

Advanced oxidation process efficiency using persulfate activation with Fe(III)-EDDS complex

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Abstract

Advanced Oxidation Processes (AOPs), based on the hydroxyl radical (HO[•]) and other radicals generation were proposed for the degradation of organic contaminants in various types of water. Recently, sulfate radical (SO₄^{•-}) which is produced by the activation of persulfate (S₂O₈²⁻) is applied to the degradation of organic pollutants in water and soil. In the present paper, 4-tert-butylphenol (4-t-BP), one of the endocrine disrupting chemicals (EDCs) with highly estrogenic effects, is used as a target pollutant to investigate the photocatalytic activity of Fe(III)-EDDS. We investigate the physicochemical properties of Fe(III)-EDDS and S₂O₈²⁻ activation using the photolysis of Fe(III)-EDDS complex for the Fe²⁺ formation. Steady state irradiation was used to investigate the effect of pH value, concentration of iron complex and oxygen on the photo activity of Fe(III)-EDDS. Activation of S₂O₈²⁻ using Fe(III)-EDDS and Fe³⁺ with UV irradiation were also investigated. The pH effects on the UV/Fe(III)-EDDS/S₂O₈²⁻ and UV/Fe(III)/S₂O₈²⁻ systems were investigated. Activation of S₂O₈²⁻ using Fe(III)-EDDS was found to be efficient at pH over 5 on the contrary of the activation via Fe³⁺ photolysis which proved to be inefficient at pH > 4.

1. Introduction

In recent years, the degradation of organic pollutants in water by green photochemical processes has become a very active research topic. Numerous studies have reported the application of Fe(III) complexes in the photodegradation of organic pollutants. They are successfully used to reduce the toxicity of toxic chemicals, convert toxic and biorecalcitrant contaminants into biodegradable byproducts, remove color, or obtain a complete mineralization of organic pollutants (Chen, 2011; De Laat, 2011; Gazi, 2010; Liu, 2010). Such positive results in terms of water decontamination are due to the irradiation of Fe(III) complexes which could produce oxidative radicals (like SO₄^{•-}, HO[•], HO₂[•], O₂^{•-}) by the ligand-to-metal charge transfer (LMCT) reactions (Li, 2010). The most obvious advantages of the application of Fe(III) complexes are the low process costs, wide irradiation wavelengths ($\lambda < 580$ nm), and a pH range that is relatively wider than that of traditional photo-Fenton processes (optimal pH 2.8) (Pignatello, 2006).

Ethylenediamine-N,N'-disuccinic acid (EDDS) is a structural isomer of EDTA and is also a strong complexing agent (Subramanian, 2011). However, it is biodegradable and has been reported as a safe and environmentally benign replacement for EDTA and can be used for environmental applications (Zhang, 2008).

4-tert-butylphenol (4-t-BP) is an alkylphenols (APs) and is one of the endocrine disrupting chemicals (EDCs) with highly estrogenic effects [Myllymäki, 2005; Barse, 2006]. It is used as a target pollutant to investigate the photocatalytic activity of Fe(III)-EDDS and the formation of $\text{SO}_4^{\cdot-}$. In this work, The effect of irradiation time, pH, Fe(III)-EDDS concentration on the photodegradation performance of 4-t-BP under UV light irradiation ($300 \text{ nm} < \lambda < 500 \text{ nm}$) was investigated.

2. Results and discussion

2.1 The molar ratio of Fe(III) and EDDS

Fe(III)-EDDS was a complex formed by Fe(III) and EDDS in specific proportion. Job's Method was used to determine the proportion between Fe(III) and EDDS in this study. Job's method was built in 1928 by chemist P. Job [Job, 1928] and was used to determine the stoichiometry of a binding event. This method was widely used in analytical chemistry, instrumental analysis, advanced chemical equilibrium texts and research articles [Huang, 1982].

The result of Job's Method was shown in Fig. 1. According to the results, the stoichiometry of Fe(III)-EDDS formation was Fe(III): EDDS = 1:1. Meanwhile, the experimental result showed that Fe(III)-EDDS solution could keep stable for at least 7 days.

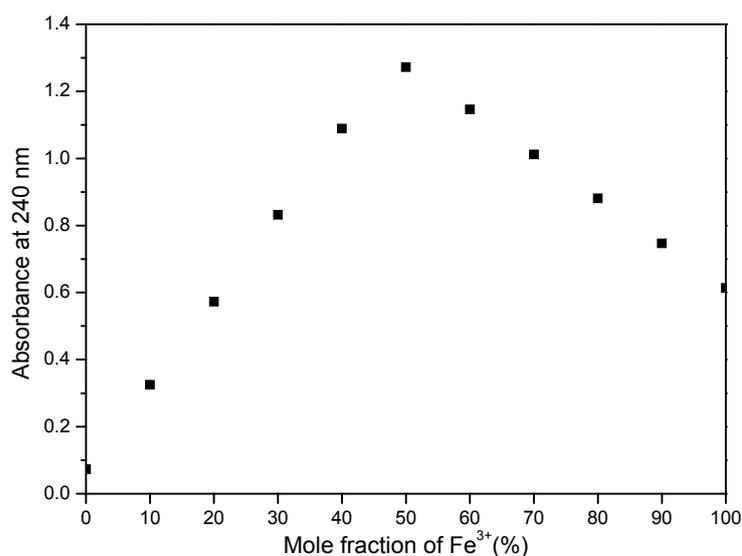


Fig. 1 Effect of molar ratio on the binding of Fe(III) and EDDS

2.2 Photochemical reactivity of Fe(III)–EDDS complex

The photoactivity of Fe(III)–EDDS was investigated following the degradation of 4-t-BP (0.05 mM) in the presence of Fe(III)–EDDS (0.1 mM) under polychromatic radiation. The results are shown in Fig. 2. Controlled experiments were also performed and the results showed its stability under direct photolysis and dark reaction. In the presence of UV light and Fe(III)–EDDS, approximately 17% of the 4-t-BP was transformed after 10 min of irradiation but only 5% of it was removed in the following 50 min. The degradation of 4-t-BP is due to the reaction with oxidative radicals (HO^\bullet , HO_2^\bullet , $\text{O}_2^{\bullet-}$) which were produced during the rapid photochemical reactions involving the Fe(III)–EDDS complex under UV light [Huang, 2012] (shown in R1-R5). In fact, the concentration of Fe(III)–EDDS was also detected and its degradation is very fast and important, around 90% degradation after 10 min of irradiation. The reaction was almost suspended after 10 min of irradiation, and it was obviously caused by the fast consumption of Fe(III)–EDDS complex at the beginning of the reaction.

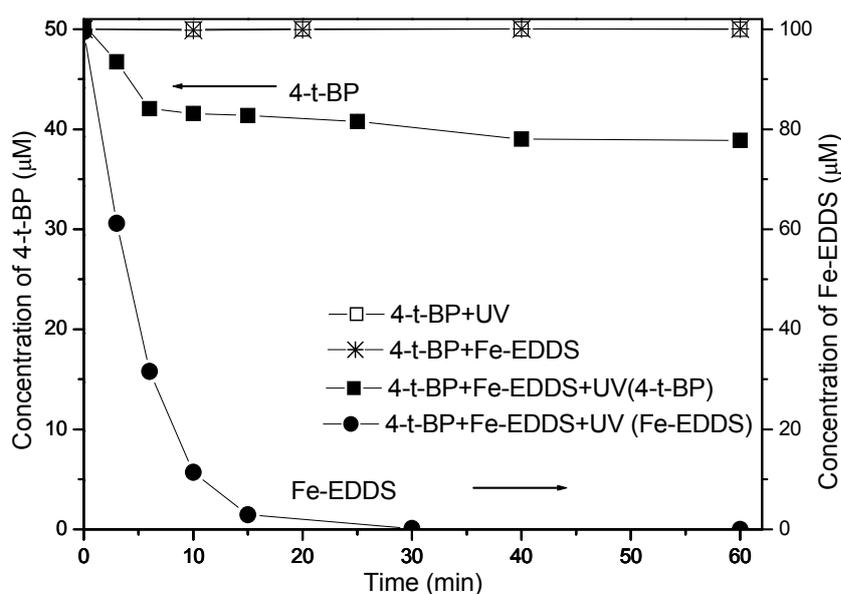
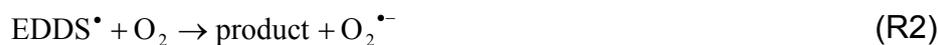


Fig. 2 Photodegradation of 4-t-BP in the presence of Fe(III)–EDDS at pH 4.0 under polychromatic wavelengths. (Filled squares represent the 4-t-BP degradation and filled rounds represent the Fe(III)–EDDS degradation)





2.3 Characteristics of Fe(III)-EDDS complex: theoretical calculations

According to the chemical structure, EDDS was tetrabasic weak acid (expressed H_4L). H_4L , H_3L^- , H_2L^{2-} , HL^{3-} and L^{4-} were the main existence form of EDDS at pH <2.4, 2.4-3.9, 3.9-6.8, 6.8-9.8 and > 9.8, respectively [Vandevivere, 2001].

Fe(III) bound with EDDS and then formed Fe(III)-EDDS. Fe(III)-EDDS also exhibited four different main forms (FeL^- , Fe(OH)L^{2-} , $\text{Fe(OH)}_2\text{L}^{3-}$ and Fe(OH)_4^-) at different pH [Orama, 2002]. Theoretical calculations with software Gaussian09 were performed and the distribution of four different forms at different pH values was shown in Fig. 3. The results from theoretical calculation showed that FeL^- was the main species present at pH lower than 6.0. Increasing the pH, Fe(OH)L^{2-} , $\text{Fe(OH)}_2\text{L}^{3-}$ and Fe(OH)_4^- were formed gradually, while the proportion of FeL^- decreases. Meanwhile, with the increase of pH, Fe(OH)_3 was gradually formed, so the total amount of soluble Fe(III) showed a gradual decline.

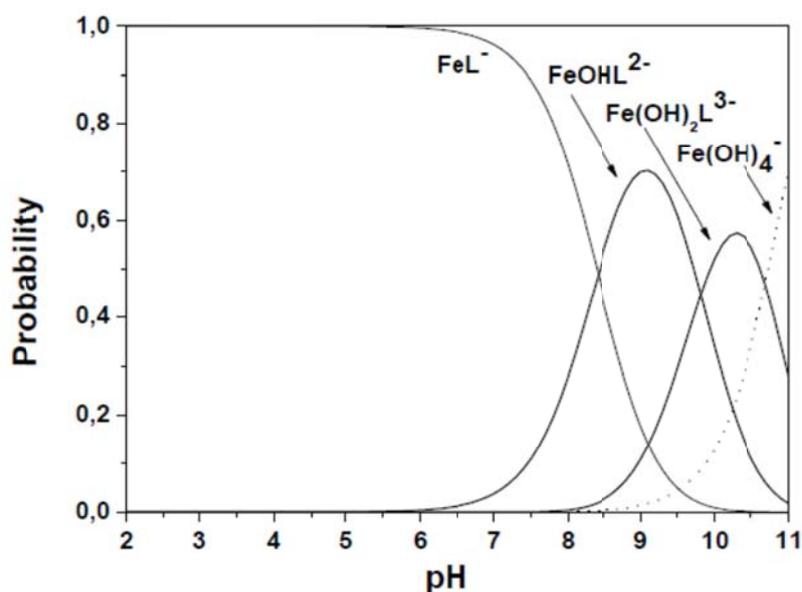


Fig. 3 Proposed theoretical model distribution of the predominant species of Fe(III)-EDDS complex as a function of pH

2.4 Effect of pH on 4-t-BP degradation in UV/Fe(III)-EDDS system

To better understand the effect of pH value during the photodegradation of 4-t-BP in the presence of Fe(III)-EDDS, experiments at different pHs between 2.6 and 9.3 were conducted. The results reported in Fig. 4 showed that the degradation rate of 4-t-BP

(R_{4-t-BP}) quickly increases between pH 2.6 and 4.5 followed by a braking up to pH 8.0 followed by a decrease at pH higher than 8.0. Similart trends were reported by Li et al. (2010) between pH 3.1 and 8.0.

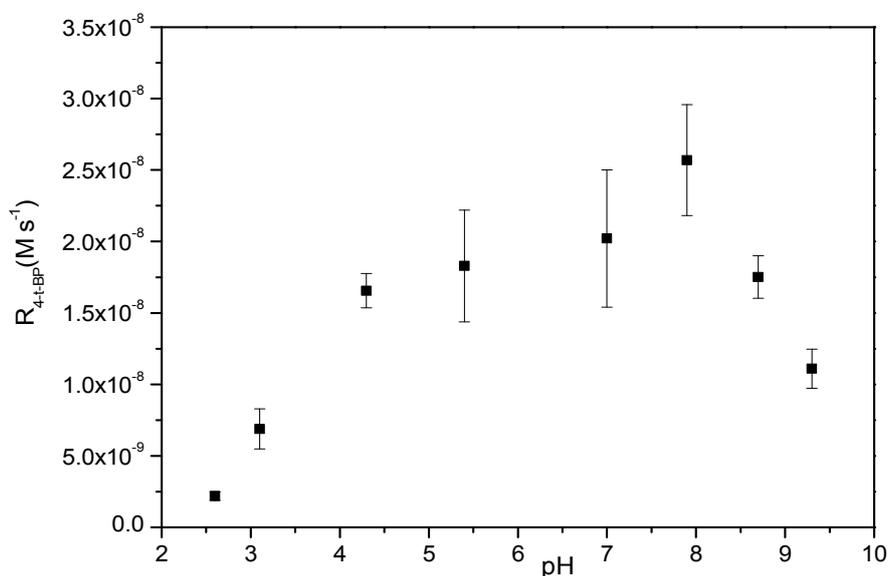
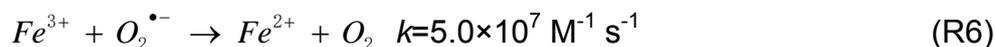


Fig. 4 Effect of pH value on the degradation rate of 4-t-BP

As reported in the paper of Huang et al. (2013), the observed effect of pH could be due to the formation of $HO_2^{\bullet}/O_2^{\bullet-}$ and to the presence of different forms of Fe(III)–EDDS as a function of pH. However, for the first part of the effect of pH, until pH 6.0, we can exclude the effect of Fe(III)–EDDS speciation. Indeed, as we evaluate by theoretical calculation the second form of the complex appears from pH 6.0 (Fig. 3). On the contrary, the decrease of R_{4-t-BP} from pH 8.0, corresponds to the presence of the second form $FeOHL^{2-}$ (with $L^{4-} = [S,S]$ -EDDS) at 50% and 50%. For the first time, we prove that the hydroxylated form $FeOHL^{2-}$ of such a complex is less efficient photochemically in terms of a photoredox process. The observed increase of R_{4-t-BP} until pH 8.0 is certainly due to the iron cycle and the relative concentration between Fe(III) and Fe(II) species. These relative concentrations are strongly impacted (R6–R9) by the presence of $HO_2^{\bullet}/O_2^{\bullet-}$ couple photogenerated from the Fe(III)–EDDS photolysis.



2.5 Degradation kinetics of 4-t-BP in $S_2O_8^{2-}$ system

The 4-t-BP concentration was followed during the reaction in the UV/Fe(III)-EDDS/ $S_2O_8^{2-}$ and UV/Fe(III)/ $S_2O_8^{2-}$ systems. The control experiments without UV irradiation or without iron were also performed. The results were shown in Fig. 5. The apparent first-order rate constant (k_1) of both processes were calculated and the results were shown in Table 1. As shown in Table 1, the k_1 obtained in UV/Fe(III)-EDDS/ $S_2O_8^{2-}$ process was three times higher than that obtained in UV/Fe(III)/ $S_2O_8^{2-}$.

According to the literatures [Zhang, 2006; Criquet, 2009], $S_2O_8^{2-}$ could be activated by UV light and decomposed to $SO_4^{\cdot-}$. But the UV activation was not the main reaction in our experiment due to the small percentage (7%) of 4-t-BP degradation in control group. In both UV/Fe(III)-EDDS/ $S_2O_8^{2-}$ and UV/Fe(III)/ $S_2O_8^{2-}$ system, the first step was the formation of Fe(II) through the photolysis of Fe(III)-EDDS/Fe(III) (R1 and R10). Fe(II) activation of $S_2O_8^{2-}$ (R11) [Xu, 2010] was the main source of $SO_4^{\cdot-}$ in this experiments and the 4-t-BP degradation rate was much higher.

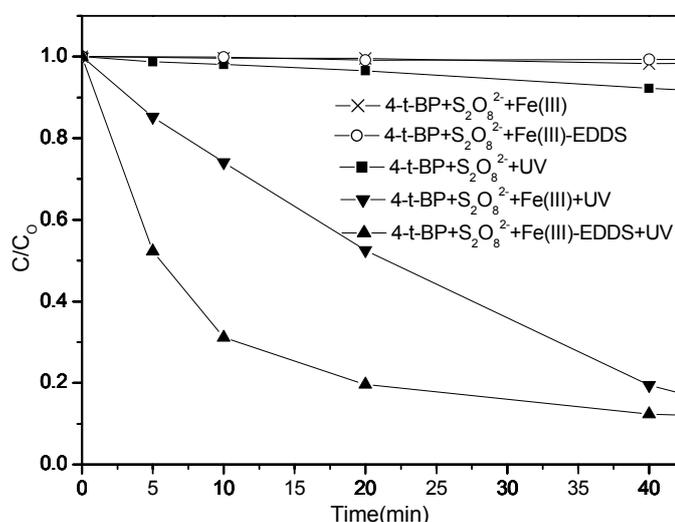
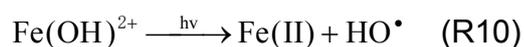


Fig.5 Degradation of 4-t-BP in $S_2O_8^{2-}$ related reactions

Table 1 The k_1 of 4-t-BP degradation in different reaction condition

System	k_1 (s^{-1})	R^2
UV/Fe(III)/ $S_2O_8^{2-}$	$5.30 \times 10^{-4} \pm 8.32 \times 10^{-6}$	0.9984
UV/Fe(III)-EDDS/ $S_2O_8^{2-}$	$1.51 \times 10^{-3} \pm 1.57 \times 10^{-4}$	0.9364

2.6 Effect of pH on 4-t-BP degradation in $S_2O_8^{2-}$ system

The pH value of aqueous solution plays a significant role during the organic compounds degradation. Experiments performed using 4-t-BP photodegradation with the $S_2O_8^{2-}/Fe(III)$ -EDDS or $S_2O_8^{2-}/Fe(III)$ reagent were carried out at pHs between 2.2 to 8.8. The R_{4-t-BP} with different pH values were obtained and are shown in Fig. 6. With the increase of pH, the efficiency of 4-t-BP degradation decreased in both reaction systems, indicating that the acidic pH is more favorable to the 4-t-BP degradation than neutral and alkaline pHs. However, the efficiency of 4-t-BP degradation decreased much more rapidly in UV/ $Fe(III)$ / $S_2O_8^{2-}$ system.

The rapidly decreased R_{4-t-BP} in the neutral and alkaline media might result from the precipitation of $Fe(III)$ in UV/ $Fe(III)$ / $S_2O_8^{2-}$ system. The precipitation of $Fe(III)$ ions occurs when $pH > 4.0$ [Xu, 2004]. But for $Fe(III)$ -EDDS complex, it is much more stable than $Fe(III)$ in the neutral and alkaline media. In our previous study, the quantum yield of $Fe(II)$ formation ($\Phi_{290-400nm}^{f, Fe(II)}$) under the irradiation of $Fe(III)$ -EDDS was estimated at pH 4.0, 6.0 and 8.6. Obtained values for $\Phi_{290-400nm}^{f, Fe(II)}$ are 0.09, 0.11 and 0.10, respectively. However, the amount of soluble $Fe(II)$ could decrease due to the formation of $FeOH^+$ complex when the pH value is higher than 4.0 [Stefánsson, 2007]. It would hinder the further reaction between $Fe(II)$ and $S_2O_8^{2-}$ which was the most important reaction for $SO_4^{\cdot-}$ formation (R11). UV/ $Fe(III)$ -EDDS/ $S_2O_8^{2-}$ system was superior to UV/ $Fe(III)$ / $S_2O_8^{2-}$ system on the performance of 4-t-BP degradation.

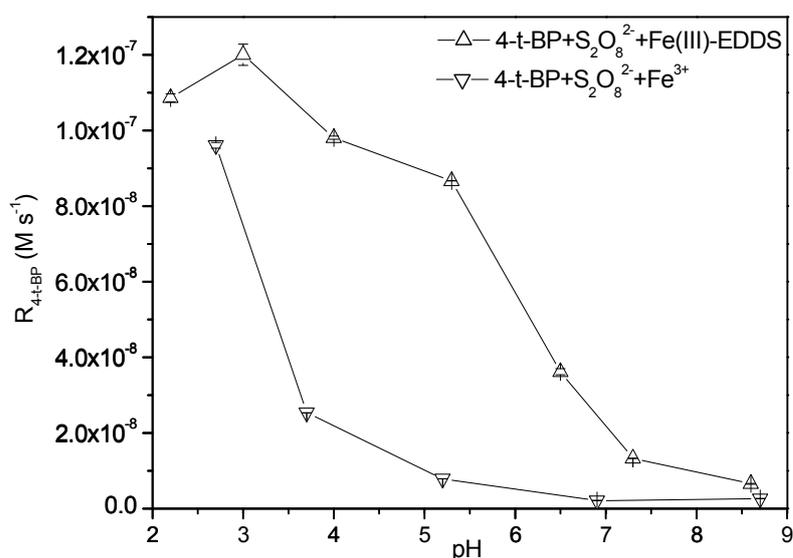


Fig. 6 Effect of pH value on the initial degradation rates of 4-t-BP

3. Conclusion

Theoretical and experimental approaches were used to investigate the speciation and photochemical reactivity of Fe(III)-EDDS complex. The activation of $S_2O_8^{2-}$ by Fe(III)-EDDS was also studied.

From this work we can conclude that before pH 6 the main process responsible for the observed trend is attributed to the iron cycle reactivity between Fe(III)/Fe(II). The main new result is coming from theoretical calculation for the distribution of the predominant species of the Fe(III)-EDDS as a function of pH. We demonstrated that the most photoactive form is the nonhydroxylated one (FeL^-) present as the majority at pH lower than 6.0. Moreover, UV/Fe(III)/ $S_2O_8^{2-}$ system was strongly effected by pH and could not applied at $pH > 4$. However, the UV/Fe(III)-EDDS/ $S_2O_8^{2-}$ system performed higher efficiency on 4-t-BP degradation and could be applied at pH 5-6.

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