

# Enhanced sorption of naphthalene and nitroaromatic compounds to bentonite by potassium and cetyltrimethylammonium cations

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## Abstract

Sorption of naphthalene, *p*-nitrotoluene, nitrobenzene and *m*-dinitrobenzene from water to original bentonite, original bentonite in KCl solutions, and an organobentonite (i.e., 100CTMAB) was compared. The affinities of sorbates with original bentonite were extremely weak and similar (sorption coefficient ( $K_d$ ) = 0.41–0.94 mL/g) regardless of their properties and structures. Sorption was dramatically enhanced by 100CTMAB due to strong retention of CTMA<sup>+</sup>-derived organic phase and the exposed-siloxane surfaces. The resultant  $K_d$  increased by 5360, 780, 40 and 200 times, respectively, for naphthalene, *p*-nitrotoluene, nitrobenzene and *m*-dinitrobenzene, reversed with their aqueous solubility. The presence of K<sup>+</sup> promoted sorption of nitroaromatic compounds (50–400 times). The enhanced-mechanism for nitrobenzene at low concentrations and *p*-nitrotoluene was derived mainly from weak van der Waals interaction between aromatic rings and siloxane surfaces, while for nitrobenzene at high concentrations and *m*-dinitrobenzene the mechanisms were attributed to primary complexation of –NO<sub>2</sub> group with K<sup>+</sup> and then strong interactions by electron donor–acceptor. Sorption of *m*-dinitrobenzene enhanced linearly with K<sup>+</sup> concentrations of 0.005–0.20 mol/L, and overshadowed the role of 100CTMAB when K<sup>+</sup> > 0.5 mol/L. These will eventually facilitate the application of modified-bentonite to abate pollutants in environments. © 2008 Elsevier B.V. All rights reserved.

**Keywords:** Sorption; Nitroaromatic compound; Naphthalene; K<sup>+</sup>-bentonite; Organobentonite

## 1. Introduction

The application of natural minerals and modified-minerals in abating pollutants has been increasing concerns in environmental community and engineering due to their high-efficient and cost-effective. Because of their powerful sorptive properties, organobentonites were introduced as a novel sorbent to remove organic pollutants in wastewater and groundwater [1–3]. Organobentonites were synthesized by replacing the naturally occurring cations (e.g. Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>) in the interlayer of original bentonite with organic cations (e.g. cetyltrimethylammonium cation, CTMA<sup>+</sup>) [4,5]. The exchanged mineral surfaces become less hydrophilic and more organophilic and thus greatly enhance sorption of nonionic organic compounds (NOCs) from water [1,5–8], such as polycyclic aromatic hydrocarbons (PAHs) [2,9], phenolic compounds [6,7], and nitroaromatic

compounds (NACs) [10]. The sorption mechanisms were also extensively elucidated in the last two decades [1,5–7,11–15]. Sorption of NOCs by CTMA<sup>+</sup>-clay was due essentially to linear solute partitioning into the microscopic organic phase formed by the large alkyl chains of the CTMA<sup>+</sup> [1,5,11]; nonlinear isotherms indicative of adsorption or cosorption were observed when tetramethylammonium (TMA<sup>+</sup>)- and trimethylphenylammonium (TPMA<sup>+</sup>)-clays were used as adsorbents [1,11]. Thereafter, Sheng et al. [12,13] proposed that multiple sorption mechanisms, including solvation with ammonium cations and mineral surfaces and partition with the CTMA<sup>+</sup> organic phase, were involved in sorption of NOCs by CTMA<sup>+</sup>-clays. Recently, respective adsorption and partition contribution of organobentonites were quantified by isotherm-separation-method [6,7]; and with increasing loadings of organic cation with long-alkyl chain, the evolvement of tightly-adhered “organic films” to a confined “phase-like medium” in the nano-interlayer of mineral was accounted for the transitional mechanism from adsorptive surface to bulk-like partition phase [14,15].

Sorption of NACs to mineral surfaces has been widely interested [16–25] in order to assess the fate of NACs in the

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subsurface and to control their mobility. This is the case for environments (e.g., typical groundwater conditions) where the organic carbon content is extremely low, and for NACs that may specifically adsorb to surface sites of natural minerals [17,20]. The strength of adsorption depends on the structure of the compound (i.e., type of substituent) and on the type of cation adsorbed to the siloxane surface [16,20]. In the presence of weakly hydrated cations (i.e., Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup>, or NH<sub>4</sub><sup>+</sup>), significant adsorption of NACs was observed, while strongly hydrated cations such as H<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, or Al<sup>3+</sup> inhibited any specific interactions [16,17,22,25]. To elucidate the enhanced-sorption of NACs with aluminosilicate surfaces of clays, an electron donor–acceptor (EDA) mechanism was proposed in which the aromatic rings of NACs function as electron acceptors and clay siloxane oxygens behave as electron donors [16–18]. Recently, Boyd and co-workers [20,23–25] concluded two-step interactions that –NO<sub>2</sub> groups in NACs primary interact with weakly hydrated exchangeable cations (e.g., K<sup>+</sup>) to form complexes, and concurrently involved interactions between the aromatic rings and siloxane surfaces via van der Waals forces or by formation of EDA complexes, proven by the planar aromatic rings align parallel to clay surfaces. The selective sorption of NACs by clay minerals saturated with type of cations provided a promising reference to develop groundwater remediation methods and regulate mobilization of NACs by subsequent electrolyte injection with weakly and strongly hydrated cations [19].

These plentiful efforts about sorption of the modified-mineral provide a fundament and practical references to implement applications of minerals in environmental remediation and pollution abatement, but more studies are still wanted. The relative magnitude of sorption of organobentonite and mineral saturated with weakly hydrated cations, and then their influential factors (e.g., organic pollutant's properties, and concentration of cation) need further elucidate. Nitroaromatic compounds (NACs) are widely used as pesticides, explosives, and inter-

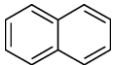
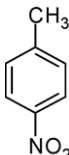
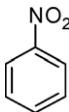
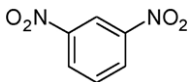
mediates in the synthesis of dyes and other chemicals. Their uses and manufacture have resulted in contamination of soils, sediments, and aquifers at military training ranges and manufacturing sites. Contamination of soils and groundwater with nitroaromatic munitions residues has recently drawn considerable public attention due to the significantly toxicological effects and the limited remediation measures. The objective of the current study is to compare enhanced-sorption of organobentonite and K<sup>+</sup>-bentonite and their mechanisms. To this end, naphthalene and three nitroaromatic compounds with different structures and properties were employed to probe sorption characteristics of original bentonite, organobentonite, and original bentonite with KCl solution at given concentrations. The effects of KCl concentrations on sorption of *m*-DNB were also investigated to intentionally establish a general relationship between sorption capabilities and the KCl concentrations.

## 2. Materials and methods

### 2.1. Materials and reagents

Naphthalene (NAPH) and three nitroaromatic compounds, such as *p*-nitrotoluene (*p*-NT), nitrobenzene (NB) and *m*-dinitrobenzene (*m*-DNB), were of analytical grade and were used without further treatment. These organic compounds are common organic contaminants in soil and sediment and have often been used in environmental research. The selected physicochemical properties and structures are presented in Table 1. Analytical grade of cetyltrimethylammonium bromide (CTMAB) was used to prepare organobentonite. An original bentonite saturated primarily with Ca<sup>2+</sup> 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<sub>2</sub> surface area (SA), organic carbon content (*f*<sub>oc</sub>), and cation-exchanged capacity (CEC) were 61 m<sup>2</sup> g<sup>-1</sup>, 0.04%, and 108 cmol kg<sup>-1</sup>, respectively.

Table 1  
Selected properties of naphthalene (NAPH), 4-nitrotoluene (4-NT), nitrobenzene (NB), and *m*-dinitrobenzene (*m*-DNB)<sup>a</sup>

Organic compounds	Formula	Structure	MW (g/mol)	<i>S</i> (μg/mL)	<i>K</i> <sub>ow</sub>	Density (g/cm <sup>3</sup> )
NAPH	C <sub>10</sub> H <sub>8</sub>		128.18	32.05	1950	0.997
4-NT	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>		137.14	350	235	1.392
NB	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		123.11	1936	71	1.196
<i>m</i> -DNB	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>		168.11	574.9	31	1.600

<sup>a</sup> MW: molecular weight, g/mol; *S*: aqueous solubility at room temperature, μg/mL; *K*<sub>ow</sub> octanol–water partition coefficient.

## 2.2. Preparation of organobentonite

An organobentonite was synthesized by reacting bentonite with aqueous solutions containing cationic surfactant. A total of 20 g of previously dried bentonite was mixed with 500 mL of aqueous solution containing 7.872 g CTMAB, equal to 100% of bentonite's CEC. The mixture was subjected to mechanical stirring for 4 h in a 60–70 °C shaker. The treated bentonite was separated from water by vacuum filtration and washed three times by distilled water. The organobentonite was 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 100CTMAB organobentonite. The organic carbon content ( $f_{oc}$ ) of 100CTMAB samples was determined using a Total Organic-Carbon Analyzer (TOC-V CPH, Shimadzu), and equal to  $f_{oc} = 18.85\%$ .

## 2.3. Batch sorption experiment

One nonpolar organic compound (e.g., NAPH) and three NACs (e.g., p-NT, NB, and m-DNB) were chosen as sorbates. An organobentonite (e.g., 100CTMAB) and an original bentonite were chosen as sorbents. All sorption isotherms were obtained using a batch equilibration technique at room temperature ( $25 \pm 0.5$  °C) in Teflon screw cap vials with aluminum foil-liners. The background solution was the deionized distilled water for sorption of the four solutes to 100CTMAB. For original bentonite, a series of solutions of the tested solutes were prepared in aqueous KCl solution. For m-DNB, the KCl concentrations were set as 0, 0.005, 0.02, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8 and 1.0 mol/L in order to investigate the effect of KCl concentration on sorption; while for p-NT, NB, and NAPH, the KCl concentrations were at 0 and 0.5 mol/L. Initial concentrations ranged from 0 to 30 mg/L for NAPH, 0–1600 mg/L for NB, 0–300 mg/L for p-NT, and 0–500 mg/L for m-DNB, which approach their individual aqueous solubility (Table 1). Sorbent were weighed into 8 mL-vials, and a series of concentrations of sorbate were added, and then the vials were sealed using aluminum foil with Teflon-lined screw caps. Isotherms consisted of ten concentration points; each point, including the blank, was run in duplicate. The vials were placed on a rotating shaker and agitated in the dark at 20 rpm for 24 h. Preliminary tests indicated apparent equilibrium was reached before 12 h. The solution was separated from remaining solids by centrifugation at 4000 rpm 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). Because 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.

All the data were processed by the logarithmic form of Freundlich equation:

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

where  $Q$  is the amount sorbed per unit weight of sorbent, mg/kg;  $C_e$  is the equilibrium concentration, mg/L;  $K_f$  is the Freundlich capacity coefficient, (mg/kg)/(mg/L)<sup>N</sup>; and  $N$  (dimensionless) describes the isotherm curvature. The linear regression were also conducted for the whole isotherms excluding nitrobenzene to all sorbents, and *m*-dinitrobenzene to original bentonite in 0.2, 0.5, 0.8, and 1.0 mol/L of KCl solution due to their strongly nonlinear, where linear isotherms were just covered at low concentration ranges. Sorption coefficients ( $K_d = Q/C_e$ ) were calculated according to the slope of practically linear equation to assess the magnitude of sorption capabilities.  $K_{oc}$  values for 100CTMAB were calculated by normalizing  $K_d$  to the carbon level ( $f_{oc}$ ) of the sorbent ( $K_{oc} = K_d/f_{oc}$ ).

## 3. Results and discussion

### 3.1. Enhanced sorption of organic compounds to bentonite by CTMA<sup>+</sup> and K<sup>+</sup> cations

Sorption isotherms of NAPH and NACs (i.e., p-NT, NB, and m-DNB) to original bentonite and organobentonite in deionized distilled water, and original bentonite in 0.5 mol/L KCl aqueous solution are presented in Fig. 1. The isotherms fit well with Freundlich equation excluding NB to original bentonite in 0.5 KCl aqueous solutions (cave-up isotherm), and the regression parameters are listed in Table 2. Sorption of NAPH and p-NT were practically linear, but nonlinear for NB. For m-DNB, sorption to original bentonite and 100CTMAB were linear, while nonlinear for sorption to original bentonite in 0.5 mol/L KCl aqueous solution. In order to compare their magnitudes of sorption capability, linear regressions were operated in the whole isotherms for practical linear isotherms and at low concentration ranges for nonlinear isotherms, and the linear parameters are also listed in Table 2. From Fig. 1 and Table 2, sorption of the tested solutes to original bentonite in water was extremely low, and the sorption coefficients ( $K_d$ ) were 0.939 mL/g, 0.405 mL/g, 0.880 mL/g and 0.876 mL/g for NAPH, p-NT, NB and m-DNB, respectively. These  $K_d$  values were almost identical regardless of their distinct differences in physicochemical properties and structures (see Table 1). Because the natural occurring cation in original bentonite was dominated by Ca<sup>2+</sup>, a typical strongly hydrated ion, the exterior and interior surfaces of the original bentonite were covered by thickly water-film and then exhibited hydrophilic properties. The presence of strongly polar water molecule significantly suppressed bentonite sorptive sites to adsorb NOCs [26]. Dissolution of NOCs in interfacial water-film of bentonite may be the only mechanism accounting for their apparently same sorption [27].

According to Fig. 1, sorption of NAPH, p-NT, NB and m-DNB to bentonite were dramatically enhanced when the Ca<sup>2+</sup> in the interior and exterior surfaces of bentonite's interlayer was replaced by an organic cation (CTMA<sup>+</sup>), due to the surfaces transition from hydrophilic to hydrophobic and additionally, a CTMA<sup>+</sup>-derived sorptive phase formed [1,5–8]. The  $K_d$  values were 5037, 318.0, 126.8 and 174.2 mL/g, respectively, for NAPH, p-NT, NB and m-DNB with 100CTMAB (Table 2), and the corresponding enhancements were 5360, 780, 40 and 200

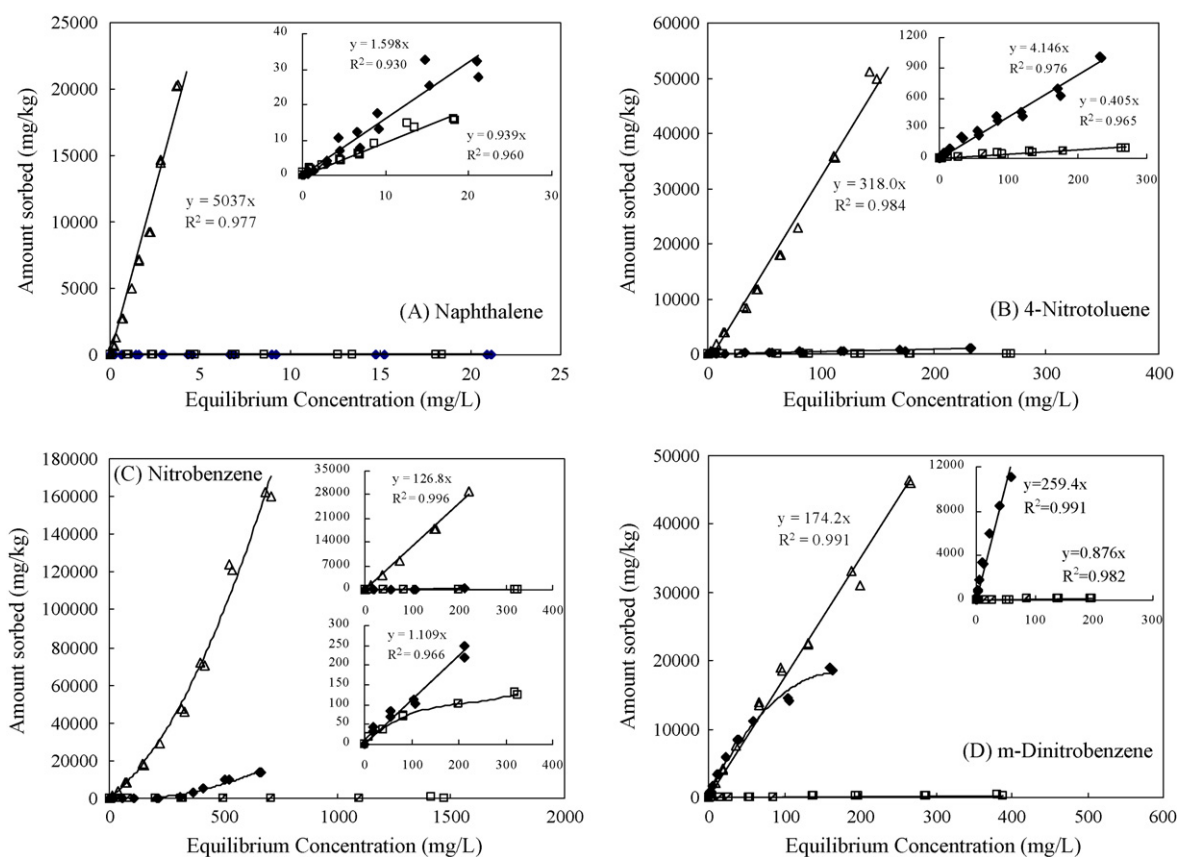


Fig. 1. Sorption isotherms of naphthalene (A), 4-nitrotoluene (B), nitrobenzene (C) and *m*-dinitrobenzene (D) to 100CTMAB ( $\Delta$ ), Ca<sup>2+</sup>-bentonite + 0.5 mol/L KCl ( $\blacklozenge$ ), and Ca-bentonite + 0 mol/L KCl ( $\square$ ).

times in comparison with the data of the original bentonite. Furthermore, the enhanced-intensity would increase to 280 times with increasing solute concentrations of NB due to its strong cave-up isotherm (Fig. 1(C)).

The presence of K<sup>+</sup> also enhanced sorption of the tested NACs to the original bentonite, consistent with previous reports [16–25]. The natural occurring of Ca<sup>2+</sup>, a strongly hydrated cation, replaced gradually by the K<sup>+</sup> cation, a weakly hydrated ion, resulted in the decrease of interfacial water-film and then partially exposed the siloxane surface of original bentonite. These evolvments favored sorption of NACs by the resultant K<sup>+</sup>-bentonite. From the insets in Fig. 1 and Table 2, with the presence of 0.5 mol/L KCl solution, the  $K_d$  values were 1.589 mL/g, 4.146 mL/g, 1.109 mL/g and 259.5 mL/g, respectively, for NAPH, p-NT, NB and m-DNB. Compared with the original bentonite in water, enhanced-sorption by original bentonite in 0.5 mol/L KCl solutions was approximately 300 times for m-DNB, and even overshadowed the role of organobentonite (100CTMAB). The enhanced-intensities were about 40 times for both of NB with high concentrations and p-NT, but none for naphthalene. These indicated that the KCl can substitute the whole or partial role of 100CTMAB to effectively remove NACs from military facility wastewaters to reduce treatment costs; and concurrently stands as an environmental friendly novel technology by injection KCl solution to groundwater to strongly intercept NACs pollution plume [19–20].

### 3.2. Effect of properties of organic compounds on sorption

Effect of the properties of organic solutes on sorption of original bentonite and 100CTMAB in water and original bentonite in 0.5 mol/L KCl solution are compared in Fig. 2. From Fig. 2(A), sorption of NAPH and NACs to original bentonite in water was almost identical again, regardless of their owning different properties and structures (Table 1). Enhanced-sorption of organic solutes to organobentonite (i.e., 100CTMAB) was observed, which was more appreciable for nonpolar organic compounds (NAPH) than polar compounds (NACs). With the decrease of their aqueous solubilities, the magnitude of sorption of the solute to 100CTMAB increased as the order of NAPH > p-NT > m-DNB > NB (Fig. 2(B)), and corresponding nonlinear sorption increased. The carbon-normalized sorption coefficients ( $K_{oc} = K_d/f_{oc}$ ) of the tested solutes to 100CTMAB are calculated in Table 2. The  $K_{oc}$  values were 26720, 1687, 923.9 and 672.7, respectively, for NAPH, p-NT, m-DNB and NB, which were 13.7, 7.2, 29.8 and 9.5 times higher than their respective  $K_{ow}$  value. Similar observations were reported [5,9,14,15]. This further suggests that the surfactant-derived organic matter formed in mineral surface functions as a powerful sorptive medium. The nonlinear isotherms for relative polar solutes (e.g., m-DNB and NB) along with extremely high ratio of  $K_{oc}/K_{ow}$  for m-DNB also indicate that besides bulk-partition additional interactions contribute to total sorption. The additional forces may

Table 2  
Regression parameters of naphthalene (NAPH), 4-nitrotoluene (4-NT), nitrobenzene (NB), and *m*-dinitrobenzene (*m*-DNB) to 100CTMAB, and original bentonite with and without the presence of KCl in solution

Sorbates	Sorbent <sup>a</sup>	KCl conc. <sup>b</sup> (mol/L)	Freundlich regression parameters <sup>c</sup>			Linear parameters <sup>d</sup>		$K_d^e$	$K_{oc}^f$
			$\log K_f$	$N$	$R^2$	Equation	$R^2$		
NAPH	Original bentonite	0	0.182	0.796	0.966	$y = 0.939x$	0.960	0.939	26720
	Original bentonite	0.5	0.029	1.1675	0.931	$y = 1.598x$	0.930	1.598	
	100CTMAB	0	3.648	1.0567	0.989	$y = 5037x$	0.977	5037	
4-NT	Original bentonite	0	0.044	0.823	0.992	$y = 0.405x$	0.965	0.405	1687
	Original bentonite	0.5	1.077	0.777	0.990	$y = 4.146x$	0.976	4.146	
	100CTMAB	0	2.371	1.052	0.997	$y = 318.0x$	0.984	318.0	
NB	Original bentonite	0	0.625	0.602	0.99	$y = 0.880x^h$	0.975	0.880	672.7
	Original bentonite	0.5 (i) <sup>g</sup>	0.658	0.712	0.946	$y = 1.109x$	0.966	1.109	
	Original bentonite	0.5 (ii) <sup>g</sup>	-6.376	3.791	0.956	$y = 38.03x$	0.984	38.03	
	100CTMAB	0	1.826	1.157	0.987	$y = 126.8x^h$	0.996	126.8	
<i>m</i> -DNB	Original bentonite	0	0.248	0.864	0.993	$y = 0.876x$	0.982	0.876	923.9
	Original bentonite	0.005	1.435	0.743	0.954	$y = 7.587x$	0.981	7.587	
	Original bentonite	0.01	1.489	0.725	0.935	$y = 10.11x$	0.923	10.11	
	Original bentonite	0.02	1.371	0.844	0.983	$y = 11.65x$	0.966	11.65	
	Original bentonite	0.05	1.319	1.112	0.996	$y = 37.38x$	0.989	37.38	
	Original bentonite	0.08	1.755	1.022	0.997	$y = 61.04x$	0.991	61.04	
	Original bentonite	0.10	1.730	1.119	0.983	$y = 81.95x$	0.972	81.95	
	Original bentonite	0.20	2.301	0.872	0.993	$y = 147.8x^h$	0.998	147.8	
	Original bentonite	0.50	2.586	0.800	0.987	$y = 259.4x^h$	0.991	259.4	
	Original bentonite	0.80	2.726	0.769	0.984	$y = 351.2x^h$	0.990	351.2	
	Original bentonite	1.00	2.792	0.746	0.987	$y = 378.6x^h$	0.982	378.6	
	100CTMAB	0	2.441	0.915	0.999	$y = 174.2x$	0.991	174.2	

<sup>a</sup> Sorbates includes original bentonite and organobentonite (i.e., 100CTMAB).

<sup>b</sup> KCl concentration in sorption solution (mol/L).

<sup>c</sup> The Freundlich parameters ( $K_f$  and  $N$ ) were calculated using the logarithmic form of the equation  $Q = K_f C_e^N$ , where  $Q$  is the amount sorbed per unit weight of sorbent (mg/kg);  $C_e$  is the equilibrium concentration, mg/L;  $K_f [(mg/kg)/(mg/L)^N]$  is the Freundlich capacity coefficient, and  $N$  (dimensionless) describes the isotherm curvature.  $R^2$  is regression coefficient.

<sup>d</sup> The linear regressions were conducted for the whole isotherms excluding nitrobenzene to all sorbents, and *m*-dinitrobenzene to original bentonite in 0.2, 0.5, 0.8, and 1.0 mol/L KCl solution.

<sup>e</sup>  $K_d$  is the sorption coefficients ( $K_d = Q/C_e$ ), calculated from the slope of linear equation.

<sup>f</sup>  $K_{oc} = K_d/f_{oc}$ , where  $f_{oc}$  is the organic carbon content of 100CTMAB ( $f_{oc} = 18.85\%$ ).

<sup>g</sup> Due to distinct shapes under and above 250  $\mu\text{g/mL}$  of nitrobenzene to the original bentonite in 0.50 mol/L KCl solution, the isotherm were separately regressed with two different dash (i.e., <250 mg/L for (i) and >250 mg/L for (ii)).

<sup>h</sup> Due to high nonlinear, linear regression for *m*-DNB to original bentonite in 0.2–1.0 mol/L KCl solution was conducted at <50  $\mu\text{g/mL}$ ; for NB to 100CTMAB and original bentonite, linear regression was regressed at <200 and <100  $\mu\text{g/mL}$ , respectively.

involve solvation with ammonium cations, directly interaction with the exposed mineral surfaces, and phase-transitional forces of adsorb-surfactant confined in the nano-interlayer and then induced by mineral interior surface [12–15].

Distinct effects of solute's properties on enhanced-sorption by 0.5 mol/L KCl are presented in Fig. 2(C). Sorption of the non-polar solute, NAPH, was hardly promoted, while for the three nitroaromatic compounds sorption was enhanced with *m*-DNB exhibiting maximum. This suggests that the attenuation intensity of water-film in mineral surface, induced by weakly dehydrated cation ( $K^+$ ) replacing strongly dehydrated cation ( $Ca^{2+}$ ), favored interaction of NACs (polar compounds) with mineral, but still disfavored for NAPH. Several studies have reported the high affinity of NACs for smectites in aqueous solution [17–25]. This has been illustrated by the formation of electron donor (clay)–acceptor (EDA) complexes facilitated by the electron withdrawing properties of the nitro ( $-NO_2$ ) group [16–18]. Alternatively, Boyd and co-workers [20,23–25] believed that the complexation of the  $NO_2$  groups of NACs with exchange-

able cations on the clay was a primary sorption mechanism [25], and then inducing additional interactions between the aromatic rings and siloxane surfaces via van der Waals forces or by formation of EDA complexes [20]. However, the enhanced-sorption of NB to the resultant  $K^+$ -bentonite depending on the equilibrium concentration of the solute was observed (Fig. 2(C) and (D)), and an apparent inflexion concentration was occurred at  $\sim 250$  mg/L. Before the inflexion concentration, the sorption of nitrobenzene was lower than that of *p*-nitrotoluene with electron repulsing property of the methyl ( $-CH_3$ ), which consistent with their hydrophobicities, i.e., octanol–water partition coefficient ( $K_{ow}$ ) (Table 1) rather than their electron withdrawing properties. Consequently, these observations cannot be explained well by the EDA mechanism alone. The enhanced-sorption of nitrobenzene at low concentrations and *p*-nitrotoluene by 0.5 mol/L KCl should be attributed to van der Waals forces (e.g.,  $\pi$ – $\pi$ ) between aromatic rings and siloxane surfaces rather than EDA mechanism, which resulted in *p*-NT > NB at low solute concentration due to *p*-NT with a larger molecular weight and a relative low

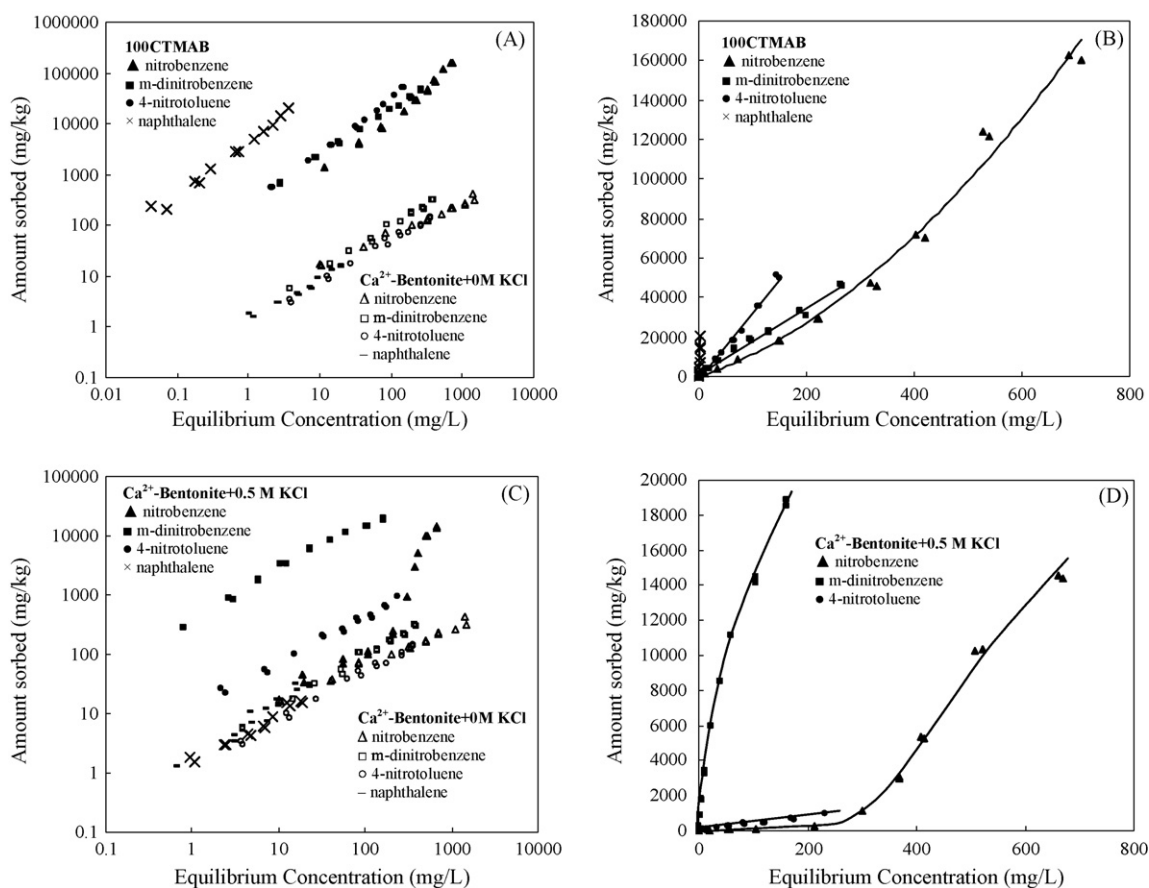


Fig. 2. Effect of organic compounds properties on the sorption of the solute to 100CTMAB, Ca<sup>2+</sup>-bentonite + 0.5 mol/L KCl, and Ca<sup>2+</sup>-bentonite + 0 mol/L KCl.

polar property. Rationally, the complexation of the  $-\text{NO}_2$  groups with  $\text{K}^+$  is not prerequisite for van der Waals interactions of NACs with mineral, but it is true for EDA mechanism. With increasing concentrations of NB, the sorbed-amount increased gradually, and then dramatically increased after the inflexion point like the behavior of m-DNB (Fig. 2(D)), which means the dominant mechanism changes from weak van der Waals interactions at low concentrations to strongly EDA interactions at high concentration. Correspondingly, sorption of m-DNB by  $\text{K}^+$ -bentonite was dominated by strong EDA interactions rather than van der Waals forces. Hence, the complexation potential of the  $\text{NO}_2$  groups of NACs with  $\text{K}^+$  was in the order of  $\text{m-DNB} > \text{NB} \gg \text{p-NT}$ .

### 3.3. Effect of concentrations of potassium ion on sorption of m-DNB to Ca<sup>+</sup>-bentonite

The effects of KCl concentration on sorption of m-DNB to Ca<sup>+</sup>-bentonite were further investigated in order to elucidate maximal sorption of NACs by electrolyte injection method. Sorption isotherms of m-DNB to original bentonite in nine KCl concentrations at the range of 0.005–1.0 mol/L are presented in Fig. 3(A), and the regression parameters are listed in Table 2. The relationships between Freundlich  $N$  factors  $\sim$  KCl concentrations, and between sorption coefficients  $\sim$  KCl concentrations

are plotted in Fig. 3(B) and (C), respectively. Enhanced-sorption of m-DNB to original bentonite by KCl solution was observed even if KCl at extremely low concentration (e.g., 0.005 mol/L), and then increased with the increase of KCl concentrations up to 1.0 mol/L, due to the creation of more sorptive  $\text{K}^+$ -sites. There occurred a peak between  $N$  values  $\sim$  KCl concentrations (Fig. 3(B)).

Interestingly, the sorption coefficients ( $K_d$ ) increased linearly with KCl concentrations from 7.586 mL/g (KCl = 0.005 mol/L) to 147.8 mL/g (KCl = 0.2 mol/L), and the regression equation was  $K_d = 755.4 \times C_{\text{KCl}}$ , where  $C_{\text{KCl}}$  is the concentration of KCl (Fig. 3(C)), indicating the binding-amount of  $\text{K}^+$  is the limited factor due to m-DNB with strongly complexation potential. With further increasing KCl concentrations, the  $K_d$  values increased from 259.4 mL/g (KCl = 0.5 mol/L) to 351.2 mL/g (0.8 mol/L), and then to 378.6 mL/g (1.0 mol/L), which were, however, lower than the prediction based on the linear equation of  $K_d \sim C_{\text{KCl}}$  (dashed line in Fig. 3(C)), due to the limited negative-charge for the coming  $\text{K}^+$  ion. The  $K_d$  values at 0.8 and 1.0 mol/L KCl were twice higher than that of 100CTMAB ( $K_d = 174.2$  mL/g), indicating KCl solution is more effective than CTMA<sup>+</sup> to enhance sorption of m-DNB to original bentonite. These observations may benefit the application of  $\text{K}^+$ -bentonite to remove m-DNB from wastewater and groundwater due to its more environmental friendly technology.

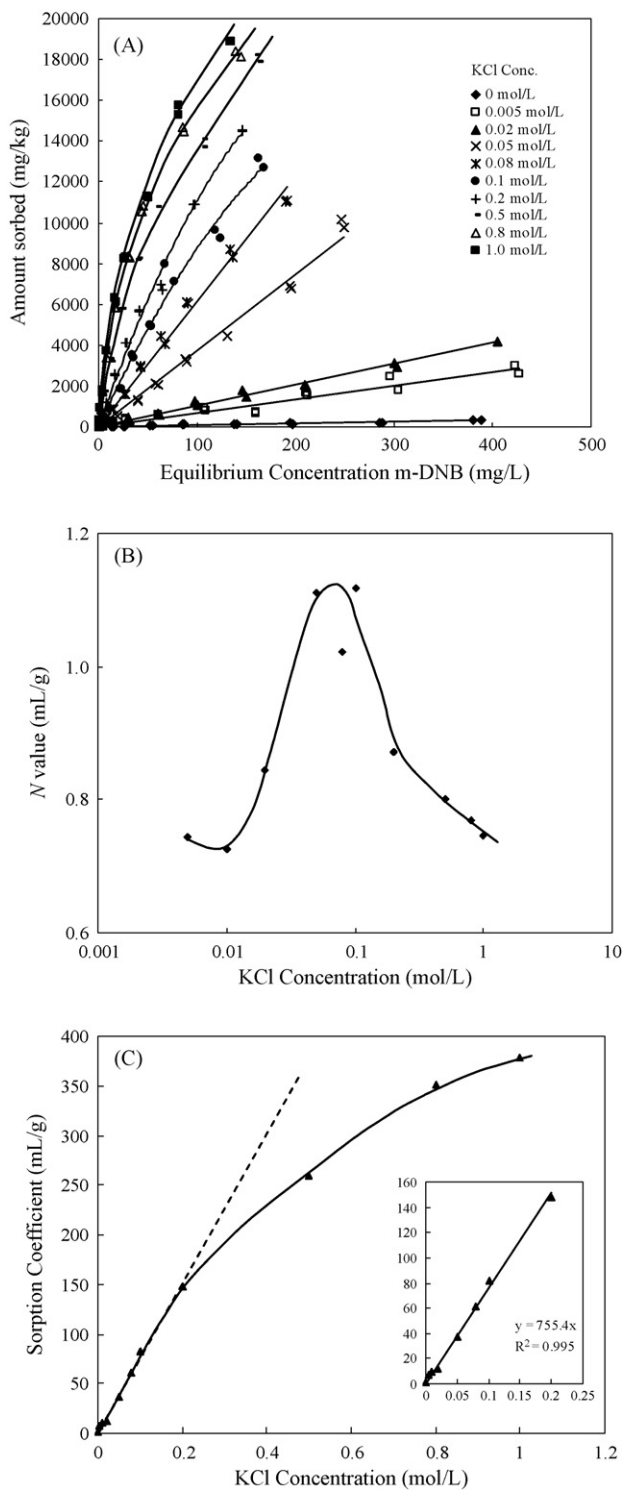


Fig. 3. Effect of KCl concentrations on the sorption of *m*-dinitrobenzene to the original bentonite. (A) Sorption isotherms of *m*-dinitrobenzene; (B) relationship of sorption coefficients ( $K_d$ ) with KCl concentration; (C) relationship of Freundlich  $N$  values with KCl concentration.

#### 4. Conclusion

Sorption of naphthalene and NACs was extremely weak and similar by  $\text{Ca}^{2+}$ -bentonite regardless of their properties and structures. When  $\text{CTMA}^+$  or  $\text{K}^+$  cation was introduced into

the interlayer of bentonite, a general enhancement in the sorption capacity was observed, depending on the types of organic solutes. The high affinity of the tested solutes with 100CTMAB (40–5000 times) was attributed to its formation of  $\text{CTMA}^+$ -derived organic matter and the exposed hydrophobic surface of mineral, more favored for nonpolar organic compounds. The presence of  $\text{K}^+$  cation enhanced sorption of NACs (50–400 times) rather than NAPH, and the enhancement was due to the reduction of interfacial water-film of bentonite replaced by  $\text{K}^+$  cation. The enhanced-mechanism for NB at low concentrations and *p*-NT was derived mainly from weak van der Waals interactions between aromatic rings and siloxane surfaces, while for NB at high concentrations and *m*-DNB the mechanisms were attributed to primary complexation of  $-\text{NO}_2$  group with  $\text{K}^+$  and then strongly interactions by electron donor–acceptor. Consequently,  $\text{K}^+$ -bentonite was most favorable to *m*-DNB. The  $K_d$  values of *m*-DNB to bentonite dramatically increased from 7.6 mL/g ( $\text{KCl} = 0.005$  mol/L) to 378 mL/g (1.0 mol/L) with the presence of KCl increasing, and the  $K_d$  values at 0.8 and 1.0 mol/L KCl were twice higher than that of 100CTMAB ( $K_d = 174.2$  mL/g). These observations provide a reference to abate aromatic compounds from wastewater and groundwater by  $\text{CTMA}^+$ -, and  $\text{K}^+$ -modified bentonites.

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