



Adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCH)

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ABSTRACT

Porous clay heterostructures (PCHs) are capable of adsorbing volatile organic compounds (VOCs). In this study, PCH was synthesized by modifying bentonite (Bent) with cetyltrimethylammonium bromide (CTMAB) and dodecylamine (DDA). Adsorption of six volatile organic compounds (VOCs) including acetone, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene by PCH was investigated. It was observed that adsorption capacities of VOCs were strongly dependent on their properties including cross-sectional area, polarizability, enthalpy of vaporization and critical volume by the multiple linear regression (MLR) approach. Furthermore, PCH had higher adsorption affinity for the aliphatic hydrocarbon compound (acetone) than that for aromatic compounds, which could be attributed to the HOMO energy effects of VOCs. Therefore, PCH could be attractive candidate adsorbents for VOC removal.

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1. Introduction

Volatile organic compounds (VOCs) are important hazard chemicals present in outdoor and indoor air. They are often noxious or carcinogenic, either directly or indirectly, having many severe environmental problems such as the adverse effects on human health at very low concentrations [1–4].

Techniques such as thermal oxidation, catalytic oxidation, bio-filtration, absorption, adsorption, condensation and membrane separation has been developed for the removal of VOCs [5–7]. Among these techniques, adsorption was widely accepted to be effective for VOC removal due to their easy operation and low cost [8], even at low concentration (ppm or sub-ppm) [9].

It is important, for the adsorption process, to find a friendly material for capturing VOCs. Activated carbon (AC), with highly developed surface area and large pore volumes, is the most frequently used adsorbent for adsorption of gases and vapors [6,8,10–12]. However, some disadvantages of AC have been frequently encountered in practice, such as flammability, pore clog, hygroscopicity, and other problems associated with regeneration [13,14]. Furthermore, the inability of AC to adsorb aromatic compounds had been addressed [15].

Attentions in adsorbents have been focused on their performance, such as high adsorption capacity, high mass transfer rates, low cost, abundance and regeneration. Natural clays such as bentonite (Bent) can be found in a number of soils and exist abundantly

[16]. Average price of commercial bentonite is US\$ 40/t [17], 500 times lower than that of AC (US\$ 20×10^3 /t – 22×10^3 /t) [18]. Porous clay heterostructures (PCHs) are new materials, having many favorable characteristics, such as large surface area (400–900 m²/g), unique combined micro- and mesopores, high adsorption capacities and high mass transfer rates [19]. Therefore, PCH may be a potential adsorbent with high-efficiency to meet the requirement of VOC adsorption/separation technology. Galarneau et al. [20] reported a way to obtain thermally stable porous materials from the cationic layered clays. Spent or virgin organic clays such as organobentonite were used as starting materials for the preparation of PCH [14,20,21]. Organobentonites can be prepared from the low-cost and abundant bentonite by intercalating cationic surfactants into the interlayer region of bentonite [20,21].

Few studies dealt with adsorption behaviors of VOCs by the new PCHs. In our previous experimental work [14], high adsorption of benzene and CCl₄ by PCHs was observed, suggesting that PCHs are attractive candidate adsorbents for VOC removal. These PCHs were synthesized using organobentonite, a waste sorbent from wastewater treatments, to reduce their cost and avoid secondary pollution of used organobentonite [14]. In this work, adsorption performance of PCH for six VOCs was examined and related to their physical/chemical properties. Aliphatic acetone was chosen due to its abundance in research laboratories or offices air. Acetone is also the most abundant carbonyl compound widely observed in outdoor and indoor air [22]. Aromatic hydrocarbons account for 22–40% of the total ambient VOCs in the modern urban environments [23]. Among aromatic VOCs, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene are most ubiquitous in indoor air [24] and have significant toxicity to human body [25,26].

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Table 1
Physical properties and adsorbed amount of nitrogen and selected VOCs^a.

Formula	Name	MW (g/mol)	P^*	μ (Debye)	V_c (cm ³ /mol)	ΔH (kJ/mol)	σ^b (nm ²)	Q_m (mmol/g)	Q_{total} (mmol/g)
N ₂	Nitrogen	28.01	1.7	0.00	90.1	6.512	0.163	5.47	12.1
C ₃ H ₆ O	Acetone	58.08	6.4	2.88	209.0	32.206	0.269	2.32	4.65
C ₇ H ₈	Toluene	92.14	12.3	0.36	315.8	38.344	0.344	1.53	3.08
C ₈ H ₁₀	Ethylbenzene	106.17	14.2	0.59	373.8	42.420	0.378	1.88	3.69
C ₈ H ₁₀	<i>o</i> -Xylene	106.17	14.9	0.62	369.2	43.740	0.375	1.84	3.28
C ₈ H ₁₀	<i>m</i> -Xylene	106.17	14.9	0.30	375.8	44.516	0.379	1.48	3.45
C ₈ H ₁₀	<i>p</i> -Xylene	106.17	14.1	0.00	379.1	41.874	0.380	1.11	3.60

MW: molecule weight; σ : cross-sectional molecule area; P^* : polarizability; μ : dipole moment; V_c : critical volume; ΔH : enthalpy of vaporization (298 K); Q_m : monolayer amount adsorbed; Q_{total} : total amount adsorbed.

^a Data from [42].

^b Data from [43].

2. Experimental

2.1. Materials

Acetone, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene are of analytical grade, which were purchased and used without further purification (Zhejiang Chemical Reagent Co., Ltd., China). Their physical/chemical properties are listed in Table 1. Cetyltrimethylammonium bromide (CTMAB), dodecylamine (DDA) and tetraethylorthosilicate (TEOS) are of analytical grade and obtained from Shanghai Bo'ao Biological Technology Co., Ltd., Sinopharm Chemical Reagent Co., Ltd. and Shanghai Wulian Chemical Plant.

2.2. Synthesis of PCH

Bentonite with a cationic exchange capacity (CEC) of 1.08 mmol/g was obtained from Inner Mongolia, China and grinded to 100 mesh for further use. The predominant clay mineral of bentonite is Ca-montmorillonite. Organobentonite (CTMA-Bent) was prepared by introducing the cationic surfactant (CTMAB) into bentonite. A suspension of 100 g previously grinded bentonite was first equilibrated with 1000 ml of surfactant solution containing 0.108 mol/L of CTMAB under stirring at 60 °C for 2 h. Then, the suspension was separated by centrifugation at 4000 rpm for 15 min, washed three times with distilled water to remove any excess surfactant, air-dried, and pestled to 100 mesh. To synthesize PCH, a co-surfactant (DDA) was intercalated with TEOS into CTMA-Bent. The intercalating of DDA and TEOS led the organosilica to a porous framework. The mass ratio of CTMA-Bent:DDA:TEOS used in this synthesis was 1:1:120. The mixture of CTMA-Bent, DDA and TEOS was stirred for 4 h. Then, PCH before calcination was collected by centrifugation, and air-dried overnight at room temperature. Subsequently, the solid was calcined at 550 °C for 6 h (3 °C/min heating rate) in air to remove the surfactant and co-surfactant and produce the PCH.

2.3. Adsorption of N₂

Nitrogen isotherms were measured at 77 K on a NOVA 2000e Surface Area & Pore Size Analyzer from Quantachrome Corp. (United States). The adsorbents were out-gassed at 378 K for 16 h in a vacuum furnace prior to analysis. The specific surface area (S_{BET}), was calculated from the adsorption branch of N₂ isotherm using the Brunauer–Emmett–Teller (BET) method in a relative vapor pressure ranging from relative pressure of 0.05 to 0.3 [27]. Pore size distribution was obtained from the desorption branch of N₂ isotherm by the Barrett–Joyner–Halenda (BJH) method [28]. The total porous volume of PCH was estimated from the adsorption capacity at relative pressure of 0.985.

2.4. Adsorption of VOCs

Adsorption isotherms of selected VOCs on PCH were determined using a dynamic method described in our previous work [14]. Nitrogen, with a purity of 99.999%, was used as the carrier gas. N₂ was divided into two flows ranging up to 600 cm³/min. The gas flow rate was adjusted using the mass flow controllers (Beijing Metron Instruments Co., Ltd.). One of the two flows was conducted to the pre-saturator containing pure liquid VOC. Other was employed as the diluted gas. The concentration of VOCs' vapor, P/P_0 , was used in this study ranged from 0 to 1.0. VOC isotherms were obtained by the gravimetric method when the changes in weight of adsorbents were less than 2 mg [14]. Before adsorption measurements, adsorbents were out-gassed at 373 K for 24 h.

3. Results and discussion

3.1. Surface area and porosity of PCH

According to adsorption–desorption isotherms of N₂ on PCH (Fig. 1(a)), pore diameter of PCH is ranged from 1.5 to 58 nm with an average value of 2.23 nm. S_{BET} and total pore volume of PCH were 740 m²/g and 0.745 cm³/g, respectively. PCH had more micropores and mesopores (Fig. 1(b)), indicating the forming of porous structure during calcination [20,29–31].

3.2. Influence of temperature on adsorption capacity

Adsorption capacity of *p*-xylene on PCH decreased with increasing temperatures (Fig. 2), indicating the exothermic nature of VOC adsorption on PCH. When temperature increased, the amount adsorbed was decreased. Thus, 298 K was chosen as the best temperature for the removal of VOCs in the subsequent study.

3.3. VOCs isotherms

Adsorption isotherms of six VOCs on PCH are shown in Fig. 3. These isotherms of all the selected VOCs were similar to that of BET. From Fig. 3, it can be observed that in general the most polar compounds (acetone) present the highest adsorption capacity, followed by the aromatic compounds (toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene). Fitted parameters of four models to the experimental data of *p*-xylene adsorption isotherm on PCH at 298 K are presented in Table 2. The best fittings were obtained by the hybrid model, i.e., the BET model for monolayer adsorption in $P/P_0 < 0.50$ and the Harkins–Jura equation for multilayer adsorption in $P/P_0 \geq 0.50$, respectively.

$P/P_0 < 0.50$:

Table 2
Fitted parameters of four models to the experimental data of *p*-xylene isotherm on PCH (298 K).

Isotherm	Model	Range of (P/P_0)	A (constants)	B (constants)	r
Freundlich	$Q = A (P/P_0)^{1/B}$	$P/P_0 < 0.90$	-2.00	1.02	0.9780
BET	$(P/P_0)/[(1 - P/P_0)Q] = A + B (P/P_0)$	$P/P_0 < 0.50$	0.172	0.496	0.9963
Harkins–Jura	$\ln(P/P_0) = A + B (1/Q^2)$	$P/P_0 > 0.50$	0.340	-4.19	-0.9921
Smith	$Q = A + B \ln(1 - P/P_0)$	$0.50 < P/P_0 < 0.95$	144	-39.0	-0.9817

$$\frac{(P/P_0)}{[(1 - P/P_0)Q]} = 0.172 + 0.496 \left(\frac{P}{P_0}\right) \quad (1)$$

$$P/P_0 \geq 0.50 :$$

$$\ln\left(\frac{P}{P_0}\right) = 0.340 - 4.19 \left(\frac{1}{Q^2}\right) \quad (2)$$

where, Q (mmol/g), P and P_0 are adsorption capacities, vapor pressures and saturated vapor pressures of VOC, respectively. Other VOCs (acetone, toluene, ethylbenzene, *o*-xylene, *m*-xylene) were also well fitted by this hybrid model.

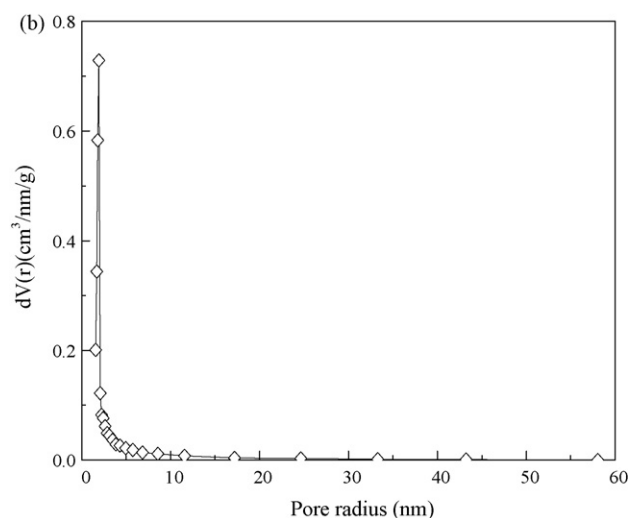
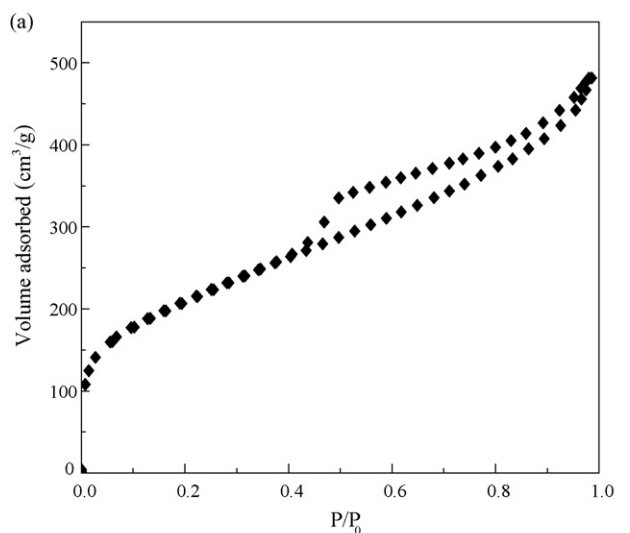


Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of PCH.

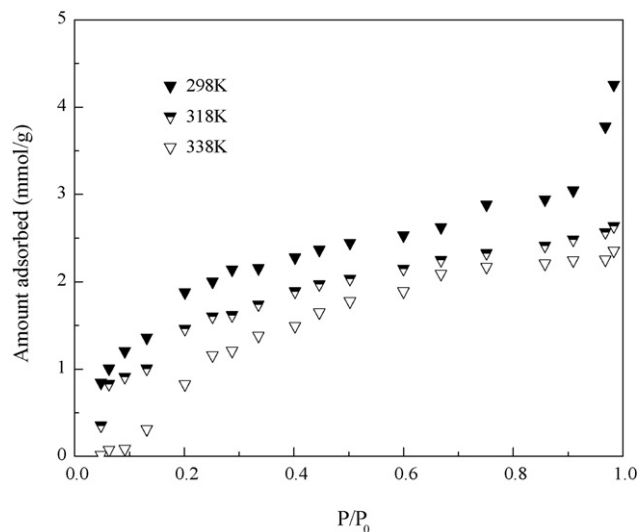


Fig. 2. Adsorption isotherms of *p*-xylene on PCH (298, 318, 338 K).

3.4. Evaluation of the monolayer and total adsorption capacities

Monolayer VOC adsorption capacity (Q_m , mmol/g) was calculated from the intercept $A = 1/(Q_m C)$ and slope $B = (C - 1)/Q_m C$ of BET equation. Monolayer adsorbed amount and total adsorbed amount (Q_{total} , mmol/g) exhibited good linear relationships with cross-sectional area of adsorbate molecule (σ , nm²) or enthalpy of vaporization (Table 1):

$$\lg Q_m = -0.386 - 0.582 \lg \sigma \quad (r^2 = 0.8743, \quad n = 7) \quad (3)$$

$$\lg Q_{total} = 0.0990 - 1.46 \lg \sigma \quad (r^2 = 0.9313, \quad n = 7) \quad (4)$$

$$Q_m = 6.00 - 0.106 \Delta H \quad (r^2 = 0.9331, \quad n = 7) \quad (5)$$

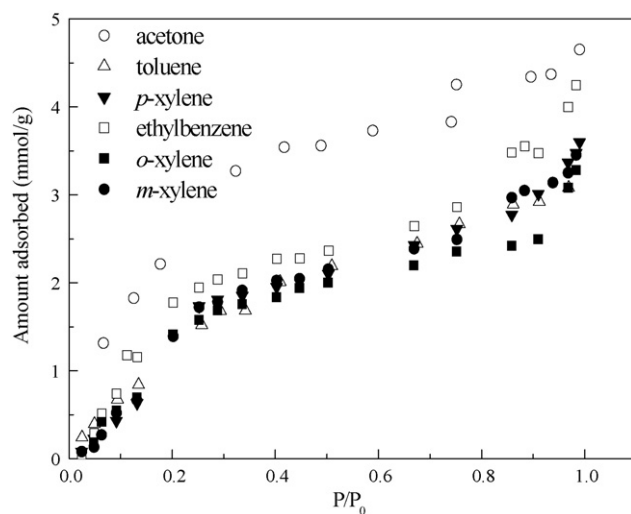


Fig. 3. Adsorption isotherms of acetone, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene on PCH (298 K).

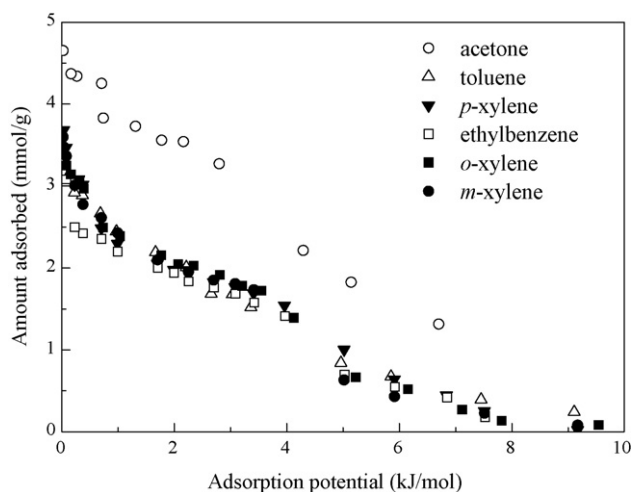


Fig. 4. Interactions of the chemical affinity and amount adsorbed between adsorbates and adsorbents (298 K).

$$Q_{\text{total}} = 13.2 - 0.234 \Delta H \quad (r^2 = 0.9480, \quad n = 7) \quad (6)$$

The properties of VOCs differed not only in the molecular sizes, but also in VOCs' polarities [13]. Polarizability (P^*) was related to intermolecular interactions [32]. Higher polarizability induced greater enthalpy of vaporization ($\Delta H = 7.61 + 2.50P^*$, $r^2 = 0.9030$, $n = 7$). Polarizability of VOCs could be related to their molecular size effects [32], showing good correlations with VOCs' critical volume (V_c) ($V_c = 59.3 + 21.6P^*$, $r^2 = 0.9903$, $n = 7$) or cross-sectional area (σ) ($\sigma = 0.148 + 0.0159P^*$, $r^2 = 0.9812$, $n = 7$).

In order to discriminate the most significant variables of VOCs, a multiple linear regression (MLR) approach was tested [33–35]. MLR approach was used for carrying out the quantitative analysis using MINITAB software which attempted to establish quantitative correlation between adsorption capacity on PCH and physical/chemical properties of VOCs (Table 1). The multiple regression equation for the response variable adsorption capacities (Q) was based on a maximum r^2 criterion and could be fitted with Eqs. (7) and (8):

$$Q_m = 16.1 - 91.3\sigma + 0.300P^* + 0.0211\Delta H + 0.0392V_c \quad (r^2 = 0.9742) \quad (7)$$

$$Q_{\text{total}} = 33.0 - 195\sigma - 0.0281P^* - 0.0567\Delta H + 0.126V_c \quad (r^2 = 0.9984) \quad (8)$$

Adsorption capacities could be predicted from the main variables rejected by MLR approach, such as σ , P^* , ΔH and V_c .

3.5. Adsorption potential

Once a gas adsorbed on adsorbent at a given P/P_0 , a decrease in chemical potential would occur. Except for the non-ideality of the adsorbates, the adsorption potential (A) was the molar work of adsorption [36]. It can be expressed as

$$A = -\Delta\mu(\text{kJ/mol}) = RT \ln \left(\frac{P_0}{P} \right) \quad (9)$$

$\Delta\mu$ is the quantitative measure of the chemical affinity of adsorbate for adsorbent. The negative plots of $\Delta\mu$ plotted against amount adsorbed of the selected VOCs (Fig. 4) served as useful criteria for the strong interactions of adsorbate–adsorbent. It was interesting to note that adsorption capacity of acetone was higher than that of BTEX during the monolayer phase. When below $0.5P/P_0$ (monolayer phase) for the selected VOCs, there

was a good linear relationship between adsorption potential and amount adsorbed (Fig. 4). The slope of the line showed that the interactions followed the same variation in the order of acetone < toluene < ethylbenzene < xylene, and there was no difference among the three xylene isomers. The constant slope depended on the difference between the melting and boiling points of VOCs and their cross-sectional molecules. When above $0.5P/P_0$, multilayered adsorption was followed by monolayered adsorption initially. The experimental results obtained showed that slope constant followed the order of ethylbenzene < xylene < acetone < toluene. However, the slope of the three isomers of xylene had no distinct difference.

3.6. Adsorption mechanism

The typical multilayer isotherm was composed of the following regions: non-cooperative adsorption and cooperative adsorption on a strongly heterogeneous surface, cooperative multilayer adsorption induced by small van der Waals [37]. A correlation between adsorption capacities at the different relative pressures and the physical/chemical properties revealed that the different mechanisms involved. As mentioned above, we tentatively explained adsorption behaviors taking into account the chemical natures of VOCs.

3.6.1. Low relative pressure ranges

It is well known that physical adsorption isotherms are linear at low pressure ranges, where Henry's Law applies. The monolayer region at relatively low pressures ($P/P_0 < 0.5$) was ascribed to physical adsorption of an adsorbent, including two regions: non-cooperative adsorption and cooperative adsorption on heterogeneous surface [37]. The adsorbates occupied most adsorption sites and adsorbent–adsorbate interactions dominated in the adsorption process [38]. The adsorption capacity ($P/P_0 < 0.5$) of acetone was higher than toluene, ethylbenzene, m -xylene, p -xylene and o -xylene due to the low boiling point and high vapor pressure at 298 K.

In order to provide energy information, the quantum-chemical descriptor (highest occupied molecular orbital (HOMO) energies), of the VOCs was calculated based on Fukui's frontier orbital theory [39] with a PM3 program. The energy of the HOMO is a measurement of the nucleophilicity of a molecule: high reactive molecules have high HOMO energy values [40]. The HOMO values of VOCs were -10.77 , -9.44 , -9.21 , -9.28 , -9.29 and -9.18 eV for acetone, toluene, ethylbenzene, o -xylene, m -xylene and p -xylene, respectively. Clearly, the degree of adsorption of these VOCs is due to HOMO energy values.

3.6.2. High relative pressure ranges

In the high relative pressure ranges ($P/P_0 \geq 0.5$), the adsorption capacity of acetone was higher than toluene, ethylbenzene, m -xylene, p -xylene and o -xylene. Mesopores allow the adsorption to proceed in relatively higher pressures region with a multilayer fashion [13]. By contrast, at relatively high pressures, multilayer adsorption occurs and adsorbate–adsorbate interactions became more prevalent, which should be taken into account [32,38]. At relatively high pressures, cooperative multilayer adsorption induced by van der Waals [37]. Van der Waals attractive forces between neutral molecules are of three types, namely induced–dipole/induced–dipole forces, dipole/induced–dipole forces and dipole–dipole forces [41]. Induced–dipole/induced–dipole forces are the only type of intermolecular attractive forces for non-polar molecules [41]. In addition, polar molecules (acetone) have two additional types of attractive force, dipole/induced–dipole forces and dipole–dipole forces [41]. So the adsorption behaviors of non-polar and polar

molecule are significantly different. PCH provided much higher adsorption capacity for acetone with increasing equilibrium concentration but lower adsorption capacity for aromatic VOCs (Fig. 3). Therefore, adsorption capacity of acetone on PCH may be increased due to interaction between dipoles of adsorbate–adsorbate at high pressure ranges.

At high relative pressures (above $0.5P/P_0$), the adsorbed amounts of VOCs exceeded the equivalent amount of a monolayer and gas molecules were not directly related to the nature of adsorbent. There are π – π dispersion interactions among molecules of aromatic ring compounds (BTEX) with face-to-face or offset face-to-face orientation. The orientation contribution is equivalent to interactions of the weak hydrogen bond. However, the dipoles of acetone are considered to align to produce dipole–dipole, dipole/induced–dipole interactions. The molecular forces are reinforced by mechanisms of dipole–dipole and dipole/induced–dipole interactions. It equals to interactions of the medium strength hydrogen bond, which is stronger than the forces donated by π electrons for aromatic compounds. Due to the stronger intermolecular interactions, acetone, therefore, was observed with a trend of higher adsorption affinity than BTEX on PCH.

4. Conclusions

Adsorption isotherms of selected VOCs on PCH, determined at ambient temperature by the gravimetric method, demonstrates different aspects of their adsorption mechanisms. Based on the qualitative and quantitative results from the proposed MLR analysis model, it was found that VOCs' cross-sectional area, polarizability, enthalpy of vaporization and critical volume were the most important parameters influencing adsorption capacities of VOCs on PCH. In general, if only the total adsorption capacities were considered, HOMO energy values were to be preferred. Thus, PCH had much higher adsorption affinity for aliphatic hydrocarbon compound such as acetone than that for aromatic compounds due to the HOMO energy values of VOCs. It was also shown that the VOC isotherms could be described by the BET–Harkins–Jura equations.

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