



Sorption behaviors of aromatic anions on loess soil modified with cationic surfactant

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Abstract

Modification of soils with hydrophobic cationic surfactants is an effective approach for enhancing the sorptive capabilities of soil in the vadose zone for the purpose of retaining organic contaminants prior to cleanup. The objective of this study was to examine the sorptive behavior of the cationic surfactant-modified loess soil for aromatic anions in the aqueous phase in an attempt to define the sorptive mechanisms. Some dominant factors governing the sorption, such as ionic strength and divalent heavy metal cation, were investigated. The sorption isotherms of 2,4-dinitrophenol (DNP) and benzoic acid (BA) in the modified soil samples were obtained using the batch equilibration method. Under the laboratory conditions, the modified loess soil utilized in this study was prepared by replacing the cations of loess soil with a cationic surfactant—hexadecyltrimethylammonium (HDTMA) bromide. The acidic aromatic compounds, DNP and BA existing as aromatic anions in the natural mixture of loess soil and aqueous phase, were selected as indicator compounds to measure the sorption behaviors of aromatic anions on the HDTMA-modified loess soil. The results confirmed that the sorptive capabilities of aromatic anions in loess soil were greatly enhanced by modification with HDTMA. The increase of ionic strength and the addition of divalent heavy metal cation Zn^{2+} significantly increased the sorption of aromatic anions on the HDTMA-modified loess soil. In binary solute systems, the sorbed amounts either of DNP or BA on the HDTMA-modified loess soil were reduced if two compounds existed simultaneously in the soil. This result indicated that competitive adsorption between the two aromatic anions occurred in soil matrix.

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1. Introduction

Sorption is seen as a viable alternate to interventionist remediation of organic compounds in contaminated soil and aquifers. Utilization of surfactant-modified soils as a sorbent for organic contaminants from an aqueous phase has been an active area of research [1–9]. Most of this research has involved the use of quaternary cation surfactants to modified natural soils. It was reported that the fundamental sorption mechanism of surfactants in a soil matrix was due to ion exchange if the loading level of cationic surfactants was more than 70% of the cation exchange capacity (CEC) of soil. At greater loadings, cationic surfactants were sorbed both by ion exchange and hydrophobic bonding [10,11]. The modification of soils with cationic surfactants through ion exchange and hydrophobic bonding can increase the soil's organic matter and significantly enhance the sorptive capabilities of soils for organic contaminants. The above studies suggested that aquifer materials or subsoils could be modified in situ by spraying or injecting cationic surfactants onto the soil to create a sorptive zone that could retard and immobilize advancing contaminant plumes in the subsurface and thus preventing further movement toward the deeper soil and groundwater. A better understanding of the sorptive properties and mechanisms of organic contaminants on surfactant-modified soils can be useful in the remediation of contaminated soils as well as assisting in ascertaining the behavior of organic contaminants affected by surfactants in soil matrix.

Many aromatic compounds with hydroxy or phenolic groups exhibit an acidic property because of the presence of carboxylic and phenolic moieties. Some of these aromatic compounds with $pK_a \ll 7$ were found as anions in aqueous phase at a pH range of natural soils. Compared to other nonionic aromatic compounds, aromatic anions are more mobile in natural environment and are not amenable to effective sorption in natural soils. For aromatic anions, the complexity and variety of possible interactions between the compounds and soil have made the mechanism studies difficult.

Westall and his co-workers [12,13] suggested two mechanisms for the distribution of the ionic forms of organic acid between octanol and water: (1) partition into octanol phase as free ions or ion pairs, i.e. organic anions combined with inorganic cations; or (2) transfer of organic ions from aqueous phase onto lipophilic surface with a counterion in electric double layer. Li and Sengupta [14] reported that ion exchange governed the overall sorption equilibrium of aromatic anions onto polymeric sorbents. Gu et al. [15] suggested that ligand-exchange mechanism between carboxylic/phenolic functional groups and the iron oxide surface was the dominant mechanism for organic acids sorption.

However, little is known about the mechanisms of the aromatic anions sorption on surfactant-modified soils. Stapleton et al. [3] hypothesized that the HDTMA-clay sorbed the neutral form of PCP via a partitioning mechanism, while the much less strongly sorbed ionic form was retained via co-adsorption with a counterion. Li et al. [9] indicated that the sorption of ionizable organic compounds on the surfactant-modified zeolite occurred via partition for the neutral form, and attraction or repulsion for the ionic form. However, no specific study dealing with the sorptive effect of cationic surfactants on aromatic anions in natural soil was reported, and the previous researches only had a little discussion on the sorption of aromatic anions in a binary solute system.

Our experiments focused on the equilibrium sorption of two aromatic anions on the HDTMA-modified loess soil. The objectives of our studies were to describe the sorptive

behavior of aromatic anions on the HDTMA-modified loess soil as a function of ionic strength, divalent heavy metal cation, and to suggest a mechanism for explaining the sorption process of aromatic anions in the modified soil environment. The research results may be used to prevent groundwater contamination from acidic aromatic compounds leaching through the vadose zone in the arid and semi-arid regions in the northwest of China, where oil fields exist on loess land. The integrated contaminant immobilization with in situ remediation would provide a comprehensive restoration technology to permanently eliminate target contaminants.

2. Materials and methods

2.1. Materials

A loess soil sample was obtained from the subsurface (50–60 cm deep) in an uncontaminated area in Lanzhou City, China. The soil contained 18.75% sand, 53.85% silt and 27.4% clay. The CEC of natural loess soils was 0.0642 meq/g. This parameter was determined by atomic absorption spectrometry with Ca^{2+} as an index cation and a 0.1 M BaCl_2 solution as the extracting reagent [16]. The soil's organic carbon content was 0.10%, as measured using $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ oxidation at 180–185 °C in an oil bath according to the methodology reported by Li et al. [16]. The chemical reagents used in this study were of the analytical grade.

Hexadecyltrimethylammonium (HDTMA) bromide was utilized as the cationic surfactant to modify the loess soil in laboratory. Being a divalent heavy metal cation, Zn^{2+} can exist as a free ion in a natural mixture of loess soil and the aqueous phase. Thus, zinc was chosen to examine the effect of divalent heavy metal cation on the sorption of aromatic anions in the HDTMA-modified loess soil.

2.2. Preparation of modified loess soil

Based on our previous sorption experiments [17], a HDTMA loading level of 1.2 times the CEC value of the loess soil was selected to prepare the HDTMA-modified soil. HDTMA bromide was dissolved in distilled water. A total of 100 g of previously dried loess soil was mixed with 1000 ml of HDTMA bromide solution in a concentration equal to 1.2 times the CEC value of the loess soil. The mixtures were mechanically agitated at room temperature for 5 h, and then repeatedly washed with distilled water until the bromide ions derived from the cation surfactant solution were undetectable as titrated by 0.01 M AgNO_3 solution. Finally, the soil sample was air-dried, passed through a 1 mm sieve, and then stored in glass bottles at room temperature for later use. The organic carbon content of the HDTMA-modified loess soil was measured as 0.88%.

2.3. Sorption procedure

Sorption isotherms were obtained by adding various dinitrophenol (DNP) or benzoic acid (BA) solutions to 50 ml Erlenmeyer flasks covered by glass caps. To ensure the sorbed

amount of the solute reached its maximum according to our previous sorption experiments [17]. A series of 5 g samples the natural and HDTMA-modified loess soils were obtained. Each sample of the two kind soils was individually mixed with 50 ml DNP or BA solutions with the different concentrations. To obtain equilibrium condition, the soil–solution mixture was initially stirred with a vortex agitator, and then placed in a shaker for continuous mixing at 200 r/min in the dark for approximating 24 h at 25 °C. After equilibration, the flasks were withdrawn and centrifuged at $3200 \times g$ for 20 min to separate the aqueous and solid phases.

The organic compound concentrations in the aqueous phase were determined using a 754 UV spectrophotometer (Shanghai, China). The sorbed amounts of DNP and BA were calculated by utilizing the difference between the initial and final concentrations of the organic compounds in aqueous phase. Meanwhile, the blank experiments conducted without adding sorbent were performed to determine a total loss of solute resulting from adsorption on the flasks walls and other losses under the same conditions.

The sorption of DNP and BA in a binary solutes system was measured using a HDTMA-modified loess soil. Sorption of DNP in the presence of BA that was added as the competitive sorbate with a constant initial concentration. This experiment was carried out. The initial concentrations of DNP were varied in this experiment. Sorption of BA in the presence of DNP as a competitive sorbate was measure by performed in a similar fashion. The aqueous phase in all experiments contained 0.1 M NaCl.

3. Results and discussion

Due to the buffering affect of the soil sample, the pH value of aqueous phase at equilibrium remained close to around 7.4 for all the concentrations of the aromatic compounds used; therefore, DNP ($pK_a = 4.09$) and BA ($pK_a = 4.20$) existed as aromatic anions in aqueous phase. All the data obtained from the batch sorption experiments were fitting the Freundlich equation (Table 1). The sorption efficiencies of the natural and HDTMA-modified loess soil for DNP and BA at the various experimental conditions also are shown here.

Table 1
Regression data for sorption isotherms and sorption efficiencies of DNP and BA on HDTMA-modified or natural loess soil at various conditions

Aromatic anions	Loess soils	Condition	Regression equation	Correlative coefficient	Sorption efficiencies (%)
DNP	Untreated HDTMA-modified		$C_S = 0.00023C_e^{0.804}$	0.993	1.43
		0.0 M NaCl	$C_S = 0.0487C_e^{0.623}$	0.996	51.9
		0.1 M NaCl	$C_S = 0.144C_e^{0.592}$	0.998	85.6
		0.025 M ZnSO ₄	$C_S = 0.523C_e^{0.459}$	0.997	95.4
		79.37 mg/l BA	$C_S = 0.205C_e^{0.557}$	0.998	82.5
BA	Untreated HDTMA-modified		$C_S = 0.00032C_e^{0.768}$	0.997	1.96
		0.0 M NaCl	$C_S = 0.0032C_e^{0.819}$	0.963	18.8
		0.1 M NaCl	$C_S = 0.00574C_e^{0.708}$	0.997	23.6
		0.025 M ZnSO ₄	$C_S = 0.00809C_e^{0.665}$	0.998	31.6
		86.4 mg/l DNP	$C_S = 0.0033C_e^{0.57}$	0.987	12.6

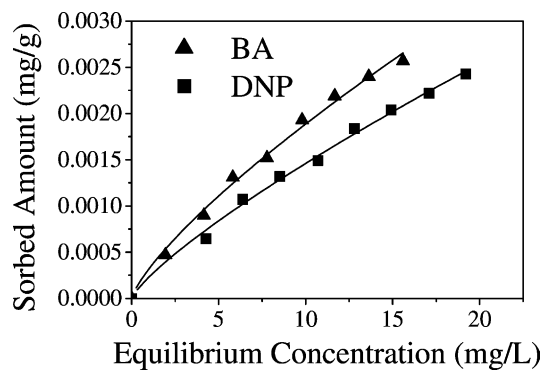


Fig. 1. Sorption isotherms of DNP and BA on natural loess soil.

3.1. The comparison of sorption isotherms on natural and modified loess soil

Sorption isotherms for DNP and BA on untreated and HDTMA-modified loess soil are shown in Figs. 1 and 2, respectively. The sorbed amounts of DNP and BA on HDTMA-modified loess soil were greater than that on untreated loess soil. Compared to the natural loess soil, the sorption efficiencies of DNP in the HDTMA-modified loess soil were

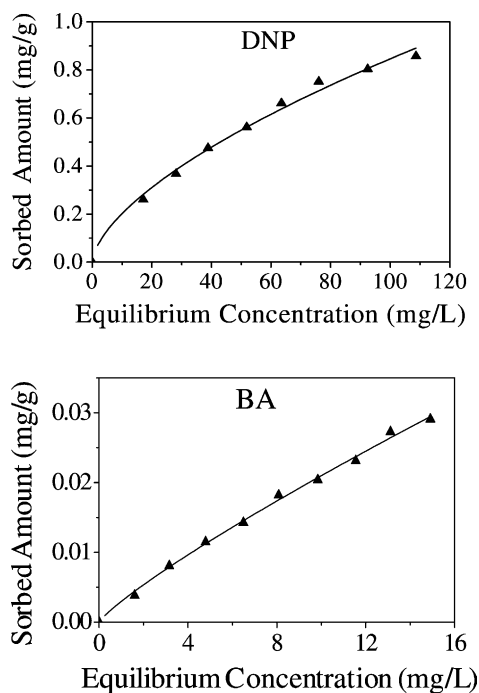


Fig. 2. Sorption isotherms of DNP (A) and BA (B) on HDTMA-modified loess soil.

increased significantly (Table 1). These results indicated that the modification of loess soil with HDTMA greatly enhanced the retention of aromatic anions and the modified soil was able to effectively retard the aromatic anions from entering the aqueous phase.

3.2. The affects of ionic strength and divalent heavy metal cation

The affects of ionic strength and divalent heavy metal cation on the sorption of DNP and BA in the HDTMA-modified loess soil are illustrated in Fig. 3. The sorbed amount of DNP and BA in the HDTMA-modified loess soil gradually increased with the additions of 0.1 M NaCl and 0.025 M ZnSO₄, respectively. The addition of 0.1 M NaCl increased the sorption efficiency of the HDTMA-modified loess soil for DNP from 51.9 to 85.6%, and for BA from 18.8 to 23.6% (Table 1). These results suggested that ionic strength effects on the sorption of aromatic anions on the HDTMA-modified loess soil and the sorption of aromatic anions is favored by higher ionic strengths.

The ionic strength of aqueous phase with 0.1 M NaCl was same as that of aqueous phase with 0.025 M ZnSO₄. The sorption efficiency increased by 10% for DNP and by 8% for BA

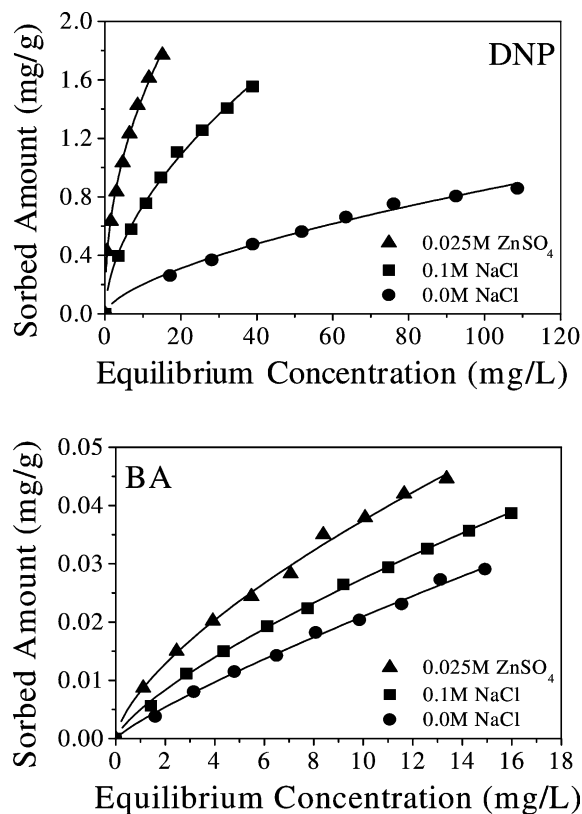


Fig. 3. The comparison of sorption isotherms of DNP (A) and BA (B) on HDTMA-modified loess soil with 0.0 M NaCl, 0.1 M NaCl or 0.025 M ZnSO₄ in the initial solutions.

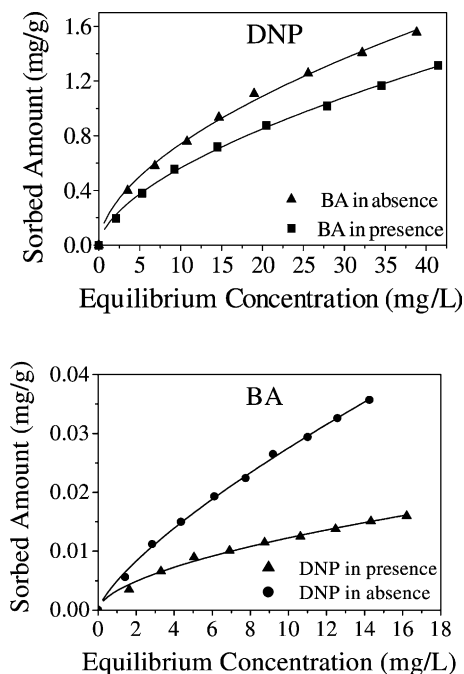


Fig. 4. Sorption isotherms of DNP (A) and BA (B) in binary solutes system containing 0.1 M NaCl on HDTMA-modified loess soil.

in the presence of 0.025 M ZnSO_4 compared with the addition of 0.1 M NaCl. The results proved that the sorptive capabilities of the HDTMA-modified loess soil for DNP and BA in the presence of Zn^{2+} were greater than that in the presence of Na^+ at the same ionic strength of aqueous phase.

3.3. Sorption of binary solutes

The sorption isotherms of aromatic anions in a binary solute system on the HDTMA-modified loess soil are shown in Fig. 4. The sorption of BA was reduced in the presence of DNP, while the presence of BA reduced the sorption of DNP. The sorption efficiencies for DNP was slightly decreased from 85.6 to 82.5% in the presence of BA, but a greater decrease in sorption efficiencies for BA was observed because of the presence of DNP, from 23.6 to 12.6%, which indicated that competitive adsorption between DNP and BA occurred on the HDTMA-modified loess soil.

3.4. Sorption mechanism of aromatic anions

Since the organic carbon content of the natural loess soil was as low as 0.10%, the sorption efficiencies of the natural loess soil on aromatic anions were quite limited. For instance, the adsorption was only 1.43% for DNP and 1.96% for BA, a result which could

be attributed to ion exchange, ligand-exchange and direct coordination with soil surface [10]. The modification with HDTMA increased the organic carbon content of the natural loess soil up to 0.88%. Consequently, the sorptive capabilities of the HDTMA-modified loess soil for aromatic anions were greater than that of the natural loess soil. It is well known that soil organic matter (SOM) is the dominant material for the sorption of organic compounds when the organic carbon on the medium is more than 0.5% [1,2]. Thus, the organic phase derived from HDTMA seemed to be the predominant phase for the sorption of aromatic anions on the HDTMA-modified loess soil.

All the sorption isotherms were nonlinear, indicating that partition was not the unique mechanism for the sorption of aromatic anions on HDTMA-modified loess soil. The dual-mode model of sorption to SOM [18,19] may be used to interpret the sorption processes of aromatic anions in the modified soil, in which solid-phase dissolution (partition) took place simultaneously with adsorption-like (hole-filling) processes. The isotherm nonlinearity results from the association of the sorbate at specific sites in the hole-filling domain within SOM. Thus, the aromatic anions as free ions or combined with inorganic cations as ion pairs, partitioned into the dissolution phase and associated with specific sites in the hole-filling domain within the organic phase derived from HDTMA.

The ionic strength of aqueous phase could have increased the ion activity of aromatic anions, and then enhanced their affinity with specific sites in the hole-filling domain within organic phase. The experiments of Westall [12] and Jafvert [13] showed that the distribution proportion of phenolate between octanol and water phase was directly related to the ionic strength in aqueous phase. The partition of phenolate into the octanol phase was favored at the higher ionic strengths because of the formation of ion pairs in the nonaqueous phase. The sorption capacities of HDTMA-modified loess soil for aromatic anions increased with an increase of ionic strength in the aqueous phase. It was explained that the high ionic strength could enhance not only the partition of aromatic anions into dissolution phase, but also the affinity of aromatic anions with specific sites in the hole-filling phase within the organic phase derived from HDTMA.

A divalent heavy metal cation Zn^{2+} was adsorbed to soil much more easily than Na^+ since a monovalent metal cation yielded a less negative surface charge, resulting in a decreased electrostatic repulsion of the aromatic anions and increased the sorption of aromatic anions on the HDTMA-modified loess soil. On the other hand, the distribution ratio of organic anions between the octanol and water phase favorably affected the aqueous solutions containing divalent inorganic cation compared to solutions that containing monovalent inorganic cations at equal ionic strength [12,13]. According to the above, Zn^{2+} could more significantly promote the partition of aromatic anions into the dissolution phase than Na^+ does as a monovalent cation within organic phase of the HDTMA-modified loess soil. Thereby, the sorptive capabilities of the HDTMA-modified loess soil for aromatic anions in presence of Zn^{2+} were greater than in the presence of Na^+ .

4. Conclusions

To strengthen the attenuation capacity of loess soil having a low organic carbon content, we successfully modified the natural loess soil by using HDTMA bromide. Taking DNP

and BA as the organic indicators for the sorption behavior, our experiments proved that the sorption capacities of the modified soil were dramatically enhanced by 36-fold for DNP and 10-fold for BA compared with the natural loess soil. The soils organic matter derived from HDTMA was the predominant phase for the sorption of aromatic anions on the HDTMA-modified loess soil. Additionally, The ionic strength affected the sorption of aromatic anions on the HDTMA-modified loess soil and the sorption of aromatic anions was favored by higher ionic strengths. The sorption efficiency increased by 10% for DNP and by 8% for BA in the presence of 0.025 M $ZnSO_4$ compared with the addition of 0.1 M NaCl. The ionic strength of aqueous phase with 0.1 M NaCl was the same as that of aqueous phase with 0.025 M $ZnSO_4$. These results indicated that the sorptive capabilities of the HDTMA-modified loess soil for DNP and BA in the presence of the high-valence cation were greater than addition of low-valence cation at the same ionic aqueous phase strength. We conducted that the ionic strength and valence of the cation were the two principal factors affecting the sorption behavior of aromatic anions on surfactant-modified loess soil. This result differed from that of nonpolar organic contaminants.

All the sorption isotherms were nonlinear and well fitted to the Freundlich equation. The results suggested that partition was not the unique mechanism for the sorption of aromatic anions on the HDTMA-modified loess soil. The sorption of aromatic anions on the HDTMA-modified loess soil could be explained with the double-mode model of sorption to SOM. Aromatic anions, as free ions or ion pairs, were partitioned into dissolution phase and associated with specific sites in the hole-filling domain within SOM derived from HDTMA. The result of this research have developed a potential procedure provides a possibility to diminish the potential of groundwater contamination through attenuation of organic contaminants in vadose zone.

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