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Impact of Porous Media Grain Size on the Transport of Multiwalled Carbon Nanotubes

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IMPACT OF POROUS MEDIA GRAIN SIZE ON THE TRANSPORT OF
MULTIWALLED CARBON NANOTUBES

(Spine Title: Grain Size Impacts on Multiwalled Carbon Nanotube Transport)

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2

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

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The University of Western Ontario
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THE UNIVERSITY OF WESTERN ONTARIO
SCHOOL OF GRADUATE AND POSTDOCTORAL STUDIES

Certificate of Examination

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Abstract

Nanomaterials possess unique physical, electrical and chemical properties which make them attractive for use in a wide range of applications. Through their use and eventual disposal, nanomaterials may ultimately be released into the subsurface environment and previous studies show that nanomaterials may pose a hazard to health. This study investigates the mobility of one important nanomaterial (multi-walled carbon nanotubes or MWNTs) through porous media. Particular focus is placed on the impact of varying mean collector grain size on MWNT retention. Results from one dimensional column experiments conducted under various physical and chemical conditions coupled with results of numerical modeling assess the suitability of traditional transport models to predict MWNT mobility. MWNTs were found to be mobile through porous media ranging from fine sand to silt. Findings suggest that a dual deposition model coupled with site blocking greatly improves model fits compared to traditional colloid filtration theory.

Keywords: multi-walled carbon nanotubes, MWNT, site blocking, grain size, dual deposition, mobility, subsurface, nanomaterial

Co-Authorship

The thesis was written in accordance with the guidelines and regulations for an integrated-article format stipulated by the School of Graduate and Postdoctoral Studies at the University of Western Ontario. The candidate conducted all the laboratory experiments; collected, interpreted and analyzed the experimental data under the close guidance and supervision of Dr. O'Carroll. The candidate wrote the manuscript draft of the follow chapters:

Chapter 3: Impact of Porous Media Grain Size on the Transport of Multiwalled Carbon Nanotubes

By: Nikolai T. Mattison and Denis M. O'Carroll

Contributions:

Nikolai T. Mattison: performed the experiments, collected and interpreted experimental results, performed mathematical modeling and wrote the draft of the paper.

Denis M. O'Carroll: initiated the research topic, developed methodology, supervised the laboratory tests, provided the mathematical model, assisted in data interpretation and mathematical modeling, and reviewed/revised the draft chapter

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List of Abbreviations

CNT	carbon nanotube
MWNT	multi-walled carbon nanotube
SWNT	single-walled carbon nanotube
CFT	colloid filtration theory
vdW	van der Waals
EDL	electrostatic double layer
NOM	natural organic matter
SGC	Stern-Gouy-Chapman
SDBS	dodecylbenzene sulfonic acid, sodium salt
RMSE	root mean square error
DDM	dual deposition model

List of Nomenclature

V_A	total van der Waals interaction energy
$V_{\max}$	maximum repulsive barrier
A	Hamaker constant,
a_1	radii of sphere 1
a_2	radii of sphere 2
h	separation distance between the two spheres
λ	"characteristic wavelength of interaction"
ζ	zeta potential
V_R	total EDL repulsion interaction energy
e	elementary charge
a	particle radius
κ	Debye-Hückel parameter
z	ionic valence
N_A	Avogadro's constant
c (aq)	aqueous concentration of ions
ϵ	dielectric permittivity
ϵ_0	dielectric permittivity of free space
k_B	Boltzman's constant
T	absolute temperature
η_0	single collector efficiency
η_G	sedimentation single collector efficiency
η_D	diffusion single collector efficiency
η_I	interception single collector efficiency
Pe	Peclet number
ρ_p	particle bulk density
g	acceleration due to gravity
ρ	solution bulk density
μ	viscosity of the bulk solution
v_0	approach velocity
d_p	particle diameter
d_c	collector diameter
l	particle length
N_R	dimensionless aspect ratio number
N_{Pe}	dimensionless Peclet number
N_{gr}	dimensionless gravitational number
N_{vdW}	dimensionless van der Waals number
N_A	dimensionless attractive number
N_G	dimensionless gravity number
A_S	dimensionless porosity number
C	aqueous phase particle concentration
D	hydrodynamic dispersion coefficient
α_1	longitudinal dispersivity
n	porosity

S	solid phase particle concentration
t	time
x	distance
k_{det}	detachment rate coefficient
k_{att}	attachment/deposition rate coefficient
α	attachment efficiency
v	pore water velocity
ψ	blocking function
S_{max}	maximum solid phase concentration
C_0	initial particle concentration
$p(k)$	bimodal distribution of k_{att}
$\bar{k}_{\text{slow}}$	mean slow deposition rate coefficient
$\bar{k}_{\text{fast}}$	mean fast deposition rate coefficient
σ_{slow}	slow deposition rate standard deviation
σ_{fast}	fast deposition rate standard deviation
f_{slow}	slow fraction of the total population of particles
f_{fast}	fast fraction of the total population of particles
$k_{\text{att.i}}$	fast/favourable attachment rate coefficient
$k_{\text{att.ii}}$	slow/unfavourable attachment rate coefficient
α_i	fast/favourable attachment efficiency
α_{ii}	slow/unfavourable attachment efficiency
d_{50}	mean collector grain size
U_1	uniformity coefficient
K	hydraulic coefficient

Chapter 1 - Introduction

1.0 Background

Nanotechnology involves the manipulation of nanomaterials (i.e., a material with one dimension under 100 nm (ASTM-International, 2006)) to form new products with enhanced properties and is thought to be one of the most promising emerging areas in science. Nanomaterials display unique electronic, optical, thermal and photoactive properties (Petosa et al., 2010) which make them very attractive for a number of applications ranging from components in advanced electronics and construction to drug delivery (Mauter and Elimelech, 2008). It has been estimated that in 2005 nanotechnology was incorporated into more than \$30 billion dollars (USD) in manufactured goods and it has been suggested that by the year 2014 products containing nanomaterials will be found in 15% of all products produced worldwide, representing 2.6 trillion dollars (Reinhart et al., 2010).

Of the 1.2 billion dollars spent in the U.S.A. on nanotechnology development in 2006 only 11 million dollars (i.e., <1 %) was devoted to research on environmental risks associated with nanomaterials (Hannah and Thompson, 2008). Given the increased production and utilization of nanomaterials there is heightened potential for their release into the environment where subsequent impacts on the ecosystem are of significant concern (Klaine et al., 2008). Research into the toxicity of nanomaterials suggests that they may be hazardous to human health (Handy and Shaw, 2007) while other findings on ecotoxicity suggest that nanoparticles can produce morbidity and mortality of organisms including bacteria through nanoparticle uptake (Hannah and Thompson, 2008). Such findings suggest that a greater understanding of the potential risks associated with nanomaterials is needed.

A key component of investigating the overall risk that nanomaterials may pose to the ecosystem is to determine the various exposure pathways that can occur. Through nanomaterial disposal in landfills or wastewater, nanoparticles may enter the subsurface environment. Subsurface systems are complex and while some literature is available, further characterization of nanomaterial behaviour is needed to better understand the transport and fate of nanomaterials in the subsurface.

1.1 Research Objectives

The objective of this research is to investigate the mobility of commercially available multi-walled carbon nanotubes (MWNTs) through porous media (quartz sand) at pore water velocities and aquatic chemistries that are representative of natural and engineered groundwater conditions. A particular focus is placed on the impact of mean collector grain or porous media diameter (d_{50}) on MWNT transport and deposition in porous media. Through the use of a one dimensional finite element model, governing parameters can be estimated from experimental data by solving governing mass balance equations. This will lead to a greater understanding of retention mechanisms governing MWNT mobility.

1.2 Thesis Outline

This thesis written in “Integrated Article Format” containing the following chapters:

Chapter 1 presents a general introduction to nanomaterial usage and associated risk as well as general research objectives.

Chapter 2 gives a review of research relevant to MWNT mobility. These studies include colloidal deposition studies investigating relevant retention mechanisms and transport studies that specifically look at carbon nanotubes (CNT) mobility through porous media. Discussion of experimental methods and results include the limitations of current research

Chapter 3 describes the research conducted in this study including methods used to investigate MWNT mobility through porous media of different mean collector grain size. This chapter includes a discussion of the results obtained from column experiments and mathematic modeling.

Chapter 4 summarizes the research undertaken in this study and presents conclusions of findings. Recommendations based on these findings are given for future directions in the investigation of MWNT mobility through porous media.

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Chapter 2 - Literature Review

2.0 Introduction

Nanomaterials are defined as materials with at least one dimension being smaller than 100 nm, with nanoparticles defined as materials with at least two dimension under 100nm (ASTM-International, 2006). Nanomaterials have unique thermal, electrical and physical properties that make them appealing for use in many existing and potential commercial and industrial applications (Wiesner and Bottero, 2007). Examples of the types of nanoparticles are (Klaine et al., 2008):

- Fullerenes and carbon nanotubes (CNTs)
- Metal oxide containing materials (e.g., TiO_2)
- Semiconductor nanocrystals (Quantum dots)
- Zero-valent metals (e.g., nano zero-valent iron)

Due to large demand for nanoparticles along with increased production and use, these particles will unavoidably end up in the environment through accidental spills or deliberate disposal. The possible human and environmental interactions of these particles are largely unknown and further research is needed to identify any possible negative impacts they may have on the environment. Understanding the transport of these nanoparticles is a key step in determining the overall level of interaction nanoparticles will have with their surroundings (Jaisi et al., 2008b). CNTs have received significant attention and are expected to be used in a wide range of applications due to their unique properties (Klaine et al., 2008). Applications include

reinforced concrete and construction materials (Mauter and Elimelech, 2008) as well as advanced bio sensors and drug delivery (Saleh et al., 2010).

There is limited literature readily available that addresses the mobility of CNTs (in the form of single walled carbon nanotubes (SWNT)) through porous media (Jaisi and Elimelech, 2009; Jaisi et al., 2008b; Lecoanet et al., 2004; Lecoanet and Wiesner, 2004), with even less which specifically looks at the mobility of multiwalled carbon nanotubes (MWNTs) (Liu et al., 2009b; Wang et al., 2008). While SWNTs and MWNTs share many of the same bulk properties they behave differently at the particle scale. Due to the differences between them they are expected to be used for dissimilar purposes (Mauter and Elimelech, 2008). For this reason it is important to understand the behaviour of both types of particles.

This chapter will first outline the principles that are essential in understanding the colloidal behaviour of nanoparticles (e.g., Derjagun-Landau-Verwey-Overbeek (DLVO) theory and traditional colloid filtration theory (CFT)). In addition some of the characteristics of nanoparticles which make their transport behaviour unique as compared to other colloids will then be highlighted. Previous studies on nanoparticle aggregation and transport will be presented along with the limitations and major findings of these studies.

2.1 DLVO Theory of Colloidal Stability

In order to gain insight into the mechanisms controlling MWNT transport in the subsurface it is necessary to understand the various forces governing nanoparticle migration in the subsurface. Due to their size and surface charge nanoparticles experience interparticle (particle-particle) and particle-surface forces that heavily influence their overall behaviour. Particle-particle forces will govern aggregation of nanoparticles while particle-surface forces

determine the deposition of nanoparticles on soil surfaces. The behaviour of colloidal particles can be considered as the result of competing forces on charged colloidal particles. In the case of MWNTs the major competing forces are attractive van der Waals (vdW) and repulsive electrostatic double layer (EDL) interactions. The sum of these forces defines the total interaction energy (V_T). When the total interaction energy is positive particles tend to agglomerate and settle out of solution. In addition to these traditional DLVO forces, particles can also experience other forces including hydration effects, hydrophobic interactions, polymer bridging and steric interactions (Elimelech et al., 1995). In most cases, where there is no polymer attached to the surface of the nanoparticle, the magnitude of these 'non-DLVO' forces can be neglected (Elimelech et al., 1995). An example of a situation where polymers may attach to the surface of the particle is in the case of natural organic matter (NOM) in the aqueous phase. Researchers have shown that this NOM can bind to CNT surfaces and increase their stability (Hyung et al., 2007; Saleh et al., 2008). In these cases, steric repulsion between particles is significant and should be included in the overall calculations of V_T .

2.2 London van der Waals attractive Forces

Attractive forces occur between two separated surfaces due to spontaneous electrical and magnetic polarization. This spontaneous polarization produces fluctuations in the electromagnetic field occurring in the space between surfaces (Elimelech et al., 1995). As molecules with permanent dipoles begin to align with the dipoles of similar adjacent molecules an attractive force will be experienced between these two molecules. This may then cause an induced dipole in a neighbouring neutrally charged molecule which will align and be attracted to the original pair of molecules. Dipoles in atoms are caused by the movement of electrons around

their nuclei; this movement is erratic and causes rapid fluctuation of dipoles even in neutrally charged atoms. This overall interaction is non-directional so even in a large group of particles where the orientations of dipoles vary significantly the net attraction will not be cancelled out (Cosgrove, 2010).

Early attempts to quantify these attractive forces led to the conventional approach, which entails the summation of all intermolecular forces between two spherical particles (Hamaker, 1937). This is done by summing the interaction of an atom on the first particle with every atom on the second particle; this process is then repeated for every atom on the first particle (Figure 2.1). All calculations of interaction done by this method can be broken down into two parts; a geometric component, which relates the radii of two particles to the separation distance between them and a constant A , the Hamaker constant. The basic Hamaker constant is related to the electronic polarisability and density of the material (Cosgrove, 2010). For the simplified case depicted in Figure 2.1 involving two spherical particles in a vacuum, the total van der Waals interaction is given by (Gregory, 1981):

$$V_A = -\frac{Aa_1a_2}{6h(a_1 + a_2)(1 + \frac{14h}{\lambda})} \quad [2-1]$$

where A is the Hamaker constant, a_1 and a_2 are the radii of spheres 1 and 2, respectively, h is the separation distance between the two spheres and λ is the “characteristic wavelength of interaction” (Gregory, 1981), typically 100 nm.

Figure 2.1: Model of microscopic approach to quantifying van der Waals force where a is the particle radius and h is the separation distance (Cosgrove, 2010)

2.3 Electrostatic Double Layer Interactions

Electrostatic principles dictate that a charged surface immersed in an electrolyte solution will attract counter ions and repel similarly charged ions. This creates an electrolyte layer which in turn attracts counter ions. For example when a negatively charged silica sand particle is placed in a solution containing NaCl, the positively charged sodium ions will be attracted towards the negatively charged silica surface (Figure 2.2). Electroneutrality is achieved when the electrolyte layer near to the surface possesses a charge that is equal in magnitude and opposite in charge to that of the surface (Cosgrove, 2010). The Stern-Gouy-Chapman (SGC) model as shown in Figure 2.2 describes this configuration by arranging ions into two main layers; the inner or Stern layer and the diffuse layer (Cosgrove, 2010). The combination of these layers is referred to as the electrostatic double layer (EDL). The Stern layer is considered to be immobile. Surrounding this layer is the diffuse layer where ions and therefore charges are thought to be mobile. Generally a shear plane is thought to exist between the immobile Stern layer and the mobile diffuse layer. It is considered that the shear plane is located just outside the Stern layer thus all charge in the Stern layer is considered immobile and all charge in the diffuse layer is mobile (Elimelech et al., 1995). The electrical potential at this shear plane is defined as the zeta potential (ζ). The zeta potential is a useful parameter used in the study of colloid

stability. Generally at lower zeta potential values particles will tend to agglomerate and deposit onto surfaces. EDL repulsion is given by (Elimelech et al. 1995)

Figure 2.2: Schematic representation of the double layer structure according to SGC model (Cosgrove, 2010)

The EDL becomes increasingly important for multiple bodies immersed in an electrolyte solution (i.e., between multiple colloidal particles in the case of aggregation and between colloidal particles and porous media, in the case of deposition). When these particles get close to each other their EDLs will overlap. This causes the ionic concentration midway between the two particles to increase and result in an osmotic pressure gradient that forces the particles away from each other (Cosgrove, 2010). The interaction energy resulting from such encounters can be calculated in two ways; direct solution of the Poisson-Boltzman equation or the formulation of an expression derived from other known relationships (summing the individual contributions of van der Waals attraction and electrostatic repulsion) for the each of the two bodies independent

of any other body. For small values of zeta potential and identical particles the interaction energy due to EDL repulsion is given by (Elimelech et al, 1995):

$$V_R = 2\pi e a \zeta^2 \exp(-\kappa h) \quad [2-2]$$

where e is the elementary charge, a is the particle radius, ζ is the zeta potential, h is the separation and κ is the Debye-Hückel parameter which can be calculated by (Elimelech et al, 1995):

$$\kappa = \left(\frac{2z^2 e^2 N_A c(aq)}{\epsilon \epsilon_0 k_B T} \right)^{\frac{1}{2}} \quad [2-3]$$

where z is the ionic valence, e is the elementary charge, N_A is Avogadro's constant, ϵ_0 is the permittivity of free space, k_B is Boltzmann's constant, T is the temperature and $c(aq)$ is the concentration of ions in the bulk electrolyte. The reciprocal of the Debye-Hückel parameter ($1/\kappa$) in theory is the total thickness of the diffuse layer and due to its relative size compared to the Stern layer, in most cases it can be considered the overall EDL thickness (Elimelech et al., 1995). This form shows the importance of ionic strength on the overall interaction as an increase in ion concentration will subsequently lead to a reduction in the values of ζ and an increase in the value of κ , which in turn decreases the overall repulsive forces experienced by two particles.

Expressions have been formulated for the potential energy of electrostatic contributions (i.e., EDL contributions) between two cylindrical particles and between a cylinder and a plate which would be analogous to (MWNT-MWNT) and (MWNT-sand grain) interactions (Ohshima, 1999; Ohshima and Hyono, 2009) however these expressions can only account for a few configurations of the cylinders (either parallel or perpendicular to the other surface). The surface

element integration (SEI) technique is an important method by which the EDL interaction energy can be estimated for non-spherical particles theoretically, including MWNT (Petosa et al., 2010). This method is useful because it can be used to directly calculate EDL forces through solving the Poisson-Boltzman equation. Unlike traditional approaches the SEI technique does not rely on the assumption that interaction distance is small compared to particle curvature (Bhattacharjee and Elimelech, 1997). Expressions describing the total interaction as a function of separation of CNTs have been developed (Khripin et al., 2009; McLean et al., 2006) however these forms can only consider few configurations of the CNTs (parallel and perpendicular to the other surface) and suffer due to a lack of published Hamaker constants for CNTs.

2.4 Interaction Energy Summary

Summation of the van der Waals attractive forces (V_A) and electrostatic double layer forces (V_R) gives the total potential energy (V_T), which can be expressed as a function of separation distance (Figure 2.3). When the plot of V_T has a positive value the force experienced by the interacting bodies will be repulsive, similarly when the value of V_T has a negative value the force experienced will be attractive. The three main features of a typical interaction profile are a primary minimum, a secondary minimum and a maximum repulsive barrier (V_{max}). The primary minimum is a deep well at small separation distance. Particles deposited in the primary minimum are considered to be irreversibly retained at the solid surface (i.e., very large energy barriers exist that make it difficult for particles to be removed from the primary minimum) (Tufenkji and Elimelech, 2005a). The secondary minimum forms at larger separation distance than the primary energy minimum. Due to the relative contributions of the V_A and V_R for a particular system, a secondary minimum may not exist while in some cases a secondary

minimum may exist for a small range of conditions. For example if the ionic strength of the system possessing a secondary minimum is reduced the value of the V_R will increase forcing the value of V_T higher (this is described by a shift of the V_T plot in the positive direction of the vertical axis in Figure 2.3) which can result in the elimination of the secondary minimum. The depth of the secondary minimum is relatively shallow compared to the primary minimum which means that deposition in the secondary minimum is reversible. Another feature of the secondary minimum is that even if a large repulsive barrier does exist which restricts deposition in the primary minimum, deposition can still occur onto collector surfaces in the secondary minimum (Petosa et al., 2010). The maximum repulsive barrier (V_{max}) occurs at an intermediate distance and forms the outer boundary of the primary minimum. For particles to deposit in the primary minimum they must overcome this energy barrier. For lower ionic strength solutions the value V_{max} increases which limits deposition of particles in the primary minimum.

Figure 2.3: Typical DLVO interaction energy profile

2.5 Traditional Filtration

The migration of particles through porous media have been extensively studied in terms of filtration (i.e., the process by which the porous media will allow a fluid to pass through it while retaining a fraction of the dispersed phase on the collector surface) (Elimelech et al., 1995). The overall process can be described in two distinct steps; the movement of particles in the dispersed phase into close proximity with the collector surface and the attachment of a particle at the solid-liquid interface between the collector and the aqueous phase. These two processes have been described using the theoretical single collector efficiency (η_0) and the attachment efficiency factor (α). The single collector efficiency (η_0) is a ratio of the number of particles striking a single collector in space to the number of particles that approach the collector while the attachment efficiency factor (α) is a ratio of the number of particles that become attached to the collector surface to the total number of particles that strike the collector surface (Swift and Friedlander, 1964).

Traditionally three key mechanisms have been considered to control the transport of particles onto the surface of collectors: gravity or sedimentation, which occurs due to the difference arising between gravitational forces and buoyant forces; interception, which occurs when the particle body is large enough that it comes into contact with the collector surface as it is moving along a streamline; and diffusion whereby small particles undergo Brownian motion which may result in the particles coming into contact with collector surfaces (Yao et al., 1971). For small particles, such as in the case of nanoparticles, diffusion is the dominant mechanism of removal however for dense particles such as metallic particles sedimentation forces can be important (Petosa et al., 2010). Yao et al. (1971) suggests that the overall η_0 for spherical

particles on a spherical collector can be approximated by the sum of the individual collector efficiency for the various mechanisms, given by:

$$\eta_0 = n_G + n_D + n_I \quad [2-4a]$$

where n_G , n_D and n_I are the single collector efficiencies for sedimentation, diffusion and settling, respectively, which for a spherical particle have been defined as

$$\eta_D = 4.04Pe^{-2/3} = 0.9 \left(\frac{k_B T}{\mu d_p d_c v_o} \right)^{2/3} \quad [2-4b]$$

$$\eta_I = \frac{3}{2} \left(\frac{d_p}{d_c} \right)^2 \quad [2-4c]$$

$$\eta_G = \frac{(\rho_p - \rho) g d_p^2}{18 \mu v_o} \quad [2-4d]$$

where Pe , ρ_p , ρ , μ , v_o , d_p , d_c , T , k_B are the Peclet number, density of the particle, density of the solution, viscosity of the bulk solution, approach velocity, diameter of the particle, diameter of the collector, absolute temperature and the Boltzmann's constant, respectively (Yao et al., 1971). A recent refinement to this model takes into account other important interactions, specifically hydrodynamic and van der Waals forces given as (Tufenkji and Elimelech, 2004a):

$$\begin{aligned} \eta_0 = & 2.4 A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.55 A_S N_R^{1.675} N_A^{0.125} \\ & + 0.22 N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053} \end{aligned} \quad [2-5]$$

where N_R , N_{Pe} , N_{gr} , N_{vdW} , N_A , N_G and A_S are dimensionless numbers related to the aspect ratio, Peclet number, gravitational number, van der Waals number, attraction number, gravity number and porosity respectively.

The above relationships have all been formulated for spherical particles. These expressions cannot be used for the transport of MWNTs as MWNTs are assumed to be cylindrical with large aspect ratios. Liu et al. (2009) developed predictive single collector efficiency relationships, based on the model of Yao et al. (1971), for particles with large aspect ratio. The single collector efficiency for 'side contact' (i.e., contact occurring with the length of the nanotube being parallel to the collector surface) is (Liu et al., 2009b):

$$\eta_0 = n_G + n_D + n_I = n_G + n_D + \left[\frac{1}{2} \left(\frac{d_p}{d_c} \right)^2 \left(3 - \frac{d_p}{d_p + d_c} \right) \right] \quad [2-6a]$$

where

$$\eta_G = \left(d_p/l \right)^{2/3} \left(\frac{0.146(\rho_p - \rho)g(d_p^2 l)^{2/3}}{\mu v_o \left[1 - \left(d_p/l \right)^2 \right]^{1/2}} \right) \ln \left(\frac{1 + \left[1 - \left(d_p/l \right)^2 \right]^{1/2}}{d_p/l} \right) \quad [2-6b]$$

η_D

$$= 4.03 \left[kT \ln \left(\frac{1 + \left(1 - \left(d_p/l \right)^2 \right)^{1/2}}{d_p/l} \right) \right]^{2/3} \left(3\pi\mu d_c v_o \left(\frac{3}{2} d_p^2 l \right)^{1/3} \left(l/d_p \right)^{2/3} \left(1 - \left(d_p/l \right)^2 \right)^{1/2} \right)^{-2/3} \quad [2-6c]$$

where l is the length of the particle.

Particle transport governed by traditional colloid filtration theory is represented by the one dimensional mass balance equations for the liquid and solid phases given as (Liu et al., 2009b) :

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} + v \frac{\partial C}{\partial x} - v \alpha_1 \frac{\partial^2 C}{\partial x^2} = 0 \quad [2-7a]$$

$$\frac{\rho_b}{n} \frac{\partial S}{\partial t} - k_{att} C + \frac{\rho_b k_{det}}{n} S = 0 \quad [2-7b]$$

where C is the concentration of MWNTs suspended in the aqueous phase, t is time, ρ_b is bulk density of the solid phase, n is porosity, S is the amount of particles attached to the solid phase, v is the pore water velocity, x is the spatial dimension in the column, k_{det} is the rate constant for detachment of particles from the surface of collectors, α_1 is the longitudinal dispersivity and k_{att} is the rate constant for attachment of particles onto the collector surface (deposition rate constant) (Tufenkji and Elimelech, 2004b) given as:

$$k_{att} = \frac{3(1-n)v}{d_c} \alpha \eta_0 \quad [2-8]$$

The attachment efficiency factor (α) has been traditionally calculated from column experiments using (Petosa et al, 2010):

$$\alpha = -\frac{2d_c}{3(1-n)\eta_0 L} \ln(C/C_o) \quad [2-9]$$

where L , C , n and C_o are the length of the packed bed, the concentration of particles measured at the outlet, the porosity and the concentration of particles measured at the inlet, respectively (Petosa et al., 2010). This solution relies upon the assumptions that the value of C/C_o does not change with time and a stable plateau is present in the breakthrough curves of column experiments. This however is not always the case and thus cannot readily be applied when other non traditional retention mechanisms are operative (e.g. straining, site blocking).

Equation 2-9 is appropriate for most situations involving traditional retention mechanisms where the major contributor to the movement of particles is advection however it may not be appropriate for situations where dispersion becomes the dominant process ($v \approx 10^{-6} \text{ m/s}$) (Logan, 1999). For these cases α can be found by fitting the breakthrough curve to the advection-dispersion equation incorporating a first order deposition rate term (Kretzschmar et al., 1999).

2.6 Non-Traditional Removal Mechanisms

The cylindrical or rod shaped nature of MWNT complicates prediction of their environmental fate as the majority of techniques described above have been developed for

spherical particles. As such predictive models and theories that have been developed require modification for application to MWNTs systems (Petosa et al., 2010). The large aspect ratio of CNTs gives rise to the possibility of additional capture mechanisms that DLVO theory does not consider (e.g., straining). Straining occurs when colloidal particles become trapped in pore throats that are too small to allow particles to flow through them (Bradford and Bettahar, 2006). One major difference between filtration and straining is that straining occurs in the pores between at least two collector surfaces, where filtration occurs at the liquid/solid interface (Bradford et al., 2006). A guideline suggests that when the ratio of particle diameter to the collector diameter (d_p/d_c) exceeds 0.005 straining will play a significant role in particle removal (Bradford et al., 2003) however this ratio assumes spherical particles and spherical collectors which is not the case for CNTs.

Another mechanism of interest is site blocking which occurs as a result of time dependent deposition of particles on the surface of collectors. When site blocking is operative initially there are a large number of available sites suitable for the particles deposition. As particles begin to deposit at these sites, they reduce (or block) the number of available sites for subsequent particle deposition (Bradford et al., 2006; Johnson and Elimelech, 1995). Charged particles blocking favourable sites can reduce the overall deposition of particles onto collectors by increasing the electrostatic repulsive forces that subsequent particles will experience on approach of the collector (Johnson and Elimelech, 1995). Site blocking phenomena can be represented mathematically through the use of a blocking function that is applied to the overall deposition rate. A blocking function based on the Langmuirian Dynamic blocking function (Li et al., 2008) can be applied such that:

$$\psi = 1 - \frac{S}{S_{max}} \quad [2-10]$$

where ψ is the blocking function which can take a value between unity and zero, S is the solid phase concentration of particles and S_{max} is the maximum solid phase concentration of particles (Li et al., 2008). The solid phase mass balance equation then becomes:

$$\frac{\rho_b}{n} \frac{\partial S}{\partial t} - k_{att} \psi C + \frac{\rho_b k_{det}}{n} S = 0$$

A more sophisticated nonlinear blocking function based on random sequential adsorption (RSA) of spherical colloidal particles onto a collector has been developed that better addresses surface exclusion effects (i.e., one particle blocking multiple sites) of larger colloidal particles at low to moderate surface coverage (Johnson and Elimelech, 1995). However since models applying RSA to non-spherical geometries have not been fully developed it is not considered in this study.

2.7 Dual Deposition Model

Traditional colloid filtration theory has been shown to poorly account for the behaviour of colloids in the presence of favourable deposition conditions (Tufenkji and Elimelech, 2005a; Tufenkji and Elimelech, 2005b). The presence of surface charge heterogeneities existing on the surface of collectors or the presence of a secondary energy minimum could lead to localized favourable deposition sites with the majority of the collector surface exhibiting unfavourable deposition sites. The result is that both favourable and non-favourable deposition sites may occur simultaneously in the porous media which cannot be described by traditional CFT. To account for the range of deposition types on a single collector a dual deposition model (DDM) can be used, where the total population is separated into particles which are subject to a slower deposition rate and particles which are subject to a faster deposition rate (analogous to

unfavourable and favourable deposition (Petosa et al., 2010)). The solutions to the one dimensional mass balance equations (Equation 2-7) for the liquid and solid phases are given as (Tufenkji and Elimelech 2004b):

$$C(x) = C_0 \int_0^\infty \exp\left[-\frac{k_{att}}{v}x\right] p(x) dk \quad [2-12a]$$

$$S(x) = \frac{nt_0 C_0}{\rho_b} \int_0^\infty k \exp\left[-\frac{k_{att}}{v}x\right] p(x) dk \quad [2-12b]$$

where $C(x)$ is the concentration of particles suspended in the dispersed phase, $S(x)$ is the concentration of particles attached to the solid phase, v is the interstitial particle velocity, n is the porosity of the porous medium, ρ_b is the porous medium bulk density, t_0 is the duration of continuous particle injection (at C_0 and $x=0$) and k_{att} is the particle deposition rate coefficient where d_c is the diameter of the collector and η is the single collector efficiency. These solutions are valid when particle detachment is not considered (i.e., $k_{det} = 0$).

The function $p(k)$ is a bimodal distribution of the deposition rate k_{att} from traditional CFT which takes the form of a linear combination of two normal (Gaussian) distributions, given as (Tufenkji and Elimelech 2004b):

$$p(k) = f_{slow} \frac{1}{\sigma_{slow} \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{k_{att} - \bar{k}_{slow}}{\sigma_{slow}}\right)^2\right] + f_{fast} \frac{1}{\sigma_{fast} \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{k_{att} - \bar{k}_{fast}}{\sigma_{fast}}\right)^2\right] \quad [2-13]$$

where $\bar{k}_{slow}$ and $\bar{k}_{fast}$ are the mean deposition rate coefficients, σ_{slow} and σ_{fast} are the corresponding standard deviations and f_{slow} and f_{fast} are the fractions of the total population of

particles associated with each mode. Use of a DDM has been shown to significantly improve the description of the behaviour of colloidal particles where mechanisms (described earlier) not accounted for by CFT are occurring (Tufenkji and Elimelech, 2004b; Tufenkji and Elimelech, 2005b). The above solution requires that site blocking is not active however Liu et al 2009 suggests this may be operative. The form of the governing mass balance equations used in this study are:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} + v \frac{\partial C}{\partial x} - v \alpha_1 \frac{\partial^2 C}{\partial x^2} = 0 \quad [2-14a]$$

$$\frac{\rho_b}{n} \frac{\partial S}{\partial t} - k_{att.i} C \psi - k_{att.ii} C + \frac{\rho_b k_{det}}{n} S = 0 \quad [2-14b]$$

where C is the concentration of MWNTs suspended in the aqueous phase, t is time, ρ_b is bulk density of the solid phase, n is porosity, S is the amount of MWNTs attached to the solid phase, v is the pore water velocity, x is the spatial dimension in the column, k_{det} is the rate constant for detachment of MWNT from the surface of collectors and α_1 is the longitudinal dispersivity, $k_{att.i}$ and $k_{att.ii}$ are the removal rate constants for fast and slow attachment, respectively and ψ is the site blocking term.

2.8 Issues Associated with Nanomaterials

Due to the relatively small sizes of nanoparticles they are much more sensitive to physical and chemical heterogeneities present in the subsurface (Song et al., 1994; Tufenkji and Elimelech, 2005a). For example smaller particles may interact with and deposit onto small surface heterogeneities which may be inaccessible to larger particles. The presence of marginal amounts of surface heterogeneity has been shown to greatly influence deposition of latex

colloidal particles under unfavourable conditions. Furthermore surfaces with significant heterogeneity drastically reduce the effect of varying ionic strength on deposition (Song et al., 1994; Tufenkji and Elimelech, 2005a).

2.9 Previous CNT Mobility Studies

A number of studies have started to investigate the transport of carbon based nanomaterials in subsurface systems, including nC60 and CNTs (e.g., Jaisi and Elimelech, 2009; Jaisi et al., 2008b; Lecoanet and Wiesner, 2004; Liu et al., 2009b; Tian et al., 2010; Wang et al., 2008). Lecoanet et al. (2004) investigated the mobility of multiple nanoparticles through a packed bed of silica glass beads ($d_{50}=355\text{ }\mu\text{m}$) at a Darcy velocity of 34.6m/d, a pH of 7 and an ionic strength of 10mM (Lecoanet et al., 2004). These experiments showed that fullerene particles such as surfactant stabilized (dodecylbenzene sulfonic acid, sodium salt (SDBS)) SWNTs and fullerol particles showed very little affinity for porous media with reported very low α values of 0.001 ± 0.0004 and 0.0001 ± 0.0001 , respectively. This led to mobility indices (i.e., the distance required to achieve a concentration of 0.1% C_0) of 10m and 14m, respectively. For the case of more hydrophobic nanoparticles (nC60) the reported attachment was much higher ($\alpha=0.298\pm0.013$) leading to a mobility index of 0.1m under the conditions investigated. These findings suggest that fullerene particles that have been modified to be more hydrophilic can be very mobile through porous media. Lecoanet and Wiesner (2004) then furthered this work by investigating what effect varying pore water velocities would have on the system and overall deposition of the considered nanoparticles. For this set of experiments the nanoparticles were injected at Darcy velocities of 121.0 m/d and 34.6 m/d and the resulting breakthrough curves were compared to evaluate any differences. It should be noted that these water velocities are

significantly larger than typical groundwater velocity. The results showed that varying the pore velocity affected the appearance of breakthrough for all the carbon based nanoparticles; breakthrough occurred sooner at the lower pore velocity than at the high pore velocity and in the case of SWNTs reached steady state sooner than the conservative tracer (NaCl). For all three nanoparticles Lecoanet and Wiesner (2004) observed dips in the breakthrough curves at the higher pore water velocity; they hypothesized this dip in effluent concentration was due to deposited particles increasing the affinity of subsequent particles for collector surfaces through site ripening. This hypothesis was supported by subsequent experiments carried out at the high flow rate with varied influent concentration. These experiments showed higher retention occurred at the higher influent concentrations. It should be noted that no other transport studies using CNTs have observed behaviour suggesting that site ripening (i.e., the increase in retention with increased deposition of particles (Bradford et al., 2003)) is an important mechanism. Tian et al. (2010), similarly showed that (SDBS stabilized) SWNTs showed very little affinity for the porous media (quartz sand, $d_{50}=500\text{ }\mu\text{m}$).

In contrast to the findings of Lecoanet and Weisner (2004) and Tian et al (2010), Jaisi et al. (2008) showed that carboxyl functionalized SWNTs showed a much greater affinity for the porous media and reported travel distances two orders of magnitude lower than Lecoanet and Weisner (2004). Jaisi et al. (2008) suggested that the transport of SWNTs through quartz sand was in qualitative agreement with traditional DLVO theory (the deposition of SWNTs decreased with increasing ionic strength) and that straining may be an important removal mechanism at low ionic strengths. This is a significant finding as the ratio of particle diameter to collector is 0.0008 which is almost an order of magnitude smaller than the 0.005 suggested by Bradford et al. (2003) (it should be noted that SWNTs have a strong tendency to form bundles in aqueous solution and

are thought to largely be in this form (Jaisi et al., 2008b) which could help account for straining behaviour). The significance of the SWNT shape in straining was shown by conducting three column experiments using SWNTs suspended in deionized water where the effluent of the first column was used as the influent of the second column and the effluent of the second column was then used for the influent of the third column. The resulting breakthrough curves were compared to each other and showed that C/C_0 increased between experiment from 0.88 to 0.95 then 0.96. This increase was proposed to be due to selective straining of larger susceptible bundles of SWNTs. Dynamic Light Scattering (DLS) measurements performed on the influent and effluent SWNTs showed that the average effective diameter of the SWNTs decreased significantly in the effluent compared to influent samples. This result further suggests that physical straining was an important removal mechanism. This study also showed that SWNT filtration decreases in the presence of humic acids leading to increased mobility of the SWNTs. This is an important result because many natural groundwater environments contain dissolved organic matter, including humic acids. Large humic acid molecules have been shown to wrap around nanotubes which introduces steric repulsion between nanotubes. This process leads to their improved stability in solution (Hyung et al., 2007). Wang et al. (2008) also showed that humic acid coated CNTs (both SWNTs and MWNTs) can be transported through quartz sand (Wang et al., 2008). The study used SWNTs and MWNTs stabilized in aqueous solution containing 25mg/L humic acid with varying ionic strengths (KCl 0.001-10mM and CaCl 0.001-10mM). The results showed that both SWNTs and MWNTs were mobile through the sand, with MWNTs being filtered to a greater extent than SWNTs. Wang et al. (2008) found deposition of CNTs (SWNTs and MWNTs) were similar to Jaisi et al. (2008) and reported travel distances of the same order of magnitude.

Straining of CNT however, was not considered as a possible removal mechanism in Wang et al. (2008).

Experiments by Jaisi et al. (2008) were conducted in a column packed with silica sand ($d_{50} = 263\mu\text{m}$) at 15.7 ± 0.2 m/d pore water velocity with varied ionic strengths involving different formulations of KCl, CaCl and humic acid. These experiments showed increased deposition of SWNTs with increased ionic strength and also showed that divalent cations (Ca^{2+}) resulted in lower stability of SWNTs particles which increased deposition and reduced overall mobility of SWNT. Following the initial breakthrough phase of the experiments the columns were rinsed with deionized water and in most cases there was an observed release of SWNTs from the grain surface. The amount of SWNTs released was more significant in the high ionic strength cases due to the elimination of larger secondary minimums. However there was no observed release of SWNTs following experiments with divalent Ca^{2+} solutions as deposition in the presence of divalent cations is thought to occur in the primary minimum (Jaisi et al., 2008b).

Jaisi and Elimelech (2009) investigated the transport of SWNTs through porous media that consisted of natural soil. Three sets of column experiments were conducted: firstly the approach velocity was altered (1.21 – 24.19 m/d) to address what impact it may have on the deposition of particles; next the mass of SWNTs injected was varied to see if SWNTs deposition followed first-order kinetics and in the third batch of experiments the ionic strength was varied by changing the concentration of KCl (0.1-100mM) and CaCl_2 (.03-10mM) in order to identify the relative importance of physiochemical filtration in the deposition of SWNTs in the packed columns. The results showed that there was a linear relationship between the log of the deposition rate coefficient and the log of the approach velocity, with a slope of 0.6. This result was an indication that the SWNT removal was not mainly due to classical filtration mechanisms.

Liu et al. (2009) also found a linear relationship between the deposition rate and the log of the approach velocity, however in this case the slope obtained was 0.33 which is consistent with removal due to mechanisms associated with classical filtration (Jaisi and Elimelech, 2009). A major difference between these two studies was the porous media used; while Liu et al. (2009) used a cleaned quartz sand ($d_{50} = 476 \mu\text{m}$), Jaisi and Elimelech (2009) used a natural soil ($d = 400\text{--}1000 \mu\text{m}$). The difference in behaviour suggests that the collector size (and by extension pore sizes) are an important parameter in determining CNT transport behaviour. Jaisi and Elimelech (2009) found that in all of the experiments conducted the SWNT breakthrough occurred before the bromide tracer. This was due to size exclusion chromatography which means that due to their size, SWNT are unable to enter the smaller pore networks that the bromide tracer can enter and are thus restricted to the larger, less tortuous and faster flow paths through the soil. This was not seen in Jaisi et al. (2008) as the porous media used in that study comprised of a uniform quartz fine sand ($d_{50} = 263 \mu\text{m}$) while the porous media used in Jaisi and Elimelech (2009) was a natural soil containing large clay fractions (29%) with average pore sizes estimated at $22 \mu\text{m}$. The experiments also showed that SWNT deposition followed first-order kinetics. The experiments showed that the presence of both salts (KCl, CaCl_2) did alter the deposition behaviour of SWNTs with the divalent calcium salts affecting deposition more strongly than the monovalent salt however even at low ionic strengths almost 80% of SWNTs were being removed from solution. The authors suggest that straining was a dominant removal mechanism of SWNTs in the natural soil column. To test this, fullerenes were injected into the column at similar experimental conditions to see what effect the shape of SWNTs had on the overall deposition. The results showed that deposition rates were much lower and sensitive to ionic strength for the spherical fullerene particles. This result may mean that due the size and shape of CNTs that other non-

traditional removal mechanisms (e.g., hydrodynamic factor as well as non-physiochemical removal mechanisms (e.g., straining)), may play a significant role in MWNT transport.

Liu et al. (2009) investigated the transport of acid functionalized MWNT through porous media (spherical glass bead and quartz sand). Experiments were conducted at varied pore water velocities (43m/d, 21m/d, 4m/d and 0.42m/d) at a solution pH of 10 and ionic strengths of 10 and 0.1mM. The results showed that above a pore velocity of 4m/d MWNTs are very mobile with similar breakthrough for the three faster pore velocities. However at the lower velocity significant retention was observed. Experiments conducted in the glass bead medium resulted in improved mobility of the MWNTs; the reason proposed was that the quartz sand exhibited more roughness and angularity which ultimately increases the number of sites that would favour physical removal of MWNTs. A non-spherical theoretical efficiency relationship was developed for MWNTs, which allowed modeling of experimental results. Simulations showed that along with traditional CFT removal mechanisms the inclusion of a site blocking term yielded behaviour that was in good agreement with observed results. The results of modeling showed that the value of S_{max} was an order of magnitude larger for the quartz sand compared to the similarly sized glass beads.

2.10 Synopsis

Many published studies on CNT deposition use porous media consisting of collectors with varied sizes. Research suggests that collector size (d_{50}) is a useful tool in determining the existence of non-physiochemical removal mechanisms (e.g., straining) (Bradford et al., 2005; Bradford et al., 2007). Additionally, it has been shown that collector size may influence the filtration of colloids (Shen et al., 2010). In this study the effects the size of collectors on MWNT

transport are examined by performing one dimensional column studies in columns with quartz sand collectors ranging from fine sand to silt.

2.11 References

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Chapter 3 - Impact of Porous Media Grain Size on the Transport of Multiwalled Carbon Nanotubes

3.0 Introduction

Increased production and utilization of engineered nanomaterials will increase the potential for their release to the environment. Carbon nanotubes (CNTs) have garnered significant attention due to their potential widespread usage (e.g., production of plastics, catalysts, water purification systems and components in the electronics, aerospace and automotive industries (Klaine et al., 2008)). CNTs are rolled up sheets of graphene made up of one or more concentric tubes (i.e., single wall nanotubes and multiwalled nanotubes, respectively). Their impact on the ecosystem is becoming an increasing concern (Klaine et al., 2008). A first step to understanding the overall impact of nanoparticles on the environment is to develop a greater understanding of their fate and behaviour.

Significant research has been conducted on interacting colloidal particles and surfaces, leading to a fundamental understanding of the forces that influence particles behaviour (Derjaguin and Landau, 1945; Grahame, 1947; Hamaker, 1937; Verwey, 1947). From this, the standard DLVO theory that describes the behaviour of charged surfaces in a liquid medium was developed. Interaction profiles can be derived from the summation of DLVO forces (van der Waals attractive forces and electrostatic double layer repulsive forces) which give a general idea of how particles are expected to interact with other bodies. Traditional colloid filtration theory (CFT) is used to predict retention of particles in porous media systems due to gravitational sedimentation, Brownian diffusion and interception (Yao et al., 1971). This theory suggests that particles are transported to and become permanently deposited in the primary minimum well of a collector of uniform surface characteristics with infinite retention capacity (Shen et al., 2007a;

Yao et al., 1971). Research suggests that additional removal mechanisms may be operative including deposition in the secondary minimum and surface charge heterogeneity (Elimelech and Omelia, 1990; Shen et al., 2007a; Shen et al., 2010; Tufenkji and Elimelech, 2004b; Tufenkji and Elimelech, 2005a). It has been suggested that physical removal mechanisms (e.g. straining which is a function of particle to pore throat size) also play a role in the removal of colloidal particles from suspension (Bradford et al., 2004; Bradford et al., 2002), and may be significant for non spherical particles with large aspect ratios like CNTs (Jaisi and Elimelech, 2009; Jaisi et al., 2008b). Research on colloidal particles has also shown that the size of collectors may not only affect the degree of straining that may be operative but also affect the attachment of particles (Shen et al., 2010; Torkzaban et al., 2007). Evidence of site blocking, where the collector surface has a finite retention capacity, has also been observed in engineered nanoparticles studies (Li et al., 2008; Liu et al., 2009b). Transport studies involving CNTs thus far have shown that CFT cannot fully describe their deposition behaviour and one or more additional mechanisms are needed to explain experimental findings (Jaisi and Elimelech, 2009; Jaisi et al., 2008b; Lecoanet et al., 2004; Lecoanet and Wiesner, 2004; Liu et al., 2009a; Liu et al., 2009b; Tian et al., 2010).

Early studies demonstrated that SWNTs were very mobile and had little affinity for porous media (quartz sand $d_{50} = 355\mu\text{m}$) with travel distances of 10m calculated using CFT (Lecoanet et al., 2004; Lecoanet and Wiesner, 2004). These studies were conducted at pore velocities significantly higher than the typical range of ground water velocities observed in the field (i.e., 35 and 121 m/d). Tian et al. (2010) similarly showed that SDBS stabilized SWNTs showed little affinity for the porous media, this may be due to the influence of surfactants on the interaction of CNTs with porous media (i.e., enhanced steric interactions may lead to larger

repulsive barriers to deposition than those derived from DLVO theory). Other studies however could not repeat these results but rather found that SWNTs had more limited mobility due to influences of increased filtration and straining on particle retention (Jaisi and Elimelech, 2009; Jaisi et al., 2008a). For example Jaisi et al. (2008) reported (functionalized) SWNT travel distances through quartz sand ($d_{50}=263\mu\text{m}$) approximately 1 to 2 orders of magnitude lower than Lecoanet et al. (2004). Jaisi et al. (2008) also investigated the impact of ionic strength on SWNT mobility and found that the transport of SWNT was at least in qualitative agreement with DLVO theory (i.e., increased deposition with increased in ionic strength). The results of Jaisi et al. (2008) studies indicate that both physiochemical filtration and straining occur concurrently with filtration being the dominant mechanism at higher ionic strengths ($>3\text{mM}$) (below 3mM the size of the repulsive barrier restricts deposition of particles). It should be noted that SWNTs have a strong tendency to form bundles in aqueous solution and are thought to largely be in this form, which contributes considerably to straining (Jaisi et al., 2008b)). Jaisi and Elimelech (2009) suggested that physiochemical filtration and straining governed deposition of SWNTs, however straining was proposed to be the dominant mechanism with filtration playing a smaller role. A natural soil ($d=420\text{-}1000\mu\text{m}$) with a significant fraction of clay particles (29%) was utilized as the porous media (Petosa et al., 2010). The large size of the SWNTs (effective diameter of 244nm) compared to the estimated pore size of the porous media ($d=22\text{nm}$), along with heterogeneity in the soil particle size and porosity greatly contributed overall degree of straining. The elements in the clay fractions of the soil used are thought to have a point of zero charge at a neutral pH, the column experiments were conducted at a pH of 5.5 – 5.8 meaning that these clay elements would possess a positive surface charge which would lead to high deposition of the negatively charged (carboxyl functionalized) SWNTs.

Relatively little work has been conducted to investigate MWNT mobility. The two experimental studies investigating the mobility of MWNTs suggest that the deposition of MWNTs in porous media can be described using an extension of traditional colloid filtration theory (Liu et al., 2009b; Wang et al., 2008). Liu et al. (2009b) observed enhanced mobility of acid functionalized MWNTs through porous media (quartz sand, $d_{50}=476\mu\text{m}$) above a critical pore water velocity, however mobility was much less at pore water velocities similar to that expected in natural subsurface conditions. Results of their study also showed decreased deposition onto the surface of uniform glass beads of similar size to the collector, meaning surface roughness and angularity of the collectors may impact the transport of the MWNTs. Their work also showed evidence of site blocking occurring as a result of an attachment rate that decreased with time; suggesting a finite number of sites appropriate for MWNT deposition, while experiments at low ionic strength (0.1mM) showed evidence of nonphysiochemical removal being present. Wang et. al, 2008 found that humic acid stabilized MWNTs ($d=35\text{nm}$) were filtered by quartz sand ($d_{50}=355\mu\text{m}$) to a higher extent than (humic acid stabilized) SWNTs ($d=1.4\text{nm}$) for all ranges of ionic strengths tested. The aforementioned studies investigating the mobility of CNTs show that their behaviour is sensitive to many experimental conditions and more research is required to identify the relative importance of parameters.

The goal of this study was to investigate the impact of mean collector size, pore water velocity and ionic strength on the mobility of MWNTs. A series of one dimensional column experiments were carried out at pore water velocities expected under both engineered and natural subsurface conditions using porous media ranging in classification from fine sand to silt. Manipulation of ionic strength facilitated an assessment of the relative importance of non traditional filtration mechanisms (e.g. straining). Multiple pulses of MWNTs were injected into

the column to determine if site blocking was operative and determine its importance to MWNT transport.

3.1 Materials and Methods

3.1.1 Multi-Walled Carbon Nanotubes

Multi-walled carbon nanotubes (MWNTs) (outer diameter of 30-50 nm and length of 10-20 μm) were purchased from Cheap Tubes Inc. (Brattleboro, VT). MWNTs were functionalized through the addition of surface carboxylic and hydroxyl groups using a 3:1 v/v ratio of sulphuric and nitric acids, 95-97% and 70%, respectively (Liu et al., 1998). This treatment enhanced their hydrophilicity. The solution was placed in a bath sonicator (Aquasonic Ultrasonic Cleaner, VWR Scientific Products, West Chester, PA) for two hours. The functionalized MWNTs were then filtered using a 0.45 μm polytetrafluoroethylene (PTFE) membrane. Deionized water was used to rinse the MWNTs until the filtrate had a neutral pH (Liu et al., 2009b). Finally MWNTs were dried in a vacuum desiccator and stored until needed.

For column experiments, a dispersion of functionalized nanotubes was prepared by placing 4 mg of MWNTs in a 250 mL beaker containing 200 mL aqueous solution. An ultrasonic probe (Fisher Sonic Dismembrator, ARTEK System Corporation, Farmingdale, NY) was placed in the beaker, which was placed in an ice-water bath, at 210 watts for 45 minutes. The dispersed nanotubes were then mixed with an additional 300 mL of aqueous solution to reach the desired concentration of 8 mg/L. The MWNT dispersions were left to sit for at least 24 hours to ensure they did not agglomerate and settle out of the aqueous solution following sonication.

3.1.2 Aqueous Solution Chemistry

Three aqueous solutions were employed in this study (two high and one of low ionic strength); all solutions had a pH of approximately 7.5. The first high ionic strength solution (AS1) had an ionic strength of 7.5 mM and was buffered to pH 7.5 with 1.26 mM monosodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), 1.73 mM (Na_2HPO_4) and 1mM NaBr. The background aqueous solution (i.e., no MWNTs) used in the high ionic strength column experiments (AS1b) had the same amount of phosphate as AS1 with the addition of 1mM NaCl instead of NaBr to act as a conservative tracer. The low ionic strength solution (AS2) (0.1mM) was obtained through dilution of AS1. In the column experiments at low ionic strength, the background solution was the same as the MWNT solution, but without MWNTs.

3.1.3 Porous Media

Four quartz sands of varying grain size (Barco, Opta Minerals Inc. Waterdown, ON) were used (Table 3.1). The values of mean collector grain size (d_{50}) and the uniformity coefficient U_1 were obtained through sieve analysis. The values of hydraulic conductivity (K) of sands were measured using a constant head permeability test, while the specific area was calculated as the ratio of surface area of an ideal spherical collector of diameter d_{50} to its volume.

Table 3.1 Grain Size Information of Sands Used

Quartz Sand	d_{50} (μm)	U_1	K (m/day)	Specific Area (m^2/m^3)
f32	476	1.6	65	1.26×10^4
f71	175	1.7	52.5	3.43×10^4
290 fraction 1	80	n/a*	3.2	7.50×10^4
290 fraction 2	50	n/a*	1.4	1.20×10^5

* the calculation of U_1 was impractical due to the small range of fractions.

The f32 and f71 sands (Barco #32 and Barco #71) size distributions were unaltered from the manufacturer. However, the desired d_{50} values of the 290 fractions 1 and 2 sands were obtained by sieving Barco #290 sand; 290 fraction 1 was the combination (1:4) of the fractions retained on the Tyler (Mentor, OH) no. 140 and Tyler no. 200 sieves while 290 fraction 2 was from sand retained on the Tyler no. 325 sieve. The sands are herein referred to by their d_{50} value to avoid confusion between the 290 fractions. The quartz sand was cleaned by washing with hydrochloric acid (0.1M) followed by hydrogen peroxide (5%) to remove any impurities from the surface of the sand grains. The sand was rinsed repeatedly with deionized water following both the acid and peroxide washing steps to ensure that all impurities had been removed from the sand and neutral pH had been achieved. The sand was then oven dried (90°C) over night, following rinsing, and stored.

3.1.4 Packing of columns

Glass columns (2.5 cm in diameter and 5 cm in length) were used in this study. A stainless steel mesh (66 μm openings) followed by a nylon screen (25 μm openings), at column ends, were used to support the porous media and evenly distribute aqueous flow through the column. The column was wet packed by filling it with 3 cm of deionized water then carefully adding sand from the top in 0.5 cm lifts. Each lift was well mixed and column gently vibrated through tapping the side prior to adding subsequent lifts. The column was then carefully capped and deionized water was pumped upwards through the column for at least 30 pore volumes to ensure that the sand was completely saturated. This packing procedure yielded an average

column porosity of 0.314 ± 0.006 for 476 μm and 175 μm sand while the finer 80 μm and 50 μm sands yielded an average porosity of 0.415 ± 0.007 .

3.1.5 Mathematical Modeling of MWNT Transport

3.1.5 Column Experiments

Columns were flushed with the appropriate background solution for 10 pore volumes following 30 pore volumes flushing with deionized water. The flow was then reduced to the experimental flow rate for least one pore volume and the direction of flow was switched to vertically downwards. Following the flow reversal, MWNT solutions were injected into the column. Multiple 60 mL plastic syringes and a syringe pump (KD Scientific, Holliston, MA) were used for solution injection. Two pulses of MWNTs were injected with sufficient time between pulses to allow column effluent absorbance to reach background levels. This was done in order to see if there is any differences in MWNT transport (breakthrough and attachment of particles) between pulses.

Once the absorbance of the column effluent had reached background levels after the second MWNTs pulse, de-ionised water was flushed through the column to determine if the sudden drop in ionic strength would mobilize any MWNTs that may have been deposited on the sand grains. The column effluent was collected using a CF-1 fraction collector (Spectrum Chromatography, Houston, TX) and the MWNT concentration determined using a UV spectrophotometer (Helios Alpha, Thermo Fisher Scientific, Mississauga, ON) at a wavelength of 400 nm. Conservative tracer concentrations (NaBr) were quantified using high performance liquid chromatography (HPLC, Waters Company, Milford, MA) of the collected fractions.

3.1.6 Mathematical Modeling of MWNT Transport

A one-dimensional finite element model, solving the following mass balance equations, was used to simulate MWNT transport (Liu et al., 2009b):

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} + v \frac{\partial C}{\partial x} - v \alpha_1 \frac{\partial^2 C}{\partial x^2} = 0 \quad [3-1]$$

$$\frac{\rho_b}{n} \frac{\partial S}{\partial t} - k_{att.i} C \psi - k_{att.ii} C = 0 \quad [3-2]$$

where C is the concentration of MWNTs suspended in the aqueous phase, t is time, ρ_b is bulk density of the solid phase, n is porosity, S is the amount of MWNTs attached to the solid phase, v is the pore water velocity, x is the spatial dimension in the column, k_{det} is the rate constant for detachment of MWNT from the surface of collectors and α_1 is the longitudinal dispersivity.

ψ is a site blocking term (Johnson and Elimelech, 1995; Li et al., 2008)

$$\psi = 1 - \frac{S}{S_{max}} \quad [3-3]$$

where S_{max} is the maximum solid phase concentration.

$k_{att.i}$ and $k_{att.ii}$ are the removal rate constants for fast and slow attachment, respectively, where fast attachment is subject to a site blocking term and the slow attachment is not. These constants are associated with traditional removal mechanisms (interception, sedimentation and diffusion) and adapted as (Yoon et al., 2006):

$$k_{att.i} = \frac{3\alpha_i \eta_0 (1 - n) v}{2d_c} \quad [3-4]$$

$$k_{att,ii} = \frac{3\alpha_{ii}\eta_0(1-n)v}{2d_c} \quad [3-5]$$

where d_c is the collector diameter, η_0 is the single collector efficiency, and α_i and α_{ii} are the attachment efficiencies associated with fast and slow deposition respectively. The single collector efficiency (η_0) was calculated using the relationship developed for rod shaped (i.e., non-spherical) MWNTs (Liu et al., 2009b) given as

$$\eta_0 = n_G + n_D + n_I = n_G + n_D + \left[\frac{1}{2} \left(\frac{d_p}{d_c} \right)^2 \left(3 - \frac{d_p}{d_p + d_c} \right) \right] \quad [3-6a]$$

where

$$\eta_G = \left(\frac{d_p}{l} \right)^{2/3} \left(\frac{0.146(\rho_p - \rho)g(d_p^2 l)^{2/3}}{\mu v \left[1 - \left(\frac{d_p}{l} \right)^2 \right]^{1/2}} \right) \ln \left(\frac{1 + \left[1 - \left(\frac{d_p}{l} \right)^2 \right]^{1/2}}{d_p/l} \right) \quad [3-6b]$$

η_D

3.2.1 Results of Column Experiments

$$\begin{aligned} &= 4.03 \left[k_B T \ln \left(\frac{1 + \left(1 - \left(\frac{d_p}{l} \right)^2 \right)^{1/2}}{d_p/l} \right) \right]^{2/3} \left(3\pi\mu d_c v \left(\frac{3}{2} d_p^2 l \right)^{1/3} \left(l/d_p \right)^{2/3} \left(1 - \left(\frac{d_p}{l} \right)^2 \right)^{1/2} \right)^{-2/3} \end{aligned} \quad [3-6c]$$

where l is the length of the particle, d_p is the particle diameter, d_c is the collector diameter, μ is the solution viscosity, k_B is Boltzman's constant, T is the absolute temperature and ρ_p, ρ are the particle

bulk density and solution bulk density respectively. The model was subject to a constant concentration (Type I) boundary at the inlet of the column with a specified flow (Type II) boundary condition at the outlet of the column. The column was discretized in ten equal lengths at 0.5cm intervals.

Independently measured parameters (v , n , d_c , ρ_b , C , C_o , t) were used to solve the mass balance equations (Equations 3-1 and 3-2), when possible. Unknown parameters (α_i , α_{ii} , $S_{\max}$ and α_1) were found by minimizing the root mean square error (RMSE) between experimentally and simulated breakthrough curves using an unconstrained nonlinear optimization routine. When repeats of the same experimental conditions were available one set of parameters was fitted to multiple breakthrough curves.

3.2 Results and Discussion

3.2.1 Results of Column Experiments

Column experiments were conducted to assess the impact of collector grain size on the transport and deposition of MWNTs. To begin with, column experiments were conducted at a higher pore water velocity (4.2 m/d) using AS1 to disperse the MWNTs and AS1b as the background solution. The first MWNT pulse exited the column noticeably later than the conservative tracer (NaBr) with the extent of retardation increasing with decreasing collector size (Figures 3.1 and 3.2). Following breakthrough MWNT normalized effluent concentration increases relatively quickly but slows at a normalized effluent concentration of approximately 0.65. When the effluent concentration plateaued (or came close to a plateau), injection of

MWNTs ceased and background solution injection commenced. In all cases normalized MWNT effluent concentrations decreased with the conservative tracer.

MWNTs breakthrough was significantly different for the second pulse. The MWNTs exited the column with the conservative tracer and showed little to no retardation. The maximum normalized concentrations for the 476, 175 and 80 μm sands were very similar, at about 0.8 for both pulses. MWNTs also exited the 50 μm sand packed column with the conservative tracer however after reaching an effluent concentration of 0.65 the MWNT concentration differed from the tracer and continued to slowly rise to a maximum value of 0.75. For the coarser textured sand experiments the effluent concentration plateau was achieved more quickly. In all cases the MWNT concentrations returned to baseline along with the conservative tracer following the second pulse.

At the low pore velocity (0.42 m/d), MWNT transport was similar to that observed in the high velocity experiments in the following ways (Figures 3.3 and 3.4): (i) the MWNTs initially do not exit the column with the conservative tracer during injection of the first pulse and also show increased retardation with decreasing collector grain size; (ii) MWNT normalized effluent concentration increases at a relatively fast rate initially until a steady state effluent concentration was achieved in some cases, while in other cases effluent concentrations increased at a much slower rate until injection of MWNT ceased; (iii) at the end of the first pulse the normalized effluent concentrations decreased with the tracer concentrations; (iv) and limited MWNT retardation was observed for the second pulse (this was more observable than during the high velocity experiments (Figures 3.3 and 3.4)). The maximum normalized concentration obtained for the 476, 175 and 80 μm sands after a second MWNT pulse were again similar (0.65). For the second pulse MWNTs exhibited a slightly delayed breakthrough in the 50 μm sand compared to

the conservative tracer and reached a maximum value of 0.5. In all cases the MWNT concentrations returned to baseline along with the conservative tracer following the second pulse. Upon completion of the second pulse (i.e., the absorbance of normalized effluent concentration returned to baseline) deionized water was injected into the columns at the experimental flow rate. For all experiments this resulted in a sharp and reproducible spike in effluent absorbance (e.g., Figure 3.5) suggesting that a fraction of the MWNTs that were loosely deposited on collector surfaces had been remobilized (Jaisi et al., 2008b). This release has been attributed to the elimination of the secondary energy minimum by lowering system ionic strength (Jaisi et al., 2008b). Jaisi et al. (2008) reported that the concentration released from collector surfaces in this way generally increased following experiments of increasing ionic strength (i.e., high experiment ionic strength leads to higher concentration of CNT in the effluent following the deionized solution flush) (Jaisi et al., 2008b). In the current study the same trend can be seen as no release on MWNTs is seen upon injection of deionized water in low ionic strength experiments (low ionic strength results discussed later).

Liu et al. (2009) investigated the transport of MWNTs (diameter = 7 to 70 nm, length = 100 to 2000 nm) in quartz sand ($d_{50} = 476 \mu\text{m}$) and found that MWNT breakthrough occurred with the conservative tracer at the 4.0 m/d, with maximum normalized effluent concentrations approaching 1.0. At a similar pore velocities effluent concentrations only achieved 0.8 in the present study. They also observed MWNTs retardation at the low pore velocity (0.42 m/d) with MWNT effluent concentrations increasing at a high rate initially and then increasing at a slower rate, similar to what was observed in this study. Differences in transport may be due to differences in MWNTs properties. In addition to differences in size, Liu et al. (2009) suspended MWNTs in an aqueous solution at pH 10 with an ionic strength of 10mM. The lower ionic

strength used in this study should yield more stable MWNTs and a greater barrier to deposition however the lower pH used in this study would have the opposite effect, reducing stability. Given that both studies used the same acid functionalization treatments the degree of surface oxidation should be similar, leading to similar hydrophilicity. These results are very different to observations by Wang et al. in their humic acid stabilized MWNT transport experiments (Wang et al., 2008). They reported that MWNT breakthrough occurred ahead of the conservative tracer at all ionic strengths investigated. The pore velocities used in their study was similar (7.7m/day) to the higher velocity used in the current study and the mean grain size was in the same range ($d_{50}=350\mu\text{m}$). They also used MWNTs with a similar diameter (35 ± 10 nm, length not reported). Given this observed differences are likely due to different stabilization methods and the resultant differences in interaction energies.

In another study Liu et al. (2009a) investigated the impact of MWNT size on their transport using similar aqueous phase conditions as their previous study (pH 10, 10mM). One of the MWNT sizes used in their study (CNT-b) was identical to the MWNTs used in this study and yielded similar transport behaviour under similar experimental conditions (i.e., pore velocity of 0.42 m/d, high ionic strength).

A suite of experiments were conducted at low pore velocity (0.42 m/d) and low ionic strength (0.1mM) in order to determine if nonphysiochemical removal mechanisms (e.g. straining) were operative (Figure 3.6). In all cases MWNTs exited the column at the same time and at a similar rate as the representative tracer in the high ionic strength experiments (Figure 3.6) (i.e., no retardation of either pulse). When the background solution flush was initiated MWNT effluent concentrations exited the column in an identical manner to representative tracer concentrations. The maximum normalized effluent concentration was approximately 0.95 except

in the case of the 50 μm sand, which had a maximum normalized effluent concentration of approximately 0.9. Following completion of the second pulse deionized water was flushed through the column and effluent absorbance remained at baseline in all cases (i.e., no detectable amounts of MWNTs were released by reducing the ionic strength). This is likely due to the relatively small change in ionic strength between the 0.1mM solution and deionized water and the negligible secondary minimum at the low ionic strength. Given the relatively large repulsive barrier that exists at the low ionic strength any MWNT removal was likely due mechanisms other than those associated with traditional filtration theory. One possible nonphysiochemical removal mechanism that may be of importance is straining (Bradford et al., 2007), although given that normalized effluent concentrations are above 0.9 for the low ionic strength solution this would suggest it is not a dominant retention mechanism.

Liu et. al (2009) observed a maximum normalized effluent concentration of MWNTs of approximately 0.65 at an ionic strength of 0.1mM which similar to the maximum concentration achieved at the high ionic strength (10mM) in that study, this may be due to significant non-physiochemical removal occurring at the low ionic strength(Liu et al., 2009b).

Results obtained at the low ionic strength case (0.1mM) in this study were similar in shape and appearance to those by Jaisi et al. (2008). In the study of Jaisi et al. (2008) SWNTs exited the column with the conservative tracer and reached a maximum normalized effluent concentration of approximately 0.93. Jaisi and Elimelech, (2009) also saw higher than expected removal occurring at low ionic strengths which due to the presence of large repulsive barriers was attributed to straining rather than filtration of the CNTs (Jaisi and Elimelech, 2009). To assess if given size fractions of the SWNTs were preferentially removed in the column Jaisi et al. (2008) measured the average effective SWNT diameter of the influent and effluent using

dynamic light scattering (DLS). This analysis implicitly assumes a spherical particle shape. Although this is not the case it does provide useful information (i.e., the SWNTs had a significant aspect ratio with a diameter ranging between 0.9 and 1.6nm, length was not reported). They reported that the average effective diameter ranged between 220 and 260 nm for the influent and approximately 200 nm for the effluent. It was postulated that this decrease may be due to larger particles being removed in the column due to straining. In the current study the influent MWNT suspension had an average effective diameter of 188nm, measured by DLS, and an average effective effluent diameter of 176nm suggesting that although some straining may be occurring, given the relatively small difference in effective diameter, which may not be statistically significant, this removal mechanism is relatively minor. Another method to assess if straining is a dominant removal mechanism is to quantify the ratio of a representative particle diameter and mean collector diameter (d_{50}) (Bradford et al., 2006). Jaisi et al. (2008) reported the ratio of both the effective diameter to the soil d_{50} (0.0008) and the SWNT diameter to the soil d_{50} (4.7×10^{-6}) for comparison with the critical straining radius reported (0.003) (Bradford et al., 2007)). For comparison, the straining ratio (particle diameter/collector diameter) in the study of Wang et al. (2008) was 4.0×10^{-6} and 0.0001 for the SWNTs and MWNTs, respectively, however their study was not designed to address the importance of straining and was thus not considered. The MWNT transport study of Liu et al. 2009 had a straining ratio of 0.0001. Lui et al. suggests that due to the non spherical nature of CNTs the diameter may not be the critical dimension controlling particle straining and presents a ratio of 0.011 and 0.0008 when the length of CNT and equivalent diameter are used, respectively. The straining ratio using the effective diameter (0.0004 to 0.0038) and the MWNT diameter (0.00008 to 0.0008) in this are all below the critical ratio proposed by Bradford et al. (2007) (0.003). Given that these values are similar to those

reported by Jaisi et al. (2008) (who concluded that straining was an important removal mechanism) for the larger fraction and in the case of the 50 μ m, exceed the ratio of 0.003 proposed by Bradford et al. (2007) this implies that straining may limit transport of MWNTs at low ionic strengths.

Traditionally the porous media is treated as a 'clean bed' which means that collectors have an unlimited capacity for deposition of particles on their surface and particle deposition rate is constant (Elimelech et al., 1995). Site blocking, which occurs when the deposition rate decreases over time (i.e., less particles are deposited onto the collector surface as it becomes covered by particles) (Ko et al., 2000), has been observed in other nanoparticle transport studies (Li et al., 2008; Liu et al., 2009a). Given the retarded MWNT breakthrough for the first pulse, and not the second pulse, in all high ionic strength experiments this suggests that site blocking may be an operative mechanism. The shape of the breakthrough curves also provides evidence for the occurrence of site blocking as the deposition rate does change with continued MWNT transport through the column (i.e., there is no stable steady state effluent concentration in some experiments but rather the maximum normalized concentration slowly increases as the deposition rate drops). These observations are consistent with previous research that has suggested site blocking is operative (Bradford et al., 2006; Ko et al., 2000; Li et al., 2008).

Figure 3.1: Breakthrough curves of MWNTs at the high pore water velocity in 476, 175 and 80 μm sand packed columns. Open circles represent conservative tracer data, squares represent MWNT data and solid lines represent the results of simulation (noted as sim.)

Figure 3.2: Breakthrough curves of MWNTs at the high pore water velocity in 50 μm sand packed columns. Open circles represent conservative tracer data, squares represent MWNT data and solid lines represent the results of simulation (noted as sim.)

Figure 3.3: Breakthrough curves of MWNTs at the low pore water velocity in 476, 175 and 80 μm sand packed columns. Open circles represent conservative tracer data, diamonds represent MWNT data and solid lines represent the results of simulation (noted as sim.)

Figure 3.4: Breakthrough curves of MWNTs at the low pore water velocity in 50 μm sand. Open circles represent conservative tracer data, squares represent MWNT data. Solid lines represent the results of simulation (noted as sim.) for mechanisms associated with traditional colloid filtration theory (CFT); traditional colloid filtration theory with site blocking (CFT + Site Blocking) and dual deposition with site blocking (DDM + Site Blocking)

Figure 3.5: Breakthrough curves of MWNTs including elution with deionized water (third pulse on graph). Open circles represent conservative tracer data, diamonds represent MWNT data.

Figure 3.6: Breakthrough curves of MWNTS for low ionic strength (0.1mM) experiment through 476,175 and 80 μm sand packed columns.

3.2.2 Results of Numerical Simulation

A series of simulations were conducted to test the ability of the numerical simulator to reproduce observed high ionic strength experiments ($I=7.5\text{mM}$), using traditional CFT and modified versions of CFT. It was assumed there was no detachment of MWNTs from the sand surface (i.e., $k_{det} = 0$) as no tailing was observed in any of the experiments. Initially simulations only incorporated mechanisms traditionally associated with CFT (i.e., $\psi = 1$ and $\alpha_{ii} = 0$) and α_i and α_1 were fitted. Model results suggest that MWNT breakthrough with the conservative tracer and achieve an effluent concentration plateau of 0.3 (Figure 3.4), other results not shown due to space limitations). Observed behaviour, which exhibited significant MWNT retardation for the first pulse, was significantly different than these simulation results. This suggests that 'clean bed' behaviour, where an effluent steady state concentration is rapidly achieved and maintained for the duration of particle injection, could not adequately describe observed experimental results. For comparison with subsequent simulations the RMSE value of this run was 2.10 (Figure 3.4).

As previously discussed, observed MWNT transport behaviour (Figure 3.1, Figure 3.2, Figure 3.3 and Figure 3.4) suggests site blocking may be operative. A Langmurian site blocking function (ψ in Equation 3-2 and 3-4) was therefore incorporated in the governing mass balance equations to account for this observed behaviour. This form of ψ suggests that as S approaches $S_{\max}$ the blocking function approaches zero. This means that once the surface becomes covered by deposited MWNTs attachment will cease and the normalized MWNT effluent concentration will increase to unity. The blocking function would be particularly useful in describing:

- i. The reduction in MWNT retardation between the first and second pulses.

- ii. The non 'clean bed' plateau observed in some cases where the normalized concentration of MWNTs slowly increases with time.

For these simulations the values of α_i , $S_{\max}$ and α_1 were fitting parameters ($\alpha_{ii} = 0$). The inclusion of site blocking significantly improved the fit to experimental results (RMSE = 0.86) however the model still did not predict MWNT retardation (Figure 3.4). Furthermore MWNT concentrations are over estimated until 6.7 pore volumes at which point the model under predicted the normalized effluent concentration of MWNTs in the first pulse. The model also over predicted the MWNT concentration during the second pulse

These model results suggest that use of the site blocking function cannot account for the similar height of the first and second pulses (i.e., as more MWNTs were injected into the column the magnitude of the blocking term decreases and thus the plateau of the second pulse should be higher than the first pulse as the deposition rate decreases as less sites remain available for deposition). This suggests that along with retention at a finite number of sites other deposition mechanisms may be operative. Straining may be operative but based on the results of the low ionic strength experiments was likely not a dominant process; another possible option could be dual deposition. Dual deposition may be due to deposition of particles in the secondary energy minimum and surface charge heterogeneity (Tufenkji and Elimelech, 2004b). Results from the de-ionized water flush, following the second MWNT pulse, support the presence of a secondary energy minimum (Figure 3.5). As previously discussed the fraction of deposited MWNTs released may be due to the elimination of the secondary minimum during the de-ionized water flush. Previous studies have used this type of model to simulate similar experimental behaviour (Tufenkji and Elimelech, 2004b; Tufenkji and Elimelech, 2005b). Tufenkji et al. (2004) found that both favourable and unfavourable sites may be present on collector surfaces. As such,

favourable and unfavourable deposition of particles can occur simultaneously where a fraction of the particles experience a fast deposition rate while others will experience a slow deposition rate.

To account for DDM a second removal rate constant ($k_{att,ii}$) was incorporated into the solid phase mass balance equation (Equation 3-2). The site blocking function ψ was only applied to the fast deposition rate and it was assumed that site blocking did not play a significant role in slow deposition. Inclusion of DDM and the site blocking term significantly improved agreement between the numerical model and experimental results (RMSE = 0.23, Figure 3.4). In Figure 3.4 the model slightly over predicted MWNT concentration at the beginning of the first and second pulses and slightly under predicted MWNTs concentration towards the end of the second pulse. Model results are in similar good agreement with experimental observations for all of the experimental data (i.e., both velocities) when both DDM and a site blocking term are incorporated in the governing mass balance equations (Figure 3.1, Figure 3.2, Figure 3.3 and Figure 3.4). Fitted parameters are presented in Table 3.2.

Table 3.2: Modeling Parameters

d_{50} (μm)	v (m/d)	RMSE	α_i	α_{ii}	S_{max} ($\mu\text{g/g}$)	α_i	η_0	$k_{att,i}$ (s^{-1})	$k_{att,ii}$ (s^{-1})
476	4.20	0.347	5.456	1.332	2.33	9.0×10^{-4}	1.99×10^{-3}	1.14×10^{-3}	2.79×10^{-4}
175	4.28	0.459	2.566	0.258	3.07	16.2×10^{-4}	3.41×10^{-3}	2.57×10^{-3}	2.59×10^{-4}
80*	4.12	0.437	1.273	0.107	5.62	5.58×10^{-3}	5.48×10^{-3}	3.65×10^{-3}	3.06×10^{-4}
50*	4.22	0.253	0.782	0.061	12.91	2.42×10^{-3}	7.18×10^{-3}	4.77×10^{-3}	3.72×10^{-4}
476	0.42	0.719	2.342	0.461	3.62	11.58×10^{-4}	1.19×10^{-2}	2.89×10^{-4}	5.68×10^{-5}
175*	0.42	0.271	1.102	0.113	4.75	3.35×10^{-3}	1.84×10^{-2}	5.88×10^{-4}	6.03×10^{-5}
80*	0.42	1.107	0.442	0.042	8.18	1.05×10^{-3}	1.79×10^{-2}	6.42×10^{-4}	6.07×10^{-5}
50	0.43	0.233	0.124	0.027	13.72	2.73×10^{-3}	3.54×10^{-2}	3.89×10^{-4}	8.62×10^{-5}

* multiple data sets for the same experimental condition, one set of parameters are fit to all repeats

Values of $S_{\max}$ obtained in this study were similar in magnitude to previous results for fullerene particles (Li et al., 2008), however were an order of magnitude greater than results obtained by Liu et al. (2009) for MWNTs (it should be noted that values of $S_{\max}$ reported by Liu et al. (2009) were 10^4 lower than actual values). This suggests that the collector surfaces have significantly larger capacities for the MWNTs used in this study in comparison to the MWNTs used in the study of Liu et al. 2009. At both high and low pore water velocities $S_{\max}$ increases as the average collector grain size decreases consistent with results reported in the fullerene nanoparticle transport study (Li et al., 2008). The increase in $S_{\max}$ with decreasing grain size is likely due to the increased surface area of collectors and corresponding total number of depositional sites. When the log of the $S_{\max}$ values are plotted versus the ideal specific surface area of collectors (surface area of sphere with diameter equal to the d_{50} of the soil divided by its volume) a strong linear relationship is observed (Figure 3.7).

Figure 3.7: Relationship between $S_{\max}$ and specific surface area of soil

Li et al. (2008) reported an increase in $S_{\max}$ as pore velocity decreases, for the same collector sizes, consistent with the results reported here. The reduction in $S_{\max}$ associated with increased pore water velocity may be due to increased tangential velocities across the collector surface which creates a 'shadow effect' down gradient of the collector due to hydrodynamic scattering (Johnson and Elimelech, 1995; Ko et al., 2000). It should be noted, $S_{\max}$ is a weaker function of pore water velocity than collector size.

Fitted attachment efficiencies (α_i and α_{ii}) both decrease with decreasing collector grain size (Table 3.2). Historically the attachment efficiency was assumed to only be related to chemical factors (e.g., ionic strength, pH) (Yao et al., 1971) however recent studies suggest that the attachment is also a function of hydrodynamic factors (Johnson and Tong, 2006; Li et al., 2005; Shen et al., 2007b; Tong and Johnson, 2006). Shen et al. (2007) showed when hydrodynamic factors are not considered (i.e., only DLVO interaction and Brownian diffusion were considered) the attachment efficiency was overestimated. Consistent with this study decreases in attachment efficiency have been reported for decreased collector size (Shen et al., 2010).

Attachment efficiency (α) is a ratio of the total number of attachments to the total number of collisions between the MWNT particles and collectors. Therefore a value greater than unity should not be possible but were fitted in this study. This may be attributed to shortcomings of the single collector efficiency (η_0) relationship used in this study. The relationship for η_0 was formulated based on mechanisms associated with traditional CFT (Liu et al., 2009b). Additional mechanisms (hydrodynamic effects and van der Waals interactions) (Tufenkji and Elimelech, 2004a) should likely be included in η_0 and may reduce α below unity.

$k_{att,i}$ and $k_{att,ii}$ increase with increasing pore water velocity consistent with previous CNTs transport studies (Jaisi and Elimelech, 2009; Liu et al., 2009b). $k_{att,i}$ and $k_{att,ii}$ also generally increase with decreasing mean collector size. It is noted that the impact of collector size on $k_{att,i}$ and $k_{att,ii}$ was significantly smaller than pore water velocity.

3.3 Significance

Results from this study suggest that commercially available MWNTs are mobile in porous media with collector sizes ranging from fine sands to silt. Differences in breakthrough curves between first and second pulse indicate that the deposition rate decreases as the experiment progresses and that site-blocking may be operative. These results could not be predicted using traditional CFT. However a dual deposition model with a site blocking term significantly improved agreement between experimental observations and model results.

Increased MWNT retardation with decreasing collector size was likely due to the increased surface area and depositional sites. Nonphysiochemical removal mechanisms (e.g. straining) may influence MWNTs deposition however low ionic strength (0.1mM) results suggest that this contribution is minor.

These findings are based on fundamental experiments incorporating ideal porous media systems. The inclusion of organic matter and both chemical and physical heterogeneity, as would be expected in subsurface environments, would impact the mobility of MWNTs. More research is needed to fully understand the complexities of CNT transport. This study does highlight the importance of collector size on MWNT transport and shows that MWNTs are mobile through increasingly finer material.

3.4 References

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Chapter 4 - Summary and Recommendations

4.1 Summary and Conclusions

The mobility of commercially available multi-walled carbon nanotubes in porous media (quartz sand) was investigated in this study. Several 1D column experiments were performed by injecting multiple pulses of functionalized MWNT aqueous solution (7.5mM) into columns packed with porous media of various mean grain sizes (d_{50}) (i.e., ranging from 476 μm down to 50 μm). The pore velocities (4.2m/d and 0.42m/d) and pH (7.5) were chosen to represent conditions that would reasonably be expected in groundwater environments. Experiments were also conducted at a lower ionic strength to determine if physical removal mechanisms were operative. Experimental results were then simulated using a 1D finite element model to solve the governing mass balance equations and fit unknown parameters.

Breakthrough curves of normalized MWNT effluent concentrations resulting from experiments at the high velocity (4.2 m/d) and high ionic strength (7.5mM) showed that the first pulse of MWNTs did not exit the column with the conservative tracer. The breakthrough curves displayed increased retardation with decreasing mean collector grain size (d_{50}). This trend was exaggerated at the low pore water velocity (0.42m/d) and similar ionic strength. The second pulse of MWNTs however did not display significant retardation and exited the column with the conservative tracer. The approximate maximum normalized concentration of MWNTs at the high pore water velocity was 0.8 in the 476, 175 and 80 μm sands and 0.75 in the 50 μm sand. The approximate maximum normalized concentration of MWNTs at the low pore water velocity was 0.65 in the 476, 175 and 80 μm sands and 0.5 in the 50 μm sand. Release of MWNTs from collector surfaces was observed following elution of de-ionized water in all high ionic strength

experiments. Breakthrough curves of MWNTs at the low pore water velocity and low ionic strength (0.1mM) exited the column with the conservative tracer and reached a maximum normalized effluent concentration of approximately 0.95 for the 476, 175 and 80 μm sands and 0.9 for the 50 μm sand. No release of MWNTs was observed following elution of de-ionized water in the low ionic strength experiments.

The results of this study suggest:

- Commercially available MWNTs are mobile through quartz sand with collector sizes ranging from fine sands to silt.
- The increased retardation of the breakthrough of MWNTs with decreasing collector size may be due to increased total specific surface area.
- Differences in breakthrough curves between the first and second pulse indicate that the deposition rate decreases as the experiment progresses. Site-blocking was proposed to account for this behaviour.
- MWNTs release from the surface of collectors following the de-ionized water flush may indicate deposition of particles in the secondary energy minimum, which is not consistent with traditional CFT.
- Traditional colloid filtration theory (CFT) does not adequately describe the behaviour of MWNTs seen in this study. A dual deposition model including site blocking was utilized to help describe the experimental findings and led to better agreement between experimental results and mathematical model fits.
- Non-physiochemical removal mechanisms, such as straining, may control deposition of MWNTs at the low ionic strength (0.1mM), however based on results of this study likely only account for 5 to 10 % removal of MWNTs.

- The capacity of collectors for MWNT deposition ($S_{\max}$) increases as collector size decreases however the attachment efficiency (α) decreases as collector size decreases.

4.2 Recommendations

This study suggests that the mean collector grain size (d_{50}) is an important parameter in determining the mobility of MWNTs beyond what is expected in CFT (i.e., the site blocking capacity ($S_{\max}$) is controlled by collector size). The experimental conditions investigated in this study are only a small fraction of the extensive potential conditions that may be seen in the environment. Therefore, further research is still needed to fully understand MWNT behaviour under varying subsurface conditions. Specific recommendations for future work include varying experimental procedure, further decreasing porous media grain size and improvement of numerical models.

To further investigate MWNT mobility, experimental conditions such as the flow velocity and ionic strength could be varied to a greater degree than investigated here. Flow velocities could be reduced to flow rates typically found in low flow areas of particular importance to potential MWNT release into the environment (e.g., underneath landfill liners). Increasing the number of pulses or the volume of pulses injections would be beneficial to determine whether surface blocking is occurring with the slow deposition rate (which due to the length of experiments was not seen in this study).

Even at the smallest fraction, straining was not a significant hindrance to particle transport. The mean collector size could be decreased beyond what was used in this study to determine the d_{50} at which straining of MWNTs becomes the dominant removal mechanism.

The development of suitable interaction energy profiles for comparison to experimental and modeling results would provide greater insight into proposed retention mechanisms.

Refinement of the single collector efficiency relationship used in this study to include removal mechanisms should be considered to yield better fits of α (e.g., hydrodynamic interactions and van der Waals attraction).

The inclusion of natural organic matter (NOM) into the system has been shown to enhance MWNT mobility. Therefore, inclusion of NOM with collectors of varying soil mineralogy would be advantageous to explore the impact of surface heterogeneities (i.e., less ideal porous media) on MWNT transport.

Appendix A – Table of Experiments

Table A.1: List of Experiments

	d₅₀ (μm)	velocity (m/d)	n	I(mM)	Label
fast					
	476	4.2	0.314	7.5	d50 =476um v=4.2m/d
	175	4.28	0.308	7.5	d50 =175um v=4.2m/d
	80	4.05	0.413	7.5	d50 =80um v=4.2m/d (Exp.A)
	80	4.12	0.406	7.5	d50 =80um v=4.2m/d (Exp.B)
	80	3.35	0.394	7.5	d50 =80um v=4.2m/d (Exp.C)
	50	4.22	0.417	7.5	d50 =50um v=4.2m/d (Exp.A)
	50	4.17	0.421	7.5	d50 =50um v=4.2m/d (Exp.B)
slow					
	476	0.416	0.318	7.5	d50 =476um v=0.42m/d
	175	0.423	0.312	7.5	d50 =175um v=0.42m/d (Exp.A)
	175	0.427	0.309	7.5	d50 =175um v=0.42m/d (Exp.B)
	80	0.328	0.402	7.5	d50 =80um v=0.32m/d (Exp.A)
	80	0.417	0.422	7.5	d50 =80um v=0.42m/d (Exp.B)
	50	0.432	0.408	7.5	d50 =50um v=0.42m/d
	476	0.415	0.326	0.1	d50 =476um v=4.2m/d I=0.1mM
	175	0.420	0.314	0.1	d50 =175um v=4.2m/d I=0.1mM
	80	0.421	0.410	0.1	d50 =80um v=4.2m/d I=0.1mM
	50	0.420	0.423	0.1	d50 =50um v=4.2m/d I=0.1mM