



Iron in non-hydroxyl radical mediated photochemical processes for dye degradation: Catalyst or inhibitor?



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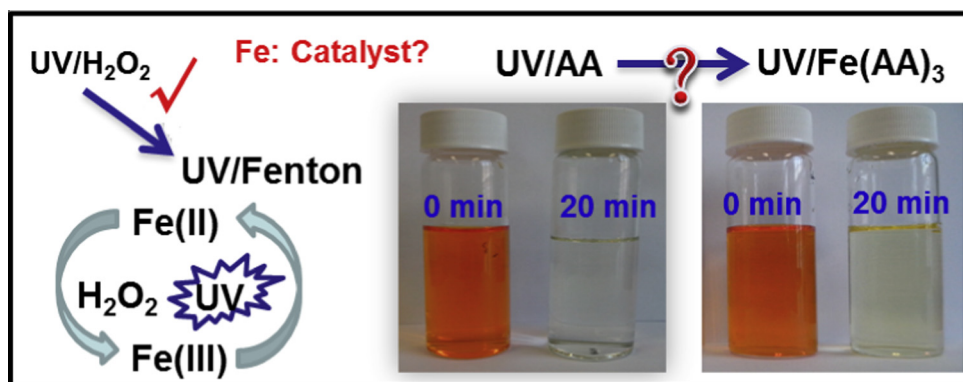
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HIGHLIGHTS

- The UV/AA process was an efficient approach for the decoloration of AO7.
- The UV/Fe(AA)₃ process was less efficient than the UV/AA process.
- Dose of iron ions reduced the efficiency of the UV/AA process.
- The enolic AA played a key role in the photo-degradation of AO7.
- Iron could not act as a catalyst but an inhibitor in the UV/AA process.

GRAPHICAL ABSTRACT



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ABSTRACT

The acetylacetone (AA) mediated photochemical process has been proven as an efficient approach for decoloration. For azo dyes, the UV/AA process was several to more than ten times more efficient than the UV/H₂O₂ process. Iron is one of the most common elements on the earth. It is well known that iron can improve the UV/H₂O₂ process through thermal Fenton and photo-Fenton reactions. What will be the role of iron in the UV/AA process? Could iron-AA complexes act as photocatalysts in environmental remediation? To answer these questions, the photo-degradation of an azo dye, Acid Orange 7 (AO7), was conducted under the variant combinations of AA with iron species in both ionic (Fe²⁺, Fe³⁺) and complex (Fe(AA)₃) forms. The pseudo-first-order decoloration rate constants of AO7 in these photochemical processes followed such an order: UV/Fe(II)/AA < UV/Fe(III)/AA < UV/Fe(AA)₃ < UV/AA. The results demonstrate that iron species, in either ionic or complex form, acts as an inhibitor rather than a catalyst in the UV/AA process. Based on spectroscopic analysis, the inner filter effect of iron and the competition between Fe(III) and AA for the complexation with AO7 were attributed to the inhibition effect of iron on the UV/AA process. The understanding of the role of iron provides insight into the practical application of the UV/AA process.

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1. Introduction

Acetylacetone (abbreviated as AA) is a β -diketone with two interesting structural isomers, keto and enol (Chart 1) (Hammond et al., 1959; Alagona et al., 2010). The enolic AA deprotonates to enolate (AA^-) in basic solutions with a $\text{p}K_{\text{a}}$ of 9.0 (Chart 1) (Stary and Liljenzin, 1982). AA has been proven as a potent photo-activator in the decoloration of dyes (Wang et al., 2013; Liu et al., 2014; Zhang et al., 2014). The decoloration rate constants of azo dyes in the UV/AA process were several to more than ten times higher than those in the well-known UV/ H_2O_2 process (Zhang et al., 2014). Furthermore, the decoloration in the UV/AA process was much more thorough and could be self-accelerated as the reactions proceed. These characteristics endow the UV/AA process with a promising application potential. It should be noted that one prominent characteristic of dyeing wastewater is the complexity of the composition. Theoretically, the UV/AA process was more target-selective than the UV/ H_2O_2 process, because direct energy and electron transfer between excited AA and dyes, rather than radical-mediated reactions, predominate in the UV/AA process (Zhang et al., 2014; Liu et al., 2014). However, to date, limited work has ever been done on the sensitivity of the UV/AA process to co-existing matters.

Iron is one of the most common elements on the earth. It is ubiquitous in water and wastewater. Due to the strong chelating ability, AA is able to form metal acetylacetonate complexes with many transition metals, including iron (Morgan and Moss, 1914; Farrar and Jones, 1964; Nakamura et al., 1972; Whitmore and Eisenberg, 1984; Mehrotra, 1988). In ferric acetylacetonate (abbreviated as $\text{Fe}(\text{AA})_3$), the enol hydrogen of AA is substituted by the iron ions (Mehrotra, 1988). The two O atoms in AA bind to the metal to form a six-membered chelate ring (Chart 1) (Morgan and Moss, 1914).

$\text{Fe}(\text{AA})_3$ has been exploited as a catalyst in organic chemistry, especially for reactions involving alkenes (Misono et al., 1966; Kioo and Saito, 1980; Richert et al., 1989; Sudo et al., 2010). For example, FeAA_3 can catalyze the dimerization of isoprene (Misono et al., 1966) or catalyze the ring-opening polymerization of 1,3-benzoxazine (Sudo et al., 2010). Based on the calculated reduction potentials and the conditional constants, $\text{Fe}(\text{AA})_3$ was regarded as an effective catalyst for the oxidation of H_2S (Eng et al., 2000). In addition to being used as a catalyst, $\text{Fe}(\text{AA})_3$ is also used to form intermediates en route to carbon–carbon bond forming reactions (Takacs et al., 1986). It is occasionally used as a catalyst precursor (Ramirez et al., 2007). However, the application of $\text{Fe}(\text{AA})_3$ is almost confined to organic solvents, such as methanol, acetonitrile, tetrahydrofuran, and dichloromethane (Emken et al.,

1966; Kimura and Muto, 1980; Cahiez et al., 2007). Limited work has been done regarding the application of $\text{Fe}(\text{AA})_3$ in aqueous solutions. The reason might be the hydrolysis of the complex in water.

At the current stage, UV light is a necessity for AA to play the role in decoloration (Zhang et al., 2014). If the photo-activity of AA could be extended to the visible light range as that of Fe-contained material (Zhang et al., 2013), the application potential of the AA-mediated photochemical process could be further improved. $\text{Fe}(\text{AA})_3$ is a red high spin complex, which absorbs visible light (Richert et al., 1989). If it could be used as a photocatalyst, the AA-mediated photochemical process might be able to happen under solar irradiation, which will greatly facilitate its practical application. To the best of our knowledge, the application possibility of $\text{Fe}(\text{AA})_3$ as an aquatic photocatalyst is still unclear.

It is well known that iron can improve the UV/ H_2O_2 process through thermal Fenton and photo-Fenton reactions (Fenton, 1894; Pignatello et al., 2006). The combination of the UV/ H_2O_2 process with Fe(II) constitutes the famous UV/Fenton process, in which the involvement of iron species significantly enhances the generation of $\cdot\text{OH}$ through the decomposition of H_2O_2 (Fenton, 1894). The iron species plays complex roles in the UV/Fenton system. Besides the Fe-involved thermal Fenton and photo-Fenton reactions, the high-valent oxoiron complexes may also participate in the Fenton chemistry (Pignatello et al., 2006). Although the mechanisms in the UV/Fenton process are still open questions, a common opinion is that iron species act as a catalyst in the UV/Fenton process (Pignatello et al., 2006). The synergistic effects of Fe(II) with the UV/ H_2O_2 process inspire us that whether the UV/ $\text{Fe}(\text{AA})_3$ process could be more effective than the UV/AA process. Could addition of exogenous iron be able to enhance the UV/AA process, like what it does in the UV/ H_2O_2 process?

To answer the above questions, the photodegradation of an azo dye in a series of iron-involved photochemical processes was systematically investigated. The roles of Fe(II), Fe(III), and $\text{Fe}(\text{AA})_3$ in the UV processes were thus demonstrated. The results are helpful for the best use of the UV/AA process.

2. Materials and methods

2.1. Materials

Acid Orange 7 (AO7, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{OSO}_3\text{Na}$), AA, $\text{Fe}(\text{AA})_3$, formic acid, acetic acid (HAc), ammonium acetate (NH_4Ac), ferric perchlorate, ferrous perchlorate, hydrochloric acid, sodium hydroxide, dichloromethane, methanol, hydroxylamine hydrochloride, and 1,10-phenanthroline were of analytical purity grade and were used as

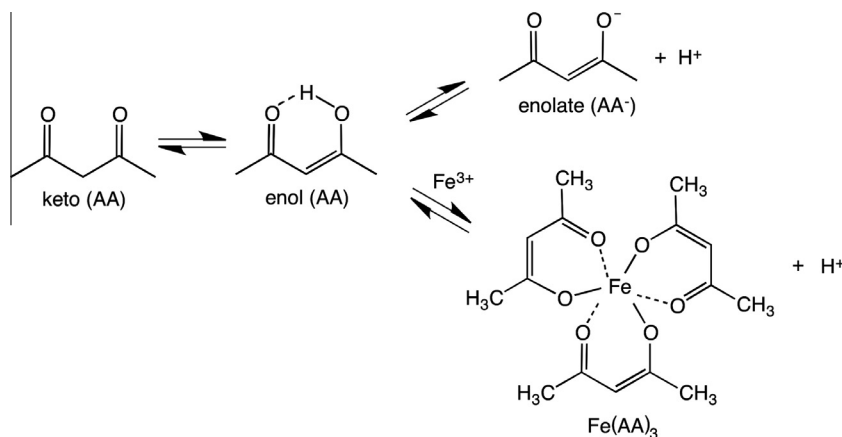


Chart 1. The molecular structures of AA and $\text{Fe}(\text{AA})_3$.

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