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RESEARCH ARTICLE

Transformation of anthracene on various cation-modified clay minerals

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Abstract In this study, anthracene was employed as a probe to explore the potential catalytic effect of clay minerals in soil environment. Clay minerals saturated with various exchangeable cations were tested. The rate of anthracene transformation follows the order: Fe–smectite >> Cu–smectite > Al–smectite ≈ Ca–smectite ≈ Mg–smectite ≈ Na–smectite. This suggests that transition-metal ions such as Fe(III) play an important role in anthracene transformation. Among Fe(III)-saturated clays, Fe(III)–smectite exhibits the highest catalytic activity followed by Fe(III)–illite, Fe(III)–pyrophyllite, and Fe(III)–kaolinite, which is in agreement with the interlayer Fe(III) content. Moreover, effects by two common environmental factors, pH and relative humidity (RH), were evaluated. With an increase in pH or RH, the rate of anthracene transformation decreases rapidly at first and then is leveled off. GC-MS analysis identifies that the final product of anthracene transformation is 9,10-anthraquinone, a more bioavailable molecule compared to anthracene. The transformation process mainly involves cation-π bonding, electron transfer leading to cation radical, and further oxidation by chemisorbed O_2. The present work provides valuable insights into the abiotic transformation and the fate of PAHs in the soil environment and the development of contaminated land remediation technologies.

Keywords Smectite · Polycyclic aromatic hydrocarbons (PAHs) · Transformation · Cation-π bonding · Electron transfer

Introduction

Polycyclic aromatic hydrocarbons (PAHs), mainly produced via incomplete combustion of fossil fuel, have been detected as one class of primary contaminants in soil and sediment. Due to their potential damage to human health and ecosystem, transformation and mobility of PAHs in soil environment have attracted great attention (Li et al. 2008; Samanta et al. 2002; Juhasz and Naidu 2000). PAH-like organic molecules may reside at the upper surface layer for a certain period of time and undergo various transformation processes such as photodecomposition, chemical transformation, and microbiological degradation (Gan et al. 2009). Although microbiological transformations are considered as an important way for PAH degradation, abiotic and biotic processes always occur simultaneously in soils (Field et al. 1992). Recently, more attention has been paid to abiotic degradation of PAHs, which is strongly affected by their interactions with chemically active soil components, such as dissolved organic matter (DOM), metal oxides, and clay minerals (Soma and Soma 1989). From this prospect, chemical transformation and photochemical processes on clay minerals are of interest for unveiling the stability and fate of hazardous substances (including PAHs) in soil environment (González-Bahamón et al. 2011; Hwang and Cutright 2002; Jia et al. 2012; Motokura et al. 2012; Wei et al. 2012).

Smectite is the most common and ubiquitous clay mineral, and its layers generally consist of a center octahedral Al–O

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sheet sandwiched between two tetrahedral Si–O sheets (Allen and Hajek 1989). The planar aluminosilicate layers typically exist in stacked assemblages. Negative charges are embedded in the individual layers (due to isomorphic substitution) in a fixed but isolated distribution and commonly neutralized by exchangeable hydrated cations that reside at or near the negatively charged sites between the layers (Sato et al. 1992). Smectite clay is usually featured with an expandable interlayer distance (between two clay sheets) ranging from 0.1 to 0.8 nm. The unique swelling, intercalation, and ion-exchange properties make smectite as the most effective one in sorption and chemical transformation of organic contaminants in soil or sediments (Hundal et al. 2001). For example, large amounts of phenanthrene can be adsorbed from water by smectite (Hundal et al. 2001). In many cases, the process of adsorption on clay minerals is followed by chemical transformation. When benzene or phenol is adsorbed on Cu(II) or Fe(III)-modified montmorillonite, higher molecular weight products are formed (Mortland and Halloran 1976). Mono-substituted benzenes such as toluene, phenol, chloro-, fluoro- and methoxybenzene can also be adsorbed on transition-metal ion-exchanged montmorillonites and undergo further transformation giving disubstituted biphenyl as final products (Soma and Soma 1985). To our knowledge, however, limited work has been done for the potential transformation process of PAHs on clay surface including critical factors involved therein such as clay structure and physiochemical properties on this chemical process.

In our preliminary experiment, it was found that the content of some PAHs compounds on Fe(III)-saturated smectite decreased with time under dark condition. This drives us to hypothesize that (1) PAHs can be transformed on the surface of certain cation-saturated clay minerals even without light irradiation, (2) modulating the cation type and composition on clay mineral surfaces could change the transformation behaviors of the surface-adsorbed compounds, and (3) the interaction between exchangeable cations and PAHs on clay surface is an important factor in the chemical transformation of PAHs. To test the hypotheses, clay minerals saturated with various exchangeable cations (i.e., Fe(III), Al(III), Cu(II), Ca(II), Mg(II), and Na(I)) were tested for the transformation of anthracene, in which anthracene is utilized as a model due to its reactivity under dark condition in our preliminary experiment. In addition, the behavior of PAHs on clay minerals is greatly governed by surface and structural properties of the sorbents and environmental factors such as the water content and pH condition, which alter the speciation and hydration status of the clay interlayers (Müller et al. 2007; Manjanna et al. 2009; Wang et al. 2009). Therefore, the objective of this study is to understand the transformation behavior of anthracene on clay surfaces, attempting to (1) reveal the effect of cation type and its oxidation state on transformation dynamics, (2) probe the importance of the clay type as well as relevant structural and surface properties, and (3) gain insight into the transformation pathway of PAHs and unveil the transformation mechanisms.

Experimental

Chemicals and materials

Anhydrous ferric chloride ($FeCl_3$), sodium chloride (NaCl), aluminum chloride ($AlCl_3$), calcium chloride ($CaCl_2$), cupric chloride ($CuCl_2$), magnesium chloride ($MgCl_2$), sodium hydroxide (NaOH), and hydrochloric acid (HCl, 36–38 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anthracene (An, 97 %) and methanol (HPLC-grade solvent) were purchased from Sigma-Aldrich (Shanghai, China). All the chemicals were used as received. Kaolinite, illite, pyrophyllite, and smectite clay minerals were obtained from Zhejiang Feng-Hong Clay Chemicals Co., Ltd. (Zhejiang, China).

Clay preparation

Fe(III)–smectite was prepared following a previously reported protocol (Arroyo et al. 2005). Briefly, smectite was first dispersed in water and then titrated to pH 6.8 with 0.5-M sodium acetate buffer (pH 5) to remove carbonate impurities. After that, the clay suspension was centrifuged for 6 min at 600 rpm to obtain sized clay particles (<2 μm) and then repeatedly treated with 0.1-M $FeCl_3$ solution for four times. The resulting Fe(III)-saturated smectite was washed using Milli-Q water until free of chloride as indicated by a negative test with $AgNO_3$ and then freeze-dried.

The speciation form of Fe(III) in Fe(III)–smectite was controlled by pH, which was adjusted to a desired value using 1.0 M HCl or 1.0 M NaOH and then freeze-dried. Smectite clays saturated by other types of cations (e.g., Al(III), Cu(II), Ca(II), Mg(II), and Na(I)) were achieved by following the same procedures as described above except replacing 0.1 M Fe(III) with the objective cations.

Reaction of anthracene at cation-modified clays

The reaction mixture was prepared by mixing anthracene dissolved in 1 mL acetone with 1 g of cation-modified clays (1 mg anthracene per g of clay). The reaction mixture was continuously stirred for 30 min to ensure complete mixing, and the use of acetone allowed removing it by simple evaporation under ambient conditions. The reaction was conducted in triplicate at room temperature (23 °C) and controlled relative humidity (RH) inside a glass desiccator. At given time intervals (0, 1, 2, 3, 4, and 5 days), samples were collected and extracted with a mixture of acetone and dichloromethane (volume ratio 1:1) in an ultrasonic bath for half an hour and then centrifuged at 10,000 rpm for 10 min to separate the supernatants from the solids. The supernatants were collected, and the solid residues were replenished with another 10 mL of extraction solution. Such procedure was repeated twice to assure that the anthracene and its reaction products were completely extracted. This method ensures that the recovery rate was up to 95 % in the present study. 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. Anthracene was quantified using a PerkinElmer HPLC equipped with a 25-cm×4.6-mm Cosmosil C18 column. An 85:15 (*v*/*v*) mixture of methanol to water ratio was employed as mobile effluent. The flow rate was 1.0 mL min^{-1}, and the ultraviolet detector was set at 254 nm. The degree of degradation was determined by comparing the amount of anthracene remaining between the control and samples. For comparison, anthracene in the control sample is extracted immediately after acetone is evaporated.

Product analysis

The extracts were concentrated and analyzed by gas chromatography–mass spectrometry (GC-MS, Agilent 7890A-5975C). GC-MS was performed on a full-scan mode (30–500 amu) for identification under the following conditions: TC-1 capillary column (length=30 m; internal diameter=250 μm; film thickness=0.25 μm). Helium was used as carrier gas at a flow rate of 1.2 mL min^{-1} with splitless injection at 230 °C. The temperature program was started at 80 °C, held for 2 min, raised from 80 to 200 °C at a step of 20 °C min^{-1}, then to 260 at 10 °C min^{-1}, then held for 2 min. The flow rate was 1.5 mL min^{-1}, the interface temperature was 260 °C, and the injection volume was 1 μL.

Results and discussion

Role of exchangeable cations

The exchangeable cations play a significant role in the surface properties of the clay mineral, thus critically affecting catalytic transformation of organic pollutants (Isaacson and Sawhney 1983). To investigate the effect of exchangeable cations, the smectites saturated with different types of cations were prepared for transformation experiments in the dark. The evolution of anthracene as a function of reaction time is presented in Fig. 1. The degradation rate at different homoionic saturated smectites follows the order Fe(III)–smectite >> Cu(II)–smectite > Al(III)–smectite ≈ Mg(II)–smectite ≈ Ca(II)–smectite ≈ Na(I)–smectite. Clearly, Fe(III) and Cu(II) both promote the transformation of anthracene at smectite, while Al(III), Ca(II), Na(I), and Mg(II) show limited effect.

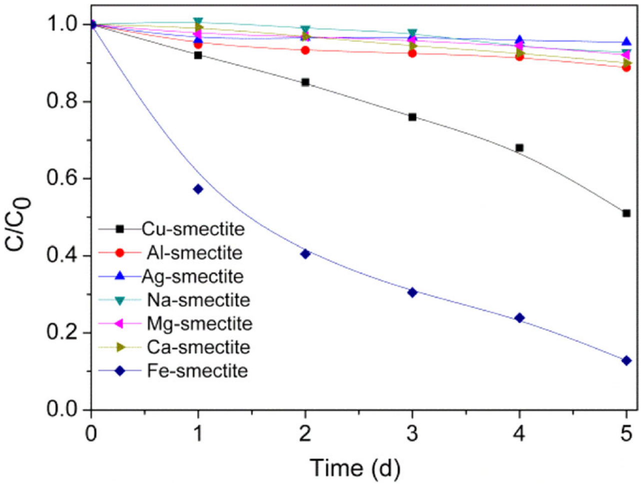

Fig. 1 The evolution of anthracene as a function of reaction time at smectite modified by various cations

The interactions between PAHs and the exchangeable cations on clay surfaces could affect PAH mobility and transformation at mineral surfaces (Zhu et al. 2004). Binding of various cations on clay surface is expected to influence the sorption and retention of organic pollutants since it will modify the structure and physical–chemical properties of the clay surface. Generally, the difference in affinity of the homoionic clays for anthracene is related to the polarizing power of exchangeable cations (Bladel and Moreale 1974; Pusino et al. 1993). The presence of transition metals on clay surface greatly facilitates the adsorption of anthracene because strong cation-π interactions and high energy exist between anthracene, a π-donor, and transition-metal ions (Zhu et al. 2004). In many cases, molecular adsorption on clay minerals is followed by chemical transformation including catalytic reduction (Elsner et al. 2004), oxidative degradation (Ebitani et al. 2002), and chemical synthesis (Gu et al. 2011a). For example, aromatic molecules adsorbed on a transition-metal ion such as Cu(II), Fe(III), VO(II), and Ru(II))-exchanged montmorillonite form colored adsorption complexes (Soma and Soma 1989). The initial step in forming these colored complexes involves an electron transfer from the adsorbed organic molecules to the interlayer transition-metal ions which may be followed by the oxidative transformations of the molecules. These reactions depend both on the ionization potential of aromatic molecules and on the oxidizing power of the interlayer metal ions (Soma and Soma 1989). Only metal ions with enough oxidizing power such as the Fe(III), Cu(II), and Ru(III) ions can produce these radical cations and induce the subsequent reactions. This suggests that transition-metal ions such as Fe(III) and Cu(II) on clay surface have the potential to play an important role in the transformation of anthracene.

On the other hand, insignificant transformation of anthracene was observed in the presence of Al(III)-saturated smectite clay. On the contrary, organic contaminants such as herbicide can be effectively degraded by Al(III)-saturated clays (González-Bahamón et al. 2011; Müller et al. 2007). Most of these reactions are believed to be catalyzed by the Brønsted acid sites (proton donating) induced by Al(III) ions on the clay surfaces (Brown and Rhodes 1997). However, the transformation of anthracene on Fe(III) or Cu(II)-modified smectite is considered to be mainly driven by electron transfer from anthracene to transition metal ions (electron-accepting sites) in clay mineral interlayers. This suggests that the strong interaction established between anthracene and Al(III) at clay surfaces has little effect on electron transfer, thus being ineffective in anthracene transformation. Therefore, insignificant transformation of anthracene on a variety of other metal ions, including Na(I), Ca(II), and Mg(II)-modified clay minerals, is understandable in terms of unfavorable redox couples involved in those systems.

Effect of Fe(III) content on clay surface

Based on the discussion above, the clay saturated with more transition metal ions may give higher reactivity. To test this, clay minerals saturated with various contents of Fe(III) were prepared for transformation experiments. As shown in Table 1, the exchangeable iron contents are ca 4.43, 0.30, 0.39, and 1.16 % for Fe(III)-saturated smectite, kaolinite, pyrophyllite, and illite, respectively. The content of Fe(III) species on clay surfaces is related to the surface negative charge density. With similar surface areas, principally, mineral with greater surface charge density attracts greater density of exchangeable cations. The structural negative charges of smectite originate from isomorphic substitution, giving greater cation exchange capacity (CEC) than other tested clays. Also, smectite is expandable with accessible cation exchange sites presented in the interlayers as well as on the external surfaces of the stacked layer assemblages. However, isomorphic substitution does not occur in kaolinite and pyrophyllite clays; hence, the exchangeable Fe primarily resides on the external surfaces and edge sites. For illite, structural charges that originated from isomorphic substitution are compensated by fixed K(I) which cannot be replaced by the added Fe(III) in the present work. Therefore, the exchangeable iron contents of clays studied here follow the order of smectite > illite > pyrophyllite > kaolinite.

Kinetic studies find that anthracene transformation observes a pseudo-first-order reaction model in the four studied clay systems, and the pseudo-first-order rate constants (k_{obs}) are listed in Table 1. As a result, the anthracene transformation rate follows the order of Fe(III)–smectite > Fe(III)–illite > Fe(III)–pyrophyllite > Fe(III)–kaolinite, which is in agreement with the exchangeable iron contents presented in the clays. The catalytic capability of Fe(III)–clay to transform anthracene may be correlated to the cation exchange capacity of the clay layered structures, which determines the populations of Fe(III) serving as electron acceptor sites. Fe(III) species are more enriched on smectite and illite surfaces, leading to a higher reactivity of anthracene transformation. Compared to smectite and illite, kaolinite and pyrophyllite provide less active sites as indicated by the number of Fe(III) species adsorbed on the clay surfaces, thereby giving a smaller rate of anthracene transformation. To confirm the effect by clay CEC on anthracene transformation, Fe(III)-modified smectite clays with different CEC amounts were tested. Consequently, the rate of anthracene transformation linearly increases with the increase in CEC content of smectites (for details, refer to SI). This supports our above proposal that the anthracene transformation is mainly correlated to the clay CEC and exchangeable iron content on Fe(III)-saturated clays.

Relationship between transformation rate and Fe(III) hydroxyl states

Fe(III) species exist in various hydroxyl states in aqueous environment depending on pH(Charles and Flynn 1984). Hydroxyl states of Fe(III) species on clay surfaces could also influence the complexes between Fe(III) and aromatic molecules, thus the electron-transfer process and anthracene transformation rate. To investigate the role of Fe(III) species on anthracene transformation, Fe(III)–smectite clays were prepared under different pH conditions, and their reactivity was evaluated by anthracene transformation. The anthracene transformation results associated with various Fe(III)–smectite samples are shown in Fig. 2a. As a trend, transformation rate decreases with increasing pH over the range of 1.8–5.5. When

Table 1 CEC and relevant reaction rates of Fe(III)-saturated smectite, kaolinite, illite, and pyrophyllite clays

Fe(III)-saturated clays	CEC (cmol(+) kg^{-1})	Exchangeable iron contents (%)	Pseudo-first-order rate constants k_{obs} (day^{-1})
Smectite	79.1	4.430	0.4424
Illite	20.7	1.159	0.0122
Kaolinite	5.35	0.300	0.0002
Pyrophyllite	6.9	0.386	0.0068

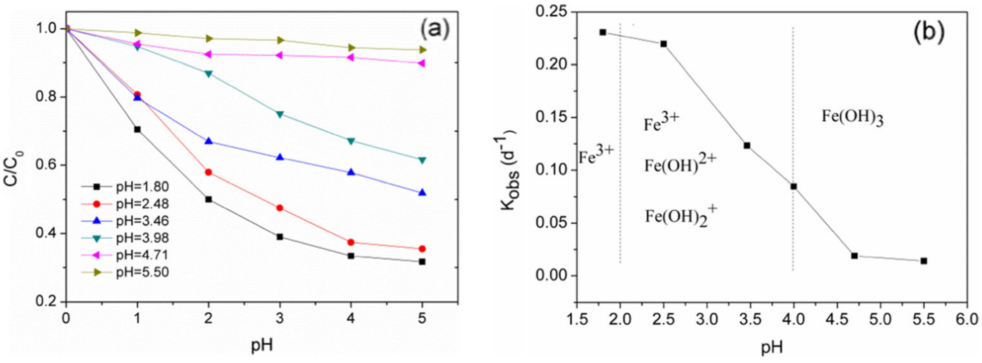

Fig. 2 **a** The evolution of anthracene as a function of reaction time at various pH values and **b** the pseudo-first-order rate constant for anthracene degradation as a function of pH value (hydrate states of Fe(III) in different pH regions are included for reference)

the pH value is 1.8, almost 70 % of anthracene is transformed in 5 days. As pH is adjusted to 2.48, 3.46, 3.98, 4.7, and 5.5, nearly 35, 52, 62, 90, and 94 % of anthracene remains as residues within the same reaction time frame, respectively. Kinetic studies suggest that anthracene transformation follows a pseudo-first-order reaction model, and the rate constants (k_{obs}) for anthracene transformation as a function of pH are shown in Fig. 2b. The k_{obs} value is 0.2307 day^{-1} when pH is 1.8, but it decreases rapidly with increasing pH value in the range of 1.8–4.7 and then is nearly leveled off when pH is further increased up to 5.5. When pH is 5.5, the transformation rate is 0.0139 day^{-1}, which is about one order of magnitude less than that at pH 1.8.

It is hypothesized that Fe(III) plays critical roles in anthracene transformation on the clay surfaces due to the formation of cation-π complexes between exchangeable cation and PAHs which is an initial step for anthracene transformation. To test this hypothesis, the transformation rate constant of anthracene (k_{obs}) is plotted against pH (Fig. 2b). It is noted that k_{obs} value decreases with increasing pH over the range of 1.8–5.5. As Fe(III) species exist in various hydroxyl states depending on pH, with the increase of pH from 1.8 to 5.5, interlayer Fe(III) is gradually hydroxylated, resulting in the decrease in interlayer Fe(III) content. The decrease in k_{obs} value is coincident with the change in the Fe(III) content in the range of pH of 1.8–5.5. This observation implies Fe(III) as the predominant species for activating anthracene transformation. Therefore, the decrease in the transformation rate of anthracene with increasing pH is presumably a result of decreasing Fe(III) content.

Transformation of anthracene under various relative humidity conditions

In general, cations on clay surface tend to be hydrated, and the hydrated status of smectite clay interlayers appears to be an important factor influencing the interaction between cations and organic molecules, and thus their transformation (Arroyo et al. 2005). RH can also be an important factor for PAH transformation at minerals similar to the observations at soot particles (Richard et al. 1988). In the present study, the reactivity of Fe(III)–smectite samples under different RH conditions was evaluated by following the process of anthracene transformation. As a result, anthracene transformation observes a pseudo-first-order reaction model at Fe(III)–smectite under different RH conditions. The pseudo-first-order rate constant (k_{obs}) as a function of RH is displayed in Fig. 3. The increase in the RH results in a steep decrease in the transformation rate; the rate constant significantly decreases from 0.147 to 0.039 h^{-1} when the RH increases from 11 to 87 %. This result is in agreement with previous reports, in which the addition of water to a system composed of arene radical cations formed by electron transfer to activated silica-alumina resulted in a rapid decay of radical cations (Rupert 1973). The suppress effect was attributed to the competition between the arene and the water molecule for the Lewis acid site (Rupert 1973).

Under moist ambient conditions, water molecules hydrate cations near the surface, and a compact water layer is formed in this interfacial region. The coverage of water molecules leads to anthracene being "pushed" off from the surface, thus slowing down the process of electron transfer from anthracene to metal cations. In other words, the presence of water which competes for the coordination sites is detrimental to PAH

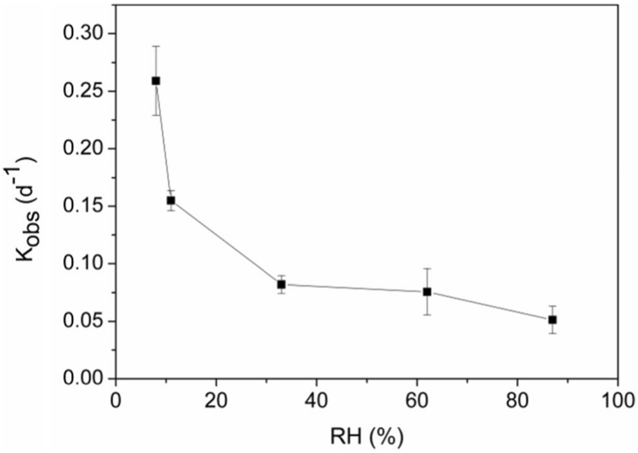

Fig. 3 The pseudo-first-order rate constant of anthracene transformation versus RH (%) value

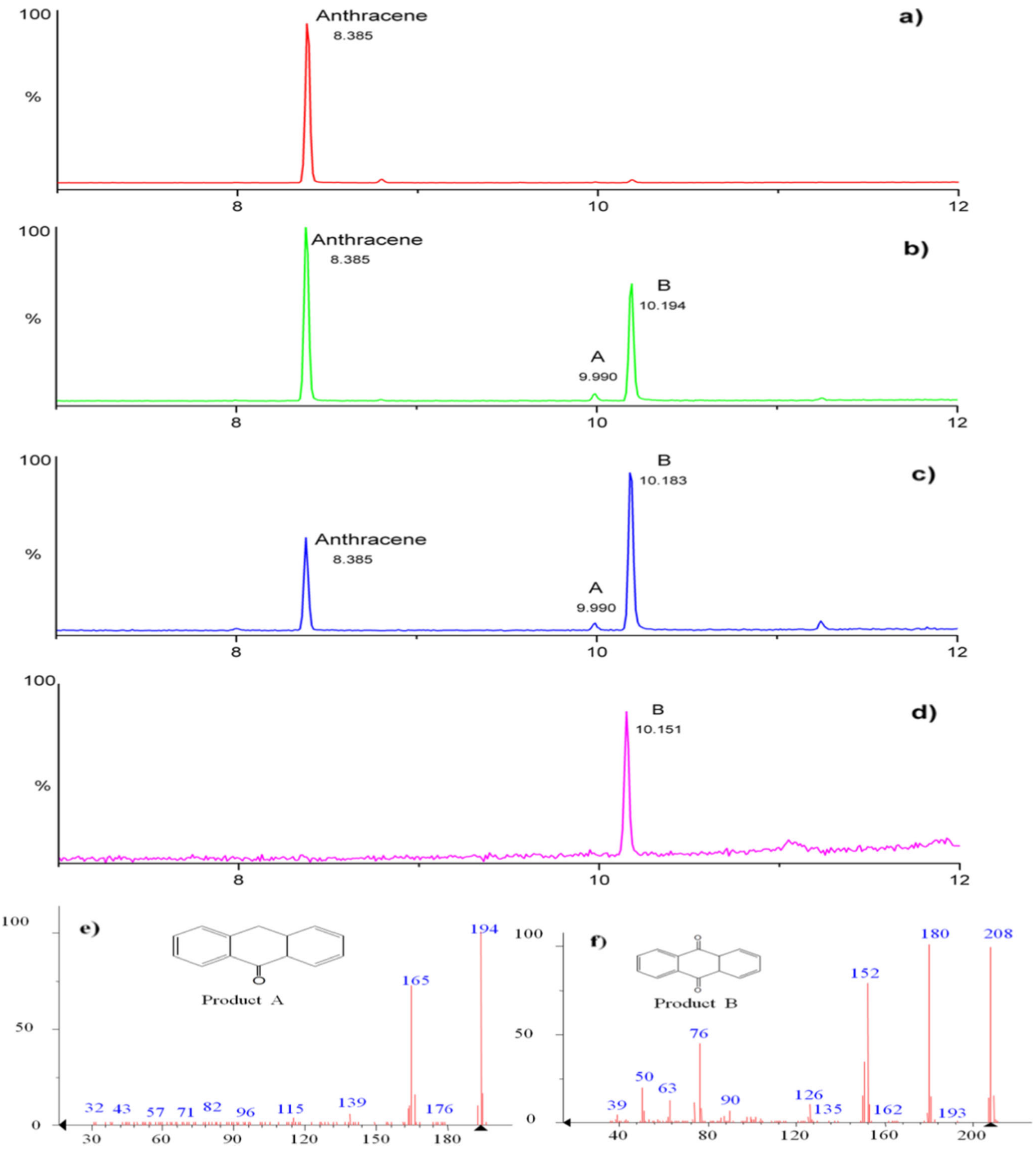

Fig. 4 GC-MS chromatograms of extracted Fe(III)-smectite/anthracene reaction mixture after **a** 0, **b** 3, **c** 5, and **d** 8-day reaction. Mass spectra of relevant products: **e** product A (retention time of 9.990 min) and **f** product B (retention time of 10.183 min)

transformation at the clay surface, and the decreasing anthracene–Fe(III) interaction on clay surface induces the decrease in electron transfer reaction rate and PAH transformation rate on clay surface (Gu et al. 2011b). Moreover, hydrated transition-metal ions are incapable of inducing the electron transfer, so the radical cation species is not formed, indicating the unique role played by the planar silicate surface (Gu et al. 2008). Therefore, water blocks the active sites and hinders the catalytic effect of the clay minerals, and the interlayer water needs to be pre-treated for the transformation of organic molecules (Soma and Soma 1989).

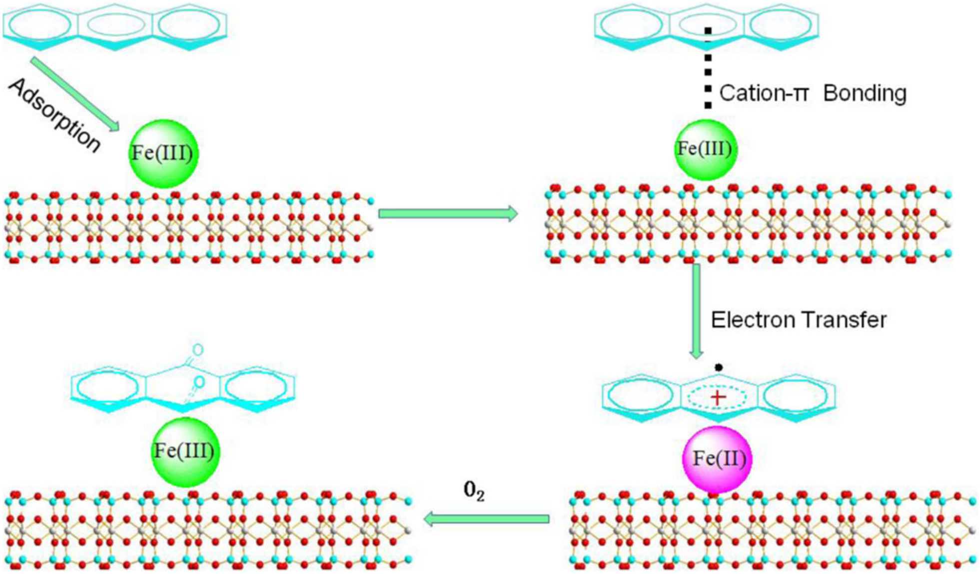

Fig. 5 Proposed mechanism for the transformation of anthracene at Fe(III)–smectite

Transformation pathway and mechanism

The transformation reaction was conducted under RH of 8 % without light exposure. At pre-selected reaction intervals (i.e., 1, 3, 5 days, etc.), the samples were extracted to obtain major products with 1:1 acetone/dichloromethane. These products were identified by GC-MS analysis. Figure 4 displays the GC-MS spectra of anthracene transformation after 0, 3, 5, and 8 days and the corresponding mass spectra related to GC peaks A and B. Notice that peak B gives the maximum *m*/*z* value of 208, which can be assigned to 9,10-anthraquinone based on the standard spectrum from the NIST library database. In addition, a minor portion of product A (shown a retention time of 9.991 min) appears during 3 and 5 days of reaction, but it goes away in 8 and 11 days of reaction in the present study. The product is tentatively assigned to compound of anthrone by analyzing the fragmentation mass patterns. On the other hand, product B, 9,10-anthraquinone, significantly increases as the reaction proceeds and becomes dominant after 5 days of reaction. This suggests the potential accumulation of 9,10-anthraquinone in soil environment, but it is more biodegradable compared to anthracene. To test if 9,10-anthraquinone could be further transformed in longer time, transformation was extended to 11 days, and no significant change was observed in GC-MS analysis. This suggests that 9,10-anthraquinone could be the final product for anthracene transformation at Fe(III)–smectite clay. The finding that 9,10-anthraquinone is the terminal product is in agreement with the work carried out by others using Mn peroxidise in white rot fungi, Mn tailings, or TiO_2 (Acevedo et al. 2011; Clarke et al. 2012; Cordeiro and Corio 2009). Furthermore, 9,10-anthraquinone has been detected as dominant oxygen-containing PAHs (OPAHs) in soil. For example, 9,10-anthraquinone which also belongs to the dominating compounds contributed on average 16 % to the Σ15 OPAHs, and its methylated derivative is the most abundant compound (Wilckea et al. 2014); the concentration of 9,10-anthraquinone ranged from 11 to 80 ng/g (Niederer 1998) and has been identified as a major component in soils from former gasworks sites (Lundstedt et al. 2007).

Based on the above GC-MS analysis, the pathways for anthracene transformation at Fe(III)-modified clay minerals are tentatively proposed as in Fig. 5. Relatively strong interactions between aromatic π-electron donors and metal cations drive the adsorption of anthracene through a predominantly electrostatic interaction (Zhu et al. 2004). In present study, the formation of cation-π bonding between anthracene molecule and Fe(III) can initiate the reaction at mineral surfaces. Exchangeable transition-metal cations such as Cu(II) or Fe(III) have been shown to play an important role in generating cation radicals through accepting electrons donated by aromatic species (dela Cruz et al. 2011; Fenn et al. 1973; Gu et al. 2011a; Pinnavaia et al. 1974). The formed cation radicals are stabilized by the presence of the planar negatively charged silicate layers in the smectite clay (Gu et al. 2008). Then, the organic radical-cations react with chemisorbed O_2 at mineral surfaces, causing the transformation of organic contaminants such as anthracene.

Conclusions

Transformation of anthracene at seven homoionic smectites has been comparatively studied. The transformation rate follows the order: Fe–smectite >> Cu–smectite > Al–smectite ≈ Mg–smectite ≈ Ca–smectite ≈ Na–smectite, suggesting that variable transition-metal ions such as Fe(III) play an important role in anthracene transformation. Among Fe(III)-saturated clays, Fe(III)–smectite exhibits the highest catalytic ability followed by Fe(III)–illite, Fe(III)–pyrophyllite, and Fe(III)–kaolinite, which is in agreement with the interlayer Fe(III) content. With the increase in pH and RH, anthracene transformation rate decreases due to the fact that hydroxylation of cations or the presence of water inhibits the electron transfer from aromatic rings to metal ions. Anthracene is finally transformed to 9,10-anthraquinone as identified by GC-MS analysis. Three steps are proposed for the transformation: (1) the formation of cation-π bonding, (2) electron transfer to form organic radical cations, and (3) oxidation by chemisorbed O_2. These present results provide valuable insights into the transformation and fate of anthracene in the natural soil environment and have important implications for remediation of contaminated land. Due to their compelling merits for effective removal of organic pollutants in soil and sediment together with great abundance in nature, clays (e.g., cation-modified smectite) hold great potential in practical treatment of PAHs in soil on a large scale.

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