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Visible light and Fe(III)-mediated degradation of Acid Orange 7 in the absence of H_2O_2

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Abstract

The photodegradation of Acid Orange 7 (AO7) was successfully achieved in the presence of Fe(III) ions only under visible light ($\lambda \geq 420$ nm). Upon adding Fe(III) to AO7 solution, ferric ions formed complexes with AO7 mainly through the azo chromophoric group. This AO7–Fe(III) complex formation was highly pH-sensitive and maximized around pH 3.7. The visible light-induced degradation of AO7 was effective only when the complex formation was favored. The AO7 photodegradation accompanied the production of ferrous (Fe^{2+}) ions and was not inhibited in the presence of excess OH radical scavenger (2-propanol), which indicated that OH radicals were not responsible for the dye degradation. The proposed mechanism of the dye degradation is the visible light-induced electron transfer from the azo chromophoric group to the iron center in the complex. Therefore, when the formation of AO7–Fe(III) complex was inhibited in the presence of excess interfering anions such as sulfites and sulfates, the photodegradation of the dye was also prevented. The photodegradation of AO7 under visible light produced *o*-phthalate and 4-hydroxybenzenesulfonate (4-HBS) as major products but did not reduce the total organic carbon (TOC) concentration. Since this process does not require the addition of hydrogen peroxide, it might be developed into an economically viable method to pretreat or decolorize azo-dye wastewaters using sunlight.

Keywords: AO7; Dye; Ferric ions; Visible light; Photolysis; Water treatment

1. Introduction

About a half of global production of synthetic textile dyes (700,000 t per year) are classified into azo compounds that have the chromophore of –N=N– unit in their molecular structure and over 15% of the textile dyes are lost in wastewater stream during dyeing operation. These azo-dyes are known to be largely non-biodegradable in aerobic conditions and to be reduced to more hazardous intermediates in anaerobic conditions [1]. Since dyes are photochemically active, there have been various approaches to destruct them efficiently using solar light, especially visible light. The photochemical treatment methods for dye pollutants under active investigations include visible light sensitized degradation of dye on TiO_2 and photo-Fenton reactions.

Unlike a typical TiO_2 photocatalysis where UV photons are absorbed to generate electron–hole pairs in the semiconductor lattice [2–4], TiO_2-based photosensitization for dye destruction uses the semiconductor conduction band to extract electrons from excited dye molecules under visible light illumination [5–9]. In this case, TiO_2 valence band does not participate in the oxidative reactions of dye molecules. Although this method could be successful in decolorizing dyes using visible light, it is not effective in mineralizing dyes (or reducing total organic carbons (TOC)) [7] and needs a separation process of TiO_2 particles from dye-containing wastewater after treatment. As for photo-Fenton reactions [10–12] utilizing UV-Vis light, OH radicals are produced from the reductive dissociation of hydrogen peroxide. Being a strong oxidant ($E^\circ = 2.81\ V_{NHE}$), hydroxyl radicals can react with almost any kind of organic pollutants to achieve full mineralization. However, this process needs H_2O_2 as an oxidizing reagent.

In the present study, we demonstrate a new photochemical remediation method for dye-polluted waters by using Fe(III) and visible light only. Acid Orange 7 (AO7) was selected as a target dye and it could be successfully decolorized under visible light ($\lambda \geq 420$ nm) at a specific pH region. AO7 forms a complex with Fe(III) and subsequently undergoes a visible light-induced electron transfer from AO7 to Fe(III), which initiates the dye degradation.

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2. Experimental section

2.1. Reagents and materials

AO7 [4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid] was obtained from Aldrich (with purity 87%). The reagent used as a Fe(III) source was $FeCl_3 \cdot 6H_2O$ (>99%, Kanto). $FeSO_4 \cdot 7H_2O$, NaCl, Na_2SO_4, Na_2SO_3 and *o*-phenanthroline (Aldrich) were of reagent grade and used as received.

2.2. Photocatalysis and analysis

AO7 stock solution was prepared at 0.1 mM in distilled-deionized water (18 MΩ cm) and stored in the dark. A fresh aqueous stock solution of Fe(III) (30 mM) was prepared daily and used within 30 min after preparation to avoid any change [13]. A half-milliliter of Fe(III) stock solution was mixed with 29.5 ml of the AO7 stock solution in a 35 ml-Pyrex glass reactor, and then the pH of the solution was adjusted to a desired value with 0.1 N NaOH or HCl standard solution. Upon adding Fe(III) to AO7 solution, the pH immediately decreased from 5.6 to 3.2. Interfering effects of sulfites, sulfates, and chlorides on the complex formation of Fe(III)–AO7 and its photolysis were investigated by adding the anions to the solution. After 30 min equilibration with stirring, the solution mixture was illuminated with visible light ($\lambda \geq 420$ nm) by a 450 W Xe Arc lamp (Oriel). Between the light source and the photoreactor, a 10 cm IR water filter, a UV cut-off filter ($\lambda \geq 420$ nm), and a focusing lens were placed.

During the photolysis, sample aliquots were taken from the reactor at a regular time interval and were filtered out to remove precipitates when necessary. The degradation of AO7 was monitored by measuring the absorbance at $\lambda = 485$ nm as a function of irradiation time with a UV-Vis spectrophotometer (Shimadzu UV-2401PC) and a 1 cm pathlength quartz cell. The absorbance was measured without filtering out the agglomerates. Fe(II) ions produced from the reaction of Fe(III) with AO7 under visible light was quantitatively analyzed by a colorimetric method using *o*-phenanthroline as a reagent. The absorbance of the Fe(II)-phenanthroline complex was measured at $\lambda = 510$ nm ($\varepsilon_{510} = 1.17 \times 10^4$ M^{-1} cm^{-1}) to determine the concentration of photo-produced Fe(II) [11,14]. Dissolved organic carbon contents were quantified using a total organic carbon analyzer (TOC-V$_{CSH}$, Shimadzu). Intermediate analysis was performed with a reverse-phase high performance liquid chromatograph (HPLC, Agilent 1100 series) that was equipped with a diode array detector. The mobile phase consisted of 0.1 M ammonium acetate in water (A) and a mixture of 0.1 M ammonium acetate and acetonitrile (8:2 by volume) (B). In case, where better separation resolution was needed, a gradient elution (100% A at 0 min and 100% B at 30 min) was used. Ionic products such as sulfate, sulfite, and nitrate were sought by using an ion chromatograph (Dionex DX-120), but not detected.

3. Results and discussion

3.1. Complex formation and photodegradation

Fig. 1 compares the UV-Vis absorption spectra of AO7, Fe(III), and the mixture of AO7 and Fe(III) in the dark at pH 3.7 and 2.0. The absorption spectrum of AO7 shows two main bands at 430 and 485 nm, which corresponds to the $n \rightarrow \pi^*$ transition of the azo and hydrazone form (see Scheme 1), respectively [15]. Other two bands at 230 and 310 nm were attributed to the $\pi \rightarrow \pi^*$ transition of benzene and naphthalene ring, respectively [16]. In the Fe(III) spectrum at pH 3.7, one broad band around 300 nm was observed, which indicated the presence of $Fe(OH)^{2+}$ or $Fe(OH)_2{}^+$ species [17,18]. When Fe^{3+} ions were added to the AO7 solution at pH 3.7 (Fig. 1a), the visible band intensities at 430 and 485 nm decreased and a residual scattering background at $\lambda > 600$ nm appeared due to the formation of particulate

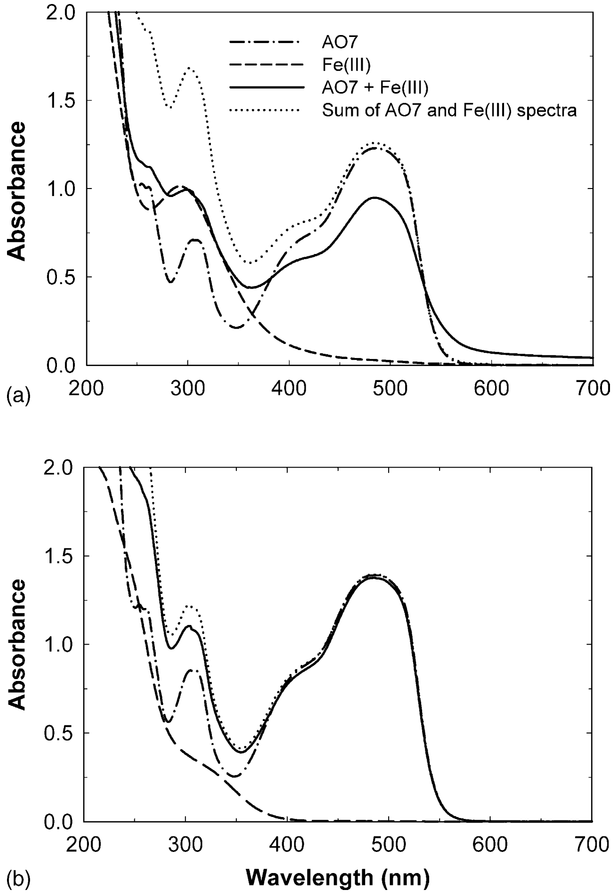
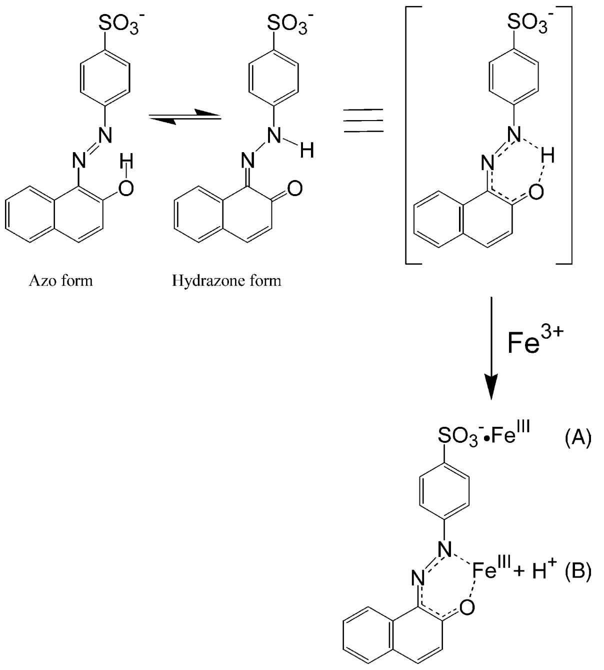


Fig. 1. UV-Vis absorption spectra of AO7 (0.1 mM), $Fe^{III}Cl_3$ (0.5 mM), and the mixture of AO7 and Fe(III) in water (a) at pH 3.70 ± 0.02 and (b) 2.00 ± 0.01. The arithmetic sum of AO7 and Fe(III) spectrum is compared with the spectrum of their mixture (AO7 + Fe(III)).



Scheme 1. Proposed structures of the complex AO7–Fe(III). AO7 undergoes fast intramolecular proton transfer (azo ↔ hydrazone). The ferric ion can be complexed to either the sulfonate group (**A**) or the azo group (**B**).

aggregates. A typical weight of the filtered agglomerate fraction (through 0.45 μm filter papers) in a 30 ml AO7+Fe(III) solution at pH 3.7 was around 0.5 mg, which accounts for 24% of the total weight of AO7 + Fe(III). The complex formation between AO7 and Fe^{3+} has been also previously reported to reduce the visible band absorption [19,20]. The solution pH decreased from 3.4 to 3.2 when 0.1 mM of AO7 was added to the ferric ion solution (0.5 mM). This observation indicated that AO7 and Fe^{3+} ions formed complexes with releasing protons. However, the absorption spectra at pH 2.0 (Fig. 1b) shows no sign of the complex formation between AO7 and Fe(III).

Table 1 lists the changes of pH when different concentrations of AO7 were added to aqueous solutions of Fe^{3+} or Fe^{2+}. Mixing of AO7 with Fe^{2+} solution little changed pH, which implied no complex formation. As for the mixing of AO7 with Fe^{3+}, the stoichiometric ratio ($\Delta[H^+]/[AO7]$) shows that about two protons were released per one AO7 molecule added in the presence of $[Fe^{3+}] \geq 0.3$ mM. Two possible structures of AO7–Fe^{3+} complex can be proposed as shown in Scheme 1: one with the terminal sulfonate group (**A**) and the other with the six-membered ring structure (**B**). Both complexing structures have been suggested in the literature [10,20]. Complex **A** does not liberate protons whereas complex **B** releases one phenolic proton with lowering pH. The mixing of benzenesulfonate and Fe^{3+} ions did not induce any pH change, which verified that the formation of complex **A** was not associated with pH change. The fact that two protons were liberated per one AO7 molecule might indicate that a 2:1 (dye:Fe^{3+}) complex was formed or that additional hydrolysis of Fe^{3+} species was induced upon complexing with an AO7 molecule. The Fe^{III} center in complex B pulls out electron density from the azo chromophoric group and reduces the intensity of the $n \rightarrow \pi^*$ transition (visible band) as exhibited in Fig. 1a. Therefore, it is quite clear that Fe^{3+} forms the complex with AO7 although the relative proportion of complex **A** and **B** could not be quantified.

Table 1
pH changes of aqueous iron solutions upon adding AO7

$[AO7]_{add}$ (mM)	$[Fe(III)]_i$ (mM)	$[Fe(II)]_i$ (mM)	pH_i	pH_f	$\Delta[H^+]$ (mM)	$\Delta[H^+]/[AO7]$
0.100[a]	–	–	5.51	5.59	<0.001	0.0
0.124	0.1	–	3.83	3.76	0.026	0.21
0.129	0.3	–	3.65	3.31	0.27	2.1
0.122	0.5	–	3.41	3.18	0.27	2.2
0.124	–	0.5	4.89	5.01	−0.0031	−0.025

[a] AO7 was added to blank distilled water.

Fig. 2a shows the photodegradation of AO7–Fe(III) complex as a function of the initial solution pH and illumination time. At pH 3.7, most AO7 degraded within 1 h illumination of visible light whereas the degradation rate became much slower at other pH regions. A dark control at pH 3.7 showed a negligible change of visible absorbance within the same time scale. The direct visible light photolysis of AO7 in the absence of ferric ions was not observed at all. The difference in initial A_{485} values among different pHs was due to the varying degree of agglomerate formation [21]. The photodegradation of AO7 accompanied gradual decreases of absorbance not only at the visible chromophoric region (400–550 nm) but also at 300 nm region (due to $\pi \rightarrow \pi^*$ transition of the naphthalene moiety) as shown in Fig. 2b. The strong dependence of AO7 photodegradation on the initial solution pH suggests that the pH-dependent Fe(III) speciation should play a critical role in this visible light-induced process. Fig. 3 compares the reduction of A_{485} after 4 h illumination with the Fe(III) speciation as a function of the initial pH. The most optimal pH region for the AO7 degradation was found to be between 3 and 4, where $Fe(OH)^{2+}$ and $Fe(OH)_2{}^+$ coexist as dominant iron species. This indicates that free Fe^{3+} species is not effective at all in inducing the visible light photolysis. On the other hand, although the color was effectively removed at pH 3.7, the soluble fraction of TOC in the solution did not decrease at all under visible light illumination. At pH 3.7, where the agglomerate formation was maximized, AO7 molecules were partitioned between the solid (agglomerates) and aqueous phase with a ratio of 7:3 before illumination. The ratio was determined by comparing the absorbance value (A_{485}) of initial AO7 solution with that of filtered AO7–Fe(III) solution. We observed that not only the aqueous solution but also the insoluble agglomerates were gradually decolorized under the visible light illumination. This implies that the AO7–Fe(III) complexes are photoactive whether they are in the solution or in the agglomerates.

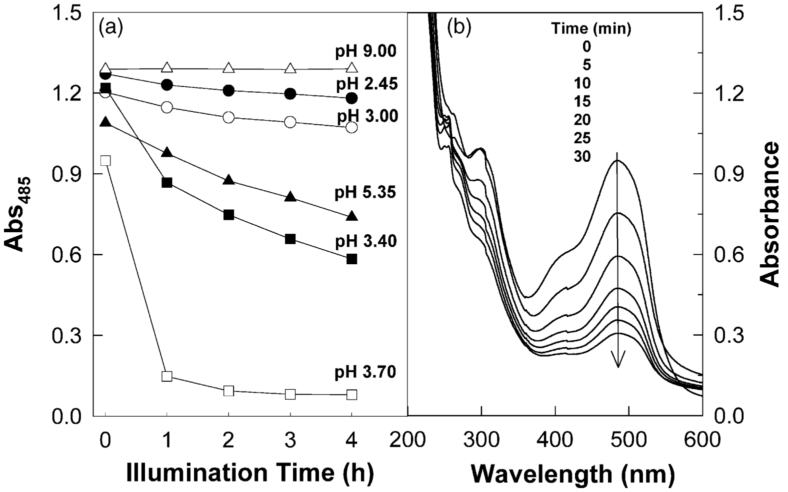


Fig. 2. (a) Degradation of AO7 (absorbance monitored at $\lambda = 485$ nm) in the presence of Fe(III) ions as a function of the visible light irradiation time at various initial pHs. (b) The absorption spectral change with the irradiation time at pH 3.70 ± 0.02. $[AO7]_i = 0.1$ mM; $[Fe(III)]_i = 0.5$ mM.

The visible light-induced degradation of AO7 could be mediated by photogenerated oxidants or direct electron transfers within the AO7–Fe(III) complexes. It is known that $Fe(OH)^{2+}$ species can be photolyzed to produce OH radicals with a quantum yield of 0.017 at 360 nm (reaction 1) [17].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO \qquad (1)$$

The degradation of organic compounds by OH radicals generated through reaction 1 has been demonstrated [22,23]. In order to check if OH radicals were involved in the AO7 degradation, the effect of adding 2-propanol, an OH radical scavenger, on the dye degradation was compared in Fig. 4. With this condition and the bimolecular rate constants (AO7 + OH ($k \sim 10^9\,M^{-1}\,s^{-1}$); 2-propanol + OH ($k = 1.9 \times 10^9\,M^{-1}\,s^{-1}$) [24]), most OH radicals, if any, should be scavenged by 2-propanol. The degradation rate of AO7 was hardly affected by adding excess 2-propanol, which indicated that OH radicals were not responsible for AO7 degradation in this system. The quantum yield of reaction 1 should be negligibly small in the visible region.

On the other hand, AO7 photodegradation accompanied a concurrent production of ferrous ions, which indicated that Fe(III) was reduced to Fe(II) as AO7 was photooxidized. Therefore, the visible light-induced degradation of AO7 seemed to be initiated within the AO7–Fe(III) complex. The fact that Fe(II) neither formed the complex with AO7 nor caused any decrease of A_{485} under visible light further verifies that the complex formation is essential for initiating AO7 degradation and that electron acceptors (i.e.

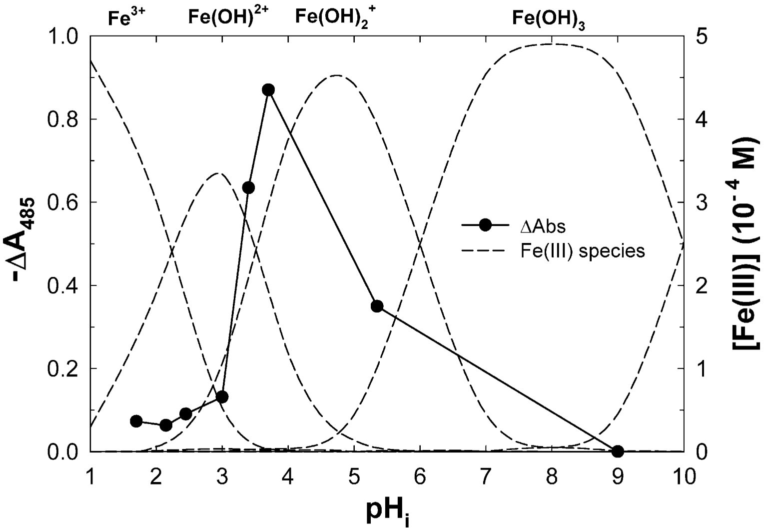


Fig. 3. Visible light-induced removal of color (A_{485}) in the AO7–Fe(III) solution and the calculated speciation of Fe(III) (dashed lines) are compared as a function of the initial pH. The experimental conditions were $[AO7]_i = 0.1$ mM; $[Fe(III)]_i = 0.5$ mM; 4 h illumination ($\lambda \geq 420$ nm).

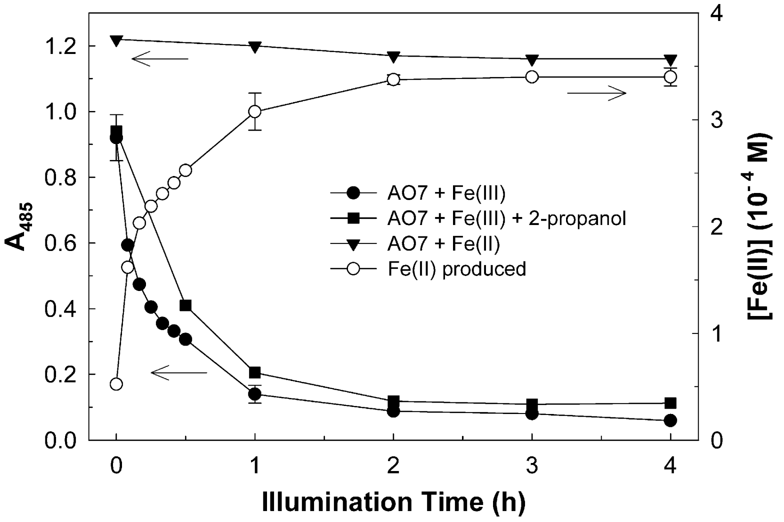


Fig. 4. Visible light-induced degradation of AO7 with or without 2-propanol. The accompanied photo-production of ferrous ions is shown as well. For a control experiment, AO7 degradation with ferrous ions (Fe^{2+}) was compared. The experimental conditions were $[AO7]_i = 0.1$ mM; $[Fe(III)]_i = 0.5$ mM; $[Fe(II)]_i = 0.5$ mM; $[2\text{-propanol}]_i = 43.5$ mM; $pH_i = 3.70 \pm 0.02$.

Fe(III)) should be present. The visible light-induced process can be proposed as follows.

$$AO7 + Fe^{III}(OH)^{2+}[\text{or } Fe^{III}(OH)_2{}^{+}] \leftrightarrow AO7 \cdots Fe^{III} \quad (2)$$

$$AO7 \cdots Fe^{III} + h\nu(\lambda \geq 420\,\text{nm}) \rightarrow AO7^{*} \cdots Fe^{III} \quad (3)$$

$$AO7^{*} \cdots Fe^{III} \rightarrow AO7^{\bullet +} \cdots Fe^{II} \quad (4)$$

$$AO7^{\bullet +} \cdots Fe^{II} \rightarrow AO7^{\bullet +} + Fe^{II}_{aq} \quad (5)$$

$$AO7^{\bullet +} \rightarrow\rightarrow \text{degradation products} \quad (6)$$

While the standard reduction potential of AO7 ($AO7/AO7^{\bullet +}$) has been reported to be 0.76 V (vs. NHE), that of the excited AO7 ($AO7^{*}/AO7^{\bullet +}$) is much more negative ($-1.24\ V_{NHE}$) [6]. Therefore, excited AO7 molecules have enough thermodynamic driving force to reduce Fe^{III} [$E^{\circ}(Fe^{2+}/Fe^{3+}) = 0.77\ V_{NHE}$] (i.e. reaction 4). A laser photolysis study of AO7 showed that the laser-induced dye bleaching around 500 nm was irreversible in the presence of Fe^{3+} [19]. The photo-production of ferrous ions reached a plateau within initial 2 h and further illumination little increased [Fe^{2+}] (Fig. 4). After most AO7 was photodegraded at pH 3.7 with reaching a steady-state of ferrous ions, a second spike of AO7 was injected into the reactor and the pH was readjusted to 3.7. Subsequent visible light illumination degraded AO7 but with a much reduced rate. The AO7 photodegradation after the third injection was even smaller than after the second injection. The successive deceleration of the AO7 photodegradation rate reflects that Fe(II) was not efficiently oxidized back to Fe(III) in this reaction mixture at pH 3.7. Even after exposing the illuminated solution to air for 24 h in the dark, the concentration of Fe(II) did not decrease. Fe(III) was used primarily as a reagent, not a catalyst in this system. Incidentally, it is noteworthy that the

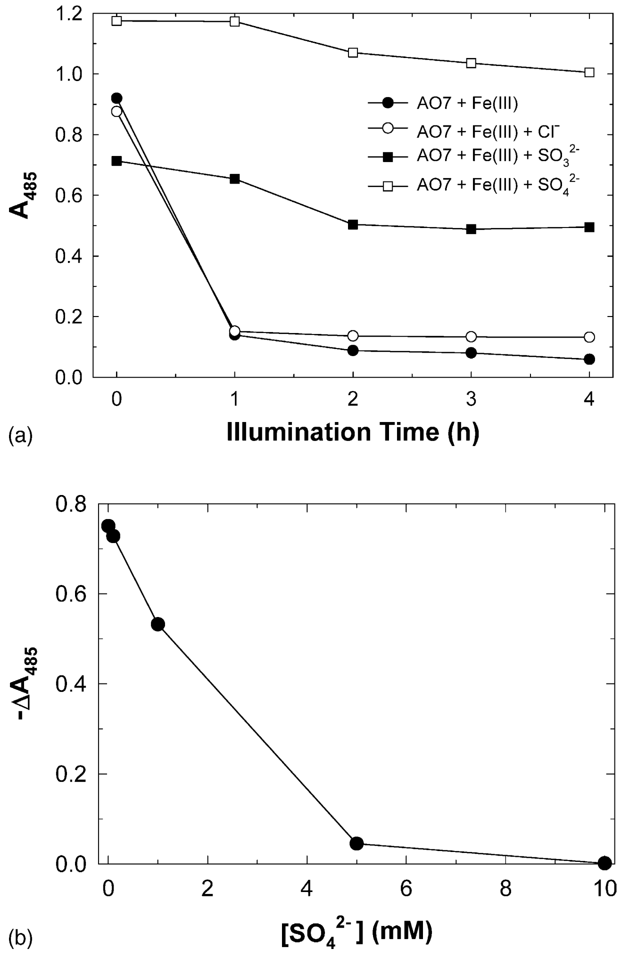


Fig. 5. (a) Effects of chloride, sulfite or sulfate ions on the photodegradation of AO7 and (b) Effect of the sulfate concentration on the photodegradation of AO7 (ΔA_{485} was measured after 4 h visible light illumination). The experimental conditions were $[AO7]_i = 0.1$ mM; $[Fe(III)]_i = 0.5$ mM; $[Cl^-]_i = [SO_3^{2-}]_i = [SO_4^{2-}]_i = 10$ mM; $pH_i = 3.70 \pm 0.02$.

visible light-induced production of Fe^{2+} (reaction 5) could be beneficial when this reaction system is combined with the Fenton reaction.

3.2. Effects of anions and complex formation

The complex formation of AO7–Fe(III) should be perturbed in the presence of anions that can complex with Fe(III) species. Therefore, adding interfering anions should reduce the photodegradation rate of AO7 under visible light. Fig. 5a shows that sulfite and sulfate greatly reduced the photodegradation of AO7 whereas chloride had little effect. A big difference in initial absorbance between the sulfate and sulfite-added mixtures should be noted, which indicates that the complex formation (AO7–Fe(III)) was affected in the presence of these anions. There was no difference in A_{485} between the AO7 only and AO7 + SO_4^{2-} (or $SO_3{}^{2-}$) solutions. As shown in Fig. 5b, increasing the sulfate concentration rapidly inhibited the photodegradation of AO7 with completely stopping the dye degradation at $[SO_4^{2-}] = 10$ mM. Fig. 6 shows the calculated speciation of Fe(III) in the presence of 0.1 or 10 mM sulfate. In the presence of 10 mM sulfate at pH 3.7, Fe(III) species distribute in the following fraction: $Fe(SO_4)^+$ (44.1%) > $Fe(OH)_2^+$ (24.1%) > $Fe(OH)^{2+}$ (15.2%) > $Fe(SO_4)_2^-$ (12.1%) > Fe^{3+} (0.48%). However, at $[SO_4^{2-}] = 0.1$ mM and pH 3.7 where the inhibition effect of sulfate was little, the order of the species distribution changes: $Fe(OH)_2{}^+$ (59.8%) > $Fe(OH)^{2+}$ (37.6%) > Fe^{3+} (1.19) > $Fe(SO_4)^+$ (0.98%) > $Fe(OH)_3$ (0.30%). Therefore, the presence of excess sulfates (≥5 mM) prevents the formation of AO7–Fe(III) complexes by sequestering most Fe(III) species as $Fe(SO_4)^+$ or $Fe(SO_4)_2{}^-$. On the contrary, with $[SO_4^{2-}] = 0.1$ mM, the total concentration of $Fe(SO_4)^+$ and $Fe(SO_4)_2{}^-$ is <2% and hardly interferes with the complex formation of AO7–Fe(III). Chloride also forms the complex with Fe(III) as $FeCl^{2+}$ or $FeCl_2{}^+$ [25] but their concentrations are negligibly small (at $[Cl^-] = 10$ mM and pH 3.7, $FeCl^{2+} + FeCl_2^+ < 0.4\%$).

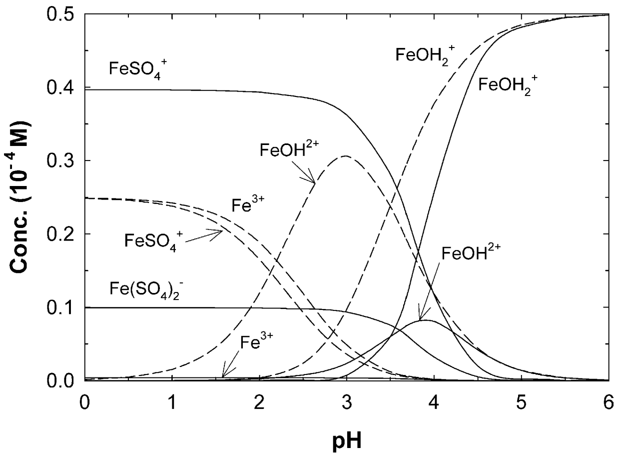
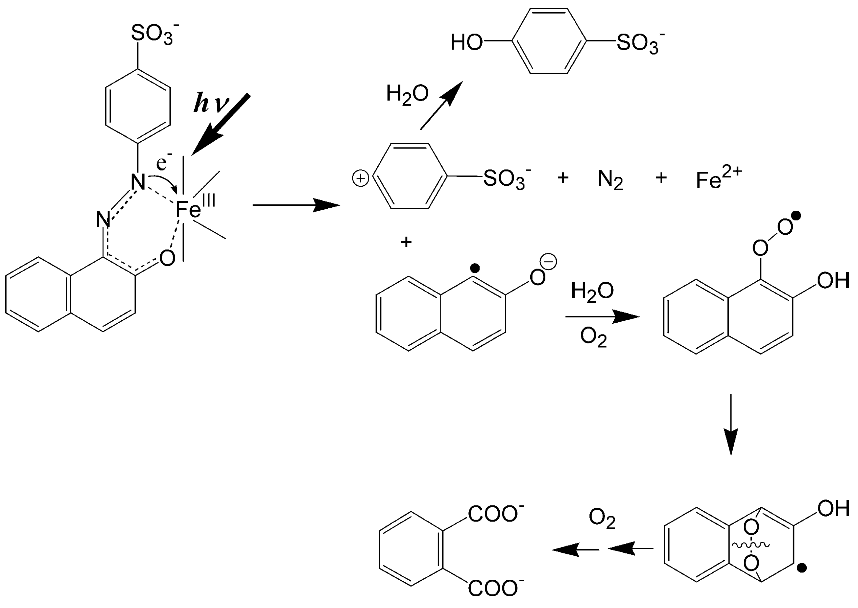


Fig. 6. Calculated pH-dependent speciation of Fe(III) ($Fe_{tot} = 0.5$ mM) in water in the presence of 0.1 mM (dashed line) or 10 mM (solid line) $SO_4{}^{2-}$. For clarity, minor species such as $Fe(OH)_3$ and $Fe(SO_4)_2{}^-$ are not shown.

3.3. Intermediate analysis and reaction pathways

The major degradation products of AO7 under visible light illumination were found to be *o*-phthalate and 4-hydroxybenzenesulfonate (4-HBS) as shown in Fig. 7 although other unknown intermediates were also detected. Since AO7 and intermediates were analyzed after filtering out the agglomerates, the measured concentrations did not



Scheme 2. Proposed reaction pathway of AO7 degradation in the presence of visible light and Fe(III) ions.

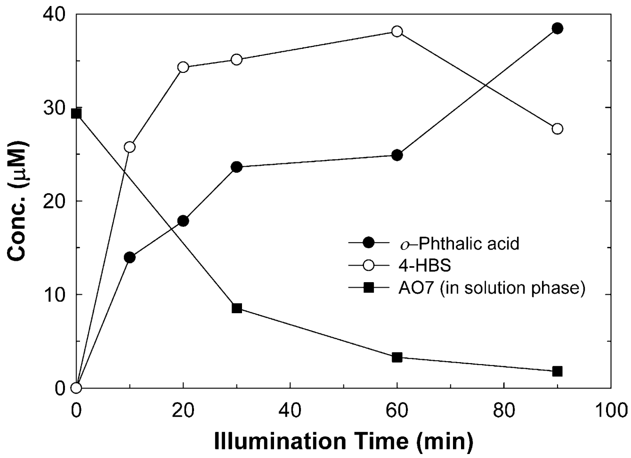


Fig. 7. Major intermediates produced from the visible light-induced degradation of AO7. [AO7] = 0.1 mM; [Fe(III)] = 0.5 mM; $pH_i = 3.70 \pm 0.02$.

take the adsorbed species into account. Scheme 2 depicts the reaction pathways of the visible light-induced degradation of AO7. Light induces an electron transfer from the azo chromophoric group to the Fe(III) center with releasing Fe^{2+}, benzenesulfonate cation, and 2-naphthol radical species. The benzenesulfonate cation subsequently reacts with water to produce 4-HBS while the reaction of 2-naphthol radical with oxygen leads to *o*-phthalate.

4. Conclusion

Development of treatment technologies for dye-polluted wastewaters has been an important research topic among environmental researchers. Although photo-Fenton processes that need H_2O_2 as an oxidant have been much studied for this purpose, this work demonstrates that a common synthetic azo-dye, AO7 can be efficiently degraded under visible light in the presence of ferric ions without H_2O_2. AO7 forms a complex with Fe(III) and the visible light induces an electron transfer from the azo chromophoric group to the Fe(III) center, which subsequently initiates the dye degradation. This method provides a basis for decolorizing dye-polluted wastewaters using sunlight and ferric salts only without H_2O_2.

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