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Adsorption of Organic Compounds by Carbon Nanomaterials in Aqueous Phase: Polanyi Theory and Its Application

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Contents

1. Introduction

Since their first discovery,[1−3] carbon nanomaterials, including fullerenes and carbon nanotubes (CNTs), have attracted special attention in terms of potential applications in catalyst supports, optical devices, quantum computers, and biomedical use.[4,5] The unique and tunable properties of carbon nanomaterials also enable a broad range of their applications in identifying and addressing environmental challenges: sorbents, high-flux membranes, depth filters, antimicrobial agents, environmental sensors, renewable energy technology, and pollution prevention strategy.[5] For example, the theoretical surface area of fullerene and single-walled CNTs is about 3000 m^2/g,[6,7] which makes them potential superior adsorbents. Carbon nanomaterials are now produced and used in significant quantities, for example, the annual global production capacity of CNTs in the year 2007/2008 was estimated as exceeding 350 tons[5] and increased future production and application are expected. A recent market report estimated the business opportunities of CNTs in electronics applications reaching $3.6 billion by 2009.[8]

Because of the current and increasing future investments and the potential widespread use, carbon nanosized particles (CNPs) will inevitably enter the environment from their production, transport, handling, use, and disposal.[9−11] Although the concentrations of CNPs measured in the environment such as air and soils are still small at the present time,[12] it has to be expected that their concentrations in the environment will increase considerably in future when their price falls and their applications in consumer products become more widespread.[13] CNPs were observed to be taken up by different cell types and evoked diverse effects in the cells and, consequently, may be toxic to human beings, plants, animals, and other organisms.[14,15] Furthermore, CNPs may accumulate along the food chain because they are totally insoluble in water and lipophilic in pristine form and possibly one of the least biodegradable man-made materials ever devised.[16,17] In addition to the toxicity, therefore, the fate, transport, and bioavailability of CNPs and their effects on common environmental contaminants need to be evaluated, which will be fundamental in determining overall environmental and health impact of CNPs once escaped into the environment[18−21]

Adsorption of organic compounds by CNPs in aqueous phases is a critical process for environmental application of CNPs in water treatment[5,22,23] and solid-phase extraction[24−27] as superior sorbents and in synthesis of functionalized CNPs with desired and tunable physical and chemical properties.[28] This process is also important for determining the environmental and health impacts of both CNPs and organic

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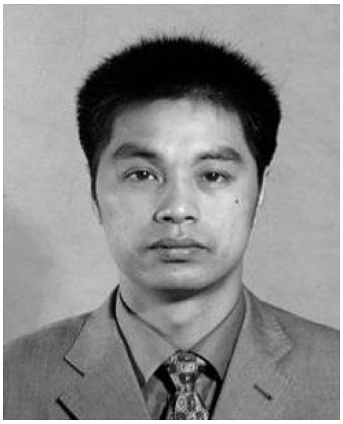

Dr. Kun Yang received his B.Sc. degree in 1999 and his Ph.D. degree in 2004 in Environmental Science from Zhejiang University, China. In 2004, he joined the Zhejiang University, where he is an active faculty member in teaching and research, and was promoted to Associate Professor in 2006. Dr. Yang was a postdoctoral fellow from 2005 to 2006 and a visiting scientist from 2008 to 2010 in the group of Professor Baoshan Xing at the University of Massachusetts, Amherst. He won the second prize of the Natural Science Award in the University of China and the National Excellent Doctoral Dissertation Nominations of China in 2007. He was selected as a New Century Excellent Talent in University by the Education Ministry of China in 2008. As the author and coauthor, Dr. Yang has published more than 30 articles in peer-reviewed technical journals, and his publications are frequently cited by his peers. His current research interests focus on the environmental behavior and toxicity of engineered nanomaterials, the sorption and fate of organic chemicals in soils and sediments, the synthesis and characterization of porous adsorbents, and the surfactant-enhanced remediation of contaminated soils with organic chemicals.

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chemicals.[10,23] First, adsorption of natural organic matter and surfactants on CNPs would enhance their suspension and stability in water and, consequently, alter the environmental fate and transport of CNPs.[29−34] Second, adsorbed organic chemicals such as hydrophobic organic compounds (HOCs) may add additional toxicity to that of CNPs when these CNPs are taken up by and accumulated in organisms.[23,35,36] Third, CNPs would act similarly to other "hard" carbon materials such as charcoal and soot[37,38] in the environment and alter the fate, transfer, and bioavailability of environmental organic pollutants by adsorption.[23,39] For example, the bioavailability and mobility of organic pollutants into organisms could be reduced and, consequently, their persistence in the environment would be enhanced if they are adsorbed by a CNP which cannot be taken up by or accumulated in the organisms.[40] Differences between CNPs and the most common carbon adsorbents (i.e., activated carbon) need to be recognized for the proper interpretation of adsorption phenomena of CNPs. First, the activated carbon consists of micropores with different sizes which provide sites for adsorption, while individual CNPs provide adsorption sites only along the external surface.[6] Second, activated carbon contains carbons of varying degree of saturation and oxidation state as well as functional groups formed during activation process,[41] while CNPs consist only of globally conjugated unsaturated carbons in three-dimensional arrays and contain few functional groups except for the carbons on their surface that are intentionally treated by oxidation techniques.[42−45]

Polanyi theory, originally used to describe gas adsorption by activated carbon[46,47] and later applied to adsorption from aqueous phases,[48,49] was observed to mechanistically capture the adsorption process of nonionic polycyclic aromatic hydrocarbons (PAHs) by CNPs in our previous work.[23] Later, this theory was successfully used to describe the competitive sorption of PAHs on CNTs[50] as well as the adsorption of ionizable organic compounds (IOCs) such as phenols and anilines.[51] Several other works[45,52−55] also applied this theory in describing organic chemical adsorption by CNPs. Polanyi theory-based models have been successfully used to fit the adsorption isotherms.[23,45,50−55] Adsorption mechanisms of organic compounds on CNTs from aqueous solution have been partly summarized by Pan and Xing.[56] Carbon nanotubes as solid-phase extraction material and sorbents have also been partly reviewed in previous works.[10,26,27] However, Polanyi theory and its application in describing organic chemical adsorption by CNPs are not discussed in these review papers. Empirical relationships, relating the adsorption capacity and affinity of CNPs with the CNP/organic chemical structures and physicochemical properties, are also not reviewed, but these empirical relationships can be helpful to explore the adsorption mechanisms and to estimate the adsorption capacity and affinity, and then one can evaluate the potential application of CNPs as sorbents and influence of adsorption on the environmental risks of both toxic organic chemicals and CNPs. With the latest publications and current understanding, a review, focused on the aqueous adsorption of organic chemicals by CNPs, therefore, is needed and will be timely provided in this paper based on the Polanyi theory and the Polanyi theory-based Dubinin−Ashtakhov (DA) model. Parameters of the DA model, identifying the adsorption capacity and affinity of organic chemicals on CNPs, will be addressed in relation with the CNP/organic chemical structures and physicochemical properties, the interaction strength between organic chemicals and CNPs, and the newly created surface characteristics as a result of surface modification.

2. Polanyi Theory

Adsorption of an adsorbate by adsorbents should be described in two aspects: adsorption capacity and affinity. Adsorption capacity is limited by the potential space of a sorbent available for adsorption of a given adsorbate, while adsorption affinity is dependent on the strength of attractive forces between adsorbate and adsorbent. The Polanyi theory[46−48,57] has been recognized as the most powerful available theory for dealing with both gas and aqueous adsorption on energetically heterogeneous surfaces such as activated carbon. This theory assumes that for a molecule located within the attractive force field (i.e., adsorption space) of a solid, there exists an (attractive) adsorption potential between the molecule and the solid surface. The adsorption potential is higher if the molecule is more close to the solid surface. This attraction derives from the induced dipole−induced dipole force of the molecule and surface atoms, which is a short-range in nature. The adsorption potential, $\varepsilon = -RT \ln(C_e/C_s)$, at a particular location in the adsorption space is defined as the energy that is required to remove the molecule from that location to a point outside the attractive force field of the solid surface; where R is the universal gas constant, T is the absolute temperature, C_s and C_e is the water solubility and the equilibrium solution phase concentration of an adsorbate, respectively, for aqueous adsorption. For a molecule in this space, therefore, the magnitude of adsorption potential varies within the adsorption space depending on its proximity to the solid surface atoms. A series of equipotential surfaces can be obtained once the points in adsorption space with the same ε are connected. In addition, the Polanyi theory assumes that the adsorption potential is independent of temperature and the adsorbed liquid has the similar properties as the corresponding bulk liquid. A direct consequence of these assumptions is that for a given adsorbent, a plot of adsorbed volume (q_v) or adsorbed mass (q_e) against equilibrium adsorption potential (ε) should yield a curve (called as "characteristic curve") that is temperature-invariant and determined by the structure of the adsorbent.[48] This temperature-invariant characteristic curve was observed for the PAH adsorption by CNPs,[23] which indicates that Polanyi theory captures this aqueous adsorption process mechanistically. Characteristic curves of phenanthrene adsorption on an multiwalled carbon nanotube sample (i.e., MWCNT15) at 25, 40, and 55 °C, as an example reported by Yang et al.,[23] are shown in Figure 1.

Application of Polanyi theory in describing the adsorption process of adsorbates by adsorbents needs a mathematical equation to relate the experimental q_v (or q_e) values with the C_e values of an adsorbate (i.e., isotherm) and extract the isotherm characteristics by employing and analyzing the parameters of the mathematical equation because the apparent relationships between q_v (or q_e) and C_e for different adsorbates and adsorbents are generally different. The most benefit to develop a mathematical equation for Polanyi theory is that the parameters of the mathematical equation for certain pairs of adsorbate and adsorbent could be related with the physicochemical properties of both adsorbate and adsorbent. Then it is possible to explore the roles of the physicochemical properties of adsorbates and adsorbents in adsorption and to estimate the adsorption capacity and affinity from the physicochemical properties. Several mathematical equations including the DA model[23,49,57] have been developed by employing the adsorption potential (ε) in the mathematical equations since the Polanyi theory was suggested.[46,47]

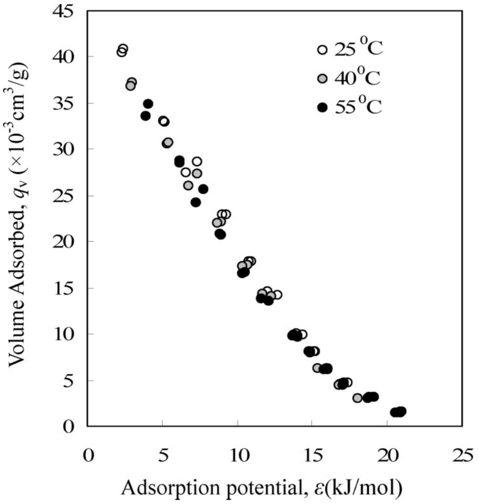

Figure 1. Characteristic curves of phenanthrene adsorption on MWCNT15 at 25, 40, and 55 °C. Reprinted with permission from ref 23. Copyright 2006 American Chemical Society.

3. Morphology and Possible Adsorption Spaces of CNPs

Monomers of fullerene and CNTs have distinct geometry, showing different spaces for adsorption. The monomer structure of fullerene is a closed graphite ball, while CNTs are rolled-up graphite sheets forming a coaxial tube (Figure 2). One single rolled-up graphite sheet forms single-walled CNTs (SWCNTs), while two or more rolled-up graphite sheets form multiwalled CNTs (MWCNTs) (Figure 2). For the spherical fullerene monomer, the available adsorption space is their external surface.[6] Besides the external surface, both inner cavity (i.e., the spaces in the innermost graphite tube) and interwall spaces (i.e., the spaces between the coaxial tubes of MWCNTs) exist in the cylindrical SWCNT or MWCNT monomer (Figure 2).[6] However, the interwall spacing would be inaccessible for nitrogen molecule with a size of 0.354 nm and common organic molecules with bigger sizes as compared with the narrow interwall spacing, 0.335 nm.[58] The inner cavities would also be inaccessible for organic molecules because these cavities would commonly be blocked by impurities such as metal catalyst and amorphous carbons.[6] Although the blocked inner pores can be opened up by acid treatment using HCl[44−59] to eliminate metal catalysts located at the end of CNTs or using H_2O_2,[43] nitric acid,[60] base,[61] or heat treatment[44] to remove the amorphous carbon, the functional groups would be created in the opened inner pores upon these treatments and bind water molecules to increase the diffusion resistance for organic molecules, thus prohibiting the access of organic molecules into the opened inner pores.[59] Therefore, available spaces of CNP monomers for adsorption are limited to their external surface.

CNP monomers conglobe spontaneously to form aggregates that exist stably in the environment.[29,62−64] In the aggregation process, CNP monomers form small aggregates first and then big aggregates (Figure 3).[6,62,63] A typical size of big aggregates of fullerene, for example, was observed to be from 20 to 50 μm, while small aggregates obtained by

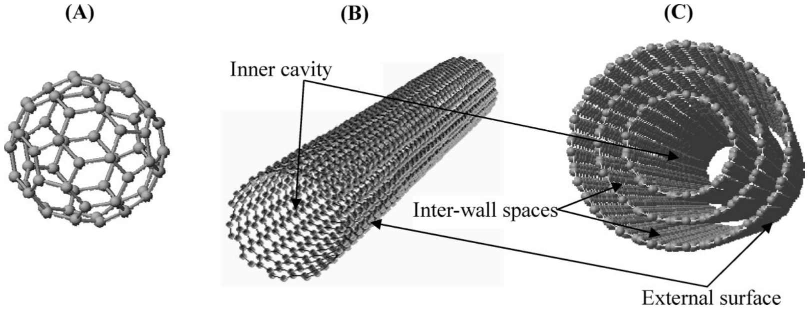

Figure 2. Schematic structures of fullerene (A), single-walled carbon nanotubes (B), and multiwalled carbon nanotubes (C), showing inner cavity, interwall spaces, and external surface. Fullerene (C_{60}) has only external surface. Reprinted with permission from ref 6. Copyright 2007 Elsevier.

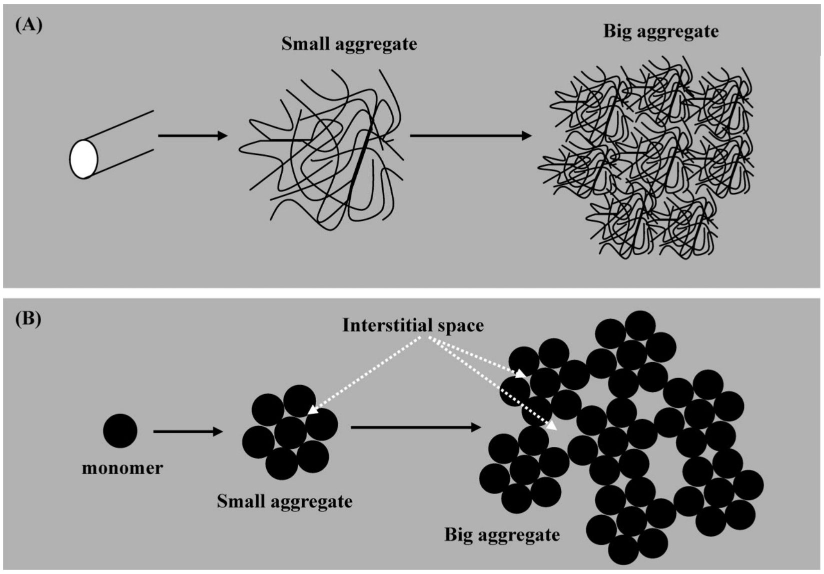

Figure 3. Schematic aggregation process of fullerene and carbon nanotubes: (A) carbon nanotubes and (B) fullerene. Reprinted with permission from ref 6. Copyright 2007 Elsevier.

extended stirring treatment were from 1 to 3 μm[62] and from 20 to 500 nm by solvent exchange.[63] The particle size of CNP aggregates in water will also be affected by pH,[65−68] acid-treatment of CNP surfaces,[67−71] and added surfactants[29,72−76] and dissolved organic matter (DOM).[30,34,65,66,71] Aggregation of spherical fullerene will result in closed interstitial spaces in its aggregates, while cylindrical CNTs cannot form closed interstitial spaces in their aggregates due to their length (Figure 3).[6] Aggregation of CNP monomers results in the decease of their exposed effective surface for adsorption.[6] Therefore, the measured surface area of fullerene and SWCNTs are much lower than their theoretically calculated surface area (i.e., as high as 3000 m^2/g).[6,7] Decrease in surface area by aggregation is larger for fullerene than for CNTs because of the formation of closed interstitial spaces in fullerene aggregates that prohibit the entrance of adsorbate molecules unless these closed spaces are opened up during the adsorption process.[6] Aggregation of CNP monomers can also form grooves in the aggregates.[53] Interstitial spaces and grooves, surrounded by the external surface of CNP monomers, are the pores of CNPs that are possibly available for adsorption.[6,53]

4. Interactions of Organic Compounds with CNPs

The net attractive forces involving the solute, solvent, and the adsorbent are assumed to be responsible for the solute adsorption by sorbents such as CNPs and activated carbon.[49,51,77] Among these forces, van der Waals force is normally the dominant force for gas or vapor adsorption onto a hydrophobic adsorbent,[77] which may also be significant for adsorption from the aqueous phase.[49,51] Considering only van der Waals forces, however, may not be applicable in cases when dipole−dipole, induced-dipole, and hydrogen-bonding donor−acceptor interactions exist, typically in aqueous phase, where these forces can be important especially for chemicals with certain functional groups.[49,51] Five possible interactions including **hydrophobic effect**, **$\pi-\pi$ bonds**, **hydrogen bonds**, and **covalent** and **electrostatic interactions** have been observed and are responsible for the adsorption of organic chemicals on CNP surface.[51,56,78] These interactions, their strengths, and contribution to the overall sorption are a function of the properties of both organic chemicals and CNPs.[51,56,78]

4.1. Hydrophobic Interaction

The surfaces of CNPs are hydrophobic, as can be demonstrated by the preference adsorption of hydrocarbon (such as hexane, benzene, and cyclohexane) over alcohols (such as ethanol and 2-propanol).[79] Therefore, hydrophobic interaction has been employed to interpret the adsorption of organic chemicals especially for HOCs by CNPs.[43,44,51,80−82] However, hydrophobic interaction alone is not enough to interpret the observed adsorption by CNPs,[51] as was also indicated by the failure in establishing a general relationship between the hydrophobic parameters of organic chemicals and their adsorption affinity parameters on CNPs.[53,56,83]

4.2. $\pi-\pi$ Bonding Interaction

$\pi-\pi$ Bonding interaction has been used to interpret the adsorption of organic molecules with a C=C double bond or a benzene ring on the surface of CNPs because these organic molecules contain π electrons to interact with the π electrons of the benzene rings on CNP surface through the $\pi-\pi$ electron coupling.[83-91] The $\pi-\pi$ bonding interaction between organic molecules and CNPs has been demonstrated by spectroscopic studies using Raman,[92] nuclear magnetic resonance (NMR), and fluorescence techniques.[93] In addition, this $\pi-\pi$ bonding interaction is affected by the relative position of the benzene ring of organic molecules to the hexagons on the CNP surface.[88,89,94]

4.3. Hydrogen Bonding Interaction

Hydrogen bonding interaction can form and play an important role in adsorption when the organic chemicals or CNPs have certain functional groups such as $-COOH$, $-OH$, and $-NH_2$.[51,95] The $-COOH$, $-OH$, and $-NH_2$ groups of organic chemicals can act as hydrogen-bonding donors and form hydrogen bonds with graphite sheets of CNPs, where the benzene rings of graphite sheets of CNPs act as the hydrogen-bonding acceptors.[51] Hydrogen bonds might also form between organic molecules and CNPs if CNPs have $-COOH$ and $-OH$ groups on their surfaces as hydrogen-bonding donors.[96,97] The insignificant effects of hydrogen-bonding interaction on adsorption of solutes without hydrogen-bonding donor ability[51,83] could be attributed to that the investigated CNPs have few functional groups on their surface and the graphite sheets of CNPs cannot be an effective hydrogen-bonding donor. Moreover, functional groups of CNPs can also form hydrogen bonds with water molecules.[97-99] This hydrogen-bonding interaction would be stronger than that between functional groups of CNPs and organic solutes, which results in the competitive sorption of water with organic solutes[97,98] and thereby the insignificant contribution of hydrogen-bonding interaction on adsorption of solutes without hydrogen-bonding donor ability.[51,83]

4.4. Covalent Bonding Interaction

Covalent bonds may occur between organic chemicals and CNPs if both of the chemicals and CNPs have certain functional groups such as $-COOH$, $-OH$, and $-NH_2$.[78,100,101] This covalent bond has been illustrated by spectroscopic studies with infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), and NMR techniques.[78,101] Relative to the noncovalent bonding interactions (e.g., hydrophobic, $\pi-\pi$ bonding, and hydrogen-bonding interactions), the attachment of organic molecules to CNPs via a covalent bond is much stronger and can resist any desorption. Therefore, covalent modification of CNPs has been widely utilized to form a variety of nanostructures with excellent physical and chemical properties.[28,102,103] Functionalizations of CNPs with covalent modification are normally achieved via reactions such as carboxylation,[104] amidation,[105] diazonium,[106] fluorination,[107] free radical chemistry,[108] bingel reaction,[109] esterification,[110] and composite formation.[111,112]

4.5. Electrostatic Interaction

Electrostatic interaction has been also utilized to interpret the adsorption decrease of natural organic matter (NOM)[31,32] and phenolic chemicals[113] on CNPs with the increase of solution pH because the facts that NOM and phenolic chemicals can be dissociated to anions and CNPs can be negatively charged as pH increased.[32] Electrostatic repulsion between the dissociated species of NOM (or phenolic chemicals) and negatively charged CNPs could result in the adsorption decrease. The electrostatic interaction is related to the charge nature of both organic chemicals and CNPs. Electrostatic attraction will occur if CNPs and organic chemicals have opposite charges; otherwise, electrostatic repulsion will occur if both CNPs and organic chemicals have the same sign of charges. The observed pH-dependent adsorption of a fluoroquinolone antibacterial agent (norfloxacin) on CNTs was also interpreted with the electrostatic interaction because norfloxacin can be positively charged (cationic), negatively charged (anionic), and/or as zwitterionic ions, depending on the solution pH.[55] However, it is difficult to separate this electrostatic interaction influence from the other interactions because dissociation of organic chemicals is always accompanied with the decrease of hydrophobic effect and hydrogen-bonding interaction of organic chemicals.[32]

Although five interactions have been recognized to be responsible for adsorption of organic chemicals on CNPs, their relative contributions on adsorption of a given organic chemical are still difficult to be quantified. The biggest challenge to determine their relative contributions is the estimation of the strength of these interactions, which depends on the ability of both organic chemicals and CNPs to form these interactions. The ability of an organic chemical to form hydrophobic interaction, $\pi-\pi$, and hydrogen bonds with CNPs can be identified quantitatively by its water solubility, $\pi-$electron polarity/polarizability, and hydrogen-bonding donor−acceptor parameters, respectively.[51] However, the ability of an organic chemical to form covalent bonds with CNPs and that of a given CNP to form the mentioned five interactions with organic chemicals still cannot be estimated. Multiple regression, which can correlate the adsorption of organic chemicals with their chemical parameters of ability to interact with CNPs if these ability parameters are available, is an useful method to evaluate the relative contributions of multiple interactions to the overall adsorption, as did in the previous studies.[49,51] Using multiple regression, the ability of CNPs to interact with organic chemicals could also be estimated by correlating the adsorption affinity parameters of reference organic chemicals with the property parameters of CNPs. For example, cyclohexane may be a good reference chemical to identify the ability of CNPs to have hydrophobic interactions.[83] Moreover, PAHs could be good reference chemicals to identify the ability of CNPs to have $\pi-\pi$ bonding interactions because the hydrophobic effects of organic chemicals on their adsorption can be largely eliminated by normalizing their adsorption affinity with their K_{HW} values or by conducting the adsorption experiments in cyclohexane solution.[53,56,83]

5. Isotherm Models and Their Fitting

Isotherm fitting with model equations is a key issue to explore sorption mechanisms. Deviation of the fitted isotherm from the true isotherm, as a statistic result, is inevitable because of experimental errors. However, large deviations of the fitted isotherm from the true isotherm could occur if few experimental data in a narrow range of equilibrium concentrations are employed for fitting (Figure 4). Large

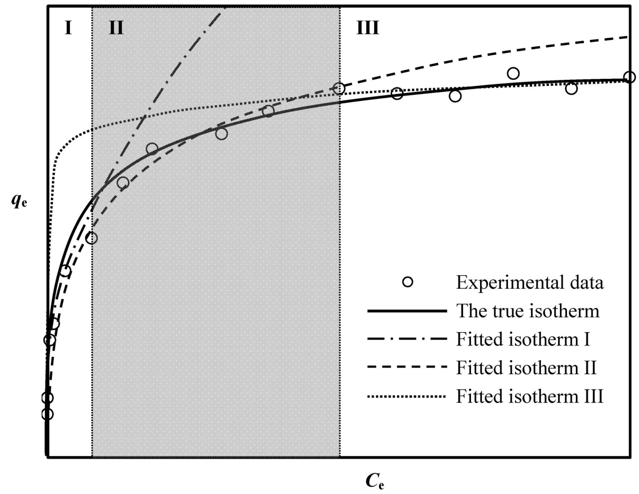

Figure 4. Possible deviations of the fitted isotherms from the true isotherm: the isotherms I, II, and III are fitted by employing the experimental data in regions I, II, and III, respectively.

deviation could confuse the researchers to give misleading interpretations and conclusions of the observed data.

In previous studies, five models have been observed having good fitting of the aqueous sorption isotherms of organic chemicals by CNPs (Table 1). They are linear, Freundlich, Langmuir, partition-adsorption, and Polanyi theory-based equations. The good fitting of linear equations was only observed for the isotherms of naphthalene adsorption by large fullerene (C_{60}) aggregates and thin C_{60} films.[62] It was also observed that isotherms of a given primary solute changed from nonlinearity toward linearity when competitors were added.[50] The partition−adsorption equation was used to interpret the adsorption−desorption hysteresis of naphthalene and 1,2-dichlorobenzene on/from small C_{60} aggregates.[114] Several studies reported the good fitting of Langmuir equation to the isotherms of organic chemicals by CNPs.[115−120] Others reported that the Freundlich equation fitted the isotherms well.[45,54,62,82,83,90,91,113,116,119−121] However, comparison of the studies regarding equation fitting of isotherms indicates that Polanyi theory-based equations had better fitting than Freundlich, Langmuir, and partition−adsorption equations for most obtained isotherms of various organic chemicals and CNPs.[23,50,51,53] Significant deviation of equation estimation from the experimental data was observed for Langmuir and partition−adsorption equations at relatively low concentrations.[23] The observations of the good fitting of Langmuir equation to the isotherms of organic chemicals by CNPs in some studies[115−120] is due to a narrow range of equilibrium concentrations (<1 order of magnitude) and few experimental data points used in these studies. The inapplicability of the partition−adsorption model was also supported by the absence of a rubbery state domain (partition medium) of CNPs for HOC partition because CNPs are predominated by the crystalline and graphitic type of carbon.[23,50] Moreover, it was observed that the partition−adsorption model failed to explain the sorption and competition data of PAHs.[50] The good fitting of the Freundlich equation was observed in some cases but varied with both the tested organic chemicals and CNPs in these model comparison studies.[23,50,53] Although the Freundlich equation was well applied to fit all the obtained isotherms in several other studies,[45,54,62,82,83,90,91,113,116,119−121] this could be attributed to the narrow range of equilibrium concentrations (<1 order of magnitude) and few experiment data points investigated in these studies. Other models such as the Brunauer−Emmett−Teller (BET) and Dual−Langmuir models are also inadequate to describe the adsorption process because significant deviation of model estimation from the experimental data was observed at relatively low concentrations.[23] The model fitting results indicate that the adsorption process of organic chemicals on CNPs (i) is neither monolayer formation on a homogeneous surface (i.e., Langmuir model) nor simple multilayer formation (i.e., BET model), (ii) is not a combination of partition and Langmuir-type adsorption domains (i.e., partition−adsorption model), and (iii) cannot be limited by two types of adsorption sites (i.e., Dual−Langmuir model). Polanyi theory-based equations seem not only applicable for pore filling but also applicable for flat surfaces,[122] supported by the fact that both the

Table 1. Models Used for Good Fitting of Isotherms

name	equation	capacity term[a]	refs
linear model	$q_e = KC_e$	K [L/g] is the affinity coefficient.	23, 62
Freundlich model	$q_e = K_f C_e^{1/n}$	K_f [(mg/g)/(mg/L)$^{1/n}$] is Freundlich affinity coefficient, and $1/n$ is the Freundlich exponential coefficient.	45, 54, 62, 82, 83, 90, 91, 113, 116, 119−121
Langmuir model	$q_e = Q^0 C_e/(K_L + C_e)$	K_L [mg/L] is the affinity coefficient.	115−120
partition−adsorption model	$q_e = K_P C_e + Q^0 C_e/(K_L + C_e)$	K_P [L/g] is the partition coefficient; K_L [mg/L] is the affinity coefficient.	114
Polanyi theory-based model	Polanyi−Manes model (PMM): $\log q_e = \log Q^0 + a(\varepsilon_{sw}/V_s)^b$ or Dubinin−Ashtakhov (DA) model: $\log q_e = \log Q^0 + (\varepsilon_{sw}/E)^b$	ε_{sw} [kJ/mol], $\varepsilon_{sw} = -RT \ln(C_e/C_s)$, is the effective adsorption potential, where R[8.314 × 10^{-3} kJ/(mol K)] and T[K], are universal gas constant and absolute temperature, respectively; V_s [cm^3/mol] is the molar volume of solute; a [(cm^3)$^{b+1}$/(kg J^b)] and b are fitting parameters of PMM model; E [kJ/mol] is the "correlating divisor"; and b is the fitting parameter of DA model.	23, 45, 50−55

[a] q_e [mg/g] is the equilibrium adsorbed concentration of solute; C_e [mg/L] is equilibrium solution phase concentration of solute; Q^0 [mg/g] is the maximum sorption capacity of solute; C_s [mg/L] is the solute solubility in water.

Freundlich model and the Polanyi theory-based models had good fits for a few cases.[23,50]

The good fitting of Polanyi theory-based models for organic chemical isotherms by CNPs was also mechanistically supported by the observed characteristic curve of Polanyi theory.[23] Though the Polanyi theory-based Polanyi−Manes model (PMM) (Table 1) has good fitting for the isotherms, the Polanyi theory-based DA model (Table 1) was later employed to fit the isotherms because molar volume (V_s) alone as the abscissa scaling factor failed to obtain a single correlation curve.[23] From the DA model (Table 1), it should be not surprising that the Freundlich equation is applicable for a few cases because the Freundlich equation is a special form of DA model at $b = 1$.[23,50] The linear model is also a special form of DA model, where $b = 1$ and $E = RT \ln 10 \approx 5.71$ kJ/mol. Therefore, the DA fitted isotherms with $b > 1$ has been called as a "typical Polanyi isotherm", showing nonlinear isotherms even in a log−log scale plot.[23,50]

To avoid large deviations from the true isotherm in fitting of sorption data as shown in Figure 4, a number of experimental data points in an extended range of equilibrium concentrations of organic chemicals should be employed. In our opinion, more than 20 experimental data points for an organic chemical distributed in the range of its equilibrium concentrations up to its solubility (Cs) from 10^{-5}−10^{-3} Cs should be employed in sorption experiments and isotherm fitting.[23] However, it is not easy to get experimental data in such an extended range of equilibrium concentrations for some organic chemicals because of their low solubility and the detection limits of the commonly used analytical techniques. Polanyi theory-based DA and PMM models have three fitting parameters, more than that of the commonly used linear, Freundlich, and Langmuir models (Table 1). It has been reported that good isotherm fitting of models may result from overparameterization of PMM and DA models,[37] and thus the effect of overparameterization should be evaluated in isotherm fitting using different models.[23] Mean weighted square error (MWSE), equal to $1/v[(q_{\mathrm{measured}} - q_{\mathrm{model}})^2/q^2_{\mathrm{measured}}]$, could be calculated to evaluate the goodness of model fitting and the effect of overparameterization,[23] where v is the degree of freedom ($v = N - 2$ for Freundlich, Langmuir, and BET models, $v = N - 3$ for partition−adsorption, PMM, and DA models, and $v = N - 4$ for Dual−Langmuir model), N is the number of experimental data points, q_{measured} is the measured equilibrium sorbed concentration, and q_{model} is the estimated equilibrium sorbed concentration by the respective models. With MWSE evaluation, the best fitting of Polanyi theory-based PMM and DA models as compared with other models for organic chemical isotherms on CNPs was demonstrated to be general and not a result from the model overparameterization.[23]

6. Polanyi Theory-Based Dubinin−Ashtakhov (DA) Model and Its Parameters

Polanyi theory-based DA equation (Table 1) has three fitting parameters, i.e., Q^0, E, and b. Figure 5 illustrates how the values of Q^0, E, and b influence the shape of the log−log scale plots of solute isotherms on a sorbent. The increase in E value is a result of the fact that the enhancement rate of the solute adsorption is higher at relatively low solute concentrations (C_e/C_s) than at relatively high solute C_e/C_s

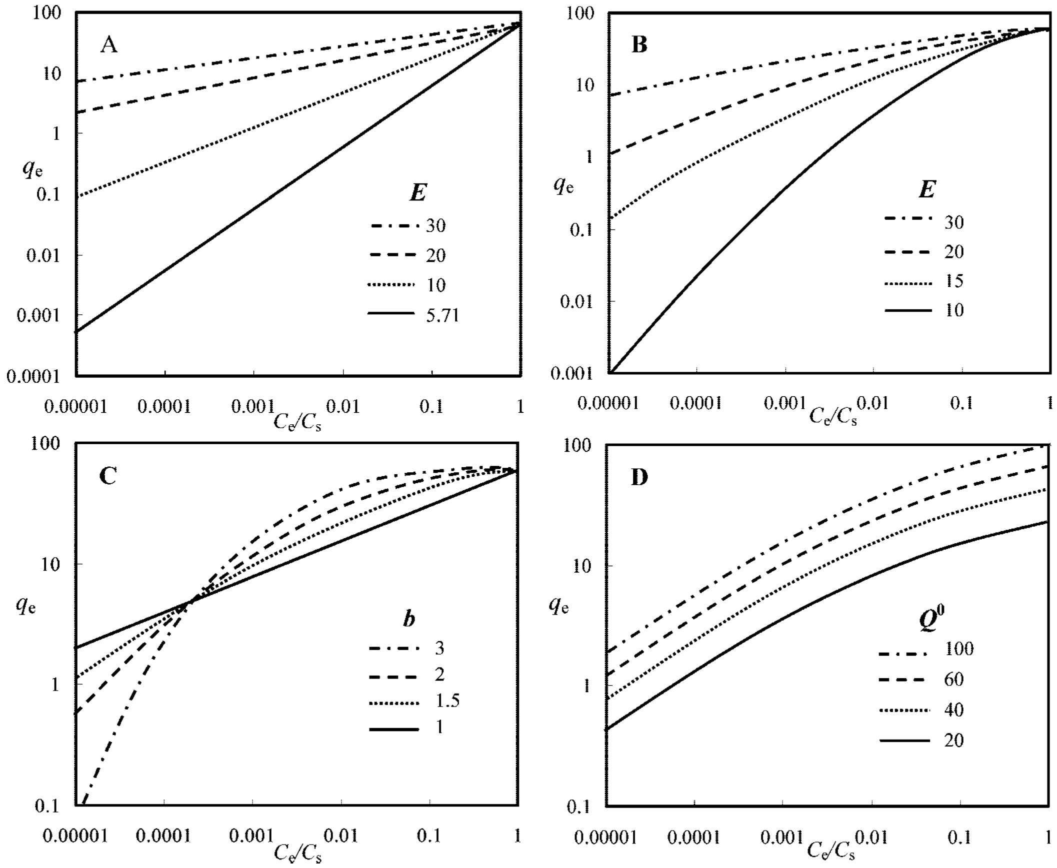

Figure 5. Influence of the increase in Q^0, E, and b on the shape of the log−log scale plots of solute isotherms on a sorbent at various relative solute concentrations (C_e/C_s): (A) $E = 5.71$, 10, 20, and 30 at $Q^0 = 60$ and $b = 1$; (B) $E = 10$, 15, 20, and 30 at $Q^0 = 60$ and $b = 1.5$; (C) $b = 1$, 1.5, 2.0, and 3.0 at $Q^0 = 60$ and $E = 20$; (D) $Q^0 = 20$, 40, 60, and 100 at $E = 20$ and $b = 1.5$.

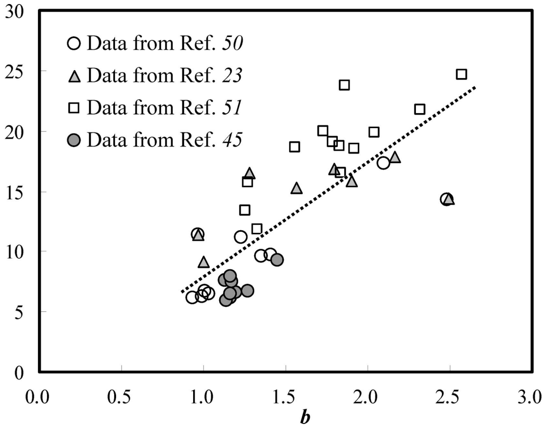

Figure 6. Linear intrinsic relationship (dotted line) between E and b values of DA model fitted isotherms for adsorption of organic chemicals on CNPs (data from refs 23, 45, 50, 51).

(Figure 5A,B). The increase in b value is a result of the enhancement rate of the solute adsorption on a sorbent that is higher at relatively high solute C_e/C_s than that at relatively low solute C_e/C_s, showing the isotherms are more nonlinear (Figure 5C). The increase in Q^0 value is a result of the fact that the enhancement rate of the solute adsorption on a sorbent is relatively equal in the entire solute concentration range (Figure 5D). Among the three fitting parameters, the saturated adsorbed solute capacity, Q^0, is limited by the available adsorption space of sorbents. The maximum potential adsorption space of sorbents is related only to the nature of adsorbent and independent of the nature of chemicals.[123] However, the available adsorption space of sorbents can varied with chemicals because of the heterogeneous nature of most sorbents, which could result in the variation of solute Q^0 with solute structures on a given sorbent. The "correlating divisor", E, is the adsorption energy for a given solute, which represents all of the interaction forces responsible for adsorption[49,51] and thus could be used to identify the adsorption affinity. A significant linear intrinsic relationship between the DA model fitted E and b values has been observed for adsorption of aniline, phenol, and their substitutes on MWCNTs.[51] This linear intrinsic relationship at the 95% confidence intervals can also be observed even if the DA model fitted E and b data of isotherms of other organic chemicals such as PAHs on various CNPs are included,[23,45,50] as is shown in Figure 6 and eq 1. These CNPs include fullerene, SWCNTs, MWCNTs, and oxidized CNTs. Moreover, this linear relationship is independent of whether competitors are added or not because the DA model fitted E and b value of isotherms in the presence of competitors[50] were included in Figure 6 and eq 1.

$$E = 9.373(\pm 1.152) \times b - 1.309(\pm 1.812) \qquad r^2 = 0.6233 \quad (1)$$

This linear intrinsic relationship suggests that the b of the DA model is also a parameter to represent the adsorption energy and the interaction forces responsible for adsorption, as is similar to the parameter E of the DA model.

According to the characteristic curve of Polanyi theory in Figure 7, the DA model fitted E and b may also describe the distribution of sorption site energy. The increase in E value means the more increase in the fraction of relatively high sorption energy than the fraction in relatively low sorption energy (Figure 7A), with respect to the more increase of solute sorption at relatively low solute C_e/C_s than at relatively high solute C_e/C_s (Figure 5B). The increase in b value means the increase in the fraction of relatively low sorption energy and the decrease in the fraction of relatively high sorption energy (Figure 7B), respective to the increase of solute sorption at relatively low solute C_e/C_s and the decrease of solute sorption at relatively high solute C_e/C_s (Figure 5C).

7. Influences of CNP Structures and Surface Properties on Adsorption

7.1. Surface Area

Different synthesis, purification, and postprocessing methods produce CNPs with different physical characteristics, which may control their adsorption for organic chemicals. Yang et al.[23] found a high adsorption capacity of PAHs (i.e., pyrene, phenanthrene, and naphthalene) with different types of CNPs (i.e., SWCNTs, MWCNTs, and fullerene). In this study, the PMM model fitted saturated adsorption capacity, Q_v^0 (cm^3/g), for a given chemical (i.e., phenanthrene) had an order of SWCNTs >MWCNTs > fullerene and seems to have a linear relationship with the surface area (A_{surf}) of CNPs. Figure 8 shows the linear relationships between Q_v^0 and A_{surf} for investigated organic chemicals in several previous studies (data of Q_v^0 and A_{surf} as well as their sources are listed in Table 2). These linear relationships indicate that the maximum adsorption capacity of a given organic chemical on CNPs depends on the CNP surface area. Dispersion

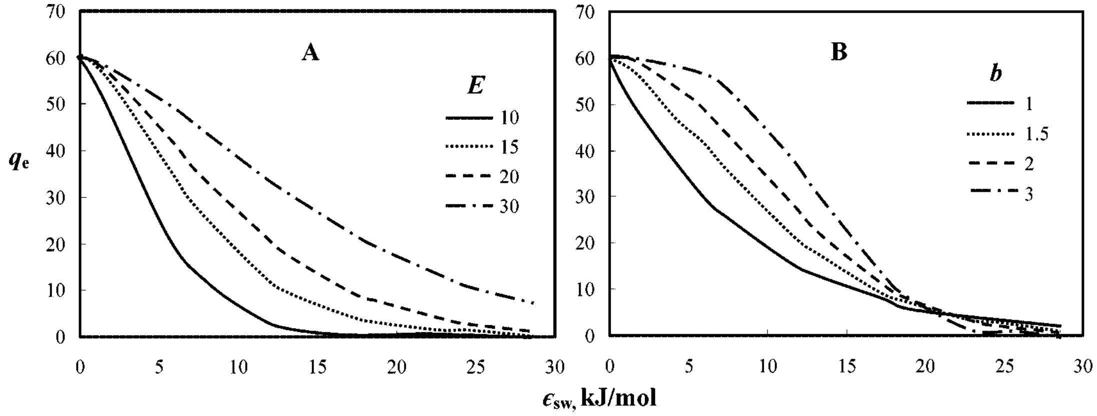

Figure 7. Influence of the increase in E and b on the shape of solute "characteristic curves" of Polanyi theory: (A) E = 10, 15, 20, and 30 at Q^0 = 60 and b = 1.5; (B) b = 1, 1.5, 2.0, and 3.0 at Q^0 = 60 and E = 20.

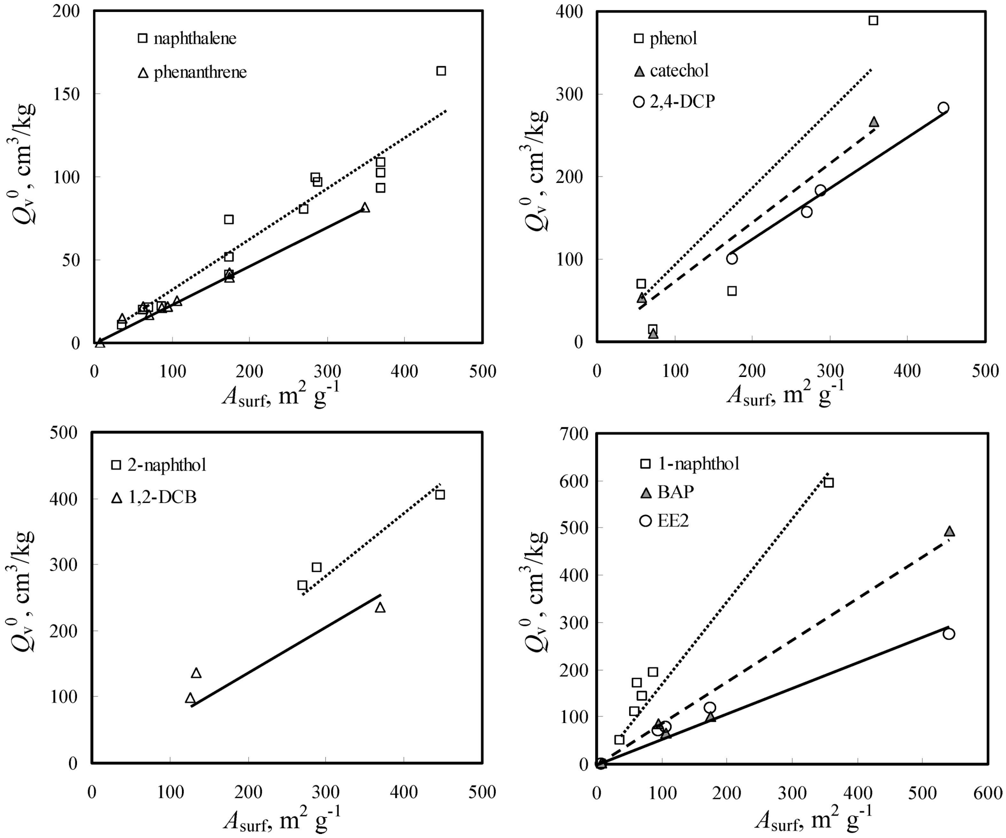

Figure 8. Maximum sorption capacity (Q_v^0) of organic chemicals on CNPs versus surface area (A_{surf}) values of CNPs. The solid and dotted lines represent the linear relationships between Q_v^0 and A_{surf} for a given organic chemical.

of large CNP aggregates to smaller aggregates can increase the surface area of CNPs and consequently be expected to enhance the organic chemical adsorption,[6,56,124] although no direct experiments have been done to examine this enhancement of adsorption at the present because of the difficulty of separating adsorbate supernatant from CNTs suspension.

The slopes of linear relationships between Q_v^0 and A_{surf} are different significantly for various organic chemicals (Figure 8), probably because part of the measured surface area of the given CNP could not be occupied by organic molecules due to the heterogeneity of the CNP surface.[56] Moreover, the available surface area of a given CNP for adsorption would be different for organic chemicals because different chemical molecular structures have different interactions with the heterogeneous surface of CNPs, as discussed in detail in section 8, Effects of Organic Chemical Structure and Properties on Adsorption. Figure 9 shows the heterogeneous nature of CNP surface and the possible influence on solute adsorption. The ratio of the available surface area to the total measured surface area could also be different for CNPs, although most of these ratios of CNPs for adsorption of a given organic chemical should be close according to the linear relationships between Q_v^0 and A_{surf} (Figure 8). For example, the observed data of A_{surf} of SWCNT and the Q_v^0 of phenanthrene on the SWCNT could not follow the observed linear relationship between Q_v^0 and A_{surf} for phenanthrene on other CNPs.[23]

7.2. Functional Groups on CNP Surface

CNPs can be used as superior adsorbents for organic chemicals basically because of the hydrophobic nature of CNP surfaces.[79] Functional groups such as $-OH$, $-C{=}O$, and $-COOH$ on the CNP surface, derived from the processes of synthesis and purification of CNPs, therefore, could be mainly responsible for the variation of the ratio of the available surface area to the total measured surface area among different CNPs. Functional groups on CNP surface can also be intentionally added by oxidation treatment[42−45] or removed by heat treatment.[121] Functional groups of CNPs can form H-bonds with water molecules, which can consequently make CNPs more hydrophilic to suppress the adsorption of organic chemicals especially HOCs through the competition of water molecules.[79,97−99,125] The competition of water molecules could be employed to interpret the reported phenomenon that oxidization of CNTs decreased their adsorption for naphthalene,[45] chlorophenol,[115] and resorcinol.[116] Functional groups of CNPs could also be expected to act as hydrogen-bonding donors and form hydrogen bonds with organic molecules as hydrogen-bonding acceptors. Relative to the hydrogen-bonding interaction between functional groups of CNPs and water molecules,[97−99] however, the hydrogen-bonding interaction between functional groups of CNPs and organic solutes should be too weak to occur in the aqueous phase, as indicated by the decreased adsorption of organic solutes from the competition of adsorbed water molecules[97,98] and no significant effects of hydrogen-bonding interaction on the adsorption of solutes without hydrogen-bonding donor ability.[51,83] The functional groups such as carboxylic groups can also act as the CNTs electron acceptors, which could consequently promote phenanthrene adsorption via enhancing the $\pi-\pi$ bond in the electron donator−acceptor (EDA) system between the CNTs and phenanthrene in organic solvents such as benzene.[44] This may not occur in aqueous systems because of the competition of adsorbed water molecules, too.[97,98,125] Among the interactions for adsorption of organic chemicals on CNPs in aqueous

Table 2. Reported Surface Area Values of CNPs and Their Maximum Sorption Capacities for Organic Chemicals[a]

chemicals	CNPs	A_{surf} (m^2 g^{-1})	Q^0 (mg/g)	$Q_v{}^0$ (cm^3/kg)	refs
phenanthrene	MWNT15	174	41.7[b]	39.2	50
	MWNT15	174	44.7[c]	42.0	50
	fullerene	7.21	0.0678	0.0637	23
	MWNT8	348	86.5	81.4	23
	MWNT15	174	42.1	39.6	23
	MWNT30	107	26.9	25.3	23
	MWNT50	94.7	23.6	22.2	23
	MWNT40	86.97		20.8	54
	HA-MWNT40	62.85		21.6	54
	PH-MWNT40	70.04		17.2	54
	PE-MWNT40	35.4		14.9	54
naphthalene	MWNT15	174	73.8	74.0	23
	r-SWNT	447	163[i]	163	91
	l-SWNT	289	96.1[i]	96.4	91
	d-SWNT	271	79.8[i]	80.0	91
	CNTs	370	108[i,d]	108	90
	CNTs	370	102[i,e]	102	90
	CNTs	370	92.7[i,f]	93.0	90
	MWNT40	86.97		21.7	54
	HA-MWNT40	62.85		19.5	54
	PH-MWNT40	70.04		20.8	54
	PE-MWNT40	35.4		10.5	54
	MWNT15	174	51.3[g]	51.4	23
	MWNT15	174	40.7[h]	40.9	23
	MWCNT	286		96.0	45
17 α-ethinyl estradiol (EE2)	fullerene	7.21	0.228	0.202	53
	SWNT	541	309	273	53
	MWNT15	174	133	118	53
	MWNT30	107	89.5	79.2	53
	MWNT50	94.7	78.4	69.4	53
bisphenol A (BPA)	fullerene	7.21	2.40	2.01	53
	SWNT	541	591	495	53
	MWNT15	174	121	101	53
	MWNT30	107	77.0	64.4	53
	MWNT50	94.7	103	86.2	53
phenol	MWNT15	174	64.6	60.3	51
	MWCNT10	357	416[i]	388	113
	MWCNT100	58	75.1[i]	70.1	113
	pristine MWCNTs	72	15.9[j]	14.8	116
1,2-dichlorobenzene (1,2-DCB)	as-grown CNTs	134	178[i]	137	121
	graphitized CNTs	126	129[i]	99.4	121
	SWNT	370	307[i]	236	83
2.4-dichlorophenol (2.4-DCP)	MWNT15	174	138	99.8	51
	r-SWNT	447	390[i]	282	91
	l-SWNT	289	253[i]	183	91
	d-SWNT	271	216[i]	156	91
2-naphthol	r-SWNT	447	494[i]	405	91
	l-SWNT	289	360[i]	295	91
	d-SWNT	271	326[i]	267	91
1-naphthol	MWCNT10	357	719[i]	593	113
	MWCNT100	58	134[i]	110	113
	MWNT40	86.97		193	54
	HA-MWNT40	62.85		170	54
	PH-MWNT40	70.04		143	54
	PE-MWNT40	35.4		49.2	54
catechol	MWCNT10	357	358[i]	266	113
	MWCNT100	58	72.2[i]	53.7	113
	pristine MWCNTs	72	14.2[j]	10.6	116

[a] A_{surf}, surface area; Q^0, maximum sorption capacity in gravimetric unit; $Q_v{}^0$, maximum sorption capacity in volumetric unit, which was calculated from Q^0 and the density (ρ) of the chemical with the equation of $Q_v{}^0 = Q^0/\rho$ if the $Q_v{}^0$ values are not directly available in the references; the density (ρ) of phenanthrene, naphthalene, EE2, BPA, phenol, 1,2-DCB, 2.4-DCP, 2-naphthol, 1-naphthol, and catechol are 1.063, 0.997, 1.13, 1.195, 1.071, 1.3, 1.383, 1.22, 1.213, and 1.344 g cm^{-3}, respectively. [b] In presence of naphthalene as the competitor. [c] In presence of pyrene as the competitor. [d] In presence of Na^+ as the competitor. [e] Iin presence of Cu^{2+} as the competitor. [f] In presence of humic acid as the competitor. [g] In presence of pyrene as the competitor. [h] In presence of phenanthrene as the competitor. [i] Q^0 was the value of q_e at $C_e = C_s$, which was calculated from the Freundlich model fitted isotherms. [j] Q^0 was obtained directly from the Langmuir model fitted isotherms.

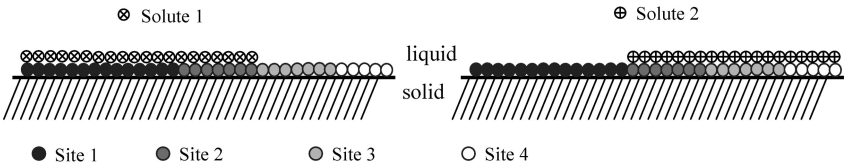

Figure 9. Possible adsorption of solute 1 (⊗) and solute 2 (⊕) on the CNP surface with different potential adsorption sites (black solid circle, site 1; dark gray solid circle, site 2; light gray solid circle, site 3; open circle, site 4). The heterogeneous nature of the CNP surface is presented by four different adsorption sites.

systems, therefore, hydrophobic interaction, hydrogen-bonding interaction, and π-bonding interaction can enhance the adsorption affinity (E) but not the adsorption capacity (Q^0) of organic chemicals on CNPs because all of these interactions can occur on the sites of CNP surface without functional groups but not the functional group occupied sites of CNP surface, which prefer to bond with water molecules. Therefore, isotherms of naphthalene on oxidized CNTs have almost a constant E value but decreased Q^0 values with increased oxygen content of CNTs[45] because only hydrophobic interaction and π-bonding interaction could occur for naphthalene adsorption on CNTs. However, functional groups of CNPs could form covalent bonds with organic chemicals in an aqueous system if these chemicals have certain functional groups such as $-$COOH and $-$OH,[78,100,101] which may add additional adsorption for organic chemicals and enhance both of the adsorption affinity (E) and the adsorption capacity (Q^0) of organic chemicals on CNPs. In addition, increase in numbers of functional groups on CNP surface may result in the conformation changes of CNP aggregates and thus the changes of exposed CNP surface area,[44,67,68,70,79,105,125] which should influence their adsorption for organic chemicals. The increase in adsorption of trihalomethanes[119] and 1,2-dichlorobenzene[121] after introducing functional groups to CNTs by oxidation treatment could possibly stem from the increase in exposed surface area of CNTs. The normalization of adsorbed capacity with the surface area of CNPs may be a useful way to rule out the influence of CNP surface area changes derived from oxidation on adsorption and thus help us to explore the interactions of organic solutes with functional groups of CNPs. In addition, surface functional groups on CNPs may possibly lead to the desorption hysteresis of organic chemicals from CNPs, which is discussed in detail in section 10, Adsorption−Desorption Hysteresis. Moreover, surface modification of CNPs with other chemicals can alter the adsorption of organic chemicals on CNPs, which is discussed in section 9, Competitive Sorption and the Role of DOM and Surfactants in Adsorption.

7.3. The Pores in CNP Aggregates

Yang et al.[23] reported that the DA model fitted E and b were linearly related to the ratios of mesopore volume to micropore volume ($R_{\mathrm{meso/micro}} = V_{\mathrm{meso}}/V_{\mathrm{micro}}$) of CNPs. According to Polanyi theory and the “characteristic curve”, the measured micropore volume could describe approximately the site fraction with relatively high sorption energies on the solid surface, while the measured mesopore volume could describe approximately the site fraction with relatively low sorption energies. Therefore, it is not surprising that the DA model fitted E and b have linear relationships with $R_{\mathrm{meso/micro}}$ ratios because both E and b of the DA model describe the distribution of the sorption energies on the solid surface as mentioned above (Figure 7). The pores (e.g., interstitial spaces and grooves) in CNP aggregates may not be available for adsorption of organic molecules if they are closed or too narrow for the adsorbing organic molecules.[6,53] This could be employed to explain why activated carbons (a similar material to CNPs) have commonly much higher surface area than CNPs but lower surface area-normalized adsorption capacity for organic chemicals relative to CNPs;[51,56] because activated carbons are porous materials having a large quantity of narrow micropores, they are inaccessible for organic molecules. Also, the higher adsorption of DOM on MWCNTs can be attributed to the larger average pore diameter and volume of MWCNTs than activated carbon.[126] Furthermore, the pores in CNP aggregates (especially fullerene) may possibly result in the desorption hysteresis of organic chemicals, which is discussed in detail in section 10, Adsorption−Desorption Hysteresis.

7.4. Surface Curvature and Defects

The surface curvature[93] and defects of CNP monomers[127] could affect their adsorption for organic solutes. Surface curvature of CNP monomers increases with their decreasing diameter. The flat surfaces of CNPs can result in more surface atoms approaching to adsorbing organic molecules, which lead to higher adsorption potential of the flat CNP surfaces and thus stronger interactions according to the Polanyi theory.[46,57] Defects of CNP monomers can also result in more surface atoms of CNPs interacting with organic molecules and thus higher adsorption potential for organic molecules.[48]

For a given organic chemical, as mentioned above, its adsorption on CNPs is dependent on the CNP structures and surface properties such as surface area, surface functional groups, surface curvature, surface defects, and the pores in CNP aggregates. The good fitting of Polanyi theory-based DA model for organic chemical isotherms on various CNPs indicates that the parameters of the DA model can be related with the CNP structures and surface properties to explore their roles on adsorption.[23,45,53] These relationships have been observed between Q^0 and CNP surface area,[23,53] between Q^0 and CNP surface oxygen content,[45] and between E (or b) and the $R_{\mathrm{meso/micro}}$ ratios of CNPs.[23] Other relationships such as Q^0 and E (or b) with the CNP structures and surface properties have not yet been obtained. Surface functionalization of CNPs with oxygen-containing groups may decrease the noncovalent adsorption of organic chemicals because of the competition of water but could increase the adsorption of other organic chemicals if they can form covalent bonds with these groups. Therefore, surface functionalization on CNPs is a primary step for the covalent modification of CNPs to form a variety of nanostructures with excellent physical and chemical properties. However, the role of a specific functional group (such as hydroxyl, carboxyl, or ketone group) in the covalent adsorption is still unclear. Comparison of the adsorption properties between CNPs containing different functional groups will help us to understand the role of a specific functional group in covalent adsorption. According to the dependence of adsorption capacity (Q^0) of organic chemicals on the surface area of CNPs, the removal of organic pollutants from water by CNPs could be enhanced by enhancing CNP surface area when they are engineered.

8. Effects of Organic Chemical Structures and Properties on Adsorption

8.1. Molecular Structure and Functional Groups

Different molecular structures of organic chemicals have different interactions with the heterogeneous surface of CNPs, which leads to the significant variation in the slopes of linear relationships between Q_v^0 and A_{surf} for various organic chemicals (Figure 8). It has been observed in a previous study by Chen et al.[83] that adsorption affinity of polar and nonpolar organic compounds on CNTs increased in the order of nonpolar aliphatic < nonpolar aromatics < nitroaromatics. Cyclohexane is a typical chemical which cannot form hydrogen and $\pi-\pi$ bonds with CNPs. Therefore, hydrophobic interaction derived from van der Waals force is responsible for adsorption of cyclohexane on CNPs,[51,83] as shown by the linear isotherm.[83] The strength of hydrophobic interaction for organic chemicals can be determined by their solubility in water.[128] Normalization of chemical adsorption with their K_{OW} or K_{HW} values can largely eliminate their hydrophobic effects on adsorption; by this treatment, the influence of other interactions on adsorption may become apparent.[83] For aromatic hydrocarbons, besides the hydrophobic effect, π-bonding interaction can play a significant role in their adsorption on CNPs.[22,43,51,83] Functional groups such as $-COOH$, $-OH$, and $-NH_2$ in organic molecules can form hydrogen bonds with CNPs and promote the adsorption of these organic molecules.[51,95] The influence of functional groups on adsorption of organic chemicals by CNPs depends on the type, number, and position of functional groups in the organic molecules. More functional groups in a molecule result in higher adsorption affinity (E) on CNPs.[51,83,116] Adsorption affinity of aniline and phenol on CNTs is altered, with their substituted groups at a given position with the following order: nitro group > chloride group > methyl group.[51] The position of substituted groups in an organic molecule could also influence the adsorption.[51,116] However, these effects are weaker than that of the type of substituted groups and cannot be interpreted directly by the group position.[51] Molecular configurations of organic chemicals may also play a role in their adsorption. For planar chemicals, SWCNTs have significantly higher adsorption capacities and site energies than MWCNTs, whereas for nonplanar chemicals, the adsorption capacity and site energy differences between SWCNTs and MWCNTs became smaller with increasing concentration of organic chemicals.[125]

8.2. Molecular Size

Molecular size of organic chemicals is another critical factor affecting their adsorption capacity on CNPs although it could not influence their adsorption affinity (E).[51] Therefore, PAHs (i.e., napththrene, phenanthrene, and pyrene) have the same types of interaction with CNPs (i.e., hydrophobic interaction and π-bonding interaction), while their adsorption capacities (Q_v^0) on a tested MWCNT sample are varied.[23] First, the volume adsorption capacity of a given organic chemical on the planar surface of CNPs should be higher if the adsorption is a result of the attachment of the end of the organic molecule (Figure 10b) on the CNP surface rather than that of the attachment of the side of the organic molecule (Figure 10c). Second, larger molecules (Figure 10b) have higher volume adsorption capacity than relatively small molecules (Figure 10a) on the planar surface of CNPs if they have a same attachment orientation. For example, the adsorption capacity of big DOM and surfactants on CNTs[32,129] is much higher than that of PAHs and other smaller organic chemicals.[23,51] However, larger molecules should have lower adsorption capacity in the pores of CNP aggregates than relatively small molecules because of the bottleneck of pores for organic chemical diffusion, i.e., organic molecules cannot enter into the pores with smaller size than the molecules. For example, small molecules (i.e., water and ethanol) have higher adsorption capacity (10 times more) than the bigger molecules (i.e., hexane) on CNPs.[95] Also, small molecules (i.e., water and ethanol) have lower diffusion rates than the bigger molecules (i.e., hexane) because the diffusion of small molecules into the inner pores of CNP aggregates is a rate-limiting process and because most of bigger molecules cannot diffuse into the inner pores of CNP aggregates.[95] With the bottleneck effect of CNP pores, larger differences in chemical molecular size result in better separation in the mixed system of organic chemicals.[130] Another possibility for larger molecules having lower adsorption capacity on CNPs is that the adsorbed phase may be different from the corresponding bulk phase.[37,131] The change of organic chemicals from bulk solid to adsorbed phase, as an example, always results in the expansion of chemical volume and density decrease. The volume expansion and density decrease are greater for big molecules as compared to smaller molecules, thus the adsorbed volume capacity (calculated from solid phase density) of a big molecular chemical is lower than smaller molecular chemicals and its actual adsorbed volume.[23] In addition, configuration of adsorbed organic molecules on CNPs may be different relative to bulk organic molecules, especially for the large molecules containing long aliphatic chains, because the long aliphatic chains are relatively “soft” as compared with the aromatic rings and easier to deform

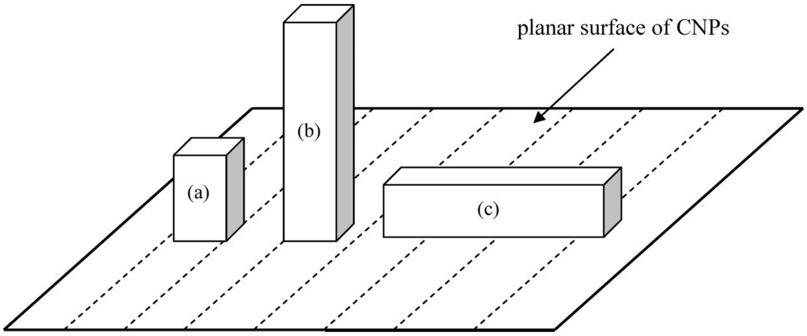

Figure 10. Adsorption of smaller molecule (a) and bigger molecules via the attachment of the end of the organic molecule (b) or the side of the organic molecule (c) on the planar surface of CNPs.

(or bend). These large molecular chemicals reported include enzymes,[132,133] lipid derivatives,[74] L-phenylalanine,[101] natural organic matter,[32,134,135] and surfactants.[129] Conformational changes of organic molecules can promote their matching with the curvature surface of CNPs to enhance their stability on the CNP surface.[74,132]

8.3. Chemical Solvatochromic Parameters

Solvatochromic parameters, in general, including the intrinsic molar volume (V_I), polarity/polarizability (π^*), hydrogen-bonding accepting ability (β_m), and hydrogen-bonding donor parameter (α_m), are useful descriptors for predicting the properties, toxicity, mobility, and environmental behavior of various organic chemicals.[49,51,136−139] These solvatochromic parameters of organic compounds can be estimated using quantitative structure−activity relationship (QSAR) modeling based on their functional and structural characteristics.[136,138] The ability of organic chemicals to form $\pi-\pi$ bonds with sorbents can be identified by their π−electron polarizability parameter (π^*).[49,51] Chemicals with more aromatic rings in their molecules have higher π^* value and lower water solubility,[136−138] and thus they are more hydrophobic and can form stronger π-bonding interaction with CNPs.[51] The ability of organic chemicals to have hydrogen-bonding interaction with sorbents can be evaluated by their hydrogen-bonding acceptor or donor parameters (β_m or α_m).[49,51] Functional groups attached to organic molecules and the type, number, and position of functional groups in the organic molecules can alter the solubility of organic chemicals in water[136,137] and their values of β_m, α_m, and π^*.[136−138] The linear solvation energy relationships (LSERs) model based on the solvatochromic parameters has been developed to predict adsorption affinity (E) of aromatics, halogenated aliphatics, and halogenated aromatics onto solid sorbents from aqueous solution by correlating solvatochromic parameters with the adsorption affinity values.[49] These solid sorbents include coal-based activated carbons, coconut shell based activated carbon, unspecified activated carbon, and synthetic polymeric adsorbents. This LSERs was observed for the adsorption of aniline, phenol, and their substitutes on a MWCNT sample (MWCNT15) as given in eq 2.[51]

$$E = 11.58(\pm 2.03) \times \alpha_m + 8.15(\pm 3.64) \times \pi^* + 5.50(\pm 3.42) \quad (r^2 = 0.785) \qquad (2)$$

The DA model fitted E data of isotherms of other organic chemicals (i.e., PAHs) on MWCNT15 reported by Yang et al.[23] also follow eq 2. In this equation, the constant intercept, 5.50 ± 3.42, is close to the DA model fitted E value (5.71) of linear isotherm ($b = 1$) and thus can be attributed to the hydrophobic effects of organic chemicals on adsorption.[51] The linear isotherm, derived from the DA model (Table 1) where E and b are given to be 5.71 and 1, respectively (eq 3), shows that the solute adsorption is limited by their solubility values (C_s) only for a given sorbent having a constant Q^0.

$$q_e = Q^0 C_e / C_s \qquad (3)$$

According to eq 2, therefore, besides the constant hydrophobic effect of organic chemicals, chemical π−electron polarizability (π^*) and hydrogen-bonding donor ability (α_m) can play an important role in their adsorption affinity on CNPs. Chemical molecular size (V_I) and hydrogen-bonding acceptor ability (β_m) have almost no influence on their adsorption affinity. The limited role of organic chemical β_m in their adsorption on CNPs could be attributed to the graphite sheet of carbon nanotubes that is not a hydrogen-bonding donor.[140] Moreover, functional groups of CNPs prefer to adsorb water molecules through hydrogen-bonding interaction, which is responsible for screening out the role of organic chemical β_m in their adsorption on the functional surface sites of CNPs.[79,97−99]

8.4. Dissociation of IOCs

IOCs including organic acids such as phenolic chemicals and organic bases such as aniline-type chemicals are different from nonionizable chemicals because they can exist either as neutral or dissociated species in the aqueous phase.[51] The occurrence of their neutral or dissociated species depends on the solution pH in relation to their dissociation constants (pK_a). At pH < pK_a, the neutral and the dissociated species (bases form cations by protonation) are dominant for organic acids and organic bases, respectively, while at pH > pK_a, the dissociated species (anion) is dominant for organic acids and the neutral species is dominant for organic bases. The fraction of neutral species for organic acids (f_A^N) and bases (f_B^N) can be respectively estimated by $f_A^N = (1 + 10^{\mathrm{pH-p}Ka})^{-1}$ and $f_B^N = (1 + 10^{\mathrm{p}Ka\mathrm{-pH}})^{-1}$, and the fraction of dissociated species for organic acids (f_A^I) and bases (f_B^I) can be estimated by $f_A^I = (1 + 10^{\mathrm{p}Ka\mathrm{-pH}})^{-1}$ and $f_B^I = (1 + 10^{\mathrm{pH-p}Ka})^{-1}$, respectively.[51] Neutral species of IOCs have higher adsorption than dissociated ones although both of neutral and dissociated species can adsorb on CNPs.[51] Therefore, adsorption of IOCs on CNPs is pH-dependent, showing that adsorption of organic acids is decreased with increasing pH[51,82,113,115,141] while adsorption of organic bases is increased with increasing pH.[51,142] For zwitterionic chemicals such as norfloxacin, their adsorption on CNPs could be either increased or decreased with pH because they can be dissociated to be cationic or anionic species.[55] Increasing pH can also decrease the adsorption of NOM on CNPs[31,32,143,144] because NOM contains abundant −COOH and phenolic groups and they are ionizable similarly to organic acids. The lower adsorption of dissociated species of IOCs on CNPs as compared with their neutral species can largely be attributed to the disappearing of hydrogen-bonding donor ability and higher solubility (i.e., lower hydrophobic effect) of dissociated species.[145] Furthermore, electrostatic repulsion between negatively charged NOM and CNP surface with increased pH could rise to decrease the NOM adsorption.[31,32] For a given solute concentration, pH dependence of the apparent adsorption coefficients K_d ($= q_e/C_e$) of organic acids and organic bases can be estimated from the following eqs 4 and 5, respectively.[51] For organic acids,

$$K_d = K_d^N \times 1/(1 + 10^{(\mathrm{pH-p}K_a)}) + K_d^I \times 1/(1 + 10^{(\mathrm{p}K_a\mathrm{-pH})}) \qquad (4)$$

and for organic bases,

$$K_d = K_d^N \times /(1 + 10^{(\mathrm{p}K_a\mathrm{-pH})}) + K_d^I \times 1/(1 + 10^{(\mathrm{pH-p}K_a)}) \qquad (5)$$

where K_d^N and K_d^I are the adsorption coefficients of neutral species and dissociated species, respectively. These two models assume that the value of either K_d^N or K_d^I is constant over the whole pH range considered for a given initial concentration. Adsorption increase with increasing pH was observed for pyrogallol and 1-naphthol,[113] and 2-naphthol and 1-naphthylamine[90] on CNPs, which is inconsistent with the reported results for other IOCs.[51,82,90,115,141] The electron donor−acceptor (EDA) interactions were suggested by Chen et al.[90] to be the primary mechanism for the pH-induced adsorption increase of naphthol and naphthylamine. One type of EDA interaction is the $\pi-\pi$ EDA interaction because hydroxyl group of naphthol and amino group of naphthylamine as $\pi-$electron donating groups make the benzene ring(s) of naphthol and naphthylamine $\pi-$electron-rich, thus allowing these two compounds via their benzene ring(s) to interact more strongly with the electron-depleted surfaces of carbon nanotubes and graphite ($\pi-$electron acceptor). Another EDA interaction was the $n-\pi$ EDA interaction because oxygen electron pairs of hydroxyl group and nitrogen electron pairs of amino group as n-electron donors might have directly interacted with the electron-depleted sites ($\pi-$electron acceptor) of carbon nanotubes and graphite. The strength of both $\pi-\pi$ and $n-\pi$ EDA interactions are enhanced when hydroxyl and amino groups are ionized to their dissociated species because of the fact that their dissociated species are even stronger electron-donating groups, and thus adsorption of naphthol and naphthylamine on the graphene surface of CNPs are increased as pH increases. In addition to the EDA interaction, Lewis acid−base interaction was also suggested by Chen et al.[90] as an extra possible mechanism contributing to the pH increased adsorption of 1-naphthylamine, especially on the oxidized carbon nanotubes. However, the observed increase in adsorption of pyrogallol, naphthol, and naphthylamine with increased pH below their $\mathrm{p}K_a$ could be due to other possible reasons. First, the pH-dependent effect of oxygen-induced oxidative coupling could lead to the adsorption of these compounds to CNTs/graphite.[146] Second, the pH-dependent oxidization of chemicals such as 1-naphthol in solution was reported,[147−149] and this oxidized loss could have accounted for increased adsorption with increasing pH, at least for naphthol. Third, measurement of IOCs in solution using the UV−vis spectrometer is generally dependent on the pH of solution because the neutral species and dissociated species of IOCs have different UV absorbance.[51,128] The pH of supernatants has to be adjusted to the pH value at which the calibration curve was obtained. In addition, adsorption increase with increased pH was also reported for nonionic nitroaromatic compounds including 2,4-dinitrotoluene,[83] 1,3-dinitrobenzene, and 1,3,5-trinitrobenzene.[91] This increase was also interpreted by Chen et al.[83,91] with the EDA interaction, for which the nitro-group (the strong electron-withdrawing group) of these aromatics make their benzene ring(s) electron depleted and act as $\pi-$electron acceptors while the oxygen containing functional groups (the electron-withdrawing groups) on surfaces of CNTs not only act as n-electron donors themselves but also make the CNT graphene surface to be $\pi-$electron-rich and thus $\pi-$electron donors. The pH-promoted electron-donor ability of oxygen containing functional groups on CNT surfaces as a result of their dissociation (e.g., $-COOH$ is a weak electron donor and acceptor, while $-COO^-$ is a strong electron donor but not an acceptor) is thus suggested to be responsible for the increased adsorption of these nitroaromatics with increasing pH. However, this increase was not observed for other nitroaromatics ($\pi-$electron acceptors) on CNTs[51] and activated carbons.[150,151] For example, the adsorption of nitrobenzene on oxidized and unoxidized activated carbon surfaces did not change significantly with the change of the solution pH from 2 to 12.[150,151] The adsorption of 1,3-dinitrobenzene, as another example, on graphitized, purified, hydroxylated, and carboxylated MWCNTs also did not change significantly with pH in the range of 2−12 (Figure 11). These observations suggest that acidic functional groups on CNP surfaces could not form EDA interactions with nitroaromatics in the aqueous phase. The much stronger interactions of water molecules to form hydrogen bonds with the acidic functional groups on CNT surfaces[97−99] would suppress the EDA interaction of nitroaromatics with oxidized CNTs, thus lower surface area normalized adsorption on the CNTs with more surface oxygen atoms was observed (Figure 11).

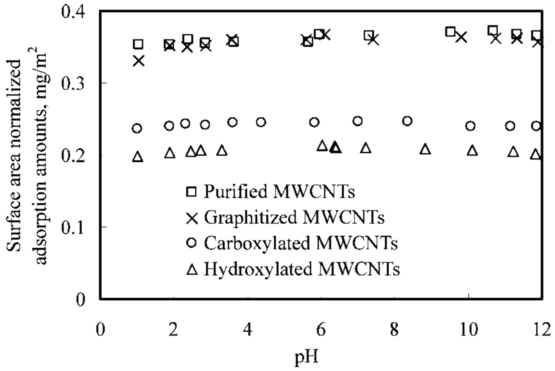

Figure 11. Effects of pH on the adsorption of 1,3-dinitrobenzene on graphitized, purified, hydroxylated, and carboxylated MWCNTs. The surface oxygen atomic percents of graphitized, purified, carboxylated, and hydroxylated MWCNTs determined by X-ray photoelectron spectroscopy (XPS) method are 0, 1.9, 6.0, and 6.4%, respectively.

Adsorption of various organic chemicals on a given CNP, as mentioned above, is a function of the chemical structures and physicochemical properties. The good fitting of Polanyi theory-based DA model for the isotherms of various organic chemicals indicates that the parameters of DA model can be related with the chemical structures and properties to probe their influence on adsorption. For example, empirical relationships between E (or b) and chemical solvatochromic parameters can be developed to explore the interactions between organic chemicals and CNPs and their strength for chemical adsorption.[51] However, the ability of organic chemicals to form covalent bonds with CNPs, as a parameter, still cannot be predicted quantitatively. Without this parameter, deviation of adsorption estimation using empirical relationships between E (or b) and chemical solvatochromic parameters would occur for organic chemicals that can be adsorbed by CNPs with covalent bonds. Moreover, Q^0 of DA model is not yet related with the chemical structures and physicochemical properties. Molecular size could be a potential parameter of organic chemicals to be related with their Q^0 values. In addition, the influence of pH on adsorption of IOCs are also not related with Q^0 and E (or b) of DA model although the pH-dependence of adsorption of IOCs can be estimated from the solution pH and chemical $\mathrm{p}K_a$ values.[51] These relationships should be developed to examine the influence of chemical structures and properties on adsorption and to estimate the adsorption in future investigations.

9. Competitive Sorption and the Roles of DOM and Surfactants in Adsorption

9.1. Competitive Sorption of PAHs

Competitive behavior of multiple organic chemicals on activated carbon and natural geosorbents has been widely reported.[37,152−155] This behavior is a key issue because multiple pollutants exist concurrently in the environment. Significant competitive sorption between PAHs was also observed on CNTs, showing the isotherm of a given primary solute changed from being significantly nonlinear to nearly linear when competitors were added.[50] Moreover, the observed competitive sorption depends on the relative equilibrium concentrations of both primary and cosolutes. Significant competition was present at relatively low concentrations of primary solute and high concentrations of competitors, while competition was much weaker in the case of relatively high concentrations of primary solute and low competitor concentrations. When the relative concentration of primary solute (C_e/C_s) approached 1, competition by other solutes seems to disappear, i.e., the adsorption capacity of a given PAH chemical on CNTs may not be changed with the addition of other PAHs as the competitors. A Polanyi-based surface adsorption mechanism with multilayer adsorption has been proposed to interpret the observed competitive adsorption of multiple organic chemicals (i.e., pyrene, phenanthrene, and naphthalene) on the CNTs.[50] The observed significant competition for PAH chemicals on CNTs and the increase of isotherm linearity could be attributed to the weaker $\pi-\pi$ electron interaction of the adsorbed PAH molecules with other PAH molecules than that with the CNT graphitic surface because the hydrophobic effect alone on solute adsorption by CNTs presents linear isotherms while additional interactions such as $\pi-\pi$ electron interaction result in the isotherm nonlinearity.[51]

9.2. Competitive Sorption with Metal Ions

Adsorption of organic chemicals such as 2,4,6-trichlorophenol, naphthalene, atrazine, 1,3-dinitrobenzene, and 1,3,5-trinitrobenzene on MWCNTs and SWCNTs can also be suppressed by metal ions (i.e., Cu^{2+}, Pb^{2+}, and Cd^{2+}), as interpreted by the formation of surface complexes of metal ions with oxygen functional groups on CNTs.[91,156,157] The suppression of the adsorption of organic chemicals by the metal ions is affected by oxygenated functional group density on CNTs.[156] This suppression could also be expected to be more significant for chemicals such as atrazine which could adsorb by forming covalent bonds with CNT functional groups than for other chemicals because: (i) CNT functional groups are mostly responsible for the adsorption of metal ions,[158] and (ii) functional group conglutinated CNT surfaces cannot be available for the adsorption of most organic chemicals because of the suppression of water[97−99] except for chemicals that can form covalent bonds with CNT functional groups.[78,100,101]

9.3. Competitive Sorption with DOM and Surfactants

DOM and surfactants can suppress the adsorption of organic chemicals such as PAHs and nitroaromatics on CNP surfaces.[54,91,129,159,160] It should be noted that the presence of DOM or surfactants reduced both of the adsorption capacity (Q^0) and the adsorption affinity (E) of these organic chemicals on CNTs.[54,129] This is different from the observed competition phenomena for PAH chemicals on CNTs,[50] in which the Q^0 for a given PAH chemical remained practically constant when other PAH chemicals were added as competitors. This competition difference could be caused by the different molecular structure between DOM (or surfactants) and PAHs as well as the structure influence on the available surface area of CNTs for adsorption. For DOM and surfactant molecules, they have a long flexible aliphatic chain in the molecule, while there are only aromatic rings in PAH molecules. Relative to the aliphatic chain, aromatic rings are hard and inflexible. The surface of CNTs occupied by DOM or surfactants could be never available for adsorption of other molecules.[129] This hypothesis was supported by the decrease of specific surface area of CNTs after they are coated with DOM or surfactants.[54,129] Additional evidence for this hypothesis was observed in other studies[161,162] that the surface area values of coated clays with cationic surfactants were far smaller than that of the uncoated clays and the specific surface area of NOM measured using N_2 adsorption−desorption is very small.[135,163] If the surface of CNTs is occupied by hard PAH molecules, however, the adsorbed PAH molecule could provide an equivalent surface area to the occupied surface area of CNTs by the PAH molecule, which is available for adsorption of other molecules,[50,129] and thus a relatively constant Q^0 remains for a given PAH chemical on CNTs with or without other PAH chemicals as competitors.[50]

9.4. Other Influence of DOM and Surfactants on Organic Chemical Adsorption

Adsorbed NOM and surfactants on CNPs can also act as a favorable media for organic chemical partition.[129,134,135] The additional sorption of organic chemicals by partitioning into the adsorbed NOM and surfactants will counteract the competition induced adsorption decrease.[129] Therefore, the apparent sorption of organic chemicals by NOM (or surfactant) coated CNPs can be attributed to: (i) adsorption of organic chemicals on unoccupied CNP surfaces and (ii) additional sorption of organic chemicals partitioning into adsorbed NOM or surfactants.[129] Adsorbed surfactants, mainly the surfactant hemimicelles as a favorable partitioning media for organic chemical sorption, should impart linear isotherms of organic chemicals.[129,162,164−166] Therefore, isotherm linearity of organic chemicals on surfactant coated CNPs increased with the increase of adsorbed surfactant amounts.[129] Moreover, the apparent sorption of organic chemicals by surfactant coated CNPs can be described by the partition−adsorption model (Table 1) including a partition fraction of chemicals into adsorbed surfactant hemimicelles and an adsorption fraction of chemicals on unoccupied CNP surfaces.[129] As compared with surfactants, adsorbed NOM can act not only as a favorable partitioning media (presenting linear isotherm) but also as an adsorbent (presenting nonlinear isotherm) for organic chemical sorption.[128,134,135,154,155] Configuration changes of NOM and surfactants might occur after they are adsorbed on CNPs, which can result in that the sorption affinity and capacity of CNP-adsorbed NOM and surfactants for organic chemicals are different from that of bulk NOM and surfactants and vary with the adsorbed amounts of NOM and surfactants on CNPs.[129,134,135] NOM fractionation might also occur upon their adsorption on CNPs, and consequently alter organic chemical sorption on adsorbed NOM as well as NOM-coated

CNPs.[134,135,167] Coadsorption of metal ions can also change the adsorption and configurations of NOM on CNPs because metal ions can bridge NOM with functional groups on CNPs, compress the double layer, and neutralize negative charges of NOM and thus weaken the repulsion between NOM molecules as well as between NOM and CNPs.[31,143,144] This should affect the sorption of organic chemicals on NOM-coated CNPs, which needs more investigations.

Dispersion of CNPs and solubility enhancement of organic chemicals by DOM and surfactants may also influence the organic chemical adsorption on CNPs.[54,56,160] It is widely observed that DOM[30,34,66,71] and surfactants[72−76] can prompt dispersion of CNPs (i.e., deaggregation of big CNP aggregates to smaller CNP aggregates), which could lead to more CNP surface sites exposed for organic chemical adsorption.[54,56,160] DOM[168−171] and surfactants[172−174] in solution could also decrease chemical adsorption on CNPs by enhancing the solubility of organic chemicals.

Although adsorption of an organic chemical on CNPs can be suppressed by other organic chemicals, metal ions, DOM, and surfactants, the isotherms of organic chemicals in the presence of these competitors can be fitted well by the Polanyi theory-based DA model,[50,54,129,156] which indicates that the influence of competition on organic chemical adsorption can be described by the variation of the parameters of DA model. Even for the other influence of DOM and surfactants on organic chemical adsorption, they can be described by the variation of the parameters of DA model, too.[129] Empirical relationships could be developed for Q^0 and E (or b) with adsorbed amounts of the competitors on CNP surfaces.[129] The pH and ionic strength could largely change the adsorption of DOM and surfactants on CNPs,[31,32,143,144,175] and thus their impact on the sorption of organic chemicals in the presence of DOM and surfactants needs to be examined. In addition to cationic surfactants,[129] anionic and nonionic surfactants have also been employed to synthesize and disperse CNPs.[76,176,177] As compared with cationic surfactants, these surfactants could have different sorption on CNPs and thus different effects on sorption of organic contaminants by CNPs. Moreover, the adsorption of surfactants on CNPs and its effects on organic contaminant sorption may depend on the various structures and functional groups of CNPs. Therefore, research using different types of surfactants and CNPs are urgently needed to examine the adsorption effects of surfactants on sorption of organic contaminants.

10. Adsorption−Desorption Hysteresis

10.1. Hysteresis Phenomenon

Adsorption−desorption hysteresis has been widely observed for the sorption of organic compounds by soils, sediments, and charcoals.[178−180] Desorption hysteresis shows greater apparent affinity of adsorbate in desorption branches than adsorption branches (Figure 12). Two types of hysteresis are often observed: reversible and irreversible hysteresis.[179,181] Reversible hysteresis means that complete desorption can be achieved without any intervention (e.g., vigorous solvent extraction), showing a closed hysteresis loop in desorption and adsorption branches of an isotherm (Figure 12A). Closed hysteresis loop is commonly observed for vapor sorption, which is attributed to formation of metastable states and network percolation effects, associated with capillary liquid condensation in fixed mesopores.[181] It was also observed for desorption of naphthalene from lignite in aqueous solutions.[182] Irreversible hysteresis means that complete desorption cannot be achieved (Figure 12B). This type of hysteresis has been observed for vapor sorption in the nanopores of glassy polymers[183] and the interlayers of dry clay[184] and for aqueous sorption of organic compounds by soils and sediments[178,185] and charcoal.[179] Irreversible pore deformation has been proposed to interpret the irreversible hysteresis in these studies.

10.2. Desorption Hysteresis on Fullerene

Irreversible hysteresis was observed for the desorption of PAHs (i.e., naphthalene, phenanthrene and pyrene), and 1,2-dichlorobenzene from fullerene into aqueous solutions,[6,62,114] while no desorption hysteresis was observed for PAHs from CNTs into aqueous solutions.[6] This difference was attributed to the distinct geometries of fullerene and CNTs.[6] Spherical monomers of fullerene may result in its aggregates having closed interstitial spaces in small aggregates or between small aggregates. Deformation and rearrangement of small aggregates can result in the penetration of adsorbate molecule into closed interstitial spaces between small aggregates during adsorption and lead to the molecular entrapment and hysteresis. The cylindrical monomers of CNTs cannot form closed interstitial spaces in their aggregates due to their length, hence no adsorption−desorption hysteresis was observed for PAHs.

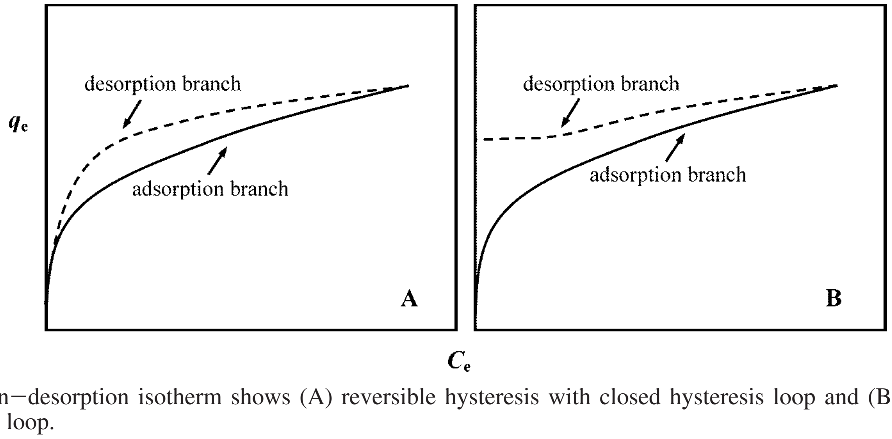

Figure 12. Adsorption−desorption isotherm shows (A) reversible hysteresis with closed hysteresis loop and (B) irreversible hysteresis with opened hysteresis loop.

10.3. Desorption Hysteresis and Immobilization on CNTs

Although no desorption hysteresis was observed for PAHs from CNTs,[6] immobilization and irreversible hysteresis have been observed for other organic chemicals such as tetra-*tert*-butylphthalocyanines[87] and bisphenol A (BPA) and 17α-ethinyl estradiol (EE2)[53] upon their desorption from CNTs into water. The strong $\pi-\pi$ coupling of benzene-ring-containing chemicals with the CNT surface was proposed by Wang et al.[87] to interpret the immobilization. However, the absence of adsorption−desorption hysteresis for naphthalene, phenanthrene, and pyrene[6] indicated that this $\pi-\pi$ coupling could not result in the immobilization. Pan et al.[53] proposed that the rearrangement of the bundles or aggregates of CNTs is responsible for the irreversible hysteresis of two estrogens (i.e., EE2 and BPA). Pan et al.[53] also attributed the absence of adsorption−desorption hysteresis for PAHs reported by Yang and Xing[6] possibly to the lower rearrangement of the bundles or aggregates of CNTs because of relatively less and weaker adsorption of PAHs as compared with that of two estrogens. This explanation may not be applicable for the significant irreversible hysteresis of the desorption of atrazine on highly oxidized CNTs (with an oxygen content of 7.07%)[156] because (i) the adsorption of atrazine on the highly oxidized CNTs is less than that on other CNTs with less oxygen content (<2.16%) and (ii) no desorption hysteresis of atrazine on CNTs with lower oxygen content was observed.[52,156] The observed irreversible hysteresis of atrazine on highly oxidized CNTs rather than other lower oxygen-containing CNTs could lead us to conclude the important role of oxygen-containing functional groups on CNT surfaces in irreversible hysteresis. Moreover, tetra-*tert*-butylphthalocyanines, EE2, BPA, and atrazine have oxygen- or nitrogen-containing functional groups in their molecules as compared with the molecular structures of PAHs. These functional groups in the molecules may possibly form covalent bonds with the oxygen-containing functional groups such as −COOH and −OH of CNTs.[78,100,101] Covalent modification of CNTs has been widely utilized to form a variety of nanostructures.[28,102,103] Therefore, we proposed here that the formation of covalent bonds between the functional groups on organic chemicals and CNTs may be partly responsible for the observed immobilization of tetra-*tert*-butylphthalocyanines[87] and irreversible hysteresis of BPA, EE2, and atrazine.[53,156] Consequently, the absence of desorption hysteresis for PAHs[6] and atrazine[52,156] from CNTs can be also attributed to (i) no covalent bonds can form between PAH molecules and CNTs because of the absence of functional groups in the PAH molecules and (ii) few covalent bonds can form between atrazine and CNTs because of these CNTs containing few functional groups.

For organic chemicals such as PAHs having no desorption hysteresis on CNTs, their desorption from CNTs into water can be estimated from their adsorption isotherms using Polanyi theory-based DA model. Although Polanyi theory and DA model can be employed to describe and estimate the adsorption of organic chemicals on fullerene and CNTs, they seem to be inadequate to describe and estimate the irreversible hysteresis of desorption of organic chemicals because the irreversible hysteresis is a result of the deformation and rearrangement of CNPs aggregates (i.e., different thermodynamic pathways between adsorption and desorption). However, irreversible hysteresis of desorption of organic chemicals from CNTs, resulting from covalent bond formation, could be described and estimated by Polanyi theory and DA model if there are parameters to describe the ability of functional groups (in organic chemicals and on CNP surfaces) to form covalent bonds.

11. Conclusions and Perspectives

The available spaces of CNPs and the strength of interactions between organic chemicals and CNPs determine the adsorption capacity and affinity of organic chemicals on CNPs, respectively. External surface of CNP monomers and the interstitial spaces and grooves surrounded by the external surface of CNP monomers are the possible spaces of CNPs for organic chemical adsorption. The availability of these possible spaces for adsorption can be altered by the surface functional groups, surface modifying chemicals, surface curvature, surface defects, pore sizes in aggregates, and pore deformation and rearrangement of CNPs. The availability of these possible spaces is also dependent on the molecular structures, functional groups, and molecular sizes of organic chemicals. There are five interactions (i.e., hydrophobic, $\pi-\pi$ bonding, hydrogen bonding, covalent bonding, and electrostatic interactions) between organic chemicals and CNPs. These interactions and their strength are influenced by the structures and functional groups of chemicals and the functional groups on CNP surfaces. Hydrophobic graphitic surfaces are the main surfaces of CNPs responsible for organic chemical adsorption. Functional group (e.g., −COOH and −OH) conglutinated hydrophilic graphitic surfaces of CNPs are not available for most organic chemicals because of the suppression of water, and thus functional groups on CNP surfaces decrease the adsorption capacity of most organic chemicals except for chemical molecules having functional groups that are able to form covalent bonds with the functional groups of CNPs. Surface modification of CNPs with “hard” organic chemicals such as PAHs containing only aromatic rings in their molecules may decrease significantly the adsorption affinity of other organic chemicals but not their adsorption capacity. However, surface modification of CNPs with “soft” organic chemicals such as NOM and surfactants containing long aliphatic chains in their molecules could not only decrease the adsorption affinity but also the adsorption capacity of other organic chemicals. Adsorption−desorption hysteresis of organic chemicals on fullerene is irreversible and can be attributed to the closed interstitial spaces between small fullerene aggregates and the penetration and entrapment of chemical molecules into these closed interstitial spaces because of the deformation and rearrangement of small aggregates, while the irreversible hysteresis on CNTs can be possibly attributed to the formation of covalent bonds between the functional groups of both of organic chemicals and CNTs.

For the application of CNPs as potential superior adsorbents, it is necessary to disperse the CNP aggregates to expose their surface area for more adsorption of organic chemicals because the adsorption is dependent on their surface area and the aggregation of CNPs always decreases their surface area. However, the common methods employed to promote the CNP dispersion such as surface functionalization with oxygen containing groups and surface modification with DOM and surfactants could not be a viable way to enhance the CNP surface area for more adsorption of organic chemicals because these methods are accompanied by the competition of water and adsorbed DOM (or surfactants) with organic chemicals and thus could result in the decrease in chemical adsorption.[54,91,97,98,129,159,160] Therefore, new methods with selecting of dispersion reagents having no competition with organic chemicals on CNP surface need to be developed to expose CNP surface area for the application of CNPs as potential superior adsorbents. Moreover, dispersion of CNPs will result in the difficulties in separating CNPs from aqueous phase, which should be solved before they are used as superior adsorbents. In addition, dispersed CNPs have been recognized to transport readily and farther with water in the environment than the undispersed ones,[29−31,33,34,186,187] which may result in higher environmental and health risks as they released into the environment.

Polanyi theory captures the aqueous adsorption process of organic chemicals by CNPs mechanistically, as evidenced by both of the observed characteristic curve of Polanyi theory and the excellent fitting Polanyi theory-based sorption models such as DA model.[23] DA model has excellent fitting for isotherms of organic chemicals on CNPs although these chemicals and CNPs have various structures and physicochemical properties.[6,23,45,51,53] The good fitting of DA model has also been observed even if other chemicals including "hard" aromatic molecules (e.g., PAHs), "soft" aliphatic molecules (e.g., NOM and surfactants), and metal ions are added as competitors.[50,54,129,156,160] Available adsorption spaces of CNPs for organic chemicals, varied with the CNP/organic chemical structures and physicochemical properties and the CNP surface modification with other chemicals, can be identified by a capacity parameter (Q^0) of DA model. Both E and b of the DA model are affinity parameters to identify the interaction forces and their strength as well as the energy distribution of CNP surface for organic chemical adsorption. Empirical relationships have been developed for Q^0 with CNP surface area,[23,53] Q^0 with CNP surface oxygen content,[45] Q^0 with adsorbed surfactant amounts on CNP surfaces,[129] E (or b) with chemical solvatochromic parameters,[51] E (or b) with the $R_{\mathrm{meso/micro}}$ ratios of CNPs,[23] E (or b) with adsorbed surfactant amounts on CNP surfaces,[129] and even for the pH-dependence of adsorption of IOCs, which can be estimated from the solution pH and chemical pK_a values.[51] These relationships may not only help us to understand the aqueous adsorption mechanisms of organic chemicals on CNPs but also represent a favorable step by estimating their adsorption capacity and affinity to evaluate the potential application of CNPs as environmental sorbents and the environmental risks of both toxic organic chemicals and CNPs after they are released into the environment. Limited by the cost and experimental difficulty of testing environmental behavior such as sorption for thousands of chemicals and materials, such estimation is usually essential when direct experimental data are unavailable. Therefore, efforts are still needed to combine these developed empirical relationships into a predictive model and develop more valid empirical relationships such as Q^0 with chemical structures and physicochemical properties. In addition, the solubility data of some organic chemicals especially for the dissociated species of IOCs is not yet available at the present, which can be a main limitation for the application of Polanyi theory-based DA model in describing adsorption of organic chemicals relative to other models such as Freundlich model.

Although there are still unanswered questions regarding the adsorption of organic chemicals on CNPs and the related environmental risks of both toxic organic chemicals and CNPs, the reported results summarized in this review have shown that Polanyi theory and the developed empirical relationships (models) between the parameters of the Polanyi theory-based DA model and the CNP/organic chemical structures and physicochemical properties can help us to better understand the adsorption mechanisms of organic chemicals on CNPs and to estimate the adsorption capacity and affinity of organic chemicals. In addition, appropriate Polanyi theory-based predictive models may help to design CNPs with specific needs, and to evaluate the potential application of CNPs as sorbents and the environmental risks of both toxic organic chemicals and CNPs. Therefore, this review may stimulate more detailed and systematic investigations for (i) effectively applying the Polanyi theory and DA model in describing the adsorption of organic chemicals on CNPs, (ii) searching for and measuring the values of useful physicochemical parameters of both organic chemicals and CNPs to develop predictive models to estimate the fitting parameters of DA model, and (iii) using the Polanyi theory and DA model to determine the desorption, hysteresis, and bioavailability of adsorbed organic chemicals on CNPs.

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