number of dye structures known. Salicylic acid derivatives of mordant azo dyes are numerically predominant and used mainly for yellow and orange hues. These dyes are non-biodegradable and show a relatively high persistence in soils and aquatic systems [1,2]. As such, researchers have tried to find various technologies to degrade these organic pollutants. It is well known that degradation of organic compounds, e.g. azo dyes, may be facilitated by oxidative processes. Two types of oxidation processes which are often used in water cleaning are photochemical degradation by use of UV, e.g. in the presence of a suitable catalyst, such as TiO_2, and chemical oxidation via O_3, O_3/H_2O_2 and Fenton's reagent [3–6]. Both types of process, generally referred to as advanced oxidation processes (AOPs), are based on in situ generation of reactive chemical species, such as hydroxyl radicals ($^{\bullet}OH$), which can oxidize almost all the organic substances, owing to their high oxidation potential ($E^0 = 2.80\,V$) [7].

It is noticeable that heterogeneous catalytic processes at mineral surfaces can be vitally important for the degradation of organic pollutants in surface soil and water [8,9]. Ferrihydrite is a natural mineral and existed in the earth's crust in great quantities. It has been found that ferrihydrite can catalyze the decomposition of hydrogen peroxide. The heterogeneous catalytic decomposition reaction of H_2O_2 with ferrihydrite in aqueous solution is an important reaction for the environment since both H_2O_2 and ferrihydrite are common constituents of natural and atmospheric waters [10]. Our group has explored the transformation from ferrihydrite to various iron (hydr)oxides such as hematite, goethite lepidocrocite and magnetite [11–13]. Based on previously published work and our own research, we have explored a new approach for the oxidative degradation of organic pollutants in aqueous solutions mediated by hydrogen peroxide in the presence of ferrihydrite. We have found that ferrihydrite can catalyze the degradation of azo dye Mordant Yellow 10 (MY10) when a trace of H_2O_2 is introduced. Ultraviolet radiation further increased the degradation rate though MY10 does not undergo any degradation in the H_2O_2/UV system without ferrihydrite. The aim of the present work was to examine the oxidation of Mordant Yellow 10, under abiotic conditions, in the presence of ferrihydrite and traces of H_2O_2, and specifically to elucidate the role of ferrihydrite in the reaction. At the same time, we have also investigated the effect of the initial concentration of H_2O_2, environmental pH value and temperature on the photoreaction.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium hydroxide (NaOH) of analytical purity and distilled water were used. The ferric salt solutions were filtered through a 0.22 μm Millipore filter

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* Corresponding authors. Tel.: +86 311 86268342.
E-mail addresses: liuhuicn@126.com (H. Liu), weiyu@mail.hebtu.edu.cn (Y. Wei).

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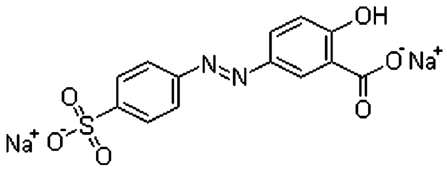
doi:10.1016/j.molcata.2010.03.037

to remove any particulate contaminants. MY10 was of guaranteed reagent grade and H_2O_2 was of analytical reagent grade. They were used without further purification.

Ferrihydrite was prepared by the following procedures. NaOH solution (6.0 M) was added into 25 mL of ferric chloride solution (2.0 M) via peristaltic pump under stirring until pH 7. The agitation was continued for an additional 30 min until the pH was adjusted to a stable one by adding NaOH (1.0 M). At the same time the total volume of the system was adjusted to 100 mL. In this system, a gel-like deposit was formed. The product was filtered and washed thoroughly with distilled water and then dried at about 40 °C [12].

For reference, the structure of MY10 is shown below.



2.2. Methods and apparatus

An 8 W ultraviolet lamp was used as the irradiation source. Aqueous ferrihydrite dispersions were prepared by the addition of 0.1 g ferrihydrite powder to 200 mL of Mordant Yellow 10 (0.2 mM) solution.

Prior to irradiation, the suspension was magnetically stirred in the dark for 60 min to establish the adsorption/desorption equilibrium between MY10 and the ferrihydrite particles. H_2O_2 was added to the reaction vessel at the beginning of the irradiation. The suspension was stirred before and throughout the experiment. At given irradiation time intervals, about 10 mL aliquots were sampled, centrifuged, and subsequently filtered through a 0.22 μm Millipore filter to remove ferrihydrite. The concentrations of MY10 in the filtrates were measured by a UV-Visible spectrophotometer (UV–vis 752 Dongxing, Hangzhou) at a wavelength of 354 nm. Total organic carbon (TOC) analysis was carried out by means of a Shimadzu TOC-V CPH total organic carbon analyzer. Following the method described in Ref. [14], the infrared (IR) spectrum (FTIR-8900 Fourier transform IR spectroscopy) was used to monitor the course of the photo-induced conversion of MY10 under UV irradiation in ferrihydrite/H_2O_2 dispersion as a function of time. The spectra were acquired over the range 4000 and 400 cm^{-1}.

2.3. Determination of the adsorption isotherm

The adsorption of MY10 on the ferrihydrite was determined by performing a batch experiment in the dark. A fixed amount of the ferrihydrite (0.025 g) was added to 50 mL of MY10, with various concentrations, in Pyrex cylindrical reactor vessel. These were agitated for 1 h and maintained at different temperatures, from 288 to 318 K, by recirculating water. The concentrations of MY10 were measured by the UV–vis spectrometer and the amount of MY10 adsorbed on the ferrihydrite was calculated based on the mass balance.

The total dissolved iron concentration was determined spectrophotometrically by the phenanthroline method [15]. The total iron concentration in solution was determined after reducing Fe(III) ions to Fe(II) with hydroxylamine.

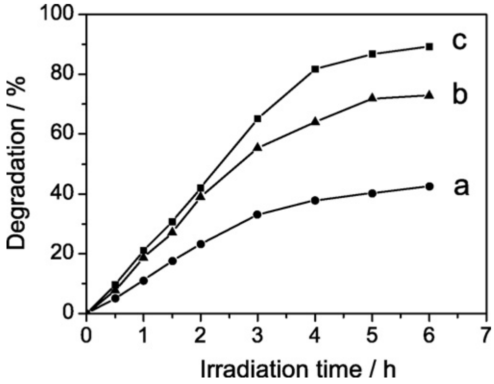


Fig. 1. The degradation rate of MY10 vs. time. (a) Adding 0.5 g L^{-1} of ferrihydrite and UV light irradiation, (b) in the presence of 0.5 g L^{-1} of ferrihydrite and 3 mM of H_2O_2 in the dark, and (c) in the presence of 0.5 g L^{-1} of ferrihydrite and 3 mM of H_2O_2 and UV light irradiation.

3. Results and discussion

3.1. Degradation of MY10 in the presence of ferrihydrite

It has been reported that some organic pollutants such as azo dyes can be photodegraded by γ-FeOOH and zerovalent iron [16,17]. To investigate the catalytic action of ferrihydrite on the degradation of MY10, four control experiments were designed. The first one was a blank experiment without ferrihydrite, in which the degradation process was carried out under UV light and in the presence of H_2O_2 (3 mM) only. Table 1 presents the changes of TOC and the concentrations of MY10 as a function of reaction time. The results showed that no degradation of MY10 was observed over several hours of irradiation, which meant that the combination of UV and H_2O_2 was ineffective. The reason for this is thought to be the fact that the photodegradation reaction was performed in a higher concentration of H_2O_2. Zhen et al. [18] had reported the treatment of nitrogen-based waste dye water with UV/H_2O_2. The concentrations of H_2O_2 used in their reaction system were much higher than ours, the smallest being 16 mM.

The other control experiments were carried out in the presence of ferrihydrite and the results are illustrated in Fig. 1. In the second experiment, about 42% of MY10 was degraded in a ferrihydrite dispersion under UV irradiation (Fig. 1a). It has been reported that the light-induced degradation of organic compounds occurs under UV irradiation in dispersions of acidic iron oxide [19,20]. For the third control experiment, more than 70% of MY10 was degraded in the presence of a ferrihydrite/H_2O_2 dispersion in the dark (Fig. 1b) for 6 h. However, the rate of degradation was higher using otherwise identical conditions as Fig. 1b but with illumination by UV light (Fig. 1c), representing the fourth control experiment. These results indicate, on the one hand, that ferrihydrite is an obvious photocatalyst and on the other hand, that the combination of ferrihydrite, H_2O_2 and UV light provides the most effective conditions for the degradation of MY10. Therefore, this reaction system

Table 1
Degradation of MY10 in the presence of H_2O_2 under UV light irradiation.

	Irradiation time/h							
	0	0.5	1	2	3	4	5	6
$C/\times10^{-4}$ M	1.00	1.00	1.00	1.00	1.01	1.01	1.01	1.01
TOC/ppm	80.00	81.46	79.32	81.14	82.32	81.77	83.19	84.02

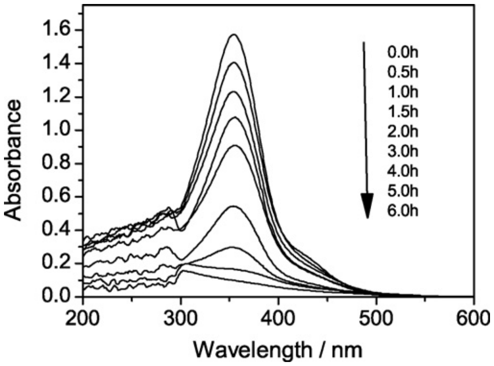


Fig. 2. The UV–vis absorption spectra for MY10 (0.2 mM) in H_2O_2 (3 mM)/ ferrihydrite (0.5 g L^{-1}) dispersion under UV irradiation at initial pH 3.

was chosen for investigation in the present paper. According to the literature [19], ferrihydrite can catalyze the decomposition of H_2O_2 during which hydroxyl radicals ($^\bullet$OH) appear. Based on the above analysis, we deduce that the cooperation of ferrihydrite and H_2O_2 leads to the formation of a large concentration of hydroxyl radicals ($^\bullet$OH) and the UV irradiation further accelerates this process.

The changes in the UV–vis spectra during the degradation of MY10 in the presence of ferrihydrite and H_2O_2 under UV light irradiation at pH 3 are displayed in Fig. 2. MY10 shows that the maximum absorption band is at 354 nm. With time, the absorption peak weakened and disappeared, illustrating the degradation of MY10. No new absorption bands appeared, either in the visible and ultraviolet regions indicating the destruction of the conjugated structure.

To verify that MY10 had not simply lost its color, a TOC analysis was performed. TOC values reflect the amount of organics in the solution, and therefore, the changes in TOC mirror the degree of degradation of an organic substrate. Fig. 3 shows the photodegradation of MY10 and the changes in TOC. About 90% of MY10 disappeared after 6 h of irradiation and a rapid decrease (40%) in the TOC was observed in the first 2 h, after which the rate of TOC removal slowed down with further irradiation. We can observe directly from this result that mineralization of MY10 accompanies the destruction of the chromophore of MY10.

IR spectroscopy was also used to monitor the evolution of the photo-induced conversion of MY10 under UV irradiation in ferrihydrite/H_2O_2 dispersions (Fig. 4) and to provide evidence for the photo-oxidation pathway. The assignments for the principal bands in the IR spectra of MY10 (before irradiation) at 1500–1670 cm^{-1} correspond to aromatic ring vibration. Vibration of the p-substituted aromatic ring is also the origin of bands at 860 cm^{-1}. The bands at 1120–1140 and 620 cm^{-1} are caused by the vibration in the $-SO_3$ group. In addition, a strong band at 1450 cm^{-1} confirms the presence of the –N=N– group.

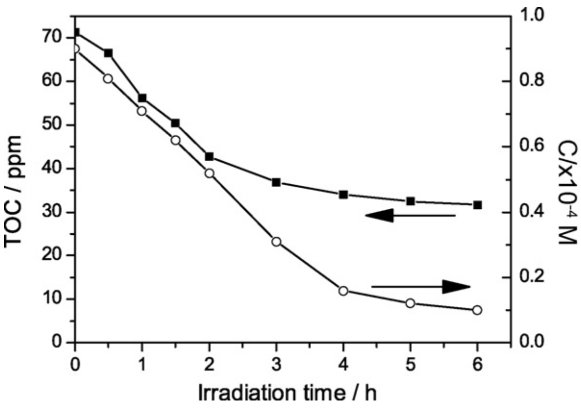


Fig. 3. The changes of TOC and the concentration of MY10 during the degradation process in the presence of H_2O_2 (3 mM) and ferrihydrite(0.5 g L^{-1}) at pH 3.

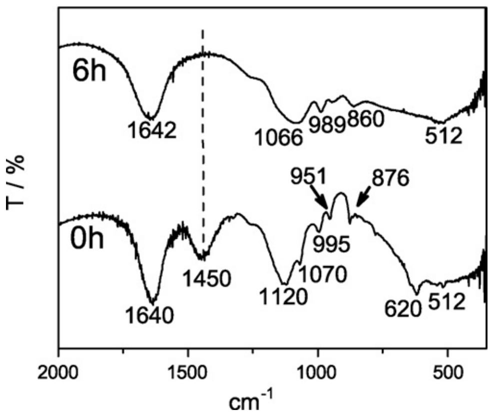


Fig. 4. IR spectra of the samples obtained at different irradiation times. (a) 0 h and (b) 6 h.

During the photo-oxidation, the characteristic bands of the –N=N– vibration disappeared after about 6 h irradiation. The characteristic bands of the $-SO_3$ group at 1120–1140 cm^{-1} became weaker and the band at 620 cm^{-1} disappeared after about 6 h irradiation. The IR results also indicate convincingly that the conjugated chromophore structure of MY10 is destroyed under UV irradiation in aqueous ferrihydrite/H_2O_2 dispersions.

3.2. The effect of pH

To choose an optimum pH for the degradation of MY10, a set of experiments was carried out at different pH values. To ensure the establishment of adsorption/desorption equilibrium, the ferrihydrite/MY10 dispersion was stirred in the dark for 60 min before UV irradiation. Fig. 5 shows the changes in absorbance with stirring time in the dark. It was found that ferrihydrite particles adsorbed more MY10 in acid media (pH 3.0) than in neutral and alkaline solutions (pH 7.0 and 9.0). The effect of solution pH in the range of 3–9 on the degradation of MY10 versus time is presented in Fig. 6. As can be seen, the degradation rate of MY10 was more rapid in acidic media (pH 3.0), with MY10 (0.2 mM) both in the bulk solution and on the particle surface being largely decomposed within 6 h. About 50% of the MY10 was degraded under UV irradiation in a ferrihydrite/H_2O_2 system at a neutral pH and less 30% in weak alkaline conditions. It is apparent that the rate of degradation is pH dependent and the activity decreases with increasing pH value. Since the point of zero charge (PZC) of ferrihydrite is 7.9–9.2, a lower

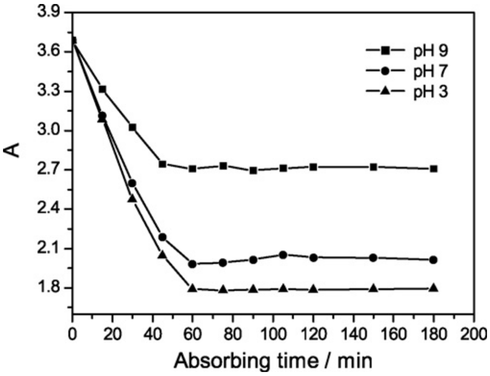


Fig. 5. The effect of initial pH on the adsorption of MY10 on ferrihydrite at 288 K.

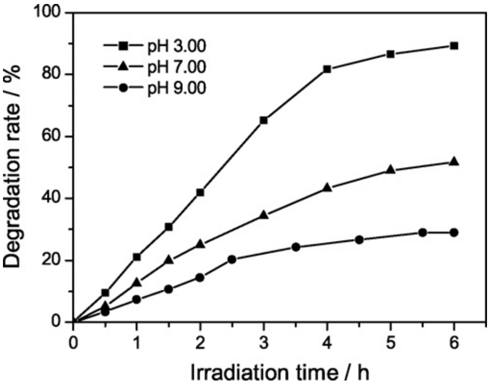


Fig. 6. The degradation of MY10 under different initial pH values in the presence of H_2O_2 (3 mM) and ferrihydrite (0.5 g L^{-1}) under UV irradiation at 288 K.

pH value causes the surface to be positively charged, which favors adsorption of the anionic dye MY10. Barreiro et al. [19] have also reported that the rate of organic compound oxidation is strongly dependent on pH, with a sharp increase in the oxidation rate from pH 3 to 4. Based on data from the literature and the results in Fig. 6, the most acidic pH (pH 3) was chosen in subsequent experiments.

3.3. *The effect of initial concentration of H_2O_2*

The initial concentration of H_2O_2 should be a key factor affecting the photodegradation of MY10 in the ferrihydrite/H_2O_2 system. To investigate the effect of the initial concentration of H_2O_2 on the photodegradation of MY10, a set of experiments were carried out with initial concentrations varying from 1 to 5 mM in the presence of MY10 and ferrihydrite at pH 3 under UV irradiation. The results are shown in Fig. 7. Clearly, the rate of degradation of MY10 increased significantly with increase of the initial concentration of H_2O_2. More than 90% of the MY10 disappeared after 4 and 6 h in the presence of 5 and 3 mM H_2O_2, respectively. However, only 50% removal of MY10 occurred in the presence of 1 mM H_2O_2 after 6 h irradiation. Although the results in Fig. 7 indicate that the rate of degradation of MY10 increased as the initial concentration of H_2O_2 increased, the rate did not obviously increase when the concentration of H_2O_2 was greater than 3 mM.

Gao et al. [21] has reported that with increase of the initial concentration of H_2O_2, the rate of formation of $^{\bullet}$OH began to increase, but then tended to stabilize in Fenton and Fenton-like systems used for the degradation of organic compounds at pH 3. Moreover, Sun and Pignatello [22] found that the utilization of H_2O_2 decreased with increasing concentration. The reason for this decrease is thought to be the fact that although hydrogen peroxide is an effective photo-electron capture reagent for the production of $^{\bullet}$OH, it is also a scavenger. The decomposition of hydrogen peroxide can be described by Eqs. (1) and (2):

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{1}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{2}$$

We deduce that the results in the current system are probably related to the mechanism of decomposition of H_2O_2 catalyzed by ferrihydrite. For example, the adsorption of H_2O_2 on ferrihydrite should create an adsorption/desorption equilibrium. Once this equilibrium is reached, the concentration of hydroxyl radicals does not increase with any further increase of the concentration of H_2O_2.

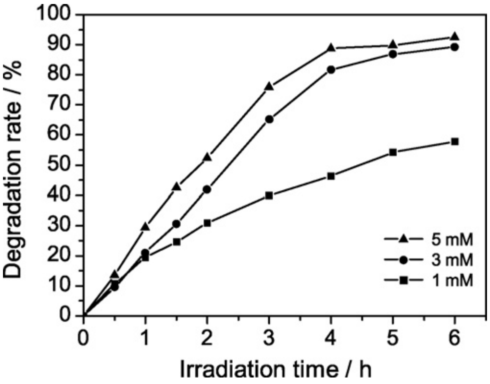


Fig. 7. The degradation of MY10 with different initial concentration of H_2O_2 with 0.5 g L^{-1} ferrihydrite under UV irradiation.

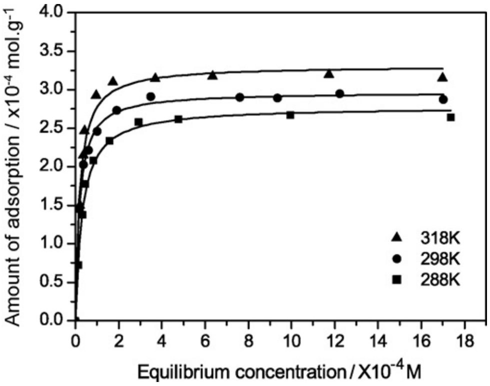


Fig. 8. The adsorption isotherms of MY10 on the surface of ferrihydrite at different temperatures by plotting the equilibrium concentration (c_e) vs. the adsorbed amounts of MY10 (Γ).

3.4. *The effect of the reaction temperature*

The adsorption isotherms of MY10 on the ferrihydrite at different temperatures were obtained by plotting c_e/Γ versus c, as shown in Fig. 8. These are well fitted by the Langmuir adsorption model given in Eq. (3).

$$\frac{c_e}{\Gamma} = \frac{1}{\Gamma_{\max}} c_e + \frac{1}{K_a \Gamma_{\max}} \tag{3}$$

where c_e is the equilibrium molar concentration in the solution, K_a is the adsorption equilibrium constant in L/mol and $\Gamma_{\max}$ is the saturated adsorption capacity in mol/g. The saturated adsorption capacity and the adsorption equilibrium constant for MY10 on to ferrihydrite are listed in Table 2. The saturated adsorption capacity is ranked in the order $\Gamma_{\max(318\,K)} > \Gamma_{\max(298\,K)} > \Gamma_{\max(288\,K)}$ while the adsorption equilibrium constant is ranked in the order $K_{a(298\,K)} \approx K_{a(318\,K)} > K_{a(288\,K)}$. A larger K_a value should denote stronger chemical adsorption [16].

The influence of temperature on the dye removal was studied by performing experiments at 288, 298 and 318 K (Fig. 9). This shows that a higher rate of oxidation of MY10 was obtained at higher temperature (318 K) and about 90% of MY10 disappeared after reaction for 1 h.

We also observed that the concentration of total dissolved iron increased during the photoreaction. Fig. 10 shows that ferrihydrite

Table 2
The saturated adsorption capacity ($\Gamma_{\max}$) and adsorption equilibrium constant (K_a) of MY10 by using the ferrihydrite at different temperatures.

Temperature/K	$\Gamma_{\max}/\times10^{-4}$ mol g^{-1}	$K_a/\times10^{5}$ L mol^{-1}	R^2
288	2.78	0.33	0.993
298	2.99	0.53	0.997
318	3.31	0.52	0.985

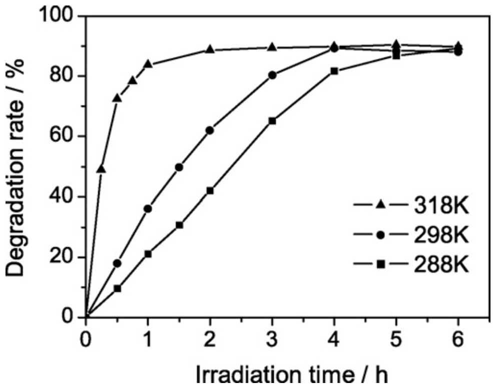


Fig. 9. The degradation of MY10 at different temperatures and pH 3.00 in the presence of H_2O_2 (3 mM) and ferrihydrite (0.5 g L^{-1}) under UV irradiation.

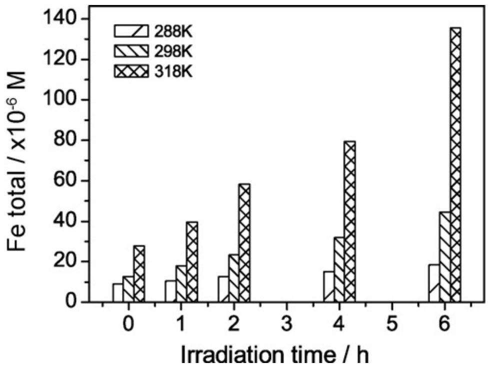


Fig. 10. The effect of temperature on total concentration of iron in solution at pH 3.00 at different reaction times.

could be easily dissolved at higher temperatures. Thus, the degradation rate of MY10 at 318 K was more rapid than that at 298 K or 288 K because of the increase in the concentration of Fe^{3+}, based on the Fenton-like reaction.

4. Conclusions

The present investigation illustrates the fact that ferrihydrite is efficient in the degradation of MY10 in the presence of traces of H_2O_2 in the dark and UV radiation further increases the degradation rate. 0.5 g L^{-1} of ferrihydrite, 3 mM of H_2O_2 and temperatures of 288–318 K are found to be highly photoactive conditions for the degradation of MY10. The rate of degradation increases with decrease of pH in the range of 3–9, with increase of H_2O_2 concentration (from 3 to 5 mM) and temperature (from 218 to 318 K). Based on these results, a mechanism has been proposed in which ferrihydrite catalyzes the decomposition of H_2O_2 to produce hydroxyl radicals ($^{\bullet}OH$), which causes the MY10 to be oxidized and degraded.

Acknowledgments

This work was supported by a grant from the Natural Science Foundation of China (20877021) and Ph.D. Programs Foundation and Key Programs of Hebei Normal University (L2005B15 and L2007z06). The authors thank International Science Editing for editing the manuscript.

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