Effect of background electrolytes on the adsorption of nitroaromatic compounds onto bentonite

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Abstract

To further elucidate interaction of nitroaromatic compounds with mineral surface, the sorption of m-dinitrobenzene (m-DNB) and nitrobenzene to original bentonite in aqueous solution containing different electrolytes (i.e., KCl, NH_4Cl, $CaCl_2$ and Tetramethy-lammonium bromide (TMAB)) was studied. The sorption of m-DNB was greatly enhanced with the presence of KCl and NH_4Cl, while little influence was observed with $CaCl_2$ and TMAB, following the order of KCl > $NH_4Cl \gg$ TMAB, $CaCl_2$, or DI water. For nitrobenzene, sorption enhancement only occurred at high nitrobenzene concentrations in the presence of KCl, and the solute equilibrium concentration at inflexion point was lowered with increasing KCl concentration. These sorption enhancements were significantly promoted with the increase of electrolyte concentration. The salting-out effect is insufficient to account for the sorption enhancement by original bentonite with increasing KCl or NH_4Cl concentration. X-ray diffraction patterns of bentonite suspensions indicated that the sorption enhancement of m-DNB was attributed to the intercalation of K^+ or NH_4^+ into bentonite interlayer and then dehydration with m-DNB to form inner-sphere complexes, which caused previously expanded bentonite interlayers to collapse in aqueous suspension, thus further enhanced the interaction of phenyl with siloxane surface. In comparison, the sorption enhancement of NB is attributed to the formation of outer-sphere complexes with K^+ at high solute-loadings (> 200–400 mg/kg). The sorption of m-DNB to initially modified TMA^+-bentonite and K^+-bentonite was almost the same as respective sorption to original bentonite in solution containing TMA^+ and K^+.

Key words: sorption; nitroaromatic compound; bentonite; cation type; wastewater treatment

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Introduction

Smectites are layered 2:1 aluminosilicates with structural negative charges, which are balanced with inorganic cations (e.g., Ca^{2+}, Mg^{2+}, Al^{3+}, K^+ and Na^+) in nature. Smectite clays can be modified through ion-exchange reactions utilizing inorganic or organic cations, and these modifications can dramatically alter the affinities of smectites for organic contaminants and pesticides (Smith *et al*., 1990; Haderlein *et al*., 1996; Zhu *et al*., 2003, 2007; Roberts *et al*., 2006; Li *et al*., 2007; Chen *et al*., 2008). Previous studies have shown that modified-smectite can be potentially used in wastewater treatment (Zhu and Chen, 2000; Zhu *et al*., 2000; Ma and Zhu, 2006, 2007; Zhu and Ma, 2008), and the implementation of *in-situ* and *ex-situ* remediation/immobilization practices in organic contaminated soil and groundwater (Boyd *et al*., 1988; Xu *et al*., 1997; Weissmahr *et al*., 1999). Nitroaromatic compounds (NACs) are commonly used as pesticides, explosives, intermediates in the synthesis of dyes, ammunition, and solvents. Their uses and manufacture have resulted in contamination of soils, sediments, and aquifers at military training and manufacturing sites. Recently, the aqueous surface chemistry of bentonites and their high affinity for NACs have attracted interests (Weissmahr *et al*., 1999; Boyd *et al*., 2001; Johnston *et al*., 2001; Sheng *et al*., 2002; Li *et al*., 2004; Charles *et al*., 2006; Chen *et al*., 2008) because the interaction of NACs with mineral surfaces plays an important role in regulating mobility, (bio)availability, toxicity and, fate of NACs in soil and groundwater (Weissmahr *et al*., 1999; Roberts *et al*., 2007a, 2007b).

Previous studies have provided inconsistent interaction mechanisms of NACs adsorption on clay surfaces (Weissmahr *et al*., 1997; Li *et al*., 2004, 2006, 2007; Charles *et al*., 2006; Chen *et al*., 2008). The adsorption of NACs with clay mineral surfaces in organic solvent was interpreted in terms of H-bonding and/or direct coordination of $-NO_2$ group(s) to exchangeable cations or hydration water of exchangeable cations (Saltzman and Yariv, 1975, 1976). Some researchers illustrate the high affinity of certain NACs for smectites in aqueous solution by considering an electron donor-acceptor (EDA) surface complex between the π-electrons of the aromatic ring and nonbonding electrons of the basal oxygen atoms on

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the siloxane surface as a potential adsorption mechanism (Haderlein and Schwarzenbach, 1993; Haderlein *et al.*, 1996; Weissmahr *et al.*, 1997). Recently, the role of EDA complexes in adsorption of NACs has been challenged. Some studies suggested that the complexation of the -NO$_2$ groups of NACs and exchangeable cations on the clay is a primary sorption mechanism for the strong affinity of nitroaromatics on aluminosilicate clay in aqueous systems (Boyd *et al.*, 2001; Johnston *et al.*, 2001; Li *et al.*, 2004, 2007). The –NO$_2$ groups can form inner- and/or outer-sphere complexes effectively with the weakly hydrated exchangeable cations (i.e., K$^+$), whereas the tightly bound water molecules surrounding more strongly hydrated cations (e.g., Ca^{2+}, Mg^{2+}, Ba^{2+}) inhibit the formation of such complexes (Li *et al.*, 2004). Partial solute dehydration associated with sorption in smectite interlayers with optimal distance (about 1.23 nm) makes the aromatic ring in nitroaromatics orient parallel to clay siloxane sheets, which enhances the stability of the complexes via nonspecific van der Waals interactions with the hydrophobic portion of clay surfaces and minimizes its contact with water (Boyd *et al.*, 2001; Johnston *et al.*, 2001; Li *et al.*, 2007).

Organobentonite has been regarded as an effective sorbent for organic pollutants removal in wastewater and groundwater. Recently, a novel technology based on simultaneously synthesis of organobentonite and removal of organic pollutants from water in one-step (termed one-step treatment) was introduced, which drastically reduces the cost of the treatment without affecting the removal efficiency (Ma and Zhu, 2007; Zhu and Ma, 2008). High affinity of NACs in aqueous solution for clay minerals presaturated with the weakly hydrated exchangeable cations (e.g., K$^+$ and NH$_4^+$) was extensively reported, but to achieve highly efficient removal of NACs from water with mixture of original bentonite and electrolytes in a one-step treatment. The studies on the adsorption of NACs by original bentonite in aqueous solution with different background electrolytes were needed.

The objective of this study was to evaluate the influence of different background electrolytes on the sorption of NACs to the original bentonite in aqueous solution. The sorption of *m*-dinitrobenzene (*m*-DNB) and nitrobenzene to the original bentonite in aqueous solution containing different electrolytes (i.e., KCl, NH$_4$Cl, CaCl$_2$ and TMAB) was evaluated. X-ray diffraction patterns of original bentonite suspension containing different electrolytes with and without NACs were recorded to quantify interlayer distances. The results help reveal the influence of electrolytes on the clay interlayer environment and hence further elucidate the interaction mechanisms of NACs with clay minerals in aqueous solution.

1 Materials and methods

1.1 Materials and reagents

Nitrobenzene (NB) and *m*-dinitrobenzene (*m*-DNB) were used as sorbates. The selected physicochemical prop-

erties and structures of sorbates are presented in Table 1. KCl, NH$_4$Cl, CaCl$_2$ and tetramethylammonium bromide (TMAB) are selected as the background electrolytes and used for synthesizing certain modified bentonite. These chemicals were all of analytical grade. Original bentonite saturated primarily with Ca^{2+} from Autonomic Inner Mongolia, China, was selected as a model mineral. The air-dried bentonite sample was sieved to obtain particles less than 165 μm in all experiments. The bentonite BET-N$_2$ surface area (SA), organic carbon content (f_{oc}), and cation-exchanged capacity (CEC) were 61 m^2/g, 0.04%, and 108 cmol/kg, respectively.

K$^+$-bentonite, NH$_4^+$-bentonite and 100TMAB-bentonite were prepared for sorption experiment and XRD analysis. K$^+$-bentonite was synthesized by reacting original bentonite with KCl solution. A total of 40 g of original bentonite was mixed with 2000 mL of 0.5 mol/L KCl aqueous solution and was stirred for 2 h. The treated bentonite was separated from water by vacuum filtration. The procedure was then repeated 9 times to replace all Ca^{2+} in the bentonite with K$^+$. The fully exchanged K$^+$-bentonite was then washed by distilled water until no Cl$^-$ was detected. Similarly, the NH$_4^+$-bentonite was prepared by exchanging Ca^{2+} with NH$_4^+$. 100TMAB-bentonite was synthesized by reacting bentonite with TMAB in aqueous solution. A total of 100 g of previously dried bentonite was mixed with 500 mL of aqueous solution containing 16.632 g TMAB, equal to 100% of bentonite's CEC. The mixture was subjected to mechanical stirring for 4 h at 60–70°C. The treated bentonite was separated from water by vacuum filtration and washed three times by distilled water. The organobentonite was then oven-dried at 80–90°C, and mechanically ground with a mortar and pestle to less than 165 μm. The final complex was named as 100TMAB-bentonite.

1.2 Batch sorption experiment

Sorption isotherms of *m*-DNB and NB by original bentonite from aqueous electrolyte solutions (KCl, NH$_4$Cl, CaCl$_2$ and TMAB) were measured using a batch equilibrium method. A series of initial *m*-DNB concentrations were prepared using aqueous KCl solutions (0 and 0.50 mol/L), NH$_4$Cl solutions (0.05, 0.08, 0.1, 0.2, 0.5, 0.8 and 1.0 mol/L), CaCl$_2$ solutions (0.50 mol/L) or TMAB solution (44.37 g/L, equal to 100% CEC of bentonite). A series of initial NB concentrations were prepared using either aqueous KCl solution (0, 0.005, 0.01, 0.02, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8 and 1.0 mol/L) or NH$_4$Cl solution (0.005, 0.05 and 0.5 mol/L). Initial concentrations ranged from 0 to 500 mg/L for *m*-DNB and from 0 to 1600

Table 1   Properties of nitrobenzene (NB) and *m*-dinitrobenzene (*m*-DNB)

	Formula	MW (g/mol)	S (μg/mL)	K_{ow}	Density (g/cm^3)
NB	C$_6$H$_5$NO$_2$	123.1	1936	71	1.196
m-DNB	C$_6$H$_4$N$_2$O$_4$	168.1	574.9	31	1.600

MW: molecular weight; *S*: aqueous solubility at room temperature; K_{ow}: octanol-water partition coefficient.

mg/L for NB, which approached their individual aqueous solubility (Table 1). Original bentonites were weighed into 8 mL-vials, and the initial solutions were added, and then the vials were sealed using Teflon-lined screw caps. Isotherms consisted of ten concentration points and each point including the blank, was run in duplicates. The vials were placed on a rotating shaker and then rotated end-over-end (20 r/min) in the dark at room temperature (25 ± 0.5°C) for 24 h. Preliminary tests indicated that apparent equilibrium was reached before 12 h. The solution was separated from remaining solids by centrifugation at 4000 r/min for 15 min. An aliquot amount of supernatant was removed and diluted with deionized distilled water. The equilibrium concentrations were measured using a UV-2550 spectrophotometer (Shimadzu, China). Because the sorption by the sample vials was minimal and no biodegradation and photo-decomposition were detected through the experiment, the sorbed-amount of sorbates was calculated by mass difference. The sorption of *m*-DNB to K$^+$-bentonite, NH$_4$$^+$-bentonite and 100TMAB-bentonite was also conducted to evaluate the one-step process.

All the data were processed by the logarithmic form of Freundlich equation (Eq. (1)):

$$\log Q = \log K_f + N \log C_e \qquad (1)$$

where, Q (mg/kg) is the amount sorbed per unit weight of sorbent; C_e (mg/L) is the equilibrium concentration; K_f ((mg/kg)/(mg/L)^N) is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature. The sorption coefficient ($K_d = Q/C_e$) of NACs was determined within the quasi-linear initial part of the NAC adsorption isotherms by batch experiments in aqueous (Weissmahr *et al.*, 1997). K_d can be used to describe the affinity of a given NAC to the clay mineral surface. The following discussion on electrolyte type and concentrations, and compound specific factors affecting the adsorption of NACs to clay minerals will primarily be based on the comparisons of K_d values of NACs (Haderlein *et al.*, 1996).

1.3 XRD patterns of bentonite suspensions

The XRD patterns of original bentonite suspensions in distilled water, 0.5 mol/L CaCl$_2$ solution, 0.5 mol/L KCl solution, 0.5 mol/L NH$_4$Cl solution and 44.37 g/L TMAB with and without 500 mg/L *m*-DNB were measured using a ARL X'TRA X-ray diffractometer (Thermo Scientific, US), equipped with CuK_α radiation with a liquid transmission cell. The XRD patterns of original bentonite suspensions in 0.5 mol/L KCl solution with different nitrobenzene-loadings were also recorded. The original suspensions were prepared by the same process based on sorption experiments (e.g., same solid-to-solution ratio and equilibrium time) except magnifying the amount of solid mass and solution volume. The NB-loadings onto bentonites were calculated from sorption isotherms. Approximately 1 mL of clay suspension was transferred to a liquid-transmission XRD cell and was analyzed using the diffractometer. The scanning angle (2θ) ranged from 1 to 32° at step of 0.05°, and the scanning time was

2 s for per step. The air-dried original bentonite, K$^+$-bentonite and NH$_4$$^+$-bentonite samples were also recorded for comparison with bentonite suspensions. The interlayer spacings (d_{001}) were calculated according to the XRD peaks.

2 Results and discussion

2.1 Sorption of *m*-DNB to original bentonite in different electrolyte solutions

Sorption isotherms of *m*-DNB to the original bentonite (Ca^{2+}-bentonite) in aqueous solution with and without electrolytes are presented in Fig. 1. Sorption isotherms for original bentonite in 0.5 mol/L KCl and 0.5 mol/L NH$_4$Cl were nonlinear with the curvature concave to the abscissa, indicating a site-limiting sorption process. Sorption isotherms for original bentonite in DI water, 0.5 mol/L CaCl$_2$ and 44.37 g/L TMAB solutions were essentially linear. The sorption data fit well with Freundlich equation (Table 2). No apparent difference in sorption *m*-DNB to original bentonite was observed in DI water, 0.5 mol/L CaCl$_2$ and 44.37 g/L TMAB solutions. The magnitudes of sorption by original bentonite in 0.5 mol/L KCl, 0.5 mol/L NH$_4$Cl were much greater than those in 0.5 mol/L CaCl$_2$ and 44.37 g/L TMAB solutions, following the order of KCl > NH$_4$Cl ≫ TMAB, CaCl$_2$, or DI water. According to the sorption coefficients (K_d, Table 2), the original bentonite adsorbed *m*-DNB in 0.5 mol/L KCl and 0.5 mol/L NH$_4$Cl solutions, respectively, were 260 and 50 times more than in DI water or 0.5 mol/L CaCl$_2$. The presence of 0.5 mol/L CaCl$_2$ had little impact on the sorption of *m*-DNB, hence sorption enhancement by 0.5 mol/L KCl and 0.5 mol/L NH$_4$Cl are not attributed to salting out effects, and this is consistent with previous study (Li *et al.*, 2007).

The size, structure and hydration properties of exchangeable cations associated with smectites strongly affected the clay interlayer environment, and hence determined the degree of NACs sorption and the sorption mechanism(s) (Boyd *et al.*, 2001; Li *et al.*, 2007). The
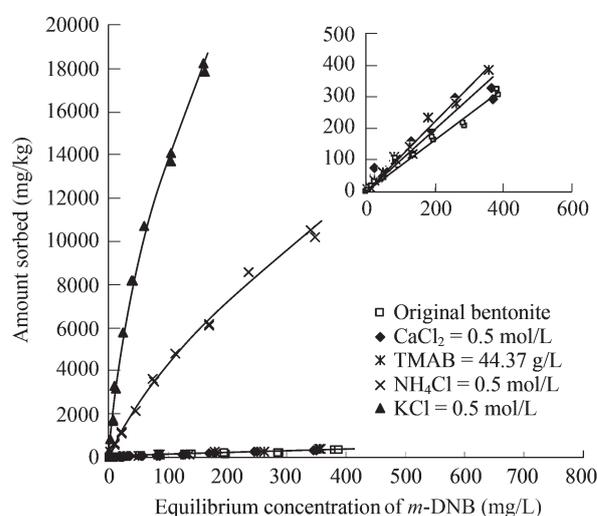
Fig. 1 Sorption isotherms of *m*-DNB to the original bentonite in different electrolyte solutions and in deionized distilled water.

Table 2   Regression parameters of nitrobenzene (NB) and m-dinitrobenzene (m-DNB) to 100TMAB, K^+-bentonite, and original bentonite with and without the presence of KCl, NH_4Cl, $CaCl_2$ and TMAB in solution

Sorbates/electrolyte	Sorbent	Electrolyte conc. (mol/L)	Freundlich regression parameters			Linear parameter		Maximum slope
			$\log K_f$	N	R^2	R^2	K_d	
m-DNB/NH_4Cl	Original bentonite	0.00	0.248	0.864	0.993	0.982	0.876	
		0.05	0.908	0.966	0.974	0.955	7.322	
		0.08	1.226	0.937	0.993	0.990	12.09	
		0.10	1.289	0.959	0.996	0.994	15.63	
		0.20	1.578	0.918	0.997	0.991	23.50	
		0.50	1.970	0.827	0.997	0.995	48.95	
		0.80	2.204	0.758	0.993	0.992	76.64	
		1.00	2.369	0.712	0.995	0.980	100.6	
m-DNB/KCl	Original bentonite	0.50	2.586	0.800	0.987	0.991	259.4	
m-DNB/$CaCl_2$	Original bentonite	0.50	0.041	1.039	0.932	0.937	0.981	
m-DNB/TMAB	Original bentonite	44.37 g/L	0.286	0.893	0.989	0.988	1.099	
m-DNB/H_2O	100TMAB-bentonite	–	0.301	0.887	0.998	0.993	1.093	
m-DNB/H_2O	K^+-bentonite	–	3.415	0.382	0.984	–	–	
NB/KCl	Original bentonite	0.00	0.625	0.602	0.990	0.975	0.880	
		0.01	–0.503	0.957	0.918	0.929	0.291	1.846
		0.02	–0.327	0.88	0.81	0.736	0.254	3.304
		0.05	–0.323	0.879	0.841	0.83	0.273	10.581
		0.08	–0.030	0.825	0.914	0.841	0.279	25.277
		0.10	0.201	0.724	0.922	0.934	0.338	28.039
		0.20	–0.285	0.951	0.951	0.978	0.386	59.882
		0.50	0.658	0.712	0.946	0.966	1.109	49.252
		0.80	0.361	0.886	0.987	0.989	1.279	59.314
		1.00	0.452	0.91	0.987	0.986	1.793	53.763
NB/NH_4Cl	Original bentonite	0.005	0.108	0.648	0.823	0.818	0.125	
		0.050	0.410	0.626	0.934	0.929	0.196	
		0.500	0.339	0.761	0.985	0.973	0.424	

For NB/KCl systems, due to distinct shapes under and above 250 μg/mL of nitrobenzene to the original bentonite in KCl solution, the isotherms were regressed over the concentration of < 250 mg/L. For m-DNB, the linear regressions were conducted for the whole isotherms excluding to original bentonite in 0.5 mol/L KCl solution and 0.5–1.0 mol/L NH_4Cl solution. Due to high nonlinear, the linear regression for m-DNB to original bentonite in 0.5 mol/L KCl solution and in 0.5–1.0 mol/L NH_4Cl solution were conducted at < 50 μg/mL and < 80 μg/mL, respectively. For NB, the linear regressions were conducted over the concentration of < 250 mg/L. Maximum slope is attained by the sharpest section of the isotherm curve of NB to original bentonite in KCl solution.

NAC adsorption is known to take place at external siloxane surfaces of two-layer clays such as kaolinites and to occur at the interlayer surfaces of three-layer clays such as bentonite (Weissmahr *et al.*, 1997). Therefore, the XRD patterns of bentonite suspensions in electrolyte solution with and without m-DNB (Fig. 2) were used to probe the interlayer environment of bentonite, and then were employed to elucidate the adsorption mechanism of m-DNB to original bentonite suspension. The interlayer spacing (d_{001}) of original bentonite (air-dried) is 1.55 nm (Fig. 2), indicating that the original bentonite is saturated with hydrated Ca^{2+} with two layers of interlayer water under ambient air-dried conditions. When the original bentonite was added into water, the d_{001} value increased to 1.90 nm, forming three to four water layers around Ca^{2+} in aqueous solution, which is independent of $CaCl_2$ and/or m-DNB. The large hydration sphere of Ca^{2+} diminishes the effective size of adsorptive domains (hydrophobic nanosites) between exchangeable cations. In addition, the great hydration energy (–1580 kJ/mol) results in more strongly held water molecules in the hydration sphere of Ca^{2+}, which inhibits the dehydration of m-DNB by replacing interlayer water molecules as well as the development of strong interactions between polar functional groups of m-DNB and Ca^{2+}. Therefore, the original bentonite in DI water or $CaCl_2$ solution can not effectively sorb m-DNB.

When the weakly hydrated cations such as NH_4^+ or K^+ (0.5 mol/L) were added, the interlayer distance (d_{001}) of wet bentonite decreased from 1.90 to 1.51 and 1.54 nm, indicating that NH_4^+ and K^+ are intercalated into the interlayer of the clay. Compared to naturally occurring inorganic exchangeable cations commonly associated with bentonite (e.g., Na^+, Ca^{2+}, Mg^{2+}), the relatively low hydration free energies for NH_4^+ (–292 kJ/mol) and K^+ (–314 kJ/mol) result in less water surrounding the cations rendering more mineral siloxane surface available for adsorption (Chen *et al.*, 2005). In the presence of m-DNB, the d_{001} value of bentonite suspension in 0.5 mol/L NH_4Cl and 0.5 mol/L KCl solutions further decreased to 1.29 nm and 1.25 nm, respectively, which are comparable to that of NH_4^+-bentonite (1.24 nm and K^+-bentonite (1.22 nm) samples (air-dried state). These phenomena suggest that NH_4^+ or K^+ in the interlayer environments is dehydrated further by m-DNB through forming inner-sphere complexes between the $-NO_2$ group and NH_4^+ (or K^+). Both O atoms of $-NO_2$ group are directly coordinated to a single NH_4^+ (or K^+) with an average band distance of 0.31 ± 0.02 nm. The clay interlayer distance at a basal spacing of 1.25–1.29 nm corresponds to the approximate thickness of the aromatic ring (0.3 nm) plus the thickness of clay layer (0.96 nm), indicating that intercalated NAC molecules align parallel to clay sheets with the planar rings directly contacting the opposing clay siloxane surfaces (Li *et al.*, 2004). The optimal interlayer distances that approx-
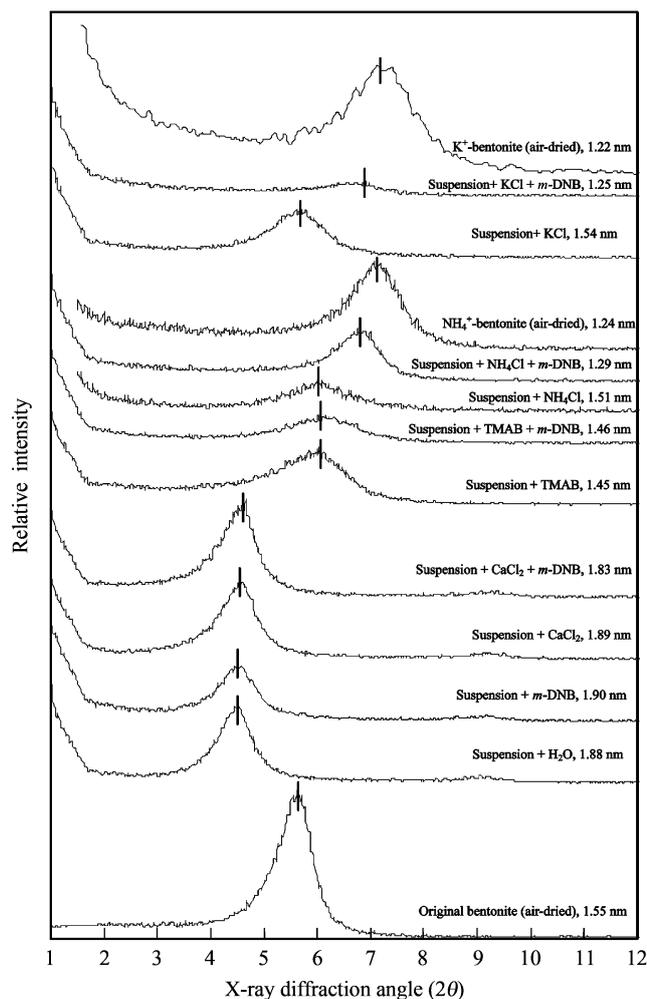
Fig. 2 X-ray diffraction patterns of original bentonite suspensions in DI water, 0.5 mol/L CaCl₂, 44.37 g/L TMAB, 0.5 mol/L NH₄Cl and 0.5 mol/L KCl solutions with and without 500 mg/L *m*-DNB (solid-to-solution ratio equals to corresponding sorption experiment), and air-dried original bentonite, K⁺-bentonite and NH₄⁺-bentonite.

imate the molecular thickness of NACs hence promoting the simultaneous interaction of the planar aromatic rings with opposing siloxane surfaces and solute dehydration (Roberts *et al.*, 2006). The bentonite suspension in 0.5 mol/L NH₄⁺ solution was at least 45 times more effective (on a unit mass basis) than the bentonite suspension in TMA⁺ solution for *m*-DNB sorption over the concentration range studied. The greater affinity of bentonite suspension for *m*-DNB in NH₄⁺ solution may result from the formation of complexes between exchanged ammonium and the –NO₂ groups of the NAC (Boyd *et al.*, 2001). Thus, –NO₂ complexes with ammonium would be expected to be stronger than those with TMA⁺, which is in agreement with previous report (Boyd *et al.*, 2001).

From Fig. 2, the interlayer spacing of the original bentonite suspension is decreased from 1.88 nm in water to 1.45 nm in TMAB solution, suggesting that the weakly hydrated TMA⁺ (hydration energy = –219 kJ/mol) is intercalated into the interlayer space by exchanging strongly hydrated Ca²⁺. Several studies have observed that the final resultants (TMAB-bentonite complex) are expected to exhibit sorption enhancement for *m*-DNB and certain

pesticide (Roberts *et al.*, 2006). It is believed that the greater affinity of NACs for TMA⁺-bentonite is due in part to complex formation between the weakly exchangeable cation and –NO₂ groups (Roberts *et al.*, 2006). But in current study, the presence of weakly hydrated TMA⁺ cation cannot promote the sorption of *m*-DNB to original bentonite. There are several reasons. First, the TMAB molecules were comparably large to occupy the interlayer space of clay to inhibit sorption (steric hindrance). Second, the cation exchange capacity of the bentonite (108 cmol/kg) was much higher than that used in the study mentioned (82 cmol/kg); bentonite with a lower surface charge density typically manifest a greater adsorption because they contain more neutral nanosized adsorptive domains on the siloxane surfaces between exchangeable cations (Li *et al.*, 2007). Third, the larger molecular size of TMA would inhibit direct interactions between –NO₂ and TMA⁺, because the locus of positive charge in TMA⁺ is buried inside four methyl groups (Boyd *et al.*, 2001). The presence of *m*-DNB can not produce dehydration of TMA⁺ in the interlayer of bentonite to the optimal interlayer distance (1.25 nm, Fig. 2) and thus inhibit additional interaction between the planar aromatic rings and opposing siloxane surfaces. Therefore, sorption enhancement is attributed to the formation of clay quasicrystals with reduced interlayer distances rather than to the salting-out effect. Dehydration of *m*-DNB is apparently a significant driving force for sorption, and sorption of *m*-DNB causes previously expanded clay interlayers to dehydrate and collapse in aqueous suspension (Li *et al.*, 2007).

2.2 Sorption of nitrobenzene to original bentonite in different electrolyte solutions

Sorption isotherms of nitrobenzene by original bentonite from KCl aqueous solutions (0, 0.005, 0.01, 0.02, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8, and 1.0 mol/L) are presented in Fig. 3. The upward isotherms suggest cooperative sorption in which weak NB-bentonite interactions are presumed to occur at low aqueous concentrations, while at higher aqueous concentrations the sorbed NB promotes further sorption due possibly to the creation of additional sorptive sites. The regression data at low and high concentration ranges are presented in Table 2. For sorption of NB in NH₄Cl as illustrated in Table 2, no significant enhancement was observed even in 0.5 mol/L NH₄Cl solution. Sorption of NB in KCl solutions at low concentrations was nearly the same as its sorption in NH₄Cl (Table 2). But at higher solute concentrations, the sorption of NB was greatly enhanced with increasing KCl concentration (Fig. 3). As shown in Fig. 3a, there exists an obvious inflexion point in each sorption isotherm, indicating a changing sorption mechanism with NB equilibrium concentration during the sorption. The equilibrium concentrations at inflexion point in each isotherms decrease with increasing KCl concentration, i.e. from 650 mg/L NB at 0.08 mol/L KCl to 244 mg/L NB at 1.0 mol/L KCl (Fig. 3b). The inflexion point turns up at a certain sorbed amount of NB (e.g., 200–400 mg/kg), which is the first report as we know.

Figure 4 shows XRD patterns of bentonite suspension
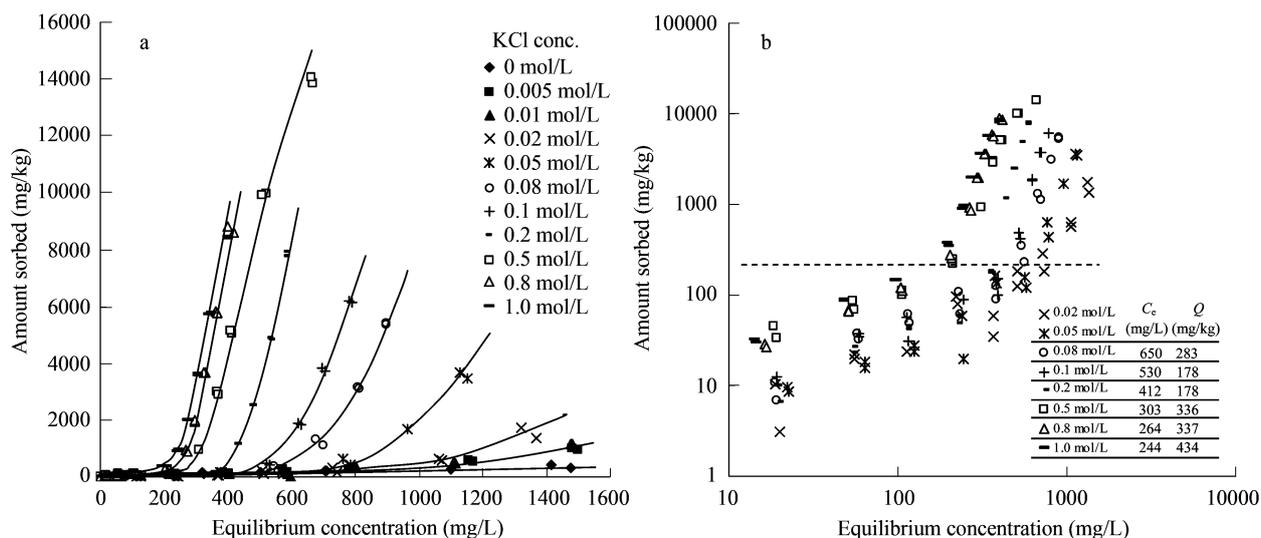
Fig. 3 Effect of KCl concentration on the sorption of nitrobenzene to original bentonite. Sorption isotherms (a) and their logarithmic forms (b). C_e and Q are the NB equilibrium concentrations and sorbed amount at the inflexion point at different KCl concentrations.

with different NB-loadings with 0.5 mol/L KCl, comparing with NB-free control. At 0.5 mol/L KCl solution, the XRD pattern of bentonite suspension without the presence of NB exhibited a broad peak centered at 5.6° (2θ). This angle corresponds to a basal spacing of 1.54 nm, which indicates two layers of water molecules between each clay layer in the quasicrystals (Li *et al.*, 2007). The interlayer spacings of these samples decreased from 1.54 to 1.51 nm, when the sorbed amount of NB increased from 0 to 1.30×10^3 mg/kg. When the sorbed amount continuously increased to 1.04×10^4 and even 1.46×10^4 mg/kg, the interlayer spacing still is 1.51 nm. At high NB concentrations, $-$NO$_2$ groups were indirectly coordinated to K$^+$ through the intermediation of water. These outer-sphere complexes exhibited average K–O distance of 0.51 ± 0.03 nm (K–NB). Unlike the sorption of *m*-DNB with bentonite suspension in KCl solution, the interlayer spacing of bentonite did not decrease as low as 1.25 nm. Generally, good electron acceptors of NACs strongly adsorb to clays, while poor

electron acceptors exhibit very low affinities (Weissmahr *et al.*, 1997). Therefore, compared with *m*-DNB, NB is a poor electron acceptor and exhibited low sorption and weak dehydration.

2.3 Effects of electrolyte concentrations in background solution on sorption enhancement

As shown in Fig. 5, the sorption enhancement of *m*-DNB to original bentonite suspension in NH$_4$Cl solution increased with the increase of NH$_4$Cl concentrations. Sorption of NB with high concentration to original bentonite suspension in KCl solution was also raised with increasing electrolyte concentration (Fig. 3). These observations are similar to our previous report that the sorption enhancement of *m*-DNB to original bentonite in KCl aqueous solutions was well in accord with the concentrations of KCl (Chen *et al.*, 2008).

The sorption coefficients (K_d, Table 2) of NACs (i.e.,
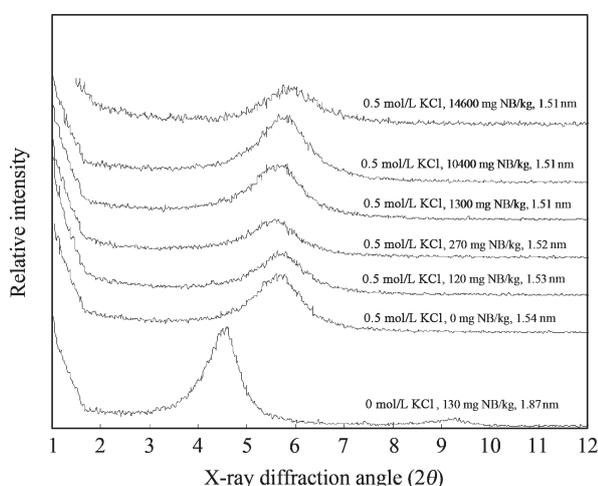
Fig. 4 X-ray diffraction patterns of original bentonite suspensions in 0.5 mol/L KCl solution with different NB-loadings (solid to solution ratio equals to that of corresponding sorption experiment).
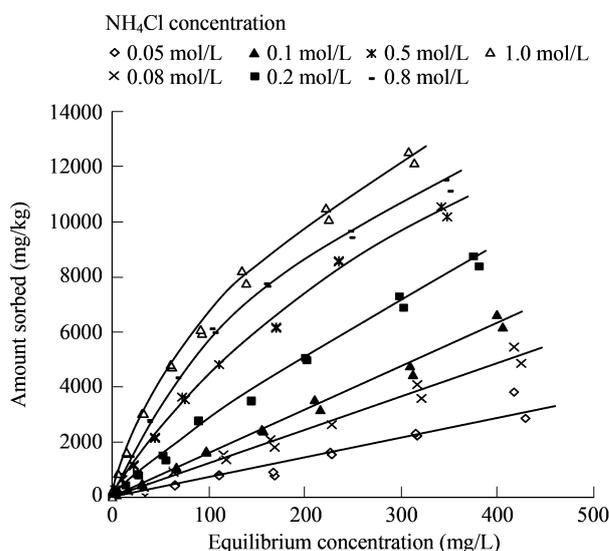
Fig. 5 Effect of NH$_4$Cl concentrations (0.05–1.0 mol/L) on the sorption of *m*-DNB to original bentonite in aqueous solution.
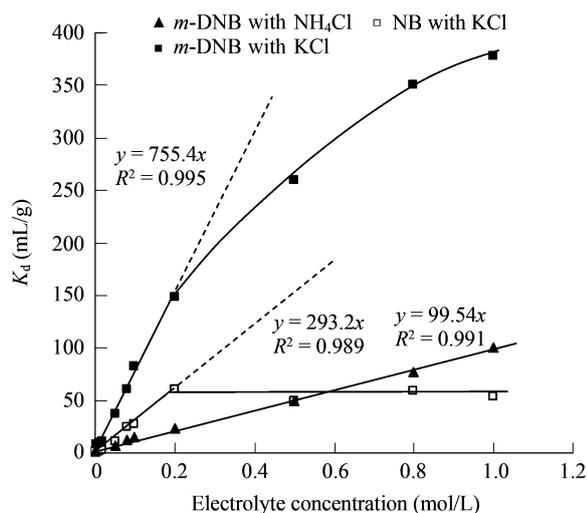
Fig. 6 Relationship of sorption coefficients (K_d) of *m*-DNB with NH$_4$Cl and KCl and relationship of maximum slopes of NB with KCl (The data of K_d for *m*-DNB–KCl were cited from Chen *et al.*, 2008).

m-DNB and NB) correlated with electrolyte concentrations (KCl or NH$_4$Cl) are shown in Fig. 6. The K_d values of *m*-DNB in NH$_4$Cl solution increase linearly with increasing electrolyte concentrations from 0.05 to 1.0 mol/L, i.e., K_d = 99.54C_{NH_4Cl} (R^2 = 0.991). The K_d values of *m*-DNB in KCl solution increased linearly with KCl concentrations at below 0.2 mol/L, i.e., K_d = 755.4C_{KCl} (R^2 = 0.995), and above 0.2 mol/L KCl the practical sorption coefficients were lower than the predicted value by the linear equation (Chen *et al.*, 2008). Enhanced adsorption of *m*-DNB with increasing KCl or NH$_4$Cl concentration was attributed to the formation of the inner-sphere complexes between -NO$_2$ in *m*-DNB and cations (K$^+$ or NH$_4^+$) and consequential reduction of the amount of water in the clay interlayers, which facilitate the intercalation of *m*-DNB in clays by specific interaction between phenyl ring and the siloxane of inner surface of the bentonite. Additionally, the sorption enhancement of *m*-DNB by KCl was 7 times that by NH$_4$Cl when electrolyte concentration below 0.2 mol/L.

The K_d value of NB in KCl solution increases linearly

with the electrolyte concentration at the range of 0.01–0.2 mol/L, i.e., K_d = 293.2C_{KCl} (R^2 = 0.989), and then reaches a constant value (55 g/mL) when the concentration of KCl exceeds 0.2 mol/L. This may be attributed to the formation of outer-sphere complexes between –NO$_2$ in NB with K$^+$ which can not further dehydrate significantly the interlayer water to induce specific interaction (e.g., EDA). The linear slope of K_d for *m*-DNB-C_{KCl} was more than 2.5 times that for NB-C_{KCl}. Compared with *m*-DNB/KCl or *m*-DNB/NH$_4$Cl systems, the absence of specific interaction of phenyl ring of NB with siloxane inner surface of bentonite resulted in a constant K_d for NB at high KCl concentrations.

As illustrated above, the sorption enhancement was attributed to the interaction between the exchanged cations (K$^+$ or NH$_4^+$) and NACs (*m*-DNB or NB), which can be described by the following Eq. (2).

$$M^+ + NACs \xrightarrow{K} M^+\text{-NACs} \qquad (2)$$

where, M$^+$ is the exchanged cations (K$^+$ or NH$_4^+$); NACs is the sorbed *m*-DNB or NB; and M$^+$-NACs is the complex. Hence, the reaction constant K could be depicted as:

$$K = \frac{C_{M^+\text{-NACs}}}{C_{M^+} \times C_{NACs}} \qquad (3)$$

$$C_{M^+\text{-NACs}} = Q \times m/V \qquad (4)$$

$$C_{NACs} = C_e \qquad (5)$$

where, m is the mass of sorbent; V is the volume of solution. According to Eqs. (3)–(5), sorption coefficient (K_d) could be calculated as follow,

$$K_d = K \times C_{M^+} \times V/m \qquad (6)$$

In our experiment, the parameters of V and m were constants, therefore, Eq. (6) could be rewritten as Eq. (7).

$$K_d = b \times K \times C_{M^+} \qquad (7)$$

This equation can be used to explain why the sorption coefficients were proportional to the concentrations
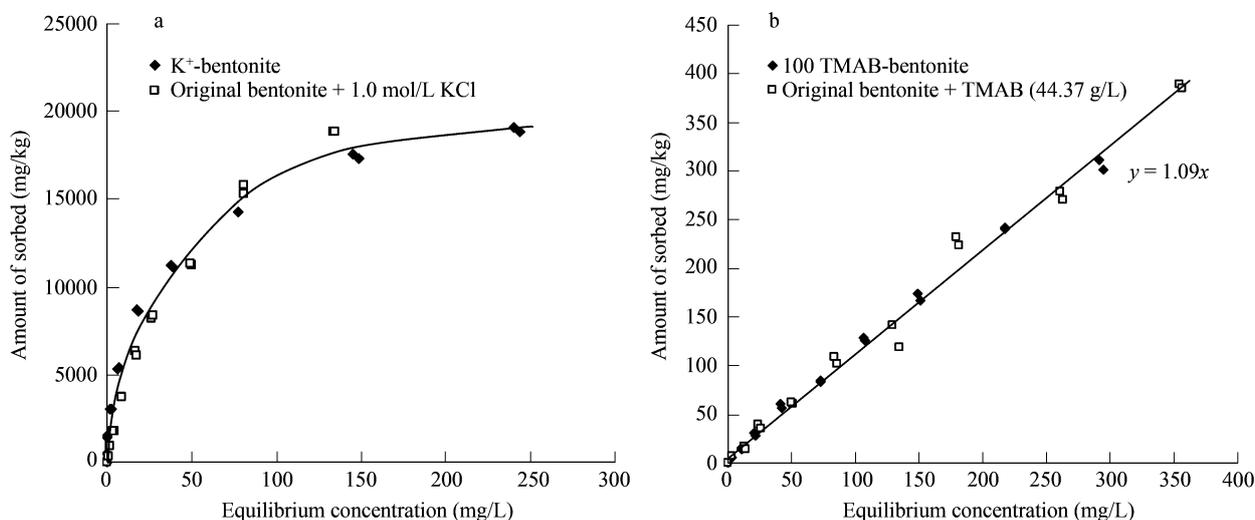
Fig. 7 Sorption isotherms of *m*-DNB to the original bentonite in KCl (1.0 mol/L) aqueous solution and K$^+$-bentonite (synthesized) (a), and isotherms of *m*-DNB to the original bentonite in TMAB 44.37 g/L aqueous solution and 100TMAB-bentonite (synthesized) (b).

of electrolytes in the background solution, and why the sorption enhancement of *m*-DNB by KCl was greater than NB in KCl and *m*-DNB in NH$_4$Cl because of a larger reaction constant of *m*-DNB-KCl.

2.4 Comparison of one-step treatment with ordinary sorption process

The sorption isotherms of *m*-DNB to K$^+$-bentonite and to 100TMAB-bentonite were also studied to examine whether there are distinct differences between sorption of *m*-DNB to primarily modified bentonite and to original bentonite suspension in solution containing the cations used in modifying bentonite. As shown in Fig. 7, no distinctive difference between the sorption of *m*-DNB to K$^+$-bentonite and to original bentonite in 1.0 mol/L KCl aqueous solution (i.e., one-step process) was observed. The sorption of *m*-DNB to 100TMAB-bentonite and to original bentonite in 44.37 g/L TMAB aqueous solution (equal to 100TMAB-bentonite sorbing *m*-DNB) was nearly the same (Fig. 7b). Therefore, there is a potential for using original bentonite suspension containing weakly hydrated cations (e.g., KCl and NH$_4$Cl) to abate the NACs pollutants in industrial wastewater.

3 Conclusions

Sorption of *m*-dinitrobenzene to the original bentonite suspension was significantly influenced by the type and concentration of coexisting cations, and the magnitude of sorption followed the order of KCl > NH$_4$Cl ≫ TMAB, CaCl$_2$, or DI water. For nitrobenzene, sorption enhancement occurred only at the high solute concentrations in KCl solution, and the solute equilibrium concentration at inflexion point was lowered with increasing KCl concentration. These sorption enhancements were significantly promoted with the increase of electrolyte concentrations. The salting-out effect was insufficient to account for the observed sorption enhancement by original bentonite with increasing KCl or NH$_4$Cl concentration. X-ray diffraction patterns of bentonite suspensions indicated that the sorption enhancement of *m*-DNB was attributed to the intercalation of K$^+$ or NH$_4^+$ into bentonite interlayer and then dehydration with *m*-DNB to form inner-sphere complexes, which caused previously expanded bentonite interlayers to collapse in aqueous suspension, thus further favoring the interaction of phenyl with siloxane surface. In comparison, the sorption enhancement of NB was attributed to the formation of outer-sphere complexes with K$^+$ at high solute-loadings (> 200–400 mg/kg). Therefore, the original bentonite suspension containing weakly hydrated cations (e.g., KCl and NH$_4$Cl) can be used to treat NACs pollutants in industrial wastewater.

Acknowledgments

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