

Adsorption Mechanism of Di-n-butyl Phthalate Ester on Brown Soil and Red Soil

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ABSTRACT: The study aimed to investigate the adsorption mechanism of di-n-butyl phthalate (DBP) on brown soil and red soil in Shenyang and Hunan province, respectively, China. Adsorption kinetics and isotherms experiments were conducted at 288, 298 and 308 K, respectively. Results of kinetics showed that adsorption of DBP exhibited a two-step process in both brown and red soil. Different models were used to simulate adsorption isotherms and the linear form of Freundlich model fitted to the data best. Sorption capacity was larger and sorption intensity was weaker on the brown soil than the red at same temperature. Sorption capacity decreased and sorption intensity enhanced with temperature increased on both soils. In addition, the thermodynamic data were analyzed which suggested that the process was a spontaneous and exothermal process on the two soils. The values of enthalpy changes were around 40 kJ/mol in the two soils, indicating that the dominant affection was physical adsorption. Furthermore the main forces were hydrogen bond and ion exchange proved by thermodynamic data and infrared spectral analyses.

Key words: DBP, Soil, Adsorption, Thermodynamics, Infrared spectral

INTRODUCTION

Phthalate acid esters (PAEs) are used as the plasticizer and softener to make plastics more flexible (Fahimeh *et al.*, 2011; Yang *et al.*, 2013). They can be found in hundreds of industrial, medical, agricultural and domestic products, such as ethylene-floor and wallpaper, medical tubes and blood bags, mulching membranes, detergents and personal care supplies (Sun *et al.*, 2012). In recent years, global production of PAEs is in the order of millions of tons per year (Julinová & Slavík, 2012). Since PAEs are not chemically bound to polymer matrixes (Mahmoud *et al.*, 2012), they can be gradually released and migrated into the environment continuously under appropriate conditions, leading to a series of ubiquitous pollutions in water (He *et al.*, 2011; Mahmoud *et al.*, 2012), atmosphere (Wang *et al.*, 2008), soil and sediment (Zeng *et al.*, 2009; Liu *et al.*, 2010b; Mahmoud *et al.*, 2012) and food (Liao *et al.*, 2009; Sun *et al.*, 2012). Moreover, PAEs are a kind of environmental hormones (Lin *et al.*, 2011) and easy to accumulate by creatures (Pant *et al.*, 2008; Liao *et al.*, 2010), which can cause a potential risk to human and animal health (Pant *et al.*, 2008; Kessler *et al.*, 2012; Susan *et al.*, 2013). Animal toxicology studies showed that DBP, di-(2-ethylhexyl) phthalate (DEHP) and diethyl

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phthalate (DEP) decreased testicular and epididymal weight, semen quality and fertility (Pant *et al.*, 2008). Liao found that DBP had toxic effects on various plants such as Bok choy (*Brassica rapa subsp. Chinensis*) (Liao *et al.*, 2006) and Chinese cabbage (*Brassica rapa var. Chinensis*) (Liao *et al.*, 2009). Therefore, PAEs are becoming a global environmental organic contamination and a matter of considerable worldwide concern (Sun *et al.*, 2012). Di-n-butyl phthalate (DBP) is one of the most widely PAEs which is listed as a priority contaminant and endocrine disrupting compound by China Environmental Monitoring Center, United States Environmental Protection Agency, the European Union and other international organizations. DBP was detected with a relatively high concentration both in municipal water, industrial sludge (Gibson *et al.*, 2005) and especially in soil (Xu *et al.*, 2008; Zeng *et al.*, 2008; Liu *et al.*, 2013). For example, research about Handan District of China showed that the residual of DBP ranged from 3.18 to 29.37 mg/kg in fluvo-aquic soils (average 14.06 mg/kg) and 2.75 to 14.62 mg/kg in black soils (average 7.60 mg/kg) (Xu *et al.*, 2008). Adsorption-desorption can directly affect the environmental behaviors and toxicological effects of contaminants in soils and plays a critical role of the

destination of pollutants (Ling *et al.*, 2005). Therefore, understanding the adsorption behaviors of PAEs on soil is extremely essential to improve the soil conditions, prevent the crops and protect the environment from PAEs. Much researches showed adsorption of PAEs increased with an increase of soil organic matter (Zeng *et al.*, 2008; Li *et al.*, 2010; Yang *et al.*, 2013), clay content (Liu *et al.*, 2013) and influenced by pH (Mohan *et al.*, 2007; Li *et al.*, 2010; Yang *et al.*, 2013). However, the thermodynamic behaviors and mechanism of DBP adsorption in different soils are not studied. It is difficult to understand the behavior and mechanism of PAEs adsorption on brown and red soil since few studies. The aims of this paper are to (1) study the effect of temperature on the adsorption of DBP on brown and red soil; (2) investigate the adsorption mechanism of DBP in two soils.

MATERIALS & METHODS

Standard reagent of DBP (96.8% purity, CAS: 84-74-2) was purchased from Lark Technology co., Ltd. (Beijing, China). Methanol (HPLC grade) was obtained from Tianjin Concord Technology co., Ltd. (Tianjin, China). Both anhydrous calcium chloride and sodium azide were analytically grade, coming from Tianjin Bodi Chemical co., Ltd. (Tianjin, China).

The standard stock solution of DBP was prepared in methanol at a concentration of 1000 µg/mL and stored at 4 °C in a refrigerator. Another standard solution of 10 µg/mL was obtained by suitable dilution with methanol from the standard stock solutions and stored at 4°C. The different concentrations of DBP were obtained by diluting the standard stock solution using the background water solution, containing 0.01M CaCl₂ (Wen *et al.*, 2007) to maintain a constant ionic strength and 200 mg/L NaNO₃ (Kasteel *et al.*, 2010) to minimize biological biodegradation. In order to minimize any cosolvent effect, the volume percentage of methanol in each system was less than 0.1% (Guo & Kannan, 2011). To avoid unnecessary contamination, plastic equipments and materials were not used during the experiment. The brown soil and red soil were collected from Agricultural University of Shenyang and Hunan Qiyang red soil experimental station of Chinese Academy of Agricultural Sciences, respectively. There was no DBP in two soils. The main clay minerals were hydromica and vermiculite in brown soil. The main composition of red soil was kaolinite,

containing lots of iron oxide and alumina. The soils were air-dried and sieved through a 0.3 mm sieve. Basic information about the soils are presented in Table 1.

DBP was detected by HPLC system (Waters e2695 series). It was equipped with a 2489 UV detector and Venusil C18 column (5µm, 250 mm×4.6 mm). The wavelength of detector was 225 nm and the temperature of column was 30 °C. The injection volume was 10 µL. Mobile phase was 90:10 (V/V) methanol: water and pumped at a flow rate of 1.0 mL min⁻¹. The retention time of DBP was 6.2 min. Two standard curves were measured and the concentration ranged from 0.1 to 1 µg/mL and 1 to 10 µg/mL, respectively. The correlation coefficients were 0.9997 and 0.9996, respectively.

0.5000 g brown soil or red soil was added into a 50 mL brown glass tube with 25 mL 2 µg/mL DBP solution. Then the samples were shaken at a controlled temperature (288, 298 and 308 K, respectively) and 200 rpm in a constant temperature oscillator, which was protected from light to avoid DBP from photo-degradation. To monitor the residual concentrations of DBP at different time intervals, the samples were taken out at appropriate time and centrifuged at 3000 rpm for 15 min. The supernatant was filtered with a 0.45 µm water-filter membrane and analyzed using the HPLC system. Each treatment was done in triplicate.

Adsorption isotherms experiments were performed according to OECD guideline 106 (OECD, 2000). Solutions with DBP concentrations of 0.5, 1, 2, 4, 8, 16 µg/mL were added to glass tubes, respectively and cultivated according to former chapter. Each treatment was done in triplicate. After an equilibrium time, all the samples were processed. According to the difference between the equilibrium concentration and the initial concentration of DBP in aqueous phase, the absorbed amount was calculated in solid phase. A blank treatment without soil was run to examine if there would be any absorption of DBP on the glassware. The result showed that there was no obvious loss of DBP in the blank sample. Therefore, the absorption of DBP could be neglected on glassware.

The adsorption data were fitted to the models as followed:

$$\text{Linear model: } C_s = K_d C_e \quad (1)$$

Table 1. Basic properties of the soils

Soil type	pH(H ₂ O)	CEC(cmol/kg)	SOM(g/kg)	Clay(%)
Brown soil	5.53	17.2	33.0	17.9
Red soil	5.42	5.90	14.9	38.3

Freundlich model: $C_s = K_f C_e^n$ (2)

Linear Freundlich model: $\log[C_s] = \log K_f + n \log[C_e]$ (3)

Where C_s ($\mu\text{g/g}$) and C_e ($\mu\text{g/mL}$) are equilibrium concentrations in solid-phase and liquid-phase, respectively. K_d (mL/g) is the adsorbate distribution coefficient of the linear model. $K_f [(\mu\text{g/g})/(\text{ug/mL})^n]$ is the affinity coefficients of Freundlich model. n is the isotherm nonlinearity index and also an indicator of the intense of adsorption. After equilibration, the solids obtained by centrifugation were analyzed by FTIR. Before FTIR analyses, the solids were lyophilized to remove residual water. The process of lyophilization would not affect the mechanism of DBP adsorption on the soil. One mg of the soil was mixed with 100 mg of FTIR-grade potassium bromide. The mixture was milled to a fine powder in an agate mortar and then pressed by a high-pressure compression machine. This pellet was placed inside the pellet cell for FTIR analysis. The FTIR spectra were recorded in the region $4000\text{-}500\text{ cm}^{-1}$ by a FTIR spectrophotometer (German, TENSOR37).

Assuming that DBP was mainly adsorbed with organic matter, the change in free energy for adsorption was calculated using the values of organic matter content of the soils K_{OM} (Sukul *et al.*, 2008):

$\Delta G = -RT \ln K_{OM}$ (4)

The value of K_{OM} was calculated by the following equation (Rea *et al.*, 1998):

$K_{OM} = 100K_f / OM\%$ (5)

Enthalpy changes and entropy change were obtained through the equation of Vant Hoff (Namasivayam & Kavitha, 2002):

$\ln K_{OM} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ (6)

Where ΔG is the free energy change (kJ/mol), R is the gas constant [$\text{J}/(\text{mol}\cdot\text{K})$], T is the absolute temperature (K), ΔH and ΔS are the standard enthalpy change and entropy change, respectively. According to equation 6, a linear regression about $\ln K_{OM} - 1/T$ is obtained. ΔH and ΔS can be got from the intercept and slope of the line, respectively.

RESULTS & DISCUSSION

The adsorption kinetic curves are shown in Fig. 1. The curves were similar and the residual concentration of DBP kept steady from 5 h after a rapidly decrease on the two soils. The residual amount of DBP between 5 h and the subsequences were no significant changes ($P < 0.05$). In order to reach a sufficient balance, 24 h was selected as the equilibrium time. Results showed that the adsorption of DBP exhibited a two-step process in both brown and red soil (Fig. 1). The first step is a surface adsorption and it can be finished usually in a few minutes to several hours. The second step is a long lasting and slowly distribution course that contaminant molecules could enter into soil organic matter and small pore of soil mineral particles. It generally takes several weeks or months or even longer time to reach final equilibrium. The theory of two-step process had been demonstrated for other hydrophobic organic pollutants on different soil medias (Kumar & Philip, 2006; Flores *et al.*, 2009; Liu *et al.*, 2013).

Adsorption data of DBP were fitted to the models referred before. The results showed that the data could be best fitted to linear form of Freundlich model. To compare the degree of nonlinearity of these isotherms

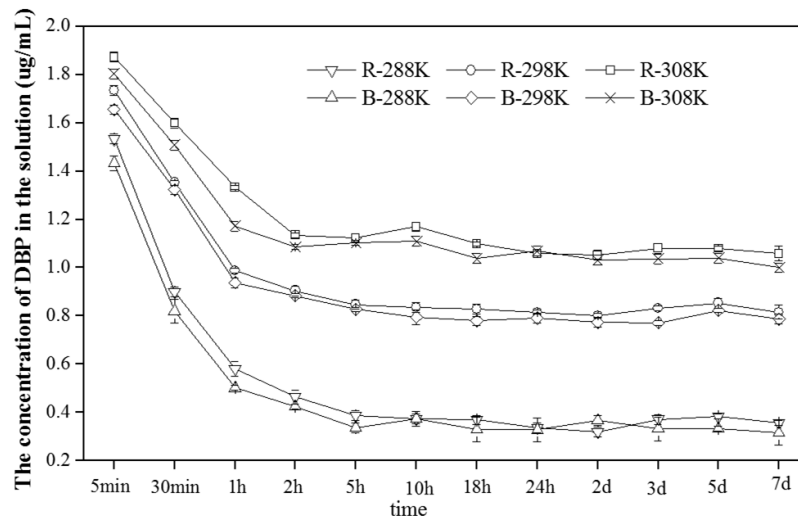
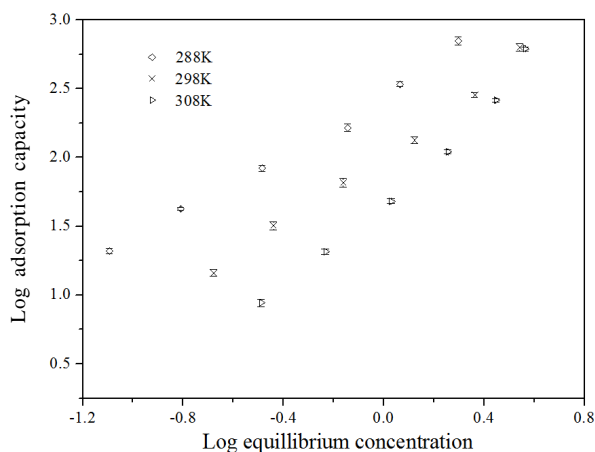
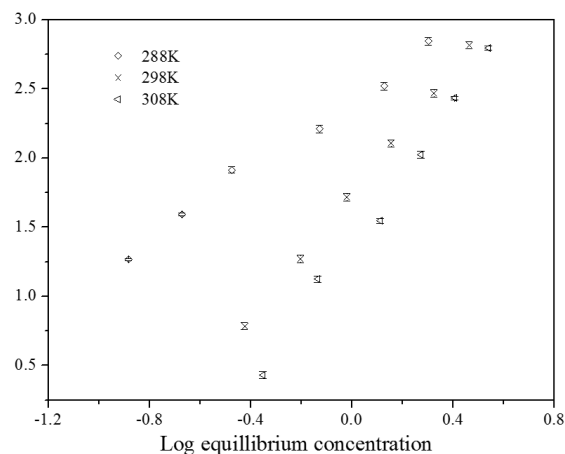


Fig. 1. Adsorption kinetic curves of DBP on two soils at different temperature in 7 days.

Table 2. Comparison of the Linear and Freundlich model for adsorption of DBP on the two soils

Soil type	Thermodynamic parameters (K)	Linear model		Linear Freundlich model		
		K_d	R^2	lgK_f	n	R^2
Brown soil	288	327	0.971	2.46	1.06	0.985
	298	156	0.869	2.03	1.28	0.993
	308	125	0.789	1.60	1.69	0.991
Red soil	288	305	0.944	2.42	1.25	0.987
	298	169	0.788	1.75	2.28	0.996
	308	128	0.725	1.46	2.58	0.990

**Fig. 2. Freundlich adsorption isotherms of DBP on brown soil.****Fig. 3. Freundlich adsorption isotherms of DBP on red soil.**

and the adsorption capacity, the parameters are given in Table 2. Adsorption isotherms were classified to S-type since n values were more than 1 on the two soils. At the same temperature, the nonlinear degree was intensified on the red soil because n value was larger than that on the brown soil. Studies showed that the type of adsorption isotherm could reflect the adsorption mechanism. Details as follows, S-type represented the adsorption affinity between adsorbent and solvent was greater than the force between adsorbent and solute at low concentration of solute (Sparks, 1995). According to this theory, the affinity between soil and DBP was relatively weaker at low concentration of DBP levels, indicating that a lower concentration was more unfavorable for DBP to be adsorbed than a higher concentration by the two of soils. The adsorption behavior of DBP onto nutshell-based activated carbon (NAC) was investigated and the results showed that the interaction between DBP and NAC was weak at low DBP concentration levels (Fang & Huang, 2009), which was same with our study.

At the same temperature, the adsorption capacity of brown soil was slightly larger since the value of lgK_f was larger on brown soil than the red. Adsorption

of pollutants can be impacted by soil properties, such as soil organic matter, cation exchange capacity, clay minerals and clay content. The dominant factors of adsorption process are various in different kinds of soil due to its composition and physicochemical properties (Weber, *et al.*, 2004; Oliver, *et al.*, 2005; Liu, *et al.*, 2013). Soil organic matter (SOM) can make a positive influence on solubilization and dissolution of PAEs because there are special sites in humic acid that can bound with PAEs.

The adsorption site increases with an increasing content of SOM, leading to a larger adsorption amount of PAEs (Zeng *et al.*, 2008; Yang *et al.*, 2013). The content of SOM (33.0 g/kg) in brown soil was more than that in red soil (14.9 g/kg), which maybe a reason for the larger adsorption capacity on brown soil. The action state of PAEs can make a cation exchange (CEC) adsorption with clay minerals causing a direct effect to adsorption amount (Wagner *et al.*, 1994). It might be another reason for a relatively higher adsorption capacity on brown soil, because the content of CEC was three times than in the red. The linear form of Freundlich adsorption isotherms of DBP on brown soil and red soil are shown in Fig. 2 and Fig. 3, respectively.

Table 3. Thermodynamics parameters of DBP adsorption on the two soils at different temperatures

soil	Thermodynamic parameters (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/(mol·K))
Brown soil	288	-20.5		
	298	-19.9	-39.0	-0.0644
	308	-19.2		
Red soil	288	-20.8		
	298	-20.1	-41.2	-0.0712
	308	-19.4		

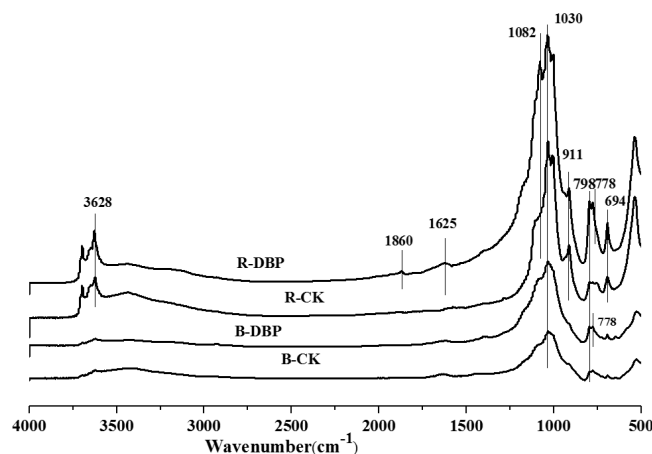


Fig. 4. Infrared spectra of blank and test soil samples.

B-CK, B-DBP, R-CK and R-DBP represented blank brown soil, adsorption sample in brown soil, blank red soil and adsorption sample in red soil, respectively.

With the increase of temperature, the adsorption isotherms of the two soils got steeper and the n value became larger, indicating that the fierce of adsorption strengthened and the isotherm of S enhanced. The reason may be that the affinity between soil and DBP at low DBP concentration decreased significantly with the increasing temperature, leading to an obvious difference of adsorption amount at different temperature, based on the theory above mentioned (Sparks, 1995).

On the other hand, research found that the adsorption theory of organics on soil was generally divided into distribution theory and sorption-site theory. The former was usually described by linear model and the later was fitted by Freundlich model (Martins & Mermoud, 1998). Therefore, the sorption-site adsorption theory was the main form of DBP absorbed by both brown and red soil.

When temperature increased, the value of $\log C_s$ reduced in the soils, indicating that the adsorption amount became smaller. It can be inferred that the adsorption was an exothermic process. Gerard *et al.* (1997) found that temperature could change water

solubility and surface activity of organic compounds, in which way adsorption behaviors was influenced. Therefore, we speculated that the surface activity of DBP was improved with an increase of temperature, making DBP more free in water and more difficult to be absorbed by soil. Chen *et al.* (2007) studied the effect of temperature on the efficiency of α -cyclodextrin-linked chitosan bead to remove PAEs and the result showed that adsorption amount decreased with the increasing temperature.

To explore the main chemical compositions of two soils and the possibility of chemisorption, infrared spectra of blank soil and absorbed samples are shown in Fig. 4.

There was such a wide absorption peak around 1000 cm^{-1} in two blank soils, which illustrated that the two soils contained a lot of silicate minerals, which could supply a sufficient medias for the exchange interactions of adsorption. There were no absorption peaks near $1500\text{-}1600\text{ cm}^{-1}$, indicating that there were little aromatic compounds in control. The absorption peaks near 694 cm^{-1} for carbon-carbon double bond and 911 cm^{-1} for triple bond were observed in red soil,

which suggested that there were relatively higher aliphatic organic matter in the red. While no obvious adsorption peaks were monitored in the brown, indicating that the organic matter were complex and various structures with tiny amount in the brown.

The absorption peaks at 1082 cm^{-1} and 3628 cm^{-1} were the stretching vibration peaks of C-OH and O-H, in adsorbed soils, respectively. It may be due to that DBP was adsorbed to the soil through hydrogen bond, causing an increase amount of C-OH and O-H. Compared to the blank samples, a weak adsorption peak at 1625 cm^{-1} appeared in the test samples, which might be induced by stretching vibration of benzene ring from DBP. Instead of 1735 cm^{-1} for ester compounds, there was a weak absorption peak at 1860 cm^{-1} in adsorbed red soil. The shift of this peak maybe the -C=O of DBP linked to another electronegative group whose electronegativity was stronger than that in its original group. Because once the C- of -C=O was connected with a stronger electronegative group, the peak would appear at a larger wavenumber. In addition, the test samples appeared a double peak phenomenon at 778 and 798 cm^{-1} , respectively, represented two different ortho substitutes of benzene. Therefore, there was also chemical adsorption in the adsorption process of the two soils.

Thermodynamics data analyses are shown in Table 3. Free energy change (ΔG) value was less than zero, indicating the adsorption behavior of DBP was a spontaneous process on the two soils. Furthermore, the ΔG value was less than 40 kJ/mol at the test temperature, which suggested the adsorption behavior was physical adsorption (Sukul *et al.*, 2008). The adsorption process of DBP was an exothermic process on the two soils since the enthalpy changes (ΔH) were negative. The value of ΔH was about 40 kJ/mol, demonstrating the adsorption type was physical sorption (Pavan *et al.*, 2008) and the main forces were hydrogen bond and ion exchange (Oepen *et al.*, 1991).

Entropy change of reaction was negative, stating that the system reached to an ordered status with a relatively lower chaos after adsorption. The reason was probable that movement was not as free as in aqueous solution and entropy change of reaction decreases after DBP molecules were adsorbed on the soil.

CONCLUSIONS

This work investigated the adsorption mechanisms of DBP on brown soil and red soil at different temperature. The results showed that the adsorption process of DBP fitted best to linear form of Freundlich model both on brown soil and red soil. At the same temperature, adsorption capacity of DBP on brown soil was larger and adsorption intense was stronger on red

soil. With the increase of temperature, the adsorption amount of DBP decreased and adsorption strength increased on two soils. Physical adsorption was the main form of DBP adsorbed on the two soils and the primary forces were the hydrogen bond and ion exchange.

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