Significantly photoinduced synergy between sodium sulfite and ammonium nitrate and the mechanism study

Wen-Na Hu, Jian Liu, Wei Liu and Xian-Feng Zhang

ABSTRACT

In this paper, a significantly photoinduced synergy between ammonium nitrate and sodium sulfite via dye decolorization was first found. This study mainly aims to explore the influences of several fundamental aspects on the photoinduced synergy as well as discuss the detailed mechanisms. The dye removal efficiencies of methyl orange and methylene blue of the synergistic system are much higher than that of a single one, and they reach 96.4% and 90.7% when the illumination is 6 and 14 min, respectively. The optimum mass ratio of sodium sulfite and ammonium nitrate in the reaction system is 1:1. The reaction process of photoinduced synergy follows the first-order reaction equation. Effects of different structures of dyes, amount of sodium sulfite and initial dye concentration on the synergistic effect were investigated. The changes of UV-vis spectra in the course of photoinduced synergy were also examined. The excellent synergistic effect can owe to the simultaneous photoreduction and photooxidation reaction with respect to photoinduced hydrated electrons (\(e_{aq}^-\)) and \(SO_4^{2-}\) active species, respectively. This work may provide some insight into detoxifying water contaminants in practical applications as well as developing other novel photoinduced synergistic systems with high performance.

Key words | ammonium nitrate, decolorization, mechanism, sulfite, synergistic effect

INTRODUCTION

Photocatalysis has attracted people’s great attention over the past decades due to its broad application prospects in a number of significant fields of environmental pollution improvement (Jiang et al. 2017; Wang et al. 2017), hydrogen production by solar energy and biology (Qiu et al. 2017), manufacturing dye-sensitized solar cells (Guo et al. 2017; Yan et al. 2017), and so on. So far, a large number of photocatalysts including metal oxides (Freitag et al. 2015), sulfides (He et al. 2014), nitrides (Wang et al. 2014), their mixed solid solutions (Kato et al. 2015), and metallic or nonmetal acid salts (Meng et al. 2015) have been extensively used to degrade organic contaminant. At the same time, numerous attempts about modification have been developed by many researchers at home and abroad, such as noble metals deposition, doping transition metals, doping non-metallic elements, surface photosensitization and construction of composites (Li et al. 2015), etc., to improve the quantum efficiency and expand the scope of practical application. However, there are still some problems to be solved in their applications, because the photocatalytic performance is limited by the low quantum efficiency, poor selectivity, the instability and undesirable structure of semiconductors themselves (Bokare & Choi 2014). Therefore, great efforts are to be devoted to developing novel photocatalysts or photoinduced reaction systems with high activity and high selectivity for their applications in the field of photocatalysis.

Recently, the bis-ions coexistence system of NH_4^+ and NO_3^- (denoted as BICS hereafter) was found to present a capability for the decolorization of soluble dyes under UV or solar light irradiation in our previous report (Chen et al. 2017). It is a remarkable fact that the color removal by BICS is a photocatalytic reduction reaction, during which ammonium nitrate plays a photocatalyst role. The reason is that NO_3^- radicals and hydrated electrons (\(e_{aq}^-\)) are produced from NO_3^- under light illumination, and then the quick reaction of \(e_{aq}^-\) with the \(\pi\) bonds in chromophore of dyes leads to an immediate decolorization. From the viewpoint of practical applications, however, the decolorization efficiency of dyes is not high and it will take a long time to decolorize them completely. Hence, there is still a quite far distance from the expected goal. To improve the
Ammonium nitrate, tert-butyl alcohol, sunset yellow FCF, carmine, orange G and ponceau S were supplied by Aladdin Industrial Corporation. Methyl orange (MO), naphthol green B, methylene blue (MB) and indigo were purchased from Shanghai Baoman Bio-Technique Co. Ltd. Ethanol was supplied by Anhui Ante Food Co. Ltd. Ammonium nitrate was dried at 70 °C in air and ground in the agate mortar before use. All chemicals were of analytically pure grade and used without further purification. Deionized water was used throughout this study.

Experimental procedure and analysis

Experiments were carried out in a photoreaction apparatus as same as our earlier report (Chen et al. 2011). Briefly, a 375 W medium pressure mercury lamp was purchased from Beijing Institute of Electric Light Source and laid in the chamber of annular quartz tube to use as the light source in the research work. The maximum emission wavelength of the lamp located at approximately 365 nm. The circulating cooling water passed through the inner thimble of annular tube to remove immediately the heat released from the lamp. A 500 mL unsealed beaker of 12 cm diameter was used as the reaction vessel. The temperature of the reaction solution is monitored no more than 25 °C during the experiment. Prior to the experiment, the 50 mL dye and 0.1 g sodium sulfite (ammonium nitrate) were put in the unsealed beaker, and a magnetic stir bar was used to blend the reaction solution. The distance between the light source and the surface of the reaction solution is 11 cm. The UV irradiation intensity (wavelengths below 400 nm) on the reaction solution surface is about 18,300 μW/cm². The schematic diagram of photoreaction apparatus is shown in Figure 1.

EXPERIMENTAL

Materials

The anhydrous sodium sulfite used in the experiments was purchased from Sinopharm Chemical Reagent Co., Ltd.
The concentration of dyes in solution was determined spectrophotometrically. At the given time intervals, the concentration of dye was determined by a spectrophotometer from its maximum absorption at a wavelength of 464 nm for MO and 664 nm for MB with deionized water as a reference sample. The photoinduced decolorization efficiency of dyes $\eta$ was calculated from the following expression:

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100$$

where $C_0$ is the initial concentration of dyes before illumination. The respective initial concentrations of MO and MB were 10.0 and 2.5 mg/L without special introductions. C is the concentration of dyes after the illumination time $t$.

### RESULTS AND DISCUSSION

#### Effects of different dye structures on the photoinduced synergy

To account for different kinds of dyes on the synergistic effect, various dyes with different structures were employed to conduct the experiments within 2 min illumination. The concentration of sodium sulfite and ammonium nitrate is 2.0 g/L, respectively. The initial concentration ($C_0$) of dyes, different structures of dyes, the synergistic decolorization efficiency ($\eta$) between ammonium nitrate and sodium sulfite are listed in Table 1. For comparison, the individual color removal efficiency of dyes by ammonium nitrate ($\eta_1$) and sodium sulfite ($\eta_2$) are also shown in the table. As shown in Table 1, various dyes such as MO, sunset yellow FCF, carmine, orange G, ponceau S, naphthol green B, MB, indigo, etc., can be decolorized by sodium sulfite and ammonium nitrate, respectively. Remarkably, it is worth noting that these dyes are more easily degraded by the synergistic system consisted of sodium sulfite and ammonium nitrate. Furthermore, it is noticeable that $\eta > \eta_1 + \eta_2$, which indicates the synergistic effect for decolorization is obvious between sodium sulfite and ammonium nitrate under the experimental conditions. For example, it is known that the color removal efficiencies of MO by ammonium nitrate ($\eta_1$), sodium sulfite ($\eta_2$) and the corresponding synergistic decolorization efficiencies ($\eta$) are 2.8%, 21.7% and 41.4%, and those of MB reaches 8.4%, 13.6% and 59.0%, respectively.

#### Effect of illumination time

MO and MB were chosen as typical representations of the familiar dyes to investigate the impact of illumination time on the synergistic effect between ammonium nitrate and sodium sulfite. The concentration of both ammonium nitrate and sodium sulfite is 2.0 g/L. Effect of illumination time on the synergistic effect for MO and MB is illustrated in Figure 2(a) and (b), respectively. For comparison, the decolorization efficiency of dyes by single ammonium nitrate or sodium sulfite was also tested under the same conditions. The blank experiment showed that the photoinduced self-degradation efficiency of dyes was little under a short-time illumination. As seen from Figure 2(a), the color removal efficiency of the mixing solution of ammonium nitrate, sodium sulfite with MO in dark could be negligible. MO can be decolorized undoubtedly by ammonium nitrate, sodium sulfite and the synergistic system consisted of them. As for MO, all of the decolorization efficiencies improve with the increasing illumination time, but the color removal efficiency for the synergistic system enhances the most rapidly among the variation tendencies. In other words, ammonium nitrate and sodium sulfite exhibit excellent synergistic effect, and the decolorization efficiency of MO can reach up to 96.4% after 6 min illumination. As shown in Figure 2(b), similar results were found in regard to MB, although the removal efficiency of the mixing solution of ammonium nitrate, sodium sulfite with MB in the dark increased slightly. The decolorization efficiency of MB improves remarkably from 0 to 85.9% with the increasing illumination time from 0 to 6 min, and then increases slowly to 90.7% when the illumination time is 14 min. The enhanced photoinduced decolorization efficiency may be attributed to the simultaneous interaction between dyes and the cumulative $e_{aq}$ as well as $SO_\text{4}^2-$ with the gradual illumination time.

#### Effect of the mass ratio of ammonium nitrate and sodium sulfite

The total mass weight of ammonium nitrate and sodium sulfite with different ratios varying from 10:1, 5:1, 1:1, 1:5, to 1:10 was 0.2 g. The experiments were performed after they were dissolved in 50 mL dyes. The mass ratio of ammonium nitrate and sodium sulfite has an obvious synergistic effect on the dye removal efficiency. The result is shown in Figure 3. From Figure 3(a) and (b), it can be seen that all of the systems containing different ratios of ammonium nitrate and sodium sulfite have good photoinduced synergy.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Dyes</th>
<th>C₀ (mg/L)</th>
<th>Structure of dyes</th>
<th>η₁ (%)</th>
<th>η₂ (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl orange (MO)</td>
<td>10.0</td>
<td><img src="image" alt="Structure MO" /></td>
<td>2.8</td>
<td>21.7</td>
<td>41.4</td>
</tr>
<tr>
<td>2</td>
<td>Sunset yellow FCF</td>
<td>10.0</td>
<td><img src="image" alt="Structure FCF" /></td>
<td>6.3</td>
<td>25.8</td>
<td>45.3</td>
</tr>
<tr>
<td>3</td>
<td>Carmine</td>
<td>10.0</td>
<td><img src="image" alt="Structure Carmine" /></td>
<td>8.2</td>
<td>27.5</td>
<td>47.6</td>
</tr>
<tr>
<td>4</td>
<td>Orange G</td>
<td>10.0</td>
<td><img src="image" alt="Structure Orange G" /></td>
<td>7.8</td>
<td>6.4</td>
<td>20.8</td>
</tr>
<tr>
<td>5</td>
<td>Ponceau S</td>
<td>10.0</td>
<td><img src="image" alt="Structure Ponceau S" /></td>
<td>8.8</td>
<td>17.2</td>
<td>34.4</td>
</tr>
<tr>
<td>6</td>
<td>Naphthol green B</td>
<td>5.0</td>
<td><img src="image" alt="Structure Naphthol green B" /></td>
<td>5.9</td>
<td>10.6</td>
<td>31.7</td>
</tr>
<tr>
<td>7</td>
<td>Methylene blue (MB)</td>
<td>5.0</td>
<td><img src="image" alt="Structure Methylene blue (MB)" /></td>
<td>8.4</td>
<td>13.6</td>
<td>59.0</td>
</tr>
<tr>
<td>8</td>
<td>Indigo</td>
<td>10.0</td>
<td><img src="image" alt="Structure Indigo" /></td>
<td>7.0</td>
<td>16.3</td>
<td>34.8</td>
</tr>
</tbody>
</table>

*aIllumination time = 2 min; Concentration of both ammonium nitrate and sodium sulfite = 2.0 g/L.

η₁: the decolorization efficiency of dyes by ammonium nitrate.

η₂: the decolorization efficiency of dyes by sodium sulfite.

η: the synergistic decolorization efficiency of dyes by sodium sulfite and ammonium nitrate.
The synergistic decolorization efficiencies of MO and MB improve remarkably with increasing ratio of ammonium nitrate and sodium sulfite, although at the higher ratios, e.g., 5:1 and 10:1, the synergistic removal efficiency decreases, suggesting that the optimal ratio of ammonium nitrate and sodium sulfite is 1:1. When the ratio is smaller or larger than 1:1, the system prevents the active radicals from producing, which implies the synergistic effect will become lower. This result also noticeably indicates that both ammonium nitrate and sodium sulfite play a vital role in enhancing the photoinduced synergy. That is to say, only ammonium nitrate and sodium sulfite have an appropriate ratio, the wonderful photoinduced synergistic effect can be highlighted. Based on the above results, it demonstrates that the photoinduced synergistic effect indeed exists between ammonium nitrate and sodium sulfite, and the initial design is correct in the present study.

**Effect of sodium sulfite concentration**

The illumination time was 2 min. The mass ratio of ammonium nitrate and sodium sulfite was fixed at 1:1. Effect of dosage of sodium sulfite (or ammonium nitrate) on the photoinduced decolorization efficiency of MO and MB are depicted in Figure 4. It is evidently seen that the synergistic degradation efficiency of MO changes extraordinarily from 17.2% to 58.3% and that of MB enhances quickly from 39.5% to 67.6%, as the sodium sulfite dosage increases from 0.5 to 4.0 g/L. While the concentration is beyond 4.0 g/L, a relatively smaller enhancement of the removal efficiency is observed. When the sodium sulfite concentration is 8.0 g/L, the photoinduced decolorization efficiency of MO and MB is 65.4% and 72.4%, respectively. Hence, the suitable amount of sodium sulfite is 4.0 g/L for the fading of the MO and MB in this study. It is known to all that NO$_3^-$ and SO$_3^{2-}$...
contain the nitrogen to oxygen double bond (\(-N=O-\)) and the sulphur to oxygen double bond (\(-S=O-\)), respectively, which conduces they are only excited by UV light. The increasing amount of sodium sulfite will improve the quantity of photons absorbed, which favors the synergistic effect and results in the enhanced decolorization efficiency. Similar results were observed in our earlier report (Liu et al. 2013).

**Effect of initial dye concentration**

As shown in Figure 5, the photoinduced decolorization efficiencies of dyes diminish with their initial concentration. As for MO, the photoinduced removal efficiency is 57.6% as the initial concentration is 5 mg/L, while that is 20.2% corresponding to 25 mg/L. With regard to MB removal, its efficiency is 59.0% and 22.8% when the respective original concentration is 2.5 and 12.5 mg/L. The decolorization occurs mediated by the direct reaction between sulfate radical (SO$_4^-$) and the dye (see section on Proposed reaction mechanisms in the present study). When both sodium sulfite and ammonium nitrate have unchanging concentration with consequently constant active species available for photoreaction, the synergistic effect tends to decrease with the increasing initial concentration of dyes. The same result was reported in previous study involved sulfite oxidation process (Wang et al. 2009).

**Reaction kinetics**

According to the method to determine the degradation kinetics for organic pollutants in previous report (Liu et al. 2013), we attempted to obtain linear function for dye removal using several usual kinetics equations. Then the first-order reaction kinetics was established by making a linear plot of \(\ln(C_0/C)\) against illumination time. The kinetics for the decolorization of MO and MB are shown in Figure 6. As shown in Figure 6(a), the
first order kinetics equation for MO removal is \( y = 0.676x - 0.64951 \) with the corresponding correlation coefficient of 0.99201. While there are two linear regions in Figure 6(b) for the photoinduced decolorization of MB, namely, when the illumination time is 0–6 min and 6–14 min, the corresponding linear equation is \( y = 0.26917x + 0.52718 \) and \( y = 0.04889x + 1.61619 \), respectively. The related coefficient of linear fitting in the plane figure is quite good to be 0.99371 and 0.99064, respectively. From Figure 6, it also can be seen that the two apparent reaction rate constants for photoinduced decolorization of MB are 0.26917 \( \text{min}^{-1} \) and 0.04889 \( \text{min}^{-1} \), respectively, and that of MO is 0.676 \( \text{min}^{-1} \). The above analysis reflects indirectly that the reaction of ammonium nitrate, sodium sulfite with dyes is independent, but they influence each other during the reaction process, namely, one ongoing reaction will give rise to the quick response of another reaction and facilitate it.

### Changes of UV-vis spectra

UV-vis absorption spectroscopy measurements were carried out using a HITACHI U-3900 UV-VIS spectrophotometer. The amount of both sodium sulfite and ammonium nitrate used was 2.0 g/L. The absorption spectra changes of MO and MB solution in the process of photoinduced synergy at given minutes are shown in Figure 7. As shown in Figure 7(a), the spectrum of MO exhibits a maximum absorption peak at 464 nm in the visible region. And that MO can be decolorized by the system consisted of ammonium nitrate and sodium sulfite, pure ammonium nitrate, and pure sodium sulfite. Nevertheless, compared to the inserted plot in Figure 7(a), it is conspicuous that the decolorization efficiency of MO by the synergistic system is far greater than that by pure ammonium nitrate and pure sodium sulfite, because of the favorable generation of photoinduced synergistic effect in the system. There is still a strong absorption intensity of MO at 464 nm by employing single ammonium nitrate or sodium sulfite after 6 min irradiation, while almost no absorption peak can be seen by using the photoinduced synergistic system under the same conditions. The results are in good agreement with the removal efficiency of MO investigated in section on Effect of illumination time in this article. Similarly, Figure 7(b) shows absorption spectral changes of MB during the fading process. It is clearly seen that there are two main absorption peaks at 664 nm and 610 nm for MB, corresponding to the characteristic structure of its monomer and dimer, respectively (Morgounova et al. 2015). The decolorization efficiency of MB at 664 nm increases rapidly at the beginning of 6 min. And then with the illumination time increasing from 6 to 14 min, the absorption intensity of dimer has almost no change, which causes the removal efficiency of MB at 664 nm improved slightly. The same results are also verified in Figure 2. These results once again demonstrated the evidence between sodium sulfite and ammonium by decolorization of dyes.

### Proposed reaction mechanisms

Based on the above results, it is known that sodium sulfite and ammonium nitrate participate in the chemical reaction simultaneously. Under UV light illumination, the \( \text{NO}_3^- \), \( \text{SO}_3^- \) radicals and hydrated electrons (\( e_{\text{aq}} \)) are produced. These electron-transfer steps are as follows (Tacconi et al. 2000):

\[
\text{NO}_3^- + h\nu \rightarrow \text{NO}_3^+ + e_{\text{aq}}
\]
As shown in Equations (2)–(4), 1 mol SO$_3^{2-}$ and NO$_3^-$ can generate 2 mol and 1 mol hydrated electron under the experimental conditions, respectively. After introducing sodium sulfite, the abundant hydrated electrons in the system accelerate the migration of eaq to the surface of dye molecules and are helpful to improve the photoreduction reaction rate as well. Because it was demonstrated that the dye removal by ammonium nitrate was a photoreduction reaction, in which the hydrated electrons (eaq) reagents immediately with the chromophore and results in the quick decolorization (Chen et al. 2011). The overall reaction for MO decolorization can be expressed as Equation (5) according to some related reactions in the literature (Földváry & Wojnárovits 2009), which is similar to MB removal. Furthermore, the ammonium nitrate served as a photocatalyst and it was proposed that NO$_3^-$ and NH$_4^+$ transformed themselves into each other, as shown in Equations (6) and (7).

\[
-N = -NH + H_2O + 2e_{aq} \rightarrow -NH - NH + OH^- 
\]  
\[
NH_4^+ + 2NO_2^- \rightarrow 3NO_2^- + 3H^+ + H^+ 
\]  
\[
NO_2^- + OH^- \rightarrow NO_3^- + H^+ 
\]

At the same time, according to the reported result (Chen et al. 2012), it is known that SO$_3^-$ anion radicals are not stable, which can react very rapidly with O$_2$ and generates SO$_5^-$ and SO$_4^{2-}$ radicals, as shown in Equations (8)–(10). Consequently, they not only produce SO$_5^-$, SO$_3^-$ and 'OH radicals but also react with molecular oxygen in the system, promoting the decolorization efficiency of dyes enhanced greatly. The fading of MB first increases rapidly before 6 min, implying unstable SO$_3^-$ transforms to other more active species. With the increasing illumination time from 6 to 14 min, the decolorization efficiency of MB improves slightly, indicating that oxygen depletion prevents the transformation of SO$_3^-$ to SO$_5^-$, even less the generation of SO$_4^{2-}$ and 'OH active radicals. These demonstrate the correctness of experimental results in sections on Effect of illumination time and Changes of UV-vis spectra in this paper. Similar results were also reported (Shi et al. 2014).

\[
SO_3^{2-} + O_2 \rightarrow SO_5^- 
\]
There exists a significant photoinduced synergy between sodium sulfite and ammonium nitrate via decolorization of dyes. The synergistic decolorization efficiencies of MO and MB in the system were much higher than that of a single one, and they reach 96.4% and 90.7% when the illumination is 6 and 14 min, respectively. The optimum mass ratio of sodium sulfite and ammonium nitrate in the reaction system is 1:1. The suitable amount of sodium sulfite is 4.0 g/L. The photoinduced synergy for dyes decolorization decreases with the increasing initial concentration of dyes. The reaction process of photoinduced synergy obeys the first-order kinetics. The photogenerated hydrated electrons and SO₄⁻ radicals in the system contribute to the greatly enhanced photoinduced synergy. The synergistic system is expected to be a good candidate for use in removal of organic. This work may provide some insight into the design of other novel photoinduced synergistic systems with high activity and high selectivity.

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