



Modeling of Fe(II)-activated persulfate oxidation using atrazine as a target contaminant



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ARTICLE INFO

Article history:

Received 7 January 2016
Received in revised form 6 April 2016
Accepted 27 May 2016
Available online 27 May 2016

Keywords:

Atrazine
Kinetic model
Ferrous ion
Persulfate
Radicals

ABSTRACT

In this paper, a mathematical model on Fe(II)-activated persulfate oxidation of atrazine (ATZ) was tested using the rate constants from literature, and the degradation kinetics and mechanism of ATZ degradation in Fe(II)/persulfate (Fe^{2+}/PS) system were investigated to verify the model. Some influence factors were taken into consideration in this model, including molar ratio of Fe^{2+} and PS, initial ATZ concentration, natural organic matter (NOM) concentration, tertiary butanol (TBA) and methanol (MeOH) concentrations. Corresponding experimental data could be predicted accurately according to this model. Both experimental data and predicted results implied that a molar ratio of Fe^{2+} and PS at 1:1, low initial ATZ and NOM concentrations were favorable for ATZ degradation. Besides, the radical species were determined via evaluating the effect of TBA and MeOH, and results confirmed that both sulfate radical ($\text{SO}_4^{\cdot-}$) and hydroxyl radical (OH^{\cdot}) existed in this system. To investigate the predominant radical in Fe^{2+}/PS system, nitrobenzene (NB) was used as a probe compound which only react with OH^{\cdot} . According to the degradation efficiency of NB and ATZ in Fe^{2+}/PS system, it could be concluded that only small amount of OH^{\cdot} were produced and $\text{SO}_4^{\cdot-}$ made a major contribution to ATZ degradation in Fe^{2+}/PS system. Experimental data, as well as the mathematical model in this study, improved our understanding on the effect of operating parameters for ATZ degradation in Fe(II)-based advanced oxidation processes.

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1. Introduction

Advanced oxidation processes (AOPs), a kind of in-situ chemical oxidation (ISCO) methods, have been extensively used for the remediation of groundwater and wastewater contaminated by a wide variety of recalcitrant organic matters, such as polychlorinated biphenyls [1], pharmaceutical and personal care products [2,3], pesticides [4–6], dyes [7,8], disinfection by-products and their precursors [9,10]. The conventional AOPs dominantly depend on the formation of reactive and non-selective hydroxyl radical (OH^{\cdot}) [11]. However, in recent years, sulfate radical ($\text{SO}_4^{\cdot-}$) based AOPs have become a hotspot and been widely studied by numerous researchers due to its high redox potential (2.5–3.1 V) and selectivity compared to OH^{\cdot} [12]. Besides, $\text{SO}_4^{\cdot-}$ is a strong one-electron oxidant, but it also readily reacts by addition to C–C double bonds and by H-abstraction, thereby it is capable of oxidizing a large number of pollutants [13]. All the aforementioned advantages make $\text{SO}_4^{\cdot-}$ an ideal alternative for OH^{\cdot} .

$\text{SO}_4^{\cdot-}$ can be activated by photolysis [6,14], thermolysis [2,14], and transition metals [15] from persulfate (PS) or peroxymonosulfate (PMS). For transition metals based AOPs, their solution could be injected in subsurface directly instead of heating or irradiating [16], which saves a big expense. Among various transition metals, ferrous ion, which is well-known as Fenton reagent, shows a fantastic ability in activating radicals [1], as exhibited in Table 1 (Reaction (1)). Therefore, Fe^{2+} -activated persulfate system (Fe^{2+}/PS) attracted many researchers' interests in last decades [1,5,17,18]. In this study, atrazine (ATZ) was chosen as a target contaminant. The use of atrazine has been banned by many European countries but some countries such as USA and China are still using it [19]. Hence, the research of ATZ degradation is still highly significant.

To date, the mechanisms and kinetics of $\text{SO}_4^{\cdot-}$ or OH^{\cdot} with ATZ have already been investigated in detail [6,13,20]. Furthermore, kinetic models have also been established successfully to predict the degradation of organic matters in $\text{Fe(III)}/\text{H}_2\text{O}_2$ system [21], and various UV-based systems [22–26]. Thus, a kinetic model that is applicable for Fe^{2+}/PS system is in demand to establish. The objectives of this study was (1) to establish and verify a mathematical model for ATZ degradation in Fe^{2+}/PS system; (2) to evaluate

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Table 1
Reactions occurred in the Fe²⁺/PS system.

No	Reaction	Reaction rates (M ⁻¹ s ⁻¹)	Reference
1	Fe ²⁺ + S ₂ O ₈ ²⁻ → Fe ³⁺ + SO ₄ ⁻ + SO ₄ ²⁻	k ₁ = 17–27	[7,27]
2	SO ₄ ⁻ + H ₂ O → H ⁺ + SO ₄ ²⁻ + OH ⁻	k ₂ < 6 × 10 ¹	[12]
3	SO ₄ ⁻ + OH ⁻ → SO ₄ ²⁻ + OH ⁻ (pH > 8.5)	k ₃ = 6.5 × 10 ⁷	[12]
4	Fe ²⁺ + SO ₄ ⁻ → Fe ³⁺ + SO ₄ ²⁻	k ₄ = 9.9 × 10 ⁸	[12]
5	Fe ²⁺ + OH ⁻ → Fe ³⁺ + OH ⁻	k ₅ = (3.0–4.8) × 10 ⁸	[7]
6	SO ₄ ⁻ + S ₂ O ₈ ²⁻ → S ₂ O ₈ ⁻ + SO ₄ ²⁻	k ₆ = 1.2 × 10 ⁶	[12]
7	SO ₄ ⁻ + SO ₄ ⁻ → S ₂ O ₈ ²⁻	k ₇ = (4.8–8.1) × 10 ⁸	[12]
8	SO ₄ ⁻ + OH ⁻ → HSO ₄ ⁻	k ₈ = 1.0 × 10 ¹⁰	[28]
9	OH ⁻ + S ₂ O ₈ ²⁻ → S ₂ O ₈ ⁻ + OH ⁻	k ₉ = 1.4 × 10 ⁷	[13]
10	SO ₄ ⁻ + ATZ → product ₁	k ₁₀ = (1.4–4.2) × 10 ⁹	[13]
11	OH ⁻ + ATZ → product ₁	k ₁₁ = (1.2–3.0) × 10 ⁹	[21]
12	SO ₄ ⁻ + NB → intermediates	k ₁₂ < 10 ⁶	[12]
13	OH ⁻ + NB → intermediates	k ₁₃ = 3.9 × 10 ⁹	[29]
<i>In the presence of TBA</i>			
14	SO ₄ ⁻ + TBA → intermediates	k ₁₄ = (4.0–9.1) × 10 ⁵	[12]
15	OH ⁻ + TBA → intermediates	k ₁₅ = 6.0 × 10 ⁸	[29]
<i>In the presence of MeOH</i>			
16	SO ₄ ⁻ + MeOH → intermediates	k ₁₆ = 1.1 × 10 ⁷	[12]
17	OH ⁻ + MeOH → intermediates	k ₁₇ = 9.7 × 10 ⁸	[29]
<i>In the presence of NOM</i>			
18	SO ₄ ⁻ + NOM → intermediates	k ₁₈ = 6.8 × 10 ³ L mg C ⁻¹ s ⁻¹	[13]
19	OH ⁻ + NOM → intermediates	k ₁₉ = 1.4 × 10 ⁴ L mg C ⁻¹ s ⁻¹	[13]
<i>In the presence of O₂</i>			
20	Fe ²⁺ + O ₂ → Fe ³⁺ + O ₂ ⁻ (pH < 7)	k ₂₀ < 10 ^{0.48}	[30]
21	Fe ²⁺ + O ₂ ⁻ + 2H ⁺ → Fe ³⁺ + H ₂ O ₂	k ₂₁ = 1.0 × 10 ⁷	[30]
22	Fe ²⁺ + H ₂ O ₂ → Fe ³⁺ + OH ⁻ + OH ⁻	k ₂₂ = 63–76	[7]
<i>Reactions between radicals and ATZ oxidation products</i>			
23	SO ₄ ⁻ + product ₁ → product ₂	k ₂₃ ≈ k ₁₀	[21]
24	OH ⁻ + product ₁ → product ₂	k ₂₄ ≈ k ₁₁	[21]
25	SO ₄ ⁻ + product ₂ → product ₃	k ₂₅ < 10 ⁵	[21]
26	OH ⁻ + product ₂ → product ₃	k ₂₆ < 10 ⁵	[21]

the key operating parameters and degradation mechanism for ATZ degradation in Fe²⁺/PS system.

2. Materials and methods

2.1. Chemicals

All chemicals were commercially available and used as received without further purification: ATZ of analytical grade was supplied by Aladdin Industrial Co. (China). Methanol (MeOH, HPLC grade, ≥99.9%) was purchased from Sigma–Aldrich Chemical Co. Ltd. (USA). Sodium persulfate (PS, Na₂S₂O₈, ≥99.5%), ferrous sulfate (FeSO₄·7H₂O, ≥99.0%), nitrobenzene (NB, ≥99.0%), and tertiary butanol (TBA, ≥98.0%) were obtained from Sinopharm Chemical Reagent Co. (China). Suwannee River natural organic matter (SRNOM, 2R101N) was purchased from International Humic Substances Society (USA), and elemental compositions of SRNOM were provided in Table S1. All solutions were prepared with ultrapure water, unless otherwise specified.

2.2. Experimental procedures

Batch experiments were conducted in a beaker containing 100 mL ATZ solution with certain concentration. Pre-determined amounts of FeSO₄·7H₂O and PS were added into the beaker. At each

designated sampling time, 1.0 mL collected sample should be filtered with 0.45 μm pore size filter. 100 μL methanol was added immediately to quench the residual oxidants [2].

The stock solutions of ATZ (40 μM) were prepared before the experiments. The required concentrations of solutions were diluted with ultrapure water when necessary. Na₂S₂O₈ and FeSO₄ stock solution was freshly prepared promptly prior to use.

2.3. Analytical methods

ATZ was measured by a High Performance Liquid Chromatography (HPLC) (Agilent 1260, USA) equipped with a Symmetry C18 column (150 mm × 4.6 mm × 5 μm, Agilent, USA) and a VWD detector (Agilent, USA). The concentrations of ATZ were measured at λ = 221 nm using a mobile phase consisting of a mixture of ultrapure water (1% formic acid) and HPLC-grade methanol (v:v = 30:70) at a flow rate of 1.0 mL/min. Injection volume was 10 μL and the column temperature was maintained at 25 °C.

All the experiments were duplicated at 25 °C. The relative standard deviations (RSD) for different batches were normally less than 10%.

2.4. Kinetic modeling

In this model, reactions of radicals with ATZ and its oxidation products (products₁ are primary products of ATZ, and products₂ are further products) have been taken into consideration. Primary oxidation products of ATZ mainly include desethylatrazine and desisopropylatrazine (Fig. S1), and the rate constants of radicals with desethylatrazine and desisopropylatrazine approximately equal to that with ATZ [4]. Further oxidation products include desethylisopropylatrazine, ammeline, cyanuric acid and so on (Fig. S1), which are much less reactive with radicals than atrazine [21], thereby reactions of radicals with products₂ can be neglected.

Table 1 summarizes the possible reactions in Fe²⁺/PS system along with their rate constants obtained from the literature, which were most cited by other researchers. To establish the kinetic model of ATZ degradation in Fe²⁺/PS system, an assumption that only reactions in Table 1 occurred during the process should be made. All of the rate constants in Table 1 were obtained from literature. The kinetic expressions of SO₄⁻, OH⁻, ATZ, Fe²⁺ and PS in the Fe²⁺/PS system are shown in Eqs. (1)–(5), where [C_i] means concentrations of scavengers of SO₄⁻ or OH⁻, including TBA, MeOH, and NOM. The derivations of the Eqs. (1)–(6) are shown in SI (Text S1).

$$\begin{aligned} \frac{d[\text{SO}_4^-]}{dt} = & k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}] - k_2[\text{H}_2\text{O}][\text{SO}_4^-] - k_4[\text{Fe}^{2+}][\text{SO}_4^-] \\ & - k_6[\text{S}_2\text{O}_8^{2-}][\text{SO}_4^-] - k_{10}[\text{ATZ}][\text{SO}_4^-] - k_{23}[\text{Products}_1] \\ & \times [\text{SO}_4^-] - \sum_i k_i[\text{C}_i][\text{SO}_4^-] \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{d[\text{OH}^-]}{dt} = & k_2[\text{H}_2\text{O}][\text{SO}_4^-] - k_9[\text{S}_2\text{O}_8^{2-}][\text{OH}^-] - k_5[\text{Fe}^{2+}][\text{OH}^-] \\ & - k_{11}[\text{ATZ}][\text{OH}^-] - k_{24}[\text{Products}_1][\text{OH}^-] - \sum_i k_i[\text{C}_i][\text{OH}^-] \end{aligned} \quad (2)$$

$$\frac{d[\text{ATZ}]}{dt} = -k_{10}[\text{ATZ}][\text{SO}_4^-] - k_{11}[\text{ATZ}][\text{OH}^-] \quad (3)$$

$$\frac{d[\text{Fe}^{2+}]}{dt} = -k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}] - k_4[\text{Fe}^{2+}][\text{SO}_4^-] - k_5[\text{Fe}^{2+}][\text{OH}^-] \quad (4)$$

$$\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = -k_1[\text{Fe}^{2+}][\text{S}_2\text{O}_8^{2-}] - k_6[\text{S}_2\text{O}_8^{2-}][\text{SO}_4^-] - k_9[\text{S}_2\text{O}_8^{2-}][\text{OH}^-] \quad (5)$$

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