INVESTIGATION ON THE ADSORPTION MECHANISMS OF IONIZABLE

COMPOUNDS ON CARBON NANOTUBES

A Thesis

by

SHIFAN LI

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Xingmao Ma
Committee Members,	Kung-Hui Chu
	Maria King
Head of Department,	Robin Autenrieth

December 2018

Major Subject: Civil Engineering

ABSTRACT

This study investigates the adsorption of several ionizable compounds on different types of carbon nanotubes, including graphitized multi-walled carbon nanotubes (G-CNTs), carboxyl functionalized multi-walled carbon nanotubes (COOH-CNTs) and hydroxyl functionalized multi-walled carbon nanotubes (OH-CNTs). The ionizable compounds investigated in this study are benzoic acid (BA), 2-naphthoic acid (2-NA), 3-hydroxy-2-naphthoic acid (3-H-2-NA), 3-methoxy-2-naphthoic acid (3-M-2-NA) and 3-amino-2-naphthoic acid (3-A-2-NA).

Adsorption isotherms of BA on all three CNTs at pH 2 and pH 7 were measured and they are highly nonlinear. The maximum capacity of functionalized CNTs for BA was invariably higher than that of G-CNTs. The results agree with a previous report that benzoate displayed strong adsorption onto functionalized CNTs and is consistent with the assumption that the negative-charged H-bonds are formed during the adsorption. OH^- stoichiometry confirmed that the adsorption of benzoate was accompanied with OH^- release. In comparison, the adsorption of BA on G-CNTs at pH 2.0 is mostly attributed to the hydrophobic force. At pH 2, functionalized CNTs show a greater adsorption for BA than G-CNTs. The forming of hydrogen bonding between O-containing functional groups on CNTs and the oxygen on the carboxyl functional group on benzene rings was deemed as the main reason for the enhanced adsorption of functionalized CNTs.

The sorption isotherms of NA at pH 2.0 and 7.0 displayed a similar adsorption patterns as BA. Hydrophobic forces play significant roles in the adsorption of the acids

at pH 2.0. At pH 7.0, the adsorption of the base exhibited strong affinity to functionalized CNTs, suggesting that similar charge-assisted hydrogen bonding has been formed during adsorption. A comparison of hydroxide ion release from BA and NA adsorption on COOH-CNTs at pH 7.0 showed that the hydroxide release from NA almost overlaps with the hydroxide release for BA adsorption, suggesting that the molecular size doesn't impact the forming of negative-charged H-bond. But the molecular structure did show a significant impact on the formation of this particularly strong intermolecular force.

ACKNOWLEDGEMENTS

CONTRIBUTORS AND FUNDING SOURCES

This work was supervised by a thesis committee consisting of Professors Xingmao Ma and Kung-hui Chu of the Zachry Department of Civil Engineering and Professor Maria King of the Department of Biological & Agricultural Engineering.

All work for this thesis was completed by the student, in collaboration with Xingmao Ma of the Zachry Department of Civil Engineering.

NOMENCLATURE

CNTs   Carbon nanotubes

G-CNTs   Graphitized carbon nanotubes

COOH-CNTs   COOH functionalized multi-walled carbon nanotubes

OH-CNTs   OH functionalized multi-walled carbon nanotubes

BA   Benzoic acid

2-NA   2-Naphthoic acid

3-H-2-NA   3-Hydroxy-2-Naphthoic acid

3-A-2-NA   3-Amino-2-Naphthoic acid

3-M-2-NA   3-Methoxy-2-Naphthoic acid

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Introduction

Carbon is an essential component of many important materials such as coal, battery core, and diamond. Recently, carbon nanotubes (CNTs) have been widely investigated as a novel material for many industrial and commercial applications. In addition to its outstanding mechanical strength and electrical conductivity [1, 2], CNTs could be a highly effective adsorbent thanks to its large specific surface area, high reactivity, and tunable surface properties [3, 4]. Currently, pollutions caused by organic chemicals such as petroleum, pesticides, and detergents are broadly recognized. Compared with other highly adsorptive carbon materials such as activated carbon (AC), CNT surface is more uniform and tunable and CNTs have displayed strong adsorption for many organic chemicals[5].

Due to their widespread uses, ionizable organic compounds are increasingly introduced into the environment. For instance, many antibiotics, pesticides, and endocrine-disrupting chemicals are all ionizable. Different from neutral compounds, the form of ionizable compounds is strongly affected by environmental pH. At a pH much greater than their pK_a, ionizable compounds may be fully deprotonated. The ionized compounds normally have lower hydrophobicity than their undissociated form and they are also more easily affected by electrostatics forces [6]. Even though there have been many studies on the adsorption of neutral compounds on CNTs, investigation on the

adsorption of ionizable compounds on CNTs is relatively rare. Emerging evidence suggests that ionized compounds may form exceptionally strong intermolecular forces with certain functional groups on CNT surfaces and exhibit much higher adsorption capacity than predicted by the hydrophobicity of these ions [7]. However, many questions remain regarding the impact of unique properties of ionized compounds on the adsorption of these compounds on CNTs

In this work, the adsorption isotherms of benzoic acid and 2-naphthoic acid, as well as several other aromatic carboxylates with more functional groups on CNTs were measured at different pH values. The main goal of the study was (1) confirm the formation of charge-assisted hydrogen bonding between benzoic acid and oxygen-containing functional groups on CNTs, and (2) to evaluate how surface functionalization of CNTs and the molecular size and structure of aromatic carboxylates may affect their adsorption on CNTs with different surface properties.

Literature review

The general background of carbon nanotubes

In 1985, a new molecule made purely of carbon, which is called sixty carbon atoms, was discovered in an experiment with a scanning tunneling microscope. After that, an infinite class of new molecules came into public view-C70, C84, etc. Each carbon in the molecules was bonded to other carbon as in graphite. In 1990, Dr. Richard Smalley found that tubular fullerene should be possible. In 1991, Sumio Iijima of NEC observed multiwalled carbon nanotubes (MWCNTs) formed in a carbon arc discharge

2

and after two years, the single-wall nanotubes (SWCNTs) were discovered by Donald Bethune at IBM independently [8]. The main difference between these two carbon nanotubes is that SWCNTs consist of one graphene cylinder whereas MWCNTs are made by several graphene cylinders. Due to the different structures, they show different properties. The SWCNTs are single surface and for exploiting especially the electronic properties which vary with their chirality, SWCNTs are the best type that can be used [9]. For MWCNTs, they show the average effect of all chiral tubes and widely used in research about mechanical and thermodynamical properties. MWCNTs are less expensive to produce and. Therefore, they are profitably used to make polymer or other composites enhancing their mechanical, thermal, and electrical production [10].

For instance, due to their high conductivity, carbon nanotubes (CNTs) may serve as a new high-advanced electrode. Some studies showed that carbon nanotubes are electrochemically active at both inner and outer tubules, thus, carbon nanotubes may be applied in batteries[11]. Meanwhile, carbon nanotubes can also be used in energy storage and energy conversion devices due to the narrow and high ordered graphitization[2]. In addition, CNTs can be incorporated into other materials to develop high-strength composites [12].

Different processes have developed to synthesize CNTs effectively. In the past decades, the chemical vapor deposition (CVD) was a commonly used method to synthesize carbon nanotubes[13]. In this approach, a substrate is prepared with metal particles and heated by $700℃$. Two gases are introduced into the reactor: one is a process gas, and the other is a carbon-containing gas. The carbon-containing gas is

broken at the surface of the metal surface and transported to the edge of metal. And Carbon nanotubes grow at the site of metal particles. The diameter of carbon nanotubes is controlled by the metal particles size [14]. Arc discharge and laser ablation are other two approaches to synthesize carbon nanotubes. Arc discharge method produces carbon nanotubes by using a current of 100 amps that is always be used to produce fullerenes[15]. In laser ablation, the laser vaporizes a graphite target in a high-temperature reactor and nanotubes are collected and develop on the cooler surface of the reactor[16].

To maximize the value of CNTs, scientist began to study the method to improve CNTs properties. The employment of hyperbranched poly in improving CNTs dispersion can increase electrical conductivity[17]. And when CNTs are connected with each other and form a branch, to form Y junctions, some new electronic properties could emerge[18, 19]. Furthermore, scientist found that the employment of hyperbranched polymers CNTs can be more reactive than non-functionalized carbon nanotubes. To enhance CNT properties, various functional groups can be added onto the surface of MWCNTs. Usually, functionalized CNTs are more effective for specific uses. Through functionalization, CNTs can fully materialize their properties. For example, the functionalized CNTs have better interfacial bonding strength. In the area of biological, functionalized carbon nanotubes have a stronger effect and better biocompatibility for cell viability [20].

As a result of the increasing environmental pollution and the emphasis of environmental cleanup, CNTs has been explored as a novel adsorptive material to

remove pollutants due to their high specific surface area, great adsorption capacity and affinity to many environmental pollutants.

The adsorption of neutral compounds on carbon nanotubes

Effects of adsorbents on the adsorption of neutral compounds on CNTs

There have been numerous studies on the adsorption of neutral compounds on CNTs in the literature. Previous studies have shown that pores of molecular dimensions can adsorb large quantities of gases owing to the enhanced density of the adsorbed material inside the pores due to the attractive potential of the pore walls [21]. CNTs typically have diameters of a few nanometers, therefore, they can attach liquids. Studies focusing on water adsorption on carbon nanotubes showed that the specific structure of carbon nanotubes is related to some physical properties like surface tension. The size of the SWCNTs was shown to be related to CNT water adsorption. Water confined in single-walled nanotube with relatively small diameter forms one-dimensional hydrogen-bonded chains in which each molecule receives one hydrogen to the next molecule along the chain. For adsorption on SWCNTs with a larger diameter, the adsorbed water is confined into layered structures.

There are also studies that indicate that SWCNTs are sensitive to the adsorption of gases. Therefore, the effect of the gas environment on electronic properties of carbon nanotubes has recently attracted certain attention. Some studies indicate that all gas molecules are weakly adsorbed on carbon nanotubes with small charge transfer. Sorption

on carbon nanotubes surface or inside of nanotubes bundle is stronger on an individual tube. In fact, there is no clear dependence of gas adsorption on tube size [21, 22].

Even though many types of research specializing in the adsorption of inorganic matters on carbon nanotubes, researches also abound on the adsorption of organic compounds on CNTs. Usually, the neutral organic compounds tend to be hydrophobic and have low solubility in water. The partition coefficient, which reveals the relation between sorbate concentration on adsorbent and equilibrium solution sorbate concentration, plays a key role in the adsorption and the low partition coefficient can decrease the maximum adsorption capacity of sorbent [23].

For the adsorption of neutral compounds to carbon nanotubes, it can be affected by many factors like hydrophobicity, π-π interaction, electrostatic interactions and H-bonding between adsorbates and carbon nanotubes [24]. There is a correlation of adsorption with CNTs morphology. Some studies indicate that the surface area can affect the adsorption and play an important role in organic chemical adsorption. Activated carbon with larger surface always has larger maximum adsorption capacity, because adsorbents with the relatively large surface area have larger pore volume and provide more adsorption site for adsorbates [25]. CNTs are intended to aggregate together due to Van der Waals force[21]. Thus, the surface area, as well as the interstitial and groove areas formed between CNTs, are main available sorption sites of CNTs but the inner pores are not [26]. Actually, the surface area is not the only physical property that can impact adsorption. Some parameters like diameter and morphology of carbon nanotubes can also affect adsorption [5]. Decreased diameter can increase surface curvature, result

6

in an increased number of multilayer and strong adsorption [27]. But for panel

molecules, increased diameter lead to stronger adsorption because panel structure

contacts better with carbon nanotubes [28]. In addition, the angle between the graphite

plane and the tube axis is related to the adsorption [29]. For adsorption on MWCNTs,

the distance between the layer of MWCNTs is too narrow for any organic molecule to fit

into [30]. The main adsorption mechanism for neutral compounds is different based on

the types of sorbates and structure of sorbents.

Functional groups are substituents that can be responsible for the specific

reaction. And some of the functional group are introduced into carbon nanotubes by

synthetic procedure and purification process [31]. Some properties can be changed by

adding functional groups. For example, functionalized CNTs can be more hydrophilic

and suitable for adsorption because functional groups can change the wettability of

CNTs [32], which make related low weight molecules adsorbed better [33]. But the

functional groups also have their own negative impact on adsorption. For organic

molecules, the functional groups may reduce the affinity and accessibility of CNTs

surface. Previous research indicates that the maximum sorption capacity is strongly

related to surface oxidation [34]. At the same time, there are serval investigations

indicate that increased oxygen-containing functional group decrease the adsorption of

chemicals which can form H-bonds. Water molecules can form hydrogen bonding with a

functional group, which will either occupy the adsorption site or form a 3-D cluster to

block nearby adsorption sites. Functionalization will result in an increase in oxygen

content, decreasing surface area and reducing hydrophobicity which can lead to reducing of adsorption for nonpolar hydrocarbons.

Effects of adsorbates for neutral compounds adsorption

The adsorption for neutral compounds is not only dependent upon the properties of adsorbents but also affected by the properties of adsorbates.

Molecular morphology is an important factor affecting the adsorption of neutral compounds. Previous research indicates that larger molecules usually have higher adsorption energy especially for organic molecules and larger molecules can also twist themselves to match with the curvature surface of CNTs to form stable complexes with CNTs [35]. On the other hand, the rate of organic chemical diffusion a is also associated with the molecule size. For smaller molecules, the diffusion into the inside of CNTs is a rate-limiting process and its diffusivities are relatively low. For larger molecules, it has higher sorption rate due to low adsorption capacity in the inner pore of CNTs [36]. Thus, the size of adsorbates results in different adsorption capacity[37].

The shape of adsorbates also affects the adsorption. For linear hydrocarbons and planar organic chemicals, these materials show strong adsorption on carbon nanotubes because they can contact carbon nanotubes surface better. The adsorption of planar molecules on CNTs has been investigated before. A study investigating the adsorption of different types of dyes on CNTs showed that the planar dyes adsorbed better than nonplanar dyes. This result illustrated that molecular morphology plays an important role in the attachment of dyes on CNTs. For planar dyes, the molecules can form π-π

bonding with carbon nanotubes and make them easier to attach on carbon nanotubes. On the contrary, the nonplanar dyes cannot form π-π bonding due to its spatial restriction [38].

Functional groups of organic chemicals also affect the adsorption through the π-π interaction. Each carbon atom in carbon nanotubes has a π electron orbit perpendicular to the surface. So, the organic chemicals containing π electron can form π- π bonding with carbon nanotubes. What is interesting is that the functional group attached to organic chemicals can greatly affect the strength of π-π bonding [39]. The functional groups of an organic molecule also greatly determine their polarity. For planar chemicals, functionalization will cause insufficient contact between carbon nanotubes and the adsorbates which decreases the adsorption of planar hydrocarbon [5].

Effects of solution conditions

Usually, the variation in pH can change the chemical speciation in a solution. Neutral compounds will maintain their chemical structure in a solution when the pH is altered. However, pH value can affect the functional groups on carbon nanotubes. For instance, when the carboxylic groups on the CNT surface were ionized at elevated pH, it can cause the enhanced formation of water cluster or reduce H-bond formation with adsorbates [40]. The pH impacts on adsorption depend on the counteracts between attractive forces (e.g., H-bond formation and hydrophobic interaction) and repulsive forces (e.g., charge repulsion).

Ionic strength is also an important factor for the adsorption of neutral compounds. The presence of metal ions can connect with organic chemicals and a functional group on carbon nanotubes. It can compress the double layer and neutralize charges of organic chemicals or carbon nanotubes to weaken the repulsion between organic chemicals and carbon nanotubes [41]. High ionic strength can result in less negative zeta potential of CNTs and reduce electrostatic repulsion between organic compounds and CNTs. Thus, the adsorbates can attach on carbon nanotubes more efficiently[42]. Previous research showed that the ionic strength can also affect the aggregation of carbon nanotubes [43].

The presence of dissolved organic matters (DOM) and surfactants in solution have been reported to suspend carbon nanotubes better [44, 45]. For instance, hydrophilic DOM fraction may suspend carbon nanotubes less efficiently than hydrophobic DOM fraction due to better contact of a hydrophobic fraction with carbon nanotubes.[5] However, the solubility of carbon nanotubes does not follow a simple relationship with hydrophobicity. There are two opposite mechanisms in the adsorption of DOMs on carbon nanotubes. On one hand, DOM can disperse carbon nanotube bundles and create more adsorption site for adsorbates to make adsorption more efficiency [46]. On the other hand, the presence of DOM can improve solubility of organic chemicals, thus decreasing their adsorption.

10

The adsorption of ionizable compounds on carbon nanotubes

Adsorption of ionizable compounds on carbon nanotubes is generally controlled by a combination of hydrophobic effects, van der Waals force as well as coulombic attraction. Factors that impact the adsorption of ionizable compounds on carbon nanotubes include the properties of carbon nanotubes and the solution chemistry.

Effects of carbon nanotubes on ionizable compounds adsorption

How the properties of carbon nanotubes affect the adsorption of ionizable is partly similar to the influence of carbon nanotubes on neutral compounds. The distance between the layers of MWCNTs, surface area, and available adsorption sites, etc. all can impact the adsorption of ionizable compounds on CNTs[5]. The functional groups also affect the adsorption through of the formation of H-bond and the alteration of CNT hydrophilicity [47]. A previous study indicated that the oxygen content of carbon nanotubes has a strong impact on the adsorption of ionizable compounds. In the study, the single-concentration point adsorption coefficient (K_d) is used to indicate the adsorption efficiency. The results showed that the K_d value decreased with increasing oxygen contents[48] is the authors attribute the results to that the oxidized carbon nanotubes are more hydrophilic so that the water molecules are adsorbed on carbon nanotubes surface to block ionizable compounds attachment [49].

Effect of solution chemistry on the adsorption of ionizable compounds

For ionizable compounds, the variation of pH can result in a change in chemical speciation, so that their adsorption is more complex. Increasing pH leads to increase solubility, ionization, and hydrophilicity. A study focusing on the adsorption of ionizable compounds on carbon nanotubes found that the equilibrium concentration of a solute on the surface of an adsorbent (q_e) decreased with increasing pH and concluded that the increasing pH is attributed to the competition between natural organic matters and OH^- on the same adsorption site [50]. The pH can also affect the electrostatic force. If the point of zero charge (pH_{pzc}) of the CNTs is higher than solution pH, high pH may lead to greater adsorption due to the electrostatic attraction. When pH is larger than pK_a of ionizable compounds and pH_{pzc} of carbon nanotubes, it can result in low adsorption because both adsorbate and adsorbent are negatively charged and there may be electrostatic repulsion [6, 51]. However, the anion appears to have an appreciable affinity for carbon nanotubes even at the strongly alkaline condition. When ionizable compounds dissociated into organoanions, the adsorption may also involve the force mentioned above, and the increased water solubility makes it easier to be attached on CNTs. The study revealed that the anion adsorption on carbon nanotubes is not only affected by the electrostatic force and hydrophobicity [52]. A particularly strong intermolecular force, the negative charge-assisted H-bond was identified as a key contributor for the adsorption of ionizable compounds on CNTs. [6]. Serval researchers investigated the adsorption of ionizable compounds on different types of carbon nanotubes. They used benzoic acid (BA), phthalic acid (PA) and 2,6-dichloro-4-

nitrophenol (DCNP) as model adsorbates. The results showed that PA^{2-} adsorbed strongly than BA^- even though PA^{2-} is more hydrophilic, and they assumed that the adsorption of ionizable compounds is not simply related with hydrophilicity, the negative charge-assisted H-bond is also an important factor. They measured the change of pH value and make stoichiometry of hydroxide release and pH as a function of organic acid adsorption on carbon nanotubes. They found that the initial stoichiometry of phthalic acid is higher than other adsorbates. This result verifies the assumption of negatively charge-assisted H-bond because PA- would react with water molecules and release the hydroxide before forming negative charge-assisted H-bond with CNTs [6]. Another study confirmed that carboxylic anion led to the split of water during the adsorption process, resulting in hydroxide ion release. This reaction drives the formation of an especially strong H-bond on the surface to offset the influence of electrostatic repulsion [52].

If ionizable compounds are adsorbed on carbon nanotubes under acidic condition, their adsorption is governed by relatively weaker forces such as van der Waals force, hydrogen bonding, and solvophobic effects. For neutral molecules, the adsorption is generally positively associated with the octanol-water partition coefficient (Kow). When pH increases beyond the pKa values of weak acids, dissolved organic acid convert to anionic forms that are more hydrophilic and it is possible to begin to form charge assisted bonding with carbon nanotubes.

Many artificial products are used in a wide variety of industries and these compounds and their affiliated product are continually introduced into the environment.

13

Many of them are ionizable compounds such as pesticides, antibiotics, and endocrine-disrupting chemicals. They are not stable and will dissociate in solutions. Due to their variable structures, the adsorption of ionizable compounds is more complex than neutral compounds. And ionizable compounds usually have higher water solubility disperse better in water, and tend to transfer into the natural environment [7, 53]. Thus, investigation on the adsorption of ionizable compounds is important and significant.

Environmental impacts of carbon nanotubes

Many different mechanisms may simultaneously contribute to the adsorption of ionizable compounds on carbon nanotubes. Each mechanism may be affected differently by the different environmental condition. The adsorption efficiency on carbon nanotubes is a result of net effects of various mechanisms. Previous studies suggested that carbon nanotubes are a better adsorbent to remove organic pollutants from water than activated carbons. Consequently, further investigation of the interaction between ionizable organic compounds and carbon nanotubes needs to be conducted.

CHAPTER II

MATERIALS AND METHODS

Carbon nanotubes

Carbon nanotubes (CNTs), which are allotropes of carbon with a cylindrical nanostructure, have unique structure. Due to their very large specific area, CNTs show a great adsorption capacity and affinity for pollutants.

Characterization of Carbon nanotubes

Three types of carbon nanotubes were investigated in this study: graphitized multi-walled carbon nanotubes (G-CNTs), OH functionalized multi-walled carbon nanotubes (OH-CNTs), COOH functionalized multi-walled carbon nanotubes (COOH-CNTs). All the CNTs were bought from US Research Nanomaterials, Inc (Houston, TX). According to the vendor, they were all manufactured using the chemical vapor deposition (CVD) method, which is widely used in industry to produce high-quality CNTs [54].

All CNTs used in this study had higher than 99.9% purity and similar sizes. Their outside diameter was in the range of 10 nm to 20nm and the inside diameter was from 5 nm to 10 nm. Transmission electron microscope (TEM) images showed that all CNTs were about 50 um long. The content of ash is lower than 0.1 wt% based on the thermogravimetric analysis. Detailed physiochemical properties of these three CNTs are summarized in **Table 1**.

Table 1. Physiochemical Properties of three CNTs

Compounds	G-CNTs	COOH-CNTs	OH-CNTs
Purity	>99.9 wt%	> 99.9 wt%	> 99.9 wt%
Outside diameter	10-20 nm	10-20 nm	10-20 nm
Inside diameter	5-10 nm	5-10 nm	5-10 nm
Length	10-30 um	10-30 um	10-30 um
SSA	$> 100 \ m^2/g$	$> 100 \ m^2/g$	$> 100 \ m^2/g$
Color	Black	Black	Black
Ash content	< 0.1 wt%	< 0.1 wt%	< 0.1 wt%
True density	$\sim 2.1 \ g/cm^3$	$\sim 2.1 \ g/cm^3$	$\sim 2.1 \ g/cm^3$
Functional group density	N/A	1.00wt%	2.48wt%
Manufacturing method	CVD	CVD	CVD

[*]: All selected nanomaterials properties are extracted from the US Research Nanomaterials' website (https://www.us-nano.com)

Other chemicals

Benzoic acid was purchased from Fisher scientific (Houston, TX). 3-amino-2-naphthoic acid was bought from CHEM-IMPEX INT'L INC (Wood Dale, IL). The 3-methoxy-2-naphthoic acid was obtained from TCI (Portland, OR). 2-naphthoic acid and 3-hydroxy-2-naphthoic acid were obtained from Alfa Aesar (Tewksbury, MA). The

molecular structures of these molecules, as well as their octanol-water partitioning coefficient (log Kow) and acid dissociation constant (pKa), are summarized in **Table 2**.

Table 2. Molecular structures and chemical parameters of the organic acids

Compounds	Structure	Log Kow	pKa	Henry constant	Vapor pressure
BA		1.87	4.19	1.08E-007	7.00E-04
2-NA		3.28	4.16	1.06E-008	6.63E-06
3-M-2-NA		2.79	N/A	6.26E-010	5.8E-006
3-H-2-NA		3.05	2.79	1.06E-008	4.88E-006
3-A-2-NA		2.54	5.02	3.74E-012	2.01E-007
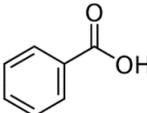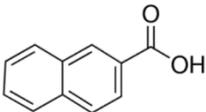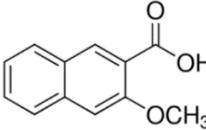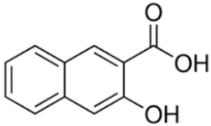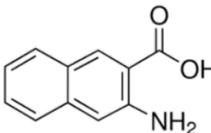
[*]: All value of Henry constant in this table is measured by bond method with the unit atm-m3/mole. All value of vapor pressure is with unit mm Hg. The names of compounds are presented by abbreviation based on nomenclature.

Experiments

Experimental setup

Batch experiments were conducted for the adsorption of organic acids on three different MWCNTs (G-CNTs, OH-CNTs, and COOH-CNTs) at different pH. For benzoic acid, 1000 mg benzoic acid solid was weighted and dissolved into 1000 mL deionized (DI) water. Solutions of benzoic acid at other concentrations (0.5-500 ppm) were obtained by serial dilution. The solution pH was then adjusted to around 2.0 and 7.0 with 0.1 N HCl or NaOH. The precise value was measured with a pH meter and recorded. 5 mg of CNTs were weighted and added into 20 mL brown vials and mixed with 10 mL solutions containing with 0.5 ppm and 5 ppm benzoic acid. 10 mg CNTs were mixed with 10 mL of 50 ppm and 200 ppm of benzoic acid solution. And 15 mg CNTs were mixed with 10 mL of 500 ppm benzoic acid in the same 20 mL brown vials. And the mixtures were then sonicated for 8 hours in a bath sonicator (EMERSON, Houston, TX). Afterward, the mixtures were placed on a shaker table with 120 rpm for 7 days at ambient temperature ($23^{o}C$). The mixtures were then centrifuged at 3000 rpm for 20 mins and the pH in the supernatant was measured again with a pH meter. The concentration of benzoic acid and benzoate was analyzed with a Perkin Elmer UV-*vis.* spectrometer at the wavelength from 200 nm to 800 nm.

The adsorption of naphthoic acids was similarly conducted. However, due to the low solubility of these acids, the concentrations used for the measurement of adsorption isotherms on CNTs fell in a narrower range. Specifically, 50 mg of 2-naphthoic acid and naphthoic acids will additional functional groups such as 3-methoxy-2-naphthoic acid, 3-

amino-naphthoic acid, and 3-hydroxy-2-naphthoic acid, were weighted and dissolved in 1000 mL DI water. Six concentrations of naphthoic acid were obtained through serial dilution, ranging from 0.5 to 50 ppm, (0.5 ppm, 5 ppm, 10 ppm, 20 ppm, 40 ppm and 50 ppm). The pH of the solutions was adjusted to 7.0. 5 mg of CNTs were weighted and mixed 10 mL of 0.5 ppm, 5 ppm and 10 ppm naphthoic acids in 20 mL brown vials. 10 mg CNTs were added to vails containing higher concentrations of naphthoic acids (20 ppm, 40 ppm, and 50 ppm). The mixtures were similarly bath sonicated for 8 hours and then put on a shaker table at room temperature at 120 rpm for seven days to allow the system to reach equilibrium. Afterward, the mixtures were centrifuged at 3000 rpm and the concentrations of these acids in the supernatant was measured with an UV-*vis* spectrometer at the wavelength from 200 to 800 nm.

Mathematical fitting of the adsorption isotherms

For every adsorption experiment, adsorbents adsorbed on carbon nanotubes were plotted with the solution concentration and figure isotherm curve, which describe the equilibrium relationship, were prepared by Excel. And the well-fitting isotherm model needs to be figured out to predicting the equilibrium distribution.

Two broadly used mathematical models: Langmuir model and Freundlich model were applied to fit the adsorption isotherms of these acids at different pH values. The Langmuir equation is shown below:

$$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e}$$

where: Ce is the equilibrium concentration of adsorbate in solution; q_e (mg/g) is the concentration of adsorbates on the solid at equilibrium; Q_{max} (mg/g) is the maximum

concentration on the solid at complete monolayer coverage; K_L (L/mg) is a constant that relates to the heat of adsorption.

The Langmuir model assumes:

1. Monolayer coverage,

2. All adsorption sites are equally probable,

3. Equilibrium model,

4. A second order reaction.

The Freundlich model is the following form

$$q_e = K_F C_e^{1/n}$$

where: K_F is an indicator of adsorption capacity. The higher the maximum capacity, the higher the K_f. $1/n$ is a measure of the intensity of adsorption. Higher the $1/n$ value, more favorable is the adsorption.

The Freundlich Model can describe sorption on heterogenous surface and multilayer sorption.

CHAPTER III

RESULTS AND DISCUSSION

Benzoic acid experiments

The adsorption isotherms of benzoic acid on multi-walled carbon nanotubes with different functional groups (G-CNTs, COOH-CNTs, and OH-CNTs) are shown in **Figure 1**. The adsorption was conducted at both pH=2.0 and pH=7.0. Dotted lines in **Figure 1** represent Freundlich model fitting. At pH 2.0, the benzoic acid is predominantly in the protonated form. At pH 7.0, however, the benzoic acid is primarily in the deprotonated form.
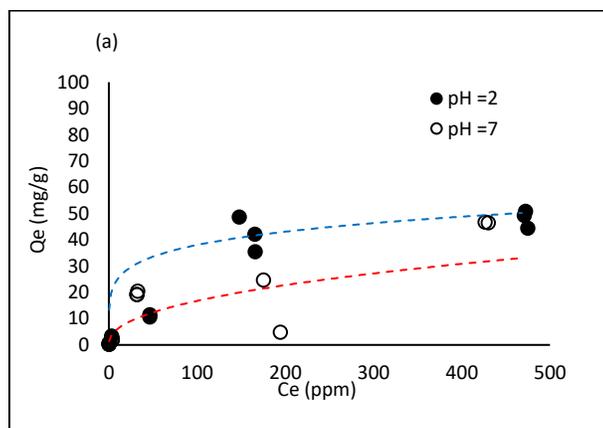
Figure 1. Isotherms of benzoic acid adsorbed on CNTs. (a) G-CNTs, (b) COOH-VNTs and (c) OH-CNTs at pH 2.0 and 7.0
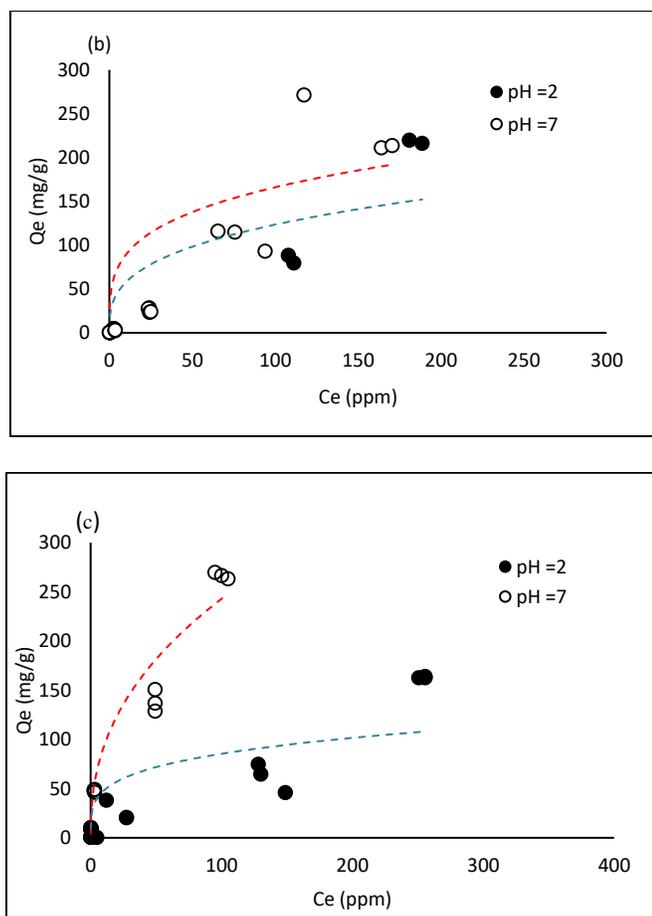
Figure 1. Continued

Effects of surface functionalization on adsorption

As expected, surface functioning played a significant role in the adsorption of benzoic acid at pH 2.0, with the –COOH functionalized G-CNTs displayed the greatest adsorption, followed by –OH functionalized CNTs and then G-CNTs. Due to the benzene rings in both the adsorbent and adsorbate, π-π interactions contribute to the adsorption of benzoic acid to G-CNTs [55], in addition to the hydrophobic force [5]. For

G-CNTs with functional groups, hydrogen bonding between the –COOH functional group on benzoic acid and the O-containing functional groups on G-CNTs surface [39]. The stronger adsorption of benzoic acid on COOH-CNTs is attributed to the formation of a dimer, **Figure 2**. Hydrogen bonding can be formed between the oxygen atom and hydrogen atom due to their different electronegativity. Two hydrogen bonding can be formed between the carboxyl functional groups, therefore, benzoic acid could form a double hydrogen-bonded dimer with the carboxyl functional group on G-CNT surface [56, 57]. However, only hydrogen bond can be formed between benzoic acid and OH-GNTs.
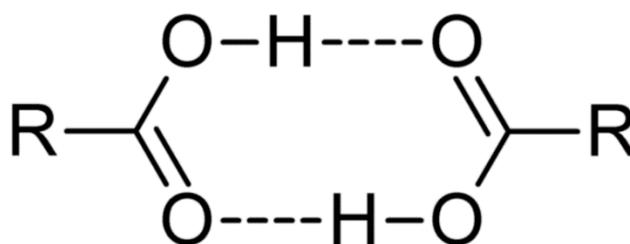
Figure 2. Chemical structure of dimer. The dimer is formed between two –COOH functional groups. Reprinted from https://en.wikipedia.org/wiki/Dimer_(chemistry).

Effects of pH on adsorption

Table 3. Point of zero charge of CNTs used in the study

Types of carbon nanotubes	G-CNTs	COOH-CNTs	OH-CNTs
Point of zero charge	2.1	10.8	10.3

At pH 2.0, benzoic acid is predominantly in the protonated form. While at pH 7.0, most benzoic acids are deprotonated as benzoate. Benzoic acid is more adsorptive on G-CNTs at pH 2.0 than at pH 7.0. The result is consistent with the general agreement that the hydrophobic force is an important intermolecular force for the adsorption of organic compounds on carbon nanotubes [5]. Interestingly, the benzoic acid at pH 7.0 or the benzoate displayed greater adsorption on the functionalized CNTs than at pH 2.0. The results suggest that other intermolecular forces in addition to the hydrophobic force play a significant role in the adsorption of benzoate on functionalized CNTs. To gain further insights, the point of zero charge of three CNTs was measured and the results are shown in **Table 3**. According to the measured point of zero charges for these CNTs, G-CNTs would be negatively charged while the other two functionalized CNTs would be positively charged at pH 7.0. Because benzoate carries a negative charge, electrostatic repulsion would further inhibit its adsorption on G-CNTs at pH 7.0 in addition to the reduced hydrophobic forces, while electrostatic attraction would enhance the adsorption of benzoate on the two functionalized CNTs [43]. Further, charge-assisted hydrogen bonding ((-)CAHB) has been suggested as an exceptionally strong hydrogen bond which

offsets the decrease of hydrophobic forces between benzoate and CNT surfaces due to the reduced hydrophobicity of benzoate. The formation of (-)CAHB requires proton exchange with water molecules so that a strong hydrogen bond between the oxygen on the carboxyl functional group on benzoate and the oxygen on the CNT surface can be formed as $O^-...H^+...O^-$. A direct consequence of the water molecule splitting is the release of hydroxide ions (OH^-) during the adsorption process [6, 52]. We measured the hydroxide ion release during the adsorption of benzoate on all CNTs. The release of hydroxide ion from G-CNTs was insignificant, however, much greater hydroxide ions were released from the COOH-CNTs and OH-CNTs, **Figure 3**, confirming the occurrence of the (-)CAHB between benzoates and the O-containing functional groups on CNTs.
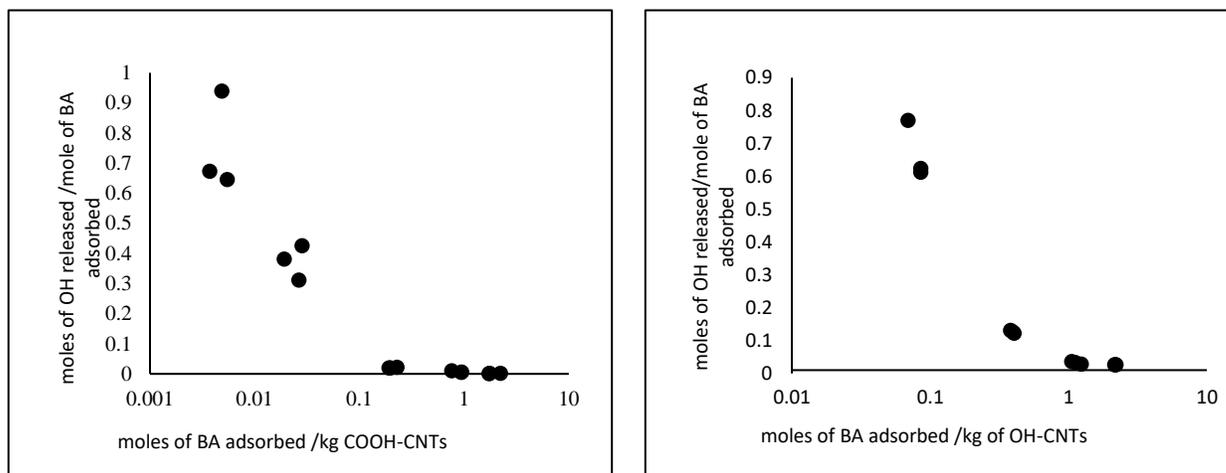
Figure 3. The stoichiometry of hydroxides release as a function of sorption of benzoic acid by CNTs at pH7. The hydroxide release from G-CNTs was close to zero and is not shown here.

25

Naphthoic acid experiments

The isotherms of each compound on two different CNTs are prepared in **Figure 4**. Each graph shows the adsorption condition of one compound on different CNTs so that comparisons among adsorbate on different CNTs can be better visualized. All isotherms are highly nonlinear.
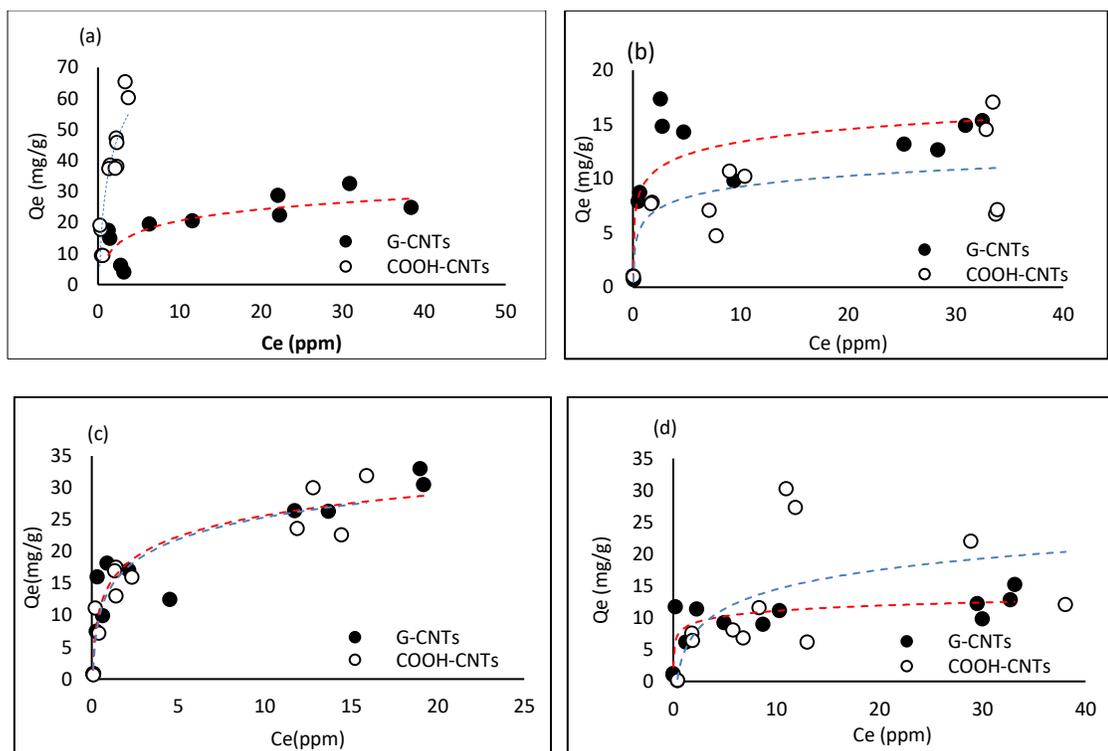
Figure 4. Comparison of sorption isotherm of given naphthoic acid on two CNTs at pH7. Dash line is the isotherm fitted by Excel. Graphitized CNTs and carboxylate CNTs are represented by G-CNTs and COOH-CNTs. (a)Isotherm of 2-naphthoic acid. (b)Isotherm of 3-hydroxy-2-Naphthoic Acid. (c)Isotherm of 3-Amino-2-Naphthoic Acid. (d)Isotherm of 3-Methoxy-2-Naphthoic acid.

The adsorption of all four compounds was conducted at pH 7.0, at which these compounds are mostly in the dissociated form. Based on our results on the point of zero charge for G-CNTs, G-CNTs was negatively charged at this pH [43], therefore, electrostatic forces discourage the adsorption of these compounds on G-CNTs. Attractive forces must overcome the repulsive forces to make the adsorption possible. Hydrophobic force is one of the primary attractive forces contributing to the adsorption of organic compounds on CNTs [26].

With the variety of CNTs types, the **Figure 4** clearly indicates that in solution with pH 7, adsorption efficiency of 2-naphthoic acid and 3-methoxy-2-naphthoic acid are better adsorbed on COOH-CNTs than on G-CNTs. We assume this result is caused by charge-assisted hydrogen bonding. Before forming the charge-assisted H-bond, the 2-naphthoic acid base is intended to react with water molecules in solution, combine with proton dissociated from water molecules and then attach on carbon nanotubes surface through negative charge-assisted H-bond [52]. The specific reactions are written as follows

$$NA^- + H_2O + COO^- - CNTS = OH^- + NA^- \cdots H^+ \cdots COO^- - CNTs \qquad \text{eq (1)}$$
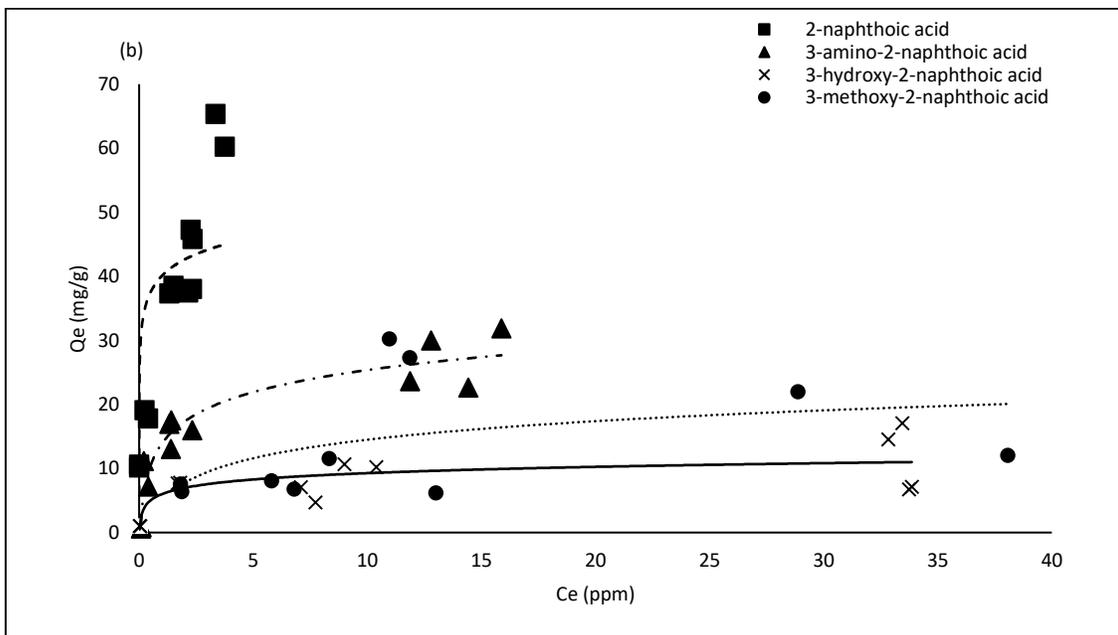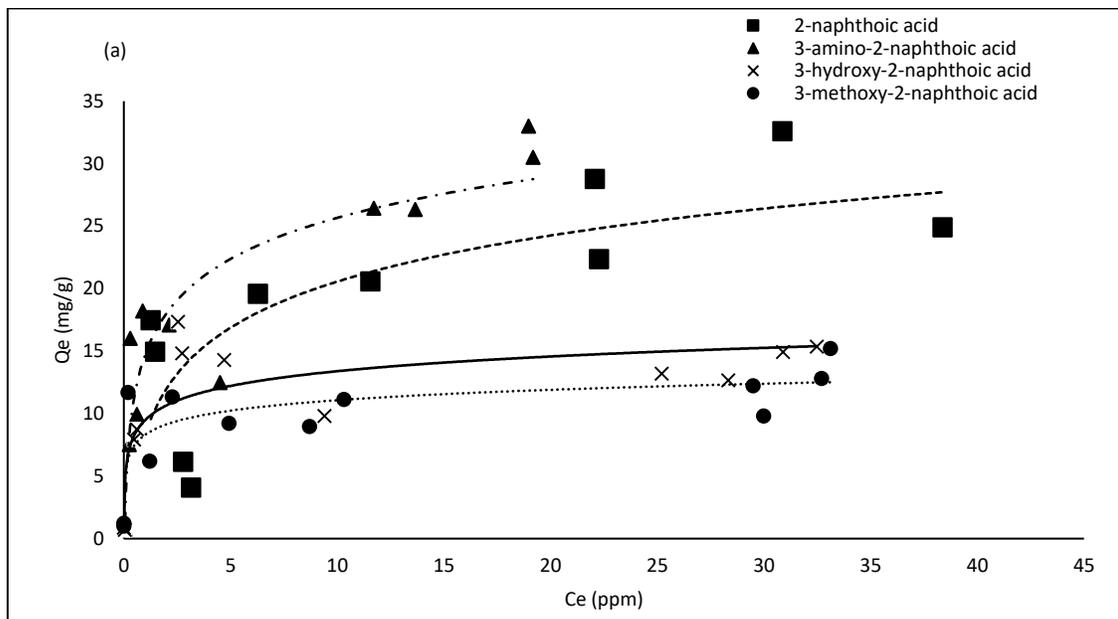
Figure 5. Comparison of sorption isotherm of given four types of naphthoic acid on CNTs at pH7. (a) Isotherm of four types naphthoic acid on G-CNTs. (b) Isotherm of four types naphthoic acid on COOH-CNTs.

Table 4. Parameter of adsorption model to naphthoic acid on G-CNTs

Compounds	Langmuir			Freundlich		
	Q_{max}	K	R^2	1/n	K_f	R^2
2-naphthoic acid	33.8983	0.1229	0.7829	0.9998	0.9993	N/A
3-methoxy-2-naphthoic acid	12.6903	0.9426	0.9501	0.2589	5.9498	0.7884
3-amino-2-naphthoic acid	33.3333	0.4392	0.9348	0.5177	8.6756	0.7231
3-hydroxy-2-naphthoic acid	14.3472	1.4196	0.9806	0.3506	5.9020	0.7520

Table 5. Parameter of adsorption model to naphthoic acid on COOH-CNTs

Compounds	Langmuir			Freundlich		
	Q_{max}	K	R^2	1/n	K_f	R^2
2-naphthoic acid	60.6061	1.7010	0.8512	0.1485	36.433	0.8089
3-methoxy-2-naphthoic acid	15.4083	0.3143	0.6623	1.0249	1.0394	0.7234
3-amino-2-naphthoic acid	30.6749	0.5086	0.9323	0.5706	8.1395	0.7258
3-hydroxy-2-naphthoic acid	9.8619	0.7776	0.7490	0.3244	3.8833	0.8003

The adsorption of these four compounds on G-CNTs generally followed the order 2-Naphthoic acid＞3-Amino-2-Naphthoic acid＞3-Hydroxy-2-Naphthoic acid＞3-Methoxy-2-Naphthoic acid. The order is partly consistent with the octanol water partitioning coefficient of these compounds, except the adsorption of 3-Amino-2-Naphthoic Acid which displayed the almost highest adsorption but is the least hydrophobic. If only partition coefficient is considered, its adsorption to G-CNTs should be smallest. In **Figure 5**, interestingly, 3-Amino-2-Naphthoic acid displayed the second highest adsorption capacity while it has the lowest hydrophobicity among the tested compounds. This result indicates that other forces contributed to the adsorption of 3-amino-2-naphthoic acid in addition to the hydrophobic force. We attribute the stronger adsorption of 3-Amino-2-Naphthoic acid to their capability to form intermolecular bonds between the adsorbate molecules. Of the molecule of 3-Amino-2-Naphthoic acid possesses two different functional group on benzene ring: amino functional group and carboxyl group. The amino functional group is an electron acceptor [58] and the carboxyl group an electron donor [59]. It is possible that the intermolecular interactions between the adsorbate molecules have resulted in higher adsorption of this otherwise more hydrophilic compounds on G-CNTs. The amino functional group and carboxyl group are likely reacted with each other and two 3-amino-2-Naphthoic acids can be connected with each other based on this mechanism and it has larger adsorption energy because of more benzene rings [37, 60]. Carboxyl group of an amino acid bind the

amino group of another amino acid forming a peptide bond with the loss of one molecule

of water [61]. The specific chemical reaction equation is shown in eq (2)

$$RCOOH + R'NH_2 \rightarrow RC(O)NHR' + H_2O \qquad\qquad\qquad \text{eq (2)}$$
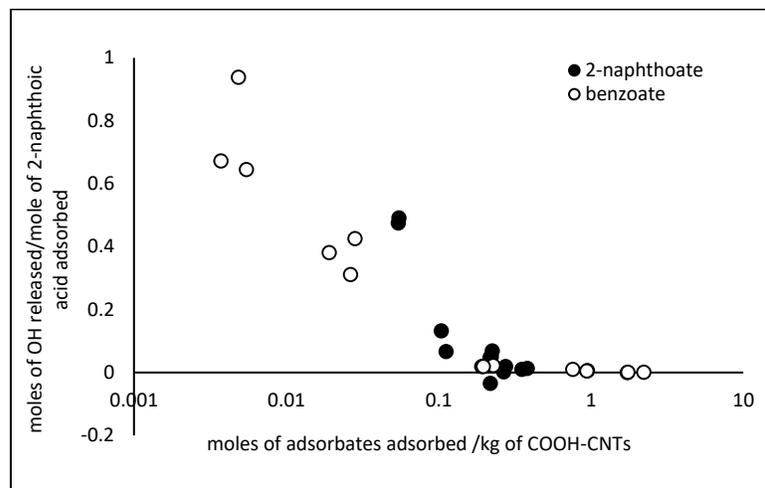
Figure 6. The stoichiometry of hydroxide ion release as a function of sorption of benzoic acid and 2-naphthoic acid by COOH-CNTs at pH7. Benzoic acid is white dot and 2-naphthoic acid is black dot.

The adsorption isotherms of these compounds on COOH-CNTs are also shown in

Figure 5 and it followed the order that 2-Naphthoic acid＞3-Amino-2-Naphthoic acid＞

3-Methoxy-2-Naphthoic acid＞3-Hydroxy-2-Naphthoic acid. Again, the adsorption

capacity of these compounds followed a different direction of the hydrophobicity of

these compounds. It is not exactly consistent with the octanol water partitioning

coefficient of these compounds but 2-naphthoic acid still is adsorbed best on COOH-

CNTs. This result indicates that hydrophobicity is one of the main mechanisms that

31

impacts on adsorption of these ionizable compounds on COOH-CNTs at pH 7, whereas there are other mechanism effects on this adsorption. At pH 7.0, all four compounds are expected to be dissociated and therefore carry a negative charge, while COOH-CNTs at pH 7.0 carry a positive charge based on the value of point of zero charge of COOH-CNTs (point of zero charge is around 10.3) [43]. Therefore, electrostatic attraction contributed to the adsorption of these compounds to COOH-CNTs. All three functional group next to the carboxyl functional group are electron donating substituents which render the benzene ring more electron-rich [62, 63] and consequently make coulombic interactions of these compounds higher than 2-naphthoic acid compounds even though 2-naphthoic acid that demonstrated the largest adsorption capacity on COOH-CNTs. In addition to the electrostatic forces, charge-assisted hydrogen bonding may also contribute to the adsorption of these compounds to COOH-CNTs like what was observed for benzoic acid. To determine the importance of this particularly strong hydrogen bonding on the adsorption of these compounds, the hydroxide release from proton exchange with water molecules was estimated. Surprisingly, the release of hydroxide ion from the adsorption acid was negligible for all three compounds with additional functional groups except for 2-naphthoic acid. The final pH after adsorption was consistently more acidic than the solution in the beginning for these three compounds, except for 2-naphthoic acid which led to the increase of pH after adsorption, indicating that the charge-assisted hydrogen bonding was not a strong contributing force for the adsorption of these molecules on COOH-CNTs except for 2-naphthoic acid. To determine the significance of charge-assisted hydrogen bond for the adsorption of 2-

32

naphthoic acid, the hydroxide ion release from water proton exchange was estimated in

Figure 6. The two curves almost overlap, indicating that the extent of hydroxide ion

release from the adsorption of these two carboxylates onto COOH-CNTs was similar.

And the result demonstrated that increasing of molecule size by one benzene ring did not

impact on the formation of this particularly strong hydrogen bonding. Detailed

mechanisms require further investigation, but the results highlight the importance of

molecular size and structure on the adsorption of aromatic carboxylates on carbon

nanotubes.

CHAPTER IV

CONCLUSION AND RECOMMENDATION

Conclusion

The adsorption of five ionizable compounds including Benzoic acid, 2-Naphthoic acid, 3-Hydroxy-2-Naphthoic acid, 3-Methoxy-2-Naphthoic acid, and 3-Amino-2-Naphthoic acid onto G-CNTs and functionalized G-CNTs were investigated. BA adsorption on CNTs is impacted by the hydrophobicity of these molecules, electrostatic forces and a particularly strong negative- charged assisted hydrogen bonding between carboxylates and functionalized CNTs at pH higher than the pK_a of these compounds. To determine whether molecular size of carboxylates affects their interactions with CNTs through the charged assisted hydrogen bonding, the release of hydroxide ions from the adsorption of benzoic acid and naphthoic acid on COOH functionalized CNTs was compared. The results indicated that increasing the adsorbate molecule size by one ring did not affect the formation of charge-assisted hydrogen bonding. However, the molecular structure was shown to strongly affect the adsorption capacity and the formation of this charged facilitated intermolecular forces. In summary, the study showed that strong intermolecular forces can be formed between ionized aromatic carboxylates and functionalized CNTs and the adsorption is strongly affected by the molecular structure of adsorbates.

Recommendations

The current study focused mostly on the adsorption efficiency of smaller carboxylates on different types of CNTs by evaluating the release of hydroxide ion and the formation of negative-charged assisted H-bond. The study can be extended in several different directions in future studies to gain more mechanistic insights into the adsorption processes. Several possible investigations are recommended for future studies including:

1. It could be valuable to further investigate the effects of molecular size on negative-charged H-bond, because of this research only examined two types of acid. Bigger molecules with similar structures should be evaluated so that the influence of molecular size on forming negative-charged H-bond can be further assessed.

2. To further study the adsorption mechanism of ionizable compounds on CNTs and implications for the removal of emerging compounds through adsorption, investigation on the energy of H-bonding forming will be valuable as well as its significance to other ionizable compounds with more complicated structures will be valuable.

3. The impact of solution chemistry on the adsorption of ionizable compounds should be determined, which will provide more realistic information on the fate and transport of ionizable compounds in the natural environment.

REFERENCES

1.   Ebbesen, T., et al., *Electrical conductivity of individual carbon nanotubes.* Nature, 1996. **382**(6586): p. 54.

2.   Baughman, R.H., A.A. Zakhidov, and W.A. De Heer, *Carbon nanotubes--the route toward applications.* science, 2002. **297**(5582): p. 787-792.

3.   Li, Y.-H., et al., *Lead adsorption on carbon nanotubes.* Chemical Physics Letters, 2002. **357**(3-4): p. 263-266.

4.   Gupta, V.K., et al., *Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review.* Advances in Colloid and Interface Science, 2013. **193**: p. 24-34.

5.   Pan, B. and B.S. Xing, *Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes.* Environmental Science & Technology, 2008. **42**(24): p. 9005-9013.

6.   Li, X., et al., *New insight into adsorption mechanism of ionizable compounds on carbon nanotubes.* Environmental science & technology, 2013. **47**(15): p. 8334-8341.

7.   Sheng, G., et al., *Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes.* Journal of hazardous materials, 2010. **178**(1-3): p. 505-516.

8.   Dresselhaus, M.S., G. Dresselhaus, and P.C. Eklund, *Science of fullerenes and carbon nanotubes: their properties and applications*. 1996: Elsevier.

9.   Odom, T.W., et al., *Atomic structure and electronic properties of single-walled carbon nanotubes.* Nature, 1998. **391**(6662): p. 62.

10.   Fan, Z., et al., *Electromagnetic and microwave absorbing properties of multi-walled carbon nanotubes/polymer composites.* Materials Science and Engineering: B, 2006. **132**(1-2): p. 85-89.

11.   Che, G., et al., *Carbon nanotubule membranes for electrochemical energy storage and production.* Nature, 1998. **393**(6683): p. 346.

12.   Yu, M.-F., et al., *Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load.* Science, 2000. **287**(5453): p. 637-640.

13.   Dai, H., *Carbon nanotubes: synthesis, integration, and properties.* Accounts of chemical research, 2002. **35**(12): p. 1035-1044.

14.   Cassell, A.M., et al., *Large scale CVD synthesis of single-walled carbon nanotubes.* The Journal of Physical Chemistry B, 1999. **103**(31): p. 6484-6492.

15.   Ebbesen, T. and P. Ajayan, *Large-scale synthesis of carbon nanotubes.* Nature, 1992. **358**(6383): p. 220.

16.   Scott, C.D., et al., *Growth mechanisms for single-wall carbon nanotubes in a laser-ablation process.* Applied Physics A, 2001. **72**(5): p. 573-580.

17.   Sahoo, N.G., et al., *Polymer nanocomposites based on functionalized carbon nanotubes.* Progress in polymer science, 2010. **35**(7): p. 837-867.

18.   Yu, H., et al., *Growth of branch carbon nanotubes on carbon nanotubes as support.* Diamond and related materials, 2006. **15**(9): p. 1447-1451.

19.   Biro, L., et al., *Carbon nanotube Y junctions: growth and properties.* Diamond and related materials, 2004. **13**(2): p. 241-249.

20.   Smart, S., et al., *The biocompatibility of carbon nanotubes.* Carbon, 2006. **44**(6): p. 1034-1047.

21.   Zhao, J., et al., *Gas molecule adsorption in carbon nanotubes and nanotube bundles.* Nanotechnology, 2002. **13**(2): p. 195.

22.   Striolo, A., et al., *Water in carbon nanotubes: Adsorption isotherms and thermodynamic properties from molecular simulation.* The Journal of chemical physics, 2005. **122**(23): p. 234712.

23.   Karickhoff, S.W., D.S. Brown, and T.A. Scott, *Sorption of hydrophobic pollutants on natural sediments.* Water research, 1979. **13**(3): p. 241-248.

24.   Chen, W., L. Duan, and D. Zhu, *Adsorption of polar and nonpolar organic chemicals to carbon nanotubes.* Environmental science & technology, 2007. **41**(24): p. 8295-8300.

25.   Tan, I., A. Ahmad, and B. Hameed, *Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies.* Journal of hazardous materials, 2008. **154**(1-3): p. 337-346.

26.   Gotovac, S., et al., *Assembly structure control of single wall carbon nanotubes with liquid phase naphthalene adsorption.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2007. **300**(1-2): p. 117-121.

27.   Crespo, D. and R.T. Yang, *Adsorption of organic vapors on single-walled carbon nanotubes.* Industrial & engineering chemistry research, 2006. **45**(16): p. 5524-5530.

28.   Gotovac, S., et al., *Adsorption of polyaromatic hydrocarbons on single wall carbon nanotubes of different functionalities and diameters.* Journal of colloid and interface science, 2007. **314**(1): p. 18-24.

29.   Tournus, F. and J.-C. Charlier, *Ab initio study of benzene adsorption on carbon nanotubes.* Physical Review B, 2005. **71**(16): p. 165421.

30.   Hilding, J.M. and E.A. Grulke, *Heat of adsorption of butane on multiwalled carbon nanotubes.* The Journal of Physical Chemistry B, 2004. **108**(36): p. 13688-13695.

31.   Yaniv, Z., *Functionalized carbon nanotubes.* 2009, Google Patents.

32.   Lu, C., Y.-L. Chung, and K.-F. Chang, *Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes.* Journal of hazardous materials, 2006. **138**(2): p. 304-310.

33.   Liao, Q., J. Sun, and L. Gao, *The adsorption of resorcinol from water using multi-walled carbon nanotubes.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **312**(2-3): p. 160-165.

34.   Cho, H.-H., et al., *Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes.* Environmental science & technology, 2008. **42**(8): p. 2899-2905.

35.   Karajanagi, S.S., et al., *Structure and function of enzymes adsorbed onto single-walled carbon nanotubes.* Langmuir, 2004. **20**(26): p. 11594-11599.

36.   Vermisoglou, E., et al., *Sorption properties of modified single-walled carbon nanotubes.* Microporous and mesoporous materials, 2007. **99**(1-2): p. 98-105.

37.   Mao, Z. and S.B. Sinnott, *Separation of organic molecular mixtures in carbon nanotubes and bundles: molecular dynamics simulations.* The Journal of Physical Chemistry B, 2001. **105**(29): p. 6916-6924.

38.   Liu, C.-H., et al., *Structure dependent interaction between organic dyes and carbon nanotubes.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **313**: p. 9-12.

39.   Chen, W., et al., *Adsorption of hydroxyl-and amino-substituted aromatics to carbon nanotubes.* Environmental science & technology, 2008. **42**(18): p. 6862-6868.

40.   Peng, X., et al., *Adsorption of 1, 2-dichlorobenzene from water to carbon nanotubes.* Chemical physics letters, 2003. **376**(1-2): p. 154-158.

41.   Hyung, H. and J.-H. Kim, *Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters.* Environmental science & technology, 2008. **42**(12): p. 4416-4421.

42.   Wang, L., et al., *Effects of ionic strength and temperature on the aggregation and deposition of multi-walled carbon nanotubes.* Journal of Environmental Sciences, 2017. **51**: p. 248-255.

43.   Lin, D., et al., *The effect of ionic strength and pH on the stability of tannic acid-facilitated carbon nanotube suspensions.* Carbon, 2009. **47**(12): p. 2875-2882.

44.   Vaisman, L., H.D. Wagner, and G. Marom, *The role of surfactants in dispersion of carbon nanotubes.* Advances in colloid and interface science, 2006. **128**: p. 37-46.

45.   Hyung, H., et al., *Natural organic matter stabilizes carbon nanotubes in the aqueous phase.* Environmental science & technology, 2007. **41**(1): p. 179-184.

46.   Carrillo-Carrión, C., et al., *Surfactant-coated carbon nanotubes as pseudophases in liquid–liquid extraction.* Analyst, 2007. **132**(6): p. 551-559.

47.   Piao, L., et al., *Adsorption of L-phenylalanine on single-walled carbon nanotubes.* The Journal of Physical Chemistry C, 2008. **112**(8): p. 2857-2863.

48.   Li, X., et al., *Adsorption of ionizable organic contaminants on multi-walled carbon nanotubes with different oxygen contents.* Journal of hazardous materials, 2011. **186**(1): p. 407-415.

49.   Yang, Y., et al., *pH-dependence of pesticide adsorption by wheat-residue-derived black carbon.* Langmuir, 2004. **20**(16): p. 6736-6741.

50.   Lu, C. and F. Su, *Adsorption of natural organic matter by carbon nanotubes.* Separation and Purification Technology, 2007. **58**(1): p. 113-121.

51.   Ayranci, E. and O. Duman, *Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth.* Journal of hazardous materials, 2005. **124**(1-3): p. 125-132.

52. Ni, J., J.J. Pignatello, and B. Xing, *Adsorption of aromatic carboxylate ions to black carbon (biochar) is accompanied by proton exchange with water.* Environmental science & technology, 2011. **45**(21): p. 9240-9248.

53. Yang, K., et al., *Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes.* Environmental science & technology, 2008. **42**(21): p. 7931-7936.

54. Ambriz-Torres, J.M., et al., *Carbon nanotubes and carbon nanobeads synthesis by one-pot chemical vapor deposition method: morphology and crystallinity.* Materials Research Express, 2018.

55. Hunter, C.A., J. Singh, and J.M. Thornton, *π-π interactions: the geometry and energetics of phenylalanine-phenylalanine interactions in proteins.* Journal of molecular biology, 1991. **218**(4): p. 837-846.

56. Etter, M.C., *Hydrogen bonds as design elements in organic chemistry.* The Journal of Physical Chemistry, 1991. **95**(12): p. 4601-4610.

57. Etter, M.C., *Encoding and decoding hydrogen-bond patterns of organic compounds.* Accounts of Chemical Research, 1990. **23**(4): p. 120-126.

58. Pullman, B. and A. Pullman, *Electron-donor and-acceptor properties of biologically important purines, pyrimidines, pteridines, flavins, and aromatic amino acids.* Proceedings of the National Academy of Sciences, 1958. **44**(12): p. 1197-1202.

59.   Burkey, K.O. and E.L. Gross, *Effect of carboxyl group modification on redox properties and electron donation capability of spinach plastocyanin.* Biochemistry, 1981. **20**(19): p. 5495-5499.

60.   Wu, T., et al., *Adsorption characteristics of acrylonitrile, p-toluenesulfonic acid, 1-naphthalenesulfonic acid and methyl blue on graphene in aqueous solutions.* Chemical Engineering Journal, 2011. **173**(1): p. 144-149.

61.   Martin, R.B., *Free energies and equilibria of peptide bond hydrolysis and formation.* Biopolymers: Original Research on Biomolecules, 1998. **45**(5): p. 351-353.

62.   Zhang, L., et al., *Relating electron donor and carboxylic acid anchoring substitution effects in azo dyes to dye-sensitized solar cell performance.* ACS Sustainable Chemistry & Engineering, 2013. **1**(11): p. 1440-1452.

63.   Gao, B., L. Chen, and T. Chen, *Effect of electron-donating substituent groups on aromatic ring on photoluminescence properties of complexes of benzoic acid-functionalized polysulfone with Eu (III) ions.* Physical Chemistry Chemical Physics, 2015. **17**(38): p. 25322-25332.