



# Characterization of volatile organic compound adsorption on multiwall carbon nanotubes under different levels of relative humidity using linear solvation energy relationship



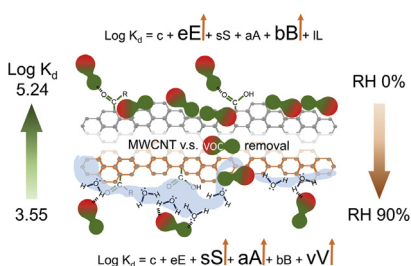
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## HIGHLIGHTS

- LSER equations successfully predicted VOC sorption on MCNT at different humidity.
- The five parameters in LSER could be narrowed down to three ones.
- Main interaction is dispersion and partly dipolarity as well as hydrogen-bonds.
- With increasing RH, it changes to cavity formation and hydrogen-bond basicity.
- This approach can facilitate the VOC control design and the fate prediction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Multiwall carbon nanotubes (MWCNTs) have been used as an adsorbent for evaluating the gas/solid partitioning of selected volatile organic compounds (VOCs). In this study, 15 VOCs were probed to determine their gas/solid partitioning coefficient ( $\text{Log } K_d$ ) using inverse gas chromatography at different relative humidity (RH) levels. Interactions between MWCNTs and VOCs were analyzed by regressing the observed  $\text{Log } K_d$  with the linear solvation energy relationship (LSER). The results demonstrate that the MWCNT carbonyl and carboxyl groups provide high adsorption capacity for the VOCs ( $\text{Log } K_d$  3.72–5.24 g/kg/g/L) because of the  $\pi$ - $n$ -electron pair interactions and hydrogen-bond acidity. The increasing RH gradually decreased the  $\text{Log } K_d$  and shifted the interactions to dipolarity/polarizability, hydrogen-bond basicity, and cavity formation. The derived LSER equations provided adequate fits of  $\text{Log } K_d$ , which is useful for VOC-removal processes and fate prediction of VOC contaminants by MWCNT adsorption in the environment.

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## 1. Introduction

Volatile organic compounds (VOCs) are widely used in the manufacture of both domestic and industrial applications/products,

but increasing VOC emissions raises a concern for both air and environmental quality. Common VOC emission sources have long been recognized to originate from solvent storage tanks, transport pipe leakage, venting of vessels, wastewater streams, and heat exchange systems. From an environmental perspective, it is essential to control and mitigate VOC air pollutants because they are linked to climate change and plant decay and impact animal and human health. Moreover, there are many indoor VOC sources,

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e.g., VOCs released through solvent usage, pressed wood products, furniture foam, and cleaners [1], which dramatically increase the daily exposure to VOCs. Because VOCs in the indoor air are known to cause severe health problems [2], much attention has been paid to the development of efficient VOC-removal processes. Many VOCs and their degradation products can be carcinogenic [3]. Consequently, there is an urgent need for the development of effective VOC-removal processes. Several techniques or technologies have been proposed for VOC control. For example, thermal oxidation, catalytic oxidation, reverse-flow reactor, and biofiltration destroy VOCs, whereas condensation, liquid solvent absorption, membrane-based processes, and carbon adsorption recover VOCs [4]. Carbon adsorption is an effective and common method for controlling VOC emissions because of its low cost and flexibility [5]. It can desorb many VOCs for regeneration [6,7]. However, because carbon adsorbents are highly diverse in structure and physicochemical properties, there is still much to learn regarding gas/particle partitioning between VOCs and carbon adsorbents.

Carbon nanotubes (CNTs), discovered by Iijima [8], have crystalline cylindrical pores that mainly consist of graphite sheets. CNTs have well-defined structures, in particular, single-wall and multiwall structures. Single-wall carbon nanotubes are composed of only one carbon layer with pores generally in the microporous levels. Multiwall carbon nanotubes (MWCNTs) comprise at least two carbon layers, and have mesoporous structure. In recent years, CNTs have been applied as adsorbents for various purposes no matter in water or air treatment, for instance, heavy metal removal [9,10], phenol removal [11], hydrogen storage [12] and adsorption of  $\text{NH}_3$  and  $\text{NO}_2$  gas [13], etc. Moreover, some studies indicate that CNTs can be used for the adsorption of organic vapors, including ethanol, *n*-hexane, *n*-nonane, and  $\text{CCl}_4$  [14,15]. The fundamental structure of CNTs, which exhibit hexagonal arrays of carbon atoms in graphene sheets, provides a strong interaction with several organic compounds and contributes to higher adsorption capacity than amorphous activated carbon. Several studies have demonstrated that CNTs have a higher adsorption efficiency than other carbon materials for removing dioxins [16], thiophene [17], 1, 2-dichlorobenzene [18], and PAHs [19]. On the other hand, the packing of CNTs in treatment equipment such as a column should be well controlled to avoid their leaks since the toxicity of CNTs also raise a concern because the CNTs could enter cells, distribute in bodies, and affect the normal function of some cell organelles [20–22]. Furthermore, the adsorption of organic contaminants on these carbonaceous materials also affects contaminants in the environment since these nano-materials such as CNTs could carry with contaminants. Therefore, the sorption of chemicals on CNTs could also play a role in their fate in the environment. However, the investigation of VOC adsorption on MWCNTs in a systematic way is limited. Moreover, modeling adsorption behaviors between various VOCs and MWCNTs in gas phase for predicting the adsorption capacity of MWCNTs for VOC removal has never been investigated. Therefore, an investigation of VOC adsorption on MWCNTs enables to obtain a better insight of relations between adsorption potential and carbon materials.

This study investigates the adsorption capacity of MWCNTs to 15 representative VOC vapors as probe chemicals under various relative humidity (RH) levels. Inverse gas chromatography (IGC) method was used to study the gas/solid partitioning coefficients of the 15 VOCs adsorbed on MWCNTs. In addition, adsorption interactions between the VOCs and MWCNTs were evaluated by the linear solvation energy relationship (LSER). The LSER-derived coefficients can be useful in predicting the performance of VOC adsorption on MWCNTs and in facilitating the design of efficient VOC-removal systems.

## 2. Experimental

### 2.1. Materials

In this study, 15 VOCs were tested, including eight of the main classes of common VOCs. *n*-Pentane, 1,1-dichloroethylene, trichloroethylene, and 2-propanol were purchased from Acros Organics. Cyclohexane, *n*-hexane, dichloromethane, trichloromethane, methanol, and acetonitrile were obtained from J.T. Baker. Tetrachloromethane and benzene were purchased from Merck. Acetone was obtained from Mallinckrodt Baker. Diethyl ether was purchased from Riedel-de Haën. All chemicals were of a purity grade higher than 95%, and there was no visible impurity peak in the IGC chromatograms [23]. Basic chemical properties of the octanol–water partition constant ( $\log K_{ow}$ ) and the solvation descriptors of these VOCs are listed in Table S1. A commercial MWCNT, purchased from Aldrich, with 95% purity was used as the adsorbent. The physical properties of the MWCNT have a Brunauer–Emmett–Teller (BET) surface area of  $108 \text{ m}^2/\text{g}$ , BET average pore size of 10.9 nm, mesopore volume of  $0.529 \text{ (cm}^3/\text{g)}$ , and micropore volume of  $0.00614 \text{ (cm}^3/\text{g)}$  [24].

### 2.2. Characterization of MWCNT

The MWCNT was characterized by observing its geometrical structure using a high-resolution transmission electron microscope (HRTEM) (JEM-2010, JEOL Ltd., Japan) and analyzing its surface functional group compositions by solid-state  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  NMR) (DSX400WB NMR spectrometer, Bruker, Germany), x-ray photoelectron spectroscopy (XPS) (ESCALAB 250, VG Scientific, England), and Fourier-transform infrared spectroscopy (FTIR) (DA8.3, Bomem, Canada). For analyzing its inner structure, the MWCNT sample was placed into a glass bottle and sonicated for 1 h. A few droplets of the MWCNT solution were added to a copper grid coated with lacey Formvar. The copper grid was first dried at 343 K for 30 min and then analyzed via HRTEM.

### 2.3. Adsorption experiments

The determination of the gas/solid partitioning coefficients of the VOCs was performed using the IGC method. Adsorption experiments of the 15 VOCs were conducted. Detailed information about column preparation and experimental conditions are as follows. The MWCNT powder (around 0.010 g) was placed in a stainless steel column of 10 cm length and 0.3175 cm outer diameter. Mechanical vibration was applied to achieve homogeneous packing. The column was sealed with silane-treated glass wool at both ends after packing. The MWCNT column was then conditioned onto a conventional gas chromatography/flame ionization detector (GC/FID) (Model 8700F, Taiwan) at 453 K overnight under a nitrogen flow rate of 5–60 mL/min. The carrier gas was nitrogen, with purity greater than 99.995%. The flow rate of nitrogen was measured using a calibrated soap bubble flowmeter. The injection volumes of the VOCs were 1–100  $\mu\text{L}$  to meet the requirements of adsorption at infinite dilution, peak symmetry, and reproducible retention times. Methane was used to correct the retention time of the GC/FID.

During the IGC experiments, the VOCs were injected into the MWCNT column under isothermal conditions, and their adsorption behavior was determined by observing their retention situation. Under sufficiently low concentrations of the injected VOCs, the adsorption equilibrium process would be reversible and exhibit a linear isotherm based on the equation as follows [25]:

$$K_d = (t_r - t_0) \frac{F_c}{m} \quad (1)$$

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