

## Sorption of Phenanthrene onto Diatomite under the Influences of Solution Chemistry: A Study of Linear Sorption based on Maximal Information Coefficient

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**ABSTRACT.** The effectiveness of diatomite as the low-cost sorbent in the removal of polycyclic aromatic hydrocarbons (PAHs) from water was investigated. The effects of ionic strength, pH, dissolved organic matter, and temperature on sorption of phenanthrene (PHE) to two types of diatomite clay (DM 545 and DM 577) were systematically studied. The maximal information coefficient (MIC) was calculated to reveal the linearity/nonlinearity in the sorption process under the influences of aqueous chemistry parameters. Results indicated that the solution parameters played an essential role in the PHE sorption behavior at the aqueous/diatomite interface. The sorption isotherms of PHE on diatomite at different temperatures could well fit the Freundlich equation. Thermodynamic studies confirmed that the sorption behavior of PHE on diatomite was spontaneous and exothermic from 283 to 303 K. The calculation of MIC revealed the linear relationship between the aqueous PAHs and sorbed PAHs at the water/diatomite interface. The results can be used to support the potential application of diatomite for the treatment of PAH-contaminated effluents.

**Keywords:** phenanthrene, linear sorption, diatomite, maximal information coefficient

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings. They are ubiquitously present and have been identified to be carcinogenic, mutagenic, and teratogenic. PAHs can be released into the environment from both natural and anthropogenic sources, such as forest fires, volcanic eruptions, vehicular emissions, industrial combustion of fossil fuels, burning of garbage, used lubricating oil and oil filters, municipal solid waste incineration and petroleum spills and discharge (Kaushik and Haritash, 2006). PAHs can transport and be accumulated in groundwater and surface water for a long period of time, and are difficult to biodegrade (Zhao et al., 2015a).

Sorption of PAHs to various sorbents is effective to remove PAHs from aqueous phase. Recently, there are emerging interests in using low-cost clay minerals such as montmorillonite, bentonite, kaolin, and palygorskite for the removal of PAHs (Zhao et al., 2015b). Among various low-cost clay sor-

bents, diatomite has received growing interest as a potential alternative to the conventional sorbents from both environmental and economic points of view. Diatomite consists of about 90% of SiO<sub>2</sub>, with a relatively small percentage of other oxides such as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MgO. It is of particular interest due to its unique properties such as high porosity, high permeability, small particle size, high surface area, low thermal conductivity, and chemical inertness. Natural and modified diatomite sorbent has been used for the removal of hazardous metal ions, including Pb(III) (Sheng et al., 2009), Zinc(II) (Caliskan et al., 2011), Th(IV) (Sheng et al., 2008), Ni(II) (Wang, 2013), Sb(III) (Sari et al., 2010), Uranium (Sprynskyy et al., 2010), and dyes (Al-Ghouti et al., 2005; Zhuang et al., 2013) because of its unique combination of physical and chemical properties. Until recently, attention has mainly been focused on the removal of heavy metals from wastewater using diatomite. However, the removal of organic compounds (e.g., PAHs) by diatomite is not well documented and its potential use in the treatment of organic wastewater is far less explored.

During the sorption process, aqueous chemistry parameters such as pH, dissolved organic matter (DOM), temperature, and ionic strength play an important role in the distribution of organic compounds at the solid/aqueous interface. For example, the maximum naphthalene removal was at pH value of 4.0 for natural bentonite and then it slightly decreased up to pH = 7 due to more negative surface charge according to the zeta potential measurements (Kaya et al., 2013). The effects

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of DOM on PHE sorption to montmorillonite was due to the changes in the surface structure, specific surface area, hydrophobic property, and average pore size of montmorillonite (Wu et al., 2011). PHE sorption on soils treated by humic substances was usually higher under lower pH and/or lower temperature conditions (Ping et al., 2006). The sorption of PHE and pyrene on glass surface increased considerably with increasing ionic strength ( $\text{CaCl}_2$ ) from 0 to 0.005 M and changed slightly thereafter (Qian et al., 2011). Although there are extensive studies which reported the sorption behaviors of PAHs, the information regarding the effects of solution chemistry on PAHs sorption to diatomite and the corresponding sorption mechanisms still need to be clarified.

A common approach to the simulation of transport of contaminants at the solid/aqueous interface is to assume that it is governed by a linear sorption isotherm. Much work was done in this area and various linear sorption isotherm models including Freundlich and Langmuir models were applied. The correlation coefficients ( $> 0.97$ ) confirmed the linear Freundlich model could well describe the sorption behavior of Pb(II) on diatomite (Sheng et al., 2009). The PHE sorption on DOM-montmorillonite was partitioning and the characteristic of sorption isotherm was linear ( $R^2 > 0.91$ ) (Wu et al., 2011). In addition, nonlinear complexity often exists in the sorption process. Brusseau (1995) investigated the effect of nonlinear sorption on transformation of contaminants during transport in porous media. Serrano (2001) studied the solute transport under nonlinear sorption and decay. Until recently, limited data have been reported on the sorption of PAHs on diatomite and the linearity/nonlinearity inherent in the process needs further investigation through some advanced mathematic methodologies.

This study will investigate the effectiveness of the diatomite as the low-cost sorbent in removing PAHs from contaminated water. The effects of aqueous chemistry parameters on PAHs sorption to diatomite clay will be explored. An approach using the maximal information coefficient (MIC) will be applied to elucidate the linear/nonlinear relationship between the aqueous PAHs and sorbed PAHs under the influences of pH, ionic strength, DOM, and temperature. The results can help establish a fundamental understanding regarding the interactions between PAHs and diatomite clay and explicate the sorption mechanisms at the aqueous/solid interface.

## 2. Materials and Methods

### 2.1. Materials

Phenanthrene (PHE) was selected as the representative PAH, and was purchased from Sigma Aldrich Chemical Co.

(WI, USA) with the purity greater than 99%. The water solubility of PHE is 1.06 mg/L at 298 K and the octanol-water coefficients ( $\log K_{ow}$ ) is 4.57. The stock solution of PHE was made by diluting the desired amount of pure PHE crystals into HPLC-grade methanol solution, and was stored in a dark place at 277 K in an amber borosilicate bottle to minimize photodegradation and volatilization. Humic acid (HA) was purchased from Sigma (WI, USA). The pH was adjusted by NaOH or HCl purchased from Sigma (WI, USA). Diatomite clay minerals were purchased from IMERYS Filtration (CA, USA). The characteristics of diatomite are given in Table 1.

### 2.2. Sorption Studies

The batch sorption experiments were conducted in 20 mL glass vials with 20 mg diatomite. The appropriate amount of PHE stock solution was added to each vial containing deionized water. The background solution also contained NaCl. The vials were sealed with Teflon-lined screw caps and were vortexed for 20 s, and then were placed in a reciprocal shaker (SHKE5000, Thermo Scientific, USA) at 283/293/303 K and 200 rpm for 24 h to reach the sorption equilibrium. Preliminary experiments showed that 24 h were sufficient for the sorption process to reach equilibrium and the experimental loss of PHE was negligible. Before testing, the samples were subsequently centrifuged at 5000 rpm (Multifuge X1R, Thermo Scientific, USA) for 30 min and 10000 rpm (Promo Legend Micro 21, Thermo Scientific, USA) for 10 min to separate diatomite from solution. An appropriate aliquot of supernatant was then carefully withdrawn with a volumetric pipette to further determine the residual amount of PHE (Wei et al., 2013; Jing et al., 2016).

### 2.3. Effect of Aqueous Chemistry Parameters

To investigate the influence of ionic strength, the sorption tests were conducted. NaCl was added at different concentrations (0.01, 0.1 and 1 M). The initial concentrations of PHE were from 0.3 to 1 mg/L and pH value was 7. Batch sorption experiments were performed in the manner as mentioned in the sorption studies. To study the effect of pH, the PHE sorption tests were carried out at pH 3, 7, and 11 (Huang et al., 2016). The pH value of solution was adjusted with standard HCl or NaOH solution, and the ion concentration in the system was kept constant at 0.01 M. The initial concentrations of PHE were ranging from 0.3 to 1 mg/L. Temperature was kept constant at 293 K. The effect of HA on the sorption behaviors of PHE was also examined. The sorption experiments were conducted in the presence of HA ranging from 0 to 50 mg organic carbon/L (OC/L). An appropriate volume of PHE

**Table 1.** Properties of the Two Types of Diatomite Clay\*

Sorbents	Density wet ( $\text{g}/\text{m}^3$ )	Loss on ignition (1000 °C, %)	pH	Surface area ( $\text{m}^2/\text{g}$ )
DM 545	0.34	0.24	4.9	3.912
DM 577	0.35	0.3	4.4	4.661

\*Error limits of parameters are less than  $\pm 3\%$ .

stock solution was added and the initial concentrations for PHE varied from 0.3 to 1 mg/L. pH and temperature were kept constant at 7 and 293 K. The vials were placed on a reciprocal shaker at 293 K and 200 rpm for 24 hours to reach the sorption equilibrium (Forsythe et al., 2015).

## 2.4. Analytical Methods

PHE was analyzed using HPLC. The HPLC instrument, an Agilent 1260 Infinity LC System (USA), was equipped with vacuum degasser, binary pump, autosampler, thermostated column compartment (set to 303 K), diode array detector (DAD), and ZORBAX Eclipse PAH column (3.5  $\mu\text{m}$  particle size, 4.6  $\times$  150 mm ID). A mobile phase consisting of acetonitrile/water (75:25, v/v) was used at a flow rate of 1.0 mL/min. PHE was monitored with DAD at 250 nm. The amount of PHE sorbed to the sorbent was the difference between the initial amount added and the amount remaining in the solution. The pH measurements were conducted through a SevenEasy S20K pH meter (Mettler-Toledo, USA).

All of the tests were conducted in duplicate and the typical error in the measurement was less than  $\pm 5\%$ . Sorption equilibrium data were fitted to the corresponding model. The sorption data were analyzed through nonlinear regression using SigmaPlot 12.0 software (Systat Software Inc., CA, USA). The statistical analyses agreed within 95% confidence demonstrating the accuracy of measurements reported in this study.

## 3. Results and Discussion

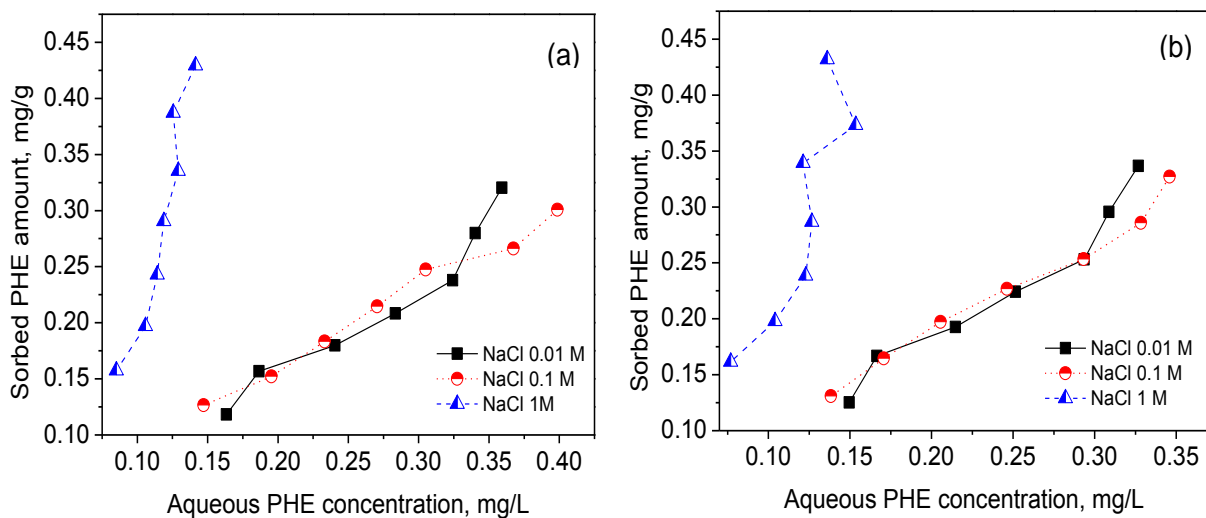
### 3.1. The Influence of Ionic Strength on PHE Sorption to Diatomite

Figure 1 shows the effect of ionic strength on sorption of PHE to two types of diatomite clays. At the ionic strength of 0.01 M, the PHE sorption ranged from 0.118 to 0.320 mg/g and from 0.125 to 0.337 mg/g for DM 545 and 577, respectively.

At the ionic strength of 0.1 M, the sorption amount ranged from 0.126 to 0.301 mg/g and from 0.131 to 0.327 mg/g for DM 545 and 577, respectively. At the ionic strength of 1 M, furthermore, there were dramatic increases of PHE sorption and the sorbed amounts ranged from 0.157 to 0.429 mg/g and from 0.162 to 0.432 mg/g for DM 545 and 577, respectively.

Results indicated that the sorption affinity of PHE to diatomite was not significantly influenced by the increasing ionic strength from 0.01 to 0.1 M. This is consistent with one study of PHE transport in the soil-water system, in which the sorption of PHE was insignificant as noticed at lower ionic strength (An et al., 2011). However, the sorption of PHE was found to increase significantly with ionic strength ranging from 0.1 to 1 M. This phenomenon could be explained by the “salting-out” effect. It is reported that the addition of ions in solution created a more homogenous water structure around the cations, which required more cavity energy for PAHs to dissolve in solution than in regular water (Qian et al., 2011). The reduction of the activity coefficients of PAHs caused an increase of sorption value. Generally, the high ionic strength values were correlated with the low mobility of PHE. The solubility of PHE decreased due to the salting-out effect and hence, the sorption of PHE increased. The presence of more salt ions resulted in a decreased diffusion of PHE from soil into aqueous phase (An et al., 2011). However, a reducing PHE sorption with increasing ionic strength was reported in a study using natural hematite nanoparticles (Li et al., 2013). The increase of ionic strength in the solution greatly increased the aggregation of soil nanoparticles, resulting in the decrease of available sites for PHE sorption.

In addition, other influencing factors, like sorbent types and solution characteristics, could also be essential to determine the influence of ionic strength on contaminant sorption behaviors. Other than salting-out effect, mechanisms such as hydrophobic effect,  $\pi$ - $\pi$  interaction, and complex formation



**Figure 1.** The sorption isotherms of PHE on (a) DM 545 and (b) DM 577 at different ionic strength levels.

interaction might also be involved to elucidate the sorption of PHE on solid particles under the influence of different ionic strength (An et al., 2016; Wang et al., 2016).

### 3.2. The Influence of pH on PHE Sorption to Diatomite

The influence of pH on PHE sorption to DM 545 and 577 is illustrated in Figure 2. The data indicated that the sorption of PHE on two diatomite soils could be affected by the pH conditions in the system. PHE sorption on DM 545 was more influenced by the solution pH due to the remarkable sorption increase when elevating pH from 3 to 11. At pH 3 and 7, the sorption amounts of PHE on DM 545 were from 0.088 to 0.303 mg/g and from 0.098 to 0.320 mg/g, respectively. The sorption amount sharply increased as pH changed to 11, especially at the low and medium PHE concentration range. With respect to DM 577, an increase in pH from 3 to 7 had no effect on the sorption of PHE. When increasing pH from 7 to 11, PHE sorption amount increased a little bit. Compared to DM 545, changes in pH caused less PHE sorption variation on DM 577. In addition, it was observed that for both DM 545 and 577, pH effect on PHE sorption was more prominent at the neutral and alkaline pH level.

The sorption of PHE on diatomite is pH-dependent, which might be caused by complicated interactive effects of surface functional groups on sorbents and specific properties of sorbates. The relative importance of the different mechanisms depends on the physical and chemical properties of the interactive sorbate-sorbent system. Generally, the  $\pi$ - $\pi$  interaction, H-bonding formation, and electron donor-acceptor interaction have been identified as the three main mechanisms in the PAHs sorption process in a solid-liquid system. Since PHE are non-polar and non-ionizable aromatic compounds, the  $\pi$ - $\pi$  interaction between the PAHs and diatomite surface would be inevitable (Yuan et al., 2010). Although PHE is non-polar regardless of solution pH, an increase of pH could modify the soil properties (e.g., amount of soil organic matter, extent of

surface deprotonation) and therefore affect the interactions between soil surface and PHE. Because DM 545 and 577 had undetectable organic contents, the enhanced dipole interaction between the charged surface (electron acceptors) and PHE with electron-rich  $\pi$  systems (electron donors) was likely to be the major reason (Fang et al., 2008). The combined mechanisms of hydrophobic effect, hydrogen-bonding interaction, and electrostatic interaction can be applied to explain the pH-dependence of PHE sorption to diatomite (Zeng et al., 2014). In addition, it is known that  $pH_{PZC}$  indicates the pH where the particle surface charge is neutral. At pH away from  $pH_{PZC}$ , the diatomite sorbent would be more stabilized due to the higher number of net charges and charge density. The surface area of diatomite could be fully exposed and more sorption sites of diatomite would be available, which was responsible for the higher PHE sorption capacity.

### 3.3. The Influence of HA on PHE Sorption to Diatomite

Because natural organic matter (such as HA) is commonly present in surface water and might interfere with the removal of organic contaminants, we investigated the effect of HA on the sorption behavior of PHE. As shown in Figure 3, PHE sorption was hindered in the presence of HA. Specifically, at the initial PHE of 0.5 mg/L, the sorption amount decreased from 0.157 to 0.148 mg/g and from 0.177 to 0.148 mg/g for DM 545 and 577 when the added dose of HA increased from 0 to 50 mg/L, respectively. At the initial PHE of 0.75 mg/L, elevating HA dose caused a reduction of PHE sorption from 0.246 to 0.225 mg/g and from 0.246 to 0.222 mg/g for DM 545 and 577, respectively. At the initial PHE of 1.0 mg/L, a decrease of PHE sorption from 0.303 to 0.270 mg/g and from 0.329 to 0.291 mg/g for DM 545 and 577 was caused by the increasing dose of HA, respectively. It is interesting that DM 577 was more influenced by the increasing HA due to its relatively larger sorption decrease.

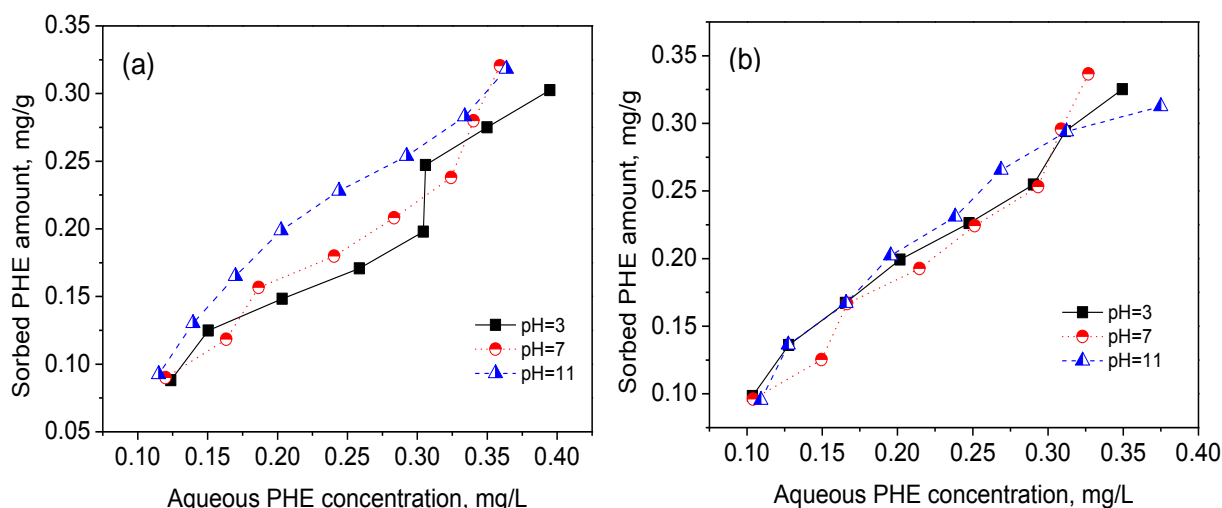
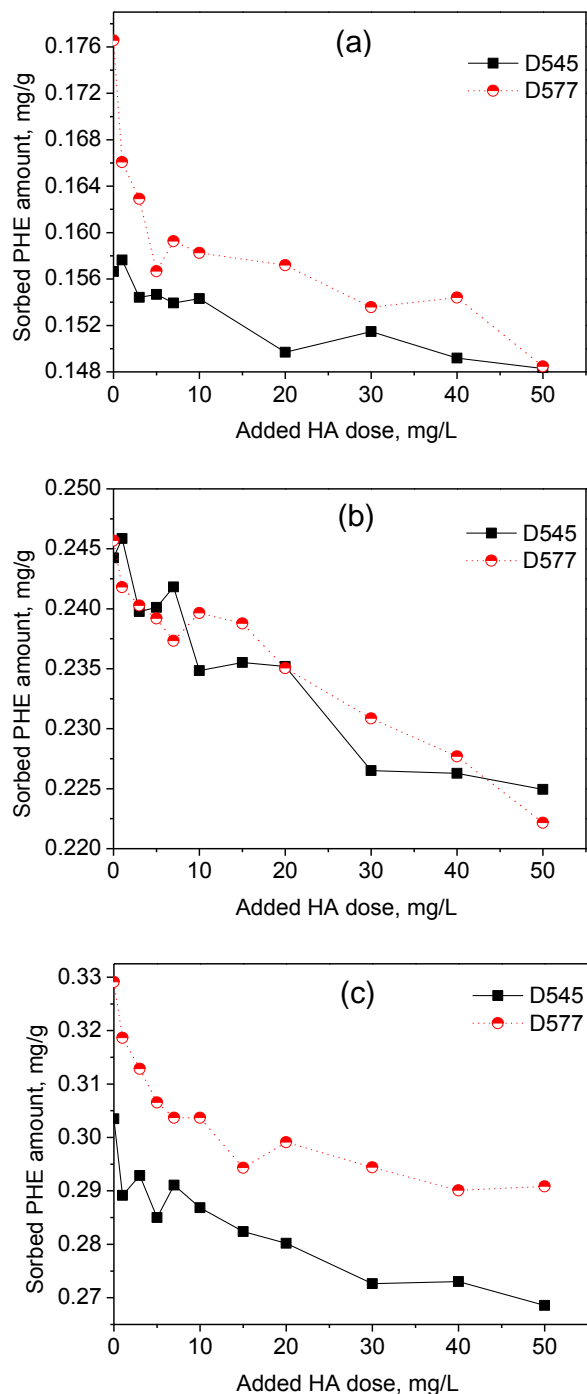


Figure 2. The sorption isotherms of PHE on (a) DM 545 and (b) DM 577 at different pH levels.

Several mechanisms might account for the considerable reduction in PHE sorption to diatomite in the presence of HA. First, PHE might compete with the HA molecules for sorption sites on the diatomite surfaces through direct site competition.



**Figure 3.** The sorption isotherms of PHE on DM 545 and DM 577, (a) initial PHE concentration 0.5 mg/L; (b) initial PHE concentration 0.75 mg/L; (c) initial PHE concentration 1 mg/L with the addition of HA from 0 to 50 mg/L.

HA was the macromolecular substance and had more functional groups that were available to simultaneously bind with the diatomite surface and to suppress PHE sorption. Such competitive sorption was also reported between nonionic organic matter and synthetic organic chemicals on carbon nanotubes (Zhang et al., 2010). Second, HA has a molecular weight which was sufficiently large to block some of the micropores on diatomite that contribute to the sorption. Therefore, the availability of sorption sites for PHE sorption was reduced. The sorption of HA molecules would occupy a great number of sorption sites on diatomite surfaces due to surface coverage and pore blockage, which would reduce sorption of PHE (Wang et al., 2009). Third, HA is mainly distributed in aqueous phase with similar function to known surfactants, which could increase the solubility of PHE, and thus decrease sorption. HA is more hydrophobic than water, thereby having higher sorption affinity for PHE than water. Sorption of PHE to the HA phase in the solution would also reduce their sorption to diatomite. Similarly, at most of the pH range, the sorption of rare earth elements in the presence of HA was much lower than that in the absence of HA, presumably due to competition for rare earth elements between HA in solution and HA sorbed onto the kaolin surface (Wan and Liu, 2006).

The effect of HA concentration on PHE sorption was due to the competition for PHE between the HA in solution and the HA sorbed onto the minerals surface. As the diatomite surface was saturated with HA, the more the concentration of HA present, the more free HA molecules existed in the aqueous phase. At the pH range in this study, HA molecules have a negative charge owing to the deprotonation of carboxyl groups or phenolic groups along the HA chain. The pHPzc values of DM 545 and 577 were approximately 4. This indicated that the surface of DM 545 and 577 carried negative charges under the test pH, resulting in enhanced HA desorption into the aqueous phase. Accordingly, the binding between HA and diatomite surface would become weaker because of electrostatic repulsion (An and Huang, 2012). Therefore, the sorption of HA with associated PHE on diatomite was inhibited. Conversely, the enhanced desorption of HA would lead to increased solubility of HA and more PHE distributing in the aqueous phase. It reveals that the distribution of HA played an essential role on the sorption behavior of PHE at the aqueous/diatomite interface.

### 3.4. The Influence of Temperature on PHE Sorption to Diatomite

Freundlich isotherm model has been widely applied to the sorption process and it is suitable for illustration of the sorption data at low and intermediate concentrations on heterogeneous surfaces (Sheng et al., 2009; Wang, 2013). The Freundlich model is written as:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (1)$$

where  $C_e$  is the equilibrium concentration of PHE in solution

and  $Q_e$  is the corresponding PHE sorption amount on solids;  $K_F$  is the Freundlich constant related to sorption capacity; and  $n$  represents the degree of dependence of sorption at equilibrium concentration. The relative parameters calculated from the model are listed in Table 2, the high  $R$  value indicating that Freundlich isotherm could adequately describe the relationship between the amount of PHE sorbed at the solid phase and its aqueous equilibrium concentration. The well fit of data to Freundlich model indicated that the sorbents used in the present work were of surface energy heterogeneity. The values of  $K_F$  increased from 283 to 303 K, implying that the sorption was enhanced with the increase in temperature. The sorption behaviors of antimony (III) on low-cost natural diatomite at different temperatures exhibited the similar trend (Sari et al., 2010), while the removal of p-cresol and di-methyl benzene from aqueous solution using diatomite clay was different (Hadjjar et al., 2011; Zaitan et al., 2013). The  $1/n$  values were largely between 0 and 1, indicating that the sorption of PHE on diatomite was favorable at studied conditions. Compared with the high-cost or complicated synthetic sorbents, diatomite can be a better candidate for PHE removal with higher sorption capacity.

### 3.5. Thermodynamic Studies of PHE Sorption to Diatomite

The thermodynamic parameters for PHE sorption on diatomite were calculated from the temperature-dependent sorption process. The Gibbs free energy of the sorption process,  $\Delta G$  (KJ/mol) was given by the following expression:

$$\Delta G = -RT \ln K \quad (2)$$

where  $R$  and  $T$  are the universal constant of the gases (8.314 J/(mol·K)) and the absolute temperature (K).  $K$  is the equi-

ilibrium constant related to the coefficients obtained from the sorption isotherms. As listed in Table 3, the evaluation of thermodynamic parameters provided an insight into the mechanism of PHE sorption to diatomite. Clearly, the Gibbs free energy change ( $\Delta G$ ) was calculated to be  $-1.25$ ,  $-0.45$ , and  $-0.55$  kJ/mol for DM 545 and  $-0.79$ ,  $-0.10$ , and  $-0.38$  kJ/mol for DM 577 at 283, 293, and 303 K, respectively. The negative  $\Delta G$  values indicated the spontaneous nature of the sorption process.  $\Delta G$  was more negative at lower temperature, indicating that the spontaneity of the sorption process decreased with the increasing temperature.

In addition, equilibrium constants  $K$  were used to calculate thermodynamic parameters such as the enthalpy change ( $\Delta H$ , KJ/mol), and the entropy change ( $\Delta S$ , KJ/(mol·K)) through the following equations:

$$\ln K = -\frac{\Delta H}{TR} + \frac{\Delta S}{R} \quad (3)$$

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

The negative  $\Delta H$  values indicated that the sorption was an exothermic process from 283 to 303 K. As indicated in Table 3, compared to the  $\Delta G$  and  $\Delta S$  values,  $\Delta H$  values were much higher. The high value of  $\Delta H$  suggested that the exothermic process of PHE sorption on diatomite was intense with the increasing temperature. Moreover, in comparison with DM 577, the exothermic process of DM 545 was much stronger due to the higher  $\Delta H$  value. This conclusion was supported by the substantial reduction of PHE sorption with the increase in temperature from 283 to 303 K, as indicated in Figure 4. This is also consistent with our previous studies, where the sorption of PHE on soil was an exothermic process with the rising temperature (Zhao et al., 2015a, 2015b, 2017a, 2017b). Fur-

**Table 2.** Freundlich Isotherm Parameters for the Sorption of PHE on DM 545 and DM 577\*

Sample	$T$ (K)	$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	$n$	$R$
DM 545	283	0.589	1.138	0.936
	293	0.832	0.970	0.932
	303	0.805	1.120	0.978
DM 577	283	0.714	1.105	0.997
	293	1.040	0.929	0.962
	303	0.860	1.144	0.987

\*Error limits of parameters are less than  $\pm 3\%$ .

**Table 3.** Thermodynamic Parameters for PHE Sorption on DM 545 and DM 577\*

Sample	$T$ (K)	$\Delta G$ (KJ/mol)	$\Delta H$ (KJ/mol)	$\Delta S$ (KJ/(mol·K))
DM 545	283	-1.25	-11.14	-0.035
	293	-0.45		
	303	-0.55		
DM 577	283	-0.79	-6.63	-0.021
	293	-0.10		
	303	-0.38		

\*Error limits of parameters are less than  $\pm 3\%$ .

therefore, the negative  $\Delta S$  value indicated the decreased randomness at the solid/aqueous interface during the sorption of PHE on the active sites of diatomite (Caliskan et al., 2011).

### 3.6. The Linearity/Nonlinearity inherent in the Sorption Process

The sorption process can be linear or non-linear (Huang et al., 1996; Yin et al., 1999; Cheng et al., 2002; Li et al., 2007, 2008, 2009, 2010; Cai et al., 2008; Lu et al., 2008; Huang and Cao, 2011; Fan et al., 2016a, 2016b). For example, linear sorption isotherms were used to elucidate the sorption and desorption behavior of 2,4-dichlorophenol in marine sediments (Fytianos et al., 2000); while the sorption of reactive contaminants in porous media was clearly a nonlinear process (Brusseu, 1995). When fitting the sorption data with some classical models, Pearson's  $r$  coefficients were widely used to reflect the linear relationship between contaminant aqueous concentration and sorption amount. To further identify the nonlinearity between the aqueous concentration variables and the correspond sorption values, maximal information coefficient (MIC) proposed by Reshef et al. (2011) was used to examine the linear/nonlinear behavior of sorption systems and analyze experimental sorption equilibrium data.

MIC was adopted to identify the linearity/nonlinearity between the equilibrium concentration in solution and the sorption capacity at the solid phase. MIC was proposed to capture a wide range of associations both functional and not, and for functional relationships provided a score that roughly equaled to the coefficient of determination ( $R^2$ ) of the data relative to the regression function (Reshef et al., 2011). The expression of MIC can be formulated as (Zhang et al., 2014):

$$MIC = \max\{I(x, y) / \log_2 \min(n_x, n_y)\} \quad (5)$$

where

$$I(x, y) = H(x) + H(y) - H(x, y) \\ = \sum_{i=1}^{n_x} p(x_i) \log_2 \frac{1}{p(x_i)} + \sum_{j=1}^{n_y} p(y_j) \log_2 \frac{1}{p(y_j)} \\ - \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} p(x_i, y_j) \log_2 \frac{1}{p(x_i, y_j)} \quad (6)$$

$$n_x n_y < B(n)$$

and

$$B(n) = n^{0.6}$$

To identify the linearity between variables  $x$  and  $y$ , the Pearson's  $r$  value ( $R_{xy}$ ) is commonly employed (de Siqueira Santos et al., 2013). The nonlinearity between two variables  $x$  and  $y$  can be examined through the calculation of MIC -  $R_{xy}^2$ .  $x$  is the aqueous concentration of PHE, and  $y$  is the sorption amount of PHE on diatomite minerals. The Pearson's  $r$  value, MIC, and nonlinearity coefficient corresponding to the PHE-diatomite sorption system are listed in Table 4.

From the table, all the MIC values approached to 1, indicating the linear characteristics inherent in the sorption process for the experimental conditions investigated. The more the MIC closed to 1, the more prominent the linearity of the process was. The linear sorption was the most significant under the influence of pH, followed by temperature, ionic strength, and added HA dose. The nonlinear relationship between PHE at the aqueous phase and PHE at the solid phase was not apparent. It is revealed that under the PHE concentrations tested in this study, the distribution of PHE between aqueous and

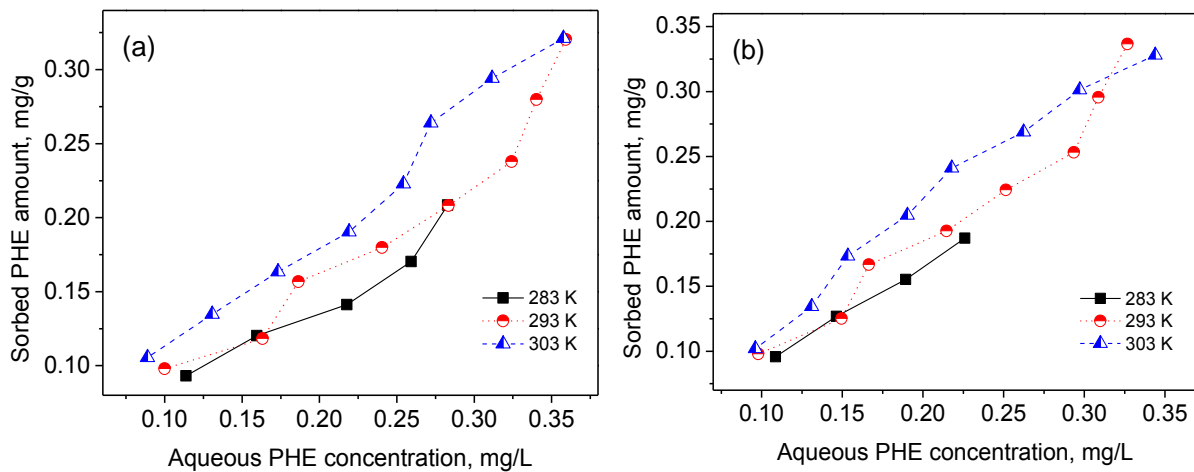


Figure 4. The sorption isotherms of PHE on (a) DM 545 and (b) DM 577 at different temperature levels.



**Table 4.** The Linearity and Nonlinearity between Aqueous PHE Concentration and Sorption Amount under the Influence of Various Operation Parameters.

	Diatomite 545			Diatomite 577		
	Pearson R	MIC	Nonlinearity	Pearson R	MIC	Nonlinearity
Ionic strength 0.01 M	0.96591	0.98523	0.05225	0.97312	0.98523	0.03826
Ionic strength 0.1 M	0.99239	0.98523	0.00039	0.98968	0.98523	0.00577
Ionic strength 1 M	0.94186	0.98523	0.09812	0.84019	0.52164	-0.18428
pH 3	0.97310	1.00000	0.05308	0.99362	1.00000	0.01273
pH 7	0.96591	0.98523	0.05225	0.97312	0.98523	0.03826
pH 11	0.98971	1.00000	0.02048	0.97964	1.00000	0.04030
Temperature 283K	0.97026	0.97095	0.02955	0.99882	1.00000	0.00235
Temperature 293K	0.96591	0.98523	0.05225	0.97312	0.98523	0.03826
Temperature 303K	0.99026	1.00000	0.01939	0.99146	1.00000	0.01701
HA 0 mg/L	0.99624	0.91830	-0.07420	0.96655	0.91830	-0.01592
HA 1 mg/L	0.91701	0.91830	0.07740	0.99994	0.91830	-0.08159
HA 3 mg/L	0.95561	0.91830	0.00510	0.99894	0.91830	-0.07958
HA 5 mg/L	0.93202	0.91830	0.04963	0.99095	0.91830	-0.06368
HA 7 mg/L	0.93722	0.91830	0.03992	0.99642	0.91830	-0.07457
HA 20 mg/L	0.93217	0.91830	0.04935	0.99160	0.91830	-0.06497
HA 30 mg/L	0.96490	0.91830	-0.01274	0.99174	0.91830	-0.06525
HA 40 mg/L	0.99512	0.91830	-0.07197	0.99997	0.91830	-0.08163
HA 50 mg/L	0.99786	0.91830	-0.07743	0.99894	0.91830	-0.07958

solid phase increased and decreased in a similar proportion.

#### 4. Conclusions

(1) The effectiveness of diatomite as the novel remediation material in treating PAHs-contaminated water was revealed and examined.

(2) The solution chemistry parameters had significant influences on PHE sorption to DM 545 and DM 577. Specifically: (a) The sorption affinity of PHE to diatomite was significantly affected by the increasing ionic strength from 0.1 to 1 M due to the salting-out effect. (b) Compared to DM 577, changes in pH caused remarkable sorption variation of PHE on DM 545. The pH effect on PHE sorption to DM 545 and DM 577 was more prominent at the neutral and alkaline pH condition, which might be caused by complicated interactive mechanisms. (c) Compared to DM 545, the PHE sorption on DM 577 was more influenced by the increasing HA due to its higher sorption reduction. The decrease of PHE sorption on both diatomite clays in the presence of HA was mainly due to the competitive sorption between PHE and HA. (d) The Freundlich isotherm model well simulated the sorption behavior of PHE on DM 545 and DM 577 at different temperatures. The sorption of PHE on diatomite was an exothermic process with the increasing temperature from 283 to 303 K.

(3) The calculation of MIC confirmed that the PHE sorption on DM 545 and DM 577 was a linear process under different aqueous chemistry parameters. The linearity was the most significant under the influence of pH, followed by temperature, ionic strength, and added HA dose. The nonlinear relationship between PHE at the aqueous phase and PHE at the

solid phase was not apparent.

(4) This study can facilitate the potential application of diatomite in PAHs-contaminated water remediation process. Future studies will be conducted to explore the combined effects of aqueous chemistry on the PAHs sorption to diatomite through factorial design techniques. The linearity/nonlinearity inhere in the sorption process will be addressed through maximal information coefficient.

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