



Research article

Linear adsorption of organic compounds on mesoporous activated carbon in bi-solute system

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ABSTRACT

Knowledge of organic compounds adsorption by adsorbents is essential for evaluating the environmental fates of organic compounds and removing them from the environment. Linear adsorption, as a supplement to the traditionally nonlinear adsorption, was previously proposed for the linear sorption of organic compounds on the mesoporous surface of carbon nanotubes (CNTs) in multi-solute system. However, CNTs are not the ideal adsorbent to verify the linear adsorption mechanism, because of their partition-like phase components such as mobile graphene layers that could be responsible for the linear sorption through linear partition mechanism instead, and thus the linear adsorption theory was argued. In this study, therefore, mesoporous activated carbon (MAC), widely accepted as the model free of partition phase components, was selected as an adsorbent to investigate the adsorption of typical organic compounds in the bi-solute system for verifying whether the linear adsorption phenomenon existed or not. The isotherm of nitrobenzene on MAC was changed from nonlinear to linear with 4-nitrophenol up to 1400 mg/L, and the linear isotherm slope decreased more as 4-nitrophenol concentration increased until 4000 mg/L. It agreed with the characteristics of adsorption (i.e., competition) but not partition (i.e., noncompetition), confirming the existence of linear adsorption. The isotherm linearity was attributed to the reduction of adsorption interactions by displacement and multi-layer adsorption. Moreover, linear adsorption of apolar compounds on MAC could occur with apolar or polar competitors, while for polar compounds, linear adsorption could occur with only polar competitors. The observed linear sorption and the competition of organic compounds in the bi-solute system on MAC free of partition phase components verified that the linear adsorption existed, which gives a new insight into the adsorption theory for organic compounds. The results could provide better fundamental theory of adsorption for improving the accuracy of environmental risk assessment of organic pollution and enhancing the efficiency of organic pollution control in the environment.

1. Introduction

Organic pollution is a worldwide and increasingly concerned environmental issue [1]. The environmental fates of organic

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contaminants and the resulted environmental and health risks could be largely affected by the sorption of natural sorbents such as black carbons and soils [2,3]. Meanwhile, the organic contaminants in the environment could be removed by the sorption of artificial sorbents such as activated carbons [4,5]. Hence, knowledge of the sorption mechanism of organic compounds is essential for the environmental risk assessment of organic pollution and the organic pollution control in the environment [3,6]. According to the classical sorption theory, there are two main sorption mechanisms of sorbates by sorbents, i.e., partition mechanism and adsorption mechanism [7–9]. Partition means that sorbates are sorbed into the bulk phase of sorbents (i.e., “bulk sorption”), accompanied with linear isotherm and noncompetitive sorption in multi-solute system [7,10]. Adsorption means that sorbates are sorbed on the external surface of sorbents (i.e., “external surface sorption”), accompanied with nonlinear isotherm and competitive sorption in multi-solute system [11–14]. During the past decades, as supplements to the classical sorption mechanism, nonlinear partition mechanism and linear adsorption mechanism were both proposed [15–17]. For example, the nonlinear partition mechanism was proposed and used to interpret the nonlinear sorption of organic compounds by soils [15,18,19]. It was verified in our studies by the nonlinear and high sorption of organic compounds to a resin ADS-12, humus-like substances humificated from rice straw, and organobentonites, respectively, all of which were with undetectable surface area [17,20–22]. The linear adsorption mechanism was also proposed and used to interpret the linear sorption of organic compounds to carbon nanotubes (CNTs) under the competitive sorption of coexisted solutes [16,23]. However, CNTs were not an ideal adsorbent for verifying the linear adsorption mechanism, because CNTs were reported to contain a certain amount of carbonaceous impurities and mobile graphene layers, which could behave like a linear partition phase for organic compounds [24–27]. It is difficult to identify that the possible mechanism for the linear isotherms of organic compounds on CNTs in multi-solute system is the linear adsorption mechanism or the linear partition mechanism. Hence, the linear adsorption mechanism as a supplement to the traditionally nonlinear adsorption was only proposed but still not verified yet. Ruling out the linear partition mechanism by selecting an adsorbent without partition phase components should be a way to verify whether the linear adsorption mechanism of organic compounds on adsorbents exists or not.

In this study, for ruling out the contribution of linear partition mechanism and better verifying whether the linear adsorption mechanism existed or not, a mesoporous activated carbon (MAC), widely accepted as an adsorbent free of partition phase, was selected as the model adsorbent [28,29] to investigate the linear sorption of typical organic compounds (i.e., nitrobenzene, 1,4-dinitrobenzene, 4-nitroaniline and 3-nitrophenol) in the presence of competitor (i.e., 4-nitrophenol and 4-chloronitrobenzene). These organic compounds are toxic pollutants and could coexist in waste water [30]. Moreover, adsorption affinity of 4-nitrophenol to carbonaceous sorbents was strong, and thus 4-nitrophenol was used as an ideal adsorption competitor in the previous study [29]. Adsorption data in multiple bi-solute systems could serve as convincing evidence to verify the existence of linear adsorption. The investigated linear adsorption mechanism of organic compounds in multi-solute system would be a supplement to the traditionally nonlinear adsorption mechanism, and could fill the knowledge gap of the adsorption theory. Therefore, the results obtained from this study would provide a better fundamental theory of adsorption for improving the accuracy of environmental risk assessment of organic pollution and enhancing the efficiency of organic pollution control in the environment.

2. Materials and methods

2.1. Organic compounds

4-Nitrophenol (4-NP, +99.5 %), nitrobenzene (NB, +99 %), 3-nitrophenol (3-NP, +99.7 %), and 1,4-dinitrobenzene (4-DNB, +98 %) were obtained from Aladdin Reagent Co. (Shanghai, China). 4-Chloronitrobenzene (4-NCB, +98 %) was purchased from Fluka Chemistry Co. (Seelze, Germany). 4-Nitroaniline (4-NA, +99.5 %) was purchased from Sinopharm Chemical Reagent Co. (Beijing, China). Their physicochemical properties are displayed in Table 1.

2.2. Mesoporous activated carbon

Mesoporous activated carbon (MAC) was purchased from Shanghai Mucklin Biochemical Co. (Shanghai, China). Adsorption-desorption isotherm of N₂ on MAC at 77 K was conducted using a physisorption analyzer (Quantachrome, Autosorb-1, USA) [32]. The C, H, and N contents of MAC were measured by a Flash EA 1112 CHN elemental analyzer (Thermo Finnigan); ash content was

Table 1
Physicochemical properties of selected organic compounds.

Compounds	Abbr	MW	S _w	λ _{max}	pK _a	V _l /100	π*	β _m	α _m	σ	logK _{ow}
4-nitrophenol	4-NP	139.11	16000	317	7.15	0.685	1.01	0.32	0.93	0.603	1.79
nitrobenzene	NB	123.11	1936	269	/	0.631	1.01	0.30	0	0.563	1.85
4-nitroaniline	4-NA	138.13	600	380	1.00	0.685	0.91	0.46	0.47	0.611	1.39
3-nitrophenol	3-NP	139.11	14000	273	8.28	0.685	1.06	0.33	0.82	0.691	2
1,4-dinitrobenzene	4-DNB	168.11	69	266	/	0.733	1.31	0.46	0	0.648	1.48
4-chloronitrobenzene	4-NCB	157.56	225	279	/	0.721	1.11	0.26	0	0.643	2.39

Abbr: abbreviation for the compound; **MW**: molecular weight (g/mol); **S_w**: water solubility (mg/L); **λ_{max}**: maximum absorption wavelength (nm); **pK_a**: dissociated constant; **V_l/100**: intrinsic molar volume (mg/mol); **π***: polarity/polarizability parameter; **β_m**: hydrogen-bonding acceptor parameter; **α_m**: hydrogen-bonding donor parameter; **σ**: the maximum cross-sectional area (nm²); **K_{ow}**: octanol/water partition coefficient. Data obtained from Ref. [31].

obtained by heating MAC at 850 °C for 4 h; O content was calculated by mass balance (Table S1) [32]. The pore size distribution (Fig. S1), mesopore volume (V_{meso} , 1.23 cm³/g), and total pore volume (V_{tot} , 1.8 cm³/g) of MAC were determined by the Density functional theory (DFT) method [33]. The surface area (S_{BET} , 1397 m²/g) and external surface area (S_{ext} , 881 m²/g) were calculated by the Brunauer-Emmett-Teller (BET) method and V-t method, respectively (Table S1) [33].

2.3. Adsorption experiments

Batch adsorption experiments in single-solute and bi-solute systems were carried out at 25 ± 1 °C, as described in our previous papers [29,34]. Chemicals were dissolved in background solution (deionized distilled water containing 0.01 mol/L CaCl₂). MAC and aqueous solution of chemicals were added into screw cap vials (8 or 40 mL). Single-point NB adsorption experiments were conducted at two initial NB concentrations (0.014 S_w and 0.60 S_w) with various 4-NP concentrations. Competitive adsorption experiments of NB by 4-NP were conducted at various NB concentrations with two fixed 4-NP concentrations (1400 and 4000 mg/L). Other competitive adsorption experiments were performed at various concentrations of target compound with saturated competitor. Solid competitor (4-NP or 4-NCB) was added to vials to maintain a saturated level. The ratios of MAC to solution were adjusted to achieve the removal rate of target chemical higher than 20 %. To avoid the dissociated effect, the final solution pH was maintained at 4.0–4.5 by adding 0.01 mol/L HCl or 0.01 mol/L NaOH solution. Vials were sealed and shaken at 150 rpm for seven days to reach apparent equilibrium based on the adsorption kinetic experiment. After equilibrium, the vials were centrifuged at 3000 r/min for 20 min to separate the solid and aqueous phases. Then, the concentrations of the chemicals in the supernatant solution were tested by the high-performance liquid chromatography (HPLC, UltiMate 3000, Dionex) with a Thermo Scientific C18 reversed-phase column (150 mm × 4.6 mm, 5 μm) and a UV detector at their maximum wavelengths (Table 1). The mobile phase consisted of a 60:40 (v/v) mixture of acetonitrile and phosphoric acid (except for 3-NP with 4-NP, v/v = 20:80) at a flow rate of 1 mL/min. Experiment uncertainties evaluated in control samples without MAC were less than 4 % of the initial chemical concentrations, and the relative errors in the measurement were not greatly dependent on concentrations. Therefore, the adsorbed amounts of chemicals were calculated directly by the mass difference of chemicals in initial and equilibrium solutions.

2.4. Extraction experiment and thermal desorption experiment

Extraction experiment was conducted as follows [35]. After adsorption equilibrium of nitrobenzene (15 mg MAC in 8.0 mL solution), the vials were centrifuged and 7.0 mL supernatant solution was quickly removed. Then, 1.0 mL extraction solvent (ethanol) was added to the vials, and the vials were sealed and shaken at 150 rpm for 12 h at 25 ± 1 °C. After extraction, the vials were centrifuged and nitrobenzene concentrations in the supernatant solution were analyzed by the HPLC method as mentioned above. Extraction efficiency of adsorbed nitrobenzene was calculated by the ratio of extracted amount to adsorbed amount of nitrobenzene on MAC.

Thermal desorption experiment was conducted as follows [36]. After adsorption equilibrium of nitrobenzene, the vials were centrifuged and supernatant solution was removed. Then, the obtained solid was freeze-dried for 3 h to obtain nitrobenzene-adsorbed MAC. These samples were heated at 150 ± 1 °C for 30 min in thermal desorption experiments. Amount of adsorbed nitrobenzene on MAC before and after thermal desorption was measured by ethanol extraction experiment. The ratio of MAC to ethanol was 15 mg–40 mL and the mixture was sealed and shaken at 150 rpm for 12 h at 25 ± 1 °C. The recovery rate measured in the control sample was 95–100 %.

2.5. Adsorption model and isotherm fitting

Freundlich model was widely used to fit isotherms of organic compounds by carbonaceous materials [37]. Moreover, the Freundlich model not only can capture nonlinear isotherms ($n < 1$), but also can capture linear isotherms ($n = 1$), and thus could well fit the nonlinear and linear isotherms in this study. Hence, the Freundlich model was used to fit the isotherms of organic compounds on MAC with or without competition.

$$q_e = K_f \times C_e^n \quad (1)$$

where q_e (mg/g) is the equilibrium adsorbed amount of adsorbate by MAC; C_e (mg/L) is the equilibrium concentration of adsorbate in solution; K_f [(mg/g)/(mg/L)ⁿ] is the Freundlich affinity coefficient; n is the Freundlich exponential coefficient.

Linear isotherms of organic compounds on MAC in bi-solute systems were fitted by linear model [37].

$$q_e = K \times C_e \quad (2)$$

where K (L/g) is the adsorption coefficient.

Mean weighted square error (MWSE) and correlation coefficients (r^2) were used to evaluate the goodness of isotherm fitting by adsorption model [33].

$$\text{MWSE} = \frac{\sum \left(\frac{q_{\text{measured}} - q_{\text{model}}}{q_{\text{measured}}} \right)^2}{v}$$

where q_{measured} is the adsorbed amount measured by experiment; q_{model} is the adsorbed amount calculated by sorption model; ν is the degree of freedom ($\nu = N-2$ for Freundlich model; $\nu = N-1$ for linear model); N is the number of experimental data points. All estimated model parameter values were obtained by commercial software (Origin 8.5).

3. Results and discussion

3.1. Single-point competitive adsorption of nitrobenzene with 4-nitrophenol on MAC

Single-point competitive adsorption of nitrobenzene at fixed initial concentrations (i.e., $0.014S_w$ and $0.60S_w$) with 4-nitrophenol at a series of concentrations on MAC (Fig. 1) were employed to figure out the effects of 4-nitrophenol concentration on the adsorption linearity of nitrobenzene on MAC [16,34]. The adsorption isotherm of nitrobenzene on MAC would be linear only if the distribution coefficient K_d (i.e., single-point slope of isotherm, q_e/C_e) were equal at all nitrobenzene concentrations [37]. It was observed that the K_d value of nitrobenzene on MAC at $0.014S_w$ (8.2 L/g) was much higher than that at $0.60S_w$ (0.56 L/g) (Fig. 1), demonstrating that adsorption affinity of nitrobenzene to MAC was stronger at a lower concentration and the adsorption isotherm of nitrobenzene on MAC should be nonlinear. A higher proportion of nitrobenzene molecules could be adsorbed on the adsorption sites with high energy at lower concentrations [14,38,39], resulting a higher K_d value of nitrobenzene at $0.014S_w$ on MAC. The K_d values of nitrobenzene on MAC at $0.014S_w$ and $0.60S_w$ both were reduced to a same value (0.38 L/g) as the 4-nitrophenol concentration increased from 0 to 1400 mg/L (Fig. 1). Subsequently, the K_d values of nitrobenzene at $0.014S_w$ and $0.60S_w$ equally decreased to a minimum value (0.25 L/g) as the 4-nitrophenol concentration increased to 4000 mg/L, and then kept constant as 4-nitrophenol concentration further increased (Fig. 1). The much higher K_d values of nitrobenzene on MAC at $0.014S_w$ than that at $0.60S_w$ as 4-nitrophenol concentration below 1400 mg/L, indicating that the adsorption isotherm of nitrobenzene on MAC is nonlinear. However, at 4-nitrophenol concentration above 1400 mg/L, the K_d values of nitrobenzene at $0.014S_w$ and $0.60S_w$ were equal, indicating that the adsorption isotherm of nitrobenzene on MAC has been changed to linear. Moreover, the K_d value of nitrobenzene on MAC at $0.014S_w$ and $0.60S_w$ both gradually decreased from 0.38 to 0.25 g/L as 4-nitrophenol concentration increased from 1400 to 4000 mg/L and then kept constant as 4-nitrophenol concentrations above 4000 mg/L, suggesting that the slope of linear adsorption isotherm of nitrobenzene on MAC should decrease as 4-nitrophenol concentration increased from 1400 to 4000 mg/L and then kept a constant at 4-nitrophenol concentration above 4000 mg/L.

3.2. Linear isotherms of nitrobenzene on MAC in the presence of 4-nitrophenol

The adsorption isotherms of nitrobenzene on MAC with 0 mg/L, 1400 mg/L, 4000 mg/L, and saturated 4-nitrophenol were displayed in Fig. 2. All the isotherms were well fitted by the Freundlich model, indicated by the high r^2 values (0.96–1.00) and low MWSE values (0.002–0.120) (Table 2). The Freundlich model fitted parameters were listed in Table 2. As displayed in Fig. 2, the adsorption isotherm of nitrobenzene without 4-nitrophenol on MAC was nonlinear, supported by the low n values of Freundlich model (0.56) (Table 2). However, the nonlinear adsorption isotherm of nitrobenzene on MAC was changed to be linear in the presence of 1400 mg/L, 4000 mg/L, and saturated 4-nitrophenol (Fig. 2), supported by the high n values of Freundlich model (i.e., 0.935, 1.045, and 1.181, respectively) (Table 2). The calculated slopes (i.e., K_{d-1400} , K_{d-4000} , and $K_{d-saturated}$) of adsorption isotherms of nitrobenzene with 1400 mg/L, 4000 mg/L, and saturated 4-nitrophenol were 0.38, 0.25, and 0.25 L/g, respectively. The change of adsorption isotherm of nitrobenzene on MAC from nonlinear to linear by the 4-nitrophenol with concentration higher than 1400 mg/L and the order of

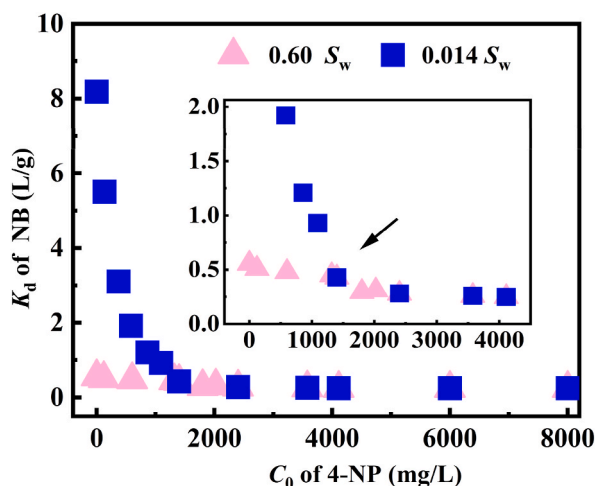


Fig. 1. Single-point distribution coefficients (K_d) of nitrobenzene (NB) at initial concentrations of $0.014 S_w$ and $0.60 S_w$ on MAC in the presence of 4-nitrophenol (4-NP) at different initial concentrations. The insert graph is an enlargement of low K_d region.

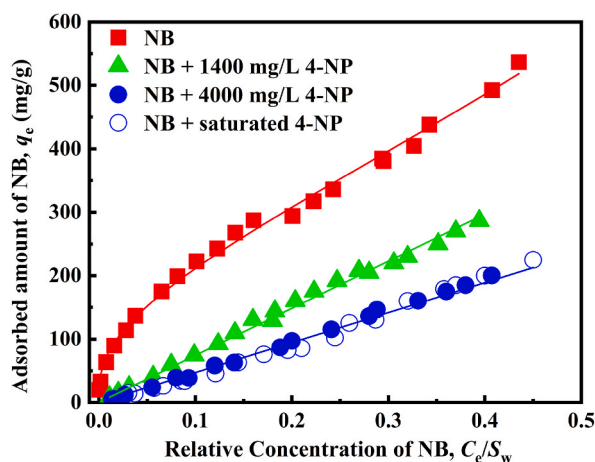


Fig. 2. Isotherms of nitrobenzene (NB) on MAC with or without 4-nitrophenol (4-NP). Solid lines are fitted isotherms by Freundlich model.

Table 2

Results of Freundlich model and linear model fits to adsorption data on MAC.

sorbates	competitor	Freundlich model				Linear model			N
		K_f [(mg/g)/(mg/L) ⁿ]	n	r ²	MWSE	K (L/g)	r ²	MWSE	
4-NP	none	29.68 ± 2.53	0.37 ± 0.010	0.9917	0.0023	/	/	/	20
4-NCB	none	39.15 ± 2.10	0.42 ± 0.013	0.9949	0.0046	/	/	/	21
NB	none	11.41 ± 1.52	0.56 ± 0.02	0.9878	0.1204	/	/	/	21
NB	1400 mg/L 4-NP	0.579 ± 0.085	0.935 ± 0.022	0.9955	0.0128	0.385 ± 0.002	0.9959	0.0010	21
NB	4000 mg/L 4-NP	0.188 ± 0.020	1.045 ± 0.016	0.9984	0.0128	0.251 ± 0.002	0.9930	0.0010	16
NB	saturated 4-NP	0.076 ± 0.014	1.181 ± 0.027	0.9954	0.1040	0.253 ± 0.002	0.9989	0.0026	17
NB	saturated 4-NCB	0.745 ± 0.116	0.973 ± 0.028	0.9968	0.0126	0.641 ± 0.002	0.9991	0.0034	10
4-DNB	none	51.30 ± 3.88	0.38 ± 0.03	0.9593	0.0168	/	/	/	21
4-DNB	saturated 4-NP	0.316 ± 0.055	1.058 ± 0.055	0.9856	0.0512	0.378 ± 0.008	0.9955	0.0094	14
4-DNB	saturated 4-NCB	1.631 ± 0.391	1.040 ± 0.080	0.9782	0.0412	1.838 ± 0.052	0.9924	0.0078	14
3-NP	none	28.43 ± 2.45	0.37 ± 0.01	0.9904	0.0050	/	/	/	23
3-NP	saturated 4-NP	0.110 ± 0.021	0.944 ± 0.022	0.9956	0.0270	0.069 ± 0.008	0.9984	0.0065	20
3-NP	saturated NCB	9.368 ± 1.099	0.486 ± 0.015	0.9933	0.0070	/	/	/	16
4-NA	none	70.35 ± 0.20	0.27 ± 0.00	0.9971	0.0090	/	/	/	20
4-NA	saturated 4-NP	0.409 ± 0.031	0.830 ± 0.014	0.9985	0.0978	0.165 ± 0.003	0.9954	0.0039	16
4-NA	saturated 4-NCB	4.110 ± 0.296	0.693 ± 0.014	0.9968	0.0090	/	/	/	18

MWSE is mean-weighted-square-errors, equal to $1/\nu[(q_{\text{measured}} - q_{\text{modeled}})^2/q_{\text{measured}}]$, where ν is the amount of freedom; $\nu = N - 2$ for Freundlich model and $\nu = N - 1$ for linear model. N: number of observations. /: fail to be fitted by the linear model. 4-NP, 4-NCB, NB, 4-DNB, 3-NP, and 4-NA are abbreviations for 4-nitrophenol, 4-chloronitrobenzene, nitrobenzene, 1,4-dinitrobenzene, 3-nitrophenol, and 4-nitroaniline.

isotherm slopes of nitrobenzene with 4-nitrophenol on MAC (i.e., $K_{d-1400} > K_{d-4000} = K_{d-saturated}$) (Fig. 2), agreed well with the results of single-point competition sorption of nitrobenzene with 4-nitrophenol as discussed above (Fig. 1).

The linear isotherms of nitrobenzene on MAC in the presence of ≥ 1400 mg/L 4-nitrophenol (Fig. 2) could not be attributed to the linear partition mechanism because: (i) the MAC was well known as a model adsorbent free of partition phase [28,29]; and (ii) the decrease of linear isotherm slope of nitrobenzene on MAC as the 4-nitrophenol concentration increased from 1400 mg/L to 4000 mg/L (Fig. 2) agreed well with the characteristic of adsorption mechanism that competitive adsorption occurred between coexisted solutes [12,13], but disagreed with the characteristic of partition mechanism that noncompetitive sorption occurred between coexisted solutes [7,10,40]. Moreover, the adsorbed 4-nitrophenol on MAC cannot act as a partition phase because the distribution coefficient (K_d) of nitrobenzene decreased as the adsorbed amount of 4-nitrophenol increased (Figs. 1 and 2), which disagreed with the characteristic of partition mechanism that the K_d of organic compound was proportional to the contents of partition phase in sorbents [21,41,42]. Hence, the linear isotherms of organic compounds on MAC in the presence of ≥ 1400 mg/L 4-nitrophenol (Fig. 2) should be attributed to the adsorption mechanism rather than the partition mechanism, i.e., linear adsorption (i.e., adsorption with linear isotherm), a quite different sorption behavior from the traditional nonlinear adsorption (i.e., adsorption with nonlinear isotherm), was verified here to be existed. To the best of our knowledge, this is the first evidence that supports the existence of linear adsorption, which is a supplement to the traditionally nonlinear adsorption mechanism and could fill the knowledge gap of the adsorption theory.

3.3. Possible mechanisms for linear adsorption of nitrobenzene on MAC

It was widely known that the nonlinearity of adsorption isotherm of organic compounds on carbonaceous adsorbents was mainly attributed to the heterogeneous adsorption interactions with different energies [11,14,38,39]. According to the previous studies [32,33,39,31], there are three main adsorption interactions, i.e., hydrogen-bonding interactions, π - π interactions, and nonspecific van der Waals force (i.e., hydrophobic effects), responsible for the adsorption of aromatic compounds on carbonaceous adsorbents (e.g., activated carbon, carbon nanotube). Moreover, significant linear solvation energy relationships (LSERs) were established between the adsorption affinity parameter (E : Dubinin-Ashtakhov (DA) model fitted parameter representing characteristic adsorption energy) and the solvatochromic parameters (α_m : hydrogen-bonding donor parameter; π^* : polarity/polarizability parameter), i.e., $E = \beta_1 \times \alpha_m + \pi_1 \times \pi^* + C$ [32,33,31]. The parameters β_1 and π_1 represented the hydrogen-bonding acceptor ability and polarity/polarizability, respectively. The items $\beta_1 \times \alpha_m$, $\pi_1 \times \pi^*$ and C represented the contributions of hydrogen-bonding interactions, π - π interactions, and nonspecific van der Waals force to the total adsorption interactions (E) between organic compounds and carbonaceous adsorbents. According to the DA model, adsorption isotherm is linear only if the DA model fitted $E = 5.71$, which represented the contribution of nonspecific van der Waals force (i.e., hydrophobic effects) [16,32,33,31]. Thus, the nonlinearity of adsorption isotherm should be derived from the nonlinear item $\Delta E = E - 5.71 = \beta_1 \times \alpha_m + \pi_1 \times \pi^* + (C - 5.71)$. The C values of multi-walled carbon nanotubes without micropores (5.0–6.6) were similar to 5.71, mainly attributed to the hydrophobic effects [31]. While the C values of single-walled carbon nanotubes (11.3) and activated carbons (8.1–14.9) were much higher than 5.71 [32,31], attributed to the adsorption in micropores in addition to the hydrophobic effects, because the adsorptive energy of adsorption sites on micropore surface were normally higher than that of adsorption sites on mesopore surface [14,38]. Thus, the item $(C - 5.71)$ could represent the contribution of high adsorption affinity on micropore surface to the total adsorption interactions (E). Hence, it is the hydrogen-bonding interactions ($\beta_1 \times \alpha_m$), π - π interactions ($\pi_1 \times \pi^*$), and high adsorption affinity on micropore surface ($C - 5.71$) that are responsible for the nonlinearity of adsorption isotherm of organic compounds on MAC. Nitrobenzene could form π - π interactions with MAC ($\pi^* = 1.01$), but could not form hydrogen-bonding interactions with MAC due to the lack of hydrogen-bonding donor ability ($\alpha_m = 0$) [32]. 4-Nitrophenol with high hydrogen-bonding donor ability ($\alpha_m = 0.93$) and polarity/polarizability ($\pi^* = 1.01$) could form strong hydrogen-bonding interactions and π - π interactions with MAC [32]. The adsorption isotherm of 4-nitrophenol was much higher than that of nitrobenzene on MAC (Fig. S2). Therefore, it can be inferred that the nonlinear adsorption of nitrobenzene on MAC should be attributed to the π - π interactions and the high adsorption affinity on micropore surface, and thus the change of nitrobenzene adsorption on MAC from nonlinear adsorption to linear adsorption by ≥ 1400 mg/L 4-nitrophenol could be attributed to the significant reduction of π - π interactions and the adsorption affinity on micropore surface because of the competitive displacement of 4-nitrophenol.

In the previous study [29], 4-nitrophenol was employed as an ideal adsorptive displacer to largely displace the adsorbed organic compounds on microporous carbonaceous adsorbents, due to the much higher adsorption affinity of 4-nitrophenol and limited adsorptive space in micropores. For example, >90 % of adsorbed o-xylene and 1,2,3-trichlorobenzene on a microporous activated carbon (F300 AC) were displaced by saturated 4-nitrophenol [29]. The disappearance of micropore peak in the pore size distribution curve of MAC with nearly saturated 4-nitrophenol (Fig. S3), indicated that most of micropores in MAC could be occupied by 4-nitrophenol. Hence, the adsorption of nitrobenzene on the micropores of MAC could be largely displaced by 4-nitrophenol, resulting in a negligible $(C - 5.71)$ item and a higher adsorption linearity. Meanwhile, it was reported that 4-nitrophenol could only partially displace the adsorbed organic compounds on mesoporous carbonaceous adsorbents, because of the formation of multilayer adsorption which could be accommodated in mesopores but not micropores [43–45]. For example, 46 % of adsorbed naphthalene on a mesoporous diesel soot was displaced by saturated 4-nitrophenol, accompanied by the multilayer adsorption of naphthalene and 4-nitrophenol on the soot [46]. Adsorption interactions (e.g., hydrogen-bonding interactions, π - π interactions) between organic molecules and the unloaded surface of carbonaceous adsorbents should be significantly higher than that between organic molecules and solute-loaded surface of adsorbent, because the hydrogen-bonding acceptor ability (β_1) and polarity/polarizability (π_1) of the unloaded surface of carbonaceous adsorbents is much higher than the solute-loaded surface [45,47–49]. Thus, multilayer adsorption affinity of organic compounds with carbonaceous adsorbent is generally much lower than monolayer adsorption affinity. Moreover, the displacement of

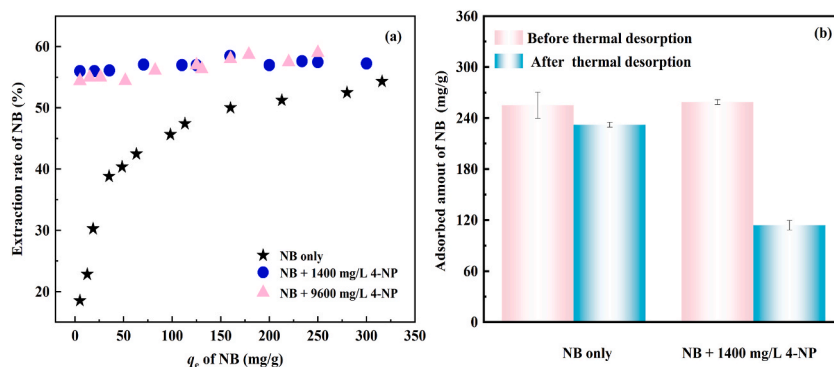


Fig. 3. Extraction rate (a) and thermal desorption data (b) of adsorbed nitrobenzene (NB) on MAC with and without 4-nitrophenol (4-NP) competition.

adsorbed organic compounds on adsorbents by competitors could be significantly alleviated by the multilayer adsorption. As displayed in Fig. 3 a-b, the extraction rates and thermal desorption rates of adsorbed nitrobenzene on MAC with 4-nitrophenol were much higher than that without 4-nitrophenol, indicating that the adsorption affinity of nitrobenzene with 4-nitrophenol on MAC was much lower than that without 4-nitrophenol. It was also observed that the adsorption isotherm of nitrobenzene on MAC was partially reduced by saturated 4-nitrophenol, although the adsorption isotherm was changed from nonlinear to linear (Fig. 2). Hence, it could be reasonable to infer that the multilayer adsorption of nitrobenzene with 4-nitrophenol occurred on the external surface of MAC. The significant decrease of hydrogen-bonding acceptor ability (β_1) and polarity/polarizability (π_1) of MAC by the adsorption of 4-nitrophenol could largely weaken the hydrogen-bonding interactions ($\beta_1 \times \alpha_m$) and π - π interactions ($\pi_1 \times \pi^*$) between nitrobenzene and MAC, resulting in higher adsorption linearity of nitrobenzene. Therefore, it is reasonable that the adsorption isotherm of nitrobenzene on MAC could be changed from nonlinear to linear, because of the significant decrease of nonlinear item $\Delta E = E - 5.71 = \beta_1 \times \alpha_m + \pi_1 \times \pi^* + (C - 5.71)$. The schematic model of the linear adsorption mechanism was shown in the Graphical Abstract. In further research, more direct characterizations of adsorption affinity of organic compounds on adsorbents are suggested to better support the mechanism of linear adsorption.

3.4. Characteristics of nonlinear and linear adsorption of organic compounds on MAC

For exploring more characteristics of nonlinear and linear adsorption, three more target organic compounds (i.e., 1,4-dinitrobenzene, 4-nitroaniline, and 3-nitrophenol) with higher polarity than nitrobenzene, and one more competitor (i.e., 4-chloronitrobenzene) with lower polarity than 4-nitrophenol were investigated. It was observed that the adsorption isotherms of 1,4-dinitrobenzene, 4-nitroaniline, and 3-nitrophenol on MAC were changed from nonlinear to linear by polar and saturated 4-nitrophenol, respectively, similar to that of nitrobenzene (Fig. 4 a-d and Table 2). Adsorption isotherms of apolar nitrobenzene and 1,4-dinitrobenzene on MAC were also changed from nonlinear to linear by apolar and saturated 4-chloronitrobenzene (Fig. 4 a-b and Table 2). However, the nonlinearity of adsorption isotherms of polar 4-nitroaniline and 3-nitrophenol on MAC were partially reduced by apolar and saturated 4-chloronitrobenzene (Fig. 4 c-d and Table 2). 1,4-Dinitrobenzene and nitrobenzene with polarity/polarizability (Table 1) could form π - π interactions but not hydrogen-bonding interactions with MAC, while 4-nitroaniline and 3-nitrophenol with hydrogen-bonding donor ability and polarity/polarizability (Table 1) could form both π - π interactions and hydrogen-bonding interactions with MAC. The polar competitor 4-nitrophenol with high hydrogen-bonding donor ability and polarity/polarizability could significantly suppress the hydrogen-bonding interactions ($\beta_1 \times \alpha_m$), π - π interactions ($\pi_1 \times \pi^*$) and high adsorption affinity on micropore surface ($C - 5.71$), resulting in the change of nonlinear adsorption to linear adsorption for both apolar organic compounds (i.e., nitrobenzene, 1,4-dinitrobenzene) and polar organic compounds (i.e., 4-nitroaniline and 3-nitrophenol) on MAC. The apolar competitor 4-chloronitrobenzene with high polarity/polarizability could suppress the π - π interactions ($\pi_1 \times \pi^*$) and high adsorption affinity on micropore surface ($C - 5.71$), but not hydrogen-bonding interactions ($\beta_1 \times \alpha_m$), resulting in change of nonlinear adsorption to linear adsorption for only apolar organic compounds (i.e., nitrobenzene, 1,4-dinitrobenzene) but not for polar organic compounds (i.e., 4-nitroaniline and 3-nitrophenol) on MAC. Meanwhile, it was observed that the isotherm slopes of organic compounds on MAC with saturated 4-nitrophenol were lower than that with saturated 4-chloronitrobenzene (Fig. 4 a-d). It could be attributed to the higher hydrogen-bonding donor ability and polarity/polarizability of 4-nitrophenol (Table 1), and also the higher displacement ability of 4-nitrophenol [12,50], as supported by the isotherms of 4-nitrophenol and 4-chloronitrobenzene on MAC (Fig. S2). Moreover, it was observed in Fig. 2 that the linear isotherm slope of nitrobenzene on MAC decreased as the 4-nitrophenol concentration increased from 1400 mg/L to 4000 mg/L, indicating that the linear adsorption of organic compounds on MAC can be competitive by competitor. Therefore, for nonlinear adsorption on carbonaceous adsorbents, apolar organic compounds could be changed to linear adsorption by both apolar and polar competitors, while polar organic compounds could be changed to linear adsorption by only polar competitor but not by apolar competitor. For linear adsorption of organic compounds on MAC with co-solutes, it is competitive if the competitors with stronger polarity or higher concentration. Linear isotherms of organic compounds on MAC in more bi-solute systems could again support the existence of linear adsorption. Moreover, the obtained characteristics of linear adsorption could be used to predict the linear adsorption for organic compounds with different polarities, which would be beneficial to the environmental risk assessment and remediation of organic pollution. In further work, linear adsorption phenomena on natural sorbents should be investigated for further improving the accuracy of environmental risk assessment of organic pollution.

4. Conclusion

In this study, MAC without partition phase components as a model adsorbent was employed to investigate the linear adsorption of typical organic compounds in bi-solute system. The existence of linear adsorption was verified by the linear adsorption of nitrobenzene on MAC in the presence of ≥ 1400 mg/L 4-nitrophenol, and the decrease of isotherm slope with the increase of 4-nitrophenol concentration from 1400 mg/L to 4000 mg/L. The verified linear adsorption mechanism could be attributed to the significant reduction of adsorption affinity by the displacement and the multilayer adsorption in bi-solute system. Different from the traditional partition mechanism with noncompetitive sorption, the verified linear adsorption is competitive by competitors. Therefore, the verified linear adsorption mechanism of organic compounds by carbonaceous adsorbents in the bi-solute system in this study is an important supplement to the traditional sorption theory (i.e., nonlinear adsorption and linear partition). The obtained results would improve the sorption theory for accessing the transport, bioavailability, and fate of organic compounds in the natural environment and promoting the removal of organic contaminants in the environment, where several solutes normally coexist.

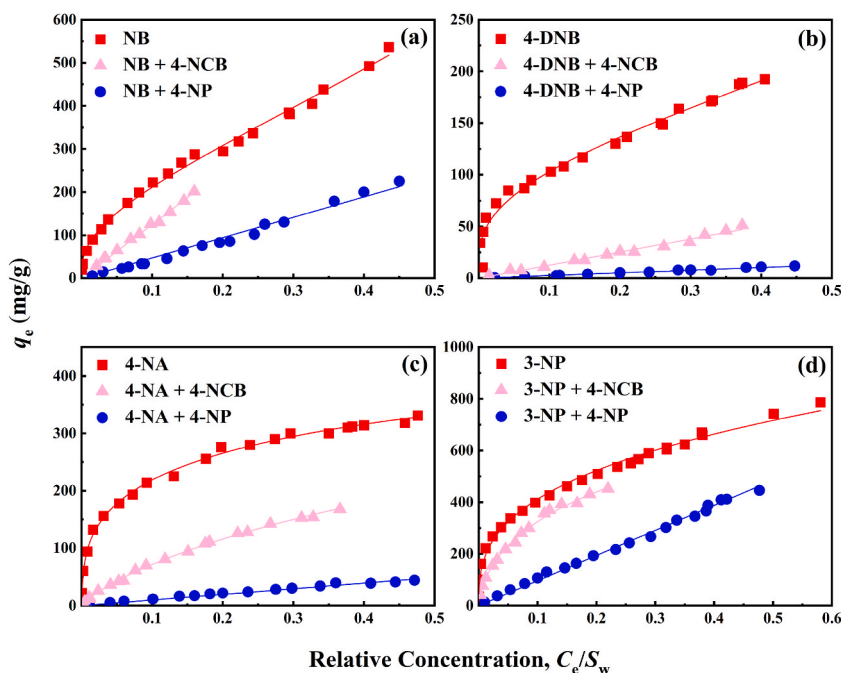


Fig. 4. Isotherms of nitrobenzene (NB, a), 1,4-dinitrobenzene (4-DNB, b), 4-nitroaniline (4-NA, c), and 3-nitrophenol (3-NP, d) on MAC with and without saturated 4-nitrophenol (4-NP) or saturated 4-chloronitrobenzene (4-NCB). Solid lines are fitted isotherms by Freundlich model.

CRedit authorship contribution statement

Xiaoyu Liu: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Wenhao Wu:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Conceptualization. **Daohui Lin:** Writing – review & editing, Methodology, Conceptualization. **Kun Yang:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e25729>.

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