

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 $\text{pH} < 2.4$, 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.

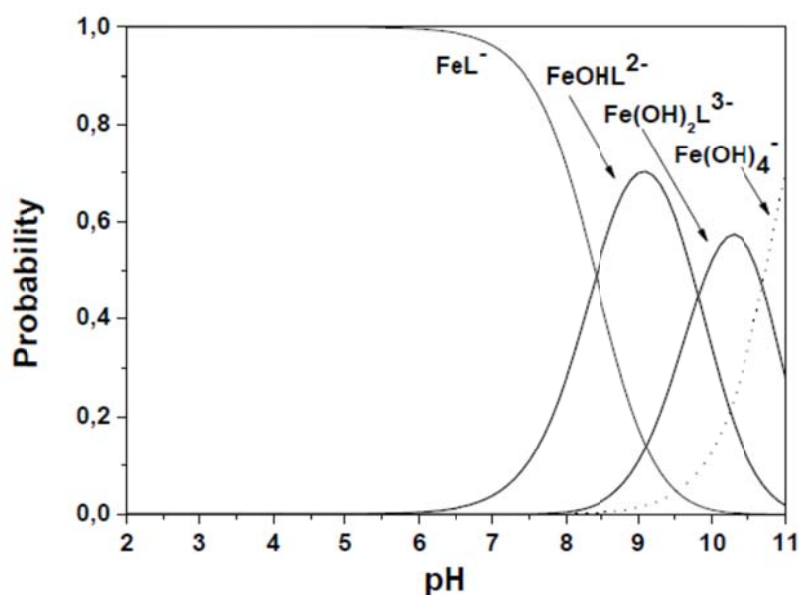


Fig. 3 Proposed theoretical model distribution of the predominant species of Fe(III)-EDDS complex as a function of pH

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.

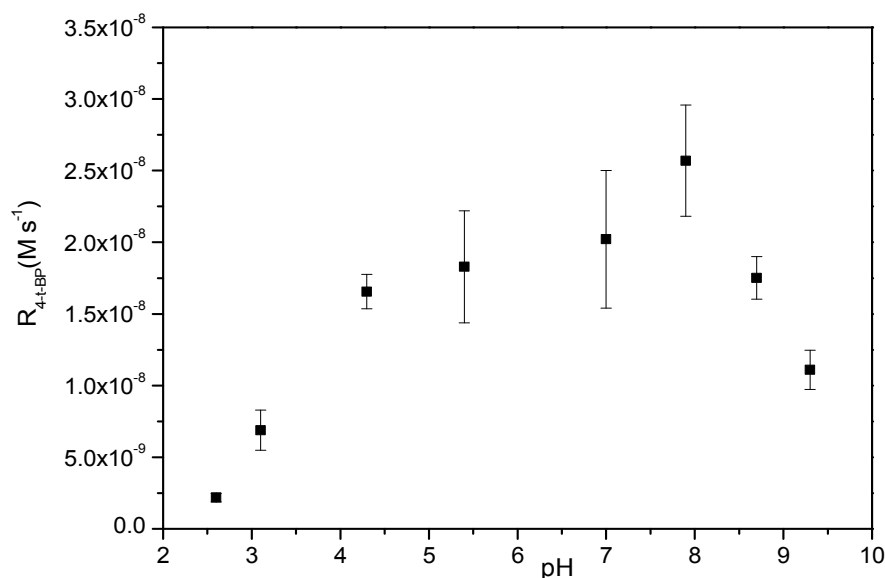
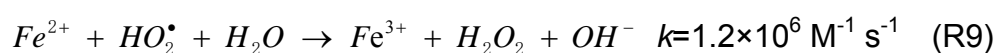
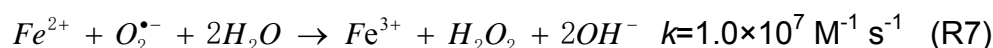
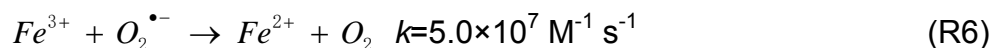


Fig. 4 Effect of pH value on the degradation rate of 4-t-BP

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.

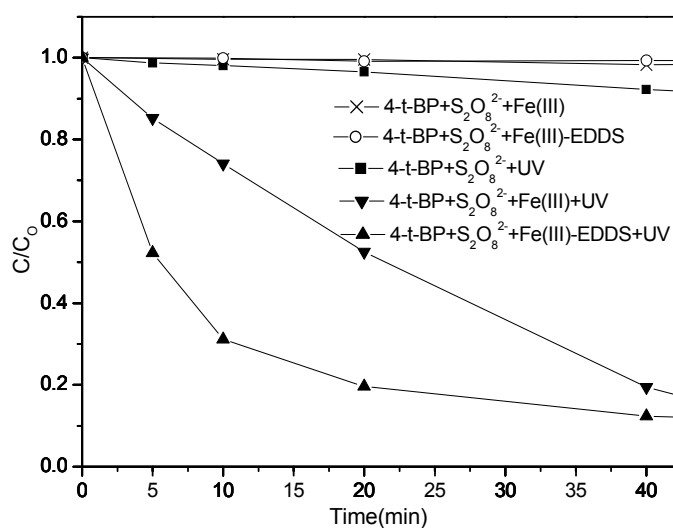
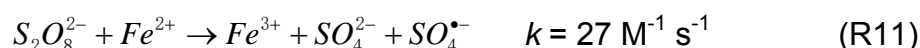
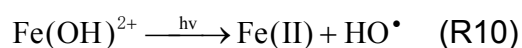


Fig.5 Degradation of 4-t-BP in $S_2O_8^{2-}$ related reactions

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.

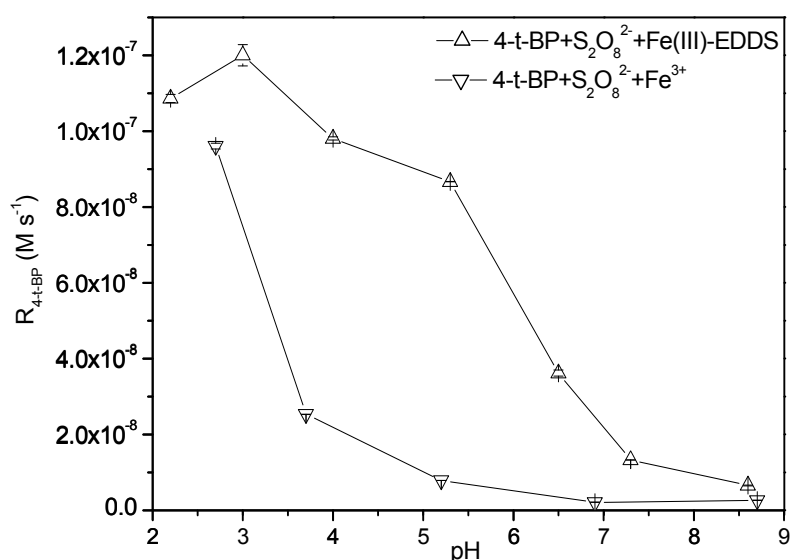


Fig. 6 Effect of pH value on the initial degradation rates of 4-t-BP

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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