Journal of Hazardous Materials 287 (2015) 16–23

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Exchangeable cations-mediated photodegradation of polycyclic aromatic hydrocarbons (PAHs) on smectite surface under visible light

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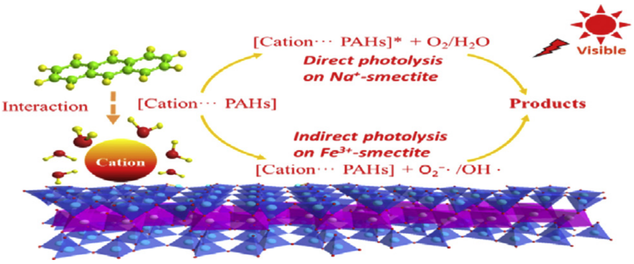
HIGHLIGHTS

- Photolysis rate are strongly dependent on the type of cations on clay surface.
- The strength of "cation–π" interactions governs the photodegradation rate of PAHs.
- Several exchangeable cations could cause a shift in the absorption spectrum of PAHs.
- Exchangeable cations influence the type and amount of reactive intermediates.

GRAPHICAL ABSTRACT

Roles of exchangeable cations in PAHs photodegradation on clay surafces under visible light.



ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form 17 August 2014
Accepted 14 January 2015
Available online 15 January 2015

Keywords:
Polycyclic aromatic hydrocarbons (PAHs)
Clay minerals
Cation–π interaction
Exchangeable cation
Photolysis

ABSTRACT

Clay minerals saturated with different exchangeable cations are expected to play various roles in photodegradation of polycyclic aromatic hydrocarbons (PAHs) via direct and/or indirect pathways on clay surfaces. In the present study, anthracene and phenanthrene were selected as molecule probes to investigate the roles of exchangeable cations on their photodegradation under visible light irradiation. For five types of cation-modified smectite clays, the photodegradation rate of anthracene and phenanthrene follows the order: $Fe^{3+} > Al^{3+} > Cu^{2+} \gg Ca^{2+} > K^+ > Na^+$, which is consistent with the binding energy of cation–π interactions between PAHs and exchangeable cations. The result suggests that PAHs photolysis rate depends on cation–π interactions on clay surfaces. Meanwhile, the deposition of anthracene at the Na^+-smectite and K^+-smectite surface favors solar light absorption, resulting in enhanced direct photodecomposition of PAHs. On the other hand, smectite clays saturated with Fe^{3+}, Al^{3+}, and Cu^{2+} are highly photoreactive and can act as potential catalysts giving rise to oxidative radicals such as $O_2^{-\bullet}$, which initiate the transformation of PAHs. The present work provides valuable insights into understanding the transformation and fate of PAHs in the natural soil environment and sheds light on the development of technologies for contaminated land remediation.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), mainly produced via fossil fuel deposit and incomplete combustion, have been recognized as one class of primary contaminants in naturally hydrophobic phases such as soil and sediment [1]. Due to their potential damaging to human health and ecosystem,

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http://dx.doi.org/10.1016/j.jhazmat.2015.01.040
0304-3894/

transformation and mobility of PAHs in soil environment have attracted great attention [2–4]. PAHs-like organic molecules may undergo various natural processes such as biodegradation, chemical transformation, and photolysis reactions [5,6]. Among those processes, the abiotic photodegradation associated with solar-light irradiation is potentially an important process for their fate and may provide an alternative way to biodegradation at the upper surface soil layer [5–8]. The photolysis process highly depends on the interactions between pollutants and chemically active soil components, such as humic substances, clay minerals, and metal oxides [6,9–12]. Recently, more attention has been paid to clay mediated photodegradation of organic pollutants in natural environments [13,14]. It is confirmed that the photolysis of organic compounds adsorbed on clay minerals is more efficient than that occurring on other minerals such as aluminum hydroxide, iron oxide (ferrihydrite), and manganese dioxide [15,16].

Smectite is a representative clay mineral, which generally consists of a center octahedral Al–O sheet sandwiched between two tetrahedral Si-O sheets. Due to isomorphic substitution in the tetrahedral Si and/or octahedral Al layers, negative charges are embedded in the individual layers in a fixed and isolated distribution. The negative charge on the clay surface is commonly neutralized by exchangeable inorganic cations that reside at or near the negative-charged sites. Binding of various cations on clay surface is expected to modify the structure and physical–chemical properties of the clay surface, and thereby influences the interaction between organic compounds and clay surface [17–20]. PAHs molecules, which have highly delocalized π-electrons, may act as strong electron-donors when interacting with electron–deficient species such as exchangeable cations [21–24]. This "cation–π" interaction has been demonstrated as an important factor regulating PAHs adsorption and mobility on mineral surfaces [17,19]. Various exchangeable cations with different electro-negative properties may possess a distinctly different capacities to accept an electron [17]. Compared to common cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+), the presence of transition metal ions (Fe^{3+} and Cu^{2+}) on clay surface facilitates the sorption of PAHs due to their strong cation–π interactions [24,25].

As reported previously, the photo-reactivity of organic contaminants is greatly altered when the chemicals are sorbed on clay surfaces [13,26]. The formation of cation–π complexes with stronger interaction is characterized by easier charge transfer, which may induce faster direct photolysis of organic pollutants [27,28]. On the other hand, the presence of various cations on clay surfaces could also influence the type and amount of formed reactive intermediates, which may initiate the photodegradation of pollutants via indirect photolysis. Therefore, the type of sorbed cations might influence both the direct and indirect photodegradation of pollutants on clay surfaces. Understanding photochemical reaction at the surface of homogeneous and well characterized clays may present a first step toward mechanistic studies on natural soil. However, how the exchangeable cations on clay minerals affect the photodegradation of PAHs has been hitherto barely studied.

It is hypothesized that modulating the cation type on clay mineral surfaces could manipulate the photolysis behavior of sorbed PAHs. To test the hypothesis, photodegradation of PAHs (such as phenanthrene and anthracene) on smectite clays saturated with various exchangeable cations was explored in the present work. The purposes of the work are to (1) probe the role of interactions between PAHs and cation-smectite in PAHs transformation; (2) evaluate the influence of surface properties of clay minerals on PAHs photodegradation; and (3) further gain insight into the mechanism responsible for PAHs photodegradation on clay surfaces. Such knowledge of the role of exchangeable cations in PAHs photodegradation and the molecular-scale forces influencing photolysis will give valuable implications on the environmental fate of PAHs.

2. Experimental

2.1. Chemicals and materials

Detailed information on the chemicals and materials used in this study is supplied in the Supporting information (SI).

2.2. Preparation of reaction mixtures

The preparation of Fe(III)-saturated clay minerals was carried out by following the method of Arroyo et al. [29]. Briefly, the clay suspension was first titrated to pH 6.8 with 0.5 M sodium acetate buffer (pH 5) to remove carbonate impurities. Clay-sized particles (<2 μm) were obtained by centrifugation of the clay suspension for 6 min at 600 rpm, and then treated with 0.1 M $FeCl_3$ solutions for 4 times. The Fe^{3+}-saturated clay was washed using Milli-Q water until free of chloride as indicated by a negative test with $AgNO_3$. To prepare Fe^{3+}-clay with different Fe^{3+} speciation forms, pH of involved suspension was adjusted to a desired value using 1.0 M HCl or NaOH, and then freeze-dried. Smectite clays saturated by other types of cations (e.g., K^+, Na^+, Ca^{2+}, Cu^{2+}, and Al^{3+}) were achieved by following the same procedures described above except substituting Fe^{3+} with K^+, Na^+, Ca^{2+}, Cu^{2+} and Al^{3+}. The reaction mixtures (PAHs contaminated clays) were prepared by mixing PAHs dissolved in 1 mL methanol with 1 g cation modified clays (0.1 mg anthracene/g clay), where the use of methanol allowed evaporating under ambient conditions.

2.3. Photochemical reaction

The reaction was conducted at room temperature (25 °C) maintained inside a container consisting of two pieces of Quartz plates (9 cm × 9 cm × 2 mm), which were plated with a clay layer of controlled thickness using the method developed by Balmer et al. [30]. Briefly, contaminated clay was placed onto the center of the quartz glass plate. The area filled with clay was controlled by a 2 mm thin Teflon gasket circular with an inner edge of 4 cm in diameter, resulting in a total surface area of 12.64 cm^2 to which clay was applied. The thickness was determined from the mass and the bulk density of clay (e.g., 0.88 g/cm^3 for smectite). After that, the second quartz plate was placed on the Teflon gasket, and they were held together with binder clips. As-obtained clay plates were placed for irradiation under visible light of 0.250 W/cm^2 generated from a xenon lamp equipped with a filter of $\lambda > 380$ nm or 420 nm. The distance between the lamp and samples was 100 mm. At pre-selected intervals, the samples were sacrificed and transferred into 50 mL Teflon centrifuge tubes. Except for the experiments of humidity effect study, all the experiments were conducted under dry conditions. For comparison, parallel experiments were conducted in dark as control. To explore the formation of oxidative radical during the photochemical reaction, experiments were conducted in the presence of coumarin and benzoquinone, which were used as $^{\bullet}OH$ radical and $O_2^{-\bullet}$ scavengers, respectively. The concentration of coumarin and benzoquinone were 1.22 and 1.65 mg/g of mineral support. At pre-selected intervals, the samples were sacrificed and transferred into 50 mL Teflon centrifuge tubes. The residual PAHs and its products were extracted and analyzed immediately.

Approximately 10 mL of extraction solution (mixture of 5 mL acetone and 5 mL dichloromethane) was added to each centrifuge tube containing sacrificed clay samples. The suspensions were extracted in an ultrasonic bath for half an hour, and this procedure was repeated twice to assure that the anthracene and its

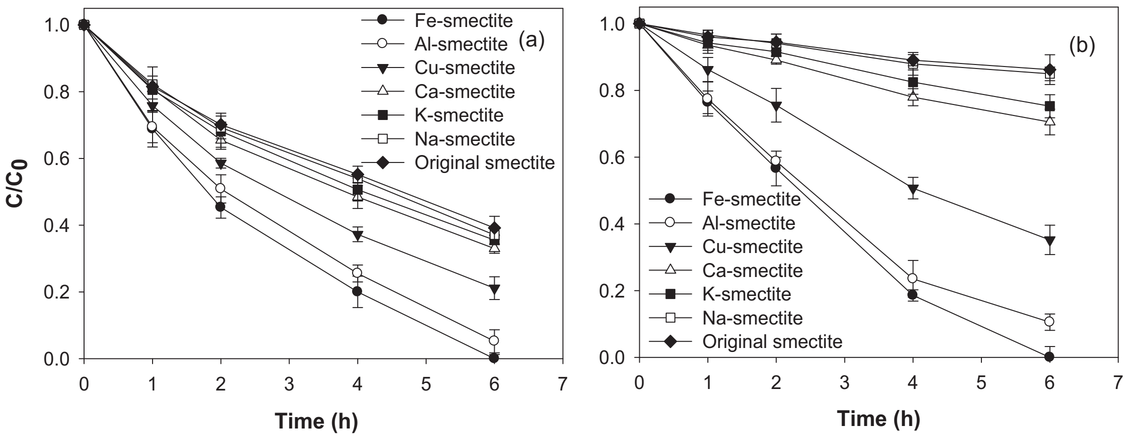

Fig. 1. Evolution of (1) anthracene and (2) phenanthrene as a function of reaction time at smectites modified by various cations.

products were completely extracted. To conduct the recovery tests, samples associated with various cation-modified smectites were extracted immediately after methanol was evaporated, and found that the mean recoveries ranged from 95 to 100%, indicating that the extraction procedure proceeded quantitatively (as shown in Supporting information Table 1). The supernatants were collected together, and 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.

2.4. Analysis of PAHs and transformation products

PAHs with photolysis were 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 employed as mobile effluent. The flow rate was 1.0 mL/min, and the ultraviolet detector was set at 254 nm. The anthracene and its intermediate products were identified using a Agilent 7890A-5975C gas chromatograph incorporated with a mass spectrometer operated on a full scan mode (30–500 amu), where a HP-5MS capillary column (length = 30 m; internal diameter = 250 μm; film thickness = 0.25 μm) was employed. Helium was used as carrier gas at a flow rate of 1.2 mL/min with splitless injection at 230 °C. The oven temperature was programmed from 80 °C to 200 °C (20 °C/min, 2 min hold), and then to 260 °C (20 °C/min, 2 min hold).

Content of Fe(II) in the reacted system was extracted with water and measured using ferrozine. Briefly, reacted iron–clay suspension was mixed using Vortex for 30 s. Then 0.5 mL of 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. Concentration of ferrozine-complexed Fe(II) was measured by UV–vis spectrophotometer at 562 nm.

2.5. Characterization

To evaluate the light response of cation-modified smectite clays and anthracene adsorbed on clays, the UV–vis diffuse reflectance spectra were measured on a spectrometer (Hitachi Co., U-3500) equipped with an internal diffuse reflectance attachment. A pellet of $MgSO_4$ was used as the reference. X-ray diffraction (XRD) patterns of air-dried powders of the cation-modified clays and anthracene-clay complexes were recorded to determine d(001) basal spacings, using an X-ray diffractometer (D8-ADVANCE) equipped with a crystal graphite monochromater, operating at 45 kV and 100 mA. XRD signals were collected with diffraction angles ranging from 2 to 10° at a scanning rate of 0.02°/min.

3. Results and discussion

3.1. Effect of cation type on photolysis

Smectite clays saturated with different types of cations were prepared for PAHs photolysis experiments. The evolution of anthracene and phenanthrene as a function of reaction time is presented in Fig. 1. After 6 h, approximately 100%, 95%, 79%, 67%, 64%, and 63% of initially added anthracene are transformed by photolysis on Fe^{3+}, Al^{3+}, Cu^{2+}, Ca^{2+}, K^+, and Na^+ saturated smectite clays, respectively. As comparison, approximately 100%, 90%, 65%, 29%, 24% and 18% of initially added phenanthrene are transformed in the same reaction time frame. On the other hand, the negative site is mainly saturated by Na^+ on original smectite clay (without cation-exchanging), and thus the photodegradation of anthracene and phenanthrene exhibits the same trend as Na^+-smectite. In addition, control experiments were conducted in the dark to evaluate possible effects of chemical and microbiological degradation during the irradiation experiment. Insignificant disappearance of PAHs was observed in dark control experiments during 6 h of reaction time (see SI Table 1). These observations suggest that photodegradation plays a crucial role in the degradation of anthracene and phenanthrene. Data fitting suggests that PAHs degradation follows a pseudo-first-order model in above stated reaction systems, and the rate constants are listed in Table 1. The relevant photodegradation rate of anthracene and phenanthrene follows the same order Fe^{3+}-smectite > Al^{3+}-smectite > Cu^{2+}-smectite > Ca^{2+}-smectite > K^+-smectite > Na^+-smectite. This observation suggests that PAHs photodegradation on clay mineral surfaces strongly depends on the type of exchangeable cations. Compared to the

Table 1
Transformation rate constant (k_{obs}, h^{-1}) of anthracene on smectite saturated with various cations.

Cation type Relative humidity		Fe^{3+} ~5%	Al^{3+} ~5%	Cu^{2+} ~5%	Ca^{2+} ~5%	K^+ ~5%	Na^+ ~5%	Al^{3+} 62%
Scavenger type	None	0.405 ± 0.044	0.339 ± 0.023	0.255 ± 0.023	0.181 ± 0.004	0.168 ± 0.004	0.154 ± 0.011	0.456 ± 0.051
	Coumarin	0.389 ± 0.031	0.363 ± 0.021	0.249 ± 0.008	0.152 ± 0.013	0.123 ± 0.008	0.128 ± 0.001	0.392 ± 0.060
	Benzoquinone	0.043 ± 0.005	0.037 ± 0.005	0.032 ± 0.001	0.050 ± 0.003	0.064 ± 0.005	0.051 ± 0.002	0.144 ± 0.022

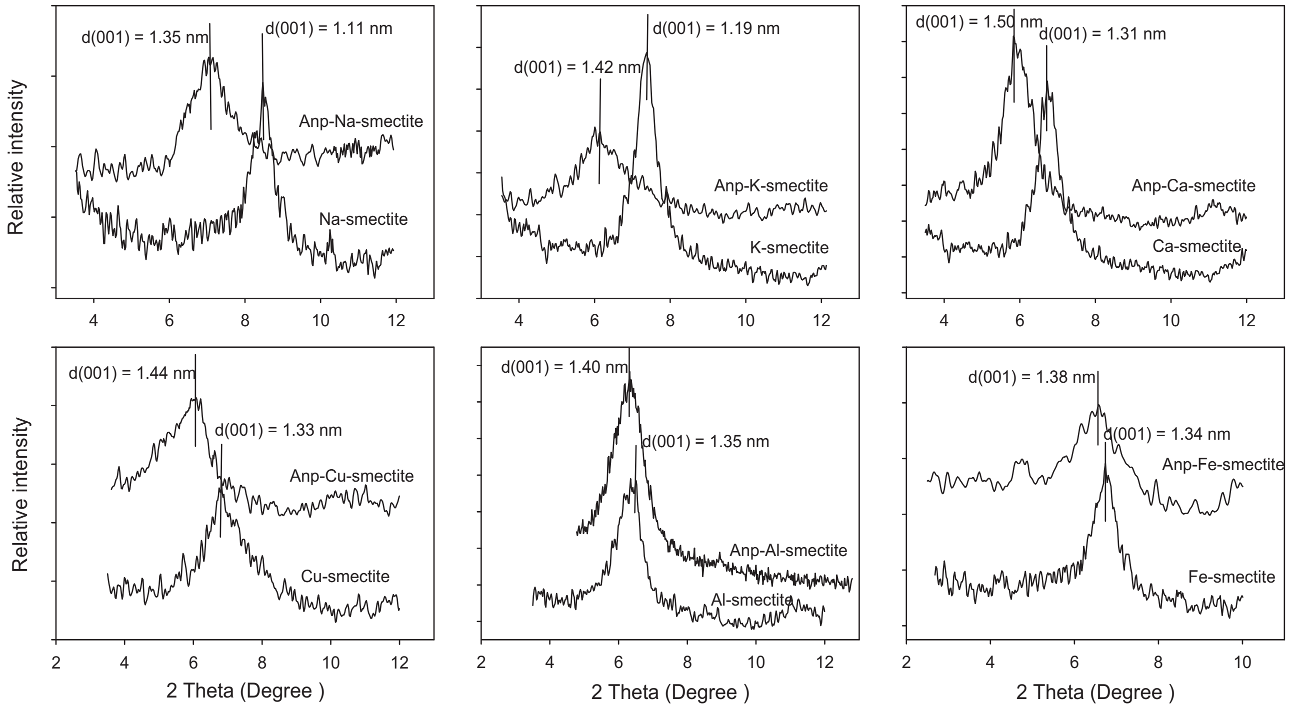

Fig. 2. X-ray diffraction patterns of various cations-modified smectite and their complexes with anthracene.

Na^+-saturated clay, the presence of cations such as Fe^{3+} increases photodegradation of anthracene and phenanthrene by about 3 and 10 times, respectively.

The interaction strength of the cation–π complex correlates well with the processes of PAHs adsorption and transformation [24,28,31]. As reported previously, PAHs molecules have planar structures and tend to be aligned parallel with clay surfaces when trapped in restricted geometries of clay interlayers [24]. Cation–π distance may be the most straightforward structure parameters to determine the strength of interaction between cation and PAHs molecule [28]. The cation–π distance can be obtained by the difference of clay interlayer distance between cation-saturated smectite and cation-smectite combined with PAHs. The basal spacing of clay minerals is calculated using the first-order reflection (001) by the Bragg equation:

$$d(001) = 1.54178/(2\sin(2\theta/2 \qquad (001)$$

where $d(001)$ refers to the basal spacing of smectite clays, and θ is the incident angle. As shown in Fig. 2, the interlayer spacings are 1.11, 1.19, 1.31, 1.33, 1.35, and 1.34 for air-dried Na^+, K^+, Ca^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}-smectite, respectively. After combined with anthracene, the interlayer spacings increase to 1.35, 1.42, 1.50, 1.44, 1.40, and 1.39 Å. Meanwhile, the diffraction peaks generally become decreased and broadened with anthracene sorption. The increase in the basal spacing and decrease in the peak intensity suggest the intercalation of anthracene in clay interlayers forming a much more disordered crystalline structure. Based on the XRD results, the cation–π distance is calculated as 0.24, 0.23, 0.21, 0.11, 0.05, and 0.04 for Na^+, K^+, Ca^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}-smectite, respectively. It is noted that the cation–π distance exhibits reverse relationship with photodegradation rate of anthracene on those cation saturated smectite clays. This indicates that the strength of interactions between cation and PAHs molecules directly affect the kinetics of photodegradation on clay mineral surfaces. Generally, the efficient energy or charge transfer can occur between adsorbed PAHs molecules and exchangeable cations [13]. The high charge valences of saturated cations, such as Al^{3+} and Fe^{3+} with great polarizability and electron-deficiency, provide strong bonding affinities toward aromatic π-donor, facilitating the electron transfer from electron-donor to electron-acceptor. This intermolecular energy transfer plays an important role in the stability and transformation of PAHs on clay surfaces under irradiation [13,32]. Stronger cation–π bonding could induce lower stabilization and higher transformation degree [33]. Therefore, the degradation rates of PAHs with Fe^{3+}, Al^{3+}, and Cu^{2+}-clay are more efficient compared with Na^+, K^+, and Ca^{2+}-smectites.

3.2. *Effect of cation hydration*

The hydration status of cations on smectite surfaces appears to be an important factor influencing the interaction between cation and PAHs, which might impact their photodegradation reactions [24]. To examine whether cation hydration influences PAHs photodegradation, smectite clay was prepared by saturating with exchangeable cations (i.e., Fe^{3+}, K^+, and Na^+) with various strengths

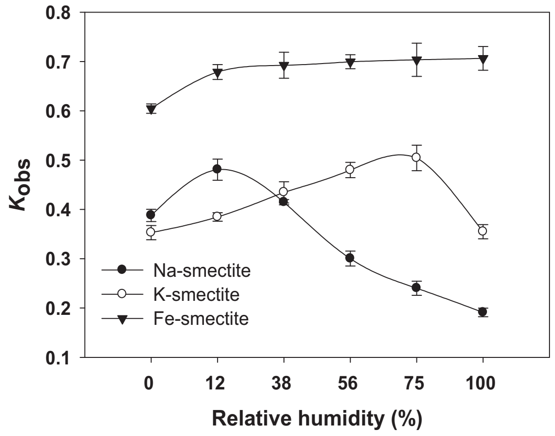

Fig. 3. Evolution of the pseudo-first-order rate constant for anthracene photodegradation as a function of relative humidity.

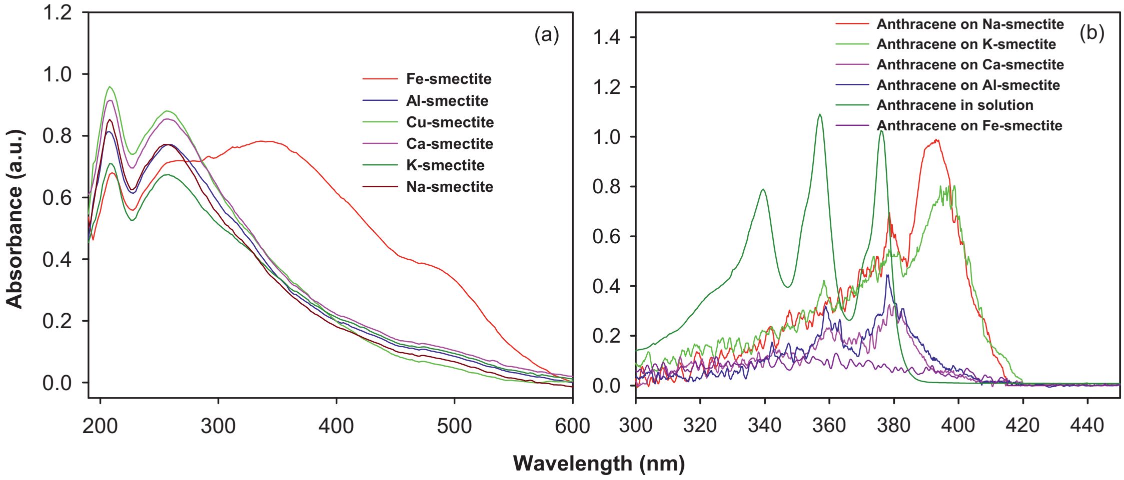

Fig. 4. Absorption spectra of (1) smectites saturated with various cations, and (2) anthracene on cation-smectites and in solution.

of hydration. The reactivity of those clay samples under various RHs was evaluated by following the process of anthracene photodegradation. Kinetic studies find that anthracene degradation observes a pseudo-first-order reaction model in those reaction systems. The evolution of pseudo-first-order rate constants (K_{obs}) as a function of RH is presented in Fig. 3. The reaction rate constant in Fe^{3+}-semctite system increases from 0.60 to 0.69/h when the RH increases from ~0 to 38%. After the RH is beyond 56%, the reaction rate constant is little changed. On the other hand, a critic RH is observed with Na^{+}-smectite (12%) and K^{+}-smectite (75%). Before reaching the critic RH, the removal of anthracene is accelerated; while after that, the photodegradation rate is suppressed. The increase in photodegradation rate with the presence of a certain amount of water can be attributed to the fact that photocatalyzed reaction involves intermediate species such as hydroxyl radicals ($^{\bullet}$OH); they can be produced by reaction of water molecular (H_2O) on clay surface under irradiation [34,35]. Hydroxyl radical is a highly oxidative species and can enhance the degradation of anthracene adsorbed on clay surfaces. As reported previously, the removal of water from smectite retarded the photodegradation of adsorbed pollutants [36]. However, the adsorption of organic compounds is thought to be restrained by ambient moisture because water molecules preferentially occupy the adsorptive sites on mineral surfaces. Under moist ambient, water molecules hydrate cations near the surface, and a compact water layer is formed in this interfacial region, thus the system would presumably cause displacement of PAHs molecules from the inner-sphere coordination sites of cations. With the increase in RH, the smectite surface becomes increasingly covered with water molecules leading to an increase in detachment of anthracene from the surface. The increasing anthracene detachment is mirrored in the monotonically decreasing values of potential bonding energy of anthracene-cation and weakening the interaction between PAHs and exchangeable cation, which might inhibit the PAHs degradation rate under visible-light.

It is noted that various exchangeable cations exhibit different critic RHs for PAHs degradation, which can be attributed to the different hydration ability of cation on clay surfaces. The hydration energy for K^{+} is −397 kJ/mol, less than that of Fe^{3+} and much less than that of Na^{+} (−1580 kJ/mol) [20]. The comparatively low hydration enthalpy of K^{+} results in a smaller hydration sphere, i.e., usually only one to two layers of water around K^{+} on smectite surface under the RH of ~100% [20]. This facilitates the interactions of aromatic rings of PAHs with K^{+}, and further makes the cation–π interaction stronger [24]. When smectites are saturated with strongly hydrated cations (e.g., Na^{+}), more water molecules are surrounding the cation, leading to ~3 layers of water surrounding cations at RH of 100% [37,38]. The strong hydration of Na^{+} inhibits direct interactions between PAHs and the exchangeable cation and weaks cation–π bonding on clay surface [24,25,39–41]. Therefore, favorable hydration of Na^{+} at relatively low RH induces the readily detachment of anthracene, thus exhibits low critic RH compared to K^{+} saturated smectite. Furthermore, the decrease in the degree of potential energy of anthracene interaction with the cation upon the surface hydration also depends on the valence and polarizability of cation on clay surface. Compared with Na^{+}, therefore, the hydration of Fe^{3+} has less impact on photodegradation rate of anthracene. This is understandable when considering that trivalent cation (such as Fe^{3+}) has stronger electrostatic interactions with PAHs [42,43].

3.3. *Potential mechanisms of anthracene photodegradation on smectite surface*

It seems that the photodegradation of PAHs is correlated to the type of exchangeable cations, but it is still unclear about the photodegradation mechanisms, via direct and/or indirect pathways [44–46]. Direct photolysis occurs when a contaminant (such as PAHs) directly absorbs light energy and undergoes a chemical reaction [47]. Photolysis rate is greatly influenced by the extent of spectral overlap between its absorption spectrum and the

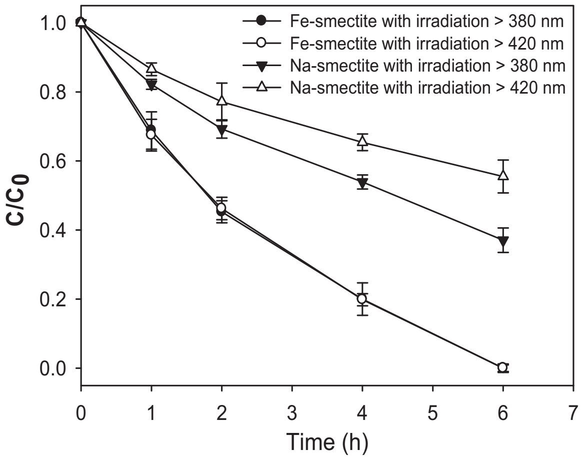

Fig. 5. Photodegradation of anthracene on Na^{+} and Fe^{3+}-smectite under irradiation at $\lambda > 380$ nm and $\lambda > 420$.

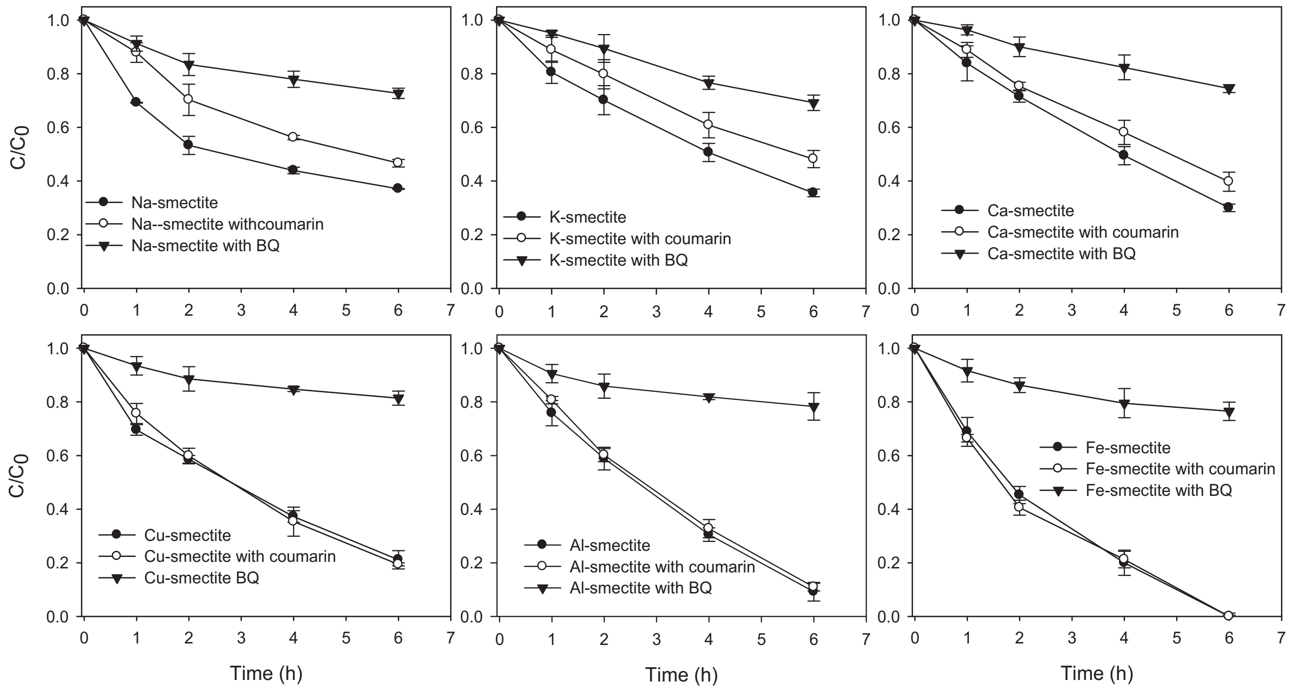

Fig. 6. Evolution of anthracene as a function of reaction time on cation-smectites in the presence of coumarin (1.22 mg/g) and benzoquinone (BQ, 1.65 mg/g).

emission spectrum of the irradiated light [36]. The type of exchangeable cations could influence the “cation–π” interaction and might cause a shift in the absorption spectrum of PAHs [13]. Therefore, PAHs can exhibit different photolysis behaviors when adsorbs on clay surface saturated by different types of cations [5]. On the other hand, clay particles can absorb light with wavelengths even higher than 360 nm and act as a photocatalyst to induce the electron transfer from aluminosilicates to adsorbed molecular oxygen or/and water [47]. This process causes the formation of active oxygen species, such as singlet oxygen ($^1O_2$), superoxide anion radical ($O_2^{-\bullet}$), and hydroxyl radical ($^\bullet OH$), which could initiate the indirect photodegradation process of PAHs [36]. The present work implies that exchangeable cations might modify their photocatalytic activity or/and the formation of reactive intermediates, thus affecting the transformation rate of substances such as PAHs.

3.3.1. Direct photolysis

Diffuse reflectance spectra of the cation-modified smectites are shown in Fig. 4a. Compared with other types of cation-modified smectites, Fe^{3+}-smectite exhibits notable absorption under visible-light (as shown in Fig. 4a). The enhanced visible-light absorption may initiate the photolysis reaction. Therefore, Fe^{3+} shows greater PAHs degradation rate associated to smectite surfaces than other cations. To have a better insight into the spectroscopic features of anthracene on clay surface, the reflection spectra of anthracene contaminated cation-modified clay samples were collected (data not shown). By subtracting the reflection part due to cation-modified smectite, the reflection spectra of anthracene on various cation-modified clays are obtained (Fig. 4b). Different spectral shifts are observed in the reflectance spectrum when anthracene is adsorbed onto various cation-modified clays. Relative to the spectrum of anthracene in methanol solution, the absorption band, appearing at ∼390 nm, of anthracene on Na^+-smectite and K^+-smectitie is red shifted. The red shift implies that smectite clay surfaces saturated by Na^+ and K^+ provide a different polarity environment compared to that saturated by water solvent. The spectral overlap between the reflectance spectrum of anthracene in solution and the visible-light emission spectrum of a xenon lamp ($\lambda > 380$ nm) is very small. However, adsorption of anthracene onto Na^+-saturated clay surface causes extended spectral overlap. This indicates that the deposition of anthracene at the Na^+-smectite surface is in favor of more efficient absorption of solar light ($\lambda > 380$ nm), which might result in the enhanced photodecomposition of PAHs [32]. This can be reflected by the photodegradation of anthracene on Na^+-smectite under different irradiation conditions. Compared to irradiation at $\lambda > 380$ nm, the photodegradation rate of anthracene is decreased when it is irradiated at $\lambda > 420$ nm (as shown in Fig. 5). On the contrary, irradiation wavelength rarely influences the degradation rate of anthracene on the Fe^{3+}-smectite (as shown in Fig. 5). Therefore, direct photolysis might be one of the possible mechanisms for the anthracene photodegradation on Na^+-smectite and K^+-smectite.

3.3.2. Indirect photolysis

As shown in Fig. 4, a spectral shift is not observed in the reflectance spectrum when anthracene is adsorbed onto smectite clays saturated with Cu^{2+}, Al^{3+}, and Fe^{3+}, and their spectral

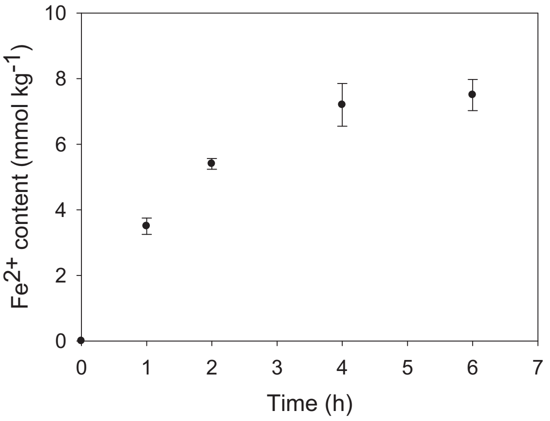

Fig. 7. The evolution of Fe^{2+} as a function of reaction time in the reaction system of anthracene transformation on Fe(III)-smectite.

overlap with the emission spectrum of the visible light is negligible. Meanwhile, an insignificant difference of transformation rate of anthrecene under irradiation >380 and >420 nm is observed (as shown in Fig. 5). Consequently, direct photolysis is unlikely to be the mechanism for the photodegradation of anthracene in those reaction systems. The observed photolysis rates of anthracene on those clay surfaces, however, can proceed via photosensitized and/or photocatalysis processes involving reactive intermediates. The clay minerals readily absorb visible-light and induce a charge separation, and the unique properties of clay enhance the electron migration from the surface to the clay structural interior enabling a stable charge separation. The separated electrons can be transferred to ground-state oxygen generating various reactive oxygen species such as $^1O_2$, $^\bullet OH$, and superoxide radical anion ($O_2^{-\bullet}$) [15].

The possible formation of reactive oxidizing radicals on different cation-modified clays was explored using coumarin and benzoquinone as two main oxidative radaicals (i.e., $^\bullet OH$, and $O_2^{-\bullet}$) quenchers. When radical scavengers such as coumarin and benzoquinone are added into the clay-based reaction system, they will adsorb on the clay surface and compete with PAHs for radical-induced reactions. Therefore, the influence by the addition of radical scavengers gives indication of the production of specific radicals. For Fe^{3+}-smectite, the presence of benzoquinone dramatically slows down the loss of anthracene, but adding coumarin shows slight change for anthracene transformation (as shown in Fig. 6 and Table 1). Likewise, the reaction systems associated with Al^{3+}-smectite and Cu^{2+}-smectite are also unaffected by coumarin. Coumarin is known to quench $^\bullet OH$, and also to quench $^1O_2$ to some extent. The result suggests that $^\bullet OH$ and $^1O_2$ may play limited role in the indirect photolysis of anthracene on clay surface saturated with Fe^{3+}, Cu^{2+}, and Al^{3+}. On the other hand, $O_2^{-\bullet}$ is suggested as the main reactive intermediate species, which is formed through an induced electron transfer process that involves the excited clay and molecular oxygen [48,49]. Such oxidative radicals play an important role in the transformation of contaminants. In addition, the presence of transition metal species (such as Fe^{3+}) could enhance the photo-absorption and sensitize the photodegradation (as shown in Fig. 4), resulting in an important increase in the observed rate constant [50]. Meanwhile, Fe^{3+} can be efficiently converted to Fe^{2+} along with the degradation of anthracene (as shown in Fig. 7). The formation of Fe^{2+} correlates with the disappearance of anthracene, indicating that the PAHs degradation associates with the electron transfer between organic molecules and clay surfaces and/or sensitization effect by transition metal ions such as Fe^{3+} and Cu^{2+} [27,51].

In the case of smectite clays saturated by Ca^{2+}, Na^+, and K^+, active oxygen such as $O_2^{-\bullet}$ still plays an important role on the photolysis (as shown in Fig. 6). However, $^\bullet OH$ species cannot be neglected. The presence of coumarin significantly slows down the photodegradation reaction, indicating that both $^\bullet OH$ and $^1O_2$ can be involved in the degradation of organic molecules [5]. The photo-irradiation of cation–PAHs complexes can generate excited states of PAHs, which can react with oxygen through energy and electron transfer processes and/or with H_2O generating reactive oxygen species (such as $^\bullet OH$ and $O_2^{-\bullet}$), thus inducing the photodegradation of PAHs [52,53]. Under high RH condition, however, the presence of coumarin in either Fe^{3+}-saturated smectite or Na^+-saturated smectite slows the reaction down to an even slower rate than that occurring in dry conditions, indicating that $^\bullet OH$ plays an important role under high RH conditions (as shown in Table 1). This is due to that the photogeneration of $^\bullet OH$ is partially derived from water on the clay surfaces [37]. Overall, indirect photolysis, i.e., reactions with the photogenerated active oxygen species, is likely to dominate the photodegradation of anthracene on these cation-modified smectite clays.

4. Conclusions

The effect of exchangeable cations on photodegradation of adsorbed PAHs on clay surface is systematically explored in this work. Saturating with various cations on clay surface is expected to influence the "cation–π" interaction between organic compounds and clay surface, thus (1) leading to modulation of PAHs photostability (such as on Al^{3+}- and Fe^{3+}-smectite surfaces); (2) causing a shift in the absorption spectrum of PAHs (such as on Na^+- and K^+-smectite surfaces); (3) enhancing the formation of reactive oxidation radicals due to the sensitization by transition cation species (such as on Cu^{2+} and Fe^{3+} on smectite surfaces). Although both indirect and direct photolysis processes of anthracene can be a potential transformation route on smectite associated with Na^+ and K^+, loss of anthracene occurs much more quickly on Fe^{3+}-smectite, Al^{3+}-smectite, and Cu^{2+}-smectite via indirect photolysis, which is more likely to occur via the reaction with reactive oxidizing radicals such as hydroxyl radicals. This work sheds light on the role of clays in the transformation of organic compounds through oxidation on the surface of clay particles in soil or even top sediments. The work also implies that clay photocatalysis could be a possible alternative/complementary technology for the destruction of organic pollutants in soil environment.

Acknowledgements

Financial support by the National Natural Science Foundation of China (grant no. 41301543 and 21173261), 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 "One Hundred Talents" program of Chinese Academy of Sciences (1029471301), the CAS "Cross-Cooperation Program" for Creative Research Teams, the CAS "Western Action Plan" (KGZD-EW-502), and the "Open Project" of State Key Laboratory of Pollution Control and Resource Reuse (PCRRF12020) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.01.040.

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