

The Effects of Inorganic Ions on Photodegradation of Humic Acids by Fe(III)/Oxalate Systems

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Abstract. The photodegradation of humic acids (HA) in aqueous solution was carried out in the presence of Fe(III) and oxalate, and the influence of inorganic ions, such as Ca²⁺, Mg²⁺, HCO₃⁻ and H₂PO₄⁻ on HA removal was investigated. 88.9 % removal of HA in solution was reached after 75 min with Xe lamp irradiation ($\lambda > 290$ nm) when the initial concentrations of oxalate and Fe(III) were 0.5 mmol/L and 0.2 mmol/L, respectively. The photodegradation of HA by Fe(III)/oxalate system is inhibited by the presence of Ca²⁺, Mg²⁺, HCO₃⁻ and H₂PO₄⁻ in solutions.

Introduction

Humic acids (HA) are ubiquitous in nature environment such as sediments, soils, and waters, and play an important role in environmental chemistry and pollutant chemistry in aquatic systems [1]. HA has a significant effect on the degradation, mobilization, and transportation of coexisting pollutants or heavy metals.

Wu et al. [2] investigated the oxidation of HA using Fenton's process and applied a new kinetic model for HA degradation. However, the use of H₂O₂ is of high cost. Several studies have reported that Fe(III)-oxalate complex, one of natural photosensitizers, can generate strong oxidant species, such as hydroxyl radical (\bullet OH), via a series of photochemical reactions upon sunlight irradiation [3,4]. It has been well proven that various contaminants (e.g. orange G, benzotriazoles, and amicarbazone) could be photodegraded by Fe(III)/oxalate system [5-7].

The issues addressed in this study were as follows: (1) examining the several factors such as Fe³⁺ and oxalate dosages that control the HA photolysis in Fe(III)/oxalate systems; (2) investigating the effects of inorganic ions (e.g. Ca²⁺, Mg²⁺, HCO₃⁻ and H₂PO₄⁻) on the photodegradation of HA with light irradiation (Xe lamp, $\lambda > 290$ nm).

Experimental Section

Materials. Commercial HA was purchased from Germany and was used as received. The HA powder was dissolved in Milli-Q water that was adjusted by NaOH to pH 7.5–8.0. Fe(NO₃)₃·9H₂O and oxalate was purchased from Tianjin Kemio Chemical Reagent Co. Ltd. A stock solution of Fe(III) ([Fe(III)]₀=100 mM) was prepared by dissolving Fe(NO₃)₃·9H₂O in water that was adjusted to pH 3 by adding 0.1M H₂SO₄. All stock solutions were stored in a refrigerator at 4 °C in the dark and used within one week. Milli-Q water (resistivity ≥ 18 M Ω ·cm) was used in all experiments.

Procedures. A certain amount of HA, Fe(III) and oxalate solution were filled into the reaction vessel. Degradation experiments were conducted at least twice. Samples were taken out at the given reaction time intervals and the absorbance of HA was analyzed by measuring the UV-vis spectra at $\lambda=254$ nm using UV-vis spectrophotometer.

The formula of degradation rate is shown as following.

$$\% \text{ Degradation} = \left(1 - \frac{A_t}{A_0} \right) * 100\%$$

Where: A₀ - the absorbance of HA at $\lambda_{254\text{nm}}$ before reaction; A_t - the absorbance of HA at $\lambda_{254\text{nm}}$ at t minutes.

A 300 W Xe lamp (Beijing Huiyixin Lighting Corporation, China) equipped with a quartz jacket was used as a sunlight source ($\lambda > 290$ nm). The reaction solutions were always magnetically stirred

during irradiation. In all the above experiments, the temperature of the solution was maintained at $25.0 \pm 1^\circ\text{C}$.

Results and discussion

The influence of oxalate and Fe(III) concentrations on HA photodegradation. It is well accepted that photodegradation of a trace organic pollutant in aqueous solution follows the first-order kinetic model (Eq. 1) well due to the relatively low substrate concentration compared to the quantum yields.[6] The C_0 and C are the concentration of HA at time 0 min and t , respectively, and k is the first-order rate constant. Half-lives ($t_{1/2}$) can be calculated as Eq. 2. As expected, the photodegradation data of HA fitted the first-order kinetic model well with all R^2 values between 0.965 and 0.990 (Fig. 1 and Table 1).

$$\ln(C_0/C) = kt \quad (1)$$

$$t_{1/2} = \ln(2)/k \quad (2)$$

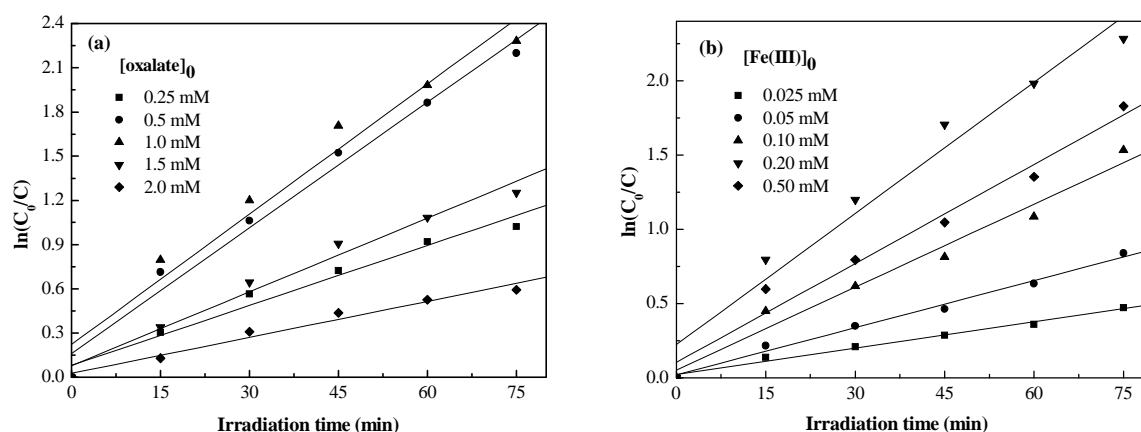


Fig. 1 The influence of oxalate and Fe(III) concentrations on HA photodegradation. (a, $[\text{Fe(III)}]_0 = 0.2$ mM, $[\text{oxalate}]_0 = 0.25\text{--}2.0$ mM; b, $[\text{Fe(III)}]_0 = 0.025\text{--}0.50$ mM, $[\text{oxalate}]_0 = 1.0$ mM)

Table 1 Kinetic parameters for HA photodegradation in aqueous solution containing different concentrations of oxalate and Fe(III)

Related coefficients	0.2 mmol/L $[\text{Fe}^{3+}]_0$					1 mmol/L $[\text{oxalate}]_0$				
	$[\text{oxalate}]_0$ (mmol/L)					$[\text{Fe}^{3+}]_0$ (mmol/L)				
	0.25	0.5	1	1.5	2	0.025	0.05	0.1	0.2	0.5
k (min^{-1})	0.013	0.028	0.029	0.016	0.008	0.005	0.010	0.018	0.029	0.022
R^2	0.972	0.981	0.965	0.980	0.975	0.988	0.990	0.974	0.965	0.974
$t_{1/2}$ (min)	53.3	24.8	23.9	43.3	86.6	138.6	69.3	38.5	23.9	31.5

Fig. 1a shows HA photodegradation kinetics curves for oxalic acid concentration of 0.25, 0.5, 1, 1.5 and 2 mM in 0.2 mM Fe(III) solutions, corresponding to the k values of 0.013, 0.028, 0.029, 0.016 and 0.008 min^{-1} , respectively. This result clearly shows that HA photodecomposition increased with increasing oxalate concentration up to 1 mM, and then decreased. One hand, the Fe(III)-oxalate complex formed at higher oxalate concentration were thought to have higher photoactivity and may be much more efficiently photolyzed than other species, greatly enhancing HA photodegradation in the presence of oxalic acid.[5] On the other hand, oxalic acid could react with reactive oxygen species (ROS) such as $\cdot\text{OH}$. Thus excess oxalic acid would compete with HA for the available $\cdot\text{OH}$ and there is a proper initial concentration of oxalic acid.

The similar trend was found in Fig. 1b that when the initial concentration of Fe(III) was in a range of 0.025-0.2 mM, the HA degradation rate increased with increasing Fe(III) dosage with

half-lives of 138.6, 69.3, 38.5 and 23.9 min, respectively, and decreased from 0.2 to 0.5 mM with half-lives from 23.9 to 31.5 min. Obviously, there is an optimum concentration of Fe(III) at 0.2 mM. Excessive iron ions are also reactive to $\bullet\text{OH}$ and then inhibit HA photodegradation.

From the experimental data shown in Fig. 1 and Table 1, the optimum degradation rate of HA (10 mg/L) is 88.9% after 75 min irradiation with the short half-lives of 24.8 min at a Fe(III)/oxalate ratio of 0.2/0.5 mM.

The influence of Ca^{2+} and Mg^{2+} on HA photodegradation. Fig.2 shows the effects of Ca^{2+} and Mg^{2+} from 0 to 1.0 mM on the photodegradation of HA in the presence of 0.20 mM Fe(III) and 0.5 mM oxalate, and the corresponding degradation rate of HA are 88.9%, 77.7%, 59.1% and 47.9% for Ca^{2+} , and 88.9%, 77.8%, 76.1% and 64.0% for Mg^{2+} , respectively.

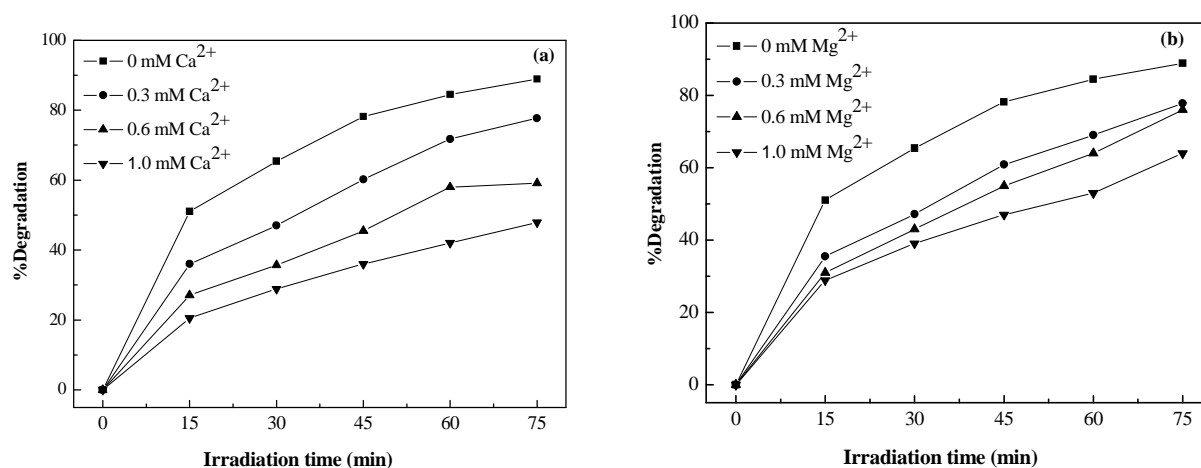
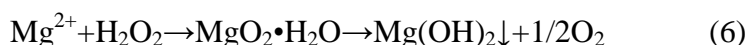
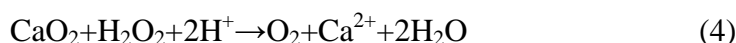
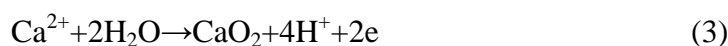


Fig. 2 The influence of Ca^{2+} (a) and Mg^{2+} (b) on HA photodegradation. ($[\text{HA}]_0=10$ mg/L, $[\text{Fe(III)}]_0=0.20$ mM, $[\text{oxalate}]_0=0.5$ mM)

It is well known that metal cations (e.g., Ca^{2+} and Mg^{2+}) can be combined with carboxyl, phenolic and hydroxyl functional groups in HA molecules to form metal-HA complexes [1]. As can be seen from Fig.2a and b, the removal rate of HA decreased with increasing the initial concentration of Ca^{2+} and Mg^{2+} , which can be attributed to the formation of Ca-HA complex and Mg-HA complex. Furthermore, Ca^{2+} (Eqs. 3 and 4) and Mg^{2+} (Eqs. 5 and 6) can react with ROS (e.g., H_2O_2) that produced in Fe(III)/oxalate systems.[8] Consequently, the concentration of H_2O_2 , which can react with Fe^{2+} to form $\bullet\text{OH}$, was reduced by the reactions with Ca^{2+} or Mg^{2+} . Higher concentration of Ca^{2+} or Mg^{2+} in solution means more H_2O_2 consumption, resulting in declining $\bullet\text{OH}$ production and reducing degradation rate of HA. Comparing Fig.2a with Fig.2b, the impact of Ca^{2+} for inhibiting HA photodegradation is greater than that of Mg^{2+} .



The influence of HCO_3^- and H_2PO_4^- on HA photodegradation. Fig.3 shows the effects of HCO_3^- and H_2PO_4^- from 0 to 0.1 mol/L on the photodegradation of HA in the presence of 0.20 mM Fe(III) and 0.5 mM oxalate, and the corresponding degradation rate of HA are 88.9%, 58.0%, 53.1% and 45.6% for HCO_3^- , and 88.9%, 66.0%, 61.9% and 35.0% for H_2PO_4^- , respectively.

Firstly, both HCO_3^- and H_2PO_4^- have strong quenching effect on $\bullet\text{OH}$, and the reaction products are $\text{CO}_3^{\bullet-}$ and $\text{H}_2\text{PO}_4^{\bullet}$, respectively, whose oxidation capacity are weaker than $\bullet\text{OH}$. Secondly, HCO_3^- will be in the strong adsorption on the surface of the catalyst, causing the activity of catalyst

decreased. Thirdly, the pH value of the HA solution was reduced after adding H_2PO_4^- , thus affecting the presence of HA and the photodegradation of HA. For these reasons, degradation of HA were inhibited. And the higher the concentration of HCO_3^- and H_2PO_4^- , more powerful inhibition of HA photodegradation occurred in Fe(III)/oxalate system.

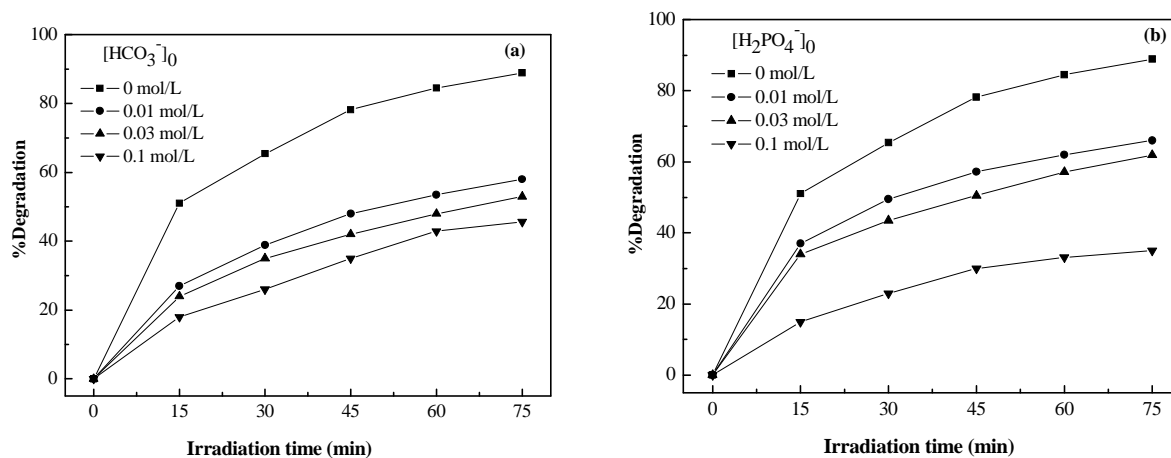


Fig. 3 The influence of HCO_3^- (a) and H_2PO_4^- (b) on HA photodegradation. ($[\text{HA}]_0=10$ mg/L, $[\text{Fe(III)}]_0=0.20$ mM, $[\text{oxalate}]_0=0.5$ mM)

Conclusions

The reaction kinetics of HA photodegradation fitted the first-order reaction and the photolysis efficiency was dependent on Fe(III) and oxalate concentrations. The optimum degradation rate of HA (10 mg/L) is 88.9% after 75 min irradiation with the short half-lives of 24.8 min at a Fe(III)/oxalate ratio of 0.2/0.5 mM. The degradation of HA was more sensitive to the presence of inorganic ions in Fe(III)/oxalate systems. Ca^{2+} , Mg^{2+} , HCO_3^- and H_2PO_4^- could either interact with HA or react with ROS such as $\cdot\text{OH}$ and H_2O_2 , therefore, the presence of these inorganic ions all inhibited the photodegradation of HA in Fe(III)/oxalate systems.

Acknowledgements

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References

- [1] F.J. Göbbels and W. Püttmann: Water Research Vol. 31(1997), p.1609
- [2] Y. Wu, S. Zhou, F. Qin, K. Zheng and X. Ye: J Hazard Mater Vol.179(2010), p. 533
- [3] G. Liu, S. Zheng, X. Xing, Y. Li, D. Yin, Y. Ding and W. Pang: Chemosphere Vol. 78(2010), p.402
- [4] D. Zhou, F. Wu and N. Deng: Chemosphere Vol.57 (2004), p. 283.
- [5] X. Ou, F. Zhang, C. Wang and Wuyunna: Asian Journal of Chemistry Vol.24(2012), p.3314
- [6] Y.S. Liu, G.G. Ying, A. Shareef and R.S. Kookana: Environ. Chem. Vol.10(2013), p.135
- [7] C.A.L. Graca, A. Correia de Velosa and A.C.S.C. Teixeira: Chemosphere Vol.184(2017), p. 981
- [8] L.A. Oste, E.J.M. Temminghoff and W.H.V. Riemsdijk: Environ. Sci. Technol. Vol.36(2002), p.208