New insights into the role of organic chelating agents in Fe(II) activated persulfate processes

Donghui Han [a], Jinquan Wan [a,b,c,*], Yongwen Ma [a,b,c], Yan Wang [a], Ying Li [a], Dongya Li [a], Zeyu Guan [a]

[a] School of Environment and Energy, South China University of Technology, Guangzhou 510006, China
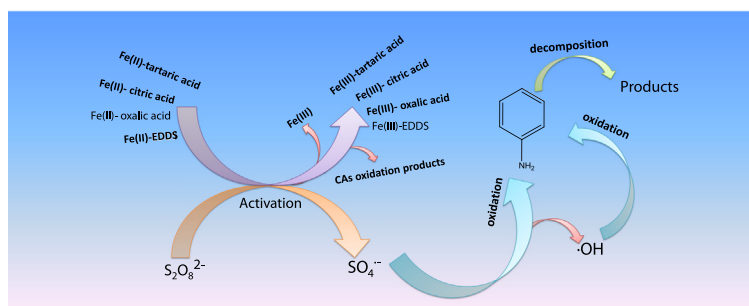[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China
[c] The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, South China University of Technology, Guangzhou 510006, China

HIGHLIGHTS

- Accessible Fe(II) in the CA–Fe(II) complex was responsible for PS activation.
- CAs molecule structure and the CA/Fe(II) ratio determined the Fe(II) accessibility.
- CAs oxidation byproducts led to the Fe(II) recovery and enhanced PS activation.
- Citric acid and tartaric acid were more effective in promoting PS activation.
- Hydroxyl radicals were the predominant oxidative radicals in studied processes.

GRAPHICAL ABSTRACT

ABSTRACT

Persulfate (PS) oxidation of aniline activated by several chelating agents (CAs) mediated ferrous iron (Fe(II)) was investigated. The effects of CAs structure, CA/Fe(II) ratios and pH on PS activation were studied in batch experiments ran for 120 min. Results showed that the accessible Fe(II) in the CA–Fe(II) complex was responsible for PS activation and appropriate Fe(II) accessibility was favored for more efficient utilization of Fe(II), which could improve the PS activation. Due to the steric hindrance, the number of chelating functional groups and the molecule size of CAs determined the Fe(II) accessibility. In addition, the Fe(II) accessibility was affected by the CA/Fe(II) ratio. When the ratio was 5/1, the Fe(II) accessibility followed the sequence: citric acid > oxalic acid > tartaric acid > (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS), but when the ratio was lower than 3/1, the accessibility followed the sequence: oxalic acid > tartaric acid > citric acid > EDDS. In tartaric acid processes, as high as 91.7% PS decomposition was obtained at initial pH 9. Although the acidification of solution might contribute to the high PS decomposition, Fe(II) buffering and Fe(II) recovery possibly played more important roles. Citric acid and tartaric acid were more effective in promoting PS activation and larger PS decomposition was observed in these processes under various initial pH. However, the intense competition for radicals by tartaric acid decreased the PS efficiency for aniline removal. The results of Electron Spin Resonance (ESR) and radicals quenching experiments indicated that both SO_4^- and ·OH contributed to the overall oxidation performance, but ·OH was the dominant oxidative species.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author at: School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China. Tel.: +86 20 39380560; fax: +86 20 87114970.
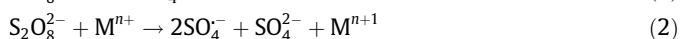E-mail address: ppjqwan@scut.edu.cn (J. Wan).

1. Introduction

With the rapid development of modern industry, more and more new types of organic compounds are being synthesized and used. However, unregulated and improper disposal of some of these compounds, such as pharmaceuticals, antibiotics, pesticides and fire retardant, causes an bioaccumulation these toxic, carcinogenic, and mutagenic compounds in the environment, posing a great risk to the ecological environment as well as human health [1,2]. However, the conventional chemical and biological treatment processes were less effective in degrading most of these persistent organic compounds [3]. Therefore, increasing interest in more efficient treatment technologies was aroused in recent years. Among these treatment methods, advanced oxidation processes (AOPs), such as ozone oxidation [4], Fenton and Fenton-like oxidation [5], and photocatalytic oxidation [6], are the most commonly used technologies. They have been proved to be highly effective to treat recalcitrant contaminants because oxidative $\cdot$OH (E^0 = 1.9–2.7 V), which can oxidize organic compounds without selectivity, is generated in these processes. However, ozone and H_2O_2 have low water solubility and short life spans, respectively, resulting in a more limited potential for contaminants oxidation [7].

More recently, SO_4^- induced AOPs have become an alternative for $\cdot$OH AOPs and are used predominantly for soil and groundwater remediation [8,9]. Compared with $\cdot$OH, SO_4^- also has a higher redox potential (E^0 = 2.5–3.1 V) [10] and presents a longer half-life. In addition, SO_4^- is more efficient at oxidizing some refractory contaminants because of its selective oxidation ability [11]. Furthermore, SO_4^- AOPs is more effective at higher pH because the pH of solution is decreased along with the SO_4^- generation process, which favors the further enhancement of SO_4^- generation [12,13].

PS and oxone (PMS) are the most commonly used oxidants for SO_4^- generation. As the more suitable option for SO_4^- generation, PS activation have been widely studied. SO_4^- generation can be achieved by UV radiation and heat activation represented as Δ and hv, respectively in Eq. (1), [14,15]

$$S_2O_8^{2-} \xrightarrow{\Delta \text{ or } hv} 2SO_4^- \qquad (1)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow 2SO_4^- + SO_4^{2-} + M^{n+1} \qquad (2)$$

Similar to the Fenton process, several low-valent transition metals (M^{n+}) such as Fe(II) and Ag^+ are effectively employed as activators as shown in Eq. (2) [16,17]. Among all the reported effective transition metals, iron is more suitable for widespread use because of its large abundance, high efficiency and environmentally friendly properties.

However, Fe(II) activated PS technologies still has its limitations. On one hand, the fast conversion of Fe(II) into Fe(III) leads to the rapid halt of PS activation, on the other hand, the excessive Fe(II) results in the well known scavenging of sulfate radicals as shown in Eq. (3) which leads to the decline of oxidation efficiency [18]:

$$SO_4^- + Fe(II) \rightarrow SO_4^{2-} + Fe(III) \quad k = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \qquad (3)$$
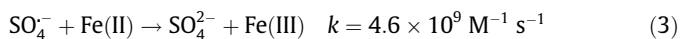
For these reasons, some heterogeneous iron activators such as zero valent iron (Fe^0) [19], minerals [20], iron oxide [21] and iron hydroxide colloids [22] had been employed to improve the oxidation efficiency by means of more sufficient utilization of Fe(II) and less radicals quenching. However, the heterogeneous reaction rate was relatively lower than that of homogeneous reaction because of either the gradual provision of limited surface reaction sites or slow release of low-level aqueous Fe(II) [19]. Moreover, the reaction must be stirred or shaken continuously which restricted its practical application. Hydroxylamine and electron was coupled with Fe(II) to improve the PS activation as well [23,24]. These

assisted methods were able to enhance the oxidation ability and reduced the formation of iron sludge by accelerating the regeneration of Fe(II), but the introduction of electricity and hydroxylamine might increase the treatment cost.

Other methods, such as employing different chelates were also found to be effective to improve PS activation by increasing the iron solubility and decreasing the reaction rate of Fe(II) [25–28]. Although it was reported that the improved solubility of Fe(II) and the Fe(II) buffering process accounted for the enhanced PS activation in a CA–Fe(II)-PS system [16], the underlying mechanism of Fe(II) buffering process and the explanation for different performance between CAs are currently poorly understood and not well documented up to date.

In this study, we proposed that the structure of CAs affected the PS activation by coordinating the reactivity of Fe(II) for the first time. We conducted experiments under different complexation ratios and pH to explain these effects. In order to investigate these potential influences, several CAs with different hydrocarbon chain lengths and dentates were selected as the representatives. As shown in Fig. 1, oxalic acid, citric acid and tartaric acid are the non-toxic and low molecular weight organic acids (LMWOA) which were commonly found in wastewater [29]. EDDS is a strong synthetic CA with better biodegradability than EDTA [30]. Aniline ($C_6H_5NH_2$), which is widely used as raw material in several industries but difficult to biodegrade and categorized as a hazardous waste [31], was selected as the probe contaminant to assess the oxidation efficiency.

2. Materials and methods

2.1. Chemicals

The following chemicals were used as received: oxalic acid dihydrate ($C_2H_2O_4\cdot2H_2O$, 99.5%), citric acid monohydrate ($C_6H_8O_7\cdot H_2O$, 99.5%), sodium tartrate dibasic dihydrate ($C_4H_4Na_2O_6\cdot2H_2O$, 99.5%), aniline ($C_6H_5NH_2$, 99.5%) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%) were obtained from Aladdin Industrial Corporation. (S,S)-Ethylenediamine-N,N′-disuccinic acid trisodium salt solution (Na3EDDS, 35% in H_2O) was purchased from Sigma-Aldrich. Sodium bicarbonate ($NaHCO_3$, 99.5%) was purchased from kermel chemical reagent Co., Ltd. Sodium persulfate ($Na_2S_2O_8$, 98%) and tert-butanol ((CH_3)$_3$COH, 99.5%) were obtained from Fuchen chemical Co., Ltd. Potassium iodide (KI, 99%) was purchased from Tianda chemical reagent Co., Ltd. Ferrous sulfate heptahydrate ($FeSO_4\cdot7H_2O$, 99%) and ethanol (C_2H_6O, 95%) were obtained from Sinopharm chemical reagent Co., Ltd. 1,10-Phenanthroline ($C_{12}H_8N_2\cdot H_2O$, 99%) was obtained from Guangzhou chemical reagent factory. Sodium thiosulfate ($Na_2S_2O_3$, 99%), sodium hydroxide (NaOH, 96%) and sulfuric acid (H_2SO_4, 98%) were purchased from the second Guangzhou chemical reagent factory.

All solutions were prepared in deionized water produced by a Milli-Q system and was purged with N_2 coupled with ultrasound for 30 min before use to eliminate the effects of dissolved oxygen.

2.2. Experimental setup

All experiments were performed in batch mode at ambient temperature and were conducted in a 250 mL conical flask with a top stopper. 50 mL of aniline stock solution was first added into the reaction flask followed by the addition of accurately weighed $FeSO_4\cdot7H_2O$ and CA at predetermined dosage. The conical flask was purged with N_2 for 5 min and was shaken for 30 min to ensure the chelating processes reached equilibrium. The initial pH was adjusted with NaOH (0.1 M) and H_2SO_4 (0.1 M) solution. Thereafter, the reaction was initiated with the addition of 50 mL PS stock solution and run for 120 min. It should be noted that in