Sorption of aromatic hydrocarbons onto montmorillonite as affected by norfloxacin

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ABSTRACT

Effect of norfloxacin (Nor) on the sorption of 1,3-dinitrobenzene (1,3-DNB), and PAHs (naphthalene (NAPH), phenanthrene (PHEN) and pyrene (PYR)) to K^+-montmorillonite was studied. Nor suppressed 1,3-DNB sorption due to their competition for the same sorption sites. 1,3-DNB was sorbed on K^+-montmorillonite surface via cation–polar interaction and n–π electron donor–acceptor interaction. Nor also was sorbed on these sites through cation exchange, cation bridging and/or surface complexation. Nor increased three PAHs sorption on montmorillonite and the enhanced magnitude was positively correlated with the π-donor strength of three PAHs. The enhanced sorption of PAHs by Nor was primarily attributed to π–π interaction between π-electron-depleted quinoline ring of Nor and π-electron-rich PAHs. Compared with cation (Nor^+) and anion (Nor^-), zwitterion ($Nor^\pm$) of Nor increased PHEN and PYR sorption more pronounced due to additional cation–π interaction between the sorbed $Nor^\pm$ and PAHs. ^{1}H NMR spectrum provided direct evidence for π–π and cation–π complexation between PAHs and Nor^+ in solution by ring-current-induced upfield chemical shifts of amino group and methylene group of Nor^+.

1. Introduction

Recently, antibiotics residue in the environment is becoming a growing concern. Many antibiotics can be accumulated to levels as high as mg kg^{-1} in soils through land application of fertilizers, sewage sludge, wastewater irrigation or discard of out-of-date pharmaceutical prescriptions [1]. Most of antibiotics have hydrophilic acidic and/or alkaline functional groups within their molecules, and can exist in aqueous solution as cation, zwitterion and/or anion. Thus, their sorption behavior in the environment is significantly different from that of other hydrophobic organic chemicals (HOCs). Past studies examined pH-dependent sorption of antibiotics onto clays [2], aluminum oxides [3,4], and amorphous iron oxides [3], goethite [4], soil and soil minerals [5,6], and carbon nanotubes [7]. The proposed mechanisms included cation exchange and cation bridging [8], surface complexation [3,4], and hydrophobic interaction [7].

Nitroaromatic compounds (NACs) are a group of polar chemicals that are widely used as explosives, pesticides, solvents, and intermediates for organic synthesis. Contamination of NACs in soils and groundwater aquifers is common and has drawn considerable

attention [8,9]. It has been recognized that clay minerals, especially those exchanged with weakly hydrated cations (K^+, Cs^+), can strongly retain NACs [10–12]. Two mechanisms have been proposed: (1) n–π electron–donor–acceptor (EDA) interaction of NACs (π-electron acceptors) with lone electron pairs of siloxane oxygens (n–donors) [10,11] and (2) cation–polar interaction of nitro groups with exchangeable cations [12–14]. There is scientific debate on the concurrence and relative importance of these two mechanisms for sorption of NACs to clay minerals for a long time. Recently, Qu et al. compared the sorption of hexafluorobenzene and dinitrobenzenes on montmorillonite, and suggested that sorption of hexafluorobenzene was dominated by n–π EDA interaction, while sorption of nitroaromatics was dominated by cation–polar interaction due to highly delocalized electrons (oxygen is partially negatively charged) on their nitro groups [15].

PAHs are a group of ubiquitous, nonionic HOCs due to their toxicity and suspected carcinogenity. PAHs sorption from water to solid phase is thought to be primarily due to their interaction with immobile organic matter [16]. However, for sorbents containing only very small amount of organic carbon, mineral phase was found to contribute significantly to the sorption of PAHs [17]. The sorption mechanisms of PAHs on clay minerals were controversial. Several models have been outlined to describe the driving forces for sorption of PAHs by mineral surfaces: (1) hydrophobic interaction, which was driven by a substantial thermodynamic gradient

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due to a combination of relatively small van der Waals forces and large entropy differences [18,19]; (2) partition from bulk aqueous phase to vicinal water film on montmorillonite surface [20,21]; (3) cation–π interaction between the accumulated "soft" cations on clay mineral surface and aromatic ring [22]; (4) capillary condensation into interlayer nano or micropores of montmorillonite [17].

It is common that antibiotics, NACs and PAHs may coexist in the contaminated environment. However, most of the past sorption studies often focused on antibiotics, NACs or PAHs separately in order to explore their underlying sorption mechanisms onto clays more easily. To our knowledge, there are very few investigations on the influence of zwitterionic chemicals on the sorption of NACs or PAHs to clays. Although natural organic matter (NOM) and surfactants were also ionic organic chemicals, and could affect the sorption of other organic chemicals [23–25]. However, such influence was generally attributed to aliphatic chains in their molecules [26]. Thus, knowledge obtained from NOM and surfactants may not be applied to other zwitterionic chemicals.

In this study, we chose norfloxacin (Nor) as a common representative of zwitterionic organic chemicals, and examined its effects on the sorption of one NACs (1,3-DNB), and three PAHs (NAPH, PHEN and PYR). Nor has two pK_a (6.22 and 8.51), and can exist either in Nor$^+$, Nor$^\pm$ or Nor$^-$ form in aqueous solution at different pH conditions due to the presence of two proton-binding sites (carboxyl and piperazinyl groups) (Fig. S1). The objectives of this study were (i) to reveal the dissociation influences of Nor on the sorption of aromatics on K$^+$-montmorillonite and (ii) to provide an insight to the interactions between Nor and four aromatics during their sorption, which helps to understand the underlying mechanisms responsible for Nor effect.

2. Materials and methods

2.1. Chemicals

Analytical reagent grade of Nor, 1,3-DNB, NAPH, PHEN, and PYR were obtained from Sigma–Aldrich Co. (St. Louis, MO). The structures and properties of these organic chemicals are shown in Table S1.

2.2. Sorbent

Montmorillonite (purity >98%) was purchased from Beijing Youlichuangjia Science and Technology Development Company (Beijing, China). A fraction of <2.0 μm was obtained by wet sedimentation and subsequently exchanged with K$^+$ using chloride salts, dialyzed free of excess salt, and freeze-dried. The freeze-dried samples were stored in plastic bottles. The cation exchange capacity (CEC) of K$^+$-montmorillonite is 107.1 cmol kg^{-1} by compulsive exchange with Ba^{2+} [27].

2.3. Sorption experiments

All sorption experiments were conducted in triplicates using a batch equilibration technique at $23 \pm 1\,^\circ$C. For sorption isotherm experiments, the suspended solution pH was between 6.9 and 7.2 (measured at the end of batch sorption). Under this pH condition, Nor is zwitterion. For the pH effect experiments, the suspended solution pH was adjusted with a weighed amount of HCl or KOH solutions. The final equilibrium pH was measured at the end of batch experiments.

For sorption of 1,3-DNB (1.0, 3.0, 6.0, 10.0, 14.0, and 20.0 mg/L), NAPH (0.1, 0.5, 1.0, 2.0, 3.0, and 5.0 mg/L), PHEN (0.1, 0.2, 0.3, 0.5, 0.7 and 1.0 mg/L), and PYR (0.01, 0.02, 0.03, 0.05, 0.07 and

0.1 mg/L) in the presence of Nor (0, 20, and 50 mg/L), the sorption experiments were carried out by mixing a certain amount of K$^+$-montmorillonite with corresponding 0.01 M KCl solution in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. Sorbates in methanol were added using a microsyringe, and the volume percentage of methanol was kept below 0.1% to minimize cosolvent effects. The prepared mixed samples were vortexed for 10 s and agitated on a flat bed shaker for 24 h at $23 \pm 1\,^\circ$C (apparent equilibrium was reached before this time). Controls (without any K$^+$-montmorillonite) were also established. Results showed that no significant loss of sorbates was observed (recoveries always >97%), indicating that sorption to glassware and degradation of these chemicals were negligible (data not shown). The suspension was centrifuged at $1667 \times g$ for 20 min to separate liquid from solid phases, and the concentrations of the solutes in the supernatant phase were determined by HPLC.

The pH effect experiments were conducted using a batch sorption approach as mentioned above. The initial concentrations of four sorbates were 0 and 50 mg/L Nor, 5.0 mg/L 1,3-DNB, 1.0 mg/L NAPH and PHEN, and 0.1 mg/L PYR, respectively. After equilibrium was reached, the suspension was centrifuged, and the sorbate concentrations in the supernatants were determined by HPLC. The sorbed mass was calculated from the differences between the initial and final equilibrium concentrations.

2.4. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurement

ATR-FTIR spectra were obtained on a Nicolet Nexus 470 FTIR spectrometer equipped with a ZnSe crystal fitted in a horizontal attenuated total reflectance (HATR) cell (Pike Technologies). A total of 256 scans with a spectral resolution of 4 cm^{-1} were employed.

Samples of Nor for ATR-FTIR analyses were prepared at pH 4.5 ± 0.1, 7.0 ± 0.1, and 9.0 ± 0.1, respectively. At pH 4.5, 7.0 or 9.0, the dominant species of Nor were cation (Nor$^+$), zwitterion (Nor$^\pm$) and anion (Nor$^-$) in solution, respectively. After sorption and centrifugation, the paste and supernatant were collected, separately, and immediately spread on the ZnSe crystal surface to obtain an appropriate thin layer. The sample holding region was sealed with a lid to prevent evaporation, and FTIR spectra were measured. FTIR spectra of K$^+$-montmorillonite in 0.01 M KCl were also measured in the absence of Nor at three defined pHs. For aqueous solution of Nor, difference spectra at each pH were obtained by subtracting the spectra of background electrolyte solution from the spectra of Nor solutions. For the sorbed Nor on K$^+$-montmorillonite, the difference spectra were obtained by subtracting the spectra of K$^+$-montmorillonite from corresponding spectra of the sorbed Nor on K$^+$-montmorillonite.

2.5. Solution-phase ^{1}H NMR

^{1}H NMR spectra were recorded at room temperature using a Bruker-DRX 500 MHz spectrometer for cationic Nor in mixtures with model π-donor compounds (NAPH, PHEN and PYR) in dimethylsulfoxide-d_6 (99.8% deuterium).

2.6. Aqueous solubility enhancement

Aqueous solubility of PAHs (NAPH, PHEN, and PYR) was measured in the Nor$^+$ and Nor$^-$ solution, respectively. Vials containing an organic compound and 20 mL different concentrations of Nor$^+$ or Nor$^-$ solution were shaken in an orbital shaker at $23 \pm 1\,^\circ$C for at least 5 d. After centrifugation, an aliquot of aqueous phase was withdrawn carefully for analysis of solute concentration.

2.7. Analysis

Solutes in the supernatants were determined by an Agilent 1200 reversed-phase HPLC (Atlantis-dC18 ODS HPLC column, 4.6 mm i.d. × 150 mm, 5 μm) equipped with UV and fluorescence detectors. The determination wavelengths were set at 262 nm for 1,3-DNB. The fluorescence wavelengths for measurement of Nor, NAPH, PHEN, and PYR were at the excitation wavelengths of 280, 225, 250 and 275 nm, and at the emission wavelengths of 450, 335, 364 and 394 nm, respectively. The mobile phase for Nor is acetonitrile:water (pH 3.0, adjusted with formic acid) (20:80, v:v) at a flow rate of 0.8 mL min^{-1}. Acetonitrile and water mixture at a volume ratio of 90% to 70% was used at a flow rate of 1.0 mL min^{-1} as the mobile phase for the determination of NAPH, PHEN and PYR.

2.8. Data analysis

Freundlich equation can be expressed as $Q = K_f C^n$, where Q (mg/g) is the amount of sorbed organic compounds by K$^+$-montmorillonite, C (mg/L) is the equilibrium concentration in solution, K_f is an empirical constant related to sorption capacity (mg$^{(1-n)}$ g^{-1} mL^n), and n is the Freundlich exponent or a site energy heterogeneity factor, often used as an indicator of isotherm nonlinearity.

3. Results and discussion

3.1. Influence of solution pH on Nor sorption

It was found that Nor sorption to K$^+$-montmorillonite was almost pH-independent between pH ∼ 4.0–8.0 (Fig. S2). When pH was > ∼8.0 Nor sorption to K$^+$-montmorillonite was remarkably decreased due to repulsion between Nor$^-$ and negatively charged surface of K$^+$-montmorillonite (Fig. S3). To examine the contributions of individual Nor species to overall sorption, we calculated species-specific equilibrium sorption contribution [28]. The overall sorbed amount at a given pH value can be represented as the sum of the contributions of individual species:

$$Cs = Cs^{Nor+} a_{Nor+} + Cs^{Nor\pm} \cdot a_{Nor\pm} + Cs^{Nor-} \cdot a_{Nor-} \qquad (1)$$

where Cs (mg/g) is the overall equilibrium sorption concentrations; Cs^{Nor+}, $Cs^{Nor\pm}$ and Cs^{Nor-} are the sorption contribution of cationic, zwitterionic and anionic species, respectively; and α_{Nor+}, $\alpha_{Nor\pm}$ and α_{Nor-} represent the mass fractions of these species in bulk solution. The best fittings were obtained for Cs^{Nor+} of 41.0 ± 0.7 mg/g, $Cs^{Nor\pm}$ of 39.2 ± 0.5 mg/g and Cs^{Nor-} of 26.4 ± 0.9 mg/g at the initial concentration of Nor 50.0 mg/L (Table S2).

ATR-FTIR was used to study the sorption mechanisms of Nor at different pHs. Fig. 1a–c shows FTIR spectra of Nor in aqueous solution at different pHs. At pH 4.5, a peak at ∼1745 cm^{-1} appeared, corresponding to C=O stretch ($\upsilon_{C=O\,carboxyl}$) of −COOH group. When pH was increased to 7.0 and 9.0, the intensity of $\upsilon_{C=O\,carboxyl}$ decreased, concurrently, the asymmetric (∼1582 cm^{-1}) and symmetric (∼1341 cm^{-1}) stretch of COO$^-$ appeared due to deprotonation of −COOH group. Assignments of the remaining vibrations observed in Fig. 1 are as follows: C=O stretch of ketone group (1629 cm^{-1}), and coupled carboxylic acid C—O stretch (υ_{COOH}) and O–H deformation (δ_{C-OH}) (1274 cm^{-1}) [3,4]. The interaction between Nor and K$^+$-montmorillonite was investigated by comparing the spectra of sorbed Nor with those of Nor in solution. When Nor was sorbed on K$^+$-montmorillonite (Fig. 1d) at pH 4.5, the spectrum of sorbed Nor$^+$ was similar to that of Nor$^+$ in aqueous solution, where the peaks of carboxyl group (1744 cm^{-1}) and keto group (1629 cm^{-1}) exhibited no shift. Because outer-sphere complexes and aqueous Nor$^+$ species had similar molecular geometries [29], outer-sphere complex was
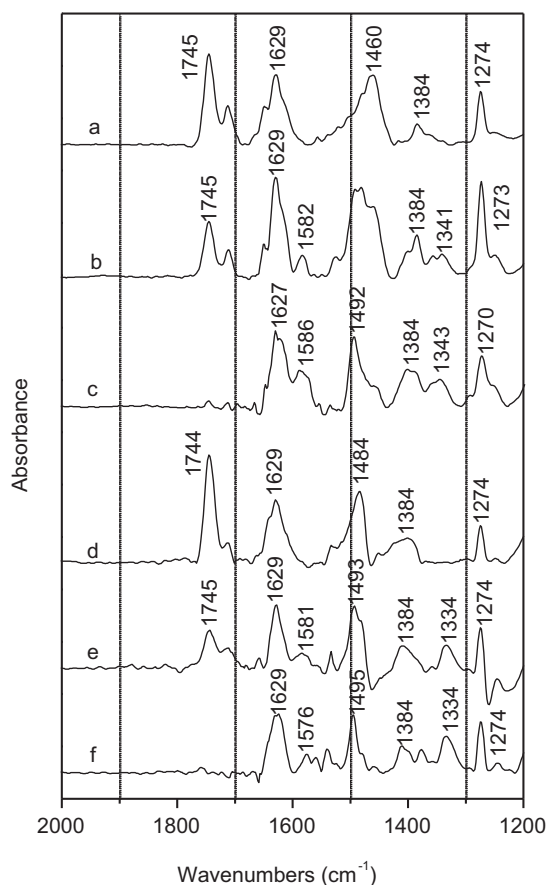

Fig. 1. FTIR spectra of Nor in solution at pH 4.5 (a), 7.0 (b), 9.0 (c) and on K$^+$-montmorillonite at pH 4.5 (d), 7.0 (e), and 9.0 (f).

expected to form for Nor$^+$ on montmorillonite surface through electrostatic interaction between negatively charged sites on mineral and protonated heterocyclic N atom of Nor$^+$. At pH 7.0, the absorbance of COO$^-$ symmetric stretch of Nor$^\pm$ shifted from 1341 to 1334 cm^{-1}, indicating that at least a portion of Nor$^\pm$ was sorbed on K$^+$-montmorillonite surface through interaction of its carboxyl group. In this case, we could not also rule out sorption of other portion of Nor$^\pm$ on montmorillonite surface through electrostatic interaction via its protonated heterocyclic N atom [6]. If pH was further increased to 9.0, the asymmetric and symmetric stretch of COO$^-$ shifted from 1586 and 1343 cm^{-1} to 1576 and 1334 cm^{-1}, respectively (Fig. 1f), indicating that carboxyl group of Nor was responsible for the sorbed Nor$^-$ on K$^+$-montmorillonite at pH 9.0 [2].

Based on the above evidences from batch sorption experiments and FTIR study it may be surmised that multiple mechanisms are expected to operate simultaneously for the sorption of Nor onto K$^+$-montmorillonite at different pH: (i) cation exchange occurred via columbic attraction of protonated heterocyclic N atom of Nor$^+$ to negatively charged surface sites on K$^+$-montmorillonite and via ion exchange with naturally occurring cations associated with sites of permanent negative charge on K$^+$-montmorillonite or pH-dependent negative charge arising from deprotonation of surface hydroxyl groups. Because in these reactions the sorption sites were not limited by the availability of cation exchange sites of K$^+$-montmorillonite but limited by Nor$^+$ and Nor$^\pm$, therefore, cation exchange appears to be the main mechanism for the sorption of Nor$^+$ at pH 4.5 and Nor$^\pm$ at pH 7.0. (ii) Cation bridging was thought to occur via interaction between COO$^-$ group and exchangeable cations of negatively charged sites of K$^+$-montmorillonite at pHs 7.0

Table 1
Freundlich constants (K_f and n) and correlation coefficients (r) of 1,3-DNB, NAPH, PHEN, and PYR sorption onto montmorillonite ($n=3$).

Sorbates	Nor (mg/L)	K_f	n	r	K_d (L/g)
1,3-DNB	0	0.333	0.70	0.97	0.23
	20	0.122	0.86	0.98	0.10
	50	0.07	0.89	0.99	0.06
NAPH	0	0.037	0.88	0.97	0.05
	20	0.043	0.84	0.98	0.07
	50	0.048	0.83	0.99	0.14
PHEN	0	0.022	0.67	0.99	0.08
	20	0.094	0.74	0.99	0.17
	50	0.294	0.85	0.99	0.42
PYR	0	0.204	0.79	0.98	0.36
	20	0.609	0.84	0.99	1.07
	50	0.626	0.83	0.98	4.31

and 9.0. (iii) Surface complexation seemed plausible via the binding of carboxyl group to surficial aluminum on the edge sites of aluminosilicate at pHs 7.0 and 9.0. Currently, it is difficult to define to what extent each mechanism contributes to the overall sorption.

3.2. Effect of Nor on the sorption of 1,3-DNB, NAPH, PHEN and PYR

Fig. 2 shows the sorption isotherms of 1,3-DNB, NAPH, PHEN, and PYR on K$^+$-montmorillonite in the presence and absence of Nor. These isotherms fitted Freundlich equation well, and were clearly nonlinear as characterized by low n values (Table 1).

As shown in Fig. 2a, the sorption of 1,3-DNB on K$^+$-montmorillonite decreased with increasing Nor concentrations from 0 to 50 mg/L, suggesting that Nor suppressed the sorption of 1,3-DNB. For example, the sorption distribution coefficients (K_d) (initial concentration of 5.0 mg/L) were used to compare the sorption behavior of 1,3-DNB (Table 1). Obviously, the K_d values decreased from 0.23 to 0.06 L/g when Nor concentrations increased from 0 to 50 mg/L. Nonlinear sorption of 1,3-DNB suggested the presence of specific interactions between 1,3-DNB and K$^+$-montmorillonite. Fig. S4 shows the FTIR spectra of sorbed 1,3-DNB on K$^+$-montmorillonite, where a red shift of υ_{asym} (NO) band of 1,3-DNB from 1542 cm^{-1} to 1536 cm^{-1} and a concomitant blue shift of υ_{sym} (NO) band from 1350 cm^{-1} to 1356 cm^{-1} were found. This suggested that 1,3-DNB was sorbed on K$^+$-montmorillonite through complexation of its −NO$_2$ groups with exchangeable K$^+$ cations of montmorillonite via cation–polar interaction and/or complexation between 1,3-DNB (e$^-$ acceptors) and oxygens on siloxane surfaces of K$^+$-montmorillonite (e$^-$ donors) via n–π electron donor–acceptor (EDA) interaction [11,13]. When Nor was added to solution together, Nor was sorbed on montmorillonite through electrostatic interaction or cation bridging, which shielded sorption sites of 1,3-DNB on mineral surface and suppressed its sorption accordingly.

Sorption isotherms of NAPH, PHEN and PYR on K$^+$-montmorillonite in the presence and absence of Nor are shown in Fig. 2b–d. For a given concentration, PYR had the highest K_d value on K$^+$-montmorillonite among three PAHs, followed by PHEN and NAPH (Table 1). The order is consistent to hydrophobicity of three PAHs [5]. Thus, for three examined PAHs, hydrophobic interaction should be a main cause for their sorption on montmorillonite [19]. When Nor/NAPH, Nor/PHEN, or Nor/PYR combination system was sorbed on K$^+$-montmorillonite (Fig. 2), the sorption of three PAHs increased with increasing Nor concentrations. The K_d values (initial concentration of 0.1 mg/L) were used to compare the sorption behavior of three PAHs (Table 1). Obviously, the K_d values increased from 0.05 to 0.14 L/g for NAPH, from 0.08 to 0.42 L/g for PHEN, and

from 0.36 to 4.2 L/g for PYR when Nor concentrations increased from 0 to 50 mg/L. Possible reason for the enhanced effect of Nor was that except for original PAHs sorption sites, the sorbed Nor formed new organic phase, thus created new sorption sites on K$^+$-montmorillonite surface, and facilitated PAHs sorption [19]. As shown in Fig. 2, the enhanced magnitude of three PAHs sorption by Nor was strongly positive correlated with π-donor strength and K_{ow} values of three PAHs (PYR > PHEN > NAPH). Therefore, it was proposed that main mechanisms about the enhancement effect of Nor on PAHs sorption likely resulted from π–π interaction between electron-depleted quinoline ring (π-electron acceptor) of Nor and PAHs (π-electron donor) and/or hydrophobic interaction between the newly formed organic phase by Nor and PAHs.

To further evaluate the role of π–π interaction on the overall enhancement effect, we chose pentachlorobenzene (PtCB) as a new sorbate, which has close hydrophobicity to PYR but has very less electron density due to electron induction effect of five chlorine atoms (Table S1). This means that there was similar hydrophobic interaction, but weaker π–π interaction between PtCB and Nor compared to that between PYR and Nor [25]. If Nor could not increased the sorption of PtCB as much as PYR, it implied that the enhanced sorption of PAHs could be ascribed to π–π interaction between Nor and PAHs [25]. As shown in Fig. S5, in the absence of Nor, PtCB and PYR had similar K_d values on K$^+$-montmorillonite. When Nor was added to solution, the sorption K_d values of PYR increased dramatically, however, the sorption K_d of PtCB only increased marginally. These results suggested that the enhanced sorption of PAHs by Nor was mainly due to π–π interaction between Nor and PAHs rather than hydrophobic interaction.

The concentrations of Nor in the supernatants were also determined simultaneously (data not shown). Nor sorption on montmorillonite varied slightly in the presence of four organic solutes. Obviously, Nor sorption was independent of the presence of 1,3-DNB, NAPH, PHEN, and PYR. This phenomenon indirectly verified that Nor was preferentially sorbed on surface of K$^+$-montmorillonite first through multiple mechanisms, and then PAHs were reacted with the sorbed Nor. It is plausible to assume that formation of ternary complex of K$^+$-montmorillonite–Nor–PAHs was likely.

3.3. Effect of different species of Nor on the sorption of 1,3-DNB, NAPH, PHEN and PYR

As described above, different species of Nor had different sorption mechanisms. And one wanted to know if different species of Nor had different effects on PAHs sorption. Fig. 3 shows the sorption of 1,3-DNB, NAPH, PHEN and PYR as a function of solution pH in the presence and absence of Nor. In the single solute system, it was found that the sorption of four adsorbates was almost independent of solution pH over the investigated pH range because these chemicals were nonionizable. When Nor was added to solution, it is found that solution pH had small effect on the sorption of 1,3-DNB on K$^+$-montmorillonite. However, for PAHs, their sorption on K$^+$-montmorillonite was changed with solution pH. As shown in Fig. 3, solution pH had little effect on the sorption of NAPH, while for PHEN and PYR, their sorption on K$^+$-montmorillonite increased significantly from pH 4.0 to 7.0, followed by a maximum at pH ∼7.1 and then decreased rapidly from pH 7.1 to 10.0. The increased sorption extent was consistent with π-donor strength of PAHs, indicating that delocalized π electrons of PAHs likely played an important role in the overall enhancement effect. It should be noted that Nor sorption on K$^+$-montmorillonite was also pH dependent at pH 7.0–10.0 (Fig. S2). To eliminate the effect of different sorption amount of Nor in different pH conditions, the K_d values of PHEN and PYR were normalized for the sorbed concentrations of Nor. As shown in Fig. S6,
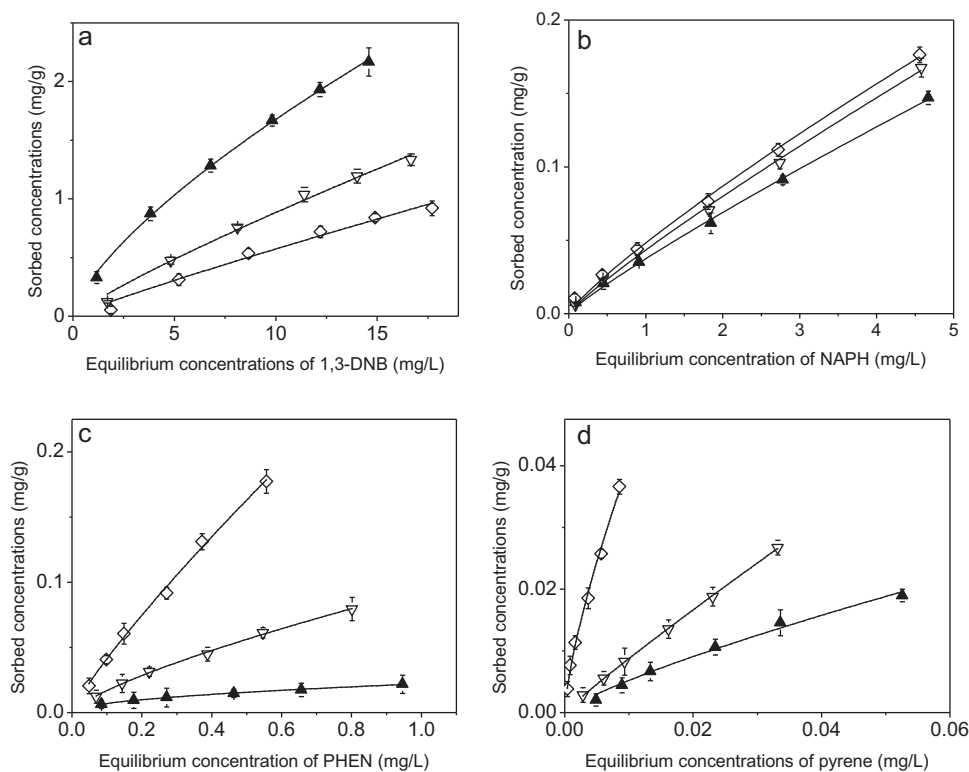
Fig. 2. Sorption isotherms of 1,3-DNB (a), NAPH (b), PHEN (c), and PYR (d) on K$^+$-montmorillonite: no Nor (▲), with 20.0 mg/L Nor (▽), and with 50 mg/L Nor (◇).

the sorption trend of PHEN and PYR as a function of pH has not been changed significantly. It was suggested that the effects of Nor on the sorption of PHEN and PYR was not only related to the sorbed amount of Nor, but also to different sorption mechanisms of Nor$^+$, Nor$^\pm$ and Nor$^-$ on K$^+$-montmorillonite.

As described above, Nor$^+$ was sorbed on K$^+$-montmorillonite through electrostatic interaction between protonated heterocyclic N atom of Nor$^+$ and negatively charged K$^+$-montmorillonite surface, leaving electron-depleted quinoline ring (π-electron acceptor) and —COOH group available freely. Several possible mechanisms
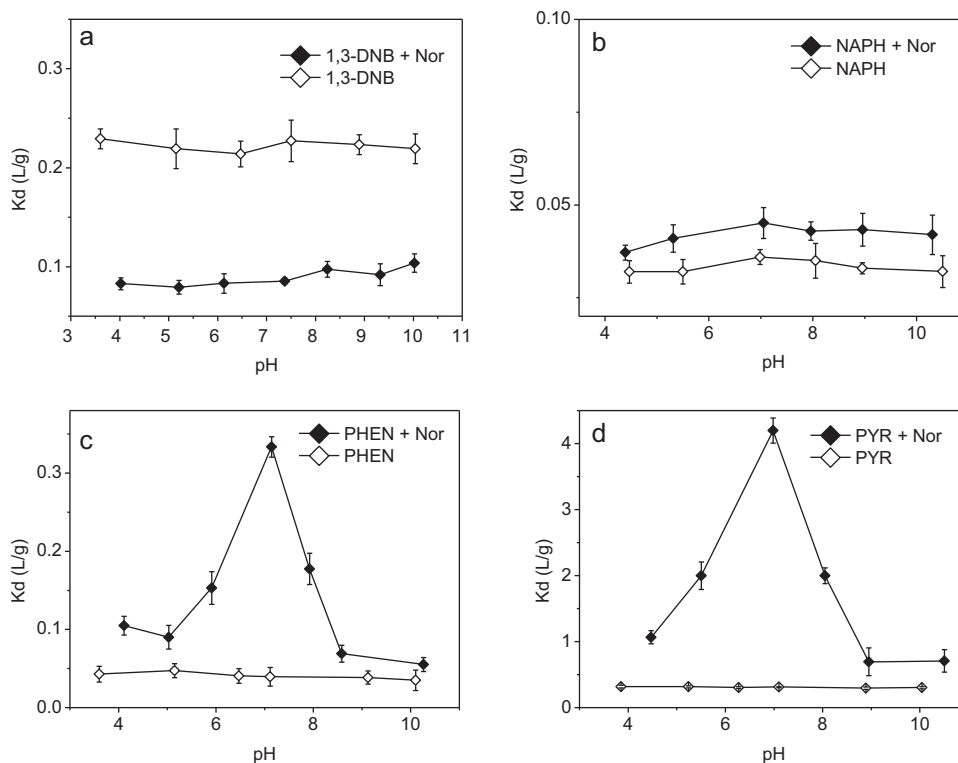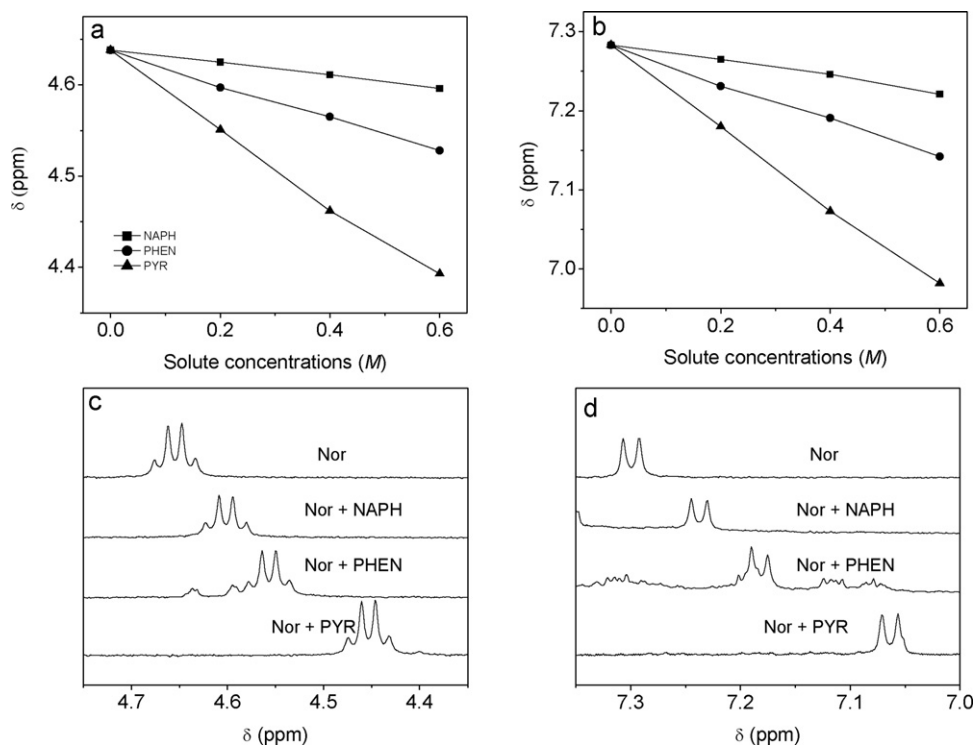

Fig. 3. Effect of equilibrium solution pH on the sorption of 1,3-DNB (a), NAPH (b), PHEN (c) and PYR (d) in the absence and presence of Nor on K$^+$-montmorillonite.

Fig. 4. ^{1}H NMR shift (δ) of Nor$^+$ (5.0 mmol/L) vs. concentration of π-donors (NAPH, PHEN, and PYR) in dimethylsulfoxide-d_6: methylene of —CH$_2$CH$_3$ group (a), —H on amino group of Nor (b). Selected NMR patterns of methylene of —CH$_2$CH$_3$ group (c), and —H on amino group of Nor (d).

should be considered based on the literature [30]: (1) π–π electron donor–acceptor (EDA) interaction between electron-depleted quinoline ring (π-electron acceptor) and PAHs (π-electron donor); (2) hydrogen–π bonding between —COOH group of sorbed Nor$^+$ and aromatic rings of PHEN or PYR. Hydrogen–π bonding was not likely a primary cause of the enhanced sorption for the following reason. When solution pH exceeds its pKa$_1$ (6.22), —COOH group on Nor would be ionized, and hydrogen–π bonding effect should have been significantly impeded. Fig. 3 shows that the sorption affinity did not decrease accordingly, while increased. At pH ~7.0, a portion of Nor$^\pm$ was sorbed on K$^+$-montmorillonite surface through interaction of its carboxyl group (Fig. 1). Thus, positively charged heterocyclic N atom of Nor$^\pm$ was far away from mineral surface and freely available to PAHs (π-electron donor). Except for π–π interaction as described above, cation–π should be another important reaction responsible for the enhanced sorption of PAHs by Nor$^\pm$. It was also the reason why the K_d values of PAHs in the presence of Nor$^\pm$ was remarkably increased compared to that in the presence of Nor$^+$ (Fig. 3). Cation–π bonding between electron-rich aromatic structures and metal ions and ammonium ions toward molecular recognition and selective metal binding had been well documented in the literatures [15,31]. For example, Qu et al. found that the presence of tetra-alkyl ammonium largely enhanced the sorption NAPH, PHEN and PYR on smectite mainly due to formation of strong cation–π EDA complexes between ammonium cation and PAHs [15]. For comparison, 1,3-DNB had an electron-depleted benzene ring, which was unfavorable for formation of cation–π interaction with Nor$^\pm$. Similarly, Nor$^-$ was sorbed on K$^+$-montmorillonite through the interaction of its carboxyl group (Fig. 1). The positive charge on heterocyclic N atom of Nor$^-$ and cation–π interaction with PAHs disappeared. π–π interaction should be responsible for the enhanced sorption of PAHs by Nor$^-$ [30]. Compared to Nor$^\pm$, PAHs sorption decreased rapidly at higher pH range (Fig. 3).

3.4. ^{1}H NMR studies

The interactions between PAHs (π-electron donors) and Nor$^+$ (π-electron acceptor) are supported by solution-phase ^{1}H NMR experiments. Placing a nucleus above or below an aromatic structure causes electronic shielding of the nucleus due to "ring current" effect. Thus, the ring current-induced upfield chemical shifts of ^{1}H NMR can serve as a strong evidence for face to face complexation of the probed molecule with aromatic structures. In previous studies, the observed ^{1}H/^{13}C NMR upfield chemical shifts have been used to support π–π EDA complexation between π-electron-acceptor compounds and PAHs (π-electron-donors) [32]. In this study, prominent [1]HNM upfield shifts are observed for Nor$^+$ in mixtures with PAHs (π-electron-donors). For example, the bands of —H on amino group and methylene on —CH$_2$CH$_3$ group of Nor$^+$ were shifted up to 0.3 ppm and 0.25 ppm in the presence of PYR, respectively (Fig. 4). The magnitudes of upfield shifts increased with an increase of PAHs concentrations and also correlated well with π-donor strength of PAHs (PYR > PHEN > NAPH). The observed trends clearly demonstrated formation of π–π EDA interaction and cation–π bonding between Nor$^+$ and PAHs in solution.

3.5. Solubility enhancement studies

To further verify the cation–π interaction between positively charged heterocyclic N atom of Nor$^+$ and PAHs, a solubility enhancement experiment was conducted. Fig. 5 shows the enhanced solubility of NAPH, PHEN, PYR vs. concentrations of Nor in aqueous solution at pH 4.0 and 9.0, respectively. Clearly, the presence of Nor increases the solubility of three PAHs, and the solubility enhancement correlates with π–donor ability of PAH (PYR > PHEN > NAPH). For example, at pH 4.0, the solubility of NAPH, PHEN and PYR increased up to 1.5 times, 2.8 times, and 17.7 times, respectively, in the presence of Nor compared to that in the absence of Nor due to possible occurrence of π–π, and cation–π interaction
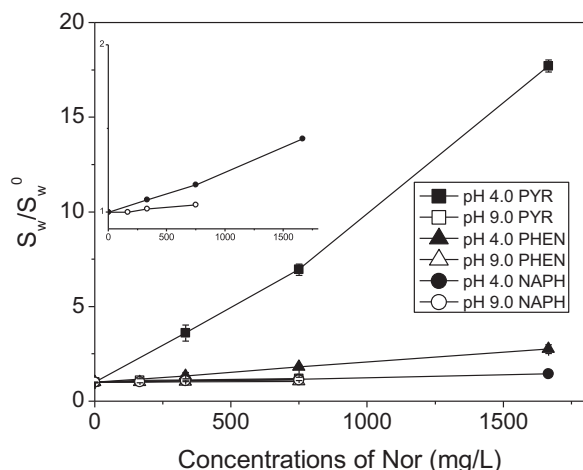
Fig. 5. Ratio of saturated solubility of NAPH, PHEN, and PYR in the presence of Nor to that in the absence of Nor vs. Nor concentrations at pH 4.0 and 9.0. The insert represents the solubility ratio of NAPH in the presence and absence of Nor.

at the examined maximum concentration of Nor^+. In contrast, Nor^- only increased the solubility of three PAHs slightly at pH 9.0 (up to 1.1 times for NAPH, 1.1 times for PHEN, and 1.2 times for PYR). These results of the maximum solubility enhancement by Nor^+ for PYR (17.7 times) than that by Nor^- (1.2 times) strongly suggested that PAHs form cation–π complexes with Nor^+ in aqueous solution.

4. Conclusions

In view of the foregoing study, it was found that Nor had different effects on different organic contaminants. For 1,3-DNB, the presence of Nor suppressed its sorption on K^+-montmorillonite due to their competition for the same sorption sites. FTIR study reveals that 1,3-DNB was sorbed on K^+-montmorillonite via cation–polar interaction of its $-NO_2$ groups with exchangeable K^+ and n–π electron donor–acceptor (EDA) interaction of 1,3-DNB (e^- acceptors) with oxygens of montmorillonite siloxane surfaces (e^- donors). While Nor was also sorbed on these sites through cation exchange, cation bridging and/or surface complexation.

In contrast, Nor increased the sorption of three PAHs on K^+-montmorillonite and the enhanced magnitude was positively correlated with π-donor strength of three PAHs. The enhanced effect of Nor on PAHs sorption was due to π–π interaction between the electron-depleted quinoline ring (π-electron acceptor) of Nor and PAHs (π-electron donor). Different species of Nor had different effects on the sorption of PAHs. Compared to Nor^+ and Nor^-, $Nor^{\pm}$ increased the sorption of PHEN and PYR more pronounced, which was attributed to additional formation of cation–π interaction between positively charged heterocyclic N atom of sorbed $Nor^{\pm}$ and PAHs.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.11.087.

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