



Role of oxygen in the degradation of atrazine by UV/Fe(III) process

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ABSTRACT

In this study, the role of oxygen in the regeneration of Fe(III) during the degradation of atrazine in UV/Fe(III) process was studied. The degradations of atrazine in UV/Fe(III) and UV-photolysis processes in the presence and absence of oxygen were compared. The results showed that the degradations of atrazine in these processes followed the pseudo-first-order kinetics well. The process exhibiting the highest rate constant (k) was UV/Fe(III)/air process, because k -value for UV/Fe(III)/air process was about 1.47, 2.23 and 2.56 times of those for UV/Fe(III)/N₂, UV/air and UV/N₂ processes, respectively. The degradation of atrazine was enhanced by oxygen in UV/Fe(III) process and the enhancement was more remarkable at higher initial concentrations of Fe(III). The investigation into the changes of Fe(III) concentrations demonstrated that the presence of oxygen led to the regeneration of Fe(III), which resulted in the enhancement of atrazine degradation. With air bubbling, the ferric ions were 25% more than those with N₂ bubbling. The experimental data showed the regeneration of Fe(III) required the excited organic molecules and oxygen and on the basis of these results, the regeneration mechanism of Fe(III) was proposed. It was also found that due to the oxidation of Fe(II), the degradation of atrazine in UV/Fe(II)/air process was effective at a low Fe(II) concentration of 7 mg/L, similar to that in UV/Fe(III)/air process. This study makes clear the role of oxygen in the regeneration of Fe(III), and thus it provides a guide to reduce the input of Fe(III) and is helpful to the application of UV/Fe(III) process in practice.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is a herbicide used for weed pre- and post-emergence control, particularly in maize crops. Because of its bioresistance, atrazine persists in soil and the aquatic environment [1]. The advanced oxidation processes (AOPs), which are based on the formation of highly active hydroxyl radicals ($\bullet\text{OH}$) to act as an oxidant, are attractive because they hold out the promise of completely mineralizing the organic compounds [2–7]. UV/Fe(III) process, in which $\bullet\text{OH}$ was formed upon excitation of Fe(III), plays a significant role in environmental processes due to the promising prospect to utilize solar energy and the ubiquitous character of Fe(III) in natural water.

In acid solution, $\text{Fe}(\text{OH})^{2+}$, a predominant form of Fe(III) in aqueous solution between pH values of 3.0 and 4.5 [8], undergoes photolysis with the highest quantum yield under UV-irradiation with wavelengths $\lambda > 300$ nm, yielding Fe(II) and $\bullet\text{OH}$, as described in Eq. (1) [9,10]. The hydroxyl radical with a strong oxidation poten-

tial of 2.80 V, reacts rapidly with most organic compounds with second order rate constants in the range of $(10^9\text{--}10^{10})\text{M}^{-1}\text{s}^{-1}$ [11] (Eq. (2)). UV/Fe(III) process has been tested as an effective method for the degradation of many pollutants such as chloroaniline, atrazine and dyes [4,12–17].



However, the production of $\bullet\text{OH}$ and the degradation of the contaminant will slow down when Fe(III) keeps being photoreduced to Fe(II) according to Reaction (1). One method to guarantee the degradation efficiency is to increase the input of Fe(III). But reducing the use of Fe(III) is the future challenge because the directives concerning the discharge standard of iron ion are becoming strict. Therefore, the simultaneous oxidation of the Fe(II) by an oxidant into Fe(III) should be the effective route to sustain the catalytic effect of Fe(III) and the degradation efficiency at the low initial concentration of Fe(III) [18]. Addition of hydrogen peroxide provides an efficient process, i.e., UV/Fenton process, for the degradation of most organic molecules. But hydrogen peroxide is not easy to handle and expensive [16].

Oxygen is well known to be a cheap oxidant and a possible oxidant agent capable to maintain a constant Fe(II)/Fe(III) ratio. Several

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papers reported that the aeration could increase the degradation efficiency of the contaminant in UV/Fe(III) process. Franch et al. [17] showed that oxygen took an active part in the mineralization of maleic acid during Fe(III) photocatalyzed degradation. The study of Mailhot et al. [13] reported that only 40% 4-chloroaniline (4-CA) was decomposed in UV/Fe(III) process in deoxygenated solution, while more than 90% 4-CA was degraded in presence of oxygen. The reports by Mailhot et al. [13] and Andreozzi and Marotta [13,16] both suggested that Fe(II) might be oxidized to Fe(III) in the presence of oxygen, enhancing the degradation. But the reoxidation mechanism of Fe(II) into Fe(III) has not been made clear. As proposed by Catastini et al. [19], a single step photoreaction among Fe(II) and oxygen could be put forward with the formation of Fe(III) and superoxide ions ($O_2^{\bullet-}$). While Mailhot et al. assumed that the reoxidation of Fe(II) into Fe(III) was probably by the reaction of Fe(II) with the oxidizing radicals such as $\bullet OH$ or HO_2^{\bullet} [13]. But the assumption proposed by Mailhot et al. had not been confirmed by experimental data and the formation of the HO_2^{\bullet} had not been studied. Due to the regeneration of Fe(III) in the presence of oxygen, the input of Fe(III) could be expected to be reduced, with no negative effect on the degradation. Therefore, understanding into the role of oxygen in the regeneration of Fe(III) is of great importance to the application of UV/Fe(III) process in practice.

In the present study, the degradation of atrazine by UV/Fe(III) process in the presence of oxygen (air bubbling) was investigated, compared with that in the absence of oxygen (nitrogen bubbling). And the detection of Fe(III) concentration demonstrated directly that the simultaneous oxidation of Fe(II) to Fe(III) by oxygenated species took place during the degradation of atrazine by UV/Fe(III)/air process. Based on the experimental results, the role of oxygen in the regeneration of Fe(III) during the degradation of atrazine in UV/Fe(III)/air process was proposed.

2. Materials and methods

2.1. Materials

Atrazine and $Fe_2(SO_4)_3$ were purchased from Hangzhou Huadong Medicine Group Co., Ltd. They were all of analytical grade. Deionized and doubly distilled water was used throughout this study.

2.2. Experimental device and procedures

The schematic diagram of the experimental set-up used in the study is shown in Fig. 1. The photoreactor is an annular quartz cylinder with a capacity of 0.56 L and a height of 200 mm, with an

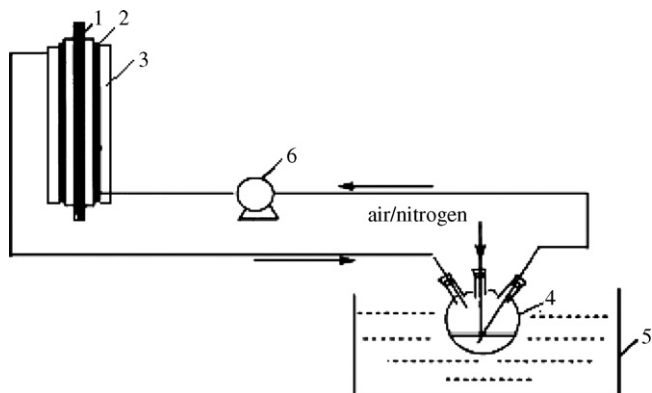


Fig. 1. Schematic diagram of photochemical reaction system experimental set-up: 1. lamp, 2. photoreactor, 3. water-cooled jacket, 4. flask, 5. thermostatic bath and 6. pump.

inner and an outer radius of 40 and 50 mm, respectively. The water-cooled jacket out of the photoreactor is annular made of quartz as well. In the axial center of the reactor, there is the light source, which consists of a high-pressure mercury (Hg) vapour lamp of 300 W (Philips), emitting mainly at 365 nm.

The procedure of UV/Fe(III)/air or UV/Fe(III)/ N_2 process was described as follows: at first, 1.0 L 30 mg/L synthetic wastewater of atrazine was introduced into the flask, which was put in the thermostatic bath, of which temperature was set at 30 °C. Ferric ions were added into the solution after pH value was adjusted to 3.0 with the concentrated H_2SO_4 . After air or N_2 (a flow rate of 0.20 m^3/h) was bubbled for 10 min, the solution was pumped into the photoreactor. When the solution flowed back to the flask, the lamp was turned on and thus the reaction was initiated. At the desired time, the sample was withdrawn from the flask for the analysis. In the direct photolysis process of UV/air or UV/ N_2 , the procedure was just the same as that of UV/Fe(III) process except that no ferric ion was added.

2.3. Analytical methods

Analysis of atrazine was performed with a Knauer HPLC system with a reversed phase C18 column and a UV–Visible absorbance detector adjusted at 235 nm. Mobile phase was the mixture of methanol and deionized water with a volume ratio of 60:40 at a flow rate of 1.0 mL/min.

The concentrations of Fe(III) and Fe(II) were measured by the *o*-phenanthroline colorimetric method ($\lambda = 510$ nm, $\epsilon = 1.1 \times 10^4 M^{-1} cm^{-1}$) [20]. The concentration of Fe(III) was determined by subtracting Fe(II) concentration from the total concentration of iron ions. UV–vis spectra were recorded with a Techcomp 8500 spectrometer.

3. Results and discussion

3.1. Enhancement of atrazine degradation by oxygen in UV/Fe(III) process

The degradation of atrazine with the reaction time in UV/Fe(III) process bubbled with air or N_2 is presented in Fig. 2. To understand better the performance of UV/Fe(III) process, the degradation of atrazine by the direct UV-photolysis is also investigated and shown in Fig. 2. The degradation rate of atrazine in various processes followed the sequence of UV/Fe(III)/air > UV/Fe(III)/ N_2 > UV/air > UV/ N_2 . Concentration of

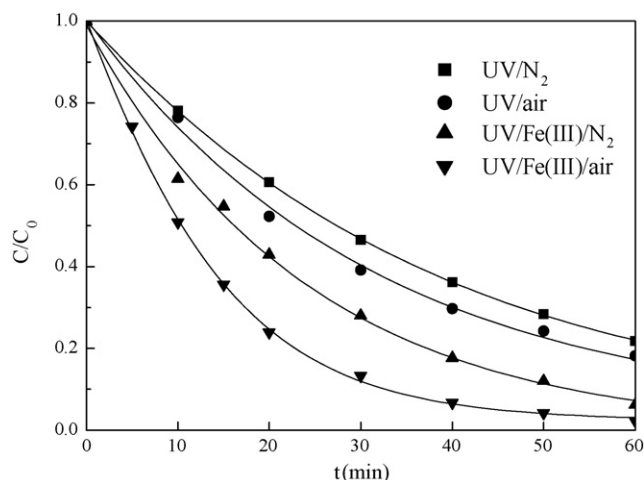


Fig. 2. Comparison of atrazine degradation in various photochemical processes: [atrazine]₀ = 30 mg/L, [Fe(III)]₀ = 7 mg/L, Q(air or N_2) = 0.20 m^3/h , pH = 3.0, T = 30 °C.

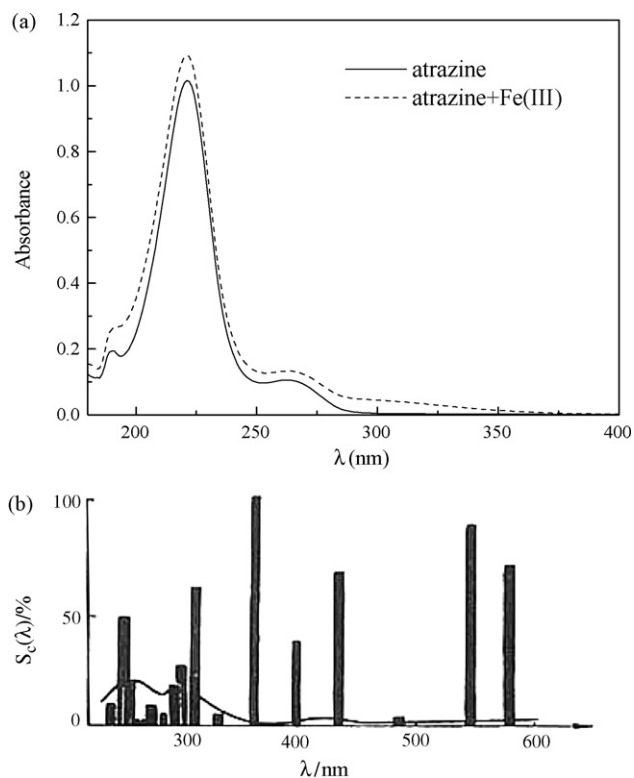


Fig. 3. (a) UV-vis spectra of atrazine solution and the mix of atrazine and Fe(III): [atrazine] = 30 mg/L, [Fe(III)] = 7 mg/L; (b) emission spectrum of the high-pressure Hg lamp.

atrazine decreased in UV/N₂ process, which meant that atrazine could be decomposed by UV-irradiation alone. As shown in Fig. 3(a), the UV-Vis spectrum of atrazine comprises two maxima, an intense one at 221 nm and a weaker one at 263 nm. Combined with the emission spectrum of Hg lamp (Fig. 3(b)), it could be found that the supplying energy as the irradiation of the lamp was absorbed by the atrazine molecule, which then passed to excited states and subsequently transformed to other intermediates [3]. However, the degradation rate of atrazine by the direct UV-photolysis was slow and about 40% atrazine remained after 40 min irradiation.

The addition of Fe(III) to UV-irradiation improved the degradation rate of atrazine greatly. The oxidation of atrazine by •OH radical was the other decomposition pathway of atrazine in UV/Fe(III) process besides the direct photolysis. The UV-vis spectrum of the solution containing atrazine and Fe(III) (Fig. 3(a)) shows atrazine does not combine with Fe(III) to form a complex, which means that •OH radical is produced from the photolysis of Fe(OH)₂²⁺ complexes. This differed from the processes of Fe(III) with low chain carboxylic acids such as citric acid and oxalic acid [14,21], in which the Fe(III)-citrate or ferrioxalate complex led to the production of •OH radical.

In the presence of oxygen, i.e., in UV/Fe(III)/air process, the degradation of atrazine was faster and more complete than that in the absence of oxygen, i.e., UV/Fe(III)/N₂ process. The enhancement of the degradation caused by oxygen was also observed in the other researches [13,17]. At 15 min, there was only 35.6% atrazine remaining in UV/Fe(III)/air process while 54.7% in UV/Fe(III)/N₂ process.

To quantify the degradation rates in these four processes, the observed kinetics in these processes was analyzed. In these processes, the degradation of atrazine all fitted a pseudo-first-order kinetics with respect to the concentration of atrazine, as described

Table 1

The kinetic data of atrazine degradation by photochemical processes.

	Value ($\times 10^{-2} \text{ min}^{-1}$)	R^2	$t_{1/2}$ (min)
$k(\text{UV}/\text{N}_2)$	2.532	0.999	27.4
$k(\text{UV}/\text{air})$	2.918	0.994	23.8
$k(\text{UV}/\text{Fe}^{3+}/\text{N}_2)$	4.408	0.995	15.7
$k(\text{UV}/\text{Fe}^{3+}/\text{air})$	6.494	0.997	10.7

in Eq. (3).

$$\ln(c/c_0) = -kt \quad (3)$$

in which, c_0 and c are the concentrations of atrazine at the initial time (mg/L) and at the reaction time t (min), respectively; k is the pseudo-first-order reaction rate constant (min^{-1}).

The calculated values of the first-order rate constants are listed in Table 1. The table also presents the value of half-life ($t_{1/2}$), that is, the time required to decrease the concentration of atrazine to half of the initial concentration. The pseudo-first-order kinetics simulated the measured dependencies of the atrazine concentration on the reaction time very well, with an excellent R^2 (R is the relative coefficient) ranging between 0.994 and 0.999.

The process exhibiting the highest k -value was UV/Fe(III)/air process. The value of k for UV/Fe(III)/air was about 1.47, 2.23 and 2.56 times of those for UV/Fe(III)/N₂, UV/air and UV/N₂ processes, respectively. Interestingly, UV-irradiation with air aeration could only improve the degradation rate of atrazine a little, but the air aeration in UV/Fe(III) process enhanced the degradation of atrazine remarkably. As seen from Table 1, in the direct UV-irradiation, the bubbling with air increased the k -value from 2.532×10^{-2} to $2.918 \times 10^{-2} \text{ min}^{-1}$ and the increment was only $0.386 \times 10^{-2} \text{ min}^{-1}$. While k -value for UV/Fe(III)/air process was $2.086 \times 10^{-2} \text{ min}^{-1}$ bigger than that for UV/Fe(III)/N₂ process. This increment was much greater than that between $k(\text{UV}/\text{air})$ and $k(\text{UV}/\text{N}_2)$, i.e., $0.386 \times 10^{-2} \text{ min}^{-1}$. In UV/Fe(III) process, atrazine is degraded by two pathways: one is the direct photolysis under the illumination of UV and the other is the oxidation by •OH radicals. The experimental result showed that by the direct photolysis, the air bubbling only improved the degradation rate of atrazine a little. Therefore, the obvious difference in atrazine degradation between UV/Fe(III)/air and UV/Fe(III)/N₂ processes should be related to the oxidation by •OH radicals, which is produced from the photolysis of Fe(OH)₂²⁺ complex. Therefore, it should be concluded that the concentration of Fe(III) in the solution was a key factor to the degradation of atrazine in UV/Fe(III) process.

3.2. Changes of the concentration of Fe(III) in UV/Fe(III)/air and UV/Fe(III)/N₂ processes

The changes of the concentration of Fe(III) during the degradation of atrazine in UV/Fe(III)/air and UV/Fe(III)/N₂ processes were measured to reveal the reason for the enhancement caused by the oxygen, as shown in Fig. 4. In general, the concentrations of Fe(III) in these two processes were UV/Fe(III)/air > UV/Fe(III)/N₂.

In UV/Fe(III)/atrazine/air process, the concentration of Fe(III) decreased slightly at the beginning of 10 min. About 80% Fe(III) remained at 10 min, and then the concentration of Fe(III) kept almost unchanged. In UV/Fe(III)/atrazine/N₂ process, the concentration of Fe(III) was much lower than that in UV/Fe(III)/atrazine/air process. With air bubbling, the concentration of ferric ion was approximately 25% higher than that in deoxygenated solution.

Although the decrease of Fe(III) concentration was slower in the presence of oxygen, the degradation of atrazine was much faster than that in UV/Fe(III)/N₂ process (as shown in Figs. 2 and 4). It gives a clear indication that Fe(II) produced was effectively reoxidized to Fe(III) in UV/Fe(III)/air process, resulting in the regeneration of

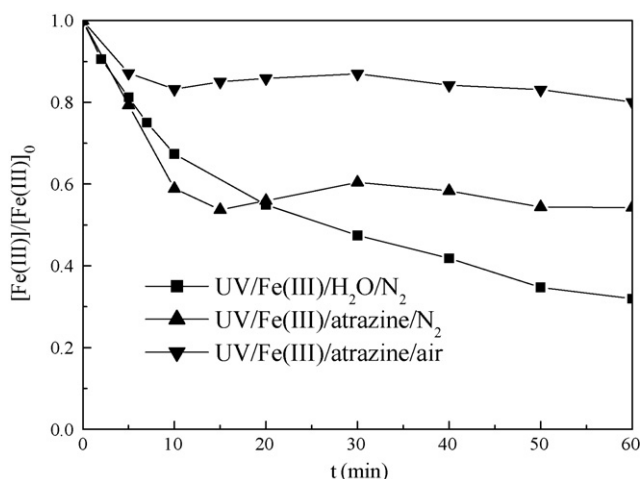


Fig. 4. Changes of the concentration of Fe(III) in UV/Fe(III)/air and UV/Fe(III)/N₂ processes: [atrazine]₀ = 30 mg/L, [Fe(III)]₀ = 7 mg/L, Q(air or N₂) = 0.20 m³/h, pH = 3.0, T = 30 °C.

Fe(III). The higher concentration of Fe(III) led to more •OH radicals be generated and thus the degradation of atrazine was enhanced.

3.3. Enhancement of atrazine degradation by oxygen under various Fe(III) input

In order to give more insight into the interaction of oxygen with iron ions, the degradations of atrazine by UV/Fe(III)/air and UV/Fe(III)/N₂ processes at different initial concentrations of Fe(III) were compared. The comparison of the pseudo-first-order rate constants in these two processes is shown in Fig. 5.

In both processes of UV/Fe(III)/air and UV/Fe(III)/N₂, the degradation of atrazine was obviously accelerated by the addition of Fe(III) into the solution. The time required to degrade the same amount of atrazine was significantly shortened with the increase of Fe(III) concentration. For example, when 3.5 and 21 mg/L Fe(III) was added, the time to degrade 75% atrazine were about 29 and 12 min, respectively in UV/Fe(III)/air process, and 38 and 25 min, respectively in UV/Fe(III)/N₂ process.

Fig. 5 also shows the enhancement of atrazine degradation by oxygen was related to the initial concentration of Fe(III). As more Fe(III) ions were put into these solutions, the increment of *k*-values

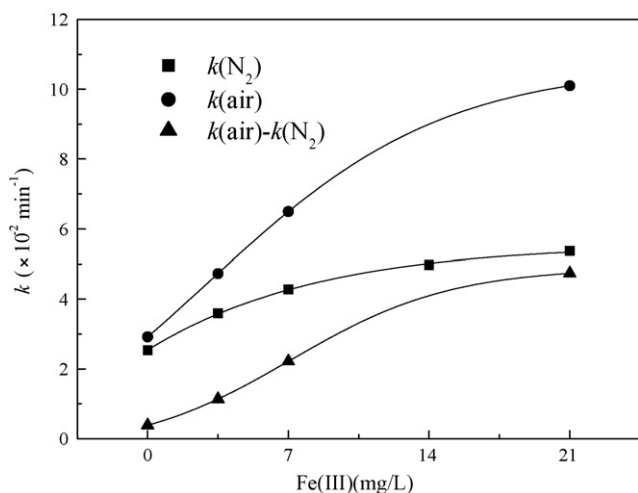
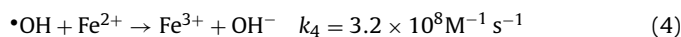


Fig. 5. Comparison of the pseudo-first-order rate constants in UV/Fe(III)/air and UV/Fe(III)/N₂ processes: [atrazine]₀ = 30 mg/L, Q(air or N₂) = 0.20 m³/h, pH = 3.0, T = 30 °C.

between UV/Fe(III)/air process and UV/Fe(III)/N₂ process increased. For example, the increment was only $1.20 \times 10^{-2} \text{ min}^{-1}$ when the initial concentration of Fe(III) was 3.5 mg/L while it enlarged to $4.73 \times 10^{-2} \text{ min}^{-1}$ at the initial Fe(III) concentration of 21 mg/L. It has been demonstrated in Section 3.3 that Fe(III) could be regenerated in the presence of oxygen. When the initial concentration of Fe(II) was low, the enhancement of the degradation caused by the oxygen was not distinct. This maybe because the amount of Fe(II) with oxygen to generate Fe(III) was few at the low initial concentrations of Fe(III). Whereas, much more Fe(II) could be oxidized to Fe(III) at higher initial concentrations of Fe(III), which caused the difference of *k*-values between UV/Fe(III)/air process and UV/Fe(III)/N₂ process increased.

3.4. Role of oxygen in the regeneration mechanism of Fe(III)

Fig. 4 shows that in UV/Fe(III)/N₂ process, the concentration of Fe(II) reaches a steady state after 15 min. Since Fe(III) in the solution keeps being photoreduced to Fe(II), it is believed that Fe(II) is oxidized to Fe(III) in UV/Fe(III)/N₂ process. The oxidant agent may be •OH because the rate constant of Fe(II) with •OH is high as $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (as shown in Eq. (4)). Mailhot et al. [13] also suggested that the reaction of Fe(II) with the oxidizing radicals such as •OH might accomplish the reoxidation of Fe(II) into Fe(III). In UV/Fe(III)/air process, Fe(II) was also oxidized by •OH, which was the same as that in UV/Fe(III)/N₂ process. But the concentration of Fe(III) was much higher than that in the air bubbling process, which indicated that there was another oxidation pathway of Fe(II) by reactive oxygen species [22].



To reveal the role of oxygen in the oxidation mechanism of Fe(II) to Fe(III) in the degradation of atrazine by UV/Fe(III)/air process, a series of controlled experiments, i.e., UV/Fe(II)/H₂O/O₂ (no atrazine), UV/Fe(II)/atrazine/N₂ (no oxygen) and Fe(II)/atrazine/O₂ (no UV illumination) were carried out to investigate the change of Fe(II) concentration. In these controlled experiments, the ratios of the concentrations of Fe(II) to the initial concentration of Fe(II) ranged from 0.963 to 1.003. In other words, the concentrations of Fe(II) were unchangeable during the reaction with the error tolerance, which demonstrated that no oxidation of ferrous ion took place in these three systems, even in UV/Fe(II)/H₂O/O₂ (no organics) process. From the results of these controlled experiments, it was concluded that the excited organic molecules and oxygen were necessary for the oxidation of Fe(II). The regeneration mechanism of Fe(III) by reactive oxygen species was not a single step photoreaction among Fe(II) and oxygen, as proposed by Catastini et al. [19].

Based on the experimental data, the role of oxygen in the regeneration mechanism of Fe(III) during the degradation of atrazine by UV/Fe(III) process was proposed. Firstly, the atrazine molecule absorbs the energy supplied by the lamp and passes to excited states, as described in Eq. (5). This has been confirmed by the experimental data of atrazine degradation of in direct photolysis process, which shown in Fig. 2. As it is well known [23–25], the excited organic molecules is active and in the presence of oxygen, it can happen that the electron transfers from the excited organic molecules (the excited atrazine or its intermediates) to the dissolved oxygen to form superoxide radical (O₂^{•-}) (Eq. (6)). As it has been accepted broadly, superoxide radical reacts with H⁺ to form the hydroperoxyl radical, i.e., HO₂[•] (Eq. (7)) and HO₂[•] could decomposed to O₂^{•-} (Eq. (8)). In the case of acidic solution of pH 3 adopted in the present study, the reaction rate of O₂^{•-} with H⁺ is $k_7 \times [\text{H}^+]$, about $10 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. While the decomposition rate is k_8 , $1.58 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Thus, in this study, the superoxide radical prefers to form the hydroperoxyl radical. HO₂[•] could both oxidize

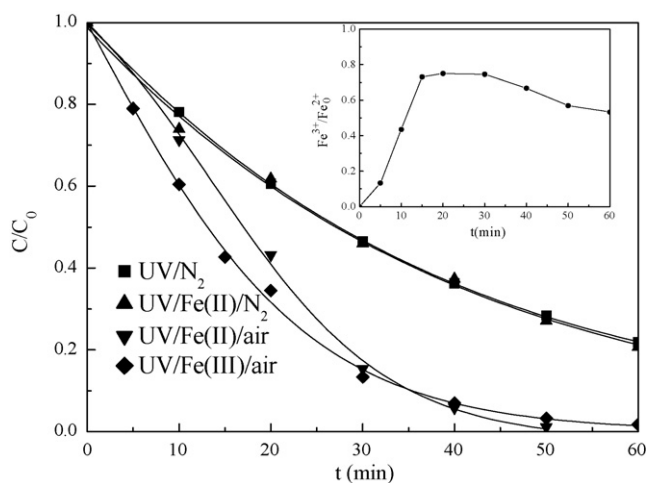
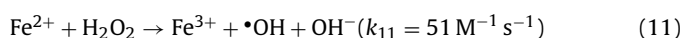
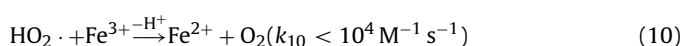
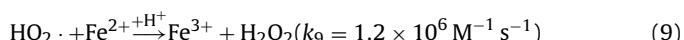
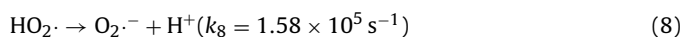
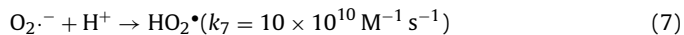


Fig. 6. Degradation of atrazine in photocatalytic processes (the insert illustration presents the changes of Fe(III) concentration in UV/Fe(II)/air process): [atrazine]₀ = 30 mg/L, [Fe(II)]₀ = 7 mg/L, Q (air or N₂) = 0.20 m³/h, pH = 3.0, T = 30 °C.

Fe(II) (Eq. (9)) and reduce Fe(III) (Eq. (10)), but the value of the oxidation rate constant was two orders of magnitude larger than that of the reduction rate constant [26]. Thus, it is concluded the main fate of the HO₂ radical is to react with Fe(II) to form Fe(III) and H₂O₂. Therefore, during UV/Fe(III)/air process, Fe(II) can be effectively reoxidized to Fe(III), which leads to the high apparent concentration of Fe(III) and the enhancement of atrazine degradation [26–28].



In addition, H₂O₂ formed in Reaction (10) could react with Fe(II) (Eq. (11)) and then •OH radical is simultaneously generated, which could also improve the degradation of atrazine.

3.5. Degradation of atrazine in UV/Fe(II)/air process

In UV/Fe(III)/air process, Fe(II) produced by the photoreduction of Fe(III) could be reoxidized to Fe(III) and thus the degradation of atrazine was enhanced. Therefore, it was supposed that the use of Fe(II) as the catalyst in UV/Fe(II)/air process could also be effective to degrade atrazine, even in a small dose of Fe(II).

Fig. 6 shows the degradation of atrazine in the processes of UV/Fe(II)/N₂ and UV/Fe(II)/air at a low concentration of Fe(II) of 7 mg/L. The degradations of atrazine in UV/N₂ and UV/Fe(III)/air processes are also presented for comparison. In the absence of oxygen, the addition of Fe(II) could not improve the degradation of atrazine and thus, the degradation of atrazine in UV/Fe(II)/N₂ process was almost the same to that in UV/N₂ process. With air bubbling, the degradation efficiency of UV/Fe(III) process was similar to that of UV process at the beginning of 10 min. However, the degradation rate of atrazine increased suddenly after 10 min and then at 40 min, the remaining atrazine was only 5%, similar to that in UV/Fe(III)/air process. The enhancement of atrazine degradation could be explained by the mechanism proposed above. At

the beginning of the reaction, atrazine was degraded only by UV-photolysis and thus the degradation rate was slow. At the same time, atrazine was excited and Eqs. (5)–(10) occurred, resulting the generation of Fe(III), as shown in the insert illustration of Fig. 6. After 10 min, the concentration of Fe(III) was considerable and UV/Fe(II)/air process changed to UV/Fe(III)/air process. Thus, the degradation of atrazine was promoted after 10 min and similar to that in UV/Fe(III)/air process. This experimental result confirmed the mechanism of Fe(II) reoxidation by reactive oxygen species proposed above.

4. Conclusion

In the presence of oxygen, the degradation of atrazine in UV/Fe(III) process was greatly enhanced. The value of first-order rate constant of the degradation atrazine in UV/Fe(III)/air process was $2.086 \times 10^{-2} \text{ min}^{-1}$ bigger than that of UV/Fe(III)/N₂ process. This increment was much greater than that between $k(\text{UV}/\text{air})$ and $k(\text{UV}/\text{N}_2)$ of $0.386 \times 10^{-2} \text{ min}^{-1}$, which meant the existence of the interaction of oxygen with iron ions in UV/Fe(III) process.

The detection of Fe(III) showed the ferric ions in the presence of oxygen were approximately 25% more than those with N₂ bubbling, which demonstrated that the regeneration of Fe(III) by reactive oxygen species took place during the process, resulting in the enhancement of atrazine degradation. The enhancement of atrazine degradation caused by oxygen increased with the initial Fe(III) concentration.

The excited organic molecules and oxygen were necessary for the regeneration of Fe(III) by reactive oxygen species. Based on the experimental results, the role of oxygen in the mechanism of Fe(III) regeneration was proposed. The electron transferred from the excited atrazine (or its intermediate) to the dissolved oxygen to form superoxide radical (O₂^{•-}). In the case of acidic solution of pH 3, O₂^{•-} was readily to combine with H⁺ to generate hydroperoxyl radical (HO₂[•]), which preferred to oxidized Fe(II) to regenerate Fe(III) and in consequence, the production of •OH and the degradation of atrazine were enhanced.

In UV/Fe(II)/air process, because of the oxidation of Fe(II) to Fe(III) by reactive oxygen species, the degradation of atrazine was similar to that in UV/Fe(III)/air process after 10 min, even at a low initial concentration of Fe(II) of 7 mg/L.

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