Degradation of Humic Acid by Ferrous Ion Activated Persulfate

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Abstract. The persulfate anions (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}) can be activated by Fe\textsuperscript{2+} to produce sulfate radicals (·SO\textsubscript{4}-) and hydroxyl radicals (·OH), which can oxidize organic compounds rapidly. Humic acid (HA) is widely found in nature and is the main limiting factor for high-concentration wastewater discharge. In this study, HA was treated by Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} system, the effects of initial pH, concentrations of Fe\textsuperscript{2+}, persulfate (PS), and HA on the removal efficiencies of HA and E\textsubscript{3}/E\textsubscript{4} were discussed. Besides UV\textsubscript{254} and UV\textsubscript{280}, we found that UV\textsubscript{250}, UV\textsubscript{270}, UV\textsubscript{300}, UV\textsubscript{365}, UV\textsubscript{400}, UV\textsubscript{436} and UV\textsubscript{465} can effectively quantified the concentrations of HA, providing more HA characterization methods. When the initial pH was 3.0, the concentrations of PS and Fe\textsuperscript{2+} were 100 mmol/L and 20 mmol/L, respectively, the removal efficiency of HA reached 72% after 5 minutes, indicating that PS/Fe\textsuperscript{2+} effectively degrade HA, and E\textsubscript{3}/E\textsubscript{4} increased from 2.6 to 5.75, suggesting the molecular weight and aromaticity of HA decreased. The removal efficiencies of HA increased as the concentrations of Fe\textsuperscript{2+} and PS increased, while the removal efficiencies of HA decreased as the initial concentration of HA increased. The addition of hydroxylamine hydrochloride (HAH) in Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} system, could effectively promoted the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} circulation and reduced the accumulation of Fe\textsuperscript{3+}, and strengthened the removal efficiency of HA. The research results indicate that Fe\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} oxidation is a promising technique for the treatment of HA in wastewater.

1. Introduction

HA is a mixture of amorphous acids with similar aromatic properties. The main functional groups on the benzene ring include ketone, ester, carboxylic acid, aldehyde, phenol, etc [1], which have an important impact on the toxicity, migration and transformation of organic pollutants [2, 3]. The excessive HA will affect the color and turbidity of water, making the water smelly, even causing aquatic eutrophication [4]. Disinfection by-products resulted from chlorination of HA, such as trihalomethane and halogenated acetic acid are carcinogenic, posing significant problems for human health and drinking water safety [5]. HA also is the main limiting factor for the standard discharge of chemical oxygen demand (COD) in high concentration wastewater, such as aged landfill leachate [6]. When the degradable organic components of the leachate disappear, most of the organic compounds are dissolved organic matter, mainly HA [6]. A large amount of HA is the main reason for the high COD of leachate
biochemical treatment effluents. Therefore, HA is often studied as a typical example of refractory organic compound.

Currently, some techniques have been successfully used for removal of HA, such as chemical coagulation [7], membrane separation [8] and adsorption [9]. However, these technologies are costly. Fe\(^{2+}\) can activate S\(_2\)O\(_8\)\(^{-2}\) under normal temperature, pressure, low energy consumption without external heating or light source, and the generated active radicals such as SO\(_4\)\(^{-}\) and OH can effectively degrade pollutants [10, 11]. Compared with other oxidation technologies, such as ozone [12, 13], UV/H\(_2\)O\(_2\) oxidation [14] or Fenton [15], the reagents used in PS activation technology are inexpensive, safe, stable, green and non-toxic, and have good selectivity for degrading targets. However, few investigations have been reported on Fe\(^{2+}/S_2O_8^{2-}\) applications for HA removal. Fe\(^{2+}/S_2O_8^{2-}\) can effectively degrade various environmental hormones, chlorine disinfection by-products and residual drugs [15, 16], and has become one of the most promising in situ repair techniques in the field of soil and groundwater organic pollution. It is very important to understand the structural changes of HA for the selection of subsequent processes, which is conducive to the discharge of sewage and the cost control of environmental engineering. To our best knowledge, the application of Fe\(^{2+}/S_2O_8^{2-}\) for HA degradation has not been reported. Hydroxylamine hydrochloride (HAH) is mainly used as a reducing agent [17, 18]. So far, although there are reports that HAH can promote Fenton process to degrade organic pollutants [19], HAH as additive in Fe\(^{2+}\)-activated S\(_2\)O\(_8\)\(^{-2}\) degradation on HA has rarely been studied. Therefore, this study selected HA as a typical refractory organic compound to fulfill the lack of knowledge about the degradation of HA during Fe\(^{2+}/S_2O_8^{2-}\) oxidation processes.

2. Materials and methods

HA and HAH (98.5\%) were obtained from McLean Biochemical Technology Co., Ltd.(Shanghai, China); Ferrous sulfate heptahydrate (FeSO\(_4\)•7H\(_2\)O) was purchased from Boyi Chemical Reagent Co., Ltd.(Chongqing, China); potassium persulfate, sodium hydroxide (NaOH) and sulfuric acid (H\(_2\)SO\(_4\)) (Analytical purity) were purchased from Kelong Chemical Reagent Factory (Chengdu, China). All reagents were analytical grade. The ultraviolet-visible spectrophotometer was produced by Shimadzu Enterprise Management (China) Co., Ltd. and the acidity meter was produced by Century Ark Technology Co., Ltd. (Chengdu, China).

2.1. Experimental procedure

The HA solution was prepared in 0.05 mol/L NaOH solution, then adjusted pH to 9.5 and adjusted to the specified concentration.100 mL 20 mg/L HA solution was transferred to a 250 mL conical flask in magnetic stirrer. After pH adjustment by H\(_2\)SO\(_4\) (5\%) or NaOH (1 mol/L), a calculated amount of ferrous sulfate was added as Fe\(^{2+}\) source. Afterwards, predetermined potassium persulfate was added into the reactor to start the reaction. Samples obtained at intervals were immediately adjusted pH to 8.0 with NaOH and H\(_2\)SO\(_4\) to quench the reaction. The ultrapure water was used as a control experiment to eliminate interference. Control group without any reagent addition were conducted to determine HA removal. All samples passed the 0.45 filter to remove possible precipitates prior to chemical analysis.

2.2. Analytical methods

UV-visible spectroscopy was used to determine the absorbance and absorbance ratio at a specific wavelength to distinguish the difference in structure, such as UV\(_{254}\) [20], UV\(_{280}\) [21], \(E_3/E_4\) [22]. In this study, we used UV\(_{254}\) represented the concentration of HA. The quotient \(E_3/E_4\) (equation 1) was inversely proportional to the degree of condensation and molecular weight of organic molecules [23]. We used the ratio of \(E_3/E_4\) to characterize the destruction level of the aromatic ring.

\[
\frac{E_3}{E_4} = \frac{\text{UV}_{300}}{\text{UV}_{400}}
\]
3. Results and discussion
As shown in Fig.1, the absorbance of HA gradually decreased as the wavelength increased. HA has a complex structure with an average molecular weight of 2000-5000. The ultraviolet absorption spectrum was generated by the transition of valence electrons in organic molecule, mostly in the range of 200-1000 nm [24]. The main spectral absorption range of HA was 200-400 nm, indicating various functional groups, such as phenolic hydroxyl group, alcoholic hydroxyl group, hydroxyanthracene, sulfhydryl group, sulfhydryl group, methoxy group and carboxyl group [1].

![Figure 1. Spectral scanning of different concentrations of HA](image)

As Fig.2 (a) shown that there were linear correlations between the concentrations of HA and UV254, and UV280. Macromolecular organics and aromatic compounds containing C=C double bonds and C=O double bonds have strong absorption at 254 nm. UV280 was reported to represent aromaticity of HA [1]. In previous studies, UV254 had been frequently used to characterize the concentration of HA [20, 25]. In this study, we found that the concentrations of HA can be measured by the UV250, UV270, UV300, UV365, UV400, UV436, UV465 with a good linear relationship ($R^2 > 0.999$) (Fig.2 (b)). Since UV254 was the most commonly and classic method [1, 20, 25, 26], the HA was also measured by spectrometer at 254 nm in this study.

![Figure 2. Correlations between HA concentrations and (a) UV254, UV280; (b) UV250, UV270, UV300, UV365, UV400, UV436 and UV465](image)

3.1. Effects of Fe²⁺ concentration
Fe²⁺ can activate S₂O₈²⁻ to produce •SO₄ with strong oxidation ability, which can rapidly oxidize most of the organic compounds to CO₂ and H₂O. Fig.3 (a) showed the effects of Fe²⁺ concentration on the HA removal in Fe²⁺/S₂O₈²⁻ system. The degradation of HA included an initial fast stage and a slow stage.
In the fast stage, the concentration of HA decreased rapidly at the first 10 minutes. In the slow stage, Fe\(^{3+}\) was slowly reduced to Fe\(^{2+}\), and Fe\(^{3+}\) was easily polymerized and hydrolyzed to form iron mud. To some extent, the cycle reaction of Fe\(^{3+}\) to Fe\(^{2+}\) was a limiting step in Fe\(^{2+}/S_2O_8^{2-}\) process. The effect of Fe\(^{2+}\) concentration was evaluated at initial Fe\(^{2+}\) concentrations of 10 mmol/L, 14.3 mmol/L, 20 mmol/L, 33 mmol/L, 100 mmol/L, with an initial PS concentration of 100 mmol/L; corresponding to [PS]/[Fe\(^{2+}\)] molar ratios of 10:1, 7:1, 5:1, 3:1 and 1:1, the removal efficiencies of HA after 10 min reaction was 43%, 63%, 85%, 83% and 82%, respectively. The results indicated that the optimal molar ratio for HA degradation was [S\(_2\)O\(_8^{2-}\)]/[Fe\(^{2+}\)] = 5:1. The higher the ferrous iron concentration was, the stronger the ability to catalyze S\(_2\)O\(_8^{2-}\), therefore, a higher amount of reactive radicals (e.g., SO\(_4^{-}\) and HO•) were produced. However, excessive Fe\(^{2+}\) concentration would increase the cost of the reaction, and the excess Fe\(^{2+}\) would react with the SO\(_4^{-}\) as reactions (2), thereby increasing the consumption of SO\(_4^{-}\). Herein, excessive Fe\(^{2+}\) competed with HA for SO\(_4^{-}\), inhibiting the removal of HA. In addition, excessive amount of Fe\(^{2+}\) also increased the chromaticity of the solution [10]. The best usage of ferrous iron should be considered in practical engineering applications.

\[
\text{Fe}^{2+} + \text{SO}_4^{−} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2−}
\]  

(2)

The increasing of E\(_3\)/E\(_4\) indicated an decreasing humification, aromaticity and molecular weight of HA [22]. As shown Fig.3 (b), the quotient E\(_3\)/E\(_4\) in the raw HA solution was 2.6, while the ratio of E\(_3\)/E\(_4\) increased to 3.1~5.7 after Fe\(^{2+}/S_2O_8^{2-}\) treatment, which indicated that the Fe\(^{2+}/S_2O_8^{2-}\) effectively decreased the molecular weight and aromaticity of HA.

![Figure 3. Effects of Fe\(^{2+}\) concentration, initial pH=3.0, [S\(_2\)O\(_8^{2-}\)]=100 mmol/L, [HA]=20 mg/L](image)

3.2. Effects of S\(_2\)O\(_8^{2-}\) concentration

The amount of oxidant is an important factor affecting the degradation of pollutants. The reaction of Fe\(^{2+}\) with S\(_2\)O\(_8^{2-}\) produces a highly oxidizing SO\(_4^{−}\), which decomposes organic pollutants into water, carbon dioxide and simple inorganic substances. As shown in Fig. 4 (a), The effect of PS concentration was evaluated at initial PS concentrations of 10 mmol/L, 25 mmol/L, 50 mmol/L, 75 mmol/L, 100 mmol/L, 150 mmol/L, 200 mmol/L, with an initial Fe\(^{2+}\) concentration of 20 mmol/L; corresponding to [PS]/[Fe\(^{2+}\)] molar ratios of 10:1, 7.5:1, 5:1, 3.75:1, 2.5:1, 1.25:1 and 0.5:1, the removal efficiencies of HA after 30 min reaction was 47%, 57%, 68%, 82%, 91%, 95% and 88%, respectively. The results shown that the removal efficiencies of HA increased with the increasing concentration of S\(_2\)O\(_8^{2-}\) in a certain range. However, excessive concentration of S\(_2\)O\(_8^{2-}\) couldn’t significantly increase the removal rate of HA. When the concentration of S\(_2\)O\(_8^{2-}\) was too high, SO\(_4^{−}\) would react with each other (as reaction (3)), thereby lowering the utilization ratio of SO\(_4^{−}\). As shown Fig.4 (b), the quotient of E\(_3\)/E\(_4\) ranged from 2.0 ([PS]/[Fe\(^{2+}\)] =0.5:1) to 5.75 ([PS]/[Fe\(^{2+}\)] =5:1) after Fe\(^{2+}/S_2O_8^{2-}\) treatment, suggesting that HA degraded to a lower degree of aromatization of organic compounds with a lower molecular weight. Therefore, the optimum concentration of PS was determined to be 100 mmol/L.
So₄•⁻ + So₄•⁻ → S₂O₈²⁻  

(3)

Figure 4. Effects of S₂O₈²⁻ concentrations; initial pH=3.0, [Fe²⁺] = 20 mmol/L, [HA]=20 mg/L

3.3. Effects of initial pH

Because different oxidants produce different free radicals at different pH, and their different standard electrode potentials determine the oxidative properties. For oxidants, the oxidizing effect is different under different pH conditions. Under the conditions of HA concentration of 20 mg/L, S₂O₈²⁻ concentration of 100 mmol/L and Fe²⁺ concentration of 20 mmol/L, the effects of different initial pH were shown in Fig. 4. When the initial pH increased from 3.0 to 11.0, the degradation efficiencies of HA decreased from 91% to 46% at reaction 30 min (Fig. 4 (a)). The removal efficiencies of HA ranged from 79% (pH = 5.0) to 93% (pH = 3.0) at reaction 60 min. In acidic conditions, the redox potential of SO₄•⁻ was higher than OH⁻ in alkaline conditions [27]. When pH > 5.0, Fe²⁺ solubility and the activation weakened, the removal efficiencies of HA decreased to 46% (pH = 11.0). Partly Fe²⁺ formed precipitates at neutral or alkaline conditions, which lost the activation [28]. At the same time, the increase of pH would promote the continuous conversion of Fe³⁺ and Fe²⁺ to iron-hydroxy complexes(as reactions (4) - (6)) [29, 30], which weakened the activation efficiencies of Fe²⁺ to S₂O₈²⁻, thereby reducing the removal efficiencies of HA. As shown in Fig. 4 (b), the ratio of E₃/E₄ was higher at pH 3.0 than that other pH ranges. Therefore, the removal efficiencies of HA in acidic conditions were much higher than those in neutral or alkaline conditions.

Fe³⁺+OH⁻ → Fe(OH)²⁺  
k₂ = 6.5×10¹¹ L/(mol·s)  

(4)

Fe(OH)²⁺ + OH⁻ → Fe(OH)₃⁺  
k₃ = 3.08×10¹⁰ L/(mol·s)  

(5)

Fe(OH)₃⁺ + OH⁻ → Fe(OH)₄⁻  

(6)

Figure 5. Effects of initial pH; [Fe²⁺] = 20 mmol/L, [S₂O₈²⁻] = 20 mmol/L, [HA]=20 mg/L
3.4. Effects of HA Concentration
As shown in Fig. 5 (a), the removal efficiencies of HA gradually decreased as the initial concentration of HA increased. When the initial concentration of HA was 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L, 30 mg/L and 40 mg/L, the removal efficiency of DEP was 85%, 74%, 72%, 64%, 49% and 34% after 5 minute, respectively. Under the same reaction condition, the generated active free radicals were constant as the concentration of PS was constant. The higher the concentrations of HA were, the larger the total amount of HA molecules were. Therefore, the degradation of HA would consume more \( \cdot \text{SO}_4^- \) and \( \cdot \text{HO}^- \). When the concentrations of target were too high, the total amount of free radicals required exceeds the amount generated from the Fe\(^{2+}/\text{S}_2\text{O}_8^{2-}\) system, leading the decreasing removal efficiencies of HA. As shown in Fig. 5(b), when the concentrations of HA increased from 10 mg/L to 50 mg/L, the values of \( \frac{E_3}{E_4} \) decreased from 7.5 to 2.1, which indicated that the molecular weight and aromaticity of HA were broken. The lower the concentration of HA was, the more severe the aromatic damage caused by free radicals was.

![Figure 6](image.png)

**Figure 6.** Effects of HA concentration; initial pH=3.0, [Fe\(^{2+}\)] =20 mmol/L, [S\(_2\)O\(_8^{2-}\)] = 20 mmol/L

3.5. Effects of HAH
The conversion of Fe\(^{3+}\) to Fe\(^{2+}\) is a limiting step in the Fe\(^{2+}/\text{S}_2\text{O}_8^{2-}\) process. By adding an electron reducing agent to the system, Fe\(^{3+}\) can be reduced to Fe\(^{2+}\) to a certain extent to weaken the accumulation of Fe\(^{3+}\). In order to promote Fe\(^{3+}/\text{Fe}^{2+}\) cycle, HAH was added to Fe\(^{2+}/\text{S}_2\text{O}_8^{2-}\) system to study the effect on the degradation of HA. In the initial pH value of 3.0, HA concentration of 20 mg/L, PS concentration of 100 mmol/L and Fe\(^{2+}\) concentration of 20 mmol/L system, the removal efficiencies of HA increased from 29% (without HAH) to 53% (added 100 mmol/L HAH) after 2 min. When the concentration of S\(_2\)O\(_8^{2-}\) was 50 mmol/L, the removal efficiencies of HA increased from 48% (without HAH) to 96% (added 100 mmol/L HAH) after 10 min. When the HA concentration of 40 mg/L, pH value of 3.0, S\(_2\)O\(_8^{2-}\) concentration of 100 mmol/L and Fe\(^{2+}\) concentration of 20 mmol/L, the removal efficiency of HA was less than 50% without HAH at 60 min, while the removal efficiency of HA reached 96% at 15 min in the HAH system. As shown in Fig.7, the ratio of \( \frac{E_3}{E_4} \) increased significantly after the addition of HAH, indicating that the molecular weight of the aromatic compound decreased rapidly. The ratio of \( \frac{E_3}{E_4} \) increased from 5.75, 2.78, 3.05, 2.43 to 6.86, 3.40, 4.12 and 3.46 after the addition of HAH. Therefore, HAH can rapidly reduce Fe\(^{3+}\) to Fe\(^{2+}\), reduce Fe\(^{3+}\) accumulation (as reactions (7) and (8)), and promote the decomposition of PS, improve the performance of HA degradation in Fe\(^{2+}/\text{PS}\) system.

\[
\text{Fe}^{3+} + \text{NH}_2\text{OH} \rightarrow \text{Fe}^{2+} + \frac{1}{2}\text{N}_2 + \text{H}^+ + \text{H}_2\text{O} \quad (7)
\]

\[
2\text{Fe}^{3+} + \text{NH}_2\text{OH} \rightarrow 2\text{Fe}^{2+} + \frac{1}{2}\text{N}_2\text{O} + 2\text{H}^+ + \frac{1}{2}\text{H}_2\text{O} \quad (8)
\]
4. Conclusion
The contents of HA can be effectively measured UV250, UV254, UV270, UV280, UV300, UV365, UV400, UV436 and UV465. The Fe2+/S2O82- system can effectively degrade HA by producing •SO4- and •OH, and the removal efficiencies of HA were affected by initial concentrations of Fe2+, S2O82-, HA, and pH. Increasing the concentration of Fe2+ and S2O82- can increase the removal efficiencies of HA. However, the excessive concentrations of Fe2+ and S2O82- wouldn’t significantly improve the removal efficiencies of HA. The removal efficiencies of HA increased with the decreasing concentration of HA. The optimal pH was 3.0 in Fe2+/S2O82- system. The addition of HAH could promote the redox cycle of Fe3+/Fe2+, alleviate the disadvantages of difficult regeneration of Fe2+, improve the utilization efficiency of S2O82-, reduce secondary pollution of iron sludge, enhance the removal of target pollutants. This study proved that the Fe2+/S2O82- system was effective for HA degradation.

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