Chemosphere 138 (2015) 266–271

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effect of low-molecular-weight organic acids on photo-degradation of phenanthrene catalyzed by Fe(III)–smectite under visible light

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HIGHLIGHTS

- Low-molecular-weight organic acids have significant influence on PAHs photolysis.
- Chelating ability of LMWOAs with Fe are critical to their roles in Phe photolysis.
- Presence of oxalic and malic acids favor Phe photodegradation on Fe(III)–clay.
- EDTA or nitrilotriacetic acid inhibits both Fe(II) formation and Phe photolysis.
- Reductive $^{\cdot}CO_2^{-}$ radicals involved in Phe photodegradation are supported by EPR.

ARTICLE INFO

Article history:
Received 19 March 2015
Received in revised form 19 May 2015
Accepted 22 May 2015
Available online 16 June 2015

Keywords:
Low-molecular-weight organic acids (LMWOAs)
Phenanthrene
Smectite
Visible light photodegradation

ABSTRACT

The photolysis of polycyclic aromatic hydrocarbons (PAHs) is potentially an important process for its transformation and fate on contaminated soil surfaces. In this study, phenanthrene is employed as a model to explore PAH photodegradation with the assistance of Fe(III)–smectite under visible-light while focusing on roles played by five low-molecular-weight organic acids (LMWOAs), i.e., malic acid, oxalic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid. Our results show that oxalic acid is most effective in promoting the photodegradation of phenanthrene, while only a slight increase in the rate of phenanthrene photodegradation is observed in the presence of malic acid. Electron paramagnetic resonance experiments confirm the formation of $^{\cdot}CO_2^{-}$ radicals in the presence of malic and oxalic acid, which provides strong evidence for generating ·OH and subsequent photoreaction pathways. The presence of EDTA or nitrilotriacetic acid significantly inhibits both Fe(II) formation and phenanthrene photodegradation because these organic anions tend to chelate with Fe(III), leading to decreases in the electron-accepting potential of Fe(III)–smectite and a weakened interaction between phenanthrene and Fe(III)–smectite. These observations provide valuable insights into the transformation and fate of PAHs in the natural soil environment and demonstrate the potential for using some LMWOAs as additives for the remediation of contaminated soil.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), are mainly produced from fossil fuel deposits and incomplete combustion, have primarily been detected in naturally hydrophobic phases, such as in soil and sediment (Li et al., 2008). Due to their tendency to degrade naturally and their potentially damaging effects on human health and ecosystems, PAHs are included in the US Environmental Protection Agency and the EU priority list of pollutants (Samanta et al., 2002). Phenanthrene is one of the most widespread PAHs, with three fused benzene rings, and is often used as a model compound to study the transformation and fate of PAHs in contaminated soils (Zhang et al., 2011). Phenanthrene may reside on the upper surface layer for a certain period and undergo various natural processes, such as biodegradation, chemical transformation, and photolysis reactions (Menager and Sarakha, 2013; Zhang et al., 2006). Among those processes, abiotic photodegradation processes, which are associated with solar-light irradiation, are potentially important for its fate and may provide an alternative

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http://dx.doi.org/10.1016/j.chemosphere.2015.05.076
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biodegradation pathway in the surface soil environment (Menager and Sarakha, 2013; Zhang et al., 2006).

The photolysis of PAHs depends highly on the soil components, such as natural minerals and organic substances (Chien et al., 2011; Jia et al., 2013). Recently, clay mediated photodegradation of organic pollutants in natural environments has received more attention (Liu et al., 2011). Indirect photolysis of several insecticides and herbicides was observed in the presence of clay suspensions (Katagi, 1990, 1993). It has been confirmed that the photolysis of organic compounds adsorbed on clay minerals is faster than on other minerals, such as aluminum hydroxide, iron oxide, or manganese dioxide (Kong and Ferry, 2003). In our previous study, the photochemical behavior of phenanthrene on various clay minerals was investigated, and high reactivity was observed with Fe(III)-saturated smectite (Jia et al., 2012). Fe(III)–smectite can generate a photo-Fenton-like system even without the addition of H_2O_2, thereby leading to an enhancement of the photodegradation of phenanthrene under visible-light irradiation (Jia et al., 2012).

In the addition to soil minerals, low-molecular-weight organic acids (LMWOAs) are abundant in natural soil and water environments as a result of microbial decomposition of organic matter and plant root exudates (Fox and Comerford, 1990). These organic acids always coexist with clay minerals and possess a strong chelating ability with multivalent cations (such as Fe(III)), have been proven to significantly affect the solubility, mobility, and fate of organic compounds in the soil (White et al., 2003). As reported previously, the photochemical process in organic acid–Fe(III) and organic acid–Fe(III)–smectite systems with the generation of $C_2O_4^{\cdot-}$ radicals are much more photoactive than other Fe(III) species for the degradation of pollutants (Sun et al., 2009; Xu et al., 2014). On the other hand, the adsorption of LMWOAs may affect the available surface charge and their interactions between clay minerals and organic pollutants, which may suppress the transformation of contaminants catalyzed by Fe(III) adsorbed on clay mineral surfaces (Sun et al., 2009).

In general, retention of LMWOAs will unavoidably modify the surface properties and reactivity of clay minerals and influence the mobility and fate of pollutants bounded thereon (Ksiezopolska and Pazur, 2011). However, the photolysis of PAHs catalyzed by Fe(III)–smectite in the presence of LMWOAs is not fully understood. Therefore, the principal objective of this study was to investigate the effects of various LMWOAs (i.e., malic acid, oxalic acid, citric acid, EDTA, and nitrilotriacetic acid) on the photodegradation of PAHs using phenanthrene as a model. We looked at the interaction between the LMWOAs and Fe(III)–smectite composite on phenanthrene photodegradation to gain further insight into the photolysis mechanisms at irradiated clay–LMWOAs complexes. The obtained knowledge of the molecular-scale forces influencing photolysis by LMWOAs in PAHs photodegradation will provide valuable insights regarding the environmental fate of PAHs.

2. Experimental section

2.1. Chemicals and materials

Detailed information for the chemicals and materials used in this study is supplied in the Supporting Information (SI). LMWOAs, such as oxalic acid, malic acid, citric acid, EDTA, and nitrilotriacetic acid were selected for this study due to their natural presence in soils. Their molecular formulas are shown in SI Fig. S1.

2.2. Preparation of phenanthrene contaminated clay

LMWOAs–Fe(III)–smectite complexes were prepared by following a similar procedure as that described previously (Jia et al., 2013). Specifically, 10 g of smectite clay was added into a 200 mL of 0.1 M $FeCl_3$ solution before shaking the mixture for 8 h. This procedure was repeated four times to ensure Fe(III) saturation. Next, Fe(III)–smectite suspensions and certain amounts of LMWOAs were mixed and shaken for 8 h. The obtained LMWOAs–Fe(III)–smectite complexes were freeze-dried and denoted as malate–Fe(III)–smectite, oxalate–Fe(III)–smectite, citrate–Fe(III)–smectite, EDTA–Fe(III)–smectite, and nitrilotriacetate–Fe(III)–smectite. The reaction mixtures (phenanthrene contaminated clays) were prepared by mixing phenanthrene dissolved in 1 mL of methanol with 1 g of various LMWOAs–Fe(III)–smectite complexes (1 mg phenanthrene/g clay). The solvent methanol was allowed to evaporate under ambient conditions.

2.3. Reaction of phenanthrene with LMWOAs–Fe(III)–smectite complexes under visible light irradiation

The photolysis reaction was conducted at room temperature (25 °C) following a previously described protocol (Jia et al., 2012). Briefly, contaminated clay minerals were placed onto the center of two quartz glass plates. Next, the clay plates were irradiated under visible light at 0.250 W cm^{-2}, which was generated from a xenon lamp and incorporated with an optical band-pass filter (the wavelength range is above 400 nm). The experiments were conducted in the presence of coumarin and benzoquinone to explore the formation of oxidative radical species during the photochemical reaction. These compounds are often used as $^{\cdot}OH$ radical and $O_2^{\cdot-}$ scavengers, respectively (Louit et al., 2005; Palominos et al., 2008). The concentrations of coumarin and benzoquinone were 1.22 and 1.65 mg per gram of mineral support. At pre-selected intervals, the samples were taken and transferred into 50 mL Teflon centrifuge tubes. The residual PAHs and their products were extracted using a mixture of 5 mL acetone and 5 mL dichloromethane (Jia et al., 2012). To investigate the availability of phenanthrene on LMWOAs–Fe(III)–smectite complexes, the extraction solution (a mixture of acetone and dichloromethane) was substituted with n-butanol using the method developed by Liste and Alexander (2002). The supernatants were filtered using a syringe filter equipped with a 0.22 μm membrane filter. The filtrates were stored in amber HPLC vials and placed in a refrigerator prior to analysis. Each experiment was repeated 3 times, and the error bars shown in the figures represent the standard deviations (SD) obtained from three parallel samples.

2.4. Analysis of phenanthrene and Fe(II)

The evolution of phenanthrene during photolysis was quantified using a Thermo Fisher Ultra 3000 HPLC equipped with a 25 cm × 4.6 mm Cosmosil C18 column. A 85:15 (v/v) mixture of methanol:water was used as the mobile effluent. The flow rate was 1.0 mL min^{-1}, and the ultraviolet detector was set at 254 nm. The amount of Fe(II) in the reacted system was extracted using water and measured using ferrozine. The reacted clay mineral suspension was mixed using a Vortex for 30 s. Next, 0.5 mL of the suspension was collected and added to 1 mL of ferrozine solution (100 mM), and the volume of the mixture was adjusted to 15 mL. The suspension was agitated for 2 h and filtered through a 0.45 μm filter. The concentration of ferrozine-complexed Fe(II) was determined using absorbance at 562 nm with a UV–vis spectrophotometer (Hitachi Co., U-3500).

2.5. EPR and redox potential test

Electron paramagnetic resonance (EPR) spectra of spin-trapping radicals by DMPO were recorded at room temperature on a Bruker EPR ELEXSYS 500 spectrometer equipped with an in situ irradiation source (a Quanta-Ray ND:YAG laser system). Typical instrumental conditions were as follows: center field, 3355 G; sweep width, 78 G; resolution, 1024 pts; microwave frequency, ~9.41 GHz; microwave power, 6.325 mW; power attenuation, 15.0 dB; modulation frequency, 100 kHz; conversion time, 30.00 ms; and receiver gain, 81 dB. To minimize experimental errors, the same quartz capillary was used for all measurements. Redox potential (Eh) measurements were carried out using an Orion expandable ion analyzer equipped with a Fisher Pt wire electrode and an Orion double junction reference electrode. The redox standard solution contained 0.1 M ferrous ammonium sulfate, 0.1 M ferric ammonium sulfate and 1.0 M H_2SO_4.

3. Results and discussion

3.1. Photodegradation of phenanthrene in the presence of different LMWOAs

Smectite clay complexes with different types of LMWOAs were prepared for phenanthrene photolysis experiments. The evolution of phenanthrene as a function of reaction time is presented in Fig. 1a. After 6 h, approximately 100%, 99%, 73%, 52%, and 29% of the initially added phenanthrene was transformed by photolysis on LMWOAs–Fe(III)–smectite complexes associated with oxalic, malic, citric, EDT, and nitrilotriacetic acid, respectively. As a comparison, approximately 90% of initially added phenanthrene was transformed by Fe(III)–smectite in the same reaction time frame. In addition, control experiments were conducted in the dark to evaluate possible effects of chemical and microbiological degradation during the irradiation experiment. An insignificant disappearance of phenanthrene was observed in the dark control experiments during 6 h of reaction. These observations suggest that photodegradation plays a crucial role in the disappearance of phenanthrene. Data fitting suggests that in the present reaction systems, phenanthrene degradation follows a pseudo-first-order model. The rate constants are listed in Table 1. Comparing the LMWOAs–Fe(III)–smectite complexes, the photodegradation rate of phenanthrene follows the following order: oxalate–Fe(III)–smectite > malate–Fe(III)–smectite > Fe(III)–smectite > citrate–Fe(III)–smectite > EDTA–Fe(III)–smectite > nitrilotriacetate–Fe(III)–smectite. Among those complexes, malate–Fe(III)–smectite and oxalate–Fe(III)–smectite were more efficient than Fe(III)–smectite in accelerating the photodegradation of phenanthrene. On the other hand, the presence of other organic acids, such as citric acid, EDTA, and nitrilotriacetic acid, is detrimental to phenanthrene photodegradation. The reaction rate is slowed down by approximately 0.6, 3, and 6 times, respectively. This observation suggests that the types of LMWOAs can influence the photodegradation of phenanthrene on clay mineral surfaces. As reported previously, the photocatalytic transformation of contaminants is strongly affected by the number of carboxylic groups in organic compounds. The initial rates of Cr(VI) reduction by different organic compounds decrease as follows: EDTA (with 4 carboxyl groups) > nitrilotriacetic acid (with 3 carboxyl groups) > iminodiacetic acid (with 2 carboxyl groups) > glycine (with 1 carboxyl group) (Lee et al., 2007). In our research system, Fe(III)–smectite complexes with bi-carboxylic acid were more photoreactive than those citrate and two other higher-carboxylic systems, and phenanthrene photodegradation did not show a linear correlation with the number of carboxylic groups that was as well as that observed in some other reports (Faust and Zepp, 1993).

Table 1
Transformation rate constant (k_{obs}, h^{-1}) of phenanthrene on various LMWOAs–Fe(III)–smectite complexes.

Scavenger type	None	Coumarin	Benzoquinone
Type of organic acid			
No acid	0.37 ± 0.023	0.34 ± 0.037	0.03 ± 0.001
Oxalic acid	0.46 ± 0.029	0.04 ± 0.001	0.10 ± 0.011
Malic acid	0.43 ± 0.041	0.12 ± 0.005	0.04 ± 0.001
Citric acid	0.22 ± 0.038	0.05 ± 0.002	0.10 ± 0.008
EDTA	0.12 ± 0.002	0.10 ± 0.007	0.03 ± 0.002
Nitrilotriacetic acid	0.06 ± 0.001	0.05 ± 0.003	0.02 ± 0.001

3.2. Fe(II) formation in the presence of different LMWOAs

During contaminant transformation processes, Fe(III) can be efficiently converted to Fe(II) from solid Fe(III) phases and dissolved Fe(III) (Kuma et al., 1995). In this study, the evolution of Fe(II) as a function of reaction time is shown in Fig. 1b. It is noted that the content of Fe(II) on a smectite surface increases significantly during the first hour of reaction. Equilibrium is reached after a certain reaction time, and the amount of produced Fe(II) remains constant until the end of the reaction. This similar phenomenon was also observed in other reports (Zuo and Deng, 1997). The photoreduction of complexed Fe(III) to Fe(II) is considered to be a photoinduced ligand (or organic pollutants) to metal charge transfer reaction (Kuma et al., 1995). As shown in Fig. 1, the amount of Fe(II) formation follows the same order with phenanthrene photodegradation rate at the various LMWOAs–Fe(III)–smectite

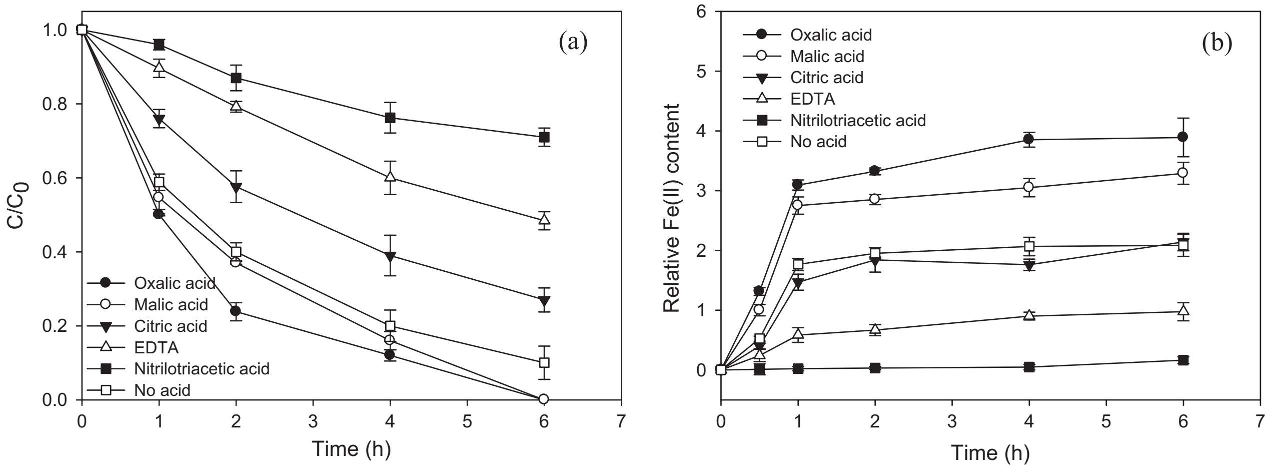

Fig. 1. The evolution of (a) phenanthrene and (b) Fe(II) as a function of reaction time in the reaction systems of various LMWOAs–Fe(III)–smectite complexes.

surfaces. The order probably depends on the ligand chelating ability of organic acids with Fe(III) on smectite surfaces and on the photo-activity of LMWOAs–Fe(III)–smectite complexes (Kuma et al., 1995). In general, the photodegradation of phenanthrene is correlated with the transformation of Fe(III) to Fe(II). This can be attributed to the fact that the Fe(II)/Fe(III) conversion acts as an electron relay that shuttles electrons from the clay surface to the contaminants in a photocatalytic cycle. This cycle consists of two processes: (1) absorption of light by organic acids–Fe(III)–phenanthrene on clay surfaces to produce Fe(II) and organic radicals, and (2) oxidation of Fe(II) to Fe(III) by O_2 or H_2O_2 accompanied by the formation of intermediates, such as $^{\cdot}OH$ and $HO_2^{\cdot}/O_2^{\cdot-}$. These radicals could act as efficient oxidative agents for the degradation of organic contaminants (Stylidi et al., 2004). Therefore, the amount of formed Fe(II) remains relatively constant after 1 h of reaction in photolysis systems associated with various LMWOAs.

3.3. Effect of LMWOAs on the formation of free radicals

In the present study, the EPR technique was employed to identify the possible short-lived radicals (such as $CO_2^{\cdot-}$ radicals) involved in the reaction systems. To avoid the interference of the quenching effect of oxygen on the carbon-centered radicals, the experiment was carried out under anaerobic conditions. As shown in Fig. 2, the formation of a major sextet signal (99%), with $a_N = 15.74$ G and $a_{\beta\text{-H}} = 18.74$ G, assigned to DMPO–$^{\cdot}COO^-$, was observed in the reaction systems of the LMWOAs–Fe(III)–smectite complexes associated with malate, oxalate, and citrate (Villamena et al., 2006). These results provide direct evidence for the generation of $CO_2^{\cdot-}$ radicals during the photolysis of LMWOAs–Fe(III)–smectite complexes. On the other hand, the DMPO–$^{\cdot}COO^-$ signal was not observed in the presence of EDTA and nitrilotriacetic acid, indicating that these organic ligands do not easily undergo photodecarboxylation on Fe(III)–smectite surfaces. The formed $CO_2^{\cdot-}$ is a strong reducing agent ($E_0 = -1.8$ V (NHE)) and can react with another organic acid molecules or reduce O_2 to produce superoxide anions ($O_2^{\cdot-}$) (Surdhar et al., 1989). The formed $O_2^{\cdot-}$ and Fe(II) could further induce the formation of H_2O_2 and hydroxyl radicals ($^{\cdot}OH$), which are considered strong oxidative species for the degradation of organic contaminants.

To verify the possible formation of reactive oxidizing radicals on different LMWOAs–Fe(III)–smectite complexes, coumarin and benzoquinone were used as quenchers for oxidative radicals (i.e., $^{\cdot}OH$) and ambivalent free radicals (i.e., $O_2^{\cdot-}$), respectively (Louit et al., 2005; Palominos et al., 2008; Kong and Davison, 1981). When radical scavengers, such as coumarin and benzoquinone, are added into the clay-based reaction system, they tend to adsorb onto the clay surface and compete with PAHs for radical-induced reactions. As a chemical trap of hydroxyl radicals, coumarin was used as a quencher for the detection of such radicals, leading to the formation of 7-hydroxycoumarin (Eq. (1)) (Louit et al., 2005).

$$^{\cdot}OH + \text{coumarin} \rightarrow \text{7-hydroxycoumarin} \quad (1)$$

On the other hand, benzoquinone, is considered as a superoxide radical quencher, has the ability to trap superoxide anions by a simple electron transfer mechanism (Eq. (2)) (Palominos et al., 2008; Wells et al., 1997).

$$\text{Benzoquinone} + O_2^{\cdot-} \rightarrow \text{Benzoquinone}^{\cdot-} + O_2 \quad (2)$$

Therefore, the addition of radical scavengers (such as coumarin and benzoquinone) hinders the production of specific radicals, and thus the photodegradation of phenanthrene. For Fe(III)–smectite, the presence of benzoquinone dramatically slows down phenanthrene degradation, but the addition of coumarin results in a slight change in phenanthrene transformation (as shown in Table 1). Likewise, the reaction systems associated with nitrilotriacetate–Fe(III)–smectite and EDTA–Fe(III)–smectite were minimally affected by coumarin, indicating that the $^{\cdot}OH$ radical potentially played a limited role in phenanthrene photolysis on the clay surfaces with associated EDTA and nitrilotriacetic acid. However, the inhibiting effect of benzoquinone on phenanthrene degradation suggests that $O_2^{\cdot-}$ is the dominant reactive intermediate species, which is mainly formed through an induced electron transfer process that involves clay and molecular oxygen (Katagi, 1993). Such oxidative radicals play an important role in the transformation of contaminants (Katagi, 1991). In the case of Fe(III)–smectite clays that form complexes with malic and oxalic acids, active oxygen, such as $O_2^{\cdot-}$, still plays an important role in photolysis (as shown in Table 1). However, the $^{\cdot}OH$ species cannot be neglected. The presence of coumarin significantly slows down the photodegradation reaction, indicating that both $^{\cdot}OH$ and $O_2^{\cdot-}$ may be involved in the degradation of organic molecules (Menager and Sarakha, 2013). This result potentially occurred because the presence of malic and oxalic acid result in the formation of $CO_2^{\cdot-}$ radicals on clay surfaces, which could induce the photogeneration of $^{\cdot}OH$ (Katagi, 1990; Wang et al., 2010).

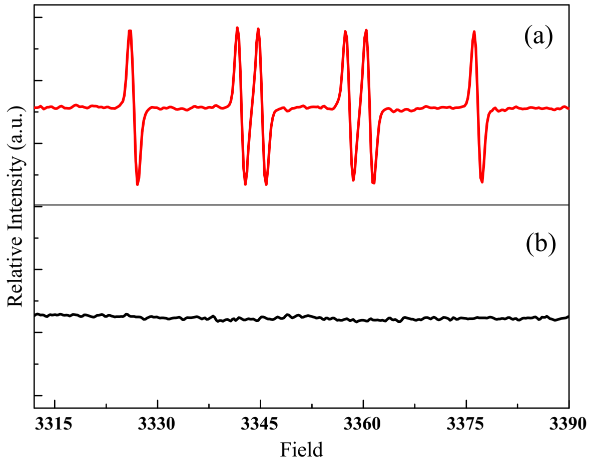

Fig. 2. EPR spectra trapped by DMPO after 2 min of visible light irradiation in phenanthrene photodegradation on LMWOAs–Fe(III)–smectite complexes associated with (a) malic acid, oxalic acid, and citric acid, and (b) EDTA, nitrilotriacetic acid, and no acid adding.

3.4. Effect of LMWOAs on redox potential of Fe(III)–smectite

The catalytic transformation of PAHs is critically related to the Lewis-acid sites (electron-accepting sites) derived from transition-metal ions (such as Fe(III)) on clay minerals (Jia et al., 2014). PAH molecules, which have highly delocalized π-electrons, may act as strong electron-donors when interacting with electron-deficient species, such as exchangeable Fe(III) (Zhu et al., 2004). The strong "cation-π" interaction, established between phenanthrene and Fe(III) at clay surfaces can facilitate electron transfer from an electron donor to an electron acceptor (Goss and Schwarzenbach, 2001). This intermolecular energy or charge transfer plays an important role in the stability and transformation of PAHs on clay surfaces that undergo irradiation (Si et al., 2004; Jia et al., 2015). Therefore, the transformation rate of phenanthrene is highly dependent on the electron-deficiency of Fe(III) on smectite surfaces. However, the presence of organic anions will lead to a decrease in the redox potential of Fe(III)–smectite clay due to their chelating effects. As shown in Fig. 3, the resulting chemical potentials are 0.2554, 0.2822, 0.4048, 0.4325, and 0.4432 V for LMWOAs–Fe(III)–smectite complexes associated with nitrilotriacetic acid, EDTA, citrate, malate, and oxalate, respectively. The phenanthrene photodegradation rate is linearly correlated with the redox potential of LMWOAs–Fe(III)–smectite complexes (Fig. 3). The higher redox potentials of organic acid–Fe(III)–smectite complexes possess a greater ability to obtain electrons from organic molecules, which results in a faster transformation rate on clay surfaces. In addition, malic and oxalic acid have a smaller acid dissociation constant (p*K*a value 3.46 and 3.34) and provide fewer anions for adsorption on the Fe(III)–smectite relative to EDTA and nitrilotriacetic acid (p*K*a values 2.0 and 1.9). Therefore, these acids may have a smaller effect on the redox potential, and the photodegradation rate of phenanthrene is linearly correlated with the p*K*a values of organic acids, as shown in Fig. 3. These observations imply that organic acids have limited effects on the redox potential of Fe(III)–smectite and, consequently, tend to favor the photodegradation of phenanthrene.

3.5. Effect of LMWOAs on interaction between phenanthrene and clay surfaces

As stated above, the interaction between cations and PAHs on smectite surfaces appears to be an important factor that influences electron and energy transfer, which could impact their photodegradation reactions (Miller and Zepp, 1979). However, the interactions between PAHs and Fe(III) are thought to be restrained by coexisting organic acids because they preferentially occupy adsorptive sites (such as Fe(III)) on mineral surfaces, thereby enhancing the desorption of organic pollutants in soil (White et al., 2003). To verify this hypothesis, a mild solvent (i.e., n-butanol) extraction experiment was conducted to explore the availability of phenanthrene on LMWOAs–Fe(III)–smectite (Ling et al., 2009). As shown in SI Fig. S2, the extractable amounts of phenanthrene in all LMWOAs–Fe(III)–smectite complexes are higher than in the Fe(III)–smectite sample. This indicates that the presence of organic acids promoted phenanthrene desorption (or availability) from the substrates, which corresponds with previously reported findings (Ling et al., 2009). Moreover, the availability of phenanthrene was enhanced in the presence of nitrilotriacetic acid and EDTA relative to in the presence of citrate, oxalate, and malate. As reported previously, the LMWOAs functioning as ligands can readily bind to metal cations (such as Fe(III)), and thus the organic contaminants complexing the clay mineral through the “bridge” of metal cations are easily broken by the addition of LMWOA (Lu et al., 2007). Therefore, the presence of organic acids would presumably result in the displacement of PAH molecules from the inner-sphere coordination sites of cations. As the molecular weight of organic acids increases, the Fe(III) on smectite surfaces becomes increasingly covered with organic acids, which leads to an increase in phenanthrene detachment from the surface. This increasing phenanthrene detachment is mirrored in the monotonically decreasing values of the potential bonding energy of the phenanthrene-cation and the weakened interaction between PAHs and exchangeable cations, which could inhibit the PAHs degradation rate under visible-light (Jia et al., 2014). Therefore, the degradation of phenanthrene on Fe(III)–clay associated with citric acid, EDTA, or nitrilotriacetic acids is less efficient than that of Fe(III)–smectites.

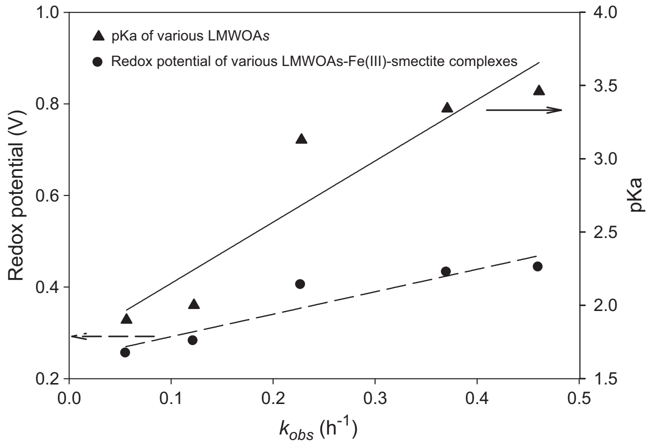

Fig. 3. Relationship between the pseudo-first-order rate constant for phenanthrene degradation and redox potential value of LMWOAs–Fe(III)–smectite complexes.

3.6. Mechanism discussion

An increase in the photodegradation rate in the presence of certain types of organic acids, such as malic and oxalic acids, can be attributed to the fact that photocatalyzed reactions involve intermediate species, such as $C_2O_4^{2-}$ radicals. These radicals can be produced by the reaction of organic acids–Fe(III) complexes under irradiation, which involves the reduction of Fe(III) to Fe(II) (Eq. (3)) (Zuo and Hoigne, 1992, 1994). Then, a strong reducing agent ($CO_2^{\cdot -}$) can be produced from $C_2O_4^{2-}$ radicals (Eq. (4)) (Xu et al., 2014). The formed $CO_2^{\cdot -}$ is ready to react with O_2, producing superoxides and hydroperoxyl radicals ($O_2^{\cdot -}$/$^{\cdot}OOH$) as key intermediates throughout the reactions (Eqs. (5) and (6)) (Faust and Zepp, 1993). Previous studies have shown that the photolysis of Fe(III)–organic acid complexes is a major pathway for the formation of H_2O_2, which can be obtained by the dismutation of $O_2^{\cdot -}$/$^{\cdot}OOH$, as shown in Eq. (8) (Zuo and Hoigne, 1992, 1994). After H_2O_2 formation, the system containing Fe(II) and H_2O_2 can perform a Fenton-like reaction to generate hydroxyl radicals ($^{\cdot}OH$) (Eq. (9)) (Zepp et al., 1992). Hydroxyl radicals are highly oxidative and can enhance the degradation of phenanthrene adsorbed on clay surfaces (Eq. (10)).

$$\text{Smectite}-\text{Fe(III)}-(C_2O_4)_n \xrightarrow{h\nu} \text{Smectite}-\text{Fe(II)}-(C_2O_4)_{n-1} + (C_2O_4)^{\cdot -} \quad (3)$$

$$(C_2O_4)^{\cdot -} \rightarrow CO_2 + CO_2^{\cdot -} \quad (4)$$

$$CO_2^{\cdot -} + O_2 \rightarrow CO_2 + O_2^{\cdot -} \quad (5)$$

$$O_2^{\cdot -} + H_2O \rightarrow HO_2^{\cdot} + OH^- \quad (6)$$

$$CO_2^{\cdot -} + \text{Smectite}-\text{Fe(III)}-(C_2O_4)_n \rightarrow \text{Smectite}-\text{Fe(II)}-(C_2O_4)_n + CO_2 \quad (7)$$

$$HO_2^{\cdot} + \text{Smectite}-\text{Fe(II)} + H^+ \rightarrow H_2O_2 + \text{Smectite}-\text{Fe(III)} \quad (8)$$

$$\text{Smectite}-\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)}-\text{smectite} + {}^{\cdot}OH + OH^- \quad (9)$$

$$\text{PAHs} + {}^{\cdot}OH \ (\text{or } {}^{\cdot}O_2^-) \rightarrow \text{degradation products} \quad (10)$$

However, photo-induced decarboxylation cannot occur on Fe(III)–smectite surfaces associated with EDTA and nitrilotriacetic acid. This results in a much lower efficiency in the generation of both Fe(II) and $CO_2^{\cdot -}$ radicals, which is unfavorable for phenanthrene photodegradation on smectite surfaces.

4. Conclusions

LMWOAs always coexist with clay minerals and have strong chelating ability with multivalent cations (such as Fe(III)) on clay surfaces. The potential effects of LMWOAs on the removal of phenanthrene catalyzed by Fe(III)–smectite under visible light have been thoroughly researched in this study and have provided fundamental information on the acceleration and quenching effects of organic acids on the photodegradation of phenanthrene. EPR results supported that Fe(III)–smectite complexes with malic and oxalic acids were very photosensitive and easily able to generate $CO_2^{\cdot -}$ radicals upon irradiation. The formed $CO_2^{\cdot -}$ can further generate reactive oxidation radicals such as $^{\cdot}OH$ or $^{\cdot}O_2^-$, thus enhancing the transformation of phenanthrene. The strong chelating ability of EDTA and nitrilotriacetic acid with Fe(III) induces a much lower efficiency in both the Fe(II) formation and the phenanthrene photodegradation. This can be attributed to the fact that the presence of EDTA and nitrilotriacetic acid influences the redox potential of Fe(III)–smectite clay and "cation-π" interactions between organic compounds and clay surfaces, thus leading to modulation of PAHs photostability. Therefore, the different photoreaction pathways and natures of radicals derived from various LMWOAs result in their different roles in phenanthrene photodegradation. The obtained results are helpful for understanding the mechanisms governing the photolysis of phenanthrene by LMWOAs and provide valuable insights regarding the photochemical processes of organic contaminants on soil surfaces.

Acknowledgements

Financial support by the National Natural Science Foundation of China (Grant No. 41301543), the Young Creative Sci-Tech Talents Cultivation Project of Xinjiang Uyghur Autonomous Region (2013721046), the "Western Light Western Doctor" Program of Chinese Academy of Sciences (XBBS201112), the CAS Cross-Cooperation Program for Creative Research Teams and the CAS/SAFEA International Partnership Program for Creative Research Teams is gratefully acknowledged.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.076.

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