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The mechanisms of reactive blue photodegradation by iron(III)/H_2O_2/HA systems

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ABSTRACT

The mechanisms of reactive blue (RB) photodegradation under simulated solar irradiation in different systems has been studied. The results show that $[H_2O_2]_0$ was the determining factor for light/H_2O_2/Fe(III) system in decomposing RB. The pH value has a significant effect on H_2O_2/Fe(III) system. At pH values of 3, 4, 5 and 6, the removal efficiencies of RB were 61%, 49%, 43% and 39%, respectively. Further, the role of humic acid (HA) was examined. The pH range of H_2O_2/Fe(III) system was extended by the existence of the HA. The mechanisms of RB photodegradation by H_2O_2/Fe(III)/HA systems included 4 pathways: the hydroxyl radical ($^{\bullet}OH$) produced from irradiated H_2O_2/Fe(III) system, the $^{\bullet}OH$ produced from irradiated H_2O_2/Fe(III)/HA system, the adsorption by Fe(III)-HA complexes and the other reactive species produced from light/H_2O_2/Fe(III)/HA system. Overall, the $^{\bullet}OH$ leading to RB degradation was the major pathway and accounted for about 72% of the total RB degradation.

Keywords: Humic acid; Photodegradation; Reactive dyes; Iron; Hydroxyl radical

1. Introduction

Humic acid (HA), widely present in natural waters, accounts for 40–60% of the dissolved organic matter (DOM). Several papers have been published on the role of HA in the photochemical degradation of organic pollutants [1–3]. Under solar (or simulated solar) irradiation, HA, via its excited triplet states ($^3HA^*$), can induce electron transfer. Also, singlet oxygen ($^1O_2$), can be produced by energy transfer from $^3HA^*$ to molecular oxygen [4]. $^3HA^*$ can also interact with H_2O to produce hydroxyl radical ($^{\bullet}OH$). $^1O_2$, $^3HA^*$ and $^{\bullet}OH$ are strong oxidizers and play a significant role in the fate of organic pollutants in natural waters [5,6].

Previous studies have shown that HA can associate itself with iron (Fe) to form Fe(III)-HA complexes [7]. Significant levels of iron are ubiquitously found in natural waters. Microbial iron reduction and iron cycling in sunlit waters are known to catalyze natural organic matter (NOM) degradation in sediments and fresh waters, and adsorption of humic matter alters the surface chemistry and colloid stability of iron oxides [8,9]. Some studies have shown that Fe(III)-HA played a key role in the degradation of organic pollutants under sunlight irradiation. The pollutant degradation by irradiated Fe(III)-HA systems is mainly attributed to the formation of reactive oxygen species (ROS) such as $^{\bullet}OH$, $^1O_2$, and triplet DOM ($^3DOM^*$) [10,11]. The types of ROS and the efficiency on pollutant degradation depend on the source of HA, its physical (e.g., molecular weight) and chemical (e.g., functional moieties) characteristics. [1,12].

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The excitation of Fe(III)-HA complex by light leads to the formation of Fe(II)-HA complex which reacts with H_2O_2 to give hydroxyl radicals and thus the photo-Fenton-like process is obtained. In a previous study, the degradation of pentachlorophenol (PCP) by H_2O_2/Fe(III) system and H_2O_2/Fe(III)/HA system at pH 5.0 was studied and the results showed although 40% of the PCP was degraded after 5 h of irradiation in the H_2O_2/Fe(III) system, more than 90% was degraded in the H_2O_2/Fe(III)/HA system [13]. Conte et al. [14] investigated the photo-Fenton degradation of 2,4-D using iron complexes such as Fe(III)-oxalate and Fe(III)-citrate complexes. Bolobajev et al. [15] reported doxycycline played a key role in Fe(III)-to-Fe(II) redox cycling and therefore in controlling the overall reaction rate of the Fenton-based process (H_2O_2/Fe(III)). Fe(III) reduction is the rate-limiting step in the Fenton-like mechanism due to the formation of Fe(II), and the presence of chelated ligands (e.g., HA, oxalate, citrate and so on) accelerated this step, which can promote the efficiency of H_2O_2/Fe(III) system.

The reactive blue (RB) is one of the reactive dyes that have been proven to have adverse effects on aquatic organisms. The potential removal pathways of reactive dyes in the surface waters may include biodegradation, sorption and photolysis [16,17]. In some cases, reactive dyes are non-biodegradable, thereby inhibiting one of the major elimination pathways. The sediment type has been shown no effects on the sorption of reactive dyes, thus the most potential major pathway is via solar mediated photodegradation.

This paper presents data on the RB photodegradation by hydrogen peroxide/ferric ions system with and without HA. And the reaction mechanism was investigated by adding potassium iodide. These data provides a good insight into the photochemical roles of HA and iron complexes in natural water.

2. Materials and methods

2.1. Materials

The Humic acid (HA) used in the present work was purchased from MP Biomedicals. Inc. (Germany) and it was extracted from soil following a protocol of the International Humic Substances Society (IHSS) [18]. Reactive blue (RB, $C_{23}H_{14}C_{l2}N_6O_8S_2$) was used as a target organic pollutant. $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and Potassium iodide (KI) were analytical grade and purchased from Tianjin Kemio Chemical Reagent Co. Ltd. Hydrogen peroxide (H_2O_2, 30% W/W) were purchased from Guoyao Chemical Reagent Co. Ltd. All the chemicals were used as received.

The ultra-pure Milli-Q water (produced by a Millipore-Academic system) was used to prepare the stock-solutions. The HA powder was dissolved in Milli-Q water that was adjusted by NaOH to pH 7.5–8.0 and the HA concentration was measured by a total organic carbon analyzer (TOC-V_{CPH}, Shimadzu, Japan). A 20 mM stock solution of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ was prepared in 0.1 M H_2SO_4. The initial concentration of stock solutions for H_2O_2 and KI were 1 M (pH = 7) and 70 mM, respectively. pH was adjusted by using 1 M HCl and 1 M NaOH solutions. All aquatic stock-solutions were stored in the dark at 4°C in a refrigerator and used within one week. The initial concentration of RB reaction solution was always 0.211 mM (150 mg/L). The concentration of RB in the dark is unchanged in two weeks.

2.2. Experimental runs and analysis

All experiments were carried out in a 200-mL stirred photo reactor. Optical experiments were conducted at room temperature (25.0 ± 1°C) with a photochemical reaction experiment apparatus, produced by Xi An Boyier, a precision instrument company. A 300 W Xe lamp in combination with a special glass filter restricting the transmission of wavelengths below 420 nm was used for visible light simulation. The reaction solutions were always magnetically stirred during irradiation. Degradation experiments were conducted at least twice.

In irradiation experiments, the solutions of HA and their complexes with Fe(III) were stirred for 1 h in the dark to reach equilibrium before adding RB. The scavenging of hydroxyl radicals ($^{\bullet}$OH) was accomplished with KI to quantify the oxidation levels from radical reactions. Before data analysis was done, all samples were withdrawn from the reactor at the given reaction time intervals (0, 5, 10, 20, 50 and 80 min) for RB analysis immediately. The absorbance of RB was analyzed by measuring the UV-vis spectra at λ = 591 nm using a WFJ2100 UV-vis spectro photo meter (Unico Co., Shanghai). The formula of degradation rate is shown as following.

$$\%\ \text{Degradation} = \left(1 - \frac{A_t}{A_0}\right) * 100\%$$

where A_0 - the absorbance of RB at λ_{591nm} before reaction; A_t - the absorbance of RB at λ_{591nm} at t minutes.

3. Results and discussion

3.1. Influence of H_2O_2 and Fe (III) initial concentration

No significant change over 80 min was observed in the RB alone solution or in 0.83 mM Fe(III) alone solution, confirming that RB photodegradation initiated by wavelengths >420 nm can be ignored over the time scale considered. Fig. 1 shows the removal rate of RB solution over a reaction time of 80 min, at different concentrations of H_2O_2 in the range of 0.80–6.68 mM. The other reaction conditions were 0.267 mM Fe(III) and pH 3.0. The value of $[H_2O_2]_0/[Fe(III)]_0$ were 3/1,5/1, 10/1, 15/1 and 25/1, respectively.

As seen in Fig. 1, $[H_2O_2]_0$ had a significant effect on RB degradation. The removal efficiencies of RB increased with the increase in the value of $[H_2O_2]_0/[Fe(III)]_0$. For the value of $[H_2O_2]_0/[Fe(III)]_0$ which were 3/1,5/1, 10/1, 15/1 and 25/1, the removal rate of RB were 30%, 45%, 59%, 72% and 81%, respectively. The primary reactions in H_2O_2/Fe(III) system may are:

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2 \cdot + H^+ \tag{1}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + HO \cdot \tag{2}$$

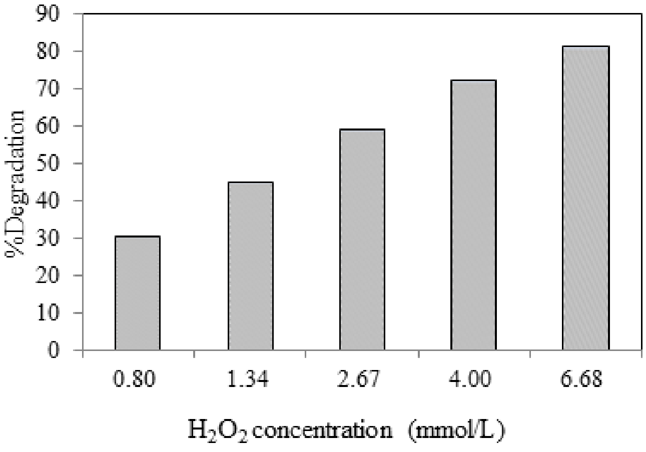

Fig. 1. Influence of the initial concentration of H_2O_2 on the RB photodegradation. pH = 3; $[Fe(III)]_0$ = 0.267 mM; $[H_2O_2]_0$ = 0.80–6.68 mM; reaction time = 80 min.

Prior study has demonstrated that Eq. (1) is several orders of magnitude slower than Eq. (2), thus Eq. (1) can be the rate-limiting step [19,20]. Therefore, with the increase in the initial concentration of H_2O_2, a significant enhanced degradation of RB was observed.

Fig. 2 shows the influence of Fe(III) concentration on the RB photodegradation. Compared to H_2O_2, the initial concentration of Fe(III) did not affect significantly the degradation of RB. For example, the increase in $[Fe(III)]_0$ from 0.11 mM to 0.89 mM resulted in the removal rate of RB from 55% to 63%, only an increase of RB removal by 8%. These data implied that under the conditions of the present experiments, $[H_2O_2]_0$ rather than $[Fe(III)]_0$, was the determinative factor for RB decomposition in the H_2O_2/Fe(III) system. According to the result presented in Fig. 2, the initial concentrations of 2.50 mM H_2O_2 and 0.83 mM Fe(III) were chosen for further experiments.

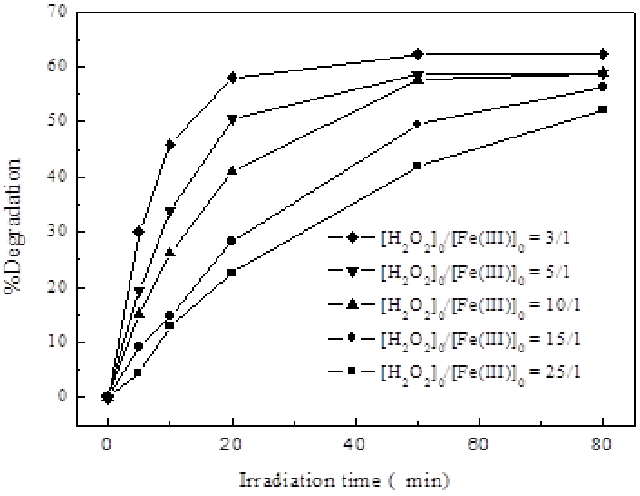

Fig. 2. Influence of the initial concentration of Fe(III) on the RB photodegradation. pH = 3; $[H_2O_2]_0$ = 2.67 mM; reaction time = 80 min.

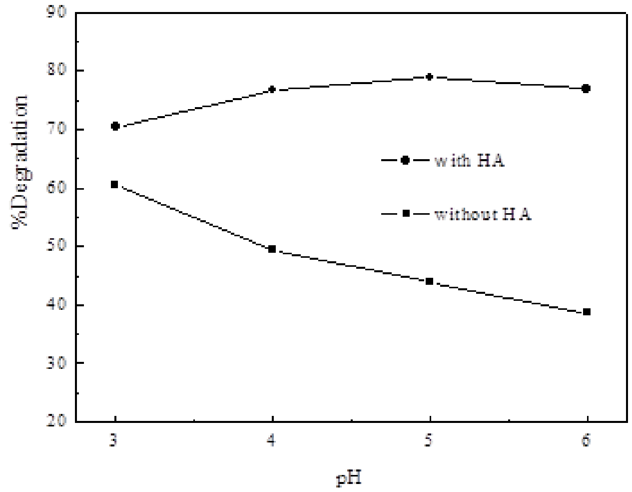

Fig. 3. Effect of pH on the photo-degradation of RB in the absence (■) and in the presence of 10 mg/L HA (●) under the visible light radiation. $[H_2O_2]_0$ = 2.50 mM; $[Fe(III)]_0$ = 0.83 mM; reaction time = 80 min.

3.2. Influence of pH on H_2O_2/Fe(III) system and H_2O_2/Fe(III)/HA system

pH was an important parameter, and it had a significant impact on the stability of H_2O_2 and the species of iron. Fig. 3 showed the removal of RB at different pH in H_2O_2/Fe(III) and H_2O_2/Fe(III)/HA system under Xe lamp irradiation.

At pH 3, 4, 5 and 6, the removal efficiencies of RB in H_2O_2/Fe(III) system were 61%, 49%, 43% and 39%, respectively. This indicated that pH can influence the generation of $^{\bullet}OH$ during H_2O_2 oxidation. The increase of pH may cause the formation of an inactive hydroperoxide anion (HO_2^-) due to H_2O_2 dissociation. Further, the HO_2^- may act as an efficient scavenger of $^{\bullet}OH$ as presented in Eq. (3), which leads to the inhibition of RB degradation [21–24]. Meanwhile, the speciation of iron is highly pH-dependent. Fe(III) reacting with H_2O_2 would be slower due to the dissolved iron concentration reduced at higher pH values.

$$HO_2^- + \cdot OH \rightarrow H_2O + O_2^{\cdot -} \qquad (3)$$

As shown in Fig. 3, there was a significant effect on the RB removal by adding 10 mg/L HA in irradiated H_2O_2/Fe(III) system. The removal of RB at pH 3, 4, 5 and 6 were 70%, 76%, 78%, and 76%, respectively. This results showed an increase of RB degradation by 10%, 27%, 35% and 37%, respectively, compared to the results obtained in absence of HA. These indicated that the presence of HA contributed to RB removal under visible light irradiation. The pH range of H_2O_2/Fe(III) system was extended by the existence of the HA.

Previous studies have shown that the speciation of iron and the solubility of HA are highly pH-dependent. Therefore, a change in pH has an effect on the complexation of Fe(III) and HA [25]. With the increase of pH, the deprotonation of HA was enhanced, more binding sites were provided and complexed with Fe(III). Fe(III)-HA complex absorbed a fraction of the visible light, generating $^{\bullet}OH$ by excitation [8,12], as presented in Eqs. (4) and (5) [26,27]. Therefore, the removal of RB was enhanced as a result of the synergetic effect of both.

$$Fe(III)-(HA)_n + hv \rightarrow Fe(II)-(HA)_{n-1} + RCOO\cdot \quad (4)$$

$$H_2O_2 + Fe(II)-(HA)_{n-1} \rightarrow \cdot OH + OH^- + Fe(III) + (HA)_{n-1} \quad (5)$$

Recently, Bianco Prevot [28] used bio-based substances (BBSs) as photo sensitizing agent in photo-Fenton system and reported when BBSs was added in solutions containing Fe and H_2O_2, the best results for caffeine photodegradation were obtained at pH about 4, instead of pH 2.8. Moreover, when ethylenediamine-N,N-disuccinic acid was used as iron complexing agent [29], the best results were reached at neutral or even slightly basic medium. These studies were of interesting that the addition of some naturally occurring organic ligands successfully overcomes the problem faced in the Fenton process, i.e., the narrow working pH range.

3.3. Influence of HA initial concentration

Influencing factors regarding the transformation and degradation of pollutants in groundwater are mainly involved with the concentration of humic substances [30]. Fig. 4 shows that the removal of RB was increased with increasing the initial concentration of HA from 0 to 10 mg/L, and was highest at 10 mg/L. When the initial concentration of HA was up to 15 mg/L, the removal of RB was reduced. The concentration of HA has a significant influence on RB removal. This is because it can act as both an accelerator and an inhibitor under the visible light irradiation. The influence of HA on photodegradation of RB is complicated due to its dual role.

As a photo sensitizer, a part of HA may interact with Fe(III) and generate $^{\bullet}OH$ by light excitation, as presented in Eq. (6) [12]. Negueroles et al. [31] also reported that addition of humic-like substances isolated from urban wastes was necessary in order to prevent iron deactivation because of the formation of non-active iron hydroxides.

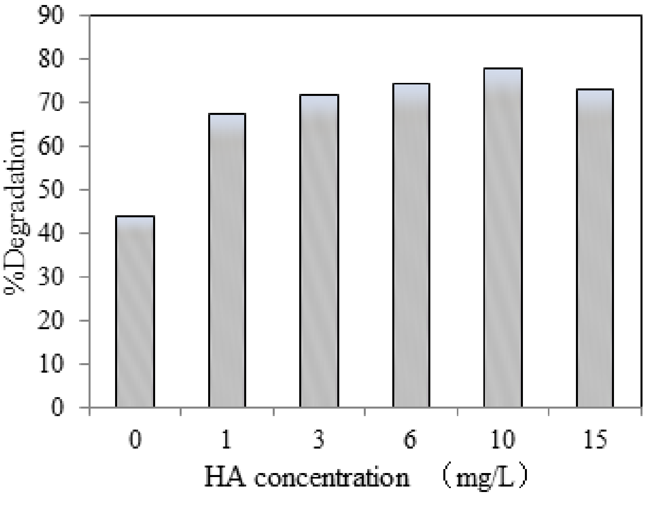

Fig. 4. The influence of HA initial concentration on the photodegradation of RB by H_2O_2/Fe(III) system. $[H_2O_2]_0$ = 2.50 mM; $[Fe(III)]_0$ = 0.83 mM; pH = 5; reaction time = 80 min.

$$Fe(III)-HA + hv \rightarrow Fe(II) + free\ radicals \quad (6)$$

The rest of the HA that didn't interact with Fe(III) can absorb a part of the light to produce reactive species and enhance the degradation of RB. This can be explained in the equations below [10].

$$HA + hv \rightarrow {}^1HA^* \rightarrow {}^3HA^* \quad (7)$$

$$^3HA^* + O_2 \rightarrow HA + {}^1O_2 \quad (8)$$

$$^3HA^* + O_2 \rightarrow HA + O_2^{-\cdot} \quad (9)$$

$$2O_2\cdot^- + 2H^+ \rightarrow H_2O_2 + O_2 \quad (10)$$

$$H_2O_2 + hv \rightarrow 2\cdot OH \quad (11)$$

$$RB + \cdot OH/{}^3HA^*/{}^1O_2 \rightarrow products \quad (12)$$

However, when the initial concentration of HA is high, HA can acts as light screening agent, presenting itself as a light absorbent and free radical quencher to inhibit RB degradation (Eq. (13)).

$$HA/{}^1HA^*/{}^3HA^*/HA^+ + \cdot OH/{}^1O_2 \rightarrow Oxidized\ HA \quad (13)$$

Therefore, the total effect on RB removal depends on the competition between the contrary roles of HA. At lower HA concentration, HA can absorb light to produce reactive species, which can react with RB and can markedly contribute to the enhanced RB degradation. When HA initial concentration was higher, RB removal was reduced due to the light screening effect and free radical quenching of HA.

3.4. The mechanism of RB photodegradation.

Several studies have showed that there is a distinction on oxidation capacities of different reactive species (such as $^{\bullet}OH$, $^1O_2$ and $^3HA^*$). The oxidation capacity of $^{\bullet}OH$ was higher than $^1O_2$ and $^3HA^*$, but it didn't mean that $^{\bullet}OH$ accounts mainly for RB degradation. Based on the prior studies, the roles of reactive species on the photodegradation of organic contaminants depend on light source [32], species of contaminants, concentration of HA, pH value of solution [3], and the coexistence of other natural water constituents, such as Fe [25], as well.

In order to examine the mechanism of RB degradation, quenching experiments were performed to determine the contribution of each reactive species to RB removal. The experiments were carried out using irradiated H_2O_2/Fe(III)/HA system, with or without potassium iodide (KI, used as a quencher for $^{\bullet}OH$) [33]. As seen in Fig. 5, the addition of KI in H_2O_2/Fe(III)/HA system resulted in a significant decrease in the observed RB removal. In the presence of 2 mM or 3 mM KI, the RB removal decreased by 44.5%. This indicates that $^{\bullet}OH$ plays an important role in RB removal. However, the addition of quencher for

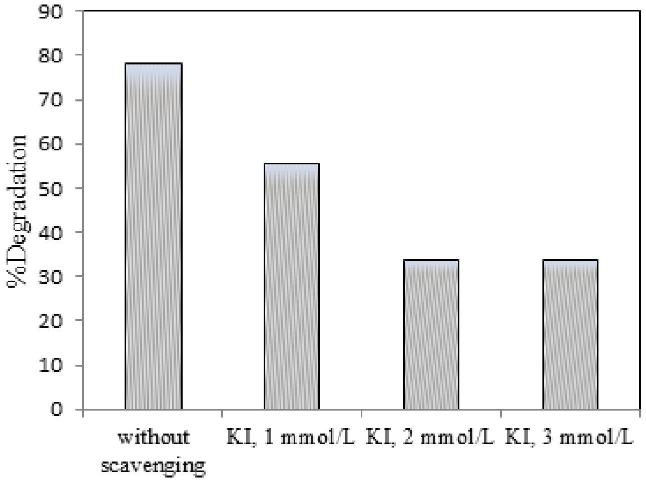

Fig. 5. The role of $^{\bullet}$OH contributed to RB photodegradation by the irradiated H_2O_2/Fe(III)/HA process in the present of 1–3 mM quencher, KI. $[H_2O_2]_0 = 2.50$ mM; $[Fe(III)]_0 = 0.83$ mM; pH = 5; reaction time = 80 min.

$^{\bullet}$OH did not completely inhibit the RB photodegradation, which implies that there were other mechanism for RB removal.

To further investigate the photodegradation mechanism of RB, controlled trials were performed to examine how the different mechanisms contribute to the RB removal in different system. Hypothesis showed that all other parameters were constant over the reaction time, and the total RB removal rate was simplified to a pseudo-first-order kinetic law (Fig. 6). It can be seen from Fig. 6 that the irradiated Fe(III) solution or alone H_2O_2 solution could not degrade RB since the light was weak. Based on the experimental data and prior studies, the mechanism for RB degradation may include four situations.

(1) RB degradation by $^{\bullet}$OH produced from H_2O_2/Fe(III) system under the visible light irradiation;
RB + $^{\bullet}$OH→ products---

$$r_{\bullet\mathrm{OH(H_2O_2/Fe)}} = \left(-\frac{dC_{\mathrm{RB}}}{dt}\right)_{\bullet OH} = k_{\bullet\mathrm{OH(H_2O_2/Fe)}} C_{RB}$$

(2) RB degradation by $^{\bullet}$OH produced from H_2O_2/Fe(III)/HA system under the visible light irradiation;
RB + $^{\bullet}$OH→ products----

$$r_{\bullet\mathrm{OH(H_2O_2/Fe/HA)}} = \left(-\frac{dC_{\mathrm{RB}}}{dt}\right)_{\bullet\mathrm{OH}} = k_{\bullet\mathrm{OH(H_2O_2/Fe/HA)}} C_{RB}$$

(3) RB degradation by adsorption of Fe(III)-HA system without visible light irradiation;
RB + adsorption→ products---

$$r_{\mathrm{adsorption}} = \left(-\frac{dC_{\mathrm{RB}}}{dt}\right)_{\mathrm{adsorption}} = k_{\mathrm{adsorption}} C_{RB}$$

(4) RB degradation by other reactive species (such as $^1O_2$ and $^3HA^*$) produced from H_2O_2/Fe(III)/HA system under the visible light irradiation;

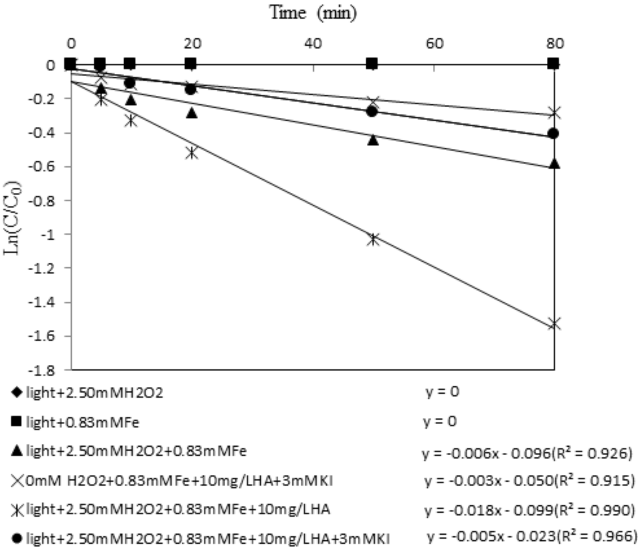

Fig. 6. The pseudo-first-order kinetic rate constants of RB degradation for different systems in the presence or absence of HA and KI. $[H_2O_2]_0 = 2.50$ mM; $[Fe(III)]_0 = 0.83$ mM; pH = 5; reaction time = 80 min.

RB + other reactive species → products---

$$r_{\mathrm{other}} = \left(-\frac{dC_{\mathrm{RB}}}{dt}\right)_{\mathrm{other}} = k_{\mathrm{other}} C_{RB}$$

Then, the total rate of RB removal can be expressed as follows:

$$\left(-\frac{dC_{\mathrm{RB}}}{dt}\right)_{\mathrm{total}} = -\left(r_{\bullet\mathrm{OH(H_2O_2/Fe)}} + r_{\bullet\mathrm{OH(H_2O_2/Fe/HA)}} + r_{\mathrm{adsorption}} + r_{\mathrm{other}}\right)$$
$$= k_{\bullet\mathrm{OH(H_2O_2/Fe)}} C_{RB} + k_{\bullet\mathrm{OH(H_2O_2/Fe/HA)}} C_{RB} + k_{\mathrm{adsorption}}$$
$$C_{RB} + k_{\mathrm{other}} C_{RB} k_{\mathrm{total}} C_{RB}$$

where $r_{\bullet\mathrm{OH(H2O2/Fe)}}$, $r_{\bullet\mathrm{OH(H2O2/Fe/HA)}}$, $r_{\mathrm{adsorption}}$ and r_{other} represent the $^{\bullet}$OH produced from light/H_2O_2/Fe(III) system, the $^{\bullet}$OH produced from light/H_2O_2/Fe(III)/HA system, the adsorption by Fe(III)-HA complexes and other reactive species that contributed to the photodegradation of RB, respectively. Further, $k_{\bullet\mathrm{OH(H2O2/Fe)}}$, $k_{\bullet\mathrm{OH(H2O2/Fe/HA)}}$, $k_{\mathrm{adsorption}}$ and k_{other} represent the pseudo-first-order kinetic rate constants for different systems and C_{RB} represents the concentration of RB.

As shown in Fig. 6, when H_2O_2 and Fe (III) were mixed to form a system under the visible light irradiation, the removal of RB increased. The pseudo-first-order kinetic rate constant for light/H_2O_2/Fe(III) system was calculated as: $k_{\bullet\mathrm{OH(H2O2/Fe)}} = 0.006$ min^{-1}. $k_{\mathrm{adsorption}}$ was obtained from Fe(III)/HA system and its value was 0.003 min^{-1}. k_{total} was obtained from light/H_2O_2/ Fe(III)/HA process and its value was 0.018 min^{-1}. The presence of 2 or 3 mM $^{\bullet}$OH quencher in the light/H_2O_2/Fe(III)/HA system inhibited the effect of $^{\bullet}$OH on RB removal. Thus, the possible photodegradation mechanism for RB was other reactive species generated from Fe(III)-HA complexes under the visible light irradiation and adsorption by Fe(III)-HA complexes. The k_{other} can be calculated as follows: $k_{\mathrm{other}} = 0.005$ min^{-1} – 0.003 min^{-1} = 0.002 min^{-1}. Similarly, $k_{\bullet\mathrm{OH(H2O2/Fe/HA)}}$ was calculated as $k_{\bullet OH(H2O2/Fe/HA)}$ = 0.018 min^{-1} – 0.006 min^{-1} -0.003 min^{-1} – 0.002 min^{-1} = 0.007 min^{-1}. All the parameter of different mechanisms are summarized in Table 1.

The important levels of different mechanisms calculated based on Table 1 in irradiated H_2O_2/Fe(III)/HA system are shown in Fig. 7. $^\bullet$OH generated from H_2O_2/Fe(III) system accounted for 33% of the total photodegradation of RB, and 33% was obtained according 0.006 min^{-1} ($k_{\cdot OH(H2O2/Fe)}$) divided by 0.018 min^{-1} (k_{total}). Correspondingly, 39%, 17% and 11% in Fig. 7 were obtained according 0.007 $\text{min}^{-1,}$ 0.003 min^{-1} and 0.002 min^{-1} divided by 0.018 min^{-1}, respectively. As seen, the $^\bullet$OH plays an important role in the RB removal, and accounted for 72% (33% + 39%) of total degradation of RB. Adsorption and other reactive species (such as $^1O_2$ and ^{3}HA*) that contributed to the degradation of RB accounted for 17% and 11%, respectively. The addition of HA increased yield of $^\bullet$OH up to 39% and the addition of HA contributed to RB photodegradation in H_2O_2/Fe(III) system. The results were consistent with Ryan's studies [34] that, for the photodegradation of trimethoprim (TMP) in solutions of effluent organic matter (EfOM), the $^\bullet$OH reaction accounted for 62% and triplet EfOM for 20% of the loss of TMP, respectively. However, Luo et al. [6] reported that $^1O_2$, $^\bullet$OH and excited state natural organic matter (^{3}NOM* and ^{1}NOM*) reactions accounted for 19%, 6% and 75%, of the total photodegradation of TMP, respectively, and postulated the reaction of TMP with ^{3}NOM* as a significant degradation pathway for the loss of TMP in sunlit waters containing natural organic matter (NOM). In another study with the presence of effluent organic matter in water, cimetidine degraded by reaction with $^1O_2$ (>95%) and caffeine degraded by reaction with $^\bullet$OH (>95%) [35]. The reasons for these differences maybe include the different photo reactivity of HA, EfOM and NOM, the light source, the metal coexist in water and the different properties of pollutants, which imply the difficulties in interpreting mechanisms in natural waters where it is possible that numerous processes occur simultaneously.

Table 1
The pseudo first order degradation rate constant of RB in different systems

k_{total}	0.018 min^{-1}
$k_{\cdot OH(H2O2/Fe)}$	0.006 min^{-1}
$k_{\cdot OH(H2O2/Fe/HA)}$	0.007 min^{-1}
$k_{adsorption}$	0.003 min^{-1}
k_{other}	0.002 min^{-1}

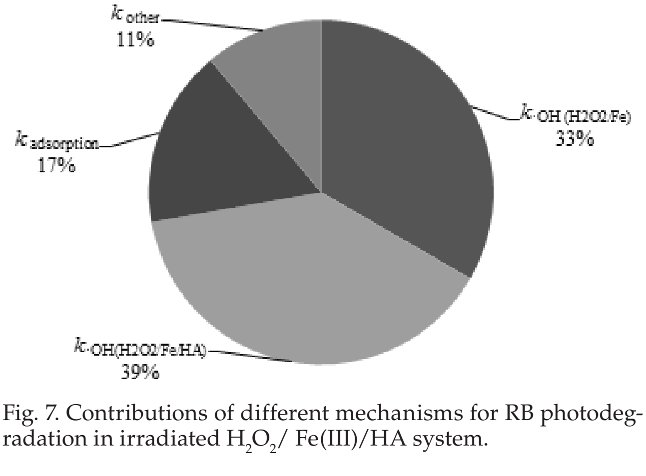

Fig. 7. Contributions of different mechanisms for RB photodegradation in irradiated H_2O_2/ Fe(III)/HA system.

4. Conclusion

The results of the present investigation demonstrated that $[H_2O_2]_0$ and pH were the important factors for irradiated H_2O_2/Fe(III) system in the decomposition of RB. HA acts either as an accelerator or an inhibitor in the H_2O_2/Fe(III) system under Xe lamp irradiation. The mechanisms of RB photodegradation in H_2O_2/Fe(III)/HA system included 4 pathways including the $^\bullet$OH produced from light/H_2O_2/Fe(III) system (33%), the $^\bullet$OH produced from light/H_2O_2/Fe(III)/HA system (39%), the adsorption by Fe(III)-HA complexes (17%) and other reactive species produced from irradiated H_2O_2/Fe(III)/HA system (11%). The $^\bullet$OH leading to the photodegradation of RB was the major pathway that accounted for up to 72% of the total degradation in RB.

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