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C_{60} Nanoparticles: Adsorption and Desorption of Organic Contaminants, and Transport in Soil

by

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ABSTRACT

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C₆₀ is a new form of carbon with unique properties due to its small size. Since it has been predicted that C₆₀ will be manufactured by tons, there is no doubt that it will ultimately find their way to the environment. Because of the insolubility of C₆₀ in water, one might expect that it would not enter groundwater in great quantities. However, “nC₆₀” (water-stable C₆₀ aggregates) can be formed in water by exchange of solvents, or simply by stirring, indicating that C₆₀ might be readily available in groundwater. Therefore it is necessary to investigate the transport of C₆₀ particles and their interactions with other environmental contaminants.

The adsorption and desorption of naphthalene and 1,2-dichlorobenzene, two common organic contaminants, with nC₆₀ in water was investigated and sorption hysteresis was observed. Naphthalene adsorption-desorption with activated carbon particles and soil organic carbon was also conducted. Similar sorption hysteresis was observed. Experimental data were fitted with different sorption models. The Dual-Equilibrium desorption model fits experimental data well. Each DED model fitting parameter has similar values for all three forms of carbon, indicating the possibility to
predict the carbonaceous nanomaterial-contaminant interactions from well known carbon materials.

The transport of nC₆₀ through a soil column was characterized by flow-through apparatus. It was observed in the transport study that nC₆₀ have limited mobility in the soil column at typical groundwater velocity, but they were more mobile at higher velocities. The effect of adsorbed nC₆₀ on naphthalene is similar to that of soil organic carbon. This study provides useful information for the environmental risk assessment of C₆₀ fullerene.
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CHAPTER 1
INTRODUCTION

Carbonaceous nanomaterials, such as single wall nanotubes and fullerenes, have attracted a great deal of attention due to their unique physical/chemical and mechanical properties. Researchers continue to find new applications of these materials in energy, medicine, space, information technology, industrial and environmental applications, to mention a few. For example, fullerenes are expected to be produced by tons in the near future (Colvin 2003), therefore it is of no doubt that those nanomaterials will ultimately enter the environment at measurable concentrations. While large scale production of these materials has begun, environmental scientists as well as the public have concerns about their environmental impacts (Borm 2002; Dagani 2003). It is necessary to investigate the fate and transport of these materials to determine possible adverse environmental impacts and to help establish guidelines for application and disposal of these materials.

Since \textit{C}_{60} is virtually insoluble in water (Ruoff, Tse et al. 1993), one might expect that this hydrophobic nanomaterial would not enter groundwater in great quantities. However, several methods have produced water-stable nC\textit{60} (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Deguchi, Alargova et al. 2001). More interestingly, it was discovered in this study that water-stable nC\textit{60} can also be formed simply by extensive stirring, without addition of any organic solvents (Cheng, Kan et al. 2004). These findings indicate that C\textit{60} might be mobile in groundwater. Recent studies have shown that this underivatized form of C\textit{60} (nC\textit{60}) causes oxidative damage to both fish
brain cells and cultured human cells (Oberdorster 2004; Sayes, Fortner et al. 2004). In addition, it has been reported that the existence of dissolved organic matter in groundwater could enhance the partition of neutral organic contaminants into water and thus enhance the transport of those compounds (Kan and Tomson 1990). It is unknown whether the release of C\textsubscript{60} and other nanosized carbonaceous nanomaterials into the environment will enhance the transport of organic contaminants and thereby spread contamination more quickly.

Many soils or sediments contain various forms of carbonaceous materials such as biogenic materials, humic substances, coals, kerogens, and black carbons (e.g., soot and char) (Allen-King, Grathwohl et al. 2002). The fate of hydrophobic organic pollutants is controlled largely by the carbonaceous matter in soil (Chiou, Peters et al. 1979; Karickhoff, Brown et al. 1979; Steinberg, Pignatello et al. 1987; Pignatello 1989; Pignatello and Xing 1996; Kan, Fu et al. 1998; Weber, Huang et al. 1998; Accardi-Dey and Gschwend 2002; Kleineidam, Schuth et al. 2002; Cornelissen and Gustafsson 2005). Black carbons are formed mostly through incomplete combustion of either plants or fossil fuels (Setton, Bernier et al. 2002). All of these carbon materials contain stacks of six-carbon aromatic rings. Instead of having six-carbon ring arranged in sheet, C\textsubscript{60} contains both six- and five-carbon rings, arranged in a spherical configuration. Kerogens, coals, and black carbons have been reported to have much higher affinity for hydrophobic organic contaminants than humic substances (McGroddy and Farrington 1995; Chiou and Kile 1998; Bucheli and Gustafsson 2000; Accardi-Dey and Gschwend 2002; Kleineidam, Schuth et al. 2002; Braida, Pignatello et al. 2003; Chun, Sheng et al. 2004; Nguyen, Sabbah et al. 2004; Zhu, Hyun et al. 2004; Cornelissen and Gustafsson 2005; James,
Sabatini et al. 2005). The existence of a small fraction of coal, kerogen, and/or black carbon in nature has been of great concern for transport and bioavailability of organic contaminants (Goldberg 1985; McGroddy, Farrington et al. 1996; Gustafsson, Haghseta et al. 1997; Bucheli and Gustafsson 2000; Ghosh, Zimmerman et al. 2003). Carbonaceous nanomaterials, such as C60 may have similarly important environmental impacts on organic contaminants.

Although sorption and desorption are important processes that control the fate and transport of both nanoparticles and environmental contaminants, few studies have addressed the adsorption-desorption of organic compounds with C60 in aqueous solutions (Ballesteros, Gallego et al. 2000; Mchedlov-Petrossyan, Klochkov et al. 2001). In this study, adsorption and desorption of naphthalene and 1,2-dichlorobenzene to C60 aggregates with different aggregation sizes ("C60 large aggregates", "C60 small aggregates", and "nC60") have been investigated and compared to that of activated carbon and soil organic carbon.

Adsorption hysteresis has been observed for organic compounds desorption from soil and sediments in many studies (Di Toro and Horzempa 1982; Pignatello and Huang 1991; Kan, Fu et al. 1994; Huang and Weber 1997; Huang, Yu et al. 1998; Kan, Fu et al. 1998; Weber, Huang et al. 1998; Xia and Pignatello 2001; Braida, Pignatello et al. 2003). It has also been observed for desorption of organic vapor molecules from C60 lattice (Rathousky, Starek et al. 1993; Rathousky and Zukal 2000). One objective of this paper is to test if hysteresis occurs when organic contaminants desorb from C60 particles in aqueous solutions.
Another focus of this work is to study the transport of “nC_{60}” in natural porous media. Previous work has been done to address the issue of C_{60} transport through glass beads, a model medium (Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004). In the natural aquatic environment, the transport of C_{60} may vary from that in model media due to the complicated conditions in natural soil, such as the medium heterogeneities, and the complex flow characteristics. This study investigates the transport of water-stable nC_{60} in natural porous media using a soil column.
CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

2.1 C₆₀

2.1.1 Introduction of C₆₀

Carbon is one of the most abundant element on the earth and the basis of all the life: protein, DNA, chromosomes, etc., are all made from combinations of carbon-containing molecules. Prior to 1984, diamond and graphite were considered to be the major forms of carbon. In 1984 Rohlfing, Cox and Kaldor (Rohlfing, Cox et al. 1984) published the first spectroscopic evidence for C₆₀ fullerene, the third form of carbon, using an apparatus designed by Professor Richard Smalley at Rice University (Dietz, Duncan et al. 1981). They found that the species had a maximum intensity at C₆₀ with C₇₀ at a little lower intensity. In 1985 Professor Smalley and other researchers published a paper in Nature describing the first model of C₆₀ (Kroto, Heath et al. 1985). They then named C₆₀ Buckminsterfullerene after R. Buckminster Fuller because of the similarity of the structure of C₆₀ to the geodesic structure widely credited to him. For this work, Kroto, Smalley and collaborator R. F. Curl were awarded the Nobel Prize in 1996.

Fullerenes are defined (Godly and Taylor 1997) as polyhedral closed cages made entirely of n three-coordinate carbon atoms and having 12 pentagonal and (n/2-10) hexagonal faces where n ≥ 20 (but uniquely, not 22). C₆₀, the most abundant fullerene, has twelve pentagons and twenty hexagons, which produces the near spherical and perfectly symmetrical structure (Figure 2.1). In a C₆₀ molecule all the pentagons are non-adjacent, and this structure with icosahedral symmetry is the most stable isomer. The lengths of
bonds in a pentagon of C\textsubscript{60} fullerene are ca. 1.45 Å, whereas those connecting two pentagons are ca. 1.40 Å (David, Ibberson et al. 1991; Yannoni, Bernier et al. 1991). And the cage-cage (centre) distances are 10.02 Å for C\textsubscript{60} fullerene.

Many instruments have been used to characterize C\textsubscript{60} and other fullerenes. Mass spectrometer is among the earliest methods which were used to locate the presence of C\textsubscript{60} and higher fullerenes. \(^{13}\)C NMR is the most widely used spectroscopic property of fullerenes, since \(^{13}\)C NMR spectrum gives a single line for C\textsubscript{60} (Taylor, Hare et al. 1990). UV/Vis spectroscopy is another powerful tool. UV/Vis spectrophotometer was used in this work to characterize C\textsubscript{60}. The UV spectrum for C\textsubscript{60} fullerene shows peaks at 213, 257, 336 and 407 nm, and the values vary slightly with the solvent used (Taylor 1999). For example, the first two peaks may not be determined for toluene because of the high intrinsic absorption of the aromatic chromophore in this spectral region. UV spectra can also be used to confirm the location of the addition for fullerenes. Other tools have also been used for the studies of the chemistry of fullerenes, for example, Fourier transform FTIR, High Pressure Liquid Chromatography (HPLC) (Hare, Kroto et al. 1991), single crystal X-ray crystallography (Hawkins, Lewis et al. 1990), and FT Raman spectroscopy (Bethune, Meijer et al. 1990; Dennis, Hare et al. 1991).

\subsection*{2.1.2 The formation of nC\textsubscript{60} in water}

Since the discovery of C\textsubscript{60} in 1985 (Kroto, Heath et al. 1985), many studies and patents have appeared suggesting its applications in various areas (Haddon, Hebard et al. 1991; Kelty, Chen et al. 1991; Ungurenasu and Airinei 2000; Innocenzi and Brusatin 2001; Ishitsuka, Niino et al. 2004). It has been reported that tons of fullerenes are
expected to be produced in the next year or two (Colvin 2003; Fortner, Lyon et al. 2005), therefore, there is no doubt that those nanomaterials will ultimately find their way in the environment at measurable concentrations. Because $C_{60}$ is essentially insoluble in water and other polar solvents such as methanol, ethanol, acetone, and acetonitrile (Ruoff, Tse et al. 1993), one might expect that this hydrophobic nanomaterial would not enter groundwater or other aqueous environments in great quantities. Instead, it might deposit to the sediments and pose no significant impact to the environment.

However, in the last two decades various methods have been developed to solubilize or disperse $C_{60}$ and other fullerenes in water in order to find better use of $C_{60}$ in biology and medicine. Various forms of fullerene-containing solutions have been synthesized, for example, water-soluble fullerene derivatives (Sijbesma, Srdanov et al. 1993; Brettreich and Hirsch 1998; Sano, Oishi et al. 2000); inclusion complexes of $C_{60}$ with $\gamma$-cyclodextrin (Andersson, Nilsson et al. 1992); $C_{60}$-micellar solutions formed by addition of surfactants or liposome (Hungerbuehler, Guldi et al. 1993; Beeby, Eastoe et al. 1994; Bensasson, Bienvenue et al. 1994); a water-soluble polymer formed by addition of polyvinylpyrrolidone into $C_{60}$-water suspension (Yamakoshi, Yagami et al. 1994), to mention a few. These approaches probably have offered more options for the application of $C_{60}$ and other fullerene nanomaterials in the industries such as materials, electronics and optics, etc. However, it might not be desirable to put those synthesized water-soluble fullerene materials directly into biological or medical use, nor health effect study use, since the additives added to solubilize fullerenes might alter or at least affect the physical/chemical properties of the parent fullerene materials. Having realized this
disadvantage, many researchers developed different approaches in order to disperse C$_{60}$ in water without introducing any chemical additives.

To the author's knowledge, the following approaches have been developed to produce water-stable C$_{60}$ nanoparticles (referred to as “nC$_{60}$” in the following text):

a) “Solvents Exchange Method”: Alargova et al. prepared colloidal dispersion of C$_{60}$ in polar solvents by first dissolving C$_{60}$ in non-polar solvents, such as toluene, followed by addition of a small volume (5-50 µl) of this solution into a larger volume (5-20 ml) of a polar solvent (acetonitrile, ethanol, or acetone) and shaking for homogenization (Alargova,Deguchi et al. 2001). The color changed from purple in the original C$_{60}$/non-polar solvents solution, to orange-brown in the final C$_{60}$/polar solvents colloidal dispersion.

Furthermore, Scrivens et al. (Scrivens, Tour et al. 1994) devised a method to produce suspensions of nano C$_{60}$ particles in water in order to study the uptake and toxicity of C$_{60}$. They started the procedure by making a saturated solution of C$_{60}$ in benzene (1.5 mg/ml, 100 µl), followed by adding this C$_{60}$/benzene solution into 10 ml tetrahydrofuran (THF). The resulting light purple-colored solution was added dropwise to 100 ml rapidly stirred acetone. Then 150 ml water was added to this predominantly acetone solution. After the addition of the first 50 ml of water, C$_{60}$ began to precipitate as a fine mustard yellow suspension. Upon complete addition of the water, the organic solvents in the suspension were removed by distillation to a final volume of 100 ml. The concentration of nC$_{60}$ in the final suspension was ~ 0.0015 mg/ml, or 1.5 mg/l.

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b) "Sonication Method": Andrievsky et al. first reported the production of nC₆₀ using this method in 1995 (Andrievsky, Kosevich et al. 1995). They first dissolved C₆₀ in toluene to a concentration of 0.2 mg/ml, added this C₆₀/toluene solution into deionized water, then this mixture was subjected to supersound under ambient conditions for a few hours until the evaporation of toluene was complete. The C₆₀/water suspension was then filtered through microfilters (pore size 0.22 μm). The final transparent suspension, containing only C₆₀ and water, showed a brownish-orange color. The concentration of nC₆₀ in the final suspension was about 0.005 mg/ml, or 5 mg/l.

c) "Redox Reaction Method": In 1997 Wei and Wu et al. reported a chemical method for the selective solution-phase generation of C₆₀ⁿ⁻ (n=1,2) and the preparation of the aqueous colloidal suspension of C₆₀ (Wei, Wu et al. 1997). They first added C₆₀ powder, excess Al-Ni alloy, solid NaOH pellets in THF, and degassed water to a Schlenk system. Upon addition, C₆₀ and Al-Ni alloy suspended in the interface between THF (upper layer) and aqueous NaOH (lower layer), while NaOH pellets dissolved in the water. As the reduction reaction proceeded, the red reaction products diffused into the THF layer, the color of which turned to dark red-purple quickly. In the reaction system, the concentrated aqueous NaOH prevented the reaction product C₆₀⁻ from dissolving in the water phase. After 10 min, the dark red-purple solution of C₆₀⁻ in THF was separated from colorless aqueous NaOH. Then 20 ml of C₆₀⁻/THF solution containing 80 mg of C₆₀ was added to 60 ml of undegassed distilled water dropwise and the aqueous colloidal C₆₀ suspension was formed.
with $C_{60}$ concentration of 1 mg/ml. As will be discussed in the next method, THF in this $C_{60}$ suspension can be removed by methods such as rotary evaporation, resulting in a final $C_{60}$/water suspension.

d) “THF Method”: This method was first proposed by Deguchi and Alargova et al. (Deguchi, Alargova et al. 2001). $C_{60}$ was first dissolved in THF to saturation, excess $C_{60}$ solids were filtered off with 0.45 μm-pore sized PTFE membrane filters. The $C_{60}$/THF was injected into an equal amount of water at a flow rate of about 200 cm$^3$/min. Finally THF in the $C_{60}$/THF/water suspension was removed by purging nitrogen gas through the solution, resulting in a water suspension of nano $C_{60}$ particles. This method was modified by Fortner and Lyon et al. (Fortner, Lyon et al. 2005). These authors added ultrapure water into the $C_{60}$/THF solution, instead of the injection of $C_{60}$/THF solution into water. And they used rotary evaporator to remove THF from the $C_{60}$/THF/water suspension to obtain the final water suspension of nC$_{60}$.

e) “Extended Stirring Method”: It was discovered by the author of this thesis that when black $C_{60}$ powder is dispersed in water and gently tumbled, the particles formed are from 20 to 50 μm in diameter, but when the powder is stirred vigorously with a magnetic stirring bar for 2–3 days or longer, the suspension becomes turbid with a brownish color. The size of “$C_{60}$ aggregates” in the resulting suspension ranged from 1 to 3 μm in diameter (Cheng, Kan et al. 2004). If this suspension is filtered with 1 μm-pore sized glass fiber membrane filters or 0.45 μm-pore sized PTFE membrane filters, a
yellow supernatant of nC$_{60}$ can be obtained. If the stirring process lasts longer, more nC$_{60}$ can be obtained in the supernatant.

2.1.3 The properties of nC$_{60}$ in water

Water suspensions of nC$_{60}$ prepared by the above methods are comprised predominantly of underivatized C$_{60}$, with diameters typically range from ~ 5 to 500 nm (Andrievsky, Klochkov et al. 1999; Alargova, Deguchi et al. 2001; Deguchi, Alargova et al. 2001; Sayes, Fortner et al. 2004; Fortner, Lyon et al. 2005). nC$_{60}$ in the water suspensions are highly stable with no precipitation after storage in the dark for months under ambient conditions, and they are stable in the case of dilution or concentration of the dispersions (Andrievsky, Kosevich et al. 1995; Alargova, Deguchi et al. 2001; Deguchi, Alargova et al. 2001; Andrievsky, Klochkov et al. 2002). Absorption spectra and particle size distribution of nC$_{60}$ in water suspensions measured immediately after preparation and after storage were indistinguishable (Deguchi, Alargova et al. 2001; Cheng 2003; Cheng, Kan et al. 2005). The colloidal stability nC$_{60}$ in their water suspensions is, however, significantly affected by addition of salt electrolytes (Mchedlov-Petrossyan, Klochkov et al. 1997; Wei, Wu et al. 1997; Andrievsky, Klochkov et al. 1999; Deguchi, Alargova et al. 2001; Cheng 2003; Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005). It has been observed that when the ionic strength of the water suspension is above 0.05 M, nC$_{60}$ will coagulate and form larger aggregates or even settle out of the colloidal suspension (Mchedlov-Petrossyan, Klochkov et al. 1997; Deguchi, Alargova et al. 2001; Cheng 2003; Brant, Lecoanet et al. 2005; Cheng, Kan et al. 2005; Fortner, Lyon et al. 2005).
Another interesting property of nC$_{60}$ in water suspensions is that nC$_{60}$ cannot be extracted by non-polar solvents, such as toluene or benzene, from their water suspensions, despite the high hydrophobicity of original C$_{60}$ solid (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Wei, Wu et al. 1997; Deguchi, Alargova et al. 2001; Cheng 2003; Cheng, Kan et al. 2005). Both the studies by Andrievsky, Klochkov et al. and by Brant, Lecoanet et al. indicated that in water suspensions of nC$_{60}$, C$_{60}$ molecules probably interact with water and form hydrated C$_{60}$. The hydration of C$_{60}$ may prevent C$_{60}$ molecules from interacting directly with hydrophobic molecules of non-polar organic solvents (Andrievsky, Klochkov et al. 2002; Brant, Lecoanet et al. 2005).

It has been reported that the surfaces of nC$_{60}$ in water suspensions are negatively charged with a $\zeta$-potential in the range of -30 ~ -50 mV at negligible electrolyte concentrations (Deguchi, Alargova et al. 2001; Brant, Lecoanet et al. 2005; Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005). The mechanisms underlying the peculiar properties of C$_{60}$ aqueous suspension are not yet fully understood. Many investigators have proposed mechanisms for the origin of the negative charge on nC$_{60}$ surfaces (Mchedlov-Petrossyan, Klochkov et al. 1997; Deguchi, Alargova et al. 2001; Andrievsky, Klochkov et al. 2002; Brant, Lecoanet et al. 2005), for example, the interaction between C$_{60}$ particles with surrounding water is possibly responsible for some properties of the C$_{60}$ aqueous dispersion, including the colloidal stability, the coagulation of C$_{60}$ on addition of electrolytes, and the difficulty to extract nC$_{60}$ from aqueous suspension into toluene. Based on the their results of FTIR, UV-Vis spectroscopy, and transmission electron microscopy (TEM) study of C$_{60}$ aqueous suspensions, Andrievsky, Klochkov et al. concluded that in the aqueous suspension of nC$_{60}$, C$_{60}$ is surrounded by water.
molecules and interacts with them (Andrievsky, Klochkov et al. 1999; Andrievsky, Klochkov et al. 2002). Furthermore, nC$_{60}$ are separated by sorbed water molecules, and thus do not interact directly with each other like C$_{60}$ molecules in the crystalline state. Recent studies concluded that (Brant, Lecoanet et al. 2005) during the formation of nC$_{60}$, C$_{60}$ (electron acceptor) formed weak donor-acceptor complexes with water (electron donor) and this charge transfer through surface hydrolysis reactions may contribute to the overall surface charge of nC$_{60}$ in water.

2.2 Adsorption and desorption

2.2.1 Basic concepts of adsorption and desorption

Sorption is the process in which chemicals become associated with solid phase. There are two types of sorption: adsorption onto a two-dimensional surface, or absorption into a three-dimensional matrix. The particular solid or mixture of solids with which a particular chemical associates is called the sorbent(s), while the chemical is called the sorbate. The term "adsorption" deals with the process in which molecules accumulate in the interfacial layer, but "desorption" denotes the converse process. Innumerable physical, chemical and biological processes take place at the boundary between two phases, or are initiated at interfaces. From an environmental point of view, sorption is very important because it dramatically affects the fate and impact of chemicals in the environment. Molecules behave very differently if they are dissolved in water as opposed to sorbed onto the exterior of solids or within a solid matrix. Since sorbed molecules may not be able to contact with atmosphere, ambient light, other chemicals or
microorganisms, their availability to phase transfer, photolysis processes, biotransformation or other chemical reactions may be substantially reduced.

Adsorption has been divided into two classes by many authors (Parfitt and Rochester 1983; Adamson and Gast 1997; Dabrowski 2001): physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption is usually due to the universal van der Walls interactions between sorbate and sorbent molecules. Therefore, sorption energy for physical adsorption is low. It is generally a reversible process. Chemisorption usually occurs with formation of some kind of chemical bond between the sorbate and sorbent surface. Therefore, compared to physisorption, chemisorption may be a slower and a more specific process. The adsorption energy of chemisorption is relatively higher than that of physisorption. And since chemisorption is considered to involve formation of specific bonds between sorbate and sorbent, it is generally an irreversible process. What's more, chemisorption usually occurs only as a monolayer, while multilayers may be formed in physisorption. Under favorable conditions, both processes can occur simultaneously.

In fact, sorption is often not a single simple process in natural environments. Rather, in a given system some combination of interactions may govern the association of sorbate(s) with sorbent(s). Nutritional organic compounds adsorb to solid surface mostly through physisorption. They may escape the water by penetrating into natural organic matter in the particulate phase, which is primarily due to the unfavorable free-energy costs of remaining in aqueous solution. This effect, called hydrophobic effect, is the force that dominates the partitioning of nonpolar hydrophobic organic compounds (Tanford 1980). The organic molecules (sorbates) may also displace water molecules from the
region near the mineral surface to some extent and then be associated with the surface via van der Walls, dipole-dipole, and other weak intermolecular forces. The above two types of association are the general sorption mechanisms that are governing the adsorption of organic chemicals to natural solids (Schwarzenbach, Gschwend et al. 2003).

Additionally, if the sorbate is ionizable in the aqueous solution, sortion can also be induced by attraction to specific surface sites exhibiting opposite charges. For some sorbate molecules, chemical bonds may be formed between sorbate and sorbent molecules (chemisorption). All of these interaction mechanisms operate simultaneously, and the mechanism(s) that dominate the overall adsorption process will depend on specific structural properties of the sorbate molecules and the solid sorbent.

### 2.2.2 Sorption isotherms

When a vapor is adsorbed onto a previously unoccupied solid surface or its pore space, the amount of the vapor adsorbed is proportional to the solid mass. The vapor uptake is also affected by temperature (T), the equilibrium partial pressure of the vapor (P), and the nature of the solid (the adsorbent) and the vapor (the adsorbate). For a vapor adsorbed on a solid at a fixed temperature, the adsorbed quantity of the adsorbate per unit mass of the solid (q or $C_s$, mass of adsorbate / mass of adsorbent, e.g., mg/kg) is then only a function of the equilibrium partial pressure of the vapor (P). At equilibrium the relationship between q and P at a given temperature is referred to as the adsorption isotherm (Chiou 2002). For adsorption of solutes from solution to a solid, similar isotherms can be constructed by relating q (or $C_s$) with the adsorbate’s concentration in the bulk solution ($C_w$, mass of adsorbate / volume of solution, e.g., mg/L).
Experimentally determined adsorption isotherms exhibit a variety of shapes for diverse combinations of adsorbates and adsorbents. Some well-defined adsorption isotherm types are described as follows:

a) Langmuir Adsorption Isotherm: This type of isotherm was originally applied to the adsorption of gases or vapors on a plane surface that contains a fixed number of identical active sites (Langmuir 1918). The amount of adsorbed gases or vapors increases monotonically until it reaches a limiting value that corresponds theoretically to the completion of a surface monolayer. Langmuir isotherm is mathematically represented by:

\[ \theta = \frac{bP}{1 + bP} \]  

(2.1)

where \( \theta \) is the fraction of the total sites occupied by the vapor at an equilibrium partial pressure \( P \), and \( b \) is the Langmuir constant, which is considered to be related to the properties of the specific adsorbate, adsorbent, and temperature, but not to the adsorbed adsorbate quantity. If one defines a limiting (monolayer) adsorption capacity, \( q_m \) (the amount of the adsorbed adsorbate per unit mass of the solid at the time when the solid surface is covered with a complete monolayer of the adsorbed vapor), then, \( \theta = q/q_m \).

The Langmuir isotherm can be expressed as:

\[ q = \frac{q_mbP}{1 + bP} \]  

(2.2)

As can be seen from Eq. (2.2), at low \( P \), \( bP \ll 1 \), therefore \( q = q_mbP \), meaning that \( q \) has a linear relationship with \( P \). At high \( P \), \( bP \gg 1 \), \( q \) approaches \( q_m \) asymptotically and the isotherm is concave toward the \( P \) axis. Although the
Langmuir isotherm (Eq. (2.2)) was originally used to describe vapor adsorption, it has been adapted to fit the adsorption data of a solute from a solution, in which case the P term was replaced by the equilibrium solute concentration ($C_w$, mass of adsorbate / volume of solution, e.g., mg/L) (Chiou 2002). By rearrangement, Eq. (2.2) can be written as:

$$\frac{1}{q} = \frac{1}{q_m bP} + \frac{1}{q_m}$$  \hspace{1cm} (2.3)

A plot of experimental data of $\frac{1}{q}$ versus $\frac{1}{P}$ should give a straight line, and the two constants $q_m$ and $b$ can be calculated from the slope and the intercept of the straight line using linear least squares.

b) Freundlich Isotherm: It is an empirical relationship which was commonly used to fit experimental adsorption data with a minimum of adjustable parameters (Schwarzenbach, Gschwend et al. 2003). The general form of the Freundlich isotherm is:

$$q = K_F C_w^n$$  \hspace{1cm} (2.4)

where $q$ is the mass of the adsorbed adsorbate per unit mass of the solid (adsorbent) at equilibrium; $C_w$ is the adsorbed vapor or solute concentration at equilibrium; $K_F$ is the Freundlich constant; and $n$ is the Freundlich exponent which relates to the intrinsic heat of vapor or solute adsorption. The Freundlich equation (Eq. (2.4)) indicates that there are multiple types of sorption sites on the energetically heterogeneous adsorbent surface, with each site type exhibiting a different sorption free energy and total site abundance.
(Weber and Digiano 1996; Chiou 2002; Schwarzenbach, Gschwend et al. 2003). The value of $n$ is commonly less than 1, in which case the isotherm is concave to the $C_w$ axis, implying that added adsorbates are bound with weaker and weaker free energies per mole as $C_w$ increases (Schwarzenbach, Gschwend et al. 2003).

c) Linear Isotherm: When the value of the exponent ($n$) in a Freundlich isotherm equals to 1, Eq. (2.4) reduces to a linear isotherm:

$$q = K_p C_w$$  \hspace{1cm} (2.5)

where $K_p$ is called the partition coefficient. The sorption of hydrophobic organic compounds from water to soil are often characterized with a linear isotherms, indicating that the partition of organic compounds to the soil organic matter is the primary process for this kind of sorption (Chiou, Peters et al. 1979; Karickhoff, Brown et al. 1979; Chiou, Porter et al. 1983). For the adsorption onto mineral surfaces, a linear isotherm often indicates a homogeneous surface with sites having equal affinity for the adsorbate molecules (Farrell and Reinhard 1994).

d) BET Isotherm: The Brunauer-Emmett-Teller (BET) equation (Brunauer, Emmett et al. 1938) in the form of:

$$\frac{q}{q_m} = \frac{C_x}{(1-x)[1+(C-1)x]}$$  \hspace{1cm} (2.6)

was developed to describe multilayer adsorption of vapor on a solid, where $q$ is the mass of the adsorbed vapor per unit mass of the solid at the relative
vapor pressure \( x = P/P^0 \), \( P \) is the equilibrium vapor pressure, \( P^0 \) is the saturation vapor pressure at the system temperature, \( q_m \) is the monolayer adsorption capacity of the vapor on the solid, and \( C \) is a constant. Eq. (2.6) can be rearranged into the form:

\[
\frac{x}{q(1-x)} = \frac{(C-1)x}{Cq_m} + \frac{1}{Cq_m}
\] (2.7)

and thus the values of \( C \) and \( q_m \) can be calculated by the slope and the intercept of the straight line, obtained by plotting \( \frac{x}{q(1-x)} \) versus \( x \). Using an inert gas as the adsorbate, the BET model has become a powerful analytical method for the surface-area measurements of solids (Adamson and Gast 1997; Chiou 2002).

e) Polanyi adsorption potential theory: Adsorption on high-surface-area microporous adsorbents, such as activated carbons, is energetically highly heterogeneous (Chiou 2002). This results in an enhanced adsorption energy (adsorption potentials) in the micropores of the carbon, owing to superposition of the fields from the opposite walls of the pores (Dubinin 1960). Figure 2.2 shows a schematic model for a region of the porous carbon surface. Under that circumstance, the Langmuir adsorption model or BET model may not be a good fit for adsorption data. The Polanyi adsorption potential theory (Polanyi 1916) has been considered the most powerful model to describe gases (or vapors) adsorption on energetically heterogeneous solids (Brunauer 1945). The original Polanyi model was clearly explained and extended to a wide
range of vapor- and liquid-phase systems by Manes and co-workers (Manes and Hofer 1969; Manes 1998).

Polanyi defined the existence of an (attractive) adsorption potential (ε) between the adsorbate molecule and the solid surface, which, at a particular location within the adsorption space, may be viewed as the energy required to remove the molecule from that location to a point outside the attractive force field of the solid. Thus the adsorption potential (ε) is the highest in the narrowest pore (or in the narrowest portion of a pore) because the adsorbate is close to more solid material (Chiou 2002). According to the Polanyi theory, the following relationship holds for ideal gas adsorption to porous adsorbents:

\[
\varepsilon = RT \ln \frac{P^0}{P_g}
\]  

(2.8)

where \(P_g\) is the vapor pressure in equilibrium with the adsorbed phase, \(P^0\) is the saturation vapor pressure, \(R\) is the ideal gas constant, and \(T\) is the absolute temperature (Polanyi 1916; Manes and Hofer 1969; Adamson and Gast 1997; Crittenden, Sanongraj et al. 1999; Allen-King, Grathwohl et al. 2002; Chiou 2002). It can be deduced from Eq. (2.8) that when the partial pressure of a vapor surrounding a porous adsorbent is increased, the adsorption of the vapor first takes place in the region with the highest adsorption potential (the narrowest pore (or the narrowest portion of a pore) and condenses to form a liquid or liquidlike adsorbate in the pore. Then the filling of the adsorbent pores with the adsorbate molecules goes gradually to lower adsorption
potential locations (wider pores, or the wider portion of a pore), until all the adsorption space is filled and the $P$ becomes $P^0$, when $\varepsilon = 0$.

f) Combined Adsorption-Partitioning Models: The sorption of hydrophobic organic contaminants by soils and sediments can be predominated by partitioning of dissolved solute between water and naturally occurring organic matter. Therefore, linear partitioning models have been used to describe sorption of those sorption processes based on the hypothesis that the natural sorbent organic matter associated with such geomaterials is a relatively homogeneous and amorphous partitioning phase for which sorption isotherms are linear over wide aqueous-phase solute concentration ranges (Chiou, Peters et al. 1979; Karickhoff, Brown et al. 1979; Means, Wood et al. 1980; Karickhoff 1981; Schwarzenbach and Westall 1981; Chiou, Porter et al. 1983). However, this simple partitioning model has been shown to be inconsistent with observed sorption behavior (Di Toro and Horzempa 1982; Miller and Weber 1986; Weber, McGinley et al. 1992; Kan, Fu et al. 1994; Kan, Fu et al. 1998). For example, experimental studies have shown that sorption isotherms measured over broad solution concentration ranges are commonly nonlinear (Miller and Weber 1986; Weber, McGinley et al. 1992; Young and Weber 1995; Allen-King, Groenevelt et al. 1996; Weber and Huang 1996); the $K_{oc}$ value for a particular hydrophobic organic contaminant often varies by more than one order of magnitude for the same sorbent depending on aqueous phase concentration (Weber, McGinley et al. 1992;
Allen-King, Groenevelt et al. 1996; Weber and Huang 1996; Huang and Weber 1997); and sorption-desorption reactions are often hysteretic (Di Toro and Horzempa 1982; Pignatello 1990; Carroll, Harkness et al. 1994; Kan, Fu et al. 1994; Kan, Fu et al. 1998). In these cases, the relationship between sorbed concentrations and dissolved concentrations of each hydrophobic organic contaminant can not be described by a single linear, Langmuir, or even a Freundlich isotherm. A combination of two types of isotherm has been proposed by many researchers (Weber, McGinley et al. 1992; Fu, Kan et al. 1994; Kan, Fu et al. 1998; Xing and Pignatello 1997; Xing and Pignatello 1997; Kan, Fu et al. 1998; Kan, Chen et al. 1999; Weber, W. et al. 1999; Xia and Ball 1999; Chen, Kan et al. 2000; Xia and Ball 2000; Xia and Pignatello 2001), to mention a few.

Weber (Weber, McGinley et al. 1992) proposed a dual reactive domain model (distributed reactivity model) by superposition of a linear type isotherm and a Langmuir type isotherm:

\[
q = x_l K_d C + x_{nl} \frac{Q^0 b C}{1 + b C} \tag{2.9}
\]

where \(q\) and \(C\) are the adsorbed phase and solution phase contaminant concentrations, respectively; \(x_l\) and \(x_{nl}\) are the mass fractions of the solid phase exhibiting linear and nonlinear sorption behavior, respectively; \(K_d\) (e.g., l/kg) is the solid-water distribution coefficient; and \(Q^0\) and \(b\) are Langmuir sorption capacity and energy parameters, respectively. Xing et al. (Xing and Pignatello 1996; Xing, Pignatello et al. 1996) also employed a dual mode model with
similar mathematical expression to interpret observed sorption-desorption data. The primary disadvantage of this model, and many other models, is that there is no theory or correlation method to predict the values of the various adjustable constants for arbitrary soil-sorbate combinations. Kan et al. overcame this problem with a slightly different model named “dual-equilibrium desorption” (DED) model wherein all the constants are predictable (Fu, Kan et al. 1994; Kan, Fu et al. 1994; Kan, Fu et al. 1997; Kan, Fu et al. 1998; Kan, Chen et al. 1999; Chen, Kan et al. 2000) to describe experimentally observed non-linear sorption and sorption-desorption hysteresis:

\[
q = K_{oc}^{1st} \cdot f_{oc} \cdot C_w + \frac{K_{oc}^{2nd} \cdot f_{oc} \cdot q_{max}^{2nd} \cdot C_w}{q_{max}^{2nd} + K_{oc}^{2nd} \cdot f_{oc} \cdot C_w}
\]  

(2.10)

where \(K_{oc}^{1st}\) is the organic carbon normalized sorption coefficient for the first compartment; \(f_{oc}\) is the fraction of organic carbon; \(K_{oc}^{2nd}\) is the organic carbon normalized sorption coefficient for the second compartment; \(q_{max}^{2nd}\) is the maximum sorption capacity for the second compartment; \(f\) is a factor representing the fraction of the second compartment that is saturated upon exposure; and \(q\) and \(C_w\) are as defined previously.

The second type of combined isotherm uses a combination of a linear isotherm and Freundlich isotherm, proposed by Accardi-Dey and Gschwend to fit experimental data from sediments known to contain black carbons (Accardi-Dey and Gschwend 2002):
\[ q = f_{oc}K_{oc}C_w + f_{bc}K_{bc}C_w^n \]  

(2.11)

where \( f_{oc} \) and \( f_{bc} \) are the weight fraction of organic carbon (OC) and black carbon (BC) in the solid phase, respectively; \( K_{oc} \) and \( K_{bc} \) are the OC-normalized and BC-normalized distribution coefficient for the compound, respectively; \( q \) and \( C_w \) are the adsorbed phase and solution phase contaminant concentrations, respectively.

### 2.2.3 Adsorption/desorption hysteresis

Sorption/desorption hysteresis means that adsorption and desorption do not follow the same \( q \) vs. \( C_w \) paths and is often observed in both laboratory and field sorption studies. If hysteresis exists, thermodynamics requires that after adsorption some rearrangement of the sorbate/sorbent system must take place (principle of microscopic reversibility) (Adamson and Gast 1997). Sorption/desorption hysteresis is traditionally evaluated by comparing the solid-water distribution coefficient \( (K_d^s) \) measured in the sorption step to that measured in the desorption step \( (K_d^d) \). Hysteresis is considered to have occurred if the measured \( K_d^s \) value is greater than the measured \( K_d^d \) value (Di Toro and Horzempa 1982).

The adsorption of many classes of organic compounds to natural soils and sediments shows hysteresis, which has been investigated by numerous researchers (Di Toro and Horzempa 1982; Karickhoff and Morris 1985; Pignatello and Huang 1991; Fu, Kan et al. 1994; Kan, Fu et al. 1998; Weber, Huang et al. 1998; Chen, Kan et al. 2000; Xia and Pignatello 2001). For example, Steinberg et al. (Steinberg, Pignatello et al. 1987) found that 1,2-dichloromethane, despite its high volatility, low affinity to soil, and rapid
biodegradation, persisted in agricultural soils for up to 19 years after its application. Kan et al. reported that the fraction of naphthalene resistant to desorption was as high as 62% after 10 successive desorption steps for 178 days (Kan, Fu et al. 1994) although naphthalene was semi-volatile and has a relatively low Kow value. Similar results were also observed by Pignatello (Pignatello 1990) for desorption of nine low molecular weight halogenated alkanes, and by Pavlostathis and Jaglal (Pavlostathis and Jaglal 1991) for the desorption of trichloroethylene, toluene, and xylene from five field-contaminated soils. Sorption/desorption hysteresis has been reported for many classes of organic compounds, including PAHs, chlorinated benzenes, phenols, halogenated aliphatic hydrocarbons, pesticides, surfactants, and PCBs (Di Toro and Horzempa 1982; Coates and Elzerman 1986; Readman, Mantoura et al. 1987; Siracusa and Somasundaran 1987; Zawadzki, Harel et al. 1987; Pignatello 1990; Pavlostathis and Jaglal 1991).

Although the mechanisms responsible for sorption/desorption hysteresis are still debatable, there have been some explanations proposed by different researchers who have been investigating this aspect for years. For example, the existence of hysteresis has been attributed to: (1) the existence of a condensed, glassy, organic polymetric matter as sorbent. The adsorption to the condensed organic matter phase could be kinetically slow, site specific, and non-linear (Weber and Huang 1996; Xing, Pignatello et al. 1996); (2) the sorbed chemicals are irreversibly entrapped in the soil organic matter matrix following sorption (irreversible adsorption) (Carroll, Harkness et al. 1994; Kan, Fu et al. 1998). The term “irreversible” here implies that desorption takes place from a molecular environment that is different from the adsorption environment and that desorption is hindered. Other possible mechanisms, such as chemisorption of organic contaminants to
various components of soil/sediment matrix (Brusseau and Rao 1989); or biotic or abiotic
degradation of the sorbate compounds (Hermosin, Cornejo et al. 1987; Miller and Pedit
1992), may also be the reason for apparently irreversible adsorption.

Numerous theories and models have been used to express the general notion that
sorption and desorption of soil organic contaminants are often different processes,
including slow desorption; bound contaminants; hysteresis; irreversible sorption;
amorphous and glassy sorption domains; to mention a few (Di Toro and Horzempa 1982;
Ball and Roberts 1991; Connaughton, Stedlinger et al. 1993; Carroll, Harkness et al.
1994; Burgos, Novak et al. 1996; Chiou and Kile 1998; Pignatello 1998; Xing and
Pignatello 1998; Gilltette, Luthy et al. 1999). All these interpretations have proposed the
existence of two distinct sorption and desorption processes: one process related to
sorption and desorption at high contaminant concentrations or initial exposure; the other
at low concentrations or “long term” weathering — “long term” typically refers to a few
days, or longer, which was predominantly observed during desorption. Furthermore,
many researchers concluded that both sorption and desorption are biphasic, consisting of
two compartments, each with unique equilibrium and kinetic characteristics (Carroll,
Harkness et al. 1994; Pignatello and Xing 1996; Weber and Huang 1996). Two
compartments have been considered as different types of sorbent matrices: amorphous
(flexible, expanded) versus glassy (rigid, dense) organic matter (Pignatello and Xing
1996; Weber and Huang 1996); soil organic matter versus high-affinity materials (Chiou
and Kile 1998); or adsorption to sediment surfaces versus entrapment in sediment pores
(Farrell and Reinhard 1994; Adamson and Gast 1997).
2.2.4 Adsorption of hydrophobic organic compounds from water to solid-phase organic carbon

Sorbents can be roughly divided into two main categories: organic sorbents, and inorganic sorbents. Since adsorption of organic compounds to hydrophobic organic surface does not require displacement of tightly bound water molecules, which was required in the process of adsorption to inorganic sorbent surface, solid-phase organic matter is a primary class of sorbents for hydrophobic organic compounds. It was found, based on studies on a large number of soils and sediments, that nonionic chemicals showed increasing solid-water distribution ratios for soils and sediments with increasing amounts of natural organic matter (Kile, Chiou et al. 1995). Typically, organic carbon accounts for 40 to 60 % of natural organic matter (Schwarzenbach, Gschwend et al. 2003), which means the amount of organic carbon in the sorbent can to a great extent determine the sorption behavior of organic chemicals. In fact, it has been reported by many research groups that the amount of organic carbon in a natural soil/sediment is one of the most significant parameters which affect the amount of sorbed organic chemicals (Kan, Fu et al. 1994; Weber, Huang et al. 1998; Chen, Kan et al. 2000; Xia and Pignatello 2001).

In soils and sediments, an organic carbon normalized sorption coefficient \( K_{oc} \) is therefore defined as:

\[
K_{oc} = \frac{K_d}{f_{oc}} = \frac{q_{oc}}{C_w}
\]  

(2.12)

where \( f_{oc} \) is the weight fraction of organic carbon, \( K_d \) (called solid-water distribution coefficient, e.g., in L/kg-solid) is defined as the ratio of the compound's total equilibrium
concentrations in the solids and in the aqueous solution: \( K_d = \frac{q}{C_w} \); and \( q_{oc} \) is the total sorbate concentration associated with the organic carbon (e.g., in mg/kg-OC). Normally each compound has its own \( K_{oc} \) value. For some organic compounds, the \( K_{oc} \) values can also be estimated by their octanol-water partition constants (\( K_{ow} \)), which can be found in most literature:

\[
\log K_{oc} = a \cdot \log K_{ow} + b
\]

(2.13)

where the values of \( a \) and \( b \) can be calculated based on large numbers of experiments.

For example, for PAHs, a relationship of \( \log K_{oc} = 0.98 \log K_{ow} - 0.32 \) has been reported (Schwarzenbach, Gschwend et al. 2003). Since organic carbon is an important parameter controlling the adsorption of organic chemicals, by normalizing the compound’s solid-water distribution coefficient (\( K_d \)) to organic carbon normalized sorption coefficient (\( K_{oc} \)), it is easier to compare the sorption behavior of the same compound in sorbents with various carbon fractions.

It was found that not only the amount of organic carbon present in the sorbent, but the structure of the carbon materials could affect the sorption of organic compounds. It has been concluded from numerous studies (Thurman 1985; Schulten and Schnitzer 1997) that organic matter present in environmental media include materials generated from various sources. Natural organic matter is recognized to be a complex mixture of macromolecules derived from the remains of organisms and modified after their release to the environment through the long process of degradation, rearrangement, or
recombination. For instance, humic materials, which can be further subdivided into humic substances and humin, are one class of materials that have a great influence on sorption of organic chemicals to natural soils and sediments (Chiou, Malcolm et al. 1986; Gauthier, Seitz et al. 1987; Schlautman and Morgan 1993; Davies and Ghabbour 1998; Huang, Senesi et al. 1998; Piccolo and Conte 2000).

Black carbon (BC) is another important class of organic carbon present in the environment. Black carbon, including charcoal, soot, active carbon etc., refers to residues from incomplete combustion of fossil fuels or biomass (Goldberg 1985). Black carbons are found in various environmental media, including atmospheric aerosols, estuarine and deep-sea sediments and soils etc. In the soils and sediments, black carbons often contribute 1 to 10% of the fco (Gustafsson and Gschwend 1998).

Black carbon has been reported to consist of single and stacked apolar and polyaromatic sheets (Goldberg 1985; Gustafsson, Bucheli et al. 2001). The carbon aromaticity, which is the ratio of aromatic carbon to total organic carbon, has been reported to be nearly 100% (Accardi-Dey and Gschwend 2002). The aromatic sheets vary in size from a few to tens of fused aromatic rings and there may be functional groups, such as anhydride, carbonyl, C-H etc., associated with black carbons. There is similarity of the structure of black carbon with that of C_{60} fullerene, which is composed of curved, very well organized aromatic sheets (the structure of C_{60} will be discussed in the following section).

Black carbon particles can be quite porous and exhibit a high affinity for many organic contaminants, particularly for planar aromatic compounds such as PAHs (Goldberg 1985; McGroddy, Farrington et al. 1996; Gustafsson, Haghseta et al. 1997;
Bucheli and Gustafsson 2000). For neutral organic sorbates, the hydrophobic organic surfaces and/or nanopores (< 1 nm) of carbonaceous materials like black carbons are the most likely sites of adsorption. Since black carbons are ubiquitous in sediments and soils, their influence on transport and bioavailability of organic contaminants is of great concern (Broman, Naf et al. 1990; McGroddy, Farrington et al. 1996; Gustafsson, Haghseta et al. 1997; Bucheli and Gustafsson 2000; Karapanagioti, Kleineidam et al. 2000). Significantly higher apparent K_{oc} values have been observed in the field compared to values predicted from simple partitioning models (Naes, Axelman et al. 1998; Kleineidam, Rugner et al. 1999; Karapanagioti, Kleineidam et al. 2000). This phenomenon has been attributed to adsorption of organic compounds to the combustion-derived black carbon fraction as well as the absorption into other biogenic or diagenetic organic carbon (Accardi-Dey and Gschwend 2003).

Since black carbon has been found to have higher affinity for organic compounds than other forms of organic carbon, it has been proposed by some researchers that the simple isotherm with one single K_{oc} value could not model field data very well. The dual-mode model (Eq. 2.11), as discussed earlier has been proposed to account for the association of organic compounds with natural sorbents that contain components exhibiting a limited number of more highly active adsorption sites (e.g., black carbon) as well as components into which organic compounds may absorb (Xing and Pignatello 1997; Xia and Ball 1999). From the field data, values of K_{bc} for the observed PAHs can be estimated via:

\[
\log K_{bc} \approx 1.6 \log K_{ow} - 1.4
\]  

(2.14)
For a specific organic sorbate, the $K_{bc}$ value estimated from Eq. (2.14) is higher than the $K_{oc}$ value estimated from conventional $K_{oc}/K_{ow}$ relationships, e.g., Eq. (2.13) + (Schwarzenbach, Gschwend et al. 2003), where $f_{bc}$ was not taken into account.

2.2.5 Studies of adsorption/desorption with $C_{60}$ solid

2.2.5.1 Simple Gas Adsorption on $C_{60}$ Solid

Since the pioneering work in the area of fullerenes, there have been a number of reports and publications addressing several aspects of this form of carbon, for example, the preparation, the properties, and the potential applications of fullerenes. However, their surface properties are considerably less known, especially their adsorption properties. Most researchers who dealt with adsorption have focused on the study of adsorptive interactions of vapors with $C_{60}$ solid (Ismail and Rodgers 1992; Kaneko, Ishii et al. 1993; Rathousky, Starek et al. 1993; Nagano, Kiyobayashi et al. 1994; Davydov, Filatova et al. 1995; Fastow, Kozirovski et al. 1995; Folman, Fastow et al. 1997; Davydov and Kalashnikova 1998; Kratschmer, Rathousky et al. 1999; Papirer, Brendle et al. 1999; Martinez-Alonso, Tascon et al. 2000; Rathousky and Zukal 2000).

In order to study the surface structure of $C_{60}$ fullerene, simple gases such as Kr, $N_2$, $O_2$, CO, $CO_2$ and Ar have been used to characterize the porous texture of the solid (Ismail and Rodgers 1992; Kaneko, Ishii et al. 1993; Nagano, Kiyobayashi et al. 1994; Fastow, Kozirovski et al. 1995; Folman, Fastow et al. 1997; Kratschmer, Rathousky et al. 1999; Martinez-Alonso, Tascon et al. 2000). Ismail and Rodgers (Ismail and Rodgers 1992) first reported gas adsorption measurements on $C_{60}$ with Kr, $N_2$, $O_2$, and $CO_2$. 

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Kaneko et al. (Kaneko, Ishii et al. 1993) studied the adsorption of N\textsubscript{2} and O\textsubscript{2} on C\textsubscript{60} and their results agreed with Ismail and Rodgers in finding evidence for the presence of micropores in C\textsubscript{60} solids. Nagano et al. (Nagano, Kiyobayashi et al. 1994) studied CO\textsubscript{2} absorption in C\textsubscript{60} solid. They found a larger amount of CO\textsubscript{2} absorbed in C\textsubscript{60} solids, compared to the amount calculated from surface area of C\textsubscript{60} and CO\textsubscript{2} cross-section area. From the infrared spectra and measurements of heat capacity anomaly of C\textsubscript{60}, they concluded that there could be lattice deformation in C\textsubscript{60} solids after treatment of C\textsubscript{60} at a temperature of 98°C, which made some voids between C\textsubscript{60} molecules available to CO\textsubscript{2} molecules. Also, according to their report, there are a lot of dislocations in C\textsubscript{60} crystal lattice, which could form microporous structures.

Folman et al. (Fastow, Kozirovski et al. 1995; Folman, Fastow et al. 1997) used infrared spectroscopy to study CO physical adsorption on C\textsubscript{60} embedded in alkali halides and C\textsubscript{60} high-area films. Their results proved that adsorption sites in C\textsubscript{60} solid are most probably the voids between C\textsubscript{60} molecules and sites on top of C\textsubscript{60} molecules, which confirmed earlier predictions from calculations of adsorption potentials. Martinez-Alonso et al. (Martinez-Alonso, Tascon et al. 2000) performed N\textsubscript{2} adsorption on C\textsubscript{60} solid and essentially reached the same conclusion.

Kratschmer et al. (Kratschmer, Rathousky et al. 1999) compared the behavior of C\textsubscript{60} and other forms of carbon as adsorbents for Kr at 77K. It was found that at low pressures the fullerene behaves similarly to a graphitized carbon black and very differently from polycrystalline diamond. Accordingly, these authors proposed that Kr is adsorbed on C\textsubscript{60} and graphite by the same mechanism in the same range of surface
coverage and that the adsorption of Kr on C\textsubscript{60} crystals with perfectly developed facets can be expected to be very similar to that on the basal plane of graphite.

### 2.2.5.2 Adsorption of Organic Vapors on C\textsubscript{60} Solids

Adsorption of organic vapors has been investigated by several researchers. Davydov et al. (Davydov, Filatova et al. 1995; Davydov and Kalashnikova 1998) studied the adsorption of vapors of some classes of organic compounds, including alkanes; aromatic hydrocarbons; phenols; chlorinated hydrocarbons etc., on C\textsubscript{60} fullerene molecular crystals by gas chromatography. Some thermodynamic characteristics of adsorption such as adsorption equilibrium constant, heat of adsorption were evaluated. Adsorption of organic vapors to graphitized carbon black was also conducted to compared with that of C\textsubscript{60}. And it was found that the adsorption potential of C\textsubscript{60} fullerene crystals was much smaller than that of graphite adsorbents.

Rathousky et al. (Rathousky, Starek et al. 1993; Rathousky and Zukal 2000) observed adsorption of cyclopentane on C\textsubscript{60} solids. They observed adsorption/desorption hysteresis on C\textsubscript{60} surfaces. Their desorption isotherm didn’t follow the same pattern as the adsorption branch, instead, a certain amount of sorbate molecules were retained on C\textsubscript{60} solids. The observed hysteresis was explained by possible penetration of the organic molecules into the bulk of C\textsubscript{60} crystals. Furthermore, they proposed that the organic molecules might break some weak van der Waals bonding between C\textsubscript{60} molecules and thus accessed some interstices between C\textsubscript{60} molecules. These observations agreed with results from other groups, such as Nagano et al. (Nagano, Kiyobayashi et al. 1994), Folman et al. (Fastow, Kozirovski et al. 1995; Folman, Fastow et al. 1997), and Martinez-
Alonso et al. (Martinez-Alonso, Tascon et al. 2000) in the finding of deformation of C_{60} crystal lattice and locations of sorbate molecules. Also their results could be one possible explanation for the observations found in this work, which will be discussed later.

2.2.5.3 Adsorption of Organic Compounds to C_{60} from Aqueous Solutions

Few reports have been found discussing the adsorption of organic compounds to C_{60} solid from water or aqueous solution. Ballesteros et al. (Ballesteros, Gallego et al. 2000) investigated the potential of C_{60} fullerene as an adsorbent for organic compounds from aqueous solutions using continuous flow configurations and gas chromatography-atomic absorption spectrometry techniques. The solid-water partition coefficient of naphthalene (the compound of interest in this work) was about one tenth of that found herein (see Chapter 3 for detail). There are at least two reasons that might be responsible for the difference. Firstly, their flow configurations, although reasonable for normal adsorbent/adsorbate study, may not be suitable for C_{60} studies because C_{60} may not be in sufficient contact with organic compounds. Secondly, whether there was enough time to reach equilibrium in their experiments is questionable. Apparently, more effective experimental design is needed to study the adsorptive interactions of organic contaminants with C_{60} solid in aqueous solutions.

2.3 Transport of nC_{60} in Porous Media

Since the manufacture of fullerenes are expected to increase rapidly, it is of no doubt that those carbonaceous nanomaterials will ultimately be present in the environment at measurable concentrations. Although the low water solubility of C_{60}.
(Ruoff, Tse et al. 1993) seems to make people expect no mobile C_{60} in aqueous environments, such as surface water and groundwater, several methods have been applied to produce water-stable nC_{60} (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Deguchi, Alargova et al. 2001). What’s more, we reported earlier that only after being stirred for a couple of days (which can be widely encountered under natural environmental conditions) did C_{60} form water-stable nC_{60} (Cheng, Kan et al. 2004). These observations indicate that C_{60} might be quite mobile in some aqueous environments. In addition, recent studies have shown that this underivatized form of C_{60} (nC_{60}) causes oxidative damage to both fish brain cells and cultured human cells, as well as being bactericidal (Oberdorster 2004; Sayes, Fortner et al. 2004; Fortner, Lyon et al. 2005; Lyon, Fortner et al. 2005). The observed toxicity of water-stable nC_{60} raised the public concern as to the potential exposure to and the health effects of those materials, as well as their possible effects to organisms in aquatic systems. Under this context, research on the transport of C_{60} is imperative.

Wiesner’s research group studied the transport of nC_{60} through columns packed with spherical glass beads and compared their mobility with that of other carbonaceous nanomaterials, such as fullerols (C_{60} hydroxide, C_{60}(OH)_{n}, n = 22-26) and single-wall carbon nanotubes (SWNTs) (Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004). Since the transport of C_{60} in natural media may vary from that in ideal model media due to the complicated conditions, such as the medium heterogeneities, this study reports the first investigation of the transport of nC_{60} through a soil column, designed to assess C_{60} transport in natural porous media, such as groundwater aquifers.
Since few theories has been proposed to evaluate the unique transport properties of new nanomaterials in porous media, a theory developed for colloidal transport in porous media (O'Melia 1989) was applied for the investigation of fullerene transport through porous media (Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004). According to this theory, the colloidal particle deposition in porous media can be described by particle transport to the media surface or “collector”, followed by particle attachment (Yao, Habibian et al. 1971; O'Melia 1990; Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004). The kinetics of particle deposition in porous media have been described by Yao and Habibian et al. (Yao, Habibian et al. 1971; O'Melia 1990) as:

\[
\frac{dC}{dL} = -\frac{3}{4} \alpha \eta \frac{(1 - \varepsilon)}{a_c} C
\]

(2.15)

where \( C \) is the concentration of particles; \( L \) is the length of travel of the particles in the porous media; \( \varepsilon \) is the porosity of the porous media; \( a_c \) is the radius of the particles comprising the porous media (assuming uniform spherical particles); \( \alpha \) is called the particle attachment efficiency; and \( \eta \) is called the single collector efficiency. The collector efficiency (\( \eta \)) is defined as the ratio of the particle flux reaching the collector surface to the particle flux approaching the collector from upstream. The attachment efficiency (\( \alpha \)) is defined as the ratio of the particle flux attaching to the collector surface to the particle flux reaching the collector surface (Yao, Habibian et al. 1971; O'Melia 1990). Therefore, the product of \( \alpha \) and \( \eta \), \( \alpha \times \eta \), describes the ratio of the flux of particles actually adhering to a stationary collector to the flux of suspended particles approaching it from upstream. Since soil particles are quite heterogeneous, Eq. (2.15) is used only as a semiempirical guide to correlate nanoparticle transport. The specific
values obtained for the terms in Eq. (2.15) can not be used to imply detailed mechanism.
Since particle transport to a collector surface can be approximated by the sum of three
transport processes that contribute to the particle transport to a collector surface:
Brownian diffusion, interception, and gravity forces (sedimentation), the value of
theoretical collector efficiency ($\eta_{\text{theor}}$) can be calculated from experimental parameters
and a few constants, including particle radius ($a_p$), collector (grain) radius ($a_c$), particle
density ($\rho_p$), fluid density, media porosity ($\varepsilon$), temperature ($T$), viscosity of water ($\mu$),
superficial or approach velocity of flow ($U$), Stokes-Einstein diffusion coefficient of the
particle ($D_p = kT/(6\pi \mu a_p)$), gravitational acceleration ($g$), Hamaker constant ($H$), and
Boltzmann’s constant ($k$) (Yao, Habibian et al. 1971; Rajagopalan and Tien 1976;
O’Melia 1990).

An equation in the form of:

$$
\alpha_{\text{exp}} = -\ln\left(\frac{C_L}{C_0}\right) \left(\frac{4a_c}{3(1-\varepsilon)\eta_{\text{theor}} L}\right)
$$

(2.16)
can be obtained by integrating Eq. (2.15) with boundary conditions that $C = C_0$ at $L = 0$
and $C = C_L$ at $L = L$. The experimental value of the attachment efficiency ($\alpha_{\text{exp}}$) can be
obtained from Eq. (2.16), using the calculated value of $\eta_{\text{theor}}$ and experimental
measurements of particle breakthrough in porous media. The calculation of theoretical
single collector efficiency ($\eta_{\text{theor}}$) and the particle attachment efficiency ($\alpha$) has been used
to evaluate the particle transport in porous media in an aquifer (Harvey, George et al.
1989; O’Melia 1990), and results agreed very well with both laboratory experiments and
theoretical prediction (Tobiason and O’Melia 1988; Harvey, George et al. 1989; O’Melia
1990).
The single collector efficiency describes the physical effects on the kinetics of particle deposition, and varies with factors such as flow velocity, media porosity, particle and collector diameters, etc. The attachment efficiency $\alpha$ generally accounts for chemical effects on the particle deposition, for example, the empirically determined value of $\alpha$ varied with solution pH, ionic strength, the nature of ions in the solution, and the surface chemistry of particles and the collector (Yao, Habibian et al. 1971; O'Melia 1990; Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004).

The particle mobility can be further illustrated by calculating the particle travel distance (Elimelech, Gregory et al. 1995; Kretzschmar and Sticher 1997; Lecoanet, Bottero et al. 2004). The maximum travel distance ($L_T$) is defined as the predicted travel distance after which 99.9% of the particles are immobilized by the porous media. It can be calculated by rearranging Eq. (2.16) and using 0.001 as the value for $\left(\frac{C_L}{C_0}\right)$. 

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Figure 2.1 Structure of a $C_{60}$ molecule.
Figure 2.2. A schematic model for a region of the porous carbon surface showing the equipotential surfaces corresponding to successively lower values of the adsorption potential with increasing pore size. The vapor liquefies wherever the adsorption potential required to concentrate it to saturation is equaled or exceeded. This picture was adopted from Manes 1998, and Chiou 2002.
CHAPTER 3
NAPHTHALENE and 1,2-DICHLOROBENZENE ADSORPTION AND DESORPTION FROM C₆₀ AGGREGATES OF DIFFERENT AGGREGATION SIZES

3.1 Introduction

Since C₆₀ is insoluble in water, one might expect that it would not enter groundwater in great quantities. However, water-stable “nC₆₀” (underivatized C₆₀ nanoparticles, stable in water for months) can be formed in water by dissolving C₆₀ in non-polar solvents, mixing into water, followed by the removal of the solvents (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Deguchi, Alargova et al. 2001). More interestingly, it was discovered in this study that water-stable “nC₆₀” can be formed simply by extensive stirring, which will easily be encountered in natural environments. These findings indicate that C₆₀ might be mobile in groundwater.

It has been reported that nC₆₀ are toxic to fish cells and cultured human cells (Oberdorster 2004; Sayes, Fortner et al. 2004), thus people may be more concerned about the potential exposure to C₆₀ if it is mobile in water. Besides, dissolved organic matter in groundwater has been reported to significantly enhance the transport of neutral organic contaminants (Kan and Tomson 1990). The release of C₆₀ and other nanosized carbonaceous nanomaterials into aqueous environments might have similar effect.

It has been reported that the existence of a small fraction of carbonaceous materials in nature could affect the transport and bioavailability of organic contaminants, due to their high adsorption capacity (Weissenfels, Klewer et al. 1992; McGroddy,
Farrington et al. 1996; Gustafsson, Haghseta et al. 1997; Chiou and Kile 1998; Bucheli and Gustafsson 2000). It is unknown whether the release of C\textsubscript{60} fullerene will significantly affect the transport and bioavailability of organic contaminants. Therefore, it is important to study the adsorptive interactions of carbonaceous nanomaterials, such as C\textsubscript{60} fullerene, with environmental contaminants.

Few studies (Ballesteros, Gallego et al. 2000; Mchedlov-Petrossyan, Klochkov et al. 2001) have addressed the adsorption of environmental organic contaminants with C\textsubscript{60} in aqueous media. In this study, C\textsubscript{60} aggregates with different size ranges were prepared and characterized. The adsorption and desorption of naphthalene and 1,2-dichlorobenzene, two common organic contaminants, with C\textsubscript{60} aggregates with different size ranges in aqueous solution was conducted and discussed. The phenomenon of desorption hysteresis has been observed and will be discussed in this chapter.
3.2 Materials and Methods

3.2.1 Materials

$C_60$ solids (purity > 99.5%) were purchased from SES Research (Houston, TX, USA). Toluene was purchased from Sigma-Aldrich with a purity of 99.8%. Tetrahydrofuran (THF, HPLC grade) used in this study was kept in the dark and was purged with nitrogen gas (Matheson UHP grade, 99.999%) after each use to prevent oxidation. Glass fiber filter membranes (Fisherbrand, 1 μm nominal pore size) were purchased from Fisher Scientific. 0.22 μm pore sized nylon filter membranes purchased from GE Osmonics Inc. Anodisc® filter membranes (20 nm pore size, Whatman) were used to separate nanoscaled $C_60$ particles from solution. The filter membrane is made of a high purity alumina matrix that is manufactured electrochemically. It has a precise, non-deformable honeycomb pore structure with no lateral crossovers between individual pores and therefore a sharp molecular weight cutoff.

$^{14}$C-radiolabeled naphthalene and $^{14}$C-radiolabeled 1,2-dichlorobenzene (1,2-DCB) with specific activities of 8.1 μCi/μmol and 8.8 μCi/μmol, respectively, were purchased from Sigma-Aldrich (St. Louis, MO) and were diluted in methanol (HPLC grade) to make stock solutions. Toluene was purchased from Sigma-Aldrich with a purity of 99.8%. Ready Safe or Ready Organic liquid scintillation cocktails for scintillation counting were supplied by Beckman Coulter, Inc. (Fullerton, CA). Biological grade sodium chloride and sodium azide (>98%) were purchased from Fisher Scientific and Eastman Kodak, respectively. Sodium azide was used to inhibit bacterial growth.
3.2.2 Methods

3.2.2.1 Preparation of C$_{60}$ aggregates with different size ranges

a) “C$_{60}$ Large Aggregates”.

Upon addition into water, the purchased C$_{60}$ black powders immediately formed aggregates with mean diameters in the micrometer range. These C$_{60}$ aggregates are referred to as “C$_{60}$ large aggregates” to differentiate from C$_{60}$ aggregates formed under other experimental conditions with different mean diameters discussed later in this chapter.

b) “C$_{60}$ Small Aggregates”.

When a water suspension of “C$_{60}$ large aggregates” is stirred vigorously with a Teflon coated stirring bar on a magnetic stirrer in the dark for two days or longer, the suspension turns very turbid with a yellow-brownish color. “C$_{60}$ large aggregates” were observed to have broken into smaller aggregates during prolonged stirring. These smaller aggregates are referred to as “C$_{60}$ small aggregates”.

c) “nC$_{60}$”.

When the purchased C$_{60}$ black powder was added into water and stirred, as discussed above, for several days to months, more “C$_{60}$ large aggregates” broke into smaller particles with sizes in the nanometer range. This turbid suspension was filtered with a 1 µm-pore-size glass fiber filter membrane (Fisherbrand, Fisher Scientific), and the resultant yellow supernatant was composed of water-stable nanometer sized aggregates of C$_{60}$ and are referred to as “nC$_{60}$”. This method of preparing “nC$_{60}$” is referred to as the “stirring method”.

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In this study, stable aqueous suspensions of “nC₆₀” were also prepared by two additional methods, similar to those described by Andrievsky et al. (1995) and Deguchi et al. (2001) and are referred to as the “sonication method” and the “THF method”, respectively.

For the sonication method, a solution of 560 mg/L C₆₀ was first prepared in toluene at room temperature. The solubility of C₆₀ in toluene is 2,800 mg/L (Taylor 1999). A total of 100 mL of 560 mg-C₆₀/l-toluene solution was added to the top of 200 ml of deionized water in a beaker. The mixture was then subjected to continuous sonication with a high-energy sonication probe (Sonifier® Cell Disruptor, W185D, Heat Systems-Ultrosonics, Inc., Farmingdale, NY) for about four hours in the dark until the mixture changed from a purplish emulsion to a yellowish suspension and the purple toluene layer on the top of the suspension evaporated. During the course of ultrasonic evaporation, a large fraction of C₆₀ aggregates (46.4 mg) was deposited on the inner wall or on the bottom of the beaker instead of being incorporated into nanoscale aggregates in water. The resultant nC₆₀ suspension was cooled and was filtered through a glass fiber filter membrane (1 μm nominal pore size, Fisherbrand, Fisher Scientific.) to remove larger aggregates.

For the THF method, about 100 mg of C₆₀ was added into 4 L THF. The solution was sparged with nitrogen (Matheson UHP grade, 99.999%) for 30 minutes and then sealed tightly and stirred overnight in the dark to dissolve C₆₀. The C₆₀ solubility in THF is approximately 9 mg/L (Deguchi, Alargova et al. 2001). A 500 mL sample of the C₆₀/THF solution was then filtered with a 0.22 μm nylon filter membrane (GE Osmonics Inc.) to remove undissolved C₆₀ and sparged with nitrogen for fifteen minutes. Deionized
water, 500 mL, was then added at a flow rate of about 100 mL/min to the C₆₀ saturated THF solution with vigorous mixing. The suspension was transferred into a rotary evaporator (Buchi Rotavapor R-200, Buchi Labortechnik AG, Flawil, Switzerland) to evaporate the THF. When the C₆₀/THF/water mixture volume was reduced to about 500 mL in about one hour, 200 mL DI water was added into the Rotavapor and the suspension volume was again reduced to about 500 mL. The suspension was diluted with another 200 mL DI water and then the evaporation was resumed for about 30 minutes until the final suspension volume was reduced to about 500 mL. The final suspension was filtered through glass fiber filter membrane (1 μm nominal pore size, Fisherbrand, Fisher Scientific.) and a suspension containing “nC₆₀” was obtained. A suspension containing higher concentrations of “nC₆₀” can be obtained by further concentrating the above suspension by evaporation.

3.2.2.2 Characterization of C₆₀

a) Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Images, and Particle Size Distribution Analysis.

A scanning electronic microscope (FEI XL-30 ESEM) was used to take images for “C₆₀ large aggregates” and “C₆₀ small aggregates”, and their approximate particle size ranges were estimated from the SEM images. The image of prepared “nC₆₀” in water suspension was produced using a transmission electronic microscope (JEOL FasTEM 2010). The TEM sample of nC₆₀ was prepared by evaporating several drops of nC₆₀ suspension on a 300-mesh carbon-coated copper grid. The particle size distribution of

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“nC₆₀” in the water suspension was analyzed using a photon correlation spectroscope (PCS System 4700 C, Malvern Instruments Inc., Southborough, MA).

b) Concentration Determination.

A calibration curve of solution absorbance at the wavelength of 407 nm, the characteristic peak for C₆₀, versus C₆₀ concentration was pre-established for C₆₀/toluene standard solutions on a UV-Vis Spectrophotometer (DR/4000, HACH Company, Loveland, CO). To measure the concentrations of “C₆₀ large aggregates” or “C₆₀ small aggregates” in the water suspension, a suspension was first filtered with a 20 nm pore size Anodisc® filter membrane (Whatman). The retained C₆₀ solids on the filter membrane were then dissolved in toluene. The absorbance of this resultant C₆₀/toluene solution was measured on the UV-Vis spectrophotometer at 407 nm. The concentration of C₆₀ in the toluene solution can be determined based on the pre-established calibration curve. Then the C₆₀ concentration in the original water suspension can be calculated.

The filtrate was scanned from the wavelength of 200 nm to 800 nm on the same spectrophotometer to verify there is no substantial C₆₀ passing through the filter membrane. It was observed that the absorbance of the filtrate was essentially zero from the wavelength of ~310 nm to 800 nm. Since the characteristic absorption peaks for C₆₀ has been observed to be at 336, 407, 540, and 595 nm (Beeby, Eastoe et al. 1994; Heymann, Bachilo et al. 2000; Bachilo, Benedetto et al. 2001; Weisman, Heymann et al. 2001; Fortner, Lyon et al. 2005), the method of filtration for C₆₀ concentration determination is considered to be appropriate.
The concentration of “nC₆₀” in their yellow water suspension was determined directly by the absorbance at 446 nm wavelength on the spectrophotometer. A series of nC₆₀ suspensions, prepared in the same batch, with different nC₆₀ concentrations were previously prepared. The absorbance of each suspension at 446 nm wavelength was measured on the spectrophotometer, and was plotted against the corresponding nC₆₀ concentration to obtain a calibration curve. Since a good correlation was obtained for the calibration curve (R²=0.999), concentrations of nC₆₀ in the yellow suspension was determined using this method. Suspensions of “nC₆₀” prepared in different batches have varied particle size distributions; therefore one calibration curve was prepared for each specific suspension.

3.2.2.3 Adsorption of Naphthalene from Aqueous Solution to “C₆₀ Large Aggregates”.

1 mg/ml C₆₀ suspension was prepared by mixing (100 ± 0.1) mg of C₆₀ fullerene in a beaker containing 100 ml of electrolyte solution. Five milliliters of C₆₀ suspension was added into each of the four 23 ml glass vials. Then ¹⁴C-radiolabeled naphthalene/methanol stock solutions were injected into the four vials with a microsyringe (Hamilton, Hamilton Company, Reno, Nevada) so that the initial naphthalene concentrations were (0.94, 1.91, 2.61, 3.72) µg/ml, respectively. The analysis of each sample of unknown concentration was repeated three times. The uncertainty of the initial naphthalene concentrations was less than ± 0.02 µg/ml, estimated by the standard deviation of the three replicated measurements. After filling with naphthalene electrolyte solutions, the headspace in each vial was typically less than.
0.1 ml. The volume fraction of methanol in solution phase in each vial was less than 0.004, which was not expected to affect the naphthalene adsorption. The vials were sealed with Teflon-septum caps and rotated end-over-end at about 1 rpm at room temperature for three days. Another four control vials were set up the same way as the four corresponding samples described above, except that no C\textsubscript{60} fullerene was added. At the end of the time period, samples and controls were filtered with 0.02 \( \mu \)m inorganic membrane filters (Anotop, Whatman Inc., Clifton, NJ, USA) and the filtrates were analyzed with a liquid-scintillation counter (Beckman Instruments Inc., Fullerton, CA, USA). The average sorption of naphthalene to the membrane filters was determined in a preliminary study to be 8.0 \%, with a standard error of \pm 0.4 \%. Thus, for those samples in which inorganic filters were used, the experimentally measured aqueous concentrations of naphthalene were corrected (by dividing the measured concentrations by 0.92) for the sorption to the filters. Solid phase naphthalene concentrations were calculated from the differences between the solution phase concentrations in the sample vials and that in the corresponding control vials.

3.2.2.4 Adsorption/Desorption of Naphthalene to/from “C\textsubscript{60} Small Aggregates”.

(21 \( \pm \) 0.1, and 24 \( \pm \) 0.1) mg of C\textsubscript{60} fullerene was added into two 28 ml glass centrifuge vials. A magnetic Teflon coated stirring bar was put in each vial. The two sample vials were then filled with electrolyte solutions (with \( \approx \) 0.1 ml headspace) and were sealed with Teflon-septum caps. Sample vials were stirred on a magnetic stirrer (Fisher Scientific.) at about 1000 rpm at room temperature for two days to produce “C\textsubscript{60} small aggregates”, as defined in earlier. Adsorption was then induced by injecting (10.0
and 17.5) μl of $^{14}$C-radiolabeled naphthalene stock solution (4990 ± 0.1 μg/ml) into the two sample vials, respectively. At the end of each adsorption step, 1 ml supernatant was sampled after centrifugation at 6000 rpm (IEC Centra MP4 Centrifuge, International Equipment) and analyzed with a scintillation counter. Successive adsorption steps were accomplished by adding identical aliquots of naphthalene stock solution and additional electrolyte solution (about 1 ml each time) to the vial to fill the headspace. Five or six adsorption steps were performed with the two samples; the time interval between adsorption steps was two days. At the end of the last adsorption step, multi-step desorption was induced by centrifugation and successively replacing each supernatant solution with naphthalene-free electrolyte solution. The time intervals between desorption steps varied from two to twenty-seven days. At the end of each desorption step, solution phase naphthalene concentration was analyzed by scintillation counting.

3.2.2.5 Adsorption/Desorption of Naphthalene to/from “nC$_{60}$”.

Batch reactors, consisting of EPA-certified glass vials (Fisher Scientific) with Teflon-septum caps, were used for adsorption and desorption experiments. At the beginning of the adsorption experiments, water suspensions of nC$_{60}$ (prepared by the sonication method, C$_{60}$ = 48 mg/L) were pipetted into seven 8-mL glass vials with PTFE septum and screw caps. A Teflon coated micro-stir bar was placed in each vial. Different volumes of $^{14}$C-radiolabeled naphthalene/methanol stock solutions were injected into the vials with a microsyringe so that the initial naphthalene concentrations were 1.10, 1.97, 2.20, 2.51, 3.30, 4.26, 5.11 μg/mL (sample nos. 3.1 to 3.7). Sample vials were closed tightly with headspace of less than 0.1 mL. The volume fraction of methanol in solution
phase in each vial was less than 0.002, which is not expected to affect the naphthalene adsorption. Another seven control vials were set up the same way as the sample vials except that no nC₆₀ was added. Control vials were designed to account for the loss of naphthalene from the aqueous phase due to volatilization or adsorption to the vessels. Sample vials and control vials were stirred slowly on magnetic stirrers in the dark at room temperature (25 ± 1 °C) for three days. At the end of each experiment, five milliliters of sample was filtered using an Anodisc® filter membrane. One milliliter filtrate was added to Ready-Safe® liquid scintillation cocktails and analyzed for naphthalene with Beckman liquid-scintillation counter (Beckman Instruments Inc., Fullerton, CA). The retention of naphthalene by Anodisc® filter membrane was measured by filtering 5 mL of naphthalene stock solution through the membrane, measuring the naphthalene concentration of the filtrate, and comparing the filtrate concentration with that of the stock solution. Approximately 8.0 ± 0.4 % of naphthalene was lost during the filtration step. Thus, for those samples in which Anodisc® filter membranes were used, experimentally measured aqueous naphthalene concentrations were divided by 0.92 to calculate the actual aqueous phase concentrations. About 1 mL of the solution in each control vial was also analyzed for aqueous phase naphthalene concentrations by liquid-scintillation counter. Naphthalene concentration in the control samples was 97.39 ± 0.11% of the original concentrations. Solid-phase naphthalene concentration in each sample vial was calculated from the difference between the solution phase naphthalene concentration in the sample vial and that in the corresponding control vial.

Desorption of naphthalene from nC₆₀ was measured for three of the seven adsorption samples (sample nos. 3.1, 3.3, 3.5). The suspension in each of these three
sample vials was filtered through Anodisc® filter membrane. The membrane containing C_{60} solids was put into a clean sample vial and naphthalene-free deionized water was added to each vial. The vials were sealed and put into a sonication bath (Solid State/Ultrasonic FS-14, Fisher Scientific) for 15 minutes to redisperse nC_{60}. Membranes were then removed carefully from the sample vials. Next, deionized water was added to each sample vial (with headspace < 0.1 mL) and samples were stirred in the dark at room temperature for three to seven days. Each of the membranes was then soaked in 1 mL of toluene to dissolve retaining C_{60}. This solution was analyzed using a UV/Vis spectrophotometer to quantify the amount of C_{60} remaining on the membrane. The loss of C_{60} during each filtration step was used to correct the mass of adsorbent in the next desorption experiment. The particle size distributions of the nC_{60} samples were measured by photon correlation spectroscopy to determine if the particle size distribution had changed. After being stirred for three to seven days, the suspension in each sample vial was filtered with Anodisc® filter membrane and aqueous phase naphthalene concentration was determined using liquid-scintillation counter. Three desorption steps were conducted for each of the three adsorption samples. Upon completion of the third desorption step, solid phase naphthalene concentrations were analyzed following filtration by dissolving C_{60} solids collected on each filter membrane in toluene. A portion of the resultant C_{60}/toluene solution was analyzed by liquid-scintillation counter to obtain solid phase naphthalene concentration. Another portion of the C_{60}/toluene solution was analyzed by UV-Vis spectrophotometry to determine C_{60} mass balance.

3.2.2.6 Adsorption/Desorption of 1,2-dichlorobenzene (1,2-DCB) to/from “nC_{60}”.

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Similar adsorption and desorption experiments of 1,2-DCB with nC\textsubscript{60} were conducted. Water suspensions of nC\textsubscript{60} (prepared by the THF method with C\textsubscript{60} concentration of 62.5 mg/L) were added to three 16-mL sample vials. A small aliquot of \textsuperscript{14}C-radiolabeled 1,2-DCB/methanol stock solution was injected into each vial with a microsyringe so that the initial 1,2-DCB concentrations were 0.89, 4.65, and 8.23 \mu g/mL, respectively. Adsorption and 3 steps of desorption were conducted with each of the 3 samples using a procedure similar to the naphthalene adsorption/desorption experiments.

3.2.2.7 Kinetics of Naphthalene Desorption from “nC\textsubscript{60}”.

Two 16-mL sample vials (sample nos. 3.8 and 3.9) were filled with nC\textsubscript{60} suspensions prepared by the THF method with C\textsubscript{60} concentration of 12.5 mg/L. A small aliquot of \textsuperscript{14}C-radiolabeled naphthalene/methanol stock solution was added into each vial so that the initial naphthalene concentrations were 8.62 and 8.67 \mu g/mL, respectively. Adsorption experiments were conducted using the same procedures as those for sample nos. 3.1 to 3.7. A total of three desorption steps were conducted with each of the two samples. During each desorption step, the time dependent naphthalene desorption was monitored periodically by measuring the aqueous phase naphthalene concentrations. At each time of sampling, 100 \mu L of the aqueous sample was filtered and the aqueous naphthalene concentration was measured by scintillation counting.

3.3 Results and Discussion

3.3.1 Characterization of C\textsubscript{60} aggregates and “nC\textsubscript{60}”
Figure 3.1 shows the SEM images of “C<sub>60</sub> large aggregates”. The formation of C<sub>60</sub> aggregates, with diameters around 20 to 50 µm, is clearly observed. Figure 3.2 is the SEM micrograph of “C<sub>60</sub> small aggregates” formed after stirring “C<sub>60</sub> large aggregates” in water for several days. These formed “C<sub>60</sub> small aggregates” looked more uniform compared to “C<sub>60</sub> large aggregates” and have the average size around 1 to 3 µm.

Representative transmission electron micrographs of “nC<sub>60</sub>” (Figure 3.3) further shows that instead of being spherical in shape (Andrievsky, Klochkov et al. 1999; Andrievsky, Klochkov et al. 2002), those “nC<sub>60</sub>” are faceted particles with sharp edges, as recently observed by Brant et al. and Fortner et al. (Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005). In this study TEM captured images indicated that most of the “nC<sub>60</sub>” have hexagonal or rectangular shaped cross sections. Fortner et al. (Fortner, Lyon et al. 2005) also observed circular and triangular shaped cross sections for “nC<sub>60</sub>” prepared using similar methods. Although those two shapes were not specifically captured in the TEM images shown here, “C<sub>60</sub> large aggregates” with triangular shaped cross sections were clearly shown in the SEM images (Figure 3.1). As pointed out by Brant et al., these particle characteristics may suggest the resemblance between the formation of C<sub>60</sub> aggregation and crystal growth (Brant, Lecoanet et al. 2005).

Particle size distributions for freshly prepared “nC<sub>60</sub>” by “stirring method”, “sonication method”, and “THF method”, respectively, were determined using photon correlation spectroscopy and are presented in Figure 3.4 (a), Figure 3.5 (a), and Figure 3.6 (a). The mean diameters (d<sub>m</sub>) for “nC<sub>60</sub>” prepared using the three methods are 342.9 nm, 165.2 nm, and 168.2 nm, respectively. The corresponding C<sub>60</sub> concentrations for the three samples are 52 mg/L, 48 mg/L, 65 mg/L, respectively.
In the study of adsorption and desorption of organic contaminants with “nC\textsubscript{60}”, as will be discussed later in this chapter, the water suspension of “nC\textsubscript{60}” was filtered and the “nC\textsubscript{60}” on the filter membrane resuspended into water to induce desorption experiments. The three “nC\textsubscript{60}” suspensions, as shown in Figure 3.4 (a), Figure 3.5 (a), and Figure 3.6 (a), were first stirred mildly in the dark for a week to simulate the adsorption process, and filtered with Anodisc\textsuperscript{®} filter membranes (20 nm pore size, Whatman). “nC\textsubscript{60}” retaining on the filter membrane were resuspended into water with a sonication bath. Finally the resuspended water suspension of “nC\textsubscript{60}” were stirred mildly in the dark again for another week to simulate the desorption process. After a week, the particle size distribution of the three suspensions (Figure 3.4 (b), Figure 3.5 (b), and Figure 3.6 (b)) was analyzed and compared with the original ones. It can be seen from Figure 3.4 to 3.6 that after going through the processes of stirring, filtration, resuspension, and restirring, there is negligible change of the mean particle diameter for the three suspensions: \(d_m\) of the particles prepared by stirring method changed from 342.9 nm to 345.4 nm, \(d_m\) of the particles prepared by sonication method changed from 165.2 nm to 166.2 nm, and \(d_m\) of the particles prepared by THF method changed from 168.2 nm to 167.3 nm. And all the suspensions remained relatively monodispersed.

It has been reported that “nC\textsubscript{60}” can be very stable in water for months with no substantial change in particle size distribution (Scrivens, Tour et al. 1994; Mchedlov-Petrosyan, Klochkov et al. 1997; Andrievsky, Klochkov et al. 1999; Deguchi, Alargova et al. 2001; Brant, Lecoanet et al. 2005). In contrast with “C\textsubscript{60} large aggregates” and “C\textsubscript{60} small aggregates”, which can be completely extracted from their water suspension into toluene and appear in the characteristic purple color of C\textsubscript{60}, “nC\textsubscript{60}” can not be extracted
substantially into nonpolar solvents, such as toluene. This indicates that $C_{60}$ forms some stable structure in water that alters its original hydrophobic property.

Addition of an electrolyte into the water suspension will coagulate those "nC$_{60}$" and make them precipitate from the water suspension (Mchedlov-Petrossyan, Klochkov et al. 1997; Wei, Wu et al. 1997; Alargova, Deguchi et al. 2001; Deguchi, Alargova et al. 2001; Andrievsky, Klochkov et al. 2002; Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005). In this study, "nC$_{60}$" coagulated when the background electrolyte concentration reached 0.2 M or higher, and this made the extraction of "nC$_{60}$" into toluene possible. This is consistent with the hypothesis that the stability of "nC$_{60}$" is a consequence of charge acquisition (Mchedlov-Petrossyan, Klochkov et al. 1997; Alargova, Deguchi et al. 2001; Deguchi, Alargova et al. 2001; Mchedlov-Petrossyan, Klochkov et al. 2001; Brant, Lecoanet et al. 2005; Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005)(+Andrievsky 2002). There was no $C_{60}$ coagulation or precipitation observed in nC$_{60}$ suspension with an ionic strength of 0.02 M (0.01 M NaCl and 0.01 M NaN$_3$) stored for one months after preparation, although other researchers found $C_{60}$ precipitation in an electrolyte solution with an ionic strength of 0.01 M (Brant, Lecoanet et al. 2005; Brant, Lecoanet et al. 2005).

The unique properties of "nC$_{60}$" in water suspension are related to the negative charge of their surfaces, which has been reported by numerous researchers (Mchedlov-Petrossyan, Klochkov et al. 1997; Alargova, Deguchi et al. 2001; Deguchi, Alargova et al. 2001; Mchedlov-Petrossyan, Klochkov et al. 2001; Brant, Lecoanet et al. 2005; Brant, Lecoanet et al. 2005; Fortner, Lyon et al. 2005). Many theories have been proposed to explained mechanisms of the surface charge of "nC$_{60}$" in water, for example, the
adsorption of ions, charge transfer, and water structuring (Mchedlov-Petrossyan, Klochkov et al. 1997; Deguchi, Alargova et al. 2001; Andrievsky, Klochkov et al. 2002; Brant, Lecoanet et al. 2005). Recently Brant and Lecoanet et al. characterized the charge characteristics of “nC₆₀” in electrolyte solutions (Brant, Lecoanet et al. 2005). They concluded, based on their work and a prior study (Andrievsky, Klochkov et al. 2002), that during the formation of “nC₆₀”, C₆₀ (electron acceptor) formed weak donor-acceptor complexes with water (electron donor) and the charge transfer through surface hydrolysis reactions may contribute to the overall surface charge of “nC₆₀” in water.

3.3.2 Adsorption of Naphthalene from Aqueous Solution to “C₆₀ Large Aggregates”.

As was discussed earlier, the term “C₆₀ large aggregates” is used to refer to the C₆₀ aggregates formed when adding purchased C₆₀ black powder into water or electrolyte solution. SEM micrographs showed that the average diameters of these “C₆₀ large aggregates” are from 20 to 50 μm.

The equilibrium data of naphthalene adsorption to “C₆₀ large aggregates” are plotted in Figure 3.7. The precision of the concentration measurements by scintillation counting was set to be less than ± 0.5 %. And the analysis of each sample was repeated at least three times and the uncertainty of the final solution phase naphthalene concentrations was calculated to be less than ± 0.05 μg/mL. At equilibrium, the solution-phase concentrations decreased by as little as 4.50% to 6.51%, indicating very little naphthalene was adsorbed to C₆₀ fullerene. Data are fitted with a linear isotherm in the form of \( q = K_p C_w \), where \( K_p \) (ml/g) denotes the partition coefficient of naphthalene.
(Schwarzenbach, Gschwend et al. 2003); \( q (\mu g/g) \) is the mass of naphthalene per unit mass of \( C_{60} \) at equilibrium; and \( C_w (\mu g/ml) \) is the naphthalene concentration in the solution phase at equilibrium. A \( K_p \) value of \( 10^{2.39} \) ml/g is obtained from adsorption data as plotted in Figure 3.7.

Since \( C_{60} \) solid presents a very hydrophobic surface, it was expected that \( C_{60} \) could be a preferred sorbent for many common organic compounds and adsorption to \( C_{60} \) was expected to be comparable to that on activated carbon, a commonly used adsorbent. Published \( K_{oc} \) (organic-carbon-based distribution coefficient) values for naphthalene sorption to various soils/sediments range from \( (10^{2.66} \text{ to } 10^{3.17}) \) ml/g-OC (Karickhoff, Brown et al. 1979; Lyman, Reehl et al. 1982; Abdul and Gibson 1986; Kan and Tomson 1990; Kan, Fu et al. 1994). The \( K_p \) value obtained for naphthalene adsorption to “\( C_{60} \) large aggregates” is considerably lower than either the \( K_p \) value of naphthalene sorption to activated carbon, or the \( K_{oc} \) value for naphthalene sorption to soil organic carbon. Ballesteros and co-workers (Ballesteros, Gallego et al. 2000) reported the chromatographic separation of organic compounds from aqueous solutions by \( C_{60} \) solids packed in a column study. A partition coefficient one order of magnitude lower than that found herein was calculated from their data.

3.3.3 Adsorption/Desorption of Naphthalene to/from “\( C_{60} \) Small Aggregates”.

The aqueous suspension of \( C_{60} \) turned very turbid with a yellow-brownish color after two days of vigorous stirring on a magnetic stirrer and \( C_{60} \) formed “\( C_{60} \) small aggregates” in water. SEM micrographs showed that \( C_{60} \) aggregation was clearly

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present, and the average size of the “C₆₀ small aggregates” formed was estimated to be 1
to 3 μm in diameter.

Successive adsorption/desorption experiments were conducted with two
separately stirred “C₆₀ small aggregates” samples. Adsorption data are fitted with
Freundlich isotherms (Figure 3.8, a and b) in the form of \( q = K_F C_w^n \), where \( K_F \) is the
Freundlich constant; \( n \) is the Freundlich exponent; \( q \) (μg/g) is the mass of sorbed
naphthalene per unit mass of sorbent at equilibrium; and \( C_w \) (μg/ml) is the naphthalene
concentration in the solution phase at equilibrium. Freundlich equations of
\[ q = 10^{4.28} C_w^{0.45} \] and \[ q = 10^{4.20} C_w^{0.45} \] are obtained for the two samples.

Since the adsorption isotherms for the “C₆₀ small aggregates” are Freundlich in
shape, this suggests that there must be a distribution of adsorption energies on the solid
particles in solution (Weber and Digiano 1996; Schwarzenbach, Gschwend et al. 2003),
which is different from the linear isotherms observed for the “C₆₀ large aggregates”.
Farrell, et al. (Farrell and Reinhard 1994) suggested that surface heterogeneities are the
most common origin of varying adsorption energies, and this would imply that the effect
of the two day vigorous stirring was to break up the aggregates of the commercial
material and, in the process, create disrupted surfaces of varying energies.

At \( C_w = 1 \) μg/ml, the solid-water distribution coefficients for naphthalene
adsorption to “C₆₀ small aggregates” \( (K_d = 10^{4.28} \text{ and } 10^{4.20} \text{ ml/g}) \) are about 1.8 ~1.9 log
units higher than the corresponding value for the “C₆₀ large aggregates” \( (10^{2.39} \text{ ml/g}) \). If
assuming spherical shape, the specific surface area can be estimated for both "C₆₀ large
aggregates" and "C₆₀ small aggregates", using the estimated particle diameters \( (20 \sim 50 \)
μm for "C₆₀ large aggregates" and \( 1 \sim 3 \) μm for "C₆₀ small aggregates"), and a density of
1.72 g/cm³ for C₆₀ (reported by SES Research Inc., 6008 West 34th, Houston, TX). The specific surface area for "C₆₀ large aggregates" is calculated to be 0.07 ~ 0.17 m²/g, which is similar to literature reported values of 0.08 ~ 0.16 m²/g (Davydov and Kalashnikova 1998; Rathousky and Zukal 2000); and the specific surface area for "C₆₀ small aggregates" is calculated to be 1.16 ~ 3.49 m²/g. The calculated specific surface area of "C₆₀ small aggregates" is over one order of magnitude higher than that of "C₆₀ large aggregates", and this might be the reason why adsorption of naphthalene to "C₆₀ small aggregates" was much stronger.

Desorption data for naphthalene from "C₆₀ small aggregates" are also presented in Figure 3.8, a and b. The apparent disagreement between the sorption and desorption isotherms suggests the occurrence of sorption "hysteresis". For these two samples, the solid-water distribution coefficient (Kₐ) values for the last desorption datum point equals to 10⁵.96 (ml/g) and 10⁵.75 (ml/g), respectively. Both Kₐ values are more than 1.5 log units higher than the corresponding Kₐ values for the last adsorption data points. By extrapolation of the desorption isotherms to the y-axes in Figure 3.8, a and b, intercept values of 10⁴.0 and 10³.9 µg-adsorbed naphthalene /g-C₆₀ can be obtained. These two quantities can be converted to mole ratio values of 1 mole of adsorbed naphthalene / (18~22) moles of C₆₀ solid, or 1 adsorbed naphthalene molecule / (18~22) C₆₀ molecules. This indicates that for every 18 to 22 C₆₀ molecules, there might be 1 naphthalene molecule "entrapped" in the C₆₀ molecules that is resistant to desorption. If these intercept values are taken as "non-desorbable", the slope of the desorption isotherm would be Kₐ(apparent) = 10³.64, and 10³.56 ml/g, very similar to the Kₐ(nc₆₀) = 10³.74, which will be discussed in the next section.
Among the few studies addressing the adsorptive properties of C_60 fullerene, Rathousky et al. observed hysteretic desorption in the adsorption/desorption of cyclopentane vapor to/from C_60 solids (Rathousky, Starek et al. 1993; Rathousky and Zukal 2000). They explained the observed hysteresis by the penetration of cyclopentane molecules into the bulk of C_60 crystals and possible entrapment of the adsorbate molecules. Interestingly, similar “entrapment” was also found in the preparation of C_60, where toluene and some other aromatics were commonly used as extraction solvents. Traces of toluene or other organic solvents were often found entrapped, or intercalated in C_60 lattice after removal of bulk toluene (Taylor 1999).

### 3.3.4 Adsorption/Desorption of Naphthalene to/from “nC_60”.

Data of naphthalene adsorption to nC_60 (sample nos. 3.1 to 3.7, Figure 3.9) can be fitted with a linear isotherm in the form of q (µg/g) = 10^{3.74} C_w (µg/ml), where the solid-water distribution coefficient K_d = 10^{3.74} ml/g (Figure 3.9). Data of naphthalene adsorption to “C_60 large aggregates” (mean diameter is 20 ~ 50 µm) and “C_60 small aggregates” (mean diameter is 1 ~ 3 µm) are included in Figure 3.9 for the purpose of comparison. As discussed in the preceding sections, data of naphthalene adsorption to “C_60 large aggregates” were fitted with a linear isotherm with the value of the solid-water distribution coefficient (K_d) equal to 10^{2.39} ml/g. Data of naphthalene adsorption to “C_60 small aggregates” can be fitted with a Freundlich isotherm in the form of q = 10^{4.28} C_w^{0.45}, where q and C_w are in the units of µg/g and µg/ml, respectively. To compare naphthalene adsorption to the above mentioned three forms of C_60 aggregates, it can be predicted from the adsorption isotherms that at C_w = 1 µg/ml, the adsorbed naphthalene concentration
would be $10^{3.39}$ µg/g on "C₆₀ large aggregates", $10^{4.28}$ µg/g on "C₆₀ small aggregates", and $10^{3.74}$ µg/g on nC₆₀.

Data of naphthalene adsorption to nC₆₀ (sample nos. 3.1 to 3.7 and 3.8 and 3.9) and 3 steps of desorption for sample nos. 3.1, 3.3, 3.5, 3.8 and 3.9 are plotted in Figure 3.10, on a logarithmic scale. As is shown in Figure 3.10, within the time frame of these experiments, desorption of naphthalene from nC₆₀ is highly hysteretic, i.e., desorption isotherm for each sample is not the reverse of the corresponding adsorption isotherm. For each sample, the solid-water distribution coefficient value ($K_d = q/C_w$) increased during the desorption process. The $K_d$ values for the last desorption data points for the five samples are $10^{5.82}$, $10^{5.73}$, $10^{5.74}$, $10^{5.55}$, and $10^{5.61}$ ml/g, respectively, each of which is about two orders of magnitude higher than the corresponding adsorption $K_d$ value ($10^{3.74}$ ml/g). Interestingly, desorption of naphthalene from "C₆₀ small aggregates" also shows hysteresis with $K_d$ values for the last desorption data points of $10^{5.78}$ and $10^{5.75}$ ml/g, similar to that of nC₆₀. It might be observed that the average of the desorption log $K_d$ values is $10^{5.87}$ ml/g, which is a little less than 2 times the log $K_d_{ads}$ values, as might be expected for interaction on two sides of naphthalene when entrapped (Kan, Fu et al. 1994).

As was discussed in the previous section, the phenomenon of sorption hysteresis was also observed in the preparation of C₆₀, where traces of toluene or other organic solvents were often found entrapped, or intercalated, in the C₆₀ lattice after removal of bulk toluene (Taylor 1999). Sorption hysteresis was also observed in the adsorption and desorption of cyclopentane vapor with C₆₀ solids, possibly caused by the penetration and
3.3.5 Adsorption/Desorption of 1,2-dichlorobenzene (1,2-DCB) to/from “nC_{60}”.

Adsorption and desorption of 1,2-dichlorobenzene (1,2-DCB) with nC_{60} were conducted similarly to the ones with naphthalene and data are plotted in Figure 3.11, on a logarithmic scale. Data of 1,2-DCB adsorption to nC_{60} are fitted with a linear isotherm \( q (\mu g/g) = 10^{3.48} C_w (\mu g/ml) \). To compare the \( K_d \) value of 1,2-DCB with that of naphthalene, the value of \( K_{d,naph} \) is about 1.6 times higher than \( K_{d,1,2\text{DCB}} \), which is not considered to be a significant difference. This similarity is consistent with the similar \( K_{ow} \) values between 1,2-DCB \( (K_{ow} = 10^{3.40}) \) and naphthalene \( (K_{ow} = 10^{3.33}) \) (Schwarzenbach, Gschwend et al. 2003).

Data of three steps of desorption for each sample are plotted in Figure 3.11, as well. It can be seen from the figure that desorption of 1,2-DCB from nC_{60} is hysteretic, similar to what was observed in naphthalene desorption from nC_{60}. The solid-water distribution coefficient value \( (K_d = q/C_w) \) for each sample increased during the desorption process. The \( K_d \) values for the last desorption data points for the three samples are \( 10^{5.52} \), \( 10^{5.34} \) and \( 10^{5.29} \) ml/g, respectively, each of which is about two orders of magnitude higher than the corresponding adsorption \( K_d \) value \( (10^{3.48} \) ml/g).

Black carbon refers to a chemically heterogeneous, biologically refractory class of carbon compounds produced by the incomplete combustion of fossil fuels or biomass. It contains over 60% carbon (Goldberg 1985; Masiello and Druffel 1998). Black carbon particles, such as coals, charcoal, soot, or char, are ubiquitous in sediments and soils.
(often contributing 1 to 10% of $f_{oc}$ (Gustafsson and Gschwend 1998; Schwarzenbach, Gschwend et al. 2003)), where they exhibit a high affinity for many organic pollutants, particularly for planar aromatic compounds (Schwarzenbach, Gschwend et al. 2003). Black carbon particles tend to sorb hydrophobic organic compounds more strongly on an organic carbon basis than macromolecular forms of natural organic matter (e.g. humic substances) (Gustafsson, Haghseta et al. 1997; Kleineidam, Rugner et al. 1999; Bucheli and Gustafsson 2000; Ghosh, Gillette et al. 2000; Karapanagioti, Kleineidam et al. 2000; Accardi-Dey and Gschwend 2002; Kleineidam, Schuth et al. 2002; Braida, Pignatello et al. 2003; Cornelissen and Gustafsson 2004; Cornelissen and Gustafsson 2005; Lohmann, Macfarlane et al. 2005). Therefore, black carbon particles are believed to play an important role in the fate of organic contaminants in soils and aquatic sediments, as well as in atmospheric chemistry (Sander and Pignatello 2005; Zhu and Pignatello 2005).

$C_{60}$ is a spherical shaped molecule consisting of 60 $sp^2$-hybridized carbon atoms, each of which is connected by a bond to exactly three neighbor atoms (Billups and Ciufolini 1993; Taylor 1999). Unlike graphite, which is comprised of layers of hexagonal carbon sheets, some of carbon atoms in $C_{60}$ are connected together in pentagons, which allow the carbon sheet to curve into the shape of a sphere (Booker and Boysen 2005). Black carbon consists primarily of stacked, condensed, and disordered polycyclic aromatic sheets (Goldberg 1985; Palotas, Rainey et al. 1996; Harris and Tsang 1997; Schmidt and Noack 2000; Gustafsson, Bucheli et al. 2001). These sheets vary in size (between a few to several tens of fused rings) and the extent to which pentagonal (i.e. fullerene-like) and heptagonal rings are dispersed throughout the hexagonal carbon framework (Harris 1999; Sander and Pignatello 2005). Since there is structural similarity
between C_{60} and black carbon, it is possible that C_{60}, like black carbon, might also play
an important role in the environmental fate of organic contaminants, such as PAHs in
soils sediments. Therefore, the sorption affinity of naphthalene and 1,2-DCB with C_{60}, in
different aggregation sizes, observed in this study was compared with that of black
carbon reported in the literature. In Table 3.1 are listed the results of logK_{oc} values of
naphthalene and 1,2-dichlorobenzene (1,2-DCB) for black carbon materials or natural
soil organic carbon (soil OC) in literature, and compared with that obtained in the present
work. It can be seen that at C_w = 1 \mu g/ml, reported K_d values for naphthalene sorption to
black carbon materials, including soot, charcoal, and lignite coke ranged from 10^{4.3} to
10^{6.82} \text{ ml/g}, which is in the same order of magnitude with the K_d value for naphthalene
sorption to “C_{60} small aggregates” (K_d = 10^{4.28} \text{ ml/g}) observed in this study. The K_d
value for naphthalene sorption to “nC_{60}” (K_d = 10^{3.74} \text{ ml/g}) is between the K_d values for
naphthalene sorption to soil OC reported in the literature (ranged from 10^{2.85} to 10^{3.51}
\text{ ml/g}), and that of black carbon materials. The K_d value for 1,2-DCB sorption to “nC_{60}”
(K_d = 10^{3.48} \text{ ml/g}) is about 10 to 20 times smaller than that of charcoal and lignite coke
(Kleineidam, Schuth et al. 2002). The reported K_d value for 1,2-DCB sorption to
activated carbon (K_d = 10^{5.44} \text{ ml/g}) (Kleineidam, Schuth et al. 2002) is almost two orders
of magnitude higher than that of “nC_{60}”, obtained in this work.

It has been observed by numerous research groups that the sorption of
hydrophobic organic compounds to natural soils and sediments exhibits hysteresis
between the sorption and desorption branches of the isotherm (Di Toro and Horzempa
1982; Karickhoff and Morris 1985; Pignatello and Huang 1991; Fu, Kan et al. 1994; Kan,
Fu et al. 1994; McGroddy, Farrington et al. 1996; Pignatello and Xing 1996; Huang and

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Weber 1997; Huang, Yu et al. 1998; Kan, Fu et al. 1998; Weber, Huang et al. 1998; Chen, Kan et al. 1999; Chen, Kan et al. 2000; Kan, Chen et al. 2000; Xia and Pignatello 2001). When hysteresis occurs, the sorbate characteristically shows greater apparent affinity for the solid in the desorption direction. Sorption hysteresis was observed in this work in naphthalene sorption to both “C60 small aggregates” and “nC60”, and it occurs in the 1,2-DCB sorption to “nC60” as well. The phenomenon of sorption hysteresis has important implications for the fate and hazardous effects of contaminants in the environment. Models dealing with physical and biological availabilities of contaminants typically assume sorption to be reversible, i.e., adsorption and desorption of the sorbate follows the same route. The sorption coefficients used in such models are based on forward-constructed sorption isotherms. If sorption is irreversible (“irreversible” here does not mean that the sorbate will not desorb, but that sorption and desorption follow different mechanistic pathways) (Lu and Pignatello 2002), i.e., if sorption hysteresis occurs these models may not correctly predict the fate and biological effects of a contaminant. It has been found that many soils or sediments contain various carbonaceous materials such as soot, hard coals, charcoals, which might behave differently from other soil organic carbon and might contribute significantly to the sorption hysteresis, or resistant release of organic compounds (McGroddy and Farrington 1995; Chiou and Kile 1998; Bucheli and Gustafsson 2000; Xia and Pignatello 2001; Braida, Pignatello et al. 2003). As more and more carbonaceous nanomaterials have been and will be manufactured, they will begin to appear in large amounts in soils and sediments, where they could possible affect the environmental fate and transport of organic contaminants. Therefore, it is important to investigate the sorption interaction of
new carbonaceous nanomaterials such as \( C_{60} \) fullerene with environmental organic contaminants such as naphthalene.

The mechanisms of sorption hysteresis has been studied for many years (Kraemer 1931; Foster 1932; McBain 1935; Cohan 1944; Everett and Whitton 1955; Bailey, Cadenhead et al. 1971; Burgess, Everett et al. 1989). Particularly, "capillary condensation" has been acknowledged to be the reason for the occurrence of sorption hysteresis in solids with mesopores (diameters between \( 20 \) and \( 500 \) Å (Farrell and Reinhard 1994)). While sorption hysteresis occurs in solids with micropores (diameters < \( 20 \) Å (Farrell and Reinhard 1994)) it is usually associated with a distortion of the solid with some irreversible change to the pore structure (Everett 1967; Bailey, Cadenhead et al. 1971; Burgess, Everett et al. 1989; Lu and Pignatello 2002; Braida, Pignatello et al. 2003). The mechanism of pore deformation in carbonaceous materials has been discussed by many researchers, among which pore dilation in carbonaceous sorbents caused by packing effects of adsorbate molecules (Olivier 1998) and the possible swelling of soot by methanol (Bucheli and Gustafsson 2000) have been observed. In many cases, the deformed pore structure did not recover to its original state even when the adsorbate was removed from the adsorbent. A minimum requirement for true adsorption/desorption hysteresis to occur is that the adsorbent surface structure can undergo physical-chemical rearrangement upon adsorption, i.e., after adsorbent rearrangement, desorption would take place in a different molecular environment from adsorption (Adamson and Gast 1997). For example, Braida et al. studied the sorption hysteresis of benzene in charcoal particles recently and concluded that the observed hysteresis is due to pore deformation by the solute and entrapment of some adsorbate as
the polyaromatic scaffold collapses during desorption (Braida, Pignatello et al. 2003). Besides, as mentioned before, entrapped toluene solvent molecules and cyclopentane molecules were observed in C_{60} solids. Since hysteresis was observed in the desorption of naphthalene and 1,2-DCB from both "C_{60} small aggregates" and "nC_{60}”, both “capillary condensation” and pore deformation could have occurred. Due to the different aggregation sizes and therefore intraparticle pore sizes in "C_{60} small aggregates" and "nC_{60}”, observed sorption hysteresis might be associated with “capillary condensation” in mesopores consisting of the interstices between microporous sub-structures, similar to that discussed by Burgess, et al., (Burgess, Everett et al. 1989).

The observed higher sorption affinity at the desorption branch may represent the concept of “two-compartment” sorption processes observed by numerous researchers: the “reversible” adsorption/desorption compartment, where naphthalene adsorbs to the external surfaces of C_{60} crystals and desorbs reversibly, and the “irreversible” adsorption/desorption compartment, where naphthalene penetrates into micropores in C_{60} crystals and may be “entrapped” and thus resistant to desorption. The fact that extensive stirring apparently does not slowly release “entrapped” naphthalene might suggest that the “entrapped” naphthalene could be a new entity, which might no longer be susceptible to desorption in the normal aqueous desorption. The impact of not stirring on desorption will be discussed in Chapter 5, on column transport study.

Consistent with many of those studies, a two-compartment irreversible sorption model has been proposed by Kan et al. to explain the phenomenon of sorption/desorption hysteresis (Kan, Fu et al. 1998). A reversible compartment and an irreversible compartment have been proposed to be responsible for the complete desorption process.
In the reversible compartment, chemicals could be readily and reversibly desorbed; while in the irreversible compartment, desorption of organic compounds could be hindered (Kan, Chen et al. 2000). The desorption distribution coefficient in the irreversible compartment was reported to be related directly to soil organic carbon content and has a value of $K'_{OC} = 10^{5.92}$ ml / g-OC for a wide range of hydrophobic organic compounds (Chen, Kan et al. 2002). It was observed in this work that naphthalene desorption $K_d$ values for the last desorption data points for "C60 small aggregates" were $10^{5.96}$ ml/g and $10^{5.75}$ ml/g, naphthalene desorption $K_d$ values for the last desorption data points for "nC60" were in the range of $10^{5.55}$ to $10^{5.82}$ ml/g, and 1,2-DCB desorption $K_d$ values for the last desorption data points for "nC60" were in the range of $10^{5.29}$ to $10^{5.52}$ ml/g. Interestingly, all these desorption $K_d$ values are in the same order of magnitude with that of $K'_{OC}$, possibly indicating the similar mechanisms for desorption from C60 and soil organic carbon materials.

3.3.6 Kinetics of Naphthalene Desorption from nC60.

The recorded naphthalene concentrations with time in the desorption process from nC60 were fitted with the empirical two-compartment first-order kinetics model (Cornelissen, Van Noort et al. 1997):

$$\frac{q_t}{q_0} = F_1 e^{-k_1 t} + F_2 e^{-k_2 t}$$ (3.1)

in which $q_t$ and $q_0$ (µg/g) are the C60-adsorbed naphthalene concentrations at time $t$ (day) and at the start of the experiment, respectively; $F_1$ and $F_2$ are the fractions of
naphthalene present in the two kinetically different desorbing compartments; $k_1$ and $k_2$ (day$^{-1}$) are the first-order rate constants for the two desorption compartments.

In Figure 3.12 $q_t/q_0$ vs. time (t, days) for desorption of naphthalene from nC$_{60}$ (sample nos. 3.8 and 3.9) are plotted. The solid lines were obtained by curve fitting experimental data with the two compartment first-order kinetic model (Eq. (3.1)) using Sigma-Plot. Parameters obtained by Sigma-Plot curve fitting are listed in Table 3.2.

It is shown that desorption data are fitted well with the two-compartment kinetic model. The standard deviations of $k_1$ values are large at the second and third desorption steps, since the majority of the adsorbed naphthalene is in the slow desorption domain. Three-step desorption experiments were conducted with both samples and with each step, desorption data were fitted with Eq. (3.1), which assumes a rapidly desorbed compartment and a slowly desorbed compartment. In the first desorption step for both samples, the fraction of naphthalene in the first compartment is relatively high ($F_1 = 29.63$ and $25.81 \%$). In the second and third desorption steps, over 90% of the desorption occurred from the second compartment ($F_2 \geq 90\%$). This indicates that at desorption step 1, a larger fraction of the sorbate mass desorb from the rapid compartment, while at desorption step 2 and 3, sorbate mass desorbs primarily from the slow desorption compartment. The rate constants for desorption from the first compartment ($k_1$) are relatively high, from 11.80 to 27.40 day$^{-1}$, while rate constants for desorption from the second compartment ($k_2$) range from 0.04 to 0.13 day$^{-1}$, more than two orders of magnitude lower than the corresponding $k_1$ value for each desorption step. It can been seen from Figure 3.12 that for each desorption step, the slopes of the $q_t/q_0$ vs. t curves
decrease gradually with time, indicating greater and greater resistance to desorption, as expected.

### 3.4 Conclusions

The virtually water-insoluble C$_{60}$ can be dispersed in water and form water-stable nanoscale aggregates (nC$_{60}$) by different methods, including extensive stirring in water without addition of any organic solvents. The surface of the formed nC$_{60}$ have net negative charges. The study of adsorption and desorption of naphthalene and 1,2-dichlorobenzene with C$_{60}$ is reported in this chapter. The different sizes of C$_{60}$ aggregates, formed under different conditions, could affect the adsorption of naphthalene by orders of magnitude. Desorption of both naphthalene and 1,2-dichlorobenzene from nC$_{60}$ exhibits hysteresis. Kinetic data of naphthalene desorption from nC$_{60}$ further indicates that desorption of naphthalene from C$_{60}$ aggregates is composed of two compartments: a labile desorption compartment, where naphthalene can be readily desorbed; and a resistant desorption compartment, where naphthalene may be entrapped in C$_{60}$ aggregates and desorption is hindered.
Table 3.1. Comparison of logK_{oc} values of naphthalene and 1,2-dichlorobenzene (1,2-DCB) adsorption to black carbon materials, activated carbons, or natural soil organic carbon (soil OC) in previous studies and the present work.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Carbon Material</th>
<th>Chemical</th>
<th>logK_{oc} at C_w = 1µg/L</th>
<th>logK_{oc} at C_w = 1mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bucheli and Gustafsson 2000)</td>
<td>Soot</td>
<td>Naphthalene</td>
<td>10^{5.16} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Accardi-Dey and Gschwend 2003)</td>
<td>Black carbon in Boston Harbor sediment</td>
<td>Naphthalene</td>
<td>10^{5.2} l/kg</td>
<td>10^{4.3} l/kg</td>
</tr>
<tr>
<td>(Zhu and Pignatello 2005)</td>
<td>Charcoal</td>
<td>Naphthalene</td>
<td>10^{4.81} l/kg</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2-DCB</td>
<td>10^{4.54} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Zhu and Pignatello 2005)</td>
<td>Graphite</td>
<td>Naphthalene</td>
<td>10^{2.62} l/kg</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2-DCB</td>
<td>10^{2.47} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Kleineidam, Schuth et al. 2002)</td>
<td>Charcoal</td>
<td>1,2-DCB</td>
<td></td>
<td>10^{5.44} l/kg</td>
</tr>
<tr>
<td></td>
<td>Lignite coke</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Activated carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Xia and Ball 1999; Schwarzenbach, Gschwend et al. 2003)</td>
<td>Black carbon</td>
<td>Naphthalene</td>
<td>10^{3.03} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Schwarzenbach, Gschwend et al. 2003)</td>
<td>Soil OC</td>
<td>Naphthalene</td>
<td>10^{2.94} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Lu and Pignatello 2004)</td>
<td>Soil OC</td>
<td>Naphthalene</td>
<td>10^{3.11} l/kg, 10^{2.86} l/kg, 10^{3.51} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Zhu, Hyun et al. 2004)</td>
<td>Soil OC</td>
<td>Naphthalene</td>
<td>10^{3.39} l/kg</td>
<td></td>
</tr>
<tr>
<td>(Kan and Tomson 1990)</td>
<td>Soil OC</td>
<td></td>
<td>10^{3.85} l/kg</td>
<td></td>
</tr>
<tr>
<td>Present research</td>
<td>C_{60} small aggregates</td>
<td>Naphthalene</td>
<td>10^{5.93} l/kg</td>
<td>10^{4.28} l/kg</td>
</tr>
<tr>
<td>Present research</td>
<td>nC_{60}</td>
<td>Naphthalene</td>
<td>10^{3.70} l/kg</td>
<td>10^{3.74} l/kg</td>
</tr>
<tr>
<td>Present research</td>
<td>nC_{60}</td>
<td>1,2-DCB</td>
<td>10^{3.48} l/kg</td>
<td>10^{3.48} l/kg</td>
</tr>
</tbody>
</table>
Table 3.2. Parameters of fitting kinetics data of naphthalene desorption from nC₆₀ to Eq. (3.1) using Sigma-Plot.

<table>
<thead>
<tr>
<th>Sample No. 3.1</th>
<th>Des step 1</th>
<th>Des step 2</th>
<th>Des step 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F₁</td>
<td>k₁ (d⁻¹)</td>
<td>F₂</td>
</tr>
<tr>
<td>Sample No. 3.1</td>
<td>0.296 ± 0.023</td>
<td>14.348 ± 4.020</td>
<td>0.704</td>
</tr>
<tr>
<td>Sample No. 3.1</td>
<td>0.095 ± 0.031</td>
<td>14.172 ± 12.086</td>
<td>0.905</td>
</tr>
<tr>
<td>Sample No. 3.1</td>
<td>0.083 ± 0.005</td>
<td>15.532 ± 3.529</td>
<td>0.917</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No. 3.2</th>
<th>Des step 1</th>
<th>Des step 2</th>
<th>Des step 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F₁</td>
<td>k₁ (d⁻¹)</td>
<td>F₂</td>
</tr>
<tr>
<td>Sample No. 3.2</td>
<td>0.258 ± 0.019</td>
<td>21.067 ± 6.151</td>
<td>0.742</td>
</tr>
<tr>
<td>Sample No. 3.2</td>
<td>0.076 ± 0.027</td>
<td>27.396 ± 36.057</td>
<td>0.924</td>
</tr>
<tr>
<td>Sample No. 3.2</td>
<td>0.056 ± 0.004</td>
<td>11.804 ± 2.970</td>
<td>0.944</td>
</tr>
</tbody>
</table>
Figure 3.1. SEM images of "C_{60} large aggregates".

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Figure 3.2. SEM images of "C₆₀ small aggregates".
Figure 3.3. TEM images of “nC$_{60}$”. The scale bars in the three pictures are 20 nm, 20 nm, and 50 nm, respectively.
Figure 3.4. Particle size distribution of nC$_{60}$ prepared by “stirring method”. $d_m$ (nm) is the mean diameter of nC$_{60}$; $f$ (%) is the fraction of scattered light intensity. (a) Freshly prepared, $d_m = 342.87$ nm; (b) after going through the process of stirring $\rightarrow$ filtration $\rightarrow$ resuspension $\rightarrow$ stirring, $d_m = 345.42$ nm.
Figure 3.5. Particle size distribution of nC_{60} prepared by “sonication method”. $d_m$ (nm) is the mean diameter of nC_{60}; $f$ (%) is the fraction of scattered light intensity. (a) Freshly prepared, $d_m = 165.17$ nm; (b) after going through the process of stirring $\rightarrow$ filtration $\rightarrow$ resuspension $\rightarrow$ stirring, $d_m = 166.23$ nm.

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Figure 3.6. Particle size distribution of nC₆₀ prepared by "THF method". $d_m$ (nm) is the mean diameter of nC₆₀; $f$ (%) is the fraction of scattered light intensity. (a) Freshly prepared, $d_m = 168.24$ nm; (b) after going through the process of stirring $\rightarrow$ filtration $\rightarrow$ resuspension $\rightarrow$ stirring, $d_m = 167.26$ nm.
Figure 3.7. Plot of experimental data of naphthalene adsorption to “C₆₀ large aggregates”. ♦, Experimental data; solid line, linear isotherm.
Figure 3.8. Plot of experimental data of naphthalene adsorption to and desorption from ‘C₆₀ small aggregates’. ♦, adsorption data; 0, desorption data; solid lines, Freundlich isotherms.
Figure 3.9. Naphthalene adsorption to “C₆₀ large aggregates”, “C₆₀ small aggregates” and nC₆₀ (sample nos. 3.1 to 3.7). ■, Naphthalene adsorption to “C₆₀ large aggregates” (same data as those in Figure 3.7); ♦, Naphthalene adsorption to “C₆₀ small aggregates” (same as the adsorption data in Figure 3.8 (a)); ▲, Naphthalene adsorption to nC₆₀ (sample nos. 3.1-3.9)
Figure 3.10. Adsorption and desorption of naphthalene with nC₆₀. ♦, adsorption of naphthalene to nC₆₀, sample nos. 3.1 to 3.9; ○, □, Δ, o and +, desorption of naphthalene from nC₆₀, sample nos. 3.1, 3.3, 3.5, 3.8 and 3.9, respectively. Straight line, a linear isotherm in the form of $q \text{(µg/g)} = 10^{3.74}C_w \text{(µg/mL)}$. 

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Figure 3.11. Adsorption and desorption of 1,2-DCB with nC₆₀. ◆, adsorption of 1,2-DCB to nC₆₀; ○, □, Δ, desorption of 1,2-DCB from nC₆₀ (3 steps of desorption for each of 3 samples). Straight line, a linear isotherm in the form of \( q (\mu g/g) = 10^{3.48} C_w (\mu g/mL) \).
Figure 3.12. Plot of $q_t/q_0$ vs. $t$ (days) for naphthalene desorption from nC$_{60}$ (sample nos. 3.8 and 3.9). $\Diamond$, sample no. 3.8; $\Delta$, sample no. 3.9. Solid lines were obtained from Sigma-Plot using the two-compartment first-order kinetics model (Eq. (3.1)).
CHAPTER 4

NAPHTHALENE 1,2-DICHLOROBENZENE ADSORPTION AND DESORPTION FROM C_{60}, ACTIVATED CARBON, AND SOIL ORGANIC CARBON — SORPTION MODELING

4.1 Introduction

The sorption of hydrophobic organic contaminants by soils and sediments is reported to be predominated by partitioning of dissolved solute between water and naturally occurring organic matter. Therefore, linear partitioning models have been used to describe sorption of those sorption processes (Chiou, Peters et al. 1979; Karickhoff, Brown et al. 1979; Means, Wood et al. 1980; Karickhoff 1981; Schwarzenbach and Westall 1981; Chiou, Porter et al. 1983). However, this simple partitioning model has been shown to be inconsistent with observed sorption behavior, for example, nonlinear sorption isotherms and hysteretic desorption are often observed in studies (Di Toro and Horzempa 1982; Miller and Weber 1986; Pignatello 1990; Weber, McGinley et al. 1992; Carroll, Harkness et al. 1994; Kan, Fu et al. 1994; Young and Weber 1995; Allen-King, Groenevelt et al. 1996; Weber and Huang 1996; Kan, Fu et al. 1998). In these cases, the relationship between sorbed concentrations and dissolved concentrations of each hydrophobic organic contaminant can not be described by a single linear isotherm.

As discussed in Chapter 3, desorption hysteresis was observed for the adsorption and desorption of naphthalene and 1,2-dichlorobenzene with three forms of carbon, i.e., C_{60}, activated carbon, and soil organic carbon. As a result, experimental data can not be fitted with a single linear isotherm. In this chapter, experimental adsorption-desorption data are fitted with different sorption models, including Freundlich model, Langmuir
model, two-compartment dual-equilibrium desorption model (DED), and Polanyi-Manes sorption model. Model fitting is compared for different models.
4.2 Materials and Methods

4.2.1 Materials

Activated carbon particles were originally obtained from Calgon Carbon Corp. (Pittsburgh, PA). The sediment used in this study was obtained from the Anacostia River in Washing D.C. area. The sediment was first dried at room temperature followed by pulverization with a pestle and mortar. The organic carbon content of the Anocostia sediment was measured by Micromeritus to be 3.7%.

$^{14}$C-radiolabeled naphthalene with specific activities of 8.1 $\mu$Ci/\mu mol was purchased from Sigma-Aldrich (St. Louis, MO) and was diluted in methanol (HPLC grade) to make stock solutions. Ready Safe liquid scintillation cocktail for scintillation counting was supplied by Beckman Coulter, Inc. (Fullerton, CA). Biological grade sodium chloride and sodium azide (>98%) were purchased from Fisher Scientific. and Eastman Kodak, respectively. Sodium azide was used to inhibit bacterial growth. Anodisc® filter membranes (20 nm pore size, Whatman) were used to separate nanoscaled C$_{60}$ particles from solution. The filter membrane is made of a high purity alumina matrix that is manufactured electrochemically. It has a precise, non-deformable honeycomb pore structure with no lateral crossovers between individual pores and therefore a sharp molecular weight cutoff.

4.2.2 Methods

4.2.2.1 Adsorption and Desorption of Naphthalene to and from “As-Received Activated Carbon Particles”.

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To study naphthalene adsorption and desorption with as-received activated carbon particles (Calgon Carbon Corp), 5 sample vials were used, each filled with 40 mg of activated carbon and 42 ml of deionized water. $^{14}$C-radiolabeled naphthalene/methanol stock solution was injected into each sample vial with a microsyringe so that initial naphthalene concentrations in the vials would be 0.97, 1.94, 2.93, 4.86, and 9.55 μg/ml, respectively. The samples were then stirred mildly for at least three days for the adsorption equilibrium. At the end of the adsorption, samples were centrifuged at 6000 rpm on a centrifuge and the supernatants were analyzed on a liquid-scintillation counter to determine the aqueous naphthalene concentrations. Over 95% of the supernatants were then removed from each sample vial. Deionized water was filled into each vial (leaving < 0.1 ml headspace) to induce the first step of desorption. Multi-step desorptions were induced similarly. At the end of each desorption step, solution-phase naphthalene concentrations were analyzed on a liquid-scintillation counter. The equilibrium time for each desorption step varied from 3 days for the first desorption step, to 14 days for the last desorption step.

4.2.2.2 Adsorption and Desorption of Naphthalene to and from “nano-activated carbon particles” (“nano-AC particles”) in water.

In the laboratory, the purchased activated carbon particles were first added into deionized water to a concentration of about 0.5 mg/ml, and the suspension was then subjected to sonication for about 1 – 2 hours with the high-energy sonication probe. A portion of the activated carbon particles were broken into nanometer sized particles after the prolonged sonication. The resulting suspension was filtered through a 0.45 μm pore
size filter membrane (Millipore). The nanometer sized activated carbon particles in the filtrate were used as sorbent for sorption of naphthalene and are referred to as “nano-AC particles”. The concentration of the obtained “nano-AC particles” in water was measured by TOC analyzer to be 12.35 mg/l.

Water suspensions containing 0.2 mg of “nano-AC particles” were added into each of four 16 ml glass vials. $^{14}$C-radiolabeled naphthalene/methanol stock solutions were injected into each of them to make the initial naphthalene concentrations to be 0.45, 1.40, 1.87, 2.36 µg/ml, respectively (sample nos. 4.1 to 4.4). Sample vials were closed tightly with headspace of less than 0.1 ml. Another four control vials were set up the same way as the sample vials except that no “nano-AC particles” was added. Control vials were designed to account for the loss of naphthalene from the aqueous phase due to volatilization or adsorption to the vessels. Sample vials and control vials were stirred slowly on magnetic stirrers in the dark at room temperature (25 ± 1 °C) for at least three days. At the end of the adsorption experiment, the suspension in each sample vial was filtered using an Anodisc® filter membrane (20 nm pore size). 1 ml of filtrate was analyzed on the Beckman liquid-scintillation counter to determine naphthalene aqueous concentrations. About 1 ml of the solution in each control vial was also analyzed for aqueous phase naphthalene concentrations by liquid-scintillation counter. Solid-phase naphthalene concentration in each sample vial was calculated from the difference between the solution phase naphthalene concentration in the sample vial and that in the corresponding control vial.

Another two sample vials, containing 0.1 mg of “nano-AC particles” in 8 ml water (Sample 4.5), and 0.2 mg of “nano-AC particles” in 16 ml water (Sample 4.6),
respectively, were set up the same way as that of sample nos. 4.1 to 4.4. The initial naphthalene concentrations are 10.02, and 9.15 µg/ml, respectively. Upon completion of the adsorption, the suspension in each sample vial was filtered and filtrates were analyzed for naphthalene aqueous concentrations, as discussed above. After filtration, the filter membranes containing C₆₀ solids were put into clean sample vials and naphthalene-free deionized water was added into each of the clean vials to induce desorption for these 2 samples (sample nos. 4.5 and 4.6). The vials were sealed tightly and put into a sonication bath (Solid State/Ultrasonic FS-14, Fisher Scientific) for 15 minutes to redisperse nC₆₀. Membranes were then removed carefully from the sample vials. Next, deionized water was added to each sample vial (with headspace < 0.1 mL) and samples were stirred at room temperature for five days for naphthalene desorption. At the end, the suspension in each sample vial was filtered with an Anodisc® filter membrane and aqueous phase naphthalene concentration was determined on the liquid-scintillation counter. 3 steps of naphthalene desorption were conducted to each of the two samples.

4.2.2.3 Adsorption and Desorption of Naphthalene to and from Anocostia sediment in water.

2g dried Anocostia sediment was added to a 40ml glass vial and the vial was filled with 0.01M NaCl and 0.01M NaN₃ electrolyte solution. ¹⁴C-radiolabeled naphthalene/methanol stock solution was injected into the vial to an initial concentration of 8.69 µg/ml. The sample was stirred mildly for at least two days for adsorption. At the end of the adsorption, the sample was centrifuged at 6000 rpm on a centrifuge and the supernatants was analyzed on a liquid-scintillation counter to determine the aqueous
phase naphthalene concentration. Over 95% of the supernatant was removed from the sample vial and deionized water was filled (leaving < 0.1 ml headspace) to induce multi-step desorption. At the end of each desorption step, the sample was centrifuged and aqueous phase naphthalene concentration was analyzed on the liquid-scintillation counter. The equilibrium time for each desorption step varied from 3 days for the first desorption step, to 7 days for the last desorption step.

4.3 Results and Discussion

4.3.1 Adsorption and Desorption of Naphthalene to and from “As-Received Activated Carbon Particles”, “nano-AC particles”, and Anocostia sediment.

The mean particle size of the “as-received activated carbon particles” was reported to be about 1 µm by the supplier (Calgon Carbon Corp., Pittsburgh, PA). Data of naphthalene adsorption to these particles are fitted with a Freundlich isotherm (Figure 4.1) in the form of \( q = 10^{5.12} C_w^{0.87} \), where \( q \), the adsorbed naphthalene concentration, is in the unit of µg/g, and \( C_w \), the aqueous phase naphthalene concentration, is in the unit of µg/ml. The corresponding linear adsorption isotherm would be \( q (\mu g/g) = 10^{5.29} C_w (\mu g/ml) \).

Data of naphthalene desorption from “as-received activated carbon particles” are also presented in Figure 4.1. Similar to what was observed in naphthalene desorption from “C-60 small aggregates” (Figure 3.8), sorption hysteresis was also observed here. For these samples, the solid-water distribution coefficient (\( K_d \)) values for the last desorption datum point for each sample are \( 10^{6.67}, 10^{6.63}, 10^{6.37}, 10^{6.62}, \) and \( 10^{6.54} \) (ml/g), respectively.
The $K_d$ value for each sample is more than one order of magnitude higher than the corresponding adsorption $K_d$ values, which are $10^{5.34}$, $10^{5.48}$, $10^{5.45}$, $10^{5.28}$ (ml/g), and $10^{5.28}$, respectively.

Data of naphthalene adsorption (sample nos. 4.1 to 4.6) to and desorption (sample nos. 4.5 and 4.6) from “nano-AC particles” are plotted in Figure 4.2. Data of naphthalene adsorption to “nano-AC particles” can be fitted with a linear isotherm in the form of $q (\mu g/g) = 10^{1.70} C_w (\mu g/ml)$ (Figure 4.2). Interestingly, this adsorption coefficient is similar to that of naphthalene adsorption to “nC60”, which has a value of $10^{3.74}$ ml/g. It has been suggested that this may be a consequence of the pores of “nC60” being filled during grinding and processing (Qilin Li, 2006, personal communication). Desorption data show that desorption of naphthalene from “nano-AC particles” is also hysteretic, i.e., for each desorption datum point, the adsorbed naphthalene concentration ($q$) is larger than that predicted from the reversible linear sorption isotherm (the solid line on Figure 4.2). As discussed in Chapter 3, this sorption hysteresis was also observed in naphthalene desorption from “nC60”.

Figure 4.3 shows naphthalene adsorption to and successive desorption from Anocostia sediment in water. The organic carbon normalized distribution coefficient ($K_{oc}$) value for adsorption is $10^{3.25}$ ml/g. On the desorption isotherm, the $K_{oc}$ values changes from $10^{3.38}$ ml/g for the first desorption step, to $10^{5.21}$ ml/g for the last desorption step. The deviation of the desorption isotherm from expected linear isotherm and the gradual increase of $K_d$ values indicate the occurrence of sorption hysteresis, as observed in numerous studies on desorption from natural soils and sediments.
4.3.2 Sorption Isotherms

4.3.2.1 Freundlich Isotherm

Freundlich isotherm is an empirical relationship which is commonly used to fit experimental adsorption data with a minimum of adjustable parameters (Schwarzenbach, Gschwend et al. 2003). It generally takes the form of:

\[ q = K_F C_w^n \]  

(4.1)

where \( K_F \) is the Freundlich sorption coefficient (e.g., \( \mu g/g \cdot (\mu g/ml)^{-n} \)); \( n \) is the Freundlich exponent; and \( q \) (\( \mu g/g \)) and \( C_w \) (\( \mu g/ml \)) are defined as before. The Freundlich isotherm assumes a distribution of site energies.

4.3.2.2 Langmuir Isotherm

This type of isotherm was originally applied to the adsorption of gases or vapors on a plane surface that contains a fixed number of identical active sites (Langmuir 1918). The amount of the sorbate increases monotonically until it reaches a limiting value that corresponds theoretically to the completion of a surface monolayer. In aqueous solutions, Langmuir isotherm can be mathematically expressed as:

\[ q = \frac{q_m b C_w}{1 + b C_w} \]  

(4.2)

where \( b \) (e.g., \( ml/\mu g \)) is the Langmuir constant, \( q_m \) is the limiting (monolayer) adsorption capacity (the amount of the adsorbed sorbate per unit mass of the solid at the time when the solid surface is covered with a complete monolayer of the sorbate), and \( q \) (\( \mu g/g \)) and \( C_w \) (\( \mu g/ml \)) are defined as before.
4.3.2.3 Combined sorption model: Dual-Equilibrium Desorption (DED) model

A linear isotherm is the simplest form of sorption isotherm, which means that at equilibrium the adsorbed concentration of a compound (q, μg/g) is directly proportional to its aqueous phase concentration (C_w, μg/ml):

\[ q = K_p C_w \]  

(4.3)

where K_p is the partition coefficient. Although early studies showed that the sorption of hydrophobic organic compounds from water to soil are often characterized with a linear isotherm (Chiou, Peters et al. 1979; Karickhoff, Brown et al. 1979; Chiou, Porter et al. 1983), this simple model has been shown to be inconsistent with observed sorption behavior (Di Toro and Horzempa 1982; Ball and Roberts 1991; Weber, McGinley et al. 1992; Carroll, Harkness et al. 1994; Kan, Fu et al. 1994; Spurlock and Biggar 1994; Young and Weber 1995; Xing, Pignatello et al. 1996). For example, experimental studies have shown that sorption isotherms measured over broad solution concentration ranges are commonly nonlinear (Miller and Weber 1986; Weber, McGinley et al. 1992; Weber and Huang 1996; Xing, Pignatello et al. 1996; Huang and Weber 1997; Chiou and Kile 1998). The K_{oc} value for a particular hydrophobic organic contaminant often varies by more than one order of magnitude for the same sorbent depending on aqueous phase concentration (Weber, McGinley et al. 1992; Allen-King, Groenevelt et al. 1996; Weber and Huang 1996). Sorption/desorption hysteresis has been widely observed in the sorption of organic compounds to natural soils (Di Toro and Horzempa 1982; Miller and Pedit 1992; Fu, Kan et al. 1994; Kan, Fu et al. 1994; Xue and Selim 1995; Huang and Weber 1997; Kan, Fu et al. 1997; Kan, Fu et al. 1998; Lu and Pignatello 2002). Among these phenomena, sorption/desorption hysteresis has important implications for the fate
and health effects of environmental contaminants. Models dealing with physical and biological availabilities of contaminants typically assume sorption to be reversible (Lu and Pignatello 2002). Sorption coefficients used in such models are invariably based on forward-constructed sorption isotherms. If sorption hysteresis occurs, those models may incorrectly predict the fate and biological effects of a contaminant. As discussed in Chapter 3 and this chapter, sorption hysteresis was observed in sorption/desorption of naphthalene and 1,2-DCB on C$_{60}$ ("C$_{60}$ small aggregates" and "nC$_{60}$"), activated carbon particles ("as-received activated carbon particles" and "nano-AC particles"), and Anocostia sediment. In these cases, the relationship between sorbed concentrations and dissolved concentrations of each hydrophobic organic contaminant may not be described by a single linear, Langmuir, or a Freundlich isotherm. A combination of two types of isotherms has been proposed by researchers to account for the observed sorption behavior (Weber, McGinley et al. 1992; Xing, Pignatello et al. 1996; Xing and Pignatello 1997; Kan, Fu et al. 1998; Weber, W. et al. 1999; Accardi-Dey and Gschwend 2002; Chen, Kan et al. 2002).

Kan et al. have proposed a “dual-equilibrium desorption” (DED) model (Kan, Fu et al. 1998; Chen, Kan et al. 2000) to describe experimentally observed sorption-desorption hysteresis. The basic concept of this model is that sorption of hydrophobic organic compounds to soils or sediments consists of two compartments, each with unique equilibrium and kinetic characteristics. In most cases, adsorption and desorption of organic contaminants at high initial concentrations (up to aqueous solubility) may be associated with the first compartment which is described by a linear term (the first term on the right-hand side of Eq. (4.4)); while at low concentration ranges most of adsorption
and desorption may be associated with the second compartment which is described by a Langmuir term (the second term on the right-hand side of Eq. (4.4)). According to this model, adsorption/desorption of organic contaminants from soils or sediments can be described by the following isotherm:

\[
q = K_{oc}^{1st} \cdot f_{oc} \cdot C_w + \frac{K_{oc}^{2nd} \cdot f_{oc} \cdot f \cdot q_{max}^{2nd} \cdot C_w}{f \cdot q_{max}^{2nd} + K_{oc}^{2nd} \cdot f_{oc} \cdot C_w}
\]  

(4.4)

where \( K_{oc}^{1st} \) is the organic carbon normalized sorption coefficient for the first compartment; \( K_{oc}^{2nd} \) is the organic carbon normalized sorption coefficient for the second compartment; \( f_{oc} \) is the fraction of organic carbon; \( q_{max}^{2nd} \) is the maximum sorption capacity for the second compartment; \( f (0 \leq f \leq 1) \) is a factor representing the fraction of the second compartment that is saturated upon exposure; and \( q \) and \( C \) are as defined previously. For adsorption and desorption of organic compounds with \( C_{60}, \) or activated carbon, \( f_{oc} = 1, \) Eq. (4.4) becomes:

\[
q = K_{d}^{1st} \cdot C_w + \frac{K_{d}^{2nd} \cdot f \cdot q_{max}^{2nd} \cdot C_w}{f \cdot q_{max}^{2nd} + K_{d}^{2nd} \cdot C_w}
\]  

(4.5)

where \( K_{d}^{1st} \) and \( K_{d}^{2nd} \) are solid-water distribution coefficients for the first and the second compartment. Weber et al. and Xing et al. also described the sorption of organic contaminants to soil organic matters using the superposition of a linear type isotherm and a Langmuir type isotherm (dual reactive domain model, or dual-mode model) (Weber, McGinley et al. 1992; Xing, Pignatello et al. 1996; Xing and Pignatello 1997; Weber, W. et al. 1999).

4.3.2.4 Polanyi-Manes sorption model
Adsorption of low-polarity organic compounds to high-surface-area carbonaceous materials, e.g. black carbons in soils and sediments, may occur in a similar manner as with activated carbon (Chiou and Kile 1998; Xia and Ball 1999). Adsorption to activated carbons may be highly energetically heterogeneous (Chiou 2002), which results in an enhanced adsorption energy (adsorption potentials) in the micropores of the carbon, owing to superposition of the fields of the opposite walls of the pores (Dubinin 1960). Under this circumstance, the Langmuir adsorption model or BET model may not be a good fit for adsorption data. The Polanyi adsorption potential theory (Polanyi 1916) has been considered the most powerful model to describe gases (or vapors) adsorption on energetically heterogeneous solids (Brunauer 1945). Since then, Polanyi adsorption theory has been successfully applied by Manes and co-workers as well as by other researchers to both gas phase adsorption and adsorption from aqueous solutions (Hansen and Fackler 1953; Manes and Hofer 1969; Reucroft, Simpson et al. 1971; Wohleber and Manes 1971; Chiou and Manes 1973; Chiou and Manes 1974; Rosene, Ozcan et al. 1976; Greenbank and Manes 1981; Greenbank and Manes 1982; Crittenden, Hand et al. 1987; Manes 1998)(+Yang, K., Zhu, L., Xing, B., Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. EST, 2006, 40, 1855-1861).

Polanyi defined the existence of an (attractive) adsorption potential ($\varepsilon$) between the adsorbate molecule and the solid surface, which, at a particular location within the adsorption space, may be viewed as the energy required to remove the molecule from that location to a point outside the attractive force field of the solid. According to the Polanyi theory, the following relationship holds for ideal gases (vapors) adsorption to porous adsorbents:
\[ \varepsilon = RT \ln \frac{P^0}{P_g} \]  

(4.6)

where \( P_g \) is the vapor pressure in equilibrium with the adsorbed phase, \( P^0 \) is the saturation vapor pressure, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature (Polanyi 1916; Manes and Hofer 1969; Adamson and Gast 1997; Crittenden, Sanongraj et al. 1999; Allen-King, Grathwohl et al. 2002; Chiou 2002). The original Polanyi model was clearly explained and extended to a wide range of vapor- and liquid-phase systems by Manes and co-workers (Manes and Hofer 1969; Manes 1998) and the effective adsorption potential can be defined as:

\[ \varepsilon = RT \ln \frac{S}{C} \]  

(4.7)

where \( S \) is the solubility of the sorbate, and \( C \) is the aqueous concentration of the sorbate.

The following empirically derived relation between adsorbed volume and adsorption potential (\( \varepsilon \)) was proposed for sorption on activated carbons (Crittenden, Hand et al. 1987; Xia and Ball 1999):

\[ q = Q_0' \rho x 10^{a'(\varepsilon/V_s)^b'} \]  

(4.8)

where \( \varepsilon \) is the net adsorption potential of the sorbate in aqueous solution, \( Q_0' \) is the maximum adsorption capacity (cm\(^3\)/kg); \( \rho \) is the liquid or solid density, \( a' \) and \( b' \) are fitting parameters; \( V_s \) is the molar volume of the solute.

Dubinin suggested that for a given solid a plot of the adsorbed volume (\( q' \)) against adsorption potential density (\( \varepsilon/V_s \)) would yield similar curves for a wide range of adsorbate chemicals (Dubinin 1960). And these curves were called "correlation curves".
4.3.3 Model fitting for experimental data of naphthalene and 1,2-dichlorobenzene (DCB) adsorption and desorption with “nC₆₀”, “nano-AC particles”, and soil organic carbon (Soil OC) in Anocostia sediment.

Experimental data of the sorption and desorption of naphthalene and 1,2-dichlorobenzene (1,2-DCB) with C₆₀, naphthalene with activated carbon, and naphthalene with soil organic carbon (Soil OC) in Anocostia sediment are fitted with the above described four sorption models and are shown in Figures 4.4-4.7: Freundlich model (Figure 4.4), Langmuir model (Figure 4.5), DED model (Figure 4.6), and Polanyi-Manes model (Figure 4.7). Values of model predicted parameters were determined using the software of SigmaPlot (version 8.0) and are listed in Table 4.1, also included are the R² values for each model fit.

The linear isotherms (dashed lines in Figures 4.4-4.7) for the adsorption of naphthalene to nC₆₀, 1,2-DCB to nC₆₀, naphthalene to nano-AC particles, naphthalene to soil OC are \( q (\mu g/g) = 10^{3.74}C_w (\mu g/ml), \) \( q (\mu g/g) = 10^{3.48}C_w (\mu g/ml), \) \( q (\mu g/g) = 10^{3.70}C_w (\mu g/ml), \) and \( q (\mu g/g) = 10^{3.25}C_w (\mu g/ml), \) respectively. As can be seen from Figures 4.4-4.7, (a) to (d) that for the three forms of carbon tested in this study, i.e., C₆₀, activated carbon, and soil organic carbon (soil OC), and two compounds, i.e., naphthalene and 1,2-DCB, the linear isotherms, as predicted from sorption data, failed to predict desorption data. The sorbed sorbate concentration for each desorption datum point, despite the sorbate and sorbent, is one to two orders of magnitude higher than that predicted from the reversible linear isotherm, indicating the occurrence of sorption hysteresis. This means that the simple linear isotherm may not be appropriate to predict observed sorption/desorption behavior.
To compare the $R^2$ values obtained from different models fits, and to compare the model fitting curves in Figures 4.4-4.7, it may be generally concluded that the Polanyi-Manes model fits most experimental data best (Figure 4.7), except for the sorption/desorption of naphthalene with Soil OC, for which either DED model or Polanyi-Manes model fit obtained a higher $R^2$ value. On the other hand, the overall data are not well described by the Langmuir model (Figure 4.5), indicated by the low $R^2$ values and the deviation of experimental data from model predicted values illustrated in the figure. The poor performance of Langmuir model is probably due to the failure of this model to predict the high sorption affinity of all three forms of carbon at low aqueous sorbate concentration range.

In Figure 4.6, (a) to (d), adsorption and desorption data of naphthalene with nC$_{60}$, nano-AC particles, and soil OC, and 1,2-DCB with nC$_{60}$ were fitted with the DED model. This model describes the sorption of organic compounds as the combination of two different processes. Sorption of the compound to the labile compartment obeys linear isotherm and desorbs reversibly, while sorption to the resistant compartment tends to be stronger and desorption hysteresis was normally observed due to the irreversible change of the pore structure of the sorbent and/or the entrapment of sorbate molecules in the sorbent (Kan, Fu et al. 1997; Lu and Pignatello 2002; Braida, Pignatello et al. 2003; Lu and Pignatello 2004). As is shown in Figure 4.6, (a) to (d), this model can predict the overall sorption data pretty well, with reasonably high $R^2$ values. As is listed in Table 4.1, the $K_{d1}^{1st}$ value ranges from $10^{2.79}$ (ml/g) for DCB sorption to nC$_{60}$, to $10^{3.68}$ (ml/g) for naphthalene sorption to nC$_{60}$; the $K_{d2}^{2nd}$ value ranges from $10^{5.73}$ (ml/g) for naphthalene sorption to nC$_{60}$, to $10^{6.69}$ (ml/g) for naphthalene sorption to nano-AC; the $q_{max}^{2nd}$ value
ranges from $10^{3.18}$ ($\mu g/g$) for naphthalene sorption to soil OC, to $10^{4.45}$ ($\mu g/g$) for naphthalene sorption to nano-AC. The values of each parameter for the three carbons varied around one order of magnitude, or smaller. It was reported by Kan et al. (1998) and Chen et al. (2002) that for many sediments/adsorbate combinations $K_{oc}^{2nd}$ was a single constant, $K_{oc}^{2nd} = 10^{5.92}$ (ml/g). The $K_{oc}^{2nd}$ values obtained in this study for model fitting of all experimental data were very similar to the $K_{oc}^{2nd}$ value obtained from soils/sediments. This similarity could possibly imply similar mechanisms. This model may possibly be used to predict the sorption behavior of new carbonaceous materials from that of other known carbons.

Model fits of experimental sorption/desorption data with the Polanyi sorption model (Eq. 4.8) are illustrated in Figure 4.7, (a) to (d). In the model fitting calculation, the molar volume ($V_s$) for naphthalene and 1,2-DCB was estimated as the ratio of the molecular weight and the density of the chemical in its pure form (Manes 1998; Xia and Ball 1999). Parameters, including $a'$, $b'$ and $Q_0'$, obtained from model fitting are listed in Table 4.1. From comparing the $R^2$ values obtained from this model to those of other models, it can be seen that is among the best to describe most experimental data of $C_{60}$ and activated carbon.

According to Polanyi theory, the sorption isotherm of adsorbed volume per unit mass of sorbent versus the adsorption potential density (called “correlation curve”) is expected to fall on a single line for all liquid sorbates if there are no specific interactions between sorbates and the sorbent surface (Manes 1998; Xia and Ball 1999). This is mostly the case for sorption of nonpolar organic sorbates from aqueous solutions (Manes and Wohleber 1971). The adsorbed volume per unit mass of $C_{60}$ ($q'$, $cm^3/10^3$kg) versus
the adsorption potential density ($\varepsilon/V_s, J/cm^3$) is plotted for the adsorption and desorption of naphthalene and 1,2-DCB with nC$_{60}$ in Figure 4.8. The obtained parameters $a'$, $b'$ and $Q_0'$ are also listed in Table 4.1. Data can be fitted with one single characteristic curve reasonably well, with a $R^2$ value of 0.9869. The goodness of the fitting of experimental data with Polanyi sorption model, as illustrated in Figures 4.7 (a) to (d) and 4.8, probably provides some evidence for the mechanism underlying the sorption of hydrophobic organic compounds to C$_{60}$ nanoparticles, that is, the sorption uptake of naphthalene and 1,2-DCB by C$_{60}$ may be the result of sorbate condensation into intra-particle micropores in nC$_{60}$. This proposed mechanism may also explain the observed sorption hysteresis since “capillary condensation” has long been believed to be one important cause for hysteretic sorption (Everett 1967; Bailey, Cadenhead et al. 1971; Burgess, Everett et al. 1989). For the sorption/desorption with soil OC data, the fit of Polanyi model is not as good as the DED model. This is probably because soil OC is composed of both normal OC and high sorption affinity carbon such as black carbons, therefore the two-compartment DED model may fit experimental data better.

It is noted that Freundlich model fits experimental data of naphthalene and 1,2-DCB on C$_{60}$ pretty well. This is not surprising since sorption sites on C$_{60}$ particles are not expected to be homogeneous and Freundlich model is the indication of multiple types of sites on the heterogeneous adsorbent surface (Weber and Digiano 1996; Chiou 2002; Schwarzenbach, Gschwend et al. 2003).

In summary, the DED model and Polanyi model both simulate experimental data presented herein reasonably well. Although three apparent parameters need to be optimized in the DED model, model fitting results showed that the values of each
parameter, \( K_{d1}^{1st} \), \( K_{d2}^{2nd} \), and \( q_{\text{max}}^{2nd} \), are similar for the three forms of carbon tested in this work, therefore, this model may be very useful in the prediction of sorptive behavior of novel carbonaceous nanomaterials from other well known carbon forms. All the three parameters in the Polanyi model, on the other hand, need to be obtained by model fitting. This is one main limitation of the Polanyi model. However, the goodness of the fitting of experimental data with the Polanyi model may have the best indication on the sorption mechanism. The single correlation curve as shown in Figure 4.8 further supports the proposed "pore-filling" mechanism.

4.4 Conclusions

Since sorption hysteresis is observed for the adsorption and desorption of naphthalene and 1,2-dichlorobenzene with C\(_{60}\), activated carbon, and soil organic carbon, i.e., desorption data deviate greatly from forward adsorption isotherm, experimental adsorption-desorption data can not be fitted with a single linear isotherm. Instead, they were fitted with four different sorption models, including Freundlich model, Langmuir model, two-compartment dual-equilibrium desorption model (DED), and Polanyi-Manes sorption model. Results show that DED model or Polanyi-Manes model fit data pretty well, while the overall data are not well described by the Langmuir model. Each DED model obtained parameter has similar values for different carbon forms, indicating that this model may possibly be used to predict the sorption behavior of new carbonaceous materials from that of other known carbons. The goodness of fitting of data with the Polanyi-Manes model implied that the intraparticle pore-filling might be the mechanism...
controlling the adsorption of organic compounds to C$_{60}$ aggregates and should be further tested.
Table 4.1. Parameters of models fit to experimental data of the sorption-desorption of naphthalene (naph) and 1,2-dichlorobenzene (DCB) with C$_{60}$, naphthalene (naph) with activated carbon (AC), and naphthalene (naph) with soil organic carbon (Soil OC) in Anocostia sediment

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbate</th>
<th>Model Parameters</th>
<th>$R^2$</th>
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<td><strong>Freundlich</strong></td>
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<td></td>
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<td>$K_F$ (pg/g) - (pg/ml)$^{1-n}$</td>
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<td>C$_{60}$</td>
<td>naph</td>
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<td>C$_{60}$</td>
<td>DCB</td>
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<td></td>
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<td>0.09</td>
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<td>#2</td>
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<td>$10^{3.97}$</td>
<td>0.20</td>
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<td>#3</td>
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<td>$10^{4.13}$</td>
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**Polanyi (q'—ε/V's)**

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Figure 4.1. Adsorption and desorption of naphthalene to and from “as-received activated carbon” particles (5 samples). ♦, Adsorption data for 5 samples; □, △, ×, ◦, and ○, 4 steps of desorption data for each of the 5 samples.
Figure 4.2. Adsorption and desorption of naphthalene to and from "nano-AC" particles. ♦, Adsorption data for sample nos. 4.1 - 4.6; +, desorption data for sample # 4.5; ◊, desorption data for sample # 4.6.
Figure 4.3. Adsorption and desorption of naphthalene to and from Anocostia sediment. ▲, Adsorption data; Δ, successive desorption data.
Figure 4.4 Adsorption and desorption of (a) naphthalene with nC\textsubscript{60}; (b) 1,2-dichlorobenzene with nC\textsubscript{60}; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Freundlich model.
Figure 4.4 Adsorption and desorption of (a) naphthalene with nC₆₀; (b) 1,2-dichlorobenzene with nC₆₀; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Freundlich model.
Figure 4.5 Adsorption and desorption of (a) naphthalene with nC60; (b) 1,2-dichlorobenzene with nC60; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Langmuir model.
Figure 4.5 Adsorption and desorption of (a) naphthalene with nC_{60}; (b) 1,2-dichlorobenzene with nC_{60}; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Langmuir model.

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Figure 4.6 Adsorption and desorption of (a) naphthalene with nC_{60}; (b) 1,2-
dichlorobenzene with nC_{60}; (c) naphthalene with nano-AC particles; (d) naphthalene with
soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols:
desorption data; dashed lines: linear isotherm assuming reversible desorption without
hysteresis; solid lines: isotherms fitted by DED model.

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Figure 4.6 Adsorption and desorption of (a) naphthalene with nC₆₀; (b) 1,2-dichlorobenzene with nC₆₀; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by DED model.
Figure 4.7 Adsorption and desorption of (a) naphthalene with nC_{60}; (b) 1,2-dichlorobenzene with nC_{60}; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Polanyi-Manes model.

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Figure 4.7 Adsorption and desorption of (a) naphthalene with nC$_{60}$; (b) 1,2-dichlorobenzene with nC$_{60}$; (c) naphthalene with nano-AC particles; (d) naphthalene with soil OC in Anocostia sediment. Filled symbols: adsorption data; open symbols: desorption data; dashed lines: linear isotherm assuming reversible desorption without hysteresis; solid lines: isotherms fitted by Polanyi-Manes model.

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Figure 4.8 Polanyi sorption isotherm for naphthalene and 1,2-dichlorobenzene desorption from “nC60”. Data are plotted as adsorbed volume (q') versus adsorption potential density (ε/V_s).
5.1 Introduction

Since fullerenes are expected to be produced by the ton (Colvin 2003), there is no doubt that these nanomaterials will ultimately be found in the environment at measurable concentrations. It is likely that the aquatic environment will be one of the most important sink for fullerene materials, although it is still unknown at what quantities they are present in the environment. Since C$_{60}$ is virtually insoluble in water (Ruoff, Tse et al. 1993), one might expect that this hydrophobic nanomaterial would not enter groundwater in great quantities. However, several methods have produced water-stable nC$_{60}$ (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Deguchi, Alargova et al. 2001), indicating that C$_{60}$ might be mobile in groundwater. Recent studies have shown that this underivatized form of C$_{60}$ (nC$_{60}$) causes oxidative damage to both fish brain cells and cultured human cells (Oberdorster 2004; Sayes, Fortner et al. 2004). If this nC$_{60}$ is indeed mobile in groundwater, people should be more concerned about the potential exposure to these materials through groundwater transport.

It has been reported that the existence of dissolved organic matter in groundwater could enhance the partition of neutral organic contaminants into water and thus enhance the transport of these compounds (Kan and Tomson 1990). Significant enhancement for naphthalene transport through groundwater was observed when the concentration of dissolved organic matter reached a critical level. It is unknown whether the release of C$_{60}$
and other nanosized carbonaceous nanomaterials into the environment will enhance the transport of organic contaminants and thereby spread contamination more quickly.

Some work has been done to address the issue of C$_{60}$ transport through glass beads, a model medium (Lecoanet, Bottero et al. 2004; Lecoanet and Wiesner 2004). In the natural aquatic environment, the transport of C$_{60}$ may vary from that in model media due to the complicated conditions in natural soil, such as the medium heterogeneities, and the complex flow characteristics. This study reports the first investigation of the transport of water-stable nC$_{60}$ through natural porous media. A soil column was packed with dried and sieved soil particles and breakthrough curves of nC$_{60}$ with that column was measured. The transport of naphthalene through the same soil column containing 0.18% deposited nC$_{60}$ was measured and will be discussed.
5.2 Materials and Methods

5.2.1 Materials.

$^{14}$C-radiolabeled naphthalene with specific activity of 6.2 µCi/µmol was purchased from Sigma-Aldrich (St. Louis, MO). A $^{14}$C-radiolabeled naphthalene stock solution with naphthalene concentration of 1129.9mg/L was prepared by diluting 100 µCi of $^{14}$C-radiolabeled naphthalene in ~1.83 mL of methanol (HPLC grade) upon receipt. Tritiated water was purchased from Amersham Co. (Arlington Hts. IL). Sodium chloride (biological grade) and sodium azide (>98%) were purchased from Fisher Scientific (Pittsburgh, PA) and Eastman Kodak Co. (Rochester, NY). Sodium azide was used to inhibit microbial activity. Toluene with a purity of 99.8% was purchased from Sigma-Aldrich. A phenylxylmethane based liquid scintillation cocktail (Ready Safe™) for scintillation counting was purchased from Beckman Coulter, Inc. (Fullerton, CA). The Ready Safe™ cocktail is much less volatile compared with traditional cocktails, and it provides very stable counting efficiency over the sample/cocktail ratio of 1-30%.

5.2.2. Soil.

Lula surface soil (fine sand), collected from a ranch near Lula, Oklahoma, was obtained from R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma. The soil is composed of 92% sand, 6% silt, and 2% clay (Wilson, Enfield et al. 1981). The soil was air-dried and sieved through 10 mesh sieve and cheese cloth to remove vegetative matter. The organic carbon content of the soil was analyzed by both dry combustion method (Galbraith Laboratories, Inc., Knoxville, TN) and chemical oxygen demand method (COD) to be 0.27%. The mean particle size of the Lula soil particles used to pack the soil
column is about 250 μm, with about 76% (wt/wt) in the 106-500 μm range (Clark 1990). The soil solid density is 2.62 g/cm³. The soil surface area was determined by BET method to be 1.24 m²/g (Micromeritics Instrument Co., Norcross, GA). The porosity of the soil column, determined from the retention volume of tritiated water, was 0.40.

5.2.3 Soil Column apparatus.

The soil column apparatus was composed primarily of a syringe pump, a soil column and an autosampler. In Figure 5.1 is a drawing of the experimental setup. The column is a borosilicate precision glass column (0.9 cm ID, 7 cm L, Spectrum Medical Industries, Inc., Los Angeles, CA). The plungers on both sides of the column were made from Type 316 stainless steel at Rice University machine shop (Houston, TX). There is a Viton O-ring (Parker Seal Group, Lexington, KY) on each plunger to provide better sealing between the glass column and plungers. Type 316 stainless steel tubing (1/16” O.D., 0.005” I.D., Small Parts Inc., Miami Lakes, FL) was used to connect the syringe pump with the column and the column with the autosampler. Input solution/suspension introduction was achieved by a syringe infusion pump (Harvard Apparatus Inc., Holliston, Massachusetts). A glass Gastight® syringe with capacity of 50 mL (Hamilton Co., Reno, Nevada) was used to load nC₆₀ suspensions or naphthalene solutions. The effluent collection was accomplished by an ISCO autosampler (ISCO Inc., Lincoln NE). The ISCO autosampler was equipped with a Type 316 stainless steel piercing device which could pierce through rubber septa during sample collection.

4.9 g air-dried and sieved soil was packed into the glass column to a depth 5 cm. The soil was retained in the column with a 10 μm stainless steel screen positioned at the
end of each plunger. 0.01M NaCl/0.01M NaN₃ electrolyte solution was passed through the soil column at a flow rate of 1 ml/hr for about 36 hrs after packing, to ensure compaction and equilibration of soil with the influent solution. Any air bubbles remaining in the soil column were removed by the electrolyte solution.

5.2.4. nC₆₀.

C₆₀ solids (purity > 99.5%) were purchased from SES Research (Houston, TX, USA). Input suspensions of nC₆₀ were prepared by mixing C₆₀/tetrahydrofuran (THF) solution with water, followed by removal of THF, as described in Chapter 3. C₆₀ concentration of the nC₆₀ suspension used as the influent in breakthrough experiments was 48 mg/L. NaCl and NaN₃ solids were dissolved in the nC₆₀ suspension to make the concentrations of NaCl and NaN₃ both 0.01M.

The image of prepared “nC₆₀” in water suspension was captured by Transmission Electronic Microscopy (JEOL FasTEM 2010) and is shown in Figure 5.2. The TEM sample of nC₆₀ was prepared by evaporating several drops of nC₆₀ suspension on a 300-mesh carbon-coated copper grid. This is the same photo as that included in Figure 3.3, and is included here for completeness.

5.2.5 Breakthrough Experiments.

5.2.5.1 nC₆₀ breakthrough experiments.

Parameters used in the nC₆₀ breakthrough experiments are listed in Table 1. The nC₆₀ suspension (C₆₀ concentration = 48 mg/L) was initially loaded in the 50-mL glass syringe and pumped into the soil column with the syringe pump at a flow rate of 1 mL/hr.
(flow velocity = 0.38 m/d). nC_{60} suspension was continuously introduced into the soil column for 148 hours (116.5 pore volumes). Next, flow rates were varied from 1 mL/hr to 10 mL/hr (flow velocity = 3.8 m/d) and 30 mL/hr (flow velocity = 11.4 m/d) to test the effect of flow rate on nC_{60} breakthrough.

Fractions of the effluent were collected in pre-weighed open-top 8-mL glass vials, and a closure was put on the vial after the collection of each sample to avoid prolonged volatilization. Collection time for each sample varied from 0.11 to 2 hrs. After the collection of all samples, glass sample vials were weighed and concentration of nC_{60} in each vial was determined by UV absorbance at 446 nm wavelength on a UV-Vis spectrophotometer (DR/4000, HACH Company, Loveland, CO). A series of nC_{60} suspensions with different nC_{60} concentrations were previously prepared. The absorbance of each suspension at 446 nm wavelength was measured on the spectrophotometer, and was plotted against the corresponding nC_{60} concentration to obtain a calibration curve. Since a good correlation was obtained for the calibration curve (R^2 = 0.999), nC_{60} concentrations in the effluent from the breakthrough experiments were determined from their absorbance.

The concentration of nC_{60} in the suspension before introducing it into the soil column, C_0, and the concentrations of nC_{60} in the effluent, C, were used to obtain a breakthrough curve of C/C_0 as a function of the number of pore volumes.

The pump was shut down for 7 days after the nC_{60} breakthrough experiments. Next, a C_{60}-free electrolyte solution (with 0.01M NaCl and 0.01M NaN_3) was loaded in a clean glass syringe and pumped into the soil column to further examine the effect of flow
rate and flow interruption on the flush-out of nC$_{60}$ particles. Electrolyte solution flow velocities of 0.38, 3.8, 11.4, 15.2 and 22.8 m/d were used.

Effluent was collected periodically with 8-mL glass vials following the same procedure as that used for collection of nC$_{60}$ effluent. Concentration of nC$_{60}$ in each collecting vial was also determined by UV absorbance at 446 nm. A total of 246 pore volumes of C$_{60}$-free electrolyte was pumped through the column.

5.2.5.2 Tracer breakthrough experiments.

Tritiated water stock solution was diluted by 0.01M NaCl/0.01M NaN$_3$ solution to make the final $^3$H$_2$O concentration equal to 0.025 µCi/mL. This solution was pumped into the soil column at a flow rate of 1mL/hr (velocity = 0.38 m/d). The effluent was collected periodically by glass scintillation vials and $^3$H$_2$O concentrations were measured in a liquid-scintillation counter (Beckman Instruments Inc., Fullerton, CA). The ratio of $^3$H$_2$O concentration in the effluent (C) and $^3$H$_2$O concentration before entering the soil column (C$_0$), was plotted against volume to obtain a tracer breakthrough curve. Three tracer tests were conducted: one was run before any nC$_{60}$ breakthrough experiments being conducted; one was run after nC$_{60}$ breakthrough experiments (but before the nC$_{60}$ flush-out experiments); and the third one was run right before conducting naphthalene breakthrough experiments.

5.2.5.3 Naphthalene breakthrough experiments.

After conducting the last tracer breakthrough experiments the column was flushed with 0.01M NaCl/0.01M NaN$_3$ background electrolyte solution at the flow rate of 1
mL/hr for more than 10 hrs until no $^3$H$_2$O was detectable in the effluent. Next, naphthalene breakthrough experiments were conducted on the soil column with $^{14}$C-naphthalene aqueous solution. The input $^{14}$C-naphthalene aqueous solution ($^{14}$C-naphthalene = 0.58 mg/L) was prepared by adding 51 µL of $^{14}$C-naphthalene/MeOH stock solution (1130 mg/L) into 100 mL 0.01M NaCl/0.01M NaN$_3$ solution. This naphthalene solution contained about 0.05% (V/V) methanol, which would only increase the solubility of organic compounds in water by about 0.5%.

The prepared $^{14}$C-naphthalene aqueous solution was loaded in the 50-mL glass syringe and pumped into the soil column with the syringe pump at a flow rate of 1 mL/hr. The introduction of naphthalene solution continued for 45 hrs. The effluent was collected hourly. 20-ml glass scintillation vials (24-400 GPI thread, Kimble Glass Inc., Vineland, NJ), each filled with 10 ml of Ready Safe™ scintillation cocktail, were pre-weighed and used for effluent collection. Open-top polypropylene closures (24-400 GPI thread, Fisher Scientific, Pittsburgh, PA) and 0.005 in. polytetrafluoroethylene (PTFE)/0.120 in. silicone rubber septa (Fisher Scientific, Pittsburgh, PA) to fit the scintillation vials were used during the effluent collection. The delivery end of the tubing was filed to be a sharp needle-shape so that it could pierce the rubber septa. The position of the needle-shape end was adjusted so that the effluent could be delivered under the cocktail surface to avoid volatilization of naphthalene. Naphthalene concentration in all sample vials was determined with a Beckman liquid-scintillation counter.

After continuous introduction of naphthalene solution for 45 hrs, naphthalene-free electrolyte solutions (0.01M NaCl, 0.01M NaN$_3$) were loaded into a clean glass syringe and pumped into the soil column at the flow rate of 1 mL/hr. The effluent was collected
following the same procedure as that used for collection of naphthalene solution. The collecting period for each sample varied from 1 hr to 2.5 hrs. Concentrations of naphthalene in the collected samples were also measured with the Beckman liquid-scintillation counter. A few empty vials were used during the sample collection to periodically collect the effluent and were then analyzed on UV-Vis spectrophotometer to monitor the nC₆₀ release from the column during the naphthalene flush-out.

The naphthalene breakthrough curve was obtained by plotting the ratio of the naphthalene concentration in the effluent (C) to the naphthalene concentration before entering the soil column (C₀), versus the number of pore volumes of solution pumped through the column.

5.3 Results and Discussion

5.3.1 nC₆₀ breakthrough experiments.

TEM image of nC₆₀ particles (Figure 5.2) shows that nC₆₀ particles are faceted particles. It was confirmed by HPLC that those particles are composed of > 99% of underivatized fullerenes, with crystal structure consistent with bulk fullerene crystals (Sayes, Fortner et al. 2004).

The transport of colloid in porous media and the attachment to the media surface or “collector” is related to two parameters, η and α (Yao, Habibian et al. 1971; O'Melia 1990). η, the single collector efficiency, describes the transport of particles to a single collector; and α, the particle attachment efficiency, describes the attaching efficiency at the collector surface.
The value of $\eta_{\text{theor}}$, the theoretical single collector efficiency, can be approximated by the sum of three transport processes that contribute to the particle transport to a collector surface: Brownian diffusion, interception, and gravity forces (sedimentation) (Yao, Habibian et al. 1971; Rajagopalan and Tien 1976; O'Melia 1990). Therefore, the value of $\eta_{\text{theor}}$ can be calculated from experimental parameters and a few constants, including particle radius, collector (grain) radius ($a_c$), particle density, fluid density, porous media porosity ($\epsilon$), temperature, viscosity of water, superficial or approach velocity of flow ($U$), gravitational acceleration, Hamaker constant, and Boltzmann's constant (Yao, Habibian et al. 1971; Rajagopalan and Tien 1976; O'Melia 1990). In the calculation of $\eta_{\text{theor}}$, it is assumed that both particles in the flowing fluid and the stationary collector grains are spherical, and there is no repulsive chemical interaction.

With the value of $\eta_{\text{theor}}$, the attachment efficiency $\alpha$ can be calculated by (Yao, Habibian et al. 1971):

\[
\alpha = -\ln \left( \frac{C_L}{C_0} \right) \cdot \left( \frac{4a_c}{3(1-\epsilon)\eta_{\text{theor}}L} \right) \tag{5.1}
\]

where $L$ is the particle travel distance in the porous media; $C_0$ and $C_L$ represent particle concentration at $L = 0$ and at $L = L$, respectively; $\epsilon$ is the porosity of the porous media; and $a_c$ is the average collector particle diameter. The calculation of theoretical single collector efficiency ($\eta_{\text{theor}}$) and the particle attachment efficiency ($\alpha$) has been used to evaluate the particle transport in porous media in an aquifer (Harvey, George et al. 1989; O'Melia 1990), and results agree very well with both laboratory experiments and theoretical prediction (Tobiason and O'Melia 1988; Harvey, George et al. 1989; O'Melia 1990).
The single collector efficiency ($\eta$) is the ratio of particle flux reaching the collector surface to the particle flux approaching the collector from upstream. It describes the physical effects on the kinetics of particle deposition, and varies with factors such as flow velocity, media porosity, particle and collector diameters, etc. The attachment efficiency $\alpha$ is defined as the ratio of the total particle deposition rate on a collector to the rate of collisions occurring between suspended particles and the collector. $\alpha$ is strongly influenced by interparticle forces between colloids and matrix surfaces, such as van der Waals and electric double layer forces, which means $\alpha$ generally accounts for chemical effects on the particle deposition. To date, $\alpha$ is often treated as an empirical parameter, for example, the empirically determined value of $\alpha$ varied with solution pH, ionic strength, the nature of ions in the solution, and the surface chemistry of the nanoparticles and the collector. In the absence of repulsive chemical interactions between the particles and collector $\alpha$ is often found to be one and the deposition rate can be theoretically predicted with reasonable accuracy (O'Melia 1990; Elimelech, Gregory et al. 1995; Kretzschmar and Sticher 1997). However, in the presence of net repulsive forces (unfavorable deposition, $\alpha<1$), current theories often fail to predict the $\alpha$ value even for well-characterized model systems (Elimelech and O'Melia 1990; Elimelech, Gregory et al. 1995; Kretzschmar and Sticher 1997).

The particle mobility can be further illustrated by calculating the particle travel distance (Elimelech, Gregory et al. 1995; Kretzschmar and Sticher 1997; Lecoanet, Bottero et al. 2004). The maximum travel distance ($L_T$) is defined as the predicted travel distance after which 99.9% of the particles are immobilized by the porous media. It can be calculated by rearranging Eq. 5.1 and using 0.001 as the value for ($C_1/C_0$).
Furthermore, the first-order deposition rate coefficient, \( k \) (T\(^{-1}\)), can be calculated from experimental measurements by: 
\[ k = - \left( \frac{v}{L} \right) \ln \left( \frac{C}{C_0} \right), \]
where \( v \) is the linear velocity for the flow through porous media.

\( nC_{60} \) breakthrough curves at the flow rate of 1 mL/hr (flow velocity = 0.38 m/d) and one tracer breakthrough curve at the same flow rate are plotted in Figure 5.3. On the graph, the x-axis represents the numbers of pore volumes of \( nC_{60} \) suspension that have passed through the soil column. The y-axis is the ratio of the \( nC_{60} \) concentration exiting the column (\( C, \text{ mg/L} \)), and the \( nC_{60} \) concentration in the input (\( C_0, \text{ mg/L} \)). The inset shows the enlarged tracer breakthrough curve at pore volumes from zero to six. The \(^3\)H\(_2\)O breakthrough reached about 100% after 1.5 pore volumes. \( nC_{60} \) particles were first observed in the effluent after about 3.2 pore volumes. After about 4.7 pore volumes \( C/C_0 \sim 0.24 \). Then, the concentration of \( nC_{60} \) particles increased gradually until it reached a peak value of 47% at about 53.5 pore volumes. Interestingly, after that, the fraction of influent \( nC_{60} \) particles exiting the column decreased sharply from 47% to 0% in only about 3 pore volumes. The introduction of \( nC_{60} \) particles was continued for another 60 pore volumes and virtually no \( nC_{60} \) particles passed through the soil column in the last 60 pore volumes, as shown in Figure 5.3. This drop of \( nC_{60} \) concentration will be discussed below.

Based on the linear flow velocity of 0.38 m/d, and a media porosity of 0.40, a superficial or approach velocity (\( U = v \cdot \varepsilon \)) of 0.152 m/d can be calculated (O'Melia 1990). Given the experimental parameters listed in Table 5.1, the value of the theoretical single collector efficiency (\( \eta_{\text{theor}} \)) was calculated using an online calculator at www.colorado.edu/ceae/environmental/ryan/cven6414/eta.xls (Yao, Habibian et al. 1971;...
An \( \eta_{\text{theor}} \) value of 1.35 (Table 5.2) was obtained for the transport of \( nC_{60} \) through soil column. At the particle size range of \( nC_{60} \) (~100 nm), the Brownian diffusion is the dominant process in the particle transport to the collector surface. The effect of direct interception and gravity forces on the particle transport is negligible.

The value for the particle attachment efficiency for the first 56.7 pore volumes (\( \alpha = 0.0046, \) Table 5.2) can be calculated with Eq. 5.1, using the \( (C_l/C_0) \) value of 0.33, and the \( \eta_{\text{theor}} \) value of 1.35. The deposition rate coefficient was calculated to be \( k = 3.37 \text{ d}^{-1} \), and it is predicted that \( nC_{60} \) could travel only 31 cm before 99.9% of the particles were removed by the soil column. It was observed that after 56.7 pore volumes, virtually no \( nC_{60} \) breakthrough occurred, i.e., “favorable deposition” (\( \alpha = 1 \)). This possibly indicated an irreversible sorption of the \( nC_{60} \) on the soil column. This may be related to the phenomenon of “filter ripening”, a process known in packed-bed filtration (O'Melia 1990). Particles that are deposited from a flowing suspension at one time can then become filter media for subsequent particles that are traveling in the pores of the media. Similar “dip” in the breakthrough curve was observed by Lecoanet and Wiesner in their transport study of \( nC_{60} \) (similar size range as used in this study) at higher velocity (121 m/d) through a column packed with glass beads (Lecoanet and Wiesner 2004). They hypothesized that the accumulation of \( nC_{60} \) on the collector surface might serve as favorable sites for subsequent \( nC_{60} \) deposition. They further observed that with higher influent \( nC_{60} \) concentration, this enhancement of \( nC_{60} \) deposition by previously deposited \( nC_{60} \) was more pronounced. Although further study is necessary to better understand the mechanisms underlying this observed “favorable deposition”, it was observed repeatedly.
in the current study under the low flow rate condition (1 mL/hr, or linear velocity of 0.38 m/d, Figure 5.3 and Figure 5.4) and may have broad environmental significance.

In the 1 mL/hr flow rate nC$_{60}$ breakthrough experiment (Figure 5.3) in this study, solution chemistry of the nC$_{60}$ suspension did not change, therefore, the increased attachment efficiency could not be attributed to solution chemistry change. The mechanism of "filter ripening" has been proposed to account for this observed increase of particle deposition. The improvement in particle deposition may indicate that the interaction between approaching particles and particles that had been already deposited is more favorable for deposition than the interaction of the approaching particles with the bare collectors. It has been observed that a relatively small number of retained particles that are destabilized can improve the deposition rate significantly (Elimelech and O’Melia 1990).

Findings obtained from particle transport studies in idealized model systems can not be directly applied to particle transport in natural porous media, such as soils and groundwater aquifers, since the natural media are too complicated and probably characterized by irregularly shaped and interconnected pores and wide pore and particle size distributions (Kretzschmar and Sticher 1997; Grolimund, Elimelech et al. 1998). However, the calculation of theoretical single collector efficiency ($\eta_{\text{theor}}$) and the measured particle attachment efficiency ($\alpha$) have been used by numerous researchers to semiempirically evaluate particle transport in laboratory and in field soils with reasonable agreement of predicted particle migration distances (Tobiason and O’Melia 1988; Harvey, George et al. 1989; O’Melia 1990; Kretzschmar and Sticher 1997; Zhuang, Jin et al. 2004).
Figure 5.4 shows the breakthrough curves of nC₆₀ particles at different flow rates. Flow rates used included 1 mL/hr (flow velocity = 0.38 m/d), 10 mL/hr (flow velocity = 3.8 m/d), and 30 mL/hr (flow velocity = 11.4 m/d). Parameters calculated for nC₆₀ particles transport in this set of experiments are listed in Table 5.2. Curve a is the breakthrough curve of nC₆₀ particles at the flow rate of 1 mL/hr, which has been shown in Figure 5.3 and is included in Figure 5.4 for comparison. Curve b is the breakthrough curve of nC₆₀ particles at the flow rate of 10 mL/hr. nC₆₀ particles were introduced into the soil column at this constant flow rate until about 55 pore volumes of the suspension has passed through the column. After about 4.4 pore volumes at 10 mL/hr, the value of C/C₀ is about 0.63, which is about 3 times that of nC₆₀ passage at flow rate of 1 mL/hr. The plateau value of nC₆₀ passage through the soil column at flow rate of 10 mL/hr was observed to be 60 ± 3%. Curve c was observed when the flow rate was changed to 30 mL/hr. At 30 mL/hr C/C₀ ≈ 0.73 after 3.9 pore volumes and remained relatively constant for the following 8 pore volumes. Following a period of a 72 hour shut-in, curve d is the breakthrough of nC₆₀ starting at 1 mL/hr for 18 pore volumes then 10 mL/hr for 8 pore volumes and finally 30 mL/hr for 24 pore volumes, all without interruption or shut-in. At the flow rate of 1 mL/hr, the percent of nC₆₀ breakthrough reached a peak value of 95% in the first 1.6 pore volumes, and that value dropped dramatically to 2.5% at 9.4 pore volumes. The C/C₀ value fluctuated slightly around zero but did not exceed 1% in the following 9 pore volumes. This observation was consistent with that observed in the 1 mL/hr flow rate nC₆₀ breakthrough experiments (Figure 5.3, and curve a in Figure 5.4), where no nC₆₀ passed through the soil column after about 56.7 pore volumes. The unexpectedly high C/C₀ value at 1.6 pore volumes (C/C₀ = 0.95) for the 1 mL/hr flow.
rate breakthrough is twice as much as that value for curve a, also at flow rate of 1 mL/hr. This difference is probably due to the flow interruption (3 days) between curve c and curve d. A similar spike of nC₆₀ following flow interruption and change was observed in nC₆₀ flush-out experiments with nC₆₀-free electrolyte solution and will be discussed in a later section. As shown in Figure 5.4 (curve d), when the flow rate was suddenly changed from 1 mL/hr to 10 mL/hr after about 18 pore volumes, nC₆₀ started to pass through the soil column and the percentage of passage reached 59% in 2.6 pore volumes. Although the plateau C/C₀ value fluctuated slightly, they were similar to those values observed in the 10 mL/hr breakthrough curve (curve b). Finally, the flow rate was increased to 30 mL/hr at 26 pore volumes and the plateau value of nC₆₀ passage was ~80%.

The mean plateau values for nC₆₀ passage at the three flow rates are listed in Table 5.2 with standard deviation. Values of collector efficiency (ηₜₜₒₑ₅ₒₑ), attachment efficiency (α), deposition rate coefficient (k, d⁻¹), and maximum travel distance (Lₜ) are calculated based on the corresponding C/C₀ values and experimental conditions listed in Table 5.1. It should be noted that for the ηₜₜₒₑ₅ₒₑ values in Table 5.2 and the particle size range of the nC₆₀ particles (~100 nm) and the velocity range used in this study, Brownian diffusion is the dominant process controlling the nC₆₀ transport to the collector surface. The contributions of the other two processes, direct interception and gravity forces, on the particle transport are negligible.

It can be seen from comparing the values in Table 5.2 that transport of nC₆₀ to collector surface is favored at lower velocity, i.e., the value of ηₜₜₒₑ₅ₒₑ decreased from 1.35 to 0.14 with increasing velocity. On the other hand, for the case of nC₆₀, the α value increased from 0.0046 to 0.0105 as flow velocity increased, suggesting that attachment of
nC_{60} was relatively favored at higher velocities. It was also observed in the transport of nC_{60} through glass beads column that $\alpha$ values increased with increasing flow velocity, although the values at 10 and 30 ml/hr are statistically indistinguishable (Lecoanet and Wiesner 2004). When considering particle transport to the collector and attachment efficiency together, the value of the product, $\alpha \cdot \eta_{\text{theor}}$, decreases with increasing flow velocity, meaning that fewer particles approaching the collector surface from upstream attach to the collector surface at higher flow velocity, as expected. Consequently, the maximum travel distance to remove 99.9% of nC_{60} to the porous media increased with increasing flow velocity, for example, at 0.152 m/d, 99.9% of nC_{60} will be removed by the soil after traveling for 31 cm; while at 4.56 m/d, 99.9% of nC_{60} will be removed by the soil only after traveling for 132 cm.

Results for nC_{60} flush-out experiments are shown in Figure 5.5, in each case $C_0 = 48$ mg/L is assumed. Data shown in Figure 5.5 (a) are from the nC_{60} flush-out experiment initiated 7 days after the completion of nC_{60} breakthrough experiments (Figure 5.4). Initial flow rate used was 10 mL/hr. A peak of nC_{60} ($C/C_0 = 0.46$) was apparently reached at 2 pore volumes, although the exact position of the peak is not known. After 4 pore volumes, no further nC_{60} breakthrough was observed, despite the fact that the flow rate was increased to 30 mL/hr without interruption at 13.8 pore volumes. Another nC_{60} flush-out experiment was conducted after 3 days of shut-in (Figure 5.5 b). Initial flow rate used in this experiment was 30 mL/hr. A peak of nC_{60} passage, $C/C_0 = 0.13$, was reached at 5.9 pore volumes. After that, the value of $C/C_0$ for nC_{60} dropped to zero, despite the fact that the flow rate was increased to 40 and then 60 mL/hr at 71 and 181 pore volumes, respectively. The last nC_{60} flush-out experiment was conducted 3 days after the second
set and data are shown in Figure 5.5 c. A single flow rate of 1 mL/hr was used. The value of \( C/C_0 \) for \( nC_{60} \) reached a peak value of 107% at 1.6 pore volumes, and then decreased gradually to zero after 7.9 pore volumes. No \( nC_{60} \) breakthrough was observed thereafter.

Three tracer breakthrough curves are shown in Figure 5.6. In all three tests, the values of tracer breakthrough reached about 50% in 1 pore volume, and 100% after about 2 pore volumes. There is no statistical difference between the three tracer breakthrough curves, suggesting that the soil column is stable with negligible physical change during the total experimental time frame.

### 5.3.2 Naphthalene breakthrough experiments.

The transport of contaminants in soil columns is generally described by a one dimensional advective-dispersive equation (ADE) (Bear 1979):

\[
r s c = d 3 / £ _ v « c (52)
\]

where \( C \) represents contaminant concentration in the flowing water; \( T \) and \( x \) are the contaminant travel time and travel distance; and \( v \) represents the linear flow velocity. \( R \) in Eq. 5.2 denotes the retardation factor:

\[
R = 1 + (\rho_b / \varepsilon)(dq / dC)
\]  

where \( \rho_b \) is the bulk density of the porous media; \( \varepsilon \) is media porosity; and \( q \) is the amount of contaminant sorbed on the porous media (e.g. soil) per gram of solid weight. If \( q = K_p C \) (a linear isotherm) then \( dq/dC = K_p \) and \( K_p \) can be calculated from measured values of \( R \).

After the completion of all \( nC_{60} \) breakthrough experiments, the mass of \( C_{60} \) retained on this soil column was calculated to be about 1.8 mg-\( C_{60}/g\)-soil, i.e., 0.18% of...
soil mass. $^{14}$C labeled naphthalene aqueous solution ($^{14}$C-naphthalene = 0.58 mg/L) was passed through this soil column at the flow rate of 1 mL/hr for 45 hrs (effluent totaled 34.1 pore volumes), followed by flushing with naphthalene-free electrolyte solution. Data are shown in Figure 5.7 (curve c). Curve a is the tracer ($^3$H$_2$O) breakthrough curve for this soil column. Naphthalene transport through the same soil has been studied by Kan and Tomson (Kan and Tomson 1990) with a different column using the same packing method. The naphthalene breakthrough curve is included Figure 5.7 (curve b) for comparison.

Since the column had been flushed with 0.01M NaCl/0.01M NaN$_3$ background electrolyte solution at the flow rate of 1 mL/hr for a few hours and there is no flow interruption between the electrolyte flushing and the following naphthalene breakthrough experiments, no C$_{60}$ release from the column was expected in the naphthalene flush-out experiment. This was verified by measuring the C$_{60}$ concentration spectroscopically in the "C$_{60}$ monitoring vials". No C$_{60}$ was detectable in any of those vials. This is consistent with that observed from nC$_{60}$ flush-out experiments (Figure 5.5), where no nC$_{60}$ was released from the column after a few pore volumes.

To compare curves b and c (Figure 5.7), it can be seen that in the breakthrough experiment with the column in this study (Lula soil with 0.18% of nC$_{60}$, curve c), only 10% of naphthalene passed through the column at 5.3 pore volumes, which is 24% of the C/C$_0$ value from the breakthrough experiment with the column packed with Lula soil only (without nC$_{60}$, curve b), at the same number of pore volumes. At 20 pore volumes, C/C$_0$ for naphthalene was 0.71 through the Lula/0.18% nC$_{60}$ column, and in the next 14.1
pore volumes $C/C_0$ increased by 0.18. Naphthalene breakthrough with the Lula soil only column reached 98.5% in 13.9 pore volumes.

In the naphthalene flush-out experiment following 34.1 pore volumes of continuous introduction of naphthalene solution, the $C/C_0$ value of naphthalene dropped from 89% at 34.1 pore volumes, to 14% at 68.2 pore volumes. During the next 37.8 pore volumes, the percentage of naphthalene breakthrough dropped from 14% to 1.4%.

The partition coefficient of naphthalene with Lula soil was reported to be $K_{soil} = 1.91 \text{ mL/g}$ (Kan and Tomson 1990) i.e., $K_{oc} = K_{soil} / f_{oc} = 1.91 / 0.0027 = 707 \text{ mL/g}$. Using this value and the porosity of 0.40 and the bulk density of 1.57 g/cm$^3$ for Lula soil, a retardation factor $R = 8.5$ can be calculated for breakthrough curve b (Figure 5.7) with Eq. 5.3. A retardation factor (denoted as $R'$) for the naphthalene breakthrough curve with the Lula/0.18% nC$_{60}$ column (curve c in Figure 5.7) is about 13.1 at $C/C_0 = 0.5$. The soil partition coefficient for naphthalene with Lula/0.18% nC$_{60}$ can be calculated from this $R'$ value with Eq. 5.3, $K_{soil, 0.18\% C_{60}} = 3.08 \text{ mL/g}$. Therefore, the organic carbon normalized partition coefficient for naphthalene with the nC$_{60}$ on Lula soil column is calculated to be $K_{oc} = 10^{3.81} \text{ mL/g}$. This $K_{oc}$ value is similar to the $K_{oc}$ value obtained for naphthalene with Lula soil ($10^{2.85} \text{ mL/g}$), but it is about 0.9 log-unit lower than the nC$_{60}$ partition coefficient $K_{nC_{60}} = 10^{3.74} \text{ mL/g}$, as was discussed in Chapter 3. In other words, if the partition coefficient of naphthalene with the 0.18% nC$_{60}$ on Lula soil column were $10^{3.74} \text{ mL/g}$, a higher retardation factor, $R' = 43.9$, would have been observed for curve c, and thus a shift far to the right. Why the observed $K_{oc}$ value is less than that for the batch experiments is not known, but it might be related to restricted physical access to the immobilized nC$_{60}$ on the soil. Also this difference between prediction and observation,
and the observed asymmetry of naphthalene breakthrough curve (the earlier breakthrough, and the “elution-front tailing”) might be related to “sorption nonequilibrium”. The effect of sorption nonequilibrium on solute transport was recognized since very early time (Wilson 1940) and is discussed in detail more recently by Brusseau and Rao (Brusseau and Rao 1989). When the sorption nonequilibrium occurs, the breakthrough curve can shift to the left and the breakthrough fails to reach 1.00, resulting in an apparently smaller value of the retardation factor. The occurrence of sorption nonequilibrium has been attributed to the result of two different classes of sorption sites on the sorbent surfaces (Giddings and Eyring 1955), or rate-limiting intra-aggregate diffusion (Rao, Green et al. 1974), or intrasorbent diffusion (particularly intraorganic matter diffusion). It was observed in the authors’ previous studies that C60 could form different sizes of aggregates under different conditions, and observed desorption hysteresis may be due to the intra-aggregate or intra-particle entrapment of naphthalene (Cheng, Kan et al. 2004; Cheng, Kan et al. 2005). The desorption kinetics of naphthalene from nC60 have been studied and was discussed in Chapter 3. Desorption of naphthalene from nC60 can be described by an empirical two-compartment first-order kinetics model. Approximately 30% of sorbed mass comprised the fast desorption compartment in the first desorption step. In a second desorption step, only less than 10% of the remaining naphthalene desorbs rapidly. This phenomenon suggests that the desorption of naphthalene from nC60 is hysteretic and slow, which is probably consistent with the observed asymmetric naphthalene breakthrough in this study. The reason might be the slow diffusion of naphthalene into aggregates of nC60, or into nC60. The mechanism is not known for certain yet, further study is needed.
5.4 Conclusions.

Although C₆₀ was expected to be very hydrophobic, which would probably lead to very limited mobility of C₆₀ in aqueous environments, water-stable nC₆₀ have been produced by different methods (Scrivens, Tour et al. 1994; Andrievsky, Kosevich et al. 1995; Deguchi, Alargova et al. 2001). This increased apparent hydrophilicity may lower the attachment efficiency of nC₆₀ and consequently increase the mobility of C₆₀. If this is true, the public may be more concerned about the exposure to the mobilized C₆₀, since there are already studies showing the toxicity of nC₆₀ to fish and to cultured human cells (Oberdorster 2004; Sayes, Fortner et al. 2004). The following are some of the observations in this study: Firstly, the plateau value of C/C₀ value for nC₆₀ transport through Lula soil column never reached 100% at any of the flow velocities used, suggesting that nC₆₀ may not be as mobile as expected. Secondly, at the lowest flow velocity (0.38 m/d), the unexpected drop of C/C₀ value to zero might also indicate that at slow groundwater flow rates, nC₆₀ may be easily immobilized by sediments. Thirdly, results from the nC₆₀ flush-out show that release of nC₆₀ may occur under complex aqueous environments, such as the interruption of flow or a sudden change of flow rate. Finally, naphthalene breakthrough experiments show that adsorbed nC₆₀ behave similar to soil organic carbon. Certainly, the transport of C₆₀ and its effect on contaminant transport in natural environment needs to be further studied, with various media/chemical combinations and experimental conditions.
Table 5.1. Parameters used in the nC$_{60}$ breakthrough experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column inner diameter</td>
<td>0.9 cm</td>
</tr>
<tr>
<td>Depth of soil in the column</td>
<td>5 cm</td>
</tr>
<tr>
<td>Soil particle radius ($a_c$)</td>
<td>125 μm</td>
</tr>
<tr>
<td>Porosity, $\varepsilon$</td>
<td>0.40</td>
</tr>
<tr>
<td>pH</td>
<td>$6.70 \pm 0.01$ ~ $7.20 \pm 0.01$</td>
</tr>
<tr>
<td>Electrolyte composition</td>
<td>0.01M NaCl, 0.01M NaN$_3$</td>
</tr>
<tr>
<td>Particle size of nC$_{60}$</td>
<td>~100 nm</td>
</tr>
<tr>
<td>Density of nC$_{60}$</td>
<td>1.41 g/cm$^3$$^a$</td>
</tr>
<tr>
<td>Initial nC$_{60}$ concentration</td>
<td>48 mg/l</td>
</tr>
<tr>
<td>Temperature</td>
<td>23 $\pm$ 0.1 °C</td>
</tr>
</tbody>
</table>

$^a$ Data from Lecoanet & Wiesner, 2004
Table 5.2. Parameters for nC₆₀ transport in Lula soil column. \( v \) (m/d) – linear flow velocity; \( U \) (m/d) – superficial or approach velocity; \( \eta_{\text{theor}} \) – theoretical single collector efficiency; \( \alpha \) – particle attachment efficiency; \( L_T \) (m) – the distance at which 99.9% of nC₆₀ \( (C_t/C_0 = 0.001) \) are removed by the porous media.

<table>
<thead>
<tr>
<th>Flow rate (ml/hr)</th>
<th>( v ) (m/d)</th>
<th>( U ) (m/d)</th>
<th>( \eta_{\text{theor}} )</th>
<th>( C/C_0 )</th>
<th>( \alpha )</th>
<th>( \alpha \cdot \eta_{\text{theor}} )</th>
<th>( L_T ) (m)</th>
<th>( k ) (d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (0-56.5 PV)a</td>
<td>0.38</td>
<td>0.152</td>
<td>1.35</td>
<td>0.33±0.07</td>
<td>0.0046</td>
<td>0.0063</td>
<td>0.32</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>±0.008</td>
<td>±0.0012</td>
<td>±0.06</td>
<td>±0.66</td>
<td></td>
</tr>
<tr>
<td>1 (56.5-116.5PV)b</td>
<td>0.38</td>
<td>0.152</td>
<td>1.35</td>
<td>0</td>
<td>1</td>
<td>1.35</td>
<td>0.0014</td>
<td>738.72</td>
</tr>
<tr>
<td>10</td>
<td>3.8</td>
<td>1.52</td>
<td>0.29</td>
<td>0.60±0.03</td>
<td>0.0098</td>
<td>0.0028</td>
<td>0.68</td>
<td>15.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>±0.0013</td>
<td>±0.0004</td>
<td>±0.10</td>
<td>±2.15</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>11.4</td>
<td>4.56</td>
<td>0.14</td>
<td>0.77±0.04</td>
<td>0.0105</td>
<td>0.0015</td>
<td>1.37</td>
<td>23.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>±0.0030</td>
<td>±0.0004</td>
<td>±0.38</td>
<td>±6.70</td>
<td></td>
</tr>
</tbody>
</table>

aValues in this line were calculated from 1 mL/hr breakthrough data from 0 to 56.5 pore volumes.

bValues in this line were calculated from 1 mL/hr breakthrough data from 56.5 to 116.5 pore volumes.
Figure 5.1. Schematic illustration of the soil column apparatus.
Figure 5.2. Representative TEM image of nC$_{60}$ with faceted edge. The average size of nC$_{60}$ is ~100nm. Scale bar on the picture is 20 nm.
Figure 5.3. nC₆₀ breakthrough curve and tracer (¹H₂O) breakthrough curve (flow rate for both is 1mL/hr). C (mg/L), nC₆₀ concentration exiting the column; C₀ (mg/L), nC₆₀ concentration in the input. The inset shows the enlarged tracer breakthrough curve.

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Figure 5.4. nC₆₀ breakthrough curves at different flow rates. ×, flow rate is 1 mL/hr ($v = 0.38$ m/d); o, flow rate is 10 mL/hr ($v = 3.8$ m/d); Δ, flow rate is 30 mL/hr ($v = 11.4$ m/d). The interruption of flow between curve a and b, b and c, c and d is 3 days each.
Figure 5.5. Plots of percentage of nC\textsubscript{60} passage through the soil column versus pore volume during the nC\textsubscript{60} flush-out experiments. ×, flow rate is 1 mL/hr (v = 0.38 m/d); o, flow rate is 10 mL/hr (v = 3.8 m/d); Δ, flow rate is 30 mL/hr (v = 11.4 m/d). ◊, flow rate is 40 mL/hr (v = 15.2 m/d); +, flow rate is 60 mL/hr (v = 22.8 m/d); The interruption of flow between curve a and b, b and c is 3 days each.
Figure 5.6. Tracer ($^3$H$_2$O) breakthrough curves. ◆, tracer breakthrough data obtained before any nC$_{60}$ breakthrough experiments being conducted; □, tracer breakthrough data obtained after nC$_{60}$ breakthrough experiments (but before the nC$_{60}$ flush-out experiments); Δ, tracer breakthrough data obtained right before conducting naphthalene breakthrough experiments.
Figure 5.7. (a) Tracer ($^3$H$_2$O) breakthrough curve; (b) naphthalene breakthrough curve from Lula soil column; and (c) naphthalene breakthrough curve from Lula soil column with 0.18% deposited nC$_{60}$.
CHAPTER 6

CONCLUSIONS

In this work, "nC₆₀" (water-stable C₆₀ aggregates) were prepared by first dissolving C₆₀ into organic solvents, such as toluene and THF, then mixing the C₆₀/solvent solution into water, followed by removal of the solvent. Interestingly, it was discovered for the first time in this work that "nC₆₀" can be formed by simply stirring in water without addition of any organic solvents. The surfaces of the formed nC₆₀ were characterized by negative surface charges. Since these nC₆₀ may be stable in water for months, this form may be the most environmentally relevant form of C₆₀.

The adsorption and desorption of naphthalene and 1,2-dichlorobenzene with C₆₀ of different sizes was investigated. It was observed that the size of C₆₀ aggregates could affect the adsorption of naphthalene by orders of magnitude. Kinetics data of naphthalene desorption from nC₆₀ indicated that desorption of naphthalene from C₆₀ aggregates may be composed of two compartments: a labile desorption compartment, where naphthalene can be readily desorbed; and a resistant desorption compartment, where naphthalene may be entrapped in C₆₀ aggregates and desorption is hindered.

Desorption of both naphthalene and 1,2-dichlorobenzene from nC₆₀ exhibits hysteresis. Adsorption and desorption of naphthalene with activated carbon and soil organic carbon was also conducted and desorption also shows hysteresis. Since sorption hysteresis is observed for the adsorption and desorption of naphthalene and 1,2-dichlorobenzene with C₆₀, activated carbon, and soil organic carbon, experimental adsorption-desorption data can not be fitted with a single linear isotherm. In this work, they were fitted with four different sorption models, including Freundlich model,
Langmuir model, two-compartment dual-equilibrium desorption model (DED), and Polanyi-Manes sorption model. Results show that DED model or Polanyi-Manes model fit data pretty well, while the overall data are not well described by the Langmuir model. Each DED model obtained parameter has similar values for different carbon forms, indicating that this model may possibly be used to predict the sorption behavior of new carbonaceous materials from that of other known carbons. The good fitting of data with the Polanyi-Manes model implied that the intraparticle pore-filling might be the mechanism controlling the adsorption of organic compounds to C\textsubscript{60} aggregates.

It was observed in the study of transport of nC\textsubscript{60} in natural porous media that nC\textsubscript{60} showed very limited mobility under typical groundwater flow velocities. Results from the nC\textsubscript{60} flush-out show that spiked release of nC\textsubscript{60} may occur under complex aqueous environments, such as the interruption of flow or a sudden change of flow rates. Naphthalene breakthrough experiments showed that adsorbed nC\textsubscript{60} behave similar to soil organic carbon.
CHAPTER 7

FUTURE WORK

• Surface structures of carbonaceous nanomaterials such as the existence of micropores need to be studied in more detail.

• Further study of interactions of nanoparticles with surrounding water molecules will be necessary for understanding their sorptive properties.

• Due to the small sizes of nanoparticles, the desorption experiments were more difficult compared to other larger sorbent particles, particularly in the separation of nanoparticles from water phase. Improvements need to be made to make the experimental technique more efficient and more reliable.

• Studies of interactions of more organic contaminants such as chlorinated benzene or PCBs, with more carbon nanomaterials such as carbon nanotubes, will be necessary to understand the mechanism(s) underlying the sorptive properties of carbon nanomaterials.

• Interactions of fullerenes and carbon nanotubes with other sorbents such as black carbons and activated carbons will possibly alter the transport of carbon nanomaterials and the interactions of contaminants with nanomaterials, and thus need to be investigated.
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