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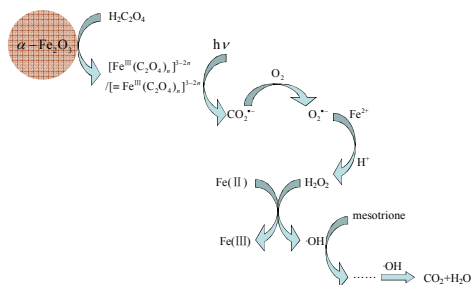


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The application of Photo-Fenton-Like system, consisted of nano $\alpha\text{-Fe}_2\text{O}_3$ /oxalate complex under UV light irradiation, on herbicide mesotrione was investigated.

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ARTICLE TYPE

Heterogeneous photodegradation of mesotrione in nano α -Fe₂O₃/oxalate system under UV light irradiation

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The aim of this study is to investigate the behavior of mesotrione herbicide photodegradation under UV light irradiation with co-existence of iron oxides and oxalic acid. α -Fe₂O₃ and oxalate can set up a novel photo-Fenton-like system under UV irradiation in nature environment without H₂O₂ additional. The adsorption capacity of mesotrione was investigated in the dark by batch experiment, and the results were well fitted by Langmuir model. The effects of the dosage of iron oxide, initial concentration of oxalic acid (C_{ox}⁰), mesotrione, and initial pH on the mesotrione photodegradation were investigated. The photoproduction of hydroxyl radicals (\bullet OH) during the photochemical process were also examined in different catalytic systems. The results indicated that mesotrione photodegradation follows pseudo-first-order kinetics. The mesotrione photodegradation gets slowly in the presence of α -Fe₂O₃ or oxalic acid. Interestingly, we found out that mesotrione photodegradation distinctly enhanced when α -Fe₂O₃ and oxalic acid were co-existed under UV irradiation. We found out that combination of α -Fe₂O₃ and oxalate system is an excellent agent to accelerate the mesotrione herbicide decomposition. The results from this study could be further applied into nature environment and facilitate environmental protecting.

Introduction

Herbicides are worldwide used for high yields of agriculture crops. Owing to its extensively production and consumption, herbicides have already been detected in a variety of soil, groundwater and surface water, which may represent a high risk to humans and ecosystem health. Once herbicides were applied in the field, the transportation and degradation processes would occur in nature environment. Knowledge of environmental fate is crucial to underestimate of the herbicide consumption. Therefore, many efforts have been undertaken to investigate the mineralization process in the surface of the earth and aquatic environments.¹

Iron oxides (including oxy-hydroxides) is a kind of natural minerals with the great content (mass ratio 5.1%) of the earth's crust. Oxalic acid, mainly secreted by plant roots, is ubiquitous in water and soil.² Iron oxides coexist with oxalic acid in nature can set up a so called photo-Fenton-like system under light irradiation.^{2,3} In fact, this photo-Fenton-like system can generate a series of strong oxidant species, such as O₂^{•-}, H₂O₂, HO₂[•] and \bullet OH, which have the high efficiency for the degradation of aqueous organic compounds, especially at very low concentrations.⁴ Thus, it would eventually influence the environmental fate and ecological risk of herbicides in the environment. Many studies showed that herbicides could be degraded in the presence of Fe(III)-oxalate complexes under solar light irradiation.⁵⁻⁷

Mesotrione (2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexanedione,⁸ its molecular structure is shown in Fig. 1) is a

selective herbicide,⁹ which belongs to the triketone group, was developed as a substitution of atrazine by Syngenta Crop Protection, and registered in Europe in 2000.¹⁰ It was marketed in 2001 under the commercial name Callisto,¹¹ and the consumption of mesotrione was indeed increasing regularly. As its extensive use, several new and advanced technologies have been developed for degradation of mesotrione, such as Fenton process,¹² electro-Fenton,¹³ photochemical degradation,¹⁴ ozonization,¹⁵ dielectric barrier discharge (DBD reactor),¹⁵ and biodegradation et al,¹⁶⁻²⁰ but little is known about the photochemical behavior of herbicides in α -Fe₂O₃ and oxalate system.

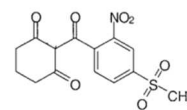


Fig.1 Chemical structure of mesotrione

The goal of this study is to investigate the photodegradation behavior of mesotrione with the co-existence of iron oxides and oxalic acid, and the mechanism of its degradation in heterogeneous system was also discussed. The α -Fe₂O₃/oxalate system was employed for its extensive exists in soil and surface water in natural environment. The photochemical degradation of mesotrione was examined in α -Fe₂O₃/oxalate system under UV irradiation at various factors, including the dosage of α -Fe₂O₃, initial concentrations oxalate, initial pH values, which may coexist with mesotrione at natural environments. To investigate the mechanism of the mesotrione heterogeneous photodegradation, the concentration of \bullet OH in the reaction

process was detected. Additional mechanistic test was performed by adding, to the irradiation experiments, phenol to scavenge hydroxyl radical. There is none report on the photodegradation of mesotrione in $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system under UV irradiation.

5 Materials and methods

Reagents

Mesotrione was obtained from Jiangsu Academy of Agricultural Sciences, China (technical grade, 98 %). $\alpha\text{-Fe}_2\text{O}_3$ (99.5 %, 30 nm) was purchased from Shanghai Ziyi Reagent Co., Ltd, China. Stock solution of mesotrione 10 g L^{-1} was prepared in acetonitrile and stored in the dark at 4°C . Oxalate (Fluka, 99.0 %) and other chemicals with analytical grades were purchased from Sinopharm Chemical Reagent Co., Ltd, China. For extraction and HPLC analysis methylene dichloride (AR), acetonitrile (HPLC grade) and phosphoric acid (GR) were used. Methyl alcohol and acetonitrile of chromatographic grade were purchased from Tedia Company, USA. Benzene (Sinopharm Chemical Reagent Co., Ltd, China) was analytical grade and used as a probe to determine the photoproduction of hydroxyl radical ($\bullet\text{OH}$) in aqueous solution. All the chemicals were used without further purification and all solutions were prepared using double distilled water.

Adsorption isotherm experiment

Adsorption of mesotrione on $\alpha\text{-Fe}_2\text{O}_3$ was determined by using the batch experiment in the dark. A fixed amount of $\alpha\text{-Fe}_2\text{O}_3$ (0.10 g) was added to 10 mL of mesotrione solution with varying concentrations in quartz tubes, which were sealed and agitated for 24h at 300 rpm at $20 \pm 1^\circ\text{C}$. The suspensions were filtered and then centrifuged (5000 rpm for 8 min) for the determination of the concentration of mesotrione in aqueous solution by liquid chromatography.

Experiments of mesotrione Photodegradation

After adsorption, the photodegradation of mesotrione was carried out in a XPA-7 photo-chemical reactor (Xujiang electromechanical plant, Nanjing, China). Before irradiation, the suspension was sealed and agitated for 30 min to reach the equilibrium of adsorption. The temperatures of the reaction solutions were maintained at $20 \pm 1^\circ\text{C}$ by cooling water circulation. A 500 W medium Hg lamp with a maximum light intensity output at 365 nm was used as an irradiation source. The lamp was put into a hollow quartz trap which located at the center of quartz tubes was measured to be $8.96 \times 10^2\text{ mW cm}^{-2}$ by a UV irradiation meter (UV-A, Beijing Normal University, China), and $7.9 \times 10^4\text{ LUX}$ by a LUX meter (AS-813, Smart Sensor, China), respectively. The initial pH of reaction solutions were adjusted with dilute hydrochloric acid solution and sodium hydroxide solution, and the final volume of the solution were adjusted to 50 mL with double distilled water. Then, the solution were put into the photochemical reactor and stirred with magnetic stirrers. At given irradiation time intervals, the analytical sample was withdraw from the suspension with a pipette and immediately filtered for further analysis in order to avoid further reaction.

Analysis

Concentrations of mesotrione in irradiated and non-irradiated

samples were obtained by the following method. Samples from adsorption and photodegradation experiments were collected and filtered using a syringe filter equipped with a $0.45\ \mu\text{m}$ membrane filter. The water samples were firstly extracted twice by methylene chloride under 20°C for 15 min. The extract liquor was then evaporated by rotary evaporator to nearly dry and dissolved in acetonitrile in constant volume. Mesotrione was quantified using a Perkin-Elmer HPLC equipped with a SPHERI-5 RP-18 column ($4.6\text{ mm} \times 150\text{ mm}$, $5\ \mu\text{m}$). The acetonitrile-phosphoric acid aqueous solution ($\text{pH} = 4.0$) was employed as mobile effluent. The flow rate was 0.5 mL min^{-1} , and the ultraviolet detector was set at 220 nm.

Aromatic hydroxylation has been proved to be one of typical reactions of $\bullet\text{OH}$ and used for the detection of $\bullet\text{OH}$ in the case of the Fenton/Fenton-like reactions.²¹⁻²³ Scavenging of $\bullet\text{OH}$ by excessive benzene was introduced into different reaction systems to determine the $\bullet\text{OH}$ quantum yield under an irradiation of a 500 W Hg lamp. The formation of phenol from the reaction of benzene and $\bullet\text{OH}$ was detected at 254 nm by HPLC (Perkin-Elmer Flexar with XDB-C18 ($5\ \mu\text{m}$, $4.6 \times 250\text{ mm}$)). A 25 % (v/v) acetonitrile was used as a mobile phase at a flowing rate of 1.0 mL min^{-1} under isocratic conditions at 25°C . Samples of $10\ \mu\text{L}$ were injected into the column through the sample loop for analysis.

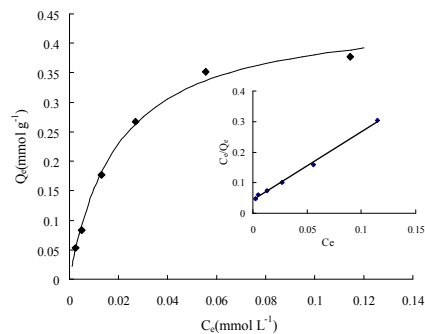
Results and discussion

80 The adsorption behavior of $\alpha\text{-Fe}_2\text{O}_3$

The adsorption isotherm of mesotrione on $\alpha\text{-Fe}_2\text{O}_3$ by plotting the equilibrium concentration (C_e) versus the amount of mesotrione adsorption (Q_e) was shown in Fig.2, which was well fitted by the Langmuir adsorption model as Eq.(1).

$$85 \quad \frac{C_e}{Q_e} = \frac{1}{Q_{\text{emax}}} \cdot C_e + \frac{1}{K \cdot Q_{\text{emax}}} \quad (1)$$

Where C_e is the equilibrium concentration in the solution in mM, K is the adsorption equilibrium constant in L mol^{-1} , and Q_{emax} is the saturated adsorption capacity in mol g^{-1} . The saturated adsorption amount (Q_{emax}) of mesotrione on $\alpha\text{-Fe}_2\text{O}_3$ was 0.447 mmol g^{-1} and adsorption equilibrium constant (K) was 52.44 L mol^{-1} with the correlative coefficient R^2 of 0.9965.



95 **Fig.2** The adsorption isotherm of mesotrione on $\alpha\text{-Fe}_2\text{O}_3$ obtained by plotting C_e versus Q_e (the inserted figure presents the dependence of C_e/Q_e on C_e).

The adsorption behaviour of mesotrione by $\alpha\text{-Fe}_2\text{O}_3$

The photodegradation of mesotrione under the different conditions were showed in Fig.3. The rate of mesotrione photodegradation was slightly at 6.8 % under UV light (500w Hg) irradiation with the absence of oxalic acid and $\alpha\text{-Fe}_2\text{O}_3$ (curve a).

When 0.2 g L⁻¹ $\alpha\text{-Fe}_2\text{O}_3$ was present with the same condition as curve a, the rate of mesotrione degradation was nearly same as curve a too and the removal of mesotrione was 9.7 % after 60 min (curve c). And the removal percentage of mesotrione was significantly increased, and was up to 21.5 % level at 60 min under UV light with 2.0 mM oxalic acid (curve b). However, when both 2.0mM oxalic acid and $\alpha\text{-Fe}_2\text{O}_3$ with 0.2 g L⁻¹ dosage were added into the reaction suspension under UV irradiation (curve d), the removal percentage of mesotrione was up to 85.9 %.

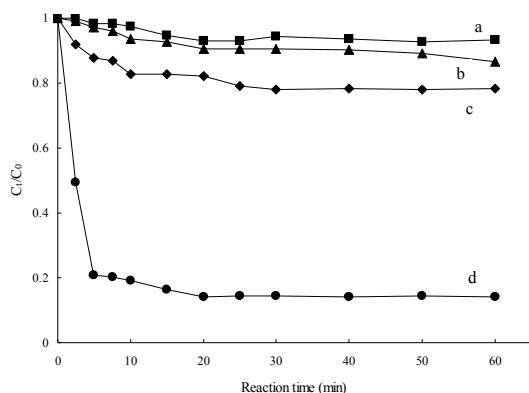
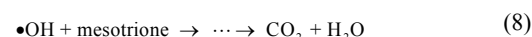
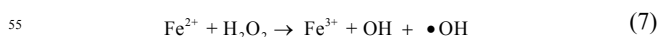
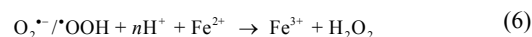
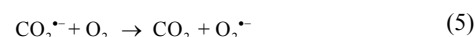
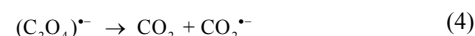
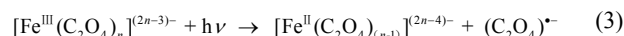
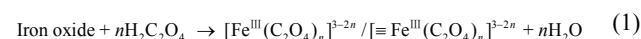


Fig.3 Photodegradation of 10 mg L⁻¹ mesotrione under UV irradiation (500 W Hg lamp) in 50mL solutions with (a) UV only; (b) UV +2.0 mM oxalic acid; (c) UV + 0.2 g L⁻¹ $\alpha\text{-Fe}_2\text{O}_3$; (d) UV + 2.0 mM oxalic acid + 0.2 g L⁻¹ $\alpha\text{-Fe}_2\text{O}_3$.

The photocatalytic degradation of mesotrione followed the first-order reaction kinetics and the first-order kinetics constants(k) for mesotrione degradation as 0.51×10^{-2} , 0.53×10^{-2} , 1.20×10^{-2} , 31.49×10^{-2} when it was degraded on different conditions as Fig.3. From curves b to d, we can see that, $\alpha\text{-Fe}_2\text{O}_3$ had low photocatalytic activities with the absence of oxalic acid, and mesotrione can be efficiently degraded by $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system under UV light irradiation. The results showed that iron oxides, oxalate and UV light should play important roles in mesotrione degradation, and mesotrione photodegradation should be greatly enhanced in the cooperation of iron oxide and oxalate.

In order to understand the photoreaction process of mesotrione degradation in $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system, the interaction of $\alpha\text{-Fe}_2\text{O}_3$ and oxalate under UV light irradiation was discussed. On the surface of $\alpha\text{-Fe}_2\text{O}_3$, oxalic acid is first adsorbed by $\alpha\text{-Fe}_2\text{O}_3$ particles to form $\alpha\text{-Fe}_2\text{O}_3$ /oxalate complexes of with high photochemical activity as described by Eq.(2). Both on the surface or in the solutions can generate Fe(II) and $\text{CO}_2^{\cdot-}$ under UV excitation as described by Eq. (3) and (4). Obviously, the higher oxalate concentration leads to the more Fe(II) concentration. Then $\text{CO}_2^{\cdot-}$ could reacts with oxygen to produce superoxide ions $\text{O}_2^{\cdot-}$ as described by Eq. (5) and (6), and Fe(II) reacts with $\text{O}_2^{\cdot-}$ to form H_2O_2 in acid solution as described by Eq. (7). After H_2O_2 was formed, $\cdot\text{OH}$ could be generated by reaction of H_2O_2 with Fe(II) as described by Eq. (8). Finally, mesotrione was oxidized by $\cdot\text{OH}$ as described by Eq. (9), which has strong oxidation potential. It should be noted that the photochemical

reactions happened both on the surface of $\alpha\text{-Fe}_2\text{O}_3$ as a heterogeneous photo-Fenton process and in the solution as homogeneous one.²⁴



The effect of $\alpha\text{-Fe}_2\text{O}_3$ dosage on mesotrione photodegradation

The dosage of $\alpha\text{-Fe}_2\text{O}_3$ on mesotrione degradation in the presence of oxalic acid with an initial concentration of 2.0 mM was showed in Fig. 5. The effect of $\alpha\text{-Fe}_2\text{O}_3$ dosage on the photodegradation of mesotrione with 2 mM oxalic acid under an irradiation of 500 W medium-pressure Hg lamp was investigated and the results were illustrated that it was very slow process with oxalate added. Approximately 20% of mesotrione was consumed after 60 min irradiation without $\alpha\text{-Fe}_2\text{O}_3$.

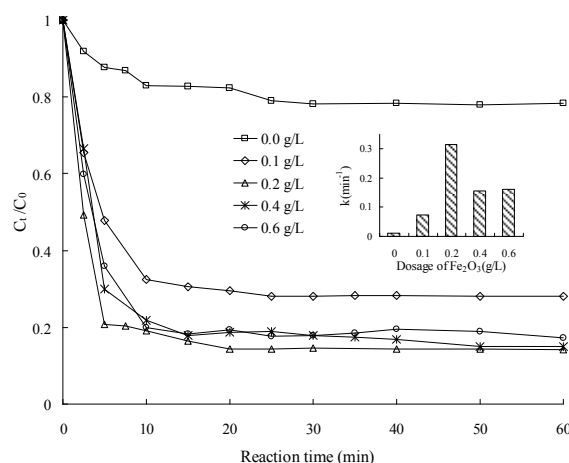


Fig.4 The effect of $\alpha\text{-Fe}_2\text{O}_3$ dosage on the photodegradation of 10 mg L⁻¹ mesotrione under UV irradiation (500 W Hg lamp) in the presence of 2.0 mM oxalic acid (the inserted figure presents the dependence of k on the dosage of iron oxide).

However, an addition of $\alpha\text{-Fe}_2\text{O}_3$ markedly accelerated the degradation of mesotrione. It is found that mesotrione with an initial concentration of 10 mg L⁻¹ was nearly reach an equilibrium in 5 min at the presence of 0.2 g L⁻¹ $\alpha\text{-Fe}_2\text{O}_3$, suggesting that $\alpha\text{-Fe}_2\text{O}_3$ was an excellent photocatalyst for mesotrione degradation assisted by oxalic acid. The removal percentage of mesotrione increased from 72.0 % to 85.9 % when $\alpha\text{-Fe}_2\text{O}_3$ increased from 0.1 to 0.2g L⁻¹, but decreased slightly when $\alpha\text{-Fe}_2\text{O}_3$ increased from 0.2 to 0.6g L⁻¹. Excessive dosage of $\alpha\text{-Fe}_2\text{O}_3$ may block

the scattering of UVA light in the reaction suspension and decrease the formation of $\bullet\text{OH}$.

The photodegradation of mesotrione in $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system followed by first-order kinetic and the first-order kinetic constants (k) versus the dosage of $\alpha\text{-Fe}_2\text{O}_3$ was plotted in Fig.4. The first-order kinetic constants (k) were 1.2×10^{-2} , 7.44×10^{-2} , 31.49×10^{-2} , 15.63×10^{-2} , $16.0 \times 10^{-2} \text{ min}^{-1}$ with 0, 0.10, 0.20, 0.4 and 0.6 g L^{-1} $\alpha\text{-Fe}_2\text{O}_3$, respectively. This suggests that the dosage of 0.2 g L^{-1} was an optimal concentration of $\alpha\text{-Fe}_2\text{O}_3$ for mesotrione photodegradation with oxalate present. The $\alpha\text{-Fe}_2\text{O}_3$, as a heterogeneous photocatalyst, can significantly accelerate the formation of $[\equiv\text{Fe}(\text{C}_2\text{O}_4)_n]^{3-2n}$. And under UV irradiation, $\bullet\text{OH}$ can be produced more during the photochemical reaction with more $[\equiv\text{Fe}(\text{C}_2\text{O}_4)_n]^{3-2n}$ formed. In fact, excessive dosage of $\alpha\text{-Fe}_2\text{O}_3$ will limit the penetration of UV light in the solution and lead to the quick decay of UV light intensity. A similar phenomenon was observed by while the investigated schwertmannite($\gamma\text{-Fe}_2\text{O}_3$) photocatalytic degradation of methyl orange by oxalate under UV irradiation.²³

20 The effect of initial concentration of oxalate (C_{ox}^0) on mesotrione photodegradation

To study the effect of initial C_{ox}^0 on the photodegradation of mesotrione, a set of experiments with initial mesotrione of 10 mg/L and $\alpha\text{-Fe}_2\text{O}_3$ dosage of 0.2 g L^{-1} were carried out under UV irradiation (500 W Hg lamp), followed by the experiments on different initial C_{ox}^0 without pH control. The initial concentration of oxalate also played an important role in the degradation of mesotrione as shown in Fig.5. In the absence of oxalate, the degradation of mesotrione was extremely slow and the concentration of mesotrione almost kept constant under the irradiation for 60 min (curve 0.0 mM). However, mesotrione degradation could be efficiently enhanced in the presence of oxalate. The increase of oxalate in the suspension of $\alpha\text{-Fe}_2\text{O}_3$ /oxalate significantly shortened the time of photodegradation of mesotrione. However, a higher oxalate concentration could not result in more rapid degradation of mesotrione. Excessive oxalate would lead to lower pH in the photochemical reaction system, and also lead to the formation of Fe^{3+} , which may reduce the formation of $\bullet\text{OH}$,²⁰ as described in Eq.(7) and Eq.(8).

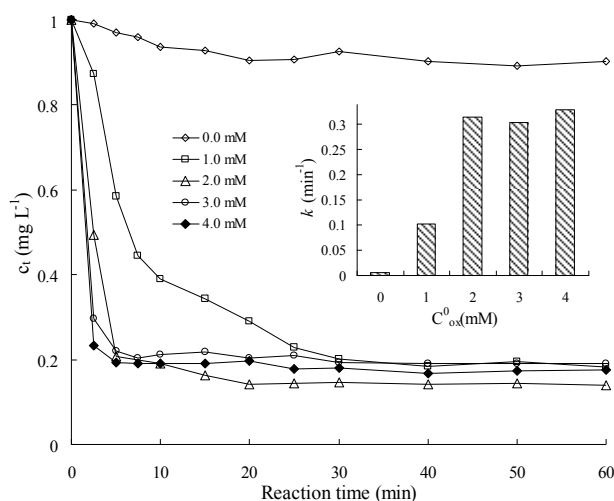


Fig.5 The effect of initial concentration of oxalic acid on the photodegradation of 10 mg L^{-1} mesotrione under UV irradiation by 0.2 g L^{-1} Fe_2O_3 (the inserted figure presents the dependence of k on the C_{ox}^0).

45 The photodegradation of mesotrione in $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system followed by first-order kinetic and the first-order kinetic constants (k) versus C_{ox}^0 was plotted as the Fig.5. The k values of mesotrione degradation were 0.53×10^{-2} , 10.24×10^{-2} , 31.49×10^{-2} , 30.35×10^{-2} and 32.89×10^{-2} when the initial concentration of oxalic acid was 0.0, 1.0, 2.0, 3.0 and 4.0 mM, respectively. The possible reason is that excessive oxalic acid would occupy the adsorbed sites on the surface of $\alpha\text{-Fe}_2\text{O}_3$ and also could react competitively with generated $\bullet\text{OH}$ together with mesotrione. Thus, it is necessary to control the optimal concentrations of $\alpha\text{-Fe}_2\text{O}_3$ and oxalate for photodegradation of mesotrione.

The effect of initial concentration of mesotrione on mesotrione photodegradation

The effect of initial concentration of mesotrione ranging from 2.0 to 20.0 mg L^{-1} on photodegradation of mesotrione was investigated in the presence of 0.2 g L^{-1} $\alpha\text{-Fe}_2\text{O}_3$ and 2.0 mM oxalic acid UV irradiation (500 W Hg lamp). The results were presented in Fig.6. The same tendency for mesotrione degradation can be observed from the curves. The k values of mesotrione degradation were 37.44×10^{-2} , 32.69×10^{-2} , 31.49×10^{-2} and 15.15×10^{-2} when the initial concentration of mesotrione was 2.0, 5.0, 10.0 and 20.0 mM, respectively. The rate of mesotrione photodegradation decrease almost linearly with the increase of initial concentration of mesotrione.

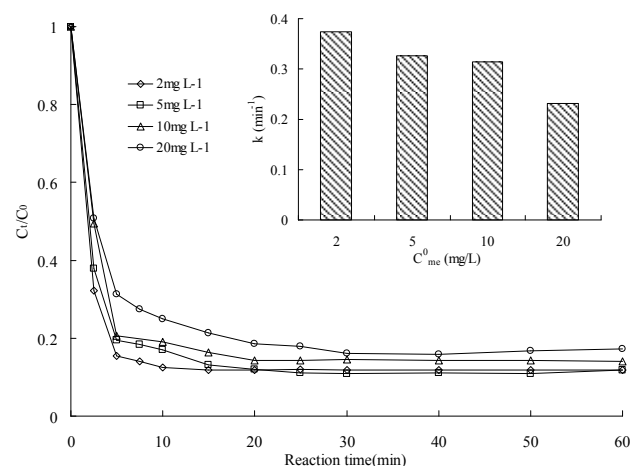


Fig.6 The effect of initial concentration of mesotrione on the photodegradation in the presence of 0.2 g L^{-1} $\alpha\text{-Fe}_2\text{O}_3$ and 2.0 mM oxalic acid under UV irradiation (the inserted figure presents the dependence of k on C_{me}^0).

The effect of initial pH value on the photodegradation of mesotrione

To investigate the effect of initial pH value on the photodegradation of mesotrione, a series of experiments were carried out at different initial pH, which was adjusted by NaOH or HCl before reaction, with initial concentration of mesotrione of 10 mg L^{-1} in the presence of 0.2 g L^{-1} $\alpha\text{-Fe}_2\text{O}_3$ and 2.0 mM oxalic acid under UV irradiation (500W Hg lamp). The results showed that the optimal initial pH value should be around 4.0, at which the photoreaction was almost completed in 20 min in Fig.7. The

first-order kinetic constants (k) were 5.36×10^{-2} , 30.2×10^{-2} , 0.92×10^{-2} , 0.12×10^{-2} , 0.17×10^{-2} when the initial pH were 2.0, 4.0, 6.0, 8.0 and 10.0 g L^{-1} , respectively.

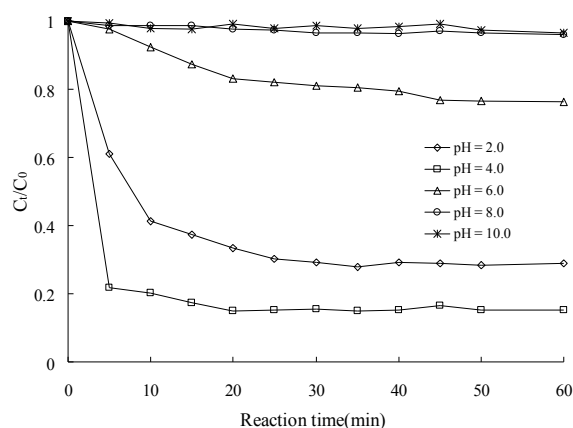


Fig.7 The effect of initial pH value on the photodegradation of mesotrione.

Several studies had reported that the main Fe(III)-oxalate species were $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^{2-}$ and $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$, which are highly photoactive when the pH was at around 4.²⁵⁻²⁷ The degradation of mesotrione would be inhibited considerably when the initial pH value interval ranges from 4 to 6. Furthermore, the degradation of mesotrione was almost neglected with the initial pH of 8.0 and 10.0, respectively. The $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system at lower initial pH value might have a higher concentration of $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$. In addition, the H_2O_2 produced in high rate in the $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system under irradiation with the pH value ranging from 1.5 to 4.0, but decreased when the pH over 4.0. When pH was over 6.0, the Fe(III) species as the formation of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ which as the precipitate in the solution, and the photochemical reaction was inhibited. On the other hand, the dissolution of $\alpha\text{-Fe}_2\text{O}_3$ by H^+ was excessive at lower initial pH 2.0. Therefore, the formation of $\alpha\text{-Fe}_2\text{O}_3$ /oxalate complex would be hindered, and less $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$ was formed. Thus the yields of $\bullet\text{OH}$ decreased, leading a lower rate of mesotrione degradation.

25 Production of hydroxyl radicals($\bullet\text{OH}$) in different reaction systems

Organic pollutants could be degraded by the hydroxyl radicals($\bullet\text{OH}$) with high oxidation potential, produced in the photochemical reactions. Therefore, the $\bullet\text{OH}$ could be an indicator for photochemical degradation in the above-mentioned $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system. To investigate the mechanism of mesotrione photodegradation in $\alpha\text{-Fe}_2\text{O}_3$ /oxalate system, the concentration of $\bullet\text{OH}$ was detected during the photochemical processes. The results were shown in Fig.8.

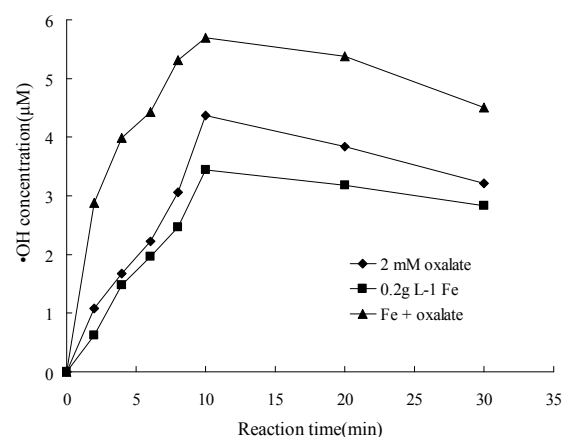


Fig.8 The production of hydroxyl radicals($\bullet\text{OH}$) in different reaction system under UV irradiation (500 W Hg lamp)

The concentration of $\bullet\text{OH}$ in the system depends on both the rates of its generation and consumption. As illustrated in Fig.8, both $\alpha\text{-Fe}_2\text{O}_3$ and oxalate alone showed a low yield of $\bullet\text{OH}$ under UV irradiation of a 500 W Hg lamp. However, in the presence of both $\alpha\text{-Fe}_2\text{O}_3$ and oxalate, a considerable number of $\bullet\text{OH}$ were detected. Hydroxyl radicals were quickly produced in initial 10 min, then the amount of $\bullet\text{OH}$ in the reaction system decreased with the $\bullet\text{OH}$ consumption by some organic compounds degradation. The maximum concentration of $\bullet\text{OH}$ observed in 10 min was approximately 60 μM .

Benzene was selected as the hydroxyl radical scavenger due to its fast reaction with the $\bullet\text{OH}$. In contrast, the photodegradation of mesotrione was significantly inhibited while benzene was added. Fig.9 shows that with 0.32 mM and 0.64 mM benzene added, mesotrione degradation rates after 30 min were 15.17 % and 5.65 % respectively, indicating that the higher benzene concentration would scavenge most of the $\bullet\text{OH}$ generated in the system, and block the mesotrione photodegradation.

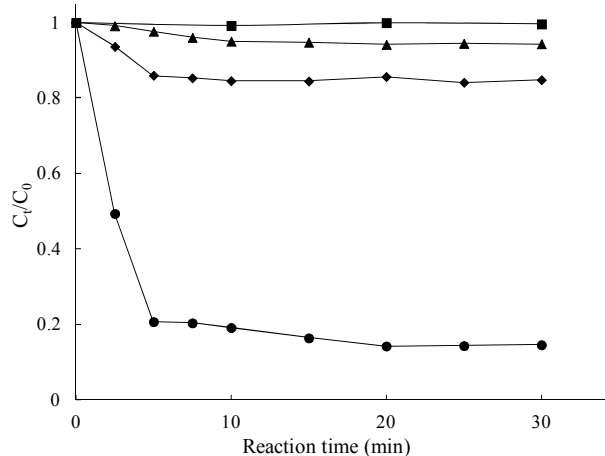


Fig.9 Effect of hydroxyl radical scavenger on mesotrione degradation performance under UV irradiation (500 W Hg lamp) with (a) blank; (b) 0.64 mM benzene; (c) 0.32 mM benzene; (d) control.

Conclusion

The photodegradation of herbicide mesotrione in the heterogeneous α -Fe₂O₃/oxalate system, as a photo-Fenton-like system without additional H₂O₂ under UV irradiation, were investigated in this study. α -Fe₂O₃ could be a efficient photocatalyst for the degradation of organic matters in nature environment. It can significantly accelerate photodegradation of herbicide mesotrione by the presence of oxalate. There are several steps for the mesotrione photodegradation which can be described as (1) oxalate is adsorbed onto the surface of α -Fe₂O₃ to form $[Fe^{III}(C_2O_4)_n]^{3-2n}$; (2) Fe(II) are generated and H₂O₂ are formed under UV irradiation; (3) •OH are generated in the Fenton-like system; (4) mesotrione are decomposed by •OH. The photodegradation of herbicide mesotrione depended strongly on the initial pH value, the doses α -Fe₂O₃, the initial concentration of oxalate and mesotrione. The optimal α -Fe₂O₃ dosage was 0.2 g L⁻¹ and the optimal C_{ox}⁰ was 2.0 mM with the UV light irradiation (500 W Hg lamp), respectively. The results obtained in this study are helpful to understand the environmental fates of mesotrione and to assess the risk of herbicide mesotrione used in the crops, and also can provide a viable technology for the removal of mesotrione from water.

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Notes and references

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