Transport and deposition of quantum dots and model polystyrene nanoparticles in granular aquatic environments

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"Success is not final, failure is not fatal: It is the courage to continue that counts"

Sir Winston Churchill

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Glossary

Abbreviations

BET	Brunauer-Emmett-Teller
CCC	critical coagulation concentration
CFT	colloid filtration theory
cPL	carboxyl-functionalized polystyrene latex nanospheres
DI	deionized water
DLS	dynamic light scattering
DLVO	Derjaguin, Landau, Verwey and Overbeek
DOM	dissolved organic molecules
ENP	engineered nanoparticle
EPM	electrophoretic mobility
EX/EM	excitation/emission wavelength
ICP	inductively coupled plasma
IS	ionic strength
nPL	carboxylated polystyrene latex

nZVI	zero-valent iron nanoparticles
NTA	nanoparticle tracking analysis
PAA	poly-acrylic acid
PEG	poly-ethylene-glycol
PDI	polydispersity index
PV	pore volumes
PZC	point of zero charge
QCM, QCM-D	quartz crystal microbalance
QD	quantum dot
SEM	scanning electron microscopy
Si-NC	silicon nanocrystal
SIOS	scanning ion occlusion spectroscopy
sPL	sulphate-functionalized polystyrene latex nanospheres
SRHA	Suwannee river humic acid
TEM	transmission electron microscopy
TOC	total organic carbon

UV	ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Symbols

A	Hamaker constant
С	effluent particle concentration
$C_{\mathfrak{b}}$	bulk concentration of particles
C_0	influent particle concentration
C/C_0	normalized effluent particle concentration
d _c	grain diameter
d_{50}	average diameter of the sand grains
$d_{ m h}$	hydrodynamic diameter
$d_{ m p}$	particle diameter
D_{∞}	diffusion coefficient in an infinite medium, D_{∞} =
	$k_{\rm B}T/(3\pi\mu d_{\rm p})$
D _n	dissipation shift from the $n_{\rm th}$ overtone
$f_{ m n}$	frequency shift from the $n_{\rm th}$ overtone

h	height of the QCM flow chamber
$k_{ m B}$	Boltzmann constant, 1.3805×10^{-23} J/K
k _d	initial deposition rate coefficient
L	packed-bed length
N _{DLVO}	DLVO number
Pe	Peclet number
<i>r</i> _d	experimental deposition rate
$r_{\rm d}{}^{\rm SL}$	theoretical deposition rate
Γr	release rate
U	approach fluid velocity
x	distance along the flow from the inlet

Greek letters

α	attachment efficiency
ε	bed porosity
£0	dielectric permittivity in vacuum
<i>E</i> r	dielectric permittivity of water

К	inverse Debye length
η_0	overall single collector contact efficiency
$\eta_{ m D}$	single collector contact efficiency for transport by
	diffusion
$\eta_{ m I}$	single collector contact efficiency for transport by
	interception
$\eta_{ m G}$	single collector contact efficiency for transport by
	gravity
$\Psi_{ m c}$	surface potential collector
Ψp	surface potential particle

ABSTRACT

Quantum dots (QDs) are luminescent semiconductor nanoparticles with relevant applications in different fields, including medical imaging, solar cells, and sensors. However, toxic effects in living organisms have been reported, and upon release, the potential ecotoxicological risks of QDs will be directly related to their transport and fate. The objective of this research was to evaluate the transport and deposition of different QDs in systems representative of natural subsurface environments and engineered granular filtration processes. Two experimental approaches were used: (i) laboratory scale columns packed with granular materials representative of the soil or filter matrix, and (ii) a quartz crystal microbalance with dissipation monitoring (QCM-D) using sensors coated with materials representative of grain-water interfaces. The transport and deposition of the QDs were determined over a broad range of solution chemistries (i.e., ionic strength, pH, cation type, natural organic molecules (NOM)). In all cases, the deposition experiments were complemented with an appropriate physicochemical characterization of the particles and collectors.

In experiments conducted with packed columns, the transport potential of a CdSe QD, a CdTe QD and model nanosized polystyrene particles was systematically investigated in two water-saturated granular matrices: *(i)* clean quartz sand and *(ii)* loamy sand obtained from Québec farm. This study provided a good starting point for the comparison of the transport behavior of engineered nanoparticles in quartz sand versus soil matrices (loamy sand), where greater retention was observed. The results obtained suggest that differences in retention are likely xvii

related to the binding affinity of surface-modified nanoparticles for specific soil constituents.

In experiments conducted with a QCM-D, the deposition kinetics of polymercoated QDs were compared with those measured for two different polystyrene latex nanoparticles onto model environmentally relevant collector surfaces (SiO₂, Al₂O₃, or Al₂O₃ coated with NOM). The results showed that QD retention is relatively low compared to that of polystyrene latex particles, and in the presence of NOM, significantly lower deposition rates of QDs were observed. Overall, the data suggested that these phenomena could be attributed to the surface coating (polymers) used to stabilize the QDs, likely due to "electrosteric repulsion".

In the final series of experiments, the deposition kinetics of functionalized siliconnanocrystals (Si-NCs) was compared by means of: columns packed with quartz sand, and a QCM-D with SiO₂ coated crystals (as a model sand surface). The Si-NCs used here were functionalized with carboxylic acids of varying alkyl-chain length, and in general, experiments conducted with both techniques revealed that the mobility of Si-NCs increases with longer alkyl-chains. QCM-D provided further insight on the nanoparticle deposition behavior, whereby the output parameters (*i.e.*, frequency and dissipation) indicated how rigidly the ENPs are bound to the surface. Yet, the interpretation of nanoparticle deposition behavior by QCM-D may be limited by the size of the particle assessed; as it was determined that in the presence of large aggregates, the acquired frequency shifts were not proportional to the deposited mass.

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RÉSUMÉ

Les points quantiques (PQs) sont des nanoparticules semi-conductrices luminescentes ayant des applications intéressantes et prometteuses dans différents domaines, comme l'imagerie médicale, les cellules solaires ou les senseurs. Cependant, des effets toxiques dans les organismes vivants ont été découverts, et après la libération des PQs dans l'environnement, les risques possibles écotoxicologiques des PQs seront directement liés à leur transport et leur destin. L'objectif de cette recherche était d'évaluer le transport et le dépôt de PQs dans différents systèmes représentatifs des milieux naturels du sol et aussi des procédés de filtration granulaire. Deux approches expérimentales ont été utilisées: (i) des colonnes (collecteurs) remplies de matériaux granulaires (correspondant à la matrice du sol), et (ii) une microbalance à cristal de quartz avec dissipation d'énergie (QCM-D) en utilisant des capteurs recouverts de matériaux pouvant modéliser les différentes interfaces sol-eau. Le transport et le dépôt des PQs ont été déterminés sur une large gamme de chimies de solution (c.-à-d, force ionique, pH, type de cation et macromolécules organiques naturelles). Dans tous les cas, les mesures de dépôt ont été complétées par une caractérisation physico-chimique appropriée pour les particules et les collecteurs.

Dans des expériences menées avec des colonnes, le potentiel de transport d'un PQ de CdSe, d'un PQ de CdTe et d'une nanoparticule modèle de latex polystyrène a été systématiquement étudié dans deux matrices granulaires saturées d'eau: *(i)* du sable de quartz propre et *(ii)* du sable glaiseux obtenu d'une ferme québécoise.

Cette étude a servi de point de départ pour comparer le comportement de transport des nanoparticules dans le sable de quartz d'une part et avec les matrices du sol (sable glaiseux) d'autre part, où, d'ailleurs, une plus grande rétention a été observée. Les résultats obtenus suggèrent que les différences de rétention sont probablement liées à ce qui constitue l'affinité des nanoparticules modifiées en surface par les constituants spécifiques du sol.

Dans des expériences menées par QCM-D, les dépôts cinétiques de PQs enrobés de polymères ont été comparés à ceux mesurés pour deux différents types de nanoparticules de latex sur des surfaces collectrices modèles représentatives de l'environnement (c.-à-d, SiO₂, Al₂O₃, Al₂O₃ ou encore recouvertes de macromolécules organiques naturelles). Les résultats ont montré que la rétention des PQs est relativement faible par rapport à celle des particules de polystyrène, et peu d'interaction se produit entre les PQs et les macromolécules organiques naturelles. Dans l'ensemble, les données suggèrent que ces phénomènes pourraient être attribués à une "répulsion électro-stérique" de la couche de surface (polymères) utilisée pour stabiliser les PQs.

Dans la dernière série d'expériences, la cinétique de dépôt des nanocristaux fonctionnalisés à base de silicium (NCs de Si), a été comparé à l'aide de: des colonnes remplies avec du sable de quartz, et un QCM-D avec de cristaux revêtus de SiO₂ (comme surface du sable modèle). Les NCs de Si utilisés ici ont été fonctionnalisés par des acides carboxyliques avec différentes longueurs de chaîne alkyle, où la mobilité de NCs de Si augmente avec des chaînes d'alkyle plus longues. QCM-D a aussi permis de mieux comprendre le comportement de dépôt de NCs de Si, de sorte que les paramètres de sortie (c.-à-d, la fréquence et la dissipation) indiquent comment les particules sont rigidement liées à la surface. Néanmoins, en présence de grands agrégats, l'interprétation du comportement de dépôt de nanoparticules par QCM-D peuvent être limitée; comme il a été déterminé, les variations de fréquence acquise pourraient ne pas être proportionnels à la masse déposée.

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PREFACE

In accordance with the "*Guidelines for Thesis Preparation*", this thesis is presented in a manuscript-based format. The results presented in these chapters are either published or in preparation for submission. In all the publications, the author of this manuscript is the primary author of this thesis. Below is a detailed description of the efforts of each contributing author:

<u>Quevedo I.R.</u>, Tufenkji N. "Mobility of Functionalized Quantum Dots and a Model Polystyrene Nanoparticles in saturated quartz sand and loamy sand". **Environmental Science and Technology** 2012, 46 (8), 4449-4457.

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I.R. Quevedo: Conducted the experimental procedures, analysis of results, wrote manuscript.

N. Tufenkji: Supervision of the research and revision of the manuscript.

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A.L.J. Olsson: Assistance in analysis of results and revision of the manuscript.

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Author's contributions:

I.R. Quevedo: Conducted the experimental procedures, analysis of results, wrote manuscript.

A.L.J. Olsson: Assistance in analysis of results and revision of the manuscript.

J.G.C. Veinot: Technical assistance and provided the silicon nanocrystals used in the study.

N. Tufenkji: Supervision of the research and revision of the manuscript.

Chapter 1: Introduction

1.1 Motivation

A large variety of engineered nanoparticles (ENPs) with unique mechanical and optical properties attributed to their size are currently available on the market¹. Quantum dots (QDs) are fluorescent ENPs with potential applications in the development of transistors, solar cells, lasers, medical imaging, and computing devices²⁻⁴. From a structural point of view, QDs are comprised of a metalloid crystalline core and a "cap" or "shell" that shields the core and renders the particles water soluble and bioavailable (Figure 1.1)⁵. The core consists of a variety of metal complexes such as inorganic semiconductors (*e.g.*, Si, CdSe, CdTe) modified with secondary coatings (*e.g.*, polymers, polyelectrolytes, surfactants)^{5, 6}.



Figure 1.1. Quantum Dot⁷

From an environmental standpoint, the introduction of QDs in the market is cause for concern because several studies have demonstrated they might exhibit toxic effects⁸⁻¹¹. The introduction of QDs may occur via waste streams from industries that synthesize or use them, as studies with other ENPs have reported¹²⁻¹⁴. Kaegi et al.,¹³ for example, indicate that significant amounts of TiO₂-ENPs, used as pigment in exterior façade paints, are transported into natural receiving waters. Benn et al.¹² reported that Ag-ENPs used as antimicrobial agent in clothes, might be released into wastewaters. Likewise, a study of the life cycle of different ENPs revealed their persistence and hazardous effects in the environment¹⁴. Hence, to properly assess the risks associated with QDs (or products containing QDs) an adequate prediction of their mobility and persistence in aquatic environments is required¹⁵.

Different experimental approaches can be used to study nanoparticle deposition in water saturated granular environments¹⁸. Water saturated columns filled with well characterized porous media (*e.g.*, glass beads, sand, or soil) are used to study the transport and deposition of ENPs following injection, by monitoring changes in the effluent particle concentration as a function of time. The quartz crystal microbalance with dissipation monitoring (QCM-D) is another approach to characterize ENP deposition onto model collector surfaces during a defined period of time.

The transport mechanisms that govern colloid transport and deposition are Brownian diffusion, interception, and sedimentation (the latter is not likely to play an important role for ENPs due to their small size)^{19, 20}.Once ENPs are transported to the surface of a collector, the likelihood of attachment is controlled by colloidal interaction forces such as Derjaguin-Landau-Verwey-Overbeek (DLVO) as well as non-DLVO interaction (including steric forces)^{21, 22}. The interaction forces are dependent on various physicochemical properties of the ENPs and collector surfaces, and can be described as being unfavorable (*i.e.*, repulsive) or favorable (*i.e.*, attractive). With respect to the QDs, the contribution of steric repulsive forces resulting from the adsorbed layers of polymers and polyelectrolytes used to stabilize them can play an important role in predicting their transport.

The deposition of ENPs onto surfaces of environmental relevance such as aquifer or filter grains is influenced by the ionic strength of the solution, the electrokinetic potentials of particles and collectors, and the particle size¹⁸. To date, only a limited number of studies²³⁻²⁶ have addressed the transport potential of QDs or other surface modified ENPs in natural subsurface environments or engineered filtration processes. Overall, these studies have concluded that the properties of the granular collector and the surface coatings used to coat the QDs have a great influence on their transport potential. Whereas QDs in packed columns with ultrapure quartz sand have been reported to exhibit high mobility²⁴⁻²⁶, an enhanced retention in the presence of mineral heterogeneities has also been observed^{23, 24}.

In this investigation, experiments with packed-bed columns and QCM have been systematically conducted to evaluate and compare the transport potential of different carboxyl-terminated commercial QDs²⁷⁻²⁹. These experiments have been conducted with different granular materials and collector mineralogies to better understand the role of surface heterogeneities and interfacial dynamics in particle-particle and particle-collector interactions. Moreover, to study the role of surface stabilizers, the results have been compared with model nanosized carboxylated 5

polystyrene latex particles. This research is one of the first attempts to study the transport of QDs in environmentally relevant matrices over a broad range of physicochemical conditions; namely ionic strength, pH, cation type, and presence of natural organic molecules.

1.2 Theoretical Background

The transport and deposition of particles in granular aquatic systems under steady state conditions is mathematically expressed by the convective-diffusion equation³⁰, generally written as:

$$\frac{\partial n_j}{\partial t} + \nabla \cdot (un_j) = \nabla \cdot (D \cdot \nabla n_j) - \nabla (\frac{D \cdot F}{kT} n_j) + \frac{\partial n_j}{\partial t_{RXN}}$$
(2.1)

where n_j is the concentration of particles of size or type *j* in the suspension; *D* is the particle diffusion tensor; *u* is the particle velocity vector induced by the flow; *F* is the external force vector and the interaction of these particles ($\partial n_j / \partial R_{RXN}$) with a surface (deposition) or with other particles (aggregation).

In packed-bed columns, the deposition phenomenon can be considered as a sequence of particle transport (to an immobile collector) followed by attachment to the surface³¹. In a granular porous medium, fluid flow can be described by the Happel sphere-in-cell model, in which grains within the porous medium are assumed to be spherical collectors, surrounded by an imaginary outer sphere³². Particles are then transported to the collector surface through a combination of interception, gravitational settling and diffusion transport mechanisms²⁰.

A correlation equation for particle transport due to Brownian diffusion, interception and gravitational settling has been reported by Tufenkji and Elimelech¹⁹ yielding a closed-form solution for the transport of particles to the surface of spherical collectors expressed as the theoretical single-collector contact efficiency (η_0):

$$\eta_0 = \eta_D + \eta_I + \eta_G \tag{2.2}$$

where η_D is the single-collector contact efficiency for transport by diffusion; η_I is the single-collector contact efficiency for transport by interception; and η_G is the single- collector contact efficiency for transport by gravity. The equation is based on the assumption that η_0 is determined by summation of the three independently determined mechanisms. The overall single-collector contact efficiency for deposition in saturated porous media is written in terms of dimensionless groups where A_s is a porosity parameter, N_R the aspect ratio, N_{Pe} the Peclet number, N_{vdW} the van der Waals number, and N_G the gravitational number, yielding the equation for the single-collector efficiency as :

$$\eta_0 = 2.44 A_{\rm s}^{1/3} N_{\rm R}^{-0.081} N_{\rm Pe}^{0.715} N_{\rm vdW}^{0.052} + 0.55 A_{\rm s} N_{\rm R}^{1.675} N_{\rm A}^{0.125} + 0.22 N_{\rm R}^{-0.24} N_{\rm G}^{1.11} N_{\rm vdW}^{0.053}$$
(2.3)

For particles in the micron size range, transport to a collector will be dominated by interception and gravitational settling mechanisms. However, ENP transport onto collectors will be typically dominated by diffusion^{16, 19}. As indicated above, observations of particle deposition in porous media over a wide range of particle sizes have shown that when particle attachment is unfavorable, only a fraction of the particles transported to the collector surface will attach; therefore, the single collector efficiency must be modified by a probability that a particle approaching a single collector will be deposited¹⁶. Measurements of particle removal across a length (*L*) in a homogeneous porous medium composed of spherical grains of diameter (*d*_c) and porosity (ε) can be combined with the calculations for particle transport to yield an estimate of the attachment efficiency (α)²⁰ :

$$\alpha = -\frac{2d_{c}}{3(1-\varepsilon)\eta_{0}L}\ln\left(\frac{C}{C_{0}}\right)$$
(2.4)

where *C* and *C*₀ are the particle number concentrations present at distance *L* in the column effluent and influent and η_0 is the single-collector contact efficiency. Using experimental *C*/*C*₀ values and theoretical values of η_0 , the efficiency can be calculated for a given particle suspension.

The deposition of particles on flat surfaces from flowing suspensions can also be studied experimentally by means of QCM-D. The QCM-D unit used in this research (E4 from Q-Sense, Sweden) comprises of four sensor flow modules which allow independent deposition measurements. Each flow module holds a 5 MHz AT-cut quartz sensor crystal coated with mineral compositions commonly present in natural or engineered aquatic environments (*e.g.*, SiO₂, Fe₂O₃ or Al₂O₃). An application using this principle has been recently reported by Chen and Elimelech^{33, 34}and Saleh et al.^{35, 36} measuring the deposition kinetics of fullerene and nanoiron particles respectively, onto silica coated quartz surfaces. The continuous increase in the mass of the crystal due to the deposited particles

induces a continuous shift in the resonance and overtone frequencies of the QCM-D, as described by the Sauerbrey relationship³⁷:

$$-\Delta f_n = -\frac{C}{n}\Delta m \tag{2.5}$$

where Δm is the mass of nanoparticles deposited, Δf_n is the shift in resonance (or overtone) frequency, with *n* being the overtone number (1, 3, 5...13), and *C* is the crystal constant (17.7 ng/Hz-cm² for a 5 MHz quartz crystal). Because the changes in resonance and overtone frequencies are proportional to the mass deposited on the crystal, the rate of deposition or release can be determined by evaluating the initial slope in the Δf_n measurements:

$$r_{\rm d} = -\frac{d\Delta f_n}{dt} \tag{2.6}$$

Because the QCM flow chamber is designed with a parallel plate geometry, the Smoluchowski-Levich approximation can be used to evaluate the theoretical particle deposition rate (r_d^{SL}) in the absence of repulsive interactions^{16, 28}:

$$r_{\rm d}^{SL} = 0.538 \frac{D_{\infty}C_{\rm b}}{a_{\rm p}} \left(\frac{Pe \cdot h}{x}\right)^{1/3}$$
(2.7)

where D_{∞} is the diffusion coefficient, C_b is the bulk concentration of QDs, a_p is the radius of the particles, *Pe* is the dimensionless particle Peclet number, *h* is the height of the QCM flow chamber, and *x* is the distance along the flow from the inlet.

1.3 Objectives and Scope of the Thesis

The overall goal of this research project was to evaluate the transport and deposition of different QDs (*i.e.*, CdTe, CdSe, Si) with consideration given to the nature of their surface coatings. The systems used were meant to be representative of natural subsurface environments or engineered filtration processes, namely, columns packed with granular materials (*i.e.*, quartz sand, loamy sand) and a QCM-D with sensors coated with materials (*i.e.*, SiO₂, Al₂O₃) representative of grain-water interfaces. Experiments were conducted over a broad range of environmentally relevant aquatic chemistry (*i.e.*, ionic strength (IS), pH, cation type, natural organic molecules). In all cases, the deposition experiments were complemented with an appropriate physicochemical characterization of the particles and collectors.

The following are the specific objectives of this study:

- To compare the mobility of QDs and polystyrene latex (as a model ENP), in water saturated columns packed with different granular porous media over a broad range of solution chemistries.
- To use a QCM-D to characterize the role of water chemistry (*i.e.*, IS, cation type, pH, dissolved natural organic molecules (DOM)) on the deposition kinetics of QDs and model polystyrene latex nanoparticles depositing onto model grain surfaces (*i.e.*, SiO₂, Al₂O₃, DOM-precoated surfaces).
• To compare the transport and deposition of functionalized silicon based QDs using packed-bed columns and QCM-D over a similar range of water chemistries (*i.e.*, IS, cation type, pH).

1.4 Thesis Organization

In Chapter 2, the mobility of two carboxyl-terminated commercial QDs (CdSe, CdTe) and a model nanosized carboxylated polystyrene latex particle were systematically assessed in packed columns with clean quartz sand (commonly used in transport studies) and loamy sand obtained from a farm near Québec City, QC, Canada. Well-controlled laboratory-scale packed column experiments were conducted to study the three ENPs in two different granular media over a broad range of environmentally relevant solutions ionic strengths (IS). Various complimentary techniques were used to obtain a comprehensive characterization of the ENPs and granular matrices used in this research. This was one of the first published studies comparing the transport behavior of ENPs in different granular matrices.

In Chapter 3, the deposition and release kinetics of a carboxyl terminated CdTe QD was studied using a QCM-D. The QCM-D is a mass sensor, where the injected flow is parallel to flat quartz sensors. The sensors used in this study were coated with SiO₂, and are therefore representative of the surface of the quartz sand grains used in the packed columns in Chapter 2. Experiments were conducted at different pHs and over a broad range of environmentally relevant water ionic

strengths (IS) of both monovalent and divalent cations, to examine the role of water chemistry on QD deposition and transport behavior.

In Chapter 4, the deposition behavior of carboxylated-QDs on chemically diverse model surfaces that may be encountered in natural or engineered aquatic environments is examined. To this end, QCM-D was used to evaluate the deposition kinetics of two commercially available polymer-coated QDs onto bare Al₂O₃ and a DOM-precoated Al₂O₃ surface over a broad range of water chemistries. The results were compared with measurements obtained using two model ENPs of comparable particle size; namely, two polystyrene latex nanospheres functionalized with carboxylic or sulfate groups. An appropriate physicochemical characterization of the particles and model collectors was performed in all cases to interpret the results.

In Chapter 5, the deposition kinetics of functionalized silicon-based QDs (Si-QDs) were characterized using columns packed with quartz sand and a QCM-D mounted with SiO₂ coated sensors. The Si-NCs used here were functionalized with carboxylic acids of varying alkyl-chain length. Overall, experiments conducted with both techniques revealed comparable deposition behaviors. An increase in solution ionic strength resulted in enhanced deposition kinetics. Yet, longer alkyl-chain lengths in the QD surface capping seemed to improve the stability of Si-QDs, thereby increasing their mobility.

Chapter 6 describes a summary of the thesis and the general conclusions of this doctoral research.

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1.5 Contributions

Because most of the ENPs available in the market are surface modified or functionalized (with polymer or polyelectrolytes), this investigation contributes to the general understanding of transport and mobility behavior of ENPs (not only QDs). To date, many of the publications on the subject of the transport of ENPs have been conducted with bare or non-functionalized particles in aquatic environments. However, since new ENPs are being introduced every year, and the findings presented here have direct implications for the evaluation of the possible risks of releasing QDs in natural subsurface environments and in deep-bed granular filtration processes.

The specific contributions of this work are listed below:

• Improved understanding of the transport and deposition behavior of QDs in aquatic systems. Although the number of studies on the environmental fate of ENPs has substantially increased in the past years, there are only limited studies with QDs. In this thesis, the transport and deposition behavior of different QDs was evaluated over a broad range of IS, environmentally relevant pH values, cation type (K⁺, Ca²⁺), and in the presence of dissolved organic molecules (DOM); namely humic acids and rhamnolipids. It was found that the transport and deposition of surface modified QDs were significantly influenced by the nature of the water chemistry.

• Demonstrated that the composition of the core and surface coatings of QDs might affect their transport potential in granular environments. The few studies conducted to assess the mobility of QDs in granular environments have used quartz sand as the material of interest, and little is known about the transport potential in more complex media. A systematic experimental investigation in laboratory scale columns packed with quartz sand and loamy sand demonstrated divergences in the transport behavior of all the ENPs. Although the granular matrices were comparable in mean grain diameters, the retention was significantly higher in loamy sand as compared to quartz sand. These differences were linked to the mineralogy of the loamy sand and the chemical composition of the polymeric coatings on the ENP surfaces.

• Comparison of the deposition behavior in columns and QCM-D experiments. Published studies have involved different experimental approaches to evaluate the transport and deposition of ENPs, but only few have combined QCM-D deposition experiments and packed bed columns. This thesis is a starting point to relate the results obtained with both experimental approaches in evaluating the deposition kinetics of ENPs over a wide range of environmentally relevant conditions.

• Improved understanding of the roles of ENP surface coatings using QCM-D. Fundamental differences between the deposition behavior of polymercoated QDs (governed by electrosteric forces) and non-coated ENPs (governed by classical DLVO interactions) were demonstrated by considering the two QCM-D

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output parameters: frequency and dissipation. It was demonstrated that the ratio of dissipation and frequency revealed key structural information about the ENP-collector interface.

• Theoretical estimation of QD deposition rates in QCM-D experiments. It was established that the approximation proposed by Smoluchowski-Levich for parallel-plate geometry is an adequate approach to estimate the deposition of ENPs in a QCM-D chamber. The theoretical calculations helped to establish the role that electrostatic and steric forces play in nanoparticle deposition studies on different collector surfaces (*i.e.*, SiO₂, Al₂O₃. Al₂O₃ precoated surfaces with DOM).

• Improved understanding of the transport and deposition behavior of aggregated ENPs. Deposition experiments with aggregated ENP systems using QCM-D have resulted in positive frequency shifts which are counterintuitive to the principle of the instrument as a mass sensor. Under these conditions, ENP aggregates (~700 nm size) are connected to the sensor via weak bridges (*i.e.*, coupled resonance-type response). Hence, experiments conducted with QCM-D to evaluate the deposition of aggregated ENP systems are limited under certain conditions.

Most of the work presented in this thesis has already been published:

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- <u>Quevedo, I.R</u>; Olsson, A.L.J.; Clark, R.; Veinot, J.; Tufenkji, N. "Effect of Surface Modifiers and Aggregate Size on the Transport and Deposition of Engineered Nanoparticles". *To be submitted to Environmental Engineering Science*
- <u>Quevedo, I.R</u>; Olsson, A.L.J.; Tufenkji, N. "Deposition Kinetics of Quantum Dots and Polystyrene Latex Nanoparticles onto Alumina: Role of Water Chemistry and Particle Coating". Environmental Science & Technology 2013, 47 (5), pp 2212–2220.
- <u>Quevedo, I.R</u> and Tufenkji, N. "Mobility of Functionalized Quantum Dots and Model Polystyrene Nanoparticles in Saturated Quartz Sand and Loamy Sand" Environmental Science & Technology 2012, 46 (8), 4449-4457.
- <u>Quevedo, I.R.</u>, and Tufenkji, N. "Influence of Solution Chemistry on the Deposition and Detachment Kinetics of a CdTe Quantum Dot Examined Using a Quartz Crystal Microbalance" Environmental Science & Technology 2009, 43, 3176–3182.

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Chapter 2: Mobility of functionalized quantum dots and a model polystyrene nanoparticle in saturated quartz sand and loamy sand

Connecting text: In aquatic environments, the transport and fate of ENPs are coupled; that is the transport of these new materials in the environment will determine their probable accumulation, potential exposure routes, and where dilution occurs. To date, not much is known about the transport of ENPs upon release, and laboratory-scale columns packed with granular materials (*e.g.*, glass beads, sand, or soil) are the most commonly used approach to evaluate the mobility of ENPs in water saturated granular porous media. This study provides a starting point for the comparison of the transport behavior of QDs and a model polystyrene latex nanoparticle in quartz sand versus soil matrices.

The results of this research have been published in this paper: Quevedo I.R., Tufenkji N. 2012. *Mobility of Functionalized Quantum Dots and a Model Polystyrene Nanoparticle in Saturated Quartz Sand and Loamy Sand*. Environ. Sci. Technol. 46 (8):4449-4457.

2.1 Introduction

It is expected that by the year 2020, the equivalent of six trillion U.S. dollars in consumer products will incorporate nanomaterials.¹ Many economic and societal benefits are expected from nanotechnology, but there are likely risks to human and ecosystem health because engineered nanoparticles (ENPs) are generally more reactive and potentially more persistent than bulk materials with similar chemical composition.^{2,3}

Quantum dots (QDs) are one example of ENPs that exhibit distinctive optical and electrical characteristics^{4,5} due to their composition and small size (typical diameters are between 2-100 nm). Because QDs have excellent fluorescent properties and narrow emission spectra compared to other fluorophores, they are particularly useful in the development of transistors, solar cells, lasers, medical imaging, and computing systems.⁶⁻⁸ Typically, QDs are composed of a binary alloy of semiconducting metals (e.g., CdTe, CdSe, InAs, InP) protected by a shell (ZnS, CdS), which is coated with polymers or polyelectrolytes to make them dispersible in aqueous media.^{4,9} Although some promising silicon-based QDs are under development,^{10,11} current commercial QDs contain toxic heavy metals and several studies demonstrate their cytotoxic effects on living organisms.¹²⁻¹⁴ QDs may be introduced into the natural environment via waste streams from industries that synthesize or use them, and via clinical and research facilities. After their release into aquatic or soil ecosystems or wastewater treatment facilities, the potential toxicological risks of QDs will be directly related to their mobility and transformation within these environments.¹⁵⁻¹⁷

The transport and fate of a wide range of ENPs in systems representative of natural subsurface environments or engineered (deep-bed) granular filtration processes have been examined in a number of laboratory investigations.¹⁸ In general, studies conducted with various surface-modified or coated ENPs suggest they possess greater mobility in water-saturated granular matrices than their bare counterparts.¹⁹⁻²⁴ For instance, several researchers have examined the transport potential of surface-modified zero-valent iron nanoparticles (nZVI) in model subsurface environments, demonstrating the effective electrosteric stabilizing efficiency of various polyelectrolytes or organic coatings.^{19,22-24} However, the variability in the experimental approach and conditions used in each study complicates the generalization of such findings to a broader range of ENPs. Moreover, only a limited number of studies²⁵⁻²⁷ have addressed the transport potential of QDs in subsurface environments. For instance, Torkzaban et al.²⁶ studied the retention of a carboxylated CdTe QD in water saturated sand packed columns as a function of solution IS (in NaCl solution). They observed little deposition of this QD in ultrapure quartz sand, but the retention was greatly enhanced in the presence of impurities on the sand surface and in columns packed with goethite-coated sand. Uyusur et al.²⁷ examined the influence of solution chemistry (IS and the presence of surfactant) and the impact of air-liquid and solid-liquid interfaces on the mobility of a CdSe QD in columns packed with sand. These researchers concluded that the mobility of the CdSe QD under unsaturated conditions is mainly controlled by capillary forces. Uyusur et al.²⁷ suggested that QDs may be highly mobile in dynamic and heterogeneous natural

subsurface environments. We also noted in a previous study²⁵ that the retention of a commercial CdTe QD on a model sand surface was very low at neutral pH.

The few studies aimed at investigating the transport behavior of QDs in granular environments have utilized quartz (clean or coated) as the collector surface of interest.²⁵⁻²⁷ There is one study in the literature reporting on the mobility of QDs in soil;²⁸ however our understanding of ENP transport potential in this more complex medium is limited. The composition of soil (*e.g.*, mineral content and organic matter content) can differ considerably from one location to another and different ENPs will likely exhibit varying affinity for different soil fractions.¹⁷ This inherent geographical and constitutional heterogeneity of natural soils presents considerable challenges to the development of functional relationships linking ENP physicochemical properties and their transport potential. Nevertheless, well-controlled laboratory studies are needed to identify potential links between measurable ENP and soil properties and the mobility of ENPs in saturated granular environments.

The purpose of this work is to systematically evaluate and compare the transport potential of two carboxyl-terminated commercial QDs and a model nano-sized carboxylated polystyrene latex (nPL) particle in the following water-saturated granular environments: (i) a clean quartz sand commonly used in ENP transport studies, and (ii) loamy sand obtained from a farm near Québec City, QC, Canada. Well-controlled laboratory-scale packed column experiments are performed to study the mobility of the three ENPs in the different granular media over a broad range of environmentally relevant solution IS, examining the influence of both 25

monovalent (K^+) and divalent cations (Ca^{2+}). This study provides a starting point for the comparison of the transport behavior of ENPs in pure quartz sand versus soil matrices (loamy sand), where greater retention may be observed.

2.2 Materials and Methods

2.2.1 Nanoparticle Suspensions

Two types of carboxyl-terminated QDs – a CdTe/CdS QD (Vive Nano, Catalog No.18010L, QDs are stabilized by poly acrylic acid derivative and suspended in water) and a CdSe/ZnS QD (Ocean Nanotechnologies, Catalog No. QSH530-04, coated with a monolayer of octadecylamine and a monolayer of undisclosed amphiphilic polymer and suspended in water) – with reported nominal sizes of 10 and 14 nm, respectively, were used in this study. In addition, carboxylated *n*PL (24 nm nominal size, Invitrogen, Catalog No. F8787) was used as a model ENP. ENP suspensions were prepared by diluting stock samples in electrolyte of varying IS (1–100 mM KCl or 1–10 mM CaCl₂ in deionized water (Biolab) at an adjusted pH of 7 (using HCl or KOH). The nanoparticle suspensions (at concentrations of 10^{12} particles/mL for the CdTe QD and *n*PL, and 5×10^{12} particles/mL for the CdSe QD) were vortexed at high speed for 30 sec, then left for 2 h at 9°C and finally at room temperature for 30 min prior to each experiment.

2.2.2 Nanoparticle Characterization

The electrophoretic mobility (EPM) of the ENPs was assessed using a Zetasizer Nano ZS (Malvern Instruments, UK). Each measurement was performed in triplicate using disposable capillary cells with an adjusted electrical field (E)between 5 and 10 \pm 0.1 V/m. To adequately characterize ENPs in aqueous suspension, we reported in a previous study the necessity of using complementary characterization techniques²⁹. Accordingly, the hydrodynamic diameter of the particles was obtained by dynamic light scattering (DLS) (ZetaSizer Nano, Malvern) and under selected conditions the particle size was assessed by transmission electron microscopy (TEM). For DLS, nanoparticle suspensions were prepared in an electrolyte solution (either KCl or CaCl₂) and sizing measurements were repeated with at least three different samples. TEM, specimens were prepared following the procedure recommended by Mavrocordatos et al.³⁰. A small droplet (20 µL) of the nanoparticle suspension was placed onto a formvar carbon-sputtered copper grid (SPI Supplies) followed by air drying overnight prior to analysis. Images were captured with a Philips CM200 TEM equipped with a $2k \times 2k$ CCD camera (Advanced Microscopy Techniques Corp., MA, USA) operating at 200 kV. The mean sizes of the ENPs were determined from the analysis of at least 40 particles per frame, in at least three randomly selected images recorded at high magnification.

2.2.3 Porous Media Preparation and Characterization

Two types of granular porous media were used in the transport experiments: (*i*) high purity quartz sand and (*ii*) loamy sand. The quartz sand (Sigma-Aldrich) was sieved to obtain a batch having an average grain diameter of 256 μ m (Figure 2.1), and then cleaned extensively³¹ to remove organic and metal impurities from the sand surface. The electrokinetic properties of the quartz sand were assessed over the range of solution chemistry used in the transport experiments and are presented in Table 2.1. Briefly, sand streaming potential was measured using an electrokinetic analyzer (Anton-Paar) and a cylindrical cell for granular material. Measured streaming potentials were converted to zeta potentials using the Helmholtz-Smoluchowski equation³².

The loamy sand was collected from the Agriculture and Agri-Food Canada (AAFC) farm in St-Augustin-de-Desmaures, QC, at a depth of 35cm. The collected medium was oven dried at 105°C for 8 hours and stored in glass jars. The loamy sand particle size distribution and cumulative weight fraction (Figure 2.1) were determined by a dry sieve analysis, while other physicochemical properties of both granular media were assessed at the Materials Characterization Laboratory of McGill University (Table 2.2).

The composition of loamy sand samples (ground into a fine powder) was studied using a field emission scanning electron microscope with energy dispersive X-ray spectrometer (SEM-EDS), and the mineralogy of the samples was analyzed using X-ray diffraction (XRD). The SEM images were recorded at an accelerating voltage of 2 keV, in high vacuum (HV) mode (FE-SEM Hitachi S-4700), and from the EDS analysis, weight percentages of major and minor elements present in the samples were determined. To identify the minerals present in the sample, XRD analysis (Philips PW 1710) was conducted on loamy sand samples containing grains that were less than 1 mm in size (this represents ~98% of the loamy sand material).

The specific surface area and porosity of the quartz and loamy sands were determined from unground samples by nitrogen BET adsorption isotherms (Micromeritics TriStar). The content of natural organic matter in the samples was determined by COD analysis using digestion tubes and a COD reactor (SCP Science).



Figure 2.1 (a) Particle size distribution for the quartz sand and loamy sand used in this study (b) Cumulative weight fraction distribution for quartz sand and loamy sand.

Table 2.1Zeta Potential of the quartz sand in the presence of electrolyte (KCl and CaCl₂) used in the transport experiments.

electrolyte	ionic strength (mM)	ζ _{sand} (mV)
	0.1	-59
	1	-52
	3	-50
KCI	10	-49
	30	-36
	100	-21
	0.1	-42
	1	-28
CaCl ₂	2.5	-25
	5	-21
	10	-14

Properties	quartz sand, 50-70 mesh particle size (Sigma-Aldrich)	AAFC farm plot at "St- Augustin-de-Desmaures", Quebec City (depth ≈ 35 cm)		
Grain size d_{50} (µm)	256	225		
Specific gravity (gr/cm ³)	2.68	2.64		
Particle size distribution	sand [99%]	sand [88.2%] clay [7.6%] silt [4.2%]		
Classification	а	loamy sand		
Organic matter	а	0.44%		
Chemical Composition	а	O, Si, Al, Fe, K, Ca, Mg, Na		
Mineralogy	quartz (SiO ₂)	quartz (SiO ₂) albite [(Na,Ca)Al(Si, Al) ₃ O ₈] orthoclase [K (Al, Fe)Si ₂ O ₈] allophane [Al ₂ O ₃ .2SiO ₂]		
Surface area (m ² /gr)	0.05	0.78		
Pore diameter (nm)	76.03	31.70		

Table 2.2Physicochemical properties of the size-fractioned porous media (quartz sand and loamy sand) used in the transport experiments.

^a not applicable or not measured.

2.2.4 Column Transport Experiments

ENP transport experiments were conducted using glass chromatography columns (10/20, Amersham Biosciences, Piscataway, NJ) with a 1 cm internal diameter and packed with either quartz sand or loamy sand to a packed bed depth of $10 \pm$ 0.5 cm. In the case of the quartz sand columns, 13.5 g of dry sand was soaked overnight in electrolyte and then packed into the column and equilibrated with 10 pore volumes (PVs) of the background electrolyte at a constant approach velocity of 1.06×10⁻⁴ m/s (equivalent to a flow rate of 0.5 mL/min). In the case of the loamy sand columns, the packed bed was prepared as described by Jaisi and Elimelech.³³ The dry packing of 11.84 g of loamy sand into the glass column was performed using gentle vibration. The packed column was purged with CO₂ in an upward flow direction for 20 min to improve water saturation as suggested by Kretzchmar et al.³⁴ Next, a solution of 20 mM CaCl₂ was injected into the column for 25 PVs, and finally, 100 PVs of the electrolyte of interest were injected into the column (downward flow direction) at an approach velocity of 1.06×10^{-4} m/s prior to injection of the ENP suspensions.

In both series of column experiments, 12.5 mL of each ENP suspension (equivalent to 3.7 or 3.3 PVs for quartz sand and loamy sand columns, respectively) were injected into the packed column, and the effluent ENP concentration (*C*) was monitored in real-time with a spectrofluorometer (Fluoromax-4, Jobin-Yvon Horiba) equipped with a flow-through cell. The

EX/EM settings for the different ENPs were as follows: 350/538 for the CdTe QD, 350/550 for the CdSe QD, and 505/550 for the *n*PL. The concentration of the influent ENP suspensions (C_0) was the same as that used for ENP characterization. ENP transport experiments were conducted over a wide range of solution IS, using both monovalent and divalent background electrolyte solutions. Each column experiment was conducted at least twice and the breakthrough behavior of an inert tracer – the fluorescent dye sodium naphtionate (Fluka Chemika) – was verified prior to injecting the ENP suspensions.

2.2.5 Interpretation of ENP Transport Experiments

To quantitatively compare the ENP transport behavior under different experimental conditions, the particle attachment efficiency (α) was calculated using colloid filtration theory (CFT), as follows³⁵:

$$\alpha = -\frac{2}{3} \frac{d_{50}}{(1-\varepsilon)L\eta_0} \ln\left(\frac{C}{C_0}\right)$$
(2.1)

where d_{50} is the average diameter of the sand grains, ε is the bed porosity, and L is the packed-bed length. The value of C/C_0 in eq 2.1 represents the normalized column effluent particle concentration for each experiment which was evaluated by numerical integration of the breakthrough curves. Values of η_0 for each experimental condition were determined using the correlation developed by Tufenkji and Elimelech³⁵.

2.2.6 Verifying QD Dissolution

The extent of dissolution of the QDs during the timescale of the transport experiments was verified as follows: QD suspensions were prepared in 30 mM KCl or 2.5 mM CaCl₂ (pH 7) in the same manner as those used for column experiments, and samples were taken at times representative of the start and end of a typical column run. The samples were transferred to conical tubes outfitted with 10 kDa membranes (Amicon, Millipore) and centrifuged at 10,000g for 5 min. The concentration of free Cd²⁺ in the filtrate was quantified by ICP-MS (Agilent 7500 CE Series). The concentration of total Cd in each sample was also determined by analyzing samples digested overnight in 30% HCl + 5% HNO3. All measurements were performed in triplicate.

2.3 Results and Discussion

2.3.1 Electrophoretic mobility (EPM) of the ENPs

The EPM of the three studied ENPs was assessed prior to each transport experiment in the presence of monovalent (KCl) and divalent (CaCl₂) salts (Table 2.3). The three ENPs are negatively charged under the conditions used in this study (pH 7, range of solution IS). The negative surface potential is attributed to the presence of carboxyl groups in the surface coatings of the ENPs.

electrolyte	ionic strength	particle	electrophoretic mobility		lectrophoretic DLS mobility Diameter			TEM Diameter					
	(mM)		(µm²	(µm².cm/V.s)		((nm)			(nm)			
	0.1		-2.1	±	0.5	72	±	1		5	±	2	
	1	CdTe QD	-2.3	±	0.4	71	±	1					
KCI	KCI ³		-2.2	±	0.2	78	±	14					
	10		-2.1	±	0.1	83	±	5					
	30 100		-1.9	±	0.7	68 114	±	12		0	т	4	
	0.1		-2.0	±	0.2	76	±	28		9	±	4	
	1		-2.5	+	0.4	144	+ +	62		5	-	2	
KCI	10	CdSe QD	-1.0	±	0.5	194	±	24					
	100		-0.4	±	0.1	175	±	54		42	±	24	
	0.1		-4.5	±	0.2	59	±	1					
	1	nPL	-3.9	±	0.3	60	±	1					
KCI	3		-4.2	±	0.2	69	±	4					
KOI	10		-3.3	±	0.3	67	±	2					
	30		-2.9	±	0.7	75	±	2					
	100		-1.7	±	0.3	86	±	5					
	0.1		-2.4	±	0.5	59	±	2					
1	1	CdTe QD	-1.5	±	0.2	59	±	1					
CaCl ₂	2.5		-1.8	±	0.1	139	±	3					
	5		-1.9	±	0.0	593	±	35					
	10		-0.2	±	0.1	447	±	351					
	0.1		-1.4	±	0.3	257	±	67					
CaCl ₂	1	CdSe QD	-1.2	±	0.1	208	±	4		74		00	
	2.5		-1.3	±	0.0	551	±	58		74	±	30	
	10		-0.2	±	0.1	074	±	140					
	U. I 4		-1.4	±	0.2	97	± ,	і л					
	۱ ۵ ۶	۳DI	-1.2	±	0.2	91	±	4 210					
	2.0 5	111° L	-1.2	Ĭ	0.∠ 0.2	201 515	± ⊥	1/2					
	10		-1.5	т +	0.2	2355	т +	816					

Table 2.3 Summary of the electrophoretic mobility and particle size of the ENPs used in this study as a function of solution IS in KCl or CaCl₂ at pH 7.

In general, when the ENPs are suspended in the monovalent salt KCl, they become less negative as the IS increases due to compression of the electrical double layer (Table 2.3). Although this decrease in the absolute EPM is quite dramatic for the *n*PL and CdSe QD when the salt concentration is increased from 0.1 to 100 mM KCl, the effect is not as significant for the CdTe QD (EPM changes only from -2.1 to -2.0 µm·cm/V·sec). The variation in EPM with IS for the *n*PL is consistent with soft particle theory; namely, the EPM becomes less negative with increasing IS but stabilizes at a non-zero value.^{36,37} The EPM of the poly-acrylic acid (PAA) coated CdTe QD also stabilizes at a non-zero value but barely changes over the wide range of IS. At low IS, the *n*PL is significantly more negative than the QDs (EPM = $-4.5 \,\mu\text{m}\cdot\text{cm/V}\cdot\text{sec}$, whereas the EPM for the CdSe QD and the CdTe QD is on the order of -1.9 and -2.1 µm·cm/V·sec, respectively). This result is consistent with the information provided by the ENP vendors: the amount of carboxylate groups on the *n*PL is on the order of 3×10^3 per particle (Invitrogen), 1.2×10² for each CdSe QD (Ocean Nano), and a similar order of magnitude for the CdTe QD (although specific details were undisclosed by Vive Nano).

The *n*PL is significantly less negative when suspended in CaCl₂ and the EPM is stable over the range of IS examined (Table 2.3). The variation in the measured EPM over the range of IS is much more important for the two QDs. The EPM changes from -2.4 to -0.2 μ m·cm/V·sec for the CdTe QD and from -1.4 to -0.2

 μ m·cm/V·sec for the CdSe QD when the IS increases from 0.1 to 10 mM CaCl₂. Both QDs nearly reach their point of zero charge (PZC) at an IS of 10 mM CaCl₂.

These EPM measurements are in general agreement with other published studies examining functionalized QDs.^{26,27,38} When converted to zeta potentials using the Henry equation³⁹ and the expression for the retardation effect of "hard spherical" particles proposed by Ohshima⁴⁰ (Table 2.5), our results are comparable to those reported by Torkzaban et al.²⁶ for a carboxylated CdTe QD. These researchers reported zeta potentials on the order of -45 to -35 mV in NaCl (pH 7.8) and Zhang et al. reported values between -30 to -20 mV in KCl (pH 7)³⁸ for a thioglycolate functionalized CdTe QD in a range of IS from 1-100 mM. Likewise, Uyusur et al.²⁷ reported values of -41 and 0 mV for a polymer coated (octylamine with modified poly-acrylic-acid) CdSe QD in 0.5 mM and 500 mM NaCl (pH 6.5), respectively. As indicated above, the ENPs studied here each have different surface coatings, but for each ENP, the terminal functional group is carboxylate.

2.3.2 Size Analysis of the ENPs

Nanoparticle size is an important parameter in the interpretation of nanoparticle transport and fate studies in granular aquatic environments.¹⁸ However, sizing suspended ENPs can be challenging given the limitations of available experimental techniques.²⁹

DLS enables rapid analysis and is one of the most widely used methods of assessing particle size in aqueous samples. DLS measurements of the QD suspensions used in this study are presented based on intensity based distributions (z-average) and generally exhibit an overall increase in hydrodynamic diameter (d_h) with increasing KCl or CaCl₂ concentration (Table 2.3). The hydrodynamic diameter increases from 72 to 114 nm for the CdTe QD, between 76 to 175 nm for the CdSe QD, and from 59 to 86 nm for the model particle *n*PL over the studied range of IS (0.1 to 100 mM) in monovalent salt solution. All of the particles exhibit significant aggregation when suspended in a divalent salt solution at the studied range of IS (0.1 to 10 mM CaCl₂). At an IS of 2.5 mM CaCl₂, the d_h increases significantly for all three ENPs (from 59 to 139 nm for CdTe QD, from 208 to 551 nm for CdSe and from 91 to 201 nm for *n*PL) (Table 2.1). The marked aggregation behavior for carboxylated QDs in the presence of multivalent cations (*e.g.*, Mg²⁺ or Ca²⁺) has been previously reported by Zhang et al.³⁸

The use of DLS has been criticized because the scattering intensity varies strongly with the particle diameter (*i.e.*, to the 6th power), which biases the interpretation of particle size (d_h) towards larger particles. Hence, DLS should not be employed as the sole characterization method. As a complementary characterization tool, TEM was employed to image the QDs under selected conditions. Although the use of TEM is not ideal due to the drying procedure used to prepare samples for imaging²⁹, this technique can be useful for evaluating the extent of aggregation of nanoparticle suspensions. The samples analyzed by TEM were prepared in the 38

same manner as those used for the column experiments, with an additional step needed for sample drying. At low IS (0.1 mM KCl, pH 7), the studied nanoparticles are generally well dispersed in the aqueous medium and large aggregates are not observed (Figure 2.2a, b, d, e). Using the image analysis software Image J, the nominal particle sizes were determined by measuring individual particles in a series of TEM images (Table 2.3). At this low IS (0.1 mM KCl) the QDs are slightly smaller than the nominal particle size reported by the manufacturer (on the order of 5 ± 2 nm for the CdTe QD and 9 ± 4 nm for the CdSe QD). When the IS is increased to 100 mM KCl, the nominal size of the CdTe QD is on the same order of magnitude (9 ± 4 nm), while the CdSe QD experienced some aggregation (42 ± 24 nm). In the presence of 2 mM IS CaCl₂, the aggregation is more significant for both QDs (Figure 2.2c and f). The particles in Figure 2.2f seem to be adhered to one another as opposed to forming aggregates.



Figure 2.2 Representative TEM micrographs of QDs suspended in electrolyte at pH 7. (a) and (b) CdTe QDs suspended in 0.1 mM KCl, and (c) in 2 mM CaCl₂. (d) and (e) CdSe QDs suspended in 0.1 mM KCl, and (f) in 2 mM CaCl₂.

This may be an artifact of the sample preparation procedure or a result of particle dissolution. However, measurements of changes in the free $[Cd^{2+}]$ during the timescale of the column experiments reveal little dissolution of both types of QDs at the experimental conditions of this study (on the order of 0.3% in KCl and on the order of 2% in CaCl₂) (Table 2.4).

Table 2.4 Time-resolved dissolved cadmium levels from polymer-coated QDs in monovalent or divalent salt solutions at pH 7.

electrolyte	particle	at <i>t</i> = 120 min (at column injection)	at <i>t</i> = 145 min (at column effluent)		
30 mM KCI	CdTe QD	0.06 ± 0.02 %	0.31 ± 0.18 %		
	CdSe QD	0.02 ± 0.01 %	0.02 ± 0.02 %		
$2 \mathrm{mM}\mathrm{CaCl}_2$	CdTe QD	1.26 ± 0.62 %	2.30 ± 0.18 %		
	CdSe QD	0.24 ± 0.24 %	2.46 ± 0.31 %		

2.3.3 Transport and Deposition of Three ENPs in Saturated Quartz Sand

Figure 2.3 shows representative particle breakthrough curves for experiments conducted with the 3 ENPs suspended in KCl solution where the normalized particle concentration at the column effluent (C/C_0) is plotted as a function of PVs (dimensionless time). The data shows that an increase in concentration of KCl does not have a major influence on the breakthrough QD concentration at the column effluent. Although we generally observe increased retention of QDs with increasing salt concentration, the effect is not dramatic. Overall, the three ENPs are highly mobile in the quartz sand in the presence of a monovalent salt (KCl). Numerical integration of the area under each breakthrough curve reveals that only 24% of the CdTe QDs are retained in the packed sand column at the highest IS examined (Table 2.5). Likewise, only 17% and 33% of the CdSe QD and nPL particles, respectively, are retained in the experiments conducted at 100 mM KCl. In the case of the model particle (nPL), the breakthrough curves at higher salt concentrations (above 10 mM) show the distinctive shape characteristic of "blocking"^{41,42}. Under certain conditions, particles deposited on the collector (sand grain) surface can "block" the deposition of suspended particles, resulting in a characteristic elution profile with rapidly increasing particle concentration with time⁴¹.



Figure 2.3 Representative ENP breakthrough curves for experiments conducted using columns packed with clean quartz sand over a range of solution ionic strengths (KCl): (a) CdTe QDs, (b) CdSe QDs, (c) *n*PL.

electrolyte i	onic strength	particle	C/C ₀	α	ζenp	ζsand
	(mM)			(T&E)	(mV)	(mV)
KCI	0.1 1 3 10 30 100	CdTe QD	0.94 0.86 0.79 0.78 0.77 0.76	0.004 0.010 0.017 0.017 0.016 0.026	-35 -36 -38 -38 -35 -28	-59 -52 -50 -49 -36 -21
KCI	0.1 1 10 100	CdSe QD	0.98 0.91 0.87 0.83	0.001 0.010 0.019 0.057	-35 -38 -20 -5	-59 -52 -49 -21
KCI	0.1 1 3 10 30 100	nPL	0.97 0.92 0.93 0.88 0.76 0.67	0.002 0.005 0.004 0.008 0.019 0.032	-64 -60 -69 -60 -56 -34	-59 -52 -50 -49 -36 -21
CaCl ₂	0.1 1 2.5 5 10	CdTe QD	0.94 0.93 0.34 0.01 0.01	0.003 0.006 0.118 0.686 1.402	-34 -22 -26 -27 -3	-42 -28 -25 -21 -14
CaCl ₂	0.1 1 2.5 10	CdSe QD	0.90 0.79 0.13 0.03	0.019 0.035 0.310 0.972	-20 -17 -18 -3	-42 -28 -25 -14
CaCl ₂	0.1 1 2.5 5 10	nPL	0.99 0.98 0.87 0.18 0.03	0.001 0.001 0.020 0.138 1.309	-19 -17 -18 -21 -22	-42 -28 -25 -21 -14

Table2.5. Summary of experiments conducted in saturated quartz sand columns with KCl and CaCl₂ at pH 7.

Figure 2.4 summarizes the calculated α values for the three ENPs when suspended in the monovalent electrolyte (KCl, Figure 2.4a) or the divalent electrolyte (CaCl₂, Figure 2.4b). In KCl, the nanoparticle attachment efficiency is relatively low (below 0.1) over the entire range of IS examined. The calculated α values increase with IS (e.g. from 0.004 to 0.026 for the CdTe QD; 0.001 to 0.057 for the CdSe QD; and from 0.002 to 0.032 for *n*PL); however, α does not reach the theoretical mass-transfer limited maximum value of unity even at 100 mM KCl. The ENP characterization data presented previously (Table 2.3) shows that the EPM (or surface potential) generally becomes less negative with increasing salt concentration. Hence, for each individual ENP, the particle attachment behavior observed in the presence of a monovalent electrolyte is generally in qualitative agreement with the DLVO theory of colloidal stability whereby the extent of physicochemical attachment increases with decreasing absolute surface potential^{43,44}.



Figure 2.4 Attachment efficiencies (α) calculated using eq.2.1 for the (\Box) CdTe QDs, (\circ) CdSe QDs, and (\diamond) nPL particles suspended in electrolyte (pH 7). Experiments were conducted using columns packed with clean quartz sand and particles were suspended in (a) KCl (open symbols) or (b) CaCl₂ (hatched symbols). Dotted lines are included as eye guides and error bars represent 95% confidence intervals.

Other studies examining the transport and deposition of polymer-coated QDs have also reported relatively low particle deposition rates on sand or model silica surfaces²⁵⁻²⁷. Using laboratory-scale packed column experiments, Torkzaban et al.²⁶ showed that the deposition of a CdTe QD was low at salt concentrations up to 100 mM NaCl (buffered to pH 7.8 with NaHCO₃). Likewise, Uyusur et al.²⁷ reported 9% and 4% retention of a CdSe QD in columns packed with quartz sand when the nanoparticles were suspended in 5 and 50 mM NaCl, respectively. Using a quartz crystal microbalance²⁵, we previously reported that the deposition of a different carboxylated CdTe QD onto silica is negligible even at high IS (>100 mM KCl, pH 7). We have also observed ²⁰ low α values (0.01 < α < 0.2) for
deposition of 50 nm sulfate-functionalized nPL onto quartz sand over a wide range of KCl concentrations (1-100 mM KCl) at pH 5.5. Hence, the results we report here are in qualitative agreement with other studies of QD and nPLdeposition on quartz.

Figure 2.4b shows the attachment efficiencies of the three ENPs when suspended in the divalent electrolyte (CaCl₂) at pH 7. A more significant change in α is noted as the IS of CaCl₂ increases from 0.1 to 10 mM (versus that observed for the monovalent salt), and for all three ENPs, α reaches the theoretical maximum (~1) at the highest IS. Also, above 1 mM IS, the ENP deposition rates are greater in CaCl₂ than in KCl. This observation is attributable to the ability of divalent cations (such as Ca²⁺) to screen particle charge but also to complex with negatively charged groups on the ENP surfaces, effectively decreasing the surface potential and the stability of the particle suspension (see Table 2.3)³⁸.

Overall, the data reported here for the transport of the two different QDs in quartz sand points to a mechanism of electrosteric stabilization resulting from the presence of the polymer and polyelectrolyte coatings on the ENP surfaces^{22,45,46}. Namely, we observe relatively low retention of the QDs over a very broad range of KCl concentrations. This stabilization effect is less apparent at high concentrations of the divalent salt CaCl₂, likely due to charge screening and compression of the macromolecules on the particle surfaces. Interestingly, comparable low extents of deposition are observed with the unmodified *n*PL particle, although such particles are generally not considered to be

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electrosterically stabilized. The limited retention of the *n*PL particle in the presence of the monovalent electrolyte is likely governed by electrostatic stabilization due to its significant surface potential (Table 2.3).

As mentioned above, there are limited studies examining the transport and deposition of QDs in saturated granular systems. Figure 2.5 presents a comparison of data from column transport studies conducted with QDs and selected other surface-modified nanomaterials in different laboratories^{21,26,27}. Data included in Figure 2.5 include those for experiments in saturated quartz sand with a CdTe QD²⁶ and CdSe QD²⁷ as well as metal oxide nanoparticles (nTiO₂ and nZnO)²¹ coated with the same PAA derivative as that used for the CdTe QD used in this study. In this figure, the particle attachment efficiency is plotted as a function of the dimensionless parameter N_{DLVO}^{47} , which takes into account the key experimental conditions used in each study (eq. 2.2):

$$N_{\rm DLVO} = \frac{\kappa A}{\varepsilon_{\rm o} \varepsilon_{\rm r} \psi_{\rm c} \psi_{\rm p}}$$
(2.2)

Here, κ is the inverse Debye length, A is the Hamaker constant for the ENP-watercollector systems¹⁸ used in each study, ψ_c is the surface (zeta) potential for the collector surface, ψ_p is the surface (zeta) potential for each ENP, ε_0 the dielectric permittivity in vacuum, and ε_r the dielectric permittivity of water. It should be noted that the dimensionless parameter N_{DLVO} does not consider the potential steric contributions of the particle surface coatings which may vary for the different ENPs examined.



Figure 2.5 Calculated ENP attachment efficiencies (α) evaluated for different ENPs in columns packed with quartz sand plotted as a function of the dimensionless parameter N_{DLVO}. Open symbols represent the ENPs used in the present study and solid symbols represent experimental data adapted from other studies^{21,26,27}.

Inspection of Figure 2.5 reveals that all of the studied ENPs (with the exception of $nTiO_2$) exhibit decreased mobility with increasing values of N_{DLVO} in watersaturated quartz sand. In many cases, the values of α fall within the same region of the plot (except for the CdSe QD data from ref²⁷ and for the *n*ZnO data from ref²¹. Values of the attachment efficiency determined from the data reported by Torkzaban et al.²⁶ (for the same CdTe QD as that used in this study) are 46 comparable to our results at moderate IS (N_{DLVO} <5), but approximately one order of magnitude larger at the highest IS examined (N_{DLVO} ≈20). Conversely, the results reported by Uyusur et al.²⁷ for a polymer-coated CdSe QD (under saturated conditions) result in lower α values than those measured here within a large range of solution IS ($0.5 < N_{\text{DLVO}} < 300$). Likewise, Petosa et al.²¹ reported very low retention for a PAA-coated ZnO nanoparticle when $N_{\text{DLVO}} < 20$. The significant mobility of the ZnO nanoparticle is surprising given that it is prepared by the same manufacturer and with the same polymeric coating as the CdTe QD used in this study (open squares in Figure 2.1c). The transport behavior of the ZnO nanoparticle was examined in the same quartz sand used in the present study²¹. However, the hydrodynamic diameter of the ZnO particles (measured by DLS) was significantly lower (on the order of 10 nm at 10-100 mM NaNO₃) than the size of the CdTe QD used in this study (on the order of 114 nm at 100 mM KCI).

In all the cases reported in Figure 2.5, the maximum α value for ENP deposition onto quartz sand is far from the theoretical maximum (α =1) even at high N_{DLVO} values. Thus, the limited data available to date on the mobility of QDs suggests that the transport potential of this ENP in water-saturated quartz sand can be significant in the absence (or at low concentrations) of divalent salts.

2.3.4 Transport and Deposition of QDs and *n*PL in Loamy Sand

An additional series of ENP transport experiments was carried out using columns packed with loamy sand obtained from a farm in St-Augustin-de-Desmaures, QC. Although the loamy sand columns were not extracted as undisturbed cores, the comparison of ENP transport and deposition in quartz sand to loamy sand is useful for evaluating the influence of collector grain properties on the filtration process. The collector media differ with respect to surface chemistry, grain size distribution, and geochemical heterogeneity.

The grain size distributions of the quartz and loamy sand obtained by sieve analysis are shown in Figure 2.1. The mean grain size (d_{50}) of the two granular materials is comparable (0.256 mm for the quartz sand versus 0.225 mm for the loamy sand), however, the size distribution of the quartz sand is more uniform (coefficient of uniformity, $d_{60}/d_{10} = 1.4$) than that of the loamy sand ($d_{60}/d_{10} = 2.1$). Figure 2 illustrates representative BTCs for transport experiments conducted with the three ENPs using columns packed with the loamy sand over a wide range of solution IS (0.1-10 mM KCl). As the concentration of KCl increases, the extent of particle retention increases for all three ENPs. However, it is interesting to note that the rate of change in the nanoparticle deposition rate with respect to IS is quite different for each ENP. For example, ~80% of the CdTe QDs are retained in the loamy sand column at 0.1 mM IS (Figure 6a) and the extent of retention increases to 90% at 10 mM. The retention of the CdSe QD (Figure 6b) ranges from 29% to 43% in the same range of IS. In contrast, the *n*PL particle exhibits a

faster change in the particle deposition rate with IS; namely, the extent of retention increases from 5% to 93% when the IS is changed from 0.1 to 10 mM (Figure 2.6c). As noted above for the experiments conducted with columns packed with quartz sand (Figure 2.3c), inspection of Figure 2.6c reveals that the BTCs for the *n*PL particle again exhibit the characteristic "blocking" profile at 1 and 10 mM IS^{41,48}. At the lower IS examined (0.1 mM), the effluent *n*PL particle concentration stabilizes at approximately 2 PVs; hence, the breakthrough curve is generally flat after this time point. For the higher IS displayed in Figure 2.6c, the breakthrough concentrations of the *n*PL particle do not reach a steady value but rather continue to increase with time. This observed increase in effluent particle concentration with time is attributed to the reduced availability of deposition sites on the collector grains as deposited particles exclude the local surrounding collector surface area from deposition of incoming particles⁴².



Figure 2.6 Representative breakthrough curves for (a) CdTe QDs, (b) CdSe QDs, and (c) *n*PL in columns packed with loamy sand at selected KCl concentrations. The breakthrough behavior of a conservative fluorescent tracer (NaP) is also shown (dashed line). The column diameter is 1 cm and the fluid approach velocity is 1.06×10^{-4} m/s.

For the sake of quantitatively comparing the results obtained from the loamy sand packed columns with the data from the quartz sand experiments (Figure 2.3 and Table 2.5), ENP attachment efficiencies were evaluated from each BTC and are presented in Figure 2.3. For the PAA-coated CdTe QDs, α values are approximately an order of magnitude greater in the sandy loam (Figure2.7) when compared to the quartz sand (Figure2.4a). The CdSe QDs also exhibit higher α values in the loamy sand matrix, but the extent of retention is generally lower than that measured for the CdTe QDs. In these loamy sand column experiments, the *n*PL particle exhibits the greatest change in α with increasing IS; namely, α increases from 0.003 to 0.18 when the salt concentration increases from 0.1 to 10 mM KCl. The *n*PL particle is also considerably less mobile in the loamy sand than in the quartz sand.



Figure 2.7 Calculated attachment efficiencies (α) for the three ENPs in loamy sand suspended in KCl at pH 7. The experimental conditions are as follows: approach velocity (U) 1.06×10⁻⁴ m/s, porosity (ε) 0.47, mean grain diameter (d_{50}) 0.225 mm, and temperature 20-22 °C. Error bars represent 95% confidence intervals.

This is the first study comparing the transport behavior of QDs in quartz sand and loamy sand in water-saturated conditions. The loamy sand characterized by nitrogen BET adsorption isotherms has considerably larger surface area and porosity than the quartz sand (Table 2.1). Characterization of the loamy sand indicates that it is mainly composed of quartz (88.2%), but it also contains claysized particles (7.6%) and organic matter (0.44%). EDS analysis reveals the heterogeneous composition of the loamy sand (mainly Si, Al, Fe) is in qualitative agreement with the mineralogical composition of the medium: silicon dioxide, feldspars (albite and orthoclase) and amorphous clay (allophane). The mineralogy of the granular collectors and the solution chemistry of the pore fluid will affect the mechanisms of ENP retention. For instance, allophane (present in the clay fraction) can exhibit positively charged sites (PZC~7.8) where negatively charged ENPs can "favorably" deposit, whereas albite (PZC~5.9) and orthoclase (PZC~1) present unfavorable conditions for retention of these ENPs⁴⁹.

This study was conducted at neutral pH; however, natural variations in pore water pH are expected to affect the fate of QDs in natural subsurface environments^{17,25,38}. Zhang et al.³⁸ reported on the stability of a polymer coated CdTe QD in monovalent electrolyte. Good colloidal stability (*i.e.* no aggregation) was observed at pHs between 5 and 12, due to the electrostatic repulsion exerted by the anionic polymer coating, conversely to low pH (3 and 2). Navarro et al.¹⁷ investigated the effect of pH on the interaction between a CdSe QD and humic substances. Here, the interaction between the humics and the QD were greatly

enhanced under acidic conditions (pH 3), compared with more alkaline conditions (pH 7 and pH 9). In an earlier study²⁵, we also reported the effect of pH on the deposition behavior of a CdTe QD onto a model sand surface; namely, the deposition rate of the CdTe QD was higher at lower pH (5 versus 7). Because pH influences critical particle and collector surface and physical properties (*e.g.*, particle aggregate size, particle surface potential, collector surface potential, etc), future studies should be aimed at clarifying the role that pH plays in QD transport and deposition in natural soil systems.

2.4 Environmental Implications

A myriad of new ENPs are being introduced onto the commercial market each year, yet the environmental fate and potential risks linked with these materials are not properly understood. Moreover, the variability in the composition of the core and surface coatings of commercial ENPs renders predictions of their transport potential and associated contamination risks very challenging. Well-controlled laboratory column experiments conducted with two representative QDs show that these nanoparticles can exhibit quite similar deposition behavior onto a clean quartz sand collector over a broad range of solution conditions (Figure 2.1). Furthermore, the selected *n*PL particle appears to be a good model material for determining conservative estimates of the transport potential of these two QDs in the quartz sand matrix. However, the transport potential of the two QDs is different in the loamy sand system, whereby the CdTe QD exhibits greater

retention than the CdSe QD (Figure2.3). This divergence in the transport behavior of the two QDs in the loamy sand matrix is likely linked to differences in the chemistry of the polymeric coatings on the ENP surfaces. The chemical composition of polymers used to functionalize ENP surfaces will influence the polymer affinity (and hence ENP affinity) for clay surfaces^{23,26}. For instance, Zaman et al.⁵⁰ found a strong bridging interaction between PAA molecules and alumina–like charged sites on the edges of clay particles. The nature of the coating molecules on ENP surfaces will also control the potential for degradation of the coatings and the likelihood for ligand exchange, which will influence the aqueous dispersibility, mobility and stability of the particles in aquatic subsurface environments²⁸. Because of the common practice of using polymeric coatings for stabilization of ENPs, additional studies aimed at understanding the role of such coatings in ENP transport, aggregation, and environmental fate is of particular importance.

The inherent heterogeneity of natural granular materials found in subsurface environments remains another major challenge for the development of functional relationships between soil properties and ENP transport potential. Although the two granular matrices used in this study have comparable mean grain diameters, the retention of the 3 ENPs is generally higher in the loamy sand versus the quartz sand. Thus, further research is needed to extend this work to a wider range of environmentally relevant granular matrices and water chemistries.

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Chapter 3: Influence of solution chemistry on the deposition and detachment kinetics of a CdTe quantum dot examined using a quartz crystal microbalance

Connecting text: In addition to column studies packed with granular materials, nanoparticle deposition studies using a quartz crystal microbalance with dissipation monitoring (QCM-D) are helpful to elucidate the transport and deposition behavior of ENPs in aquatic environments. In Chapter 3, a QCM-D was used to assess the kinetics of deposition and release of a carboxylated-CdTe QD on a model sand surface (*i.e.*, silica-coated QCM-D sensor) over a wide range of solution conditions. It is important to mention, that in this chapter, the technique is referred as QCM because the dissipation factor measurements are not discussed.

The results of this research have been published in this paper: Quevedo I.R., Tufenkji N. 2009. *Influence of Solution Chemistry on the Deposition and Detachment Kinetics of a CdTe Quantum Dot Examined Using a Quartz Crystal Microbalance*. Environ. Sci. Technol. 43 (9):3176-3182.

3.1 Introduction

In 2004, about 0.1% of the world's manufactured goods contained nanoparticles, but this is expected to rise to 15% of global output by 2014, with a commercial value of more than \$1 trillion¹. Massive investment in research and development has led to an amazing array of new products, as evidenced by an exponential increase in the number of patents pending for products and processes involving engineered nanoparticles². For example, nanoparticles can be used to deliver pharmaceuticals more efficiently, as antibacterial agents in clothing and sanitation equipment, and to store and transmit electronic data on computer chips and microsensors^{3,4}. Despite the numerous anticipated benefits of nanotechnology, there is great concern that we do not yet fully understand the environmental and health risks associated with this technology.

Quantum dots (QD) are one example of novel engineered nanomaterials that may be used in medical imaging, solar cells, and sensors because of their unique optical and electrical properties⁵⁻⁸. QDs consist of a metalloid crystalline core and a protective shell (*e.g.*, ZnS, CdS) that shields the core and renders the QD bioavailable. The core can consist of a variety of metal complexes that include semiconductors, noble metals, or magnetic transition metals (*e.g.*, CdTe, CdSe). To render QDs biologically compatible or active, they are functionalized with secondary coatings which improve water solubility and core durability⁹. Some researchers have reported that the surface coatings of QDs are subject to photolysis or oxidation^{10,11} which may result in dissolution of the core and hence release of toxic metals as hydrated ions. Currently, very little is known regarding the stability of QDs in the environment, product lifetimes, or how these materials partition into environmental media (*i.e.*, air, water, and soil phases). However, it is theorized that the toxicity of QDs depends on their physicochemical properties which may vary under different environmental conditions; namely, particle size, surface charge, outer coating bioactivity (capping material, functional groups), and oxidative, photolytic, and mechanical stability¹¹. Gagne et al.¹² have reported the toxicity of CdTe QDs to freshwater mussels. These researchers found that exposure to QDs suspended in aqueous media led to oxidative stress in the gills of the organism and DNA damage in both the gills and digestive glands. Male et al.¹³ found that CdSe QDs exhibited direct cytotoxicity to fibroblasts, whereas CdTe QDs also exhibited indirect toxicity due to release of free cadmium. The introduction of QDs into environmental media may occur via waste streams from industries that synthesize or use QDs and via clinical and research settings. Once released into natural aquatic systems, the potential environmental and health risks associated with QDs will be influenced by their fate and transport within these systems.

The transport and retention of nanomaterials in water saturated granular porous matrices representative of groundwater environments or engineered (deep-bed) granular filtration systems has traditionally been investigated using chromatography columns packed with model granular materials (*e.g.*, glass beads, sand, or soil)¹⁴⁻¹⁹. In these bench-scale studies, aqueous suspensions of nanoparticles are injected into columns packed with granular media and particle

retention in the granular matrix is commonly interpreted using classical clean-bed filtration theory²⁰. Using this approach, Lecoanet et al.¹⁵ investigated the transport and deposition behavior of various engineered nanomaterials (fullerols, titanium dioxide, carbon nanotubes, etc) in a water saturated glass bead matrix. These researchers observed considerably differing migration potential for the nanomaterials examined. The transport potential of nanosized zerovalent iron (nZVI) has also been investigated by several researchers^{17,18,21,22}. A number of these laboratory column studies have shown that various types of nZVI, with a wide range of surface modifiers, and sizes ranging from 10 to 200 nm, are transported very efficiently in uncontaminated granular porous media, primarily due to the stabilizing effect of surface modifiers^{17,18,21,22}. Recent studies have demonstrated how quartz crystal microbalance (QCM) technology can be used to examine the retention and release of nanoparticles onto surfaces in an aqueous environment^{17,23,24}. Chen and Elimelech^{23,24} used this approach to measure the deposition and detachment of fullerene nanoparticles over a broad range of solution chemistries. They noted that the deposition kinetics of fullerene nanoparticles onto clean silica surfaces are controlled by electrostatic and van der Waals interactions in the presence of monovalent and divalent salts. In contrast, nanoparticle deposition rates were significantly hindered in the presence of humic acid and alginate due to steric stabilization²⁴. Saleh et al.¹⁷ also used QCM to study the transport and deposition of bare and surface modified nZVI onto a silica coated crystal surface. Their experiments showed how surface modification of the nZVI significantly reduced deposition of the particles onto the silica surface as a

result of electrosteric stabilization. In these studies, the silica coated QCM crystal is considered a model collector representing the surface of a sand grain that may been countered by nanoparticles migrating in a groundwater matrix.

The objective of this work is to examine the deposition and release kinetics of a carboxyl terminated CdTe QD using the QCM. This QD was selected as it is commercially available and representative of functionalized QDs that are stable in aqueous media. Experiments were conducted at two different pHs and a broad range of environmentally relevant solution ionic strengths (IS), examining the influence of both monovalent and divalent cations. Dynamic light scattering (DLS)and transmission electron microscopy (TEM) were used to characterize the size of the QDs at different water chemistries. Particle electrophoretic mobilities (EPMs) were also evaluated.

3.2 Materials and Methods

3.2.1 Preparation and Characterization of QDs

Carboxyl terminated CdTe/CdS QDs with a reported diameter of 10nm (determined by the manufacturer using transmission electron microscopy) were obtained from Northern Nanotechnologies. QD suspensions at a concentration of 2×10^{13} particles/mL were prepared by diluting the 0.8 µM stock in filtered (0.2 µm nylon filter, Fisher) electrolyte solutions of varying solution chemistry. Analytical reagent-grade KCl and CaCl₂ (Fisher) and deionized (DI) water (Biolab) were used to prepare electrolyte solutions. Salt concentrations were varied over a wide range of ionic strengths (1-300 mM) and the pH of the

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suspensions was adjusted to 5 or 7 by the addition of HCl or KOH (0.1 mM). Prepared QD suspensions were stored at 9 °C for 24 h prior to each experiment.

The hydrodynamic diameter of the QDs was assessed using dynamic light scattering (DLS) (ZetaSizer Nano, Malvern). Laser Doppler velocimetry (ZetaSizer Nano, Malvern) was used to evaluate QD electrophoretic mobility (EPM). For sizing and EPM measurements, QD suspensions were prepared in the electrolyte solution of interest and each measurement was repeated with at least three different samples. At selected solution conditions, transmission electron microscopy (TEM) was used to confirm the measured size of the particles. Samples were prepared by placing a drop of a QD suspension on a Formvar grid, which was left to air-dry overnight prior to analysis. Measurements were performed on a Philips CM200 microscope equipped with an AMT CCD camera and operating at 200 kV with a LaB₆ filament.

3.2.2 Quantum Dot Deposition and Release Experiments

QD deposition onto a silica surface was examined using a QCM instrument mounted with silica coated crystals (E4, Q-Sense AB). When the 5 MHz crystals are mounted in the QCM flow modules, the injected flow is parallel to the flat SiO₂ surface (Figure 3.1).



Figure 3.1Schematic of the QCM instrument (also known as QCM-D).

A peristaltic pump (Reglo-Digital IPC-N 4, Ismatec) was used to first inject DI water (100 μ L/min) to obtain a stable baseline. Next, the background electrolyte solution of interest was injected into the flow module, followed by a QD suspension in the same electrolyte solution for up to 20 min. The QD suspension was followed by an injection of particle-free electrolyte solution of the same composition. During particle injection into the flow module, deposition of QDs onto the silica surface results in an increase in mass (*m*) which is recorded as a decrease in the resonance frequency (*f*) of the quartz crystal. This direct relationship between the resonance frequency of the crystal and the mass adhered to the crystal surface was first reported by Sauerbrey²⁵:

$$-\Delta f_n = \frac{C}{n} \Delta m \tag{3.1}$$

where *n* is the overtone (*i.e.*, harmonic) number (1, 3, etc...) and *C* is the crystal constant (17.7 Hz·ng/cm²). Hence, measurement of variations in the crystal 69

resonance frequency during QD injection provides a means to monitor changes in the mass of deposited QDs with time. The detection limit of the QCM is on the order of ~1 ng/cm which may be limiting when examining low levels of deposition (*e.g.*, when highly repulsive particle-surface interactions predominate). The QD deposition rate (r_d) was evaluated as the rate of change of the frequency shift in a given time period (t), as follows:

$$r_{\rm d} = -\frac{d\Delta f_3}{dt} \tag{3.2}$$

As shown in eq. 3.2, the QD deposition rate can be determined from the initial slope in the frequency shift measurements. Once a stable deposition rate was observed, the flow was changed to particle free electrolyte at the same ionic strength (to flush the chamber of any undeposited QDs). Next, the chamber was flushed with DI water for 10 min to examine the potential release of QDs from the silica surface. Hence, the rate of QD release (r_r) is determined from the rate of change of the frequency shift during injection of DI water. QCM experiments were repeated at least three times using suspensions prepared on different days.

3.3 Results and Discussion

3.3.1 Size and Electrophoretic Mobility of Quantum Dots.

To explore the influence of the physicochemical properties of QDs on their deposition behavior, the QD electrophoretic mobility (EPM) and size were

evaluated as a function of the electrolyte species and concentration. The QD EPM is negative over the entire range of solution chemistries examined (Figure 3.2). This negative surface charge can be attributed to the presence of carboxyl functional groups in the shell coating of the QDs. The particles generally become less negative with increasing concentration of either KCl or CaCl₂ as a result of compression of the diffuse double-layer of ions at the particle surface. Inspection of Figure 3.2 reveals large error bars in the reported QD EPMs. These large variations in the measurements suggest that the QD suspensions are not fully stabilized and monodispersed.

In the presence of the monovalent salt (KCl), the QD EPM was less negative at lower pH with values ranging between -2.4 and -2.1 μ m·cm/V·sec at pH 5, whereas at pH7, the EPM varied between-3.1 and-2.5 μ m·cm/V·sec (Figure3.2a). If the Smoluchowski equation is used to evaluate the QD zeta potentials from the EPMs, they are found to range from-40 to -45 mV in KCl at pH 7 and from -30 to -35 mV in KCl at pH 5²⁶. The results obtained in Figure 3.2 are in general agreement with those reported by Zhang et al.²⁷, where they observed a decrease in the absolute zeta potential of thioglycolate functionalized QDs with increasing IS.

The QD EPM measured in KCl at pH 7 has a lower absolute value than that of carboxyl-modified latex nanospheres under similar conditions^{28,29}. Behrens et al.²⁸ reported EPMs on the order of -4 μ m·cm/V·sec for 52 nm latex particles suspended in KCl at pH 7, whereas Tufenkji and Elimelech²⁹ reported a zeta potential of -50 to -58.5 mV for 63 nm carboxyl-modified latex particles

suspended in KCl at pH 8. In the presence of the divalent cation (Ca²⁺), we noted a significant decrease in the absolute value of the QD EPM, with absolute values ranging between-1.8 and-1.5 μ m·cm/ V·sec (Figure 3.2b). These findings are also in agreement with the measurements of Zhang et al.²⁷ obtained in the presence of the divalent ions Mg²⁺ and Ca²⁺.



Figure 3.2 Electrophoretic mobility of quantum dots suspended in different electrolytes: (a) KCl (pH 5 and 7), (b) CaCl₂ (pH 5). Data represent the mean \pm 95% confidence interval.

The mean diameters and particle size distributions of the ODs were studied over a broad range of ionic strengths at two different pHs using DLS (Figure 3.3). In general, the size of the QDs increased with electrolyte concentration. This was particularly clear at pH 5 in both salts. When the QDs are suspended in KCl (pH 5), the hydrodynamic diameter is between 45 and 100 nm below 155 mM IS but demonstrates considerable instability above this IS (*i.e.*, the error bars for these measurements are quite large) (Figure 3.3a). At pH 7, the particle size measured by DLS remains in the same range (45-100 nm) below 100 mM but again becomes more unstable at higher IS (Figure 3.3a). When the QDs are suspended in a CaCl₂ solution, marked aggregation is observed with increasing salt concentration (Figure 3.3b). In the presence of CaCl₂, the critical coagulation concentration (CCC) is much lower (12 mM) than that observed for the monovalent salt (\sim 155 mM) (note: in this discussion, the CCC is estimated from the data presented in Figure 3.3). Because the scattering intensity of the particles is roughly proportional to d^6 (Rayleigh approximation), DLS measurements are strongly influenced by the presence of aggregates. Hence, the values reported in Figure 3.3 are expected to be larger than those assessed with microscopic techniques such as transmission electron microscopy (TEM). In Figure 3.4a, a TEM image of a QD sample suspended in 15 mM KCl reveals the presence of irregularly shaped QDs on the order of 10-20 nm. On the other hand, when the QDs are suspended in 12 mM CaCl2 (Figure 3.4b), the particles tend to aggregate in irregular clusters of more than 100 nm in size. These results are consistent with those reported by Zhang et al.²⁷ where considerable aggregation of QDs was

observed in the presence of calcium, even with a relatively low concentration of the divalent cation.



Figure 3.3 Average hydrodynamic diameter of QDs determined by dynamic light scattering (DLS) when suspended in (a) KCl and (b) CaCl₂. Data represent the mean \pm 95% confidence interval. Quantum Dot particle size distribution at pH 5: (c) 15 mM KCl, and (d) 255 mM KCl.





Figure 3.4 TEM images of quantum dots prepared in the following electrolytes: (a) 15 mM KCl, (b) 12 mM CaCl₂.

A comparison of particle size distributions of selected samples determined by DLS are shown in Figure 3.3c and 3.3d.At lower ionic strength (15 mM), the particle size distribution resembles a log-normal distribution, whereas at higher salt concentration (255 mM) the QD suspension exhibits a broader size distribution. At the higher IS examined (above the CCC), the particle suspension is very unstable and the DLS technique captures a bimodal distribution in the particle size.

3.3.2 Deposition of Quantum Dots onto a Silica Surface

Figure 3.5a shows representative QCM measurements (frequency shifts) for an experiment where the QDs are suspended in KCl at pH 5.In step A, DI water is injected to achieve a stable baseline (constant frequency) followed by 205 mM KCl (pH 5), whereas in step B a suspension containing QDs with the same concentration of salt and pH is injected into the QCM flow chamber. Because the

measured frequency shift is proportional to the amount of mass on the silica surface, the QD deposition rate onto the clean silica surface is determined by calculating the initial slope of the measured frequency shifts as a function of time (as described in eq 3.2).



Figure 3.5 (a) Representative QCM experiment showing injection of (phase A) 205 mM KCl at pH 5; (phase B) QDs suspended in 205 mM KCl at pH 5; (phase C) 205 mM KCl at pH 5, and (phase D) DI water. (b) Representative measured frequency shifts during injection of QDs suspended in KCl at different solution IS (pH 5).

Figure 3.5b shows representative measurements of the frequency shift from QD deposition experiments at different solution IS (KCl, pH 5). As the solution IS increases, we note an increase in the slope of the frequency shift, and hence, an increase in the QD deposition rate, r_d (based on eq 3.2). Values of the deposition rate determined from experiments conducted over a broad range of solution IS at two different pHs are presented in Figure 3.4. In this figure, the data are presented in terms of ng/min where the mass of deposited nanoparticles was evaluated using the Sauerbrey relation (eq 3.1).

At pH 5 (open squares in Figure 3.6a), the QD deposition rate increases significantly with increasing solution IS up to 155 mM KCl. The observed increase in the QD deposition rate with increasing salt concentration is in qualitative agreement with other studies of nanoparticle retention conducted under conditions deemed unfavorable for deposition^{14,23,29,30}. Namely, when the nanoparticles and collector surfaces (*e.g.*, glass beads or silica surfaces) are both negatively charged, an increase in solution ionic strength results in a decrease in the range and magnitude of repulsive electrostatic interactions, and hence, a decrease in the extent of deposition.



Figure 3.6 Comparison of experimental values of the QD deposition rate (r_d) determined using eq 3.2 and theoretical rates (\Rightarrow) determined using the Smoluchowski-Levich approximation for a parallel-plate flow chamber (eq 3.3) for QDs suspended in (a) KCl solution at pH 5; (b) KCl solution at pH 7; and (c) CaCl₂ at pH 7. Data represent the mean ± 95% confidence interval.

When the solution IS exceeds 155 mM (at pH 5), the measured QD deposition rate decreases (Figure 3.6a). This behavior can be attributed to a loss in stability of the QD suspension at high salt concentrations. The sizing data reported in Figure 3.3 show that the average diameter of the QDs increases at high solution IS and the DLS measurements are more unstable (larger error bars) under these conditions. The data in Figure 3.3 suggest that the CCC of the QDs is between 155 and 200 mM at pH 5. The larger QD aggregates formed at high solution IS have a significantly lower diffusion coefficient than the stable QDs and hence will experience lowered convective-diffusive transport to the silica-coated surface. Similar behavior was observed by Chen and Elimelech for the deposition of fullerene nanoparticles onto bare or humic coated silica surfaces^{23,24}.

The results of QCM experiments conducted at pH 7 are presented in Figure 3.6b as solid symbols. At this higher pH, the QD deposition rate is near zero over the entire range of solution IS examined. These results contrast with the data obtained at pH 5 where significantly higher QD deposition rates were measured. At pH 7, the QDs exhibit a more negative zeta potential (Figure 3.2), and the silica surface is also more negatively charged³¹. This greater absolute potential of the like-charged surfaces gives rise to more significant repulsive electrical double-layer interactions upon approach of the QD to the silica surface. Hence, the results shown in Figure 3.6b suggest that, even at high solution IS, the carboxyl-terminated QDs are not expected to be effectively retained on sand surfaces at neutral pH in the presence of the monovalent salt, KCI.
To examine the influence of a divalent cation on QD deposition kinetics, QCM experiments were conducted with QDs suspended in a CaCl₂ electrolyte solution at pH 5 (Figure 3.6c). Comparison of the results obtained in Figure 3.6a and 3.6c shows that the QD deposition rate is significantly higher in the presence of the divalent cation versus the monovalent cation. In the case of CaCl₂, the QD deposition rate (r_d) increases with increasing salt concentration up to an IS of 12 mM. Above this critical concentration, the QD deposition rate onto the silica surface exhibits more instability and tends to decrease. This behavior can again be explained by considering the stability of the QD suspension over the range of salt concentrations examined. At ionic strengths below 12 mM, the QDs are relatively stable (Figure 3.3b), however above this CCC, the QDs tend to form larger aggregates (Figure 3.4b) and will therefore experience lessened convectivediffusive transport to the silica surface. Hence, even though the QD electrophoretic mobility (and hence zeta potential) becomes less negative with increasing concentration of $CaCl_2$ (Figure 3.2b), the QD deposition rate decreases above the CCC due to the formation of aggregates. It is interesting to note that the QD CCC in CaCl₂ is considerably lower (12 mM) than in the monovalent salt (155 mM).

To confirm the proposed hypothesis that the measured QD deposition rates decrease at high solution IS due to QD aggregation and a corresponding decrease in convective-diffusive transport, the experimental data in Figure 3.6 can be compared to the theoretical particle deposition rates.

The theoretical particle deposition rate (r_d^{SL}) in the absence of electrostatic interactions can be evaluated using the Smoluchowski-Levich approximation which is a valid approximation for the E4 QCM flow chamber³²:

$$r_{\rm d}^{\rm SL} = 0.538 \frac{D_{\infty}C_{\rm b}}{a_{\rm p}} \left(\frac{Pe \cdot h}{x}\right)^{\frac{1}{3}}$$
 (3.3)

where D_{∞} is the diffusion coefficient, C_b is the bulk concentration of QDs, a_p is the radius of the QDs based on DLS measurements (Figure 3.3), *Pe* is the dimensionless particle Péclet number, *h* is the height of the QCM flow chamber, and *x* is the distance along the flow from the inlet.

Equation 3.3 was used to calculate the theoretical QD deposition rates and the results are compared to the experimental measurements in Figure 3.6. At low solution IS where repulsive electrostatic interactions predominate, QD deposition rates measured in KCl at pH 5 are significantly lower than r_d^{SL} . As the IS increases, the experimental rates approach values of r_d^{SL} . As noted above, when the KCl concentration exceeds 155 mM, the measured QD deposition rates decrease with increasing solution IS (Figure 3.6a). A similar trend is noted for the theoretical particle deposition rates represented by the open stars. In Figure 3.6b, the QD deposition rates measured in KCl at pH 7 are significantly lower than r_d^{SL} .

over the entire range of IS examined. This difference between theoretical and experimental deposition rates is caused by the presence of strong repulsive electrostatic interactions at the higher pH. Similar behavior is noted for experiments conducted at low solution IS with QDs suspended in CaCl₂ (Figure 3.6c); namely, values of r_d^{SL} are much greater than the experimental rates under conditions deemed unfavorable for deposition. In contrast, when the IS of the CaCl₂ solution is increased above 8 mM, experimental QD deposition rates are nearly equivalent to r_d^{SL} (Figure 3.6c). In summary, the results shown in Figure 3.6 reveal that for all three cases, the theoretical particle deposition rate (represented by open stars in Figure 3.6a,b,c) decreases over the range of solution IS as a result of particle aggregation and a corresponding decrease in convective-diffusive transport.

3.3.3 Release Kinetics of Quantum Dots

In the natural subsurface environment, changes in solution chemistry might cause release of colloids from soil surfaces. For instance, a rainfall can result in significant decreases in water IS, potentially causing detachment of particles from the soil grain surfaces³³. To better understand the reversibility of QD retention on the silica surface, a series of release experiments were conducted whereby the QCM chamber was rinsed with DI water at the same flowrate used during nanoparticle injection. Representative QCM measurements during the injection of DI water are shown in Figure 3.5a (phase D). In these experiments, the QD release rate $(r_{\rm r})$ can be determined by calculating the slope of the frequency shift during injection of DI water. Calculated values of $r_{\rm r}$ are compared to calculated values of r_d in Figure 3.7a and Figure 3.7b for experiments conducted in KCl (pH 5) or CaCl₂ (pH 5), respectively. Figure 3.7a shows that for QDs deposited in the presence of KCl, the rate of QD release from the silica surface was nearly equal to the rate of QD deposition over the range of IS examined. In contrast, when QDs were deposited in the presence of CaCl₂ (Figure 3.7b), the rate of QD release (r_r) is low in comparison to the rate of QD deposition (r_d). In fact, the values of r_r are near zero over the range of CaCl₂ concentrations, except near the CCC. The higher rate of QD release at the CCC may be caused by the breakup and/or release of weakly formed QD aggregates.



Figure 3.7Calculated values of the QD deposition (r_d) and release (r_r) rates for QDs suspended in (a) KCl solution and (b) CaCl₂ at pH 5. Data represent the mean \pm 95% confidence interval.

The fraction of QDs released during injection of DI water was calculated from the measured frequency shifts and is plotted in Figure 3.8. These calculations show that a small fraction of QDs is released when the particles are deposited at a relatively low IS (below the CCC); namely, the fraction released is less than ~20% in KCl, and less than ~10% in CaCl₂. On the other hand, the fraction of QDs released is greater when particles are deposited at IS above the CCC. This finding is counter-intuitive in that particles deposited in the presence of the divalent cation are expected to be irreversibly attached, particularly when deposited at higher salt concentrations³⁴. Hence, this result further supports the hypothesis that the higher release rate (and fraction of particles released) observed at the CCC (12 mM) in CaCl₂ can be attributed to breakup and/or release of weakly formed QD aggregates. This would also explain the greater release of particles noted for the experiments conducted in high IS KCI (Figure 3.8a).



Figure 3.8(a) Fraction of particles released for experiments conducted in KCl (pH 5). (b) Fraction of particles released for experiments conducted in CaCl₂ (pH 5). The vertical dashed line represents the approximate IS of the critical coagulation concentration (CCC).

3.4 Environmental Implications

Following the release of quantum dots in the natural environment, their potential risks to ecosystems and public health will be governed by their transport and fate. The data reported in this study begins to fill the knowledge gaps regarding the physicochemical properties and transport potential of one type of manufactured QD in aqueous media. Northern Nanotechnologies sells this material for a wide range of applications, including fluorescence-based biological sensing and solar devices. In the presence of a monovalent cation, the selected QD is shown to be relatively stable at low solution IS, but significant aggregation is observed at higher IS (above 155 mM). The QDs aggregate at much lower solution IS (12 mM) in the presence of a divalent cation. EPM measurements are challenging with

this nanoscale system that tends to aggregate, but reveal observable variations with water chemistry. At pH 5, the extent of QD deposition increases with IS until it reaches the CCC. Above this salt concentration, the QD deposition rate decreases due to decreased convective-diffusive transport to the silica surface. Very little QD deposition is observed at neutral pH suggesting that the transport potential of this nanomaterial is significant at pH 7. The rate of particle detachment from the silica surface is quite important at pH 5, suggesting that additional investigations examining the potential re-mobilization of QDs upon changes in water chemistry are needed to better understand the contamination risks associated with this nanomaterial.

Complementary studies conducted using laboratory-scale packed columns will provide additional insights into the migration behavior of QDs in water saturated granular systems. Natural groundwater can contain a wide range of components, including dissolved organic matter, biological exudates, and biocolloids. Continuing research in our laboratory aims at extending this work to examine the transport of QDs in aquatic environments over a wider range of environmentally relevant conditions. Moreover, preliminary experiments in our laboratory illustrate the varying behavior of QDs composed of different core materials and having different surface functionalizations. Many commercial QDs are CdSe/ZnS based, whereas the product used in this study is CdTe/CdS based. Hence, additional studies are needed to better characterize the transport potential of these engineered nanomaterials on a case-by-case basis.

3.5 References

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Chapter 4: Deposition kinetics of quantum dots and polystyrene latex nanoparticles onto alumina: Role of water chemistry and particle coating

Connecting text: In previous chapters, polymer coated QDs exhibited high mobility on SiO₂ surfaces. However in experiments conducted in water saturated columns packed with loamy sand (Chapter 2) it was determined that the presence of mineral heterogeneities enhanced the retention. Since the deposition behavior of QDs onto mineral surfaces (other than SiO₂) and the role of dissolved organic molecules are unknown. In this chapter the deposition kinetics of two commercially available carboxylated-QDs were assessed onto Al₂O₃ and surfaces precoated with dissolved organic molecules (*i.e.*, a humic substance, and a biosurfactant).

The results of this research have been published in this paper: Quevedo I.R., Olsson, A.L.J. Tufenkji N. 2013.*Deposition Kinetics of Quantum Dots and Polystyrene Latex Nanoparticles onto Alumina: Role of Water Chemistry and Particle Coating*. Environ. Sci. Technol. 47 (5), pp. 2212–2220

4.1 Introduction

Quantum dots (QDs) are engineered nanoparticles (ENPs) that exhibit fluorescent properties, which makes them attractive for applications in visual technologies, biomedical imaging, solar energy conversion and information technology¹⁻³. Major investments are now being targeted towards the industrial production of QDs and the rising demand of these ENPs will likely result in their increased presence in the environment⁴. Therefore, the potential toxicity and fate of these particles in the environment must be evaluated⁵⁻⁸.

QDs are comprised of a metalloid core (*e.g.*, CdTe, CdSe), a protective shell (CdS, ZnS) and, typically, a second polymer or polyelectrolyte coating, which renders them stable in aqueous suspensions⁷. Yet, recent research suggests that there is a substantial risk of Cd²⁺, Te²⁺, or Se²⁺release from the QD core and subsequent toxicity^{5,6}. Other studies also suggest that their harmfulness can be enhanced by the polymer coatings used to encapsulate the QDs^{7,8}. The introduction of ENPs into the environment may occur via waste streams, and once released, the potential risks associated will be influenced by their transport and fate⁹.

ENP transport in the subsurface aquatic environment or engineered water treatment facilities has been typically studied using packed bed columns, in water saturated granular porous matrices that are representative of the aquifer or deepbed filter matrix¹⁰. Using this technique, few studies have addressed the transport and retention of QDs¹¹⁻¹⁴. Whereas high mobility of QDs in packed bed columns

with ultrapure quartz sand has been reported¹²⁻¹⁵, an enhanced retention in the presence of mineral heterogeneities has also been observed^{11,13,14}. Overall, these studies have concluded that QD surface coatings and their potential degradation under natural conditions might play an important role in their transport and fate in the environment. However, the interaction of different ENPs with metal oxide patches (such as alumina) present on aquifer or filter grain surfaces has not been examined; particularly, in the presence of dissolved organic molecules (DOM).

DOM such as organic acids (e.g., fulvic and humic acids) and biosurfactants produced and secreted by microorganisms can be present in natural or engineered aquatic environments where they may adsorb onto collector or nanoparticle surfaces^{16,17}. Suwannee River humic acid (SRHA) is a model and well characterized type of organic acid, which consists of a mixture of polycyclic aromatic subfractions. Rhamnolipids are biosurfactants produced and released by *Pseudomonas* strains^{17,18} and consist of a rhamnose moiety and a 3- (hydroxyalkanoyloxy) alkanoic acid fatty acid tail. Both humic substances and rhamnolipids may influence the transport and fate of ENPs in aquatic environments when adsorbed on particle or collector surfaces¹⁶⁻²⁰. For example, humic substances have been reported to stabilize polystyrene latex particles in aqueous media^{21,22}, and rhamnolipids have been shown to stabilize zerovalent iron and ZnS nanoparticles in aqueous suspensions^{17,18,20} and prevent the deposition of zerovalent iron nanoparticles on silica²⁰.

Recently, the quartz crystal microbalance with dissipation monitoring (OCM-D) was introduced as a useful technique to study the deposition kinetics of ENPs onto various surfaces^{20,23-26}. One advantage of using QCM-D is that this highly sensitive mass sensor (~1 ng/cm²) can be coated with mineral compositions commonly present in natural or engineered aquatic environments (e.g., SiO₂, Fe₂O₃ or Al₂O₃). To the best of our knowledge, there are only two studies wherein OCM-D has been used to study the deposition kinetics of ODs^{25,26}. Park et al.²⁵ studied the retention of a carboxylated CdSe QD onto SiO₂ that had been modified with self-assembled monolayers having different end groups (e.g., -NH₂, -CH₃, -COOH).At different pHs (6 to 10), higher retention was observed on the surface modified with $-NH_2$ groups, reaching a maximum at pH ~7.5. Moreover, it was shown that the interaction between the QD and the substrate followed a Langmuirian model. In a previous study, we showed that the deposition rate of a carboxylated CdTe QD onto SiO₂ increased with salt concentration and was significantly greater in the presence of divalent salt as compared to a monovalent salt²⁶. However, at very high dissolved Ca²⁺ concentrations, the CdTe QD experienced aggregation and the extent of deposition decreased due to lessened convective-diffusive particle transport to the SiO₂ surface.

To date, the deposition behavior of commercial QDs onto mineral surfaces other than SiO₂ and in the presence of dissolved organic molecules (DOM) remains unexplored. The objective of this work is to improve our understanding of the deposition behavior of QDs on chemically diverse model surfaces that may be encountered in natural or engineered aquatic environments²⁷. To this end, a QCM-96 D was used to measure the deposition kinetics of two commercially available polymer-coated QDs onto bare Al_2O_3 and a DOM-precoated Al_2O_3 surface over a broad range of solution IS. The results are compared with two model ENPs of comparable particle size: polystyrene latex nanospheres functionalized with carboxylic (*c*PL) or sulphate groups (*s*PL). An appropriate physicochemical characterization of the particles and model collectors has been performed in all the cases.

4.2 Materials and Methods

4.2.1 Preparation of ENP Suspensions

Two types of carboxyl-terminated QDs were used in this study: a CdTe/CdS QD (Vive Crop Protection, Catalog No.18010 L) stabilized with a polyacrylic-acid (PAA) derivative and suspended in water, and a CdSe/ZnS QD (T2MP–Evitags, fromEvident Technologies) coated withpoly-ethylene-glycol (PEG) and suspended in water. Results obtained with the QDs were compared against two model ENPs (surfactant free preparations): a carboxyl-functionalized (*c*PL) and a sulphate-functionalized (*s*PL) polystyrene latex nanosphere (Invitrogen). All ENPs were suspended in KCl (analytical reagent grade, Fisher) electrolyte (prepared with deionized water)over a range of IS (from 0.1 up to 500 mM in select cases) to final concentrations of 2×10^{13} particles/mL, at an adjusted pH of 5 (using HCl or KOH). All ENP suspensions were stored overnight (12 hours) at 9°C prior to each deposition experiment and measurement of particle properties.

In experiments conducted to study the influence of the presence of DOM on nanoparticle deposition, two organic molecules were selected; namely SRHA and rhamnolipid (JBR215). SRHA (International Humic Substances Society) or JBR215 (Jeneil Biosurfactant Co., WI), which is a 10% mixture of the two rhamnolipids RLL ($C_{26}H_{48}O_9$) and RRLL ($C_{32}H_{58}O_{13}$) prepared at an equivalent concentration of 2 mg/L (expressed as total organic carbon), were used to precoat the Al₂O₃ surface and to prepare ENP suspensions. The selected molecules are highly soluble in water due to their relatively low molecular weight; the SRHA is on the order of 1490 Da²⁸, and the rhamnolipids RLL and RRLL are504 and 650 Da, respectively (as reported by the vendor).

The hydrodynamic diameter of the PAA polyelectrolyte (0.8 mg/mL, Vive Crop Protection) used to stabilize the CdTe QD was also measured at different solution IS (1, 10, and 100 mM KCl) at the same concentration (*i.e.*, 4%) as that present in the CdTe QD suspensions.

4.2.2 Characterization of the ENPs

The general physicochemical properties of each ENP (namely, size and electrophoretic mobility) were characterized immediately prior to conducting QCM-D experiments. The nominal particle sizes reported by the vendors were: 10 nm for the CdTe QD, 25 nm for the CdSe QD, 24 nm for the *c*PL and 22 nm for the *s*PL. Hydrodynamic particle sizes and polydispersity indexes (PDI) of the different ENPs (and PAA) were determined by dynamic light scattering (DLS) (ZetaSizer Nano, Malvern) using at least three different samples of each

suspension. The size of the QDs was also evaluated by transmission electron microscopy (TEM) for selected conditions (Phillips CM200). Samples were placed onto SiO Formvar grids (SPI Supplies), following the procedure described previously¹³. The electrophoretic mobility (EPM) of the ENPs at different IS was determined by measuring the velocity of the particles via Laser Doppler velocimetry (ZetaSizer Nano ZS, Malvern); each measurement was performed in triplicate using disposable capillary cells with an adjusted electrical field (*E*) between 5 and 10 ± 0.1 V/m.

4.2.3 Effect of water chemistry on the fluorescence and dissolution of QDs

The extent of dissolution and fluorescence of the CdSe and CdTe QDs during the timescale of the transport experiments was verified as follows: QD suspensions were prepared in KCl (1 mM and 100 mM IS) and at 100 mM KCl supplemented with DOM (pH 5) in the same manner as those used for the deposition experiments. Samples were taken at different time intervals, within an equilibration period of 12 hrs, transferred to conical tubes outfitted with 10 kDa membranes (Amicon, Millipore) and centrifuged at 10,000g for 5 min. The concentration of free Cd2+ ions from the core in the filtrate was quantified by ICP-OES (Thermo Scientific iCAP 6000 Series). The concentration of total Cd+2 in each sample was also determined by analyzing samples digested overnight in 30% HCl + 5% HNO3. All measurements were performed in triplicate. The fluorescence was monitored by placing QD samples in a quartz cuvette and

measured using a spectrofluorometer (Fluoromax-4, Jobin-Yvon Horiba). The EX/EM settings used were: 350/538 for the CdTe QD, 350/550 for the CdSe QD.

4.2.4 Nanoparticle Deposition Experiments

ENP deposition rates on Al₂O₃-coated QCM sensors (QSX–309,Q-Sense AB, Gothenburg, Sweden) were measured using QCM-D(E4, Q-Sense AB). The QCM-D measures deposited mass (Δm) in terms of a negative shift in resonance frequency (Δf) of an AT-cut quartz crystal. In addition, dissipative energy losses (dissipation, *D*) induced by the adsorbed mass, are measured in terms of the crystal's oscillation decay time. Dissipation plays an essential role in the interpretation of molecular adsorption since it provides information about the mechanical and viscoelastic properties of the adsorbed film²⁹. Rigidly adsorbed films express minimal dissipation, whereupon the frequency shift (- Δf_n) is linearly proportional to the adsorbed mass (Δm),as described by the Sauerbrey relationship³⁰:

$$-\Delta f_{\rm n} = \frac{C}{n} \Delta m \tag{4.1}$$

Here, the mass sensitivity constant, *C*, is equal to 17.7 Hz·ng/cm² for a 5MHz crystal and *n* is the resonance overtone number. Note that the frequency shift obtained from QCM-D (Q-Sense) is already normalized, *i.e.*, divided by the overtone number (*n*). Because $-\Delta f_n$ is proportional to the total change in mass

 (Δm) (eq. 4.1), the rate at which frequency shift changes during a given time period (- f_{n_slope} , eq.4.2) describes the rate at which mass is deposited on the Al₂O₃ surface:

$$-f_{n_slope} = -\frac{d\Delta f_n}{dt}$$
(4.2)

This approach has often been used in studies of ENP deposition and it relies on the interpretation of mass proposed by Sauerbrey for rigidly adsorbed films^{23,24,26,30,31}. This is a valid assumption as long as the adsorbed mass causes low dispersion in the normalized frequency shifts between different overtones and/or the dissipation shift is small compared to the frequency shift (*i.e.* the so called $\Delta D_n/\Delta f_n$ ratio)²⁹. Whereas the manufacturer of QCM-D (Q-Sense)³² suggests a $-\Delta D_n/\Delta f_n$ value of 1×10^{-7} Hz⁻¹ as the threshold below which Sauerbrey's interpretation still applies, Reviakine et al.²⁹ proposed a value of 4×10^{-7} Hz⁻¹. Otherwise, when the dissipative energy losses are too large within the adsorbed film, the frequency shift is generally considered to underestimate the adsorbed mass^{29,33,34}. Hence, in some cases, the rate at which dissipation changes in time (D_{n_slope}) has been used instead to monitor the deposition kinetics of colloidal particles^{20,31,35}.

In this study, the frequency and dissipation shifts were monitored at different overtones (n=1, 3, 5...), but because the criteria for Sauerbrey interpretation (*i.e.*

low dispersion in $-\Delta f_n/n)^{29}$ is fulfilled; for the sake of clarity only normalized frequency and dissipation of the third overtone are presented. The ENP deposition experiments were conducted according to the following steps and an illustrative measurement is shown in Figure 4.1a. First, particle-free electrolyte was allowed to flow through the QCM-D chamber until stable baselines of Δf_3 and ΔD_3 were established. Next, ENP suspensions were injected while Δf_3 and ΔD_3 were continuously recorded during the entire experiment. In experiments designed to study the effect of DOM, the surface was pre-coated prior to the injection of the ENP suspension, by injection of either SRHA or rhamnolipid solution (2 mg TOC/L) in 1 mM KCl. Adsorption of DOM onto the Al₂O₃-coated crystal shifted the resonance frequency by approximately 10 Hz (Figure 4.1b) which is equivalent to a layer thickness on the order of 1 nm. X-ray photoelectron spectroscopy (XPS) and streaming potential analyses of the coated crystals were used to confirm adsorption of DOM onto the Al₂O₃ surfaces. Temperature and flow rates were kept constant throughout the duration of the experiment at 20°C and 100 μ L/min, respectively. Each experiment was repeated using at least three different samples prepared on different days. After each experiment, the crystals, QCM-D chambers, and tubing were rinsed with 20 mL of 2% Hellmanex (Fisher Scientific) and 30 mL of DI. The crystals were further cleaned by soaking in 2% Hellmanex overnight, rinsed with DI, dried under N2 and then exposed to UV/ozone treatment for 10 min prior to any additional measurement.



Figure 4.1 Representative QCM-D experiments from the 3rd overtone measurements (frequency (\circ) and dissipation (\bullet)). (a) Deposition of a CdSe QD onto Al₂O₃ in 1 mM KCl at pH 5. Phase A: baseline upon background electrolyte injection; phase B, injection of CdSe QD in the same electrolyte; and phase C, rinse with particle-free electrolyte. The deposition rates from the measurements ($-f_3$ slope, D_3 slope) were calculated from the initial phase of the injection step (*i.e.*, phase B). (b) Deposition of a CdSe QD in electrolyte supplemented with SRHA onto a SRHA-coated Al₂O₃ crystal. Phase A: baseline upon background electrolyte injection (1 mM KCl at pH 5); followed by B: injection of 2 mg/L SRHA in 1 mM KCl for crystal coating; phase C, rinse with particle-free background electrolyte; and phase D, injection of CdSe QD in 100 mM KCl (pH 5) supplemented with 2 mg/L SRHA. The deposition rates $(-f_{3 \text{ slope}}, D_{3 \text{ slope}})$ were calculated from the data obtained in the first minute of phase D. In all cases, $-f_3$ slope and D_3 slope are calculated as the rate of change in the frequency shift (f_3) or dissipation (D_3) in a given time period (t).

4.3 Results and Discussion

4.3.1 Electrokinetic Characterization of ENPs and Collector Surfaces.

The EPMs of the ENPs were evaluated over the entire range of solution chemistries (Table 4.1). In KCl electrolyte, the QDs are less charged than the model ENPs (cPL, sPL). For example, for KCl concentrations between 0.1 to 100 mM, the highest absolute measured EPM for the QDs is 2.4 µm cm/V sec, whereas the lowest absolute value for the latex nanoparticles is $3.2 \,\mu m \cdot cm/V \cdot sec.$ Moreover, data in Table 4.1 show that the CdTe QD is less sensitive to changes in IS than the CdSe QD. For instance, when the salt concentration is varied from 0.1to 100 mM KCl, the EPM of the CdTe QD varies between -2.4 µm cm/V sec and -1.8 µm·cm/V·sec. In contrast, the EPM of the CdSe QD varies by 5-fold within the same range of IS. Notably, the presence of DOM (*i.e.*, SRHA, rhamnolipid) had a less important effect on the EPM of the QDs than that of the model latex nanoparticles (Table 4.1). When EPM measurements are converted to zeta potential (Table 4.2), the obtained values are in qualitative agreement with previously published QD studies^{14,15,36}. Zhang et al.³⁶ reported a decrease in the absolute zeta potential of a CdTe QD(from -30 to -20 mV) when the KCl concentration was increased from 1 to 100 mM (at pH 7). Likewise, within the same range of IS, Torkzaban et al.¹⁴ reported a decrease in zeta potential from -45 to -35 mV for a carboxylated CdTe QD in NaCl at pH 8. Uyusur et al.¹⁵ also observed a decrease in zeta potential with increasing solution IS for a polymer coated (octylamine with modified poly acrylic-acid) CdSe QD in NaCl at pH 6.5.

The Electrokinetic properties of bare Al_2O_3 and DOM-coated Al_2O_3 were also assessed over the range of solution chemistries using a streaming potential analyzer³⁷ (EKA, Brookhaven Instruments, Holtsville, NY) (Table 4.3). Overall, an increase in IS has a screening effect in the zeta potential of the bare and DOMcoated collector surfaces. While on bare Al_2O_3 , the zeta potential is positive (13 to 2 mV) at all conditions investigated, coating the surface with the selected organic molecules resulted in charge reversal (on the order of -27 to -13 mV for SRHA, and between -16 to -8 mV with rhamnolipids).

		KCI		KCI + SRHA			KCI + rhamnolipid				
particle	ionic strength	electrophoretic mobility	DLS diameter	PDI	TEM diameter	electrophoretic mobility	DLS diameter	PDI	electrophoretic mobility	DLS diameter	PDI
	(mM)	(µm.cm/V.s)	(nm)		(nm)	(µm.cm/V.s)	(nm)		(µm.cm/V.s)	(nm)	
CdTe QD	0.1	-2.4 ± 0.0	62 ± 3	0.2		-2.5 ± 0.1	57 ± 3	0.3	-2.1 ± 0.1	70 ± 3	0.5
	1	-1.8 ± 0.0	59 ± 4	0.2	29 ± 4	-2.4 ± 0.1	55 ± 3	0.5	-2.0 ± 0.1	59 ± 4	0.6
	10	-1.9 ± 0.0	88 ± 19	0.4		-2.1 ± 0.1	50 ± 3	0.3	-1.8 ± 0.0	75 ± 19	0.4
	30	-1.9 ± 0.0	206 ± 2	0.3		-1.7 ± 0.0	46 ± 3	0.2	-1.8 ± 0.3	70 ± 2	0.5
	100	-1.8 ± 0.1	192 ± 3	0.2	67 ± 46	-1.9 ± 0.1	74 ± 3	0.2	-1.6 ± 0.2	54 ± 3	0.2
CdSe QD	0.1	-1.6 ± 0.4	163 ± 50	0.5		-2.4 ± 0.1	52 ± 0	0.6	-1.6 ± 0.4	57 ± 2	0.5
	1	-0.7 ± 0.1	196 ± 68	0.4	30 ± 20	-1.1 ± 0.1	56 ± 1	0.5	-0.7 ± 0.1	79 ± 5	0.5
	10	-0.7 ± 0.1	244 ± 26	0.7		-0.7 ± 0.0	48 ± 3	0.6	-0.3 ± 0.3	279 ± 0	0.6
	30	-0.3 ± 0.3	370 ± 45	0.6		-0.2 ± 0.1	55 ± 4	0.6	-0.7 ± 0.3	224 ± 1	0.3
	100	-0.3 ± 0.1	257 ± 30	0.3	202 ± 172	-0.4 ± 0.0	52 ± 3	0.5	-0.3 ± 0.1	289 ± 26	0.6
cPL	0.1	-5.2 ± 0.3	62 ± 1	0.3		-5.6 ± 0.2	62 ± 1	0.3	-4.7 ± 0.2	60 ± 1	0.3
	1	-4.9 ± 0.5	60 ± 2	0.3		-5.1 ± 0.1	60 ± 2	0.3	-4.4 ± 0.1	58 ± 0	0.3
	10	-4.7 ± 0.1	61 ± 1	0.4		-4.6 ± 0.2	61 ± 0	0.3	-4.1 ± 0.3	54 ± 1	0.4
	30	-3.9 ± 0.4	70 ± 12	0.3		-4.7 ± 0.7	68 ± 6	0.4	-3.7 ± 0.3	77 ± 3	0.5
	100	-4.1 ± 0.2	61 ± 5	0.3		-2.7 ± 0.3	61 ± 3	0.4	-3.1 ± 0.3	63 ± 7	0.4
	500	-3.0 ± 2.7	923 ± 36	0.6							
sPL	0.1	-4.1 ± 0.1	56 ± 1	0.2		-3.7 ± 0.1	56 ± 1	0.2	-3.5 ± 0.2	57 ± 1	0.2
	1	-3.6 ± 0.2	58 ± 2	0.2		-3.7 ± 0.1	55 ± 1	0.2	-3.4 ± 0.1	56 ± 2	0.2
	10	-3.6 ± 0.1	55 ± 0	0.2		-2.5 ± 0.3	50 ± 1	0.2	-3.4 ± 0.4	54 ± 1	0.2
	30	-3.2 ± 0.1	73 ± 2	0.5		-2.5 ± 0.3	76 ± 14	0.8	-2.6 ± 1.1	51 ± 1	0.7
	100	-3.2 ± 0.2	944 ± 674	1.0		-2.3 ± 0.1	234 ± 20	0.7	-2.5 ± 0.1	515 ± 292	0.8

Table 4.1 Electrophoretic mobility, particle size, and polydispersity index (PDI) of the ENPs over a range of ionic strength (pH5) in simple electrolyte (KCl) and electrolyte supplemented with DOM (2 mg/L SRHA or rhamnolipid).

Table 4.2 Zeta potentials determined from the measured particle EPMs over a range of ionic strength in simple electrolyte (KCl) and in electrolyte supplemented with 2 mg/L SRHA or rhamnolipid (pH 5). The zeta potentials were obtained using the Henry equation³⁸ and the expression for the retardation effect of spherical particles proposed by Ohshima³⁹.

ionic strength	particle	KCI	KCI + SRHA	KCI + rhamnolipid			
(mM)		Zeta Potential (mV)					
0.1 1 10 30 100	CdTe QD	-34 ± 1 -26 ± 1 -26 ± 0 -27 ± 0 -25 ± 1	-35 ± 1 -34 ± 1 -29 ± 1 -24 ± 0 -27 ± 2	$\begin{array}{r} -29 \pm 2 \\ -28 \pm 1 \\ -26 \pm 0 \\ -25 \pm 4 \\ -22 \pm 3 \end{array}$			
0.1 1 10 30 100	CdSe QD	-22 ± 6 -10 ± 1 -10 ± 1 -4 ± 4 -4 ± 2	-34 ± 2 -16 ± 1 -10 ± 0 -3 ± 1 -5 ± 0	-16 ± 2 -18 ± 1 -10 ± 1 -5 ± 1 -0.1 ± 0			
0.1 1 10 30 100 500	сPL	-73 ± 4 -69 ± 6 -67 ± 1 -55 ± 6 -58 ± 3 -3 ± 4	-79 ± 3 -72 ± 1 -65 ± 2 -66 ± 9 -39 ± 4	-67 ± 3 -63 ± 3 -58 ± 4 -52 ± 5 -44 ± 5			
0.1 1 10 30 100	sPL	-58 ± 2 -51 ± 2 -50 ± 1 -46 ± 2 -46 ± 3	-60 ± 6 -53 ± 1 -54 ± 3 -35 ± 5 -33 ± 1	-50 ± 2 -48 ± 2 -48 ± 5 -37 ± 6 -35 ± 2			

Table 4.3 Zeta potentials (mV) of bare and DOM-coated Al₂O₃ determined over a range of ionic strength (pH 5). Standard microscope glass slides (coated with Al₂O₃) and slides coated with 2 mg/L SRHA or rhamnolipid were used (instead of QCM-D sensors) due to geometric limitation to fit the asymmetric clamping cell. Zeta potentials were obtained from streaming potential measurements using the Smoluchowski-Helmholtz approach³⁸.

ionic strength	substrate	KCI	KCI + SRHA	KCI + rhamnolipid		
(mM)		Zeta Potential (mV)				
0.1		13 ± 1	-27 ± 1	n.m.		
1		8 ± 1	-27 ± 0	-16 ± 0		
10	AI_2O_3	6 ± 3	-15 ± 0	n.m.		
30		3 ± 2	-13 ± 0	-8 ± 0		
100		2 ± 0	n.m.	n.m.		

n.m.: not measured.

The mean ENP size at the different solution chemistries was measured using two methods: (*i*) dynamic light scattering (DLS) and (*ii*) transmission electron microscopy (TEM). The hydrodynamic diameters obtained by DLS at the different solution chemistries and in the absence/presence of DOM are presented in Table 1. In KCl, at low IS, the particle size is on the order of 60 nm for the *c*PL and 55 nm for the *s*PL, and for both particles, aggregation is observed at high salt concentrations (100 mM for the *s*PL and 500 mM for the *c*PL), with corresponding high values of the polydispersity index (PDI) (*i.e.*, PDI > 0.5). Overall, the addition of DOM does not have a significant effect on the size of the latex nanoparticles. However, the addition of DOM resulted in decreased aggregation of the *s*PL at 100 mM IS.

Overall, the QD sizes obtained here are in agreement with other QD studies at comparable solution chemistries^{14,15,26}. In general, the particle size for both QDs increases with the KCl concentration: the CdTe QD yields hydrodynamic diameters between 59 and 206 nm, whereas the size of the CdSe QD ranges between 163 and 370 nm. The measured hydrodynamic diameters of the QDs are larger than the particle sizes reported by the vendors, especially for the CdSe QD. This may be explained by partial degradation of the particle surface coatings and dissolution of Cd^{2+} from the core of the QDs during the 12 hr suspension equilibration phase^{40,41}. Changes in dissolved Cd^{2+} during the 12 hr equilibration

period were measured by ICP-OES for suspensions prepared at 1 or 100 mM KCl (Table 4.4). Greater dissolution of Cd²⁺ is observed at the higher IS. Because free Cd²⁺ may contribute to particle bridging⁴⁰ via complexation with the polymers coating the particle surface, this would explain the larger QD sizes measured at high IS. Changes in QD fluorescence can also be an indication of degradation of the QD surface coating⁴¹. Significant decrease in fluorescence of the QDs were measured over the 12 hr suspension equilibration period (Figure 4.2), pointing to a certain extent of degradation of the QD surface coating. Such degradation of the QD surface surface coating would also contribute to aggregation of the QD suspensions as a result of decreased electrosteric stabilization.

It is generally accepted that DOM stabilizes ENPs in suspension^{16,17}. However, noteworthy differences are observed in the effectiveness of each organic molecule in stabilizing the QDs used here within the range of IS examined; whereas the SRHA yields particle sizes on the same order of magnitude, the presence of rhamnolipid does not appear to effectively stabilize the CdSe QD at the higher IS examined (Table 4.1). Humic substances have been reported to overcoat QDs improving their stability in aqueous suspensions⁴². However, the nature of the specific interactions between rhamnolipids and ENPs (*i.e.*, QDs) are not fully understood yet¹⁸, and further studies are required to clarify them. Overall, the results shown here are in agreement with other studies of polymer-coated QDs in electrolyte supplemented with different DOM^{43,44}.

The particle size and the state of aggregation of the QDs were further corroborated at selected conditions using TEM. Figure 4.3 shows representative images of the CdTe and CdSe QDs suspended in 1 mM and 100 mM KCl. For both QDs, the images show sizes that are larger than those reported by the vendors (*i.e.*,10 and 24 nm for the CdTe and CdSe QDs, respectively) even at low salt concentration (1 mM KCl, pH 5).TEM image analysis (using Image J software) was done on at least 150 particles in randomly selected images from three TEM grids. Images recorded at high magnification reveal spherical and well dispersed ENPs (average nominal sizes of 29±4 nm for the CdTe QD and 30±20 nm for the CdTe QD). In comparison, at 100 mM KCl, particles of an average size of 67±46 nm for the CdTe QD and 202±172 nm for the CdSe QD are observed (Table 4.1).

particle	time (hrs)	1 mMKCI	100 mM KCl
CdTe/CdS QD	0	0.6 +/- 0.3 %	16.5 +/- 0.3 %
(PAA coated)	4	0.5 +/- 0.1 %	18.0 +/- 1.5 %
	8 12	2.4 +/- 0.0 %	23.4 +/- 0.4 %
	12	1.9 +/- 0.0 %	22.3 +/- 2.3 %
CdSe/ZnS QD	0	1.3 +/- 0.7 %	5.0 +/- 1.4 %
(PEG coated)	4	4.1 +/- 0.4 %	10.0 +/- 1.1 %
	8	2.9 +/- 0.4 %	9.5 +/- 0.5 %
	12	6.0 +/- 0.6 %	15.5 +/- 5.2 %

Table 4.4 Time-resolved free dissolved Cd^{2+} from QD suspensions in KCl at pH 5 expressed as percentage of the total Cd^{2+} . The values represent the mean \pm standard deviation.



Figure 4.2 Fluorescence of CdTe and CdSe QDs at different time intervals (N) normalized to that obtained at time zero (N_0) when suspended in KCl (1 or 100 mM) at pH 5.



Figure 4.3Representative TEM micrographs of QDs suspended in simple electrolyte at pH 5.

4.3.3 Deposition kinetics of ENPs onto bare Al₂O₃

Figure 4.4a presents the initial deposition kinetics of the polystyrene latex particles as evaluated from the change in the frequency shift with time (*i.e.*, - f_{3_slope}) during the first ~1 minute of particle deposition. The initial particle deposition rates ($-f_{3_slope}$) for both polystyrene latex particles are greatest at the lowest IS examined and decrease significantly at the highest IS. These results are in qualitative agreement with the DLVO theory of colloidal stability^{45,46} for the interaction of negatively charged particles (*c*PL, *s*PL) with a positively charged bare Al₂O₃surface. These trends also agree with previous studies where colloid deposition onto oppositely charged collectors has been studied^{23-25,47}.

However, there are some notable differences in the deposition behavior of the two model latex particles depending on the surface functional group. For instance, at the lowest IS (0.1 mM), the $-f_{3_slope}$ is nearly twice as steep for *s*PL as for *c*PL. The *s*PL also seems more sensitive to changes in IS, as the $-f_{3_slope}$ varied between 101 to 0.6 Hz/min, whereas the $-f_{3_slope}$ of the *c*PL is on the order of 49 to 9.3 Hz/min. The observed significant decrease in the *s*PL and *c*PL particle deposition rate at the highest IS can also partially be attributed to a decrease in the convective-diffusive transport of particles towards the collector as a result of particle aggregation^{23,26}.

In order to effectively compare the trends in deposition of the ENPs studied, we have converted the values of $-f_{3_slope}$ to particle deposition rate (r_d) and normalized the values with respect to the theoretical particle deposition rate(r_d^{SL}), as described

previously²⁶. The value of r_d^{SL} is obtained under the assumption that the deposition rate of the ENPs is by pure convective-diffusive transport^{10,48}. In theory, in the absence of repulsive or attractive electrostatic forces, the ratio $r_{\rm d}/r_{\rm d}^{\rm SL}$ should approach unity. As expected, for both polystyrene latex particles, the ratio (r_d/r_d^{SL}) is greatest at the lowest IS (0.1 mM) and it remains close to 1 over a broad range of salt concentrations (Figure 4.4b). The large variations (note large error bars) in the ratio r_d/r_d^{SL} at the highest IS are likely the result of the error propagation of two parameters with large standard deviations (*i.e.*, $r_{\rm d}$ and $r_{\rm d}^{\rm SL}$) in the aggregated system (Table 4.1). Comparing the two polystyrene particles, it is interesting that higher normalized deposition rates are observed for sPL than for cPL at most IS examined. This difference could be due to the surface properties of each model particle; according to the manufacturer, the sPL particle is hydrophobic, whereas the *c*PL is hydrophilic and made by grafting polymers containing carboxylic groups onto a hydrophobic particle. The external "hairy" layer on the surface of the cPL is only a few angstroms thick, but might provide an additional barrier to prevent the deposition compared to the *s*PL⁴⁹.



Figure 4.4 Deposition rates $(-f_{3_slope})$ of ENPs suspended in KCl (pH 5) on bare Al₂O₃. (a) polystyrene latex nanoparticles: *c*PL (Δ) and *s*PL (\diamond), and (c) quantum dots: CdSe QD (\circ), CdTe QD (\Box). Data represent the mean \pm standard deviation. In (b) and (d) normalized retention presented as a ratio of the experimental deposition rate (r_d) to the theoretical particle deposition rate (r_d^{SL}). r_d^{SL} was estimated using the Smoluchowski-Levich approximation^{26,48} with parameters determined from DLS measurements (Table 4.1). The dashed line represents the theoretical deposition by pure convective-diffusive transport. Data represent the ratio $r_d/r_d^{SL} \pm$ standard deviation.
In Figure 4.4c,d, the deposition rates ($-f_3$ slope) and the normalized retention of the coated QDs (r_d/r_d^{SL}) are presented as a function of IS. Overall, the QDs display lower $-f_{3 \text{ slope}}$ as compared to the polystyrene latex particles (by approximately one order of magnitude). We attribute these differences to steric repulsion exerted by the polymeric coatings used to functionalize the QDs^{7,50,51}. Steric stabilization of surface-modified ENPs is well documented in the literature^{52,53}. For example, different studies using QCM-D have confirmed the efficiency of various polyelectrolytes or organic coatings in reducing the deposition of surfacemodified zero-valent iron nanoparticles (nZVI), demonstrating the effective electrosteric stabilizing efficiency of the surface modifiers^{20,54,55}. Moreover, others have proposed that the types of surface modifiers used to coat the QDs studied herein (namely PAA and PEG) can enhance particle stability by a mechanism of electrosteric repulsion^{40,51}. Comparison of the two QDs reveals that the deposition rate of the CdSe QD decreases as the solution IS increases, while the opposite trend is observed for the CdTe QD. Whereas the CdSe QD reaches its highest deposition rate at 0.1 mM KCl (~12 Hz/min), the CdTe QD is at its minimum deposition rate at this condition (~2 Hz/min) and reaches a maximum value at 30 mM IS (~9 Hz/min). As described above for the polystyrene latex nanoparticles, the deposition behavior of the CdSe QD is in qualitative agreement with DLVO theory of colloidal stability for the deposition of a negatively charged particle on a positively charged surface. To interpret the results obtained with the CdTe QD, we must take into account that the surface coating present on this QD is an anionic polyelectrolyte (PAA) that can be strongly affected by changes in

solution IS^{33,40}. At low IS, due to the strong repulsion between the anionic groups of the PAA, the coating is likely to adopt an extended conformation, resulting in considerable steric hindrance³³. This explains the very low deposition rate measured at the lowest IS (for the CdTe QD). However, as the salt concentration increases, the intramolecular and intermolecular electrostatic repulsion between PAA molecules decreases, leading to collapse of the polyelectrolyte layer, and a decrease in the extent of steric stabilization³³. DLS measurements of a PAA suspension confirmed the decrease in size of the free PAA molecules from 19.5 to15.6 and 8.2 nm when the IS increased from1 to10, and 100 mM IS, respectively. Hence, it is likely that the greater deposition rates of the CdTe QD upon an increase in solution IS (Figure 4.4c) are caused by conformational changes of the PAA coating^{33,40}. Figure 4.4d shows the normalized deposition rates (r_d/r_d^{SL}) for the two QDs over a range of IS. As expected, the ratio r_d/r_d^{SL} for these sterically stabilized ENPs are lower than unity $(r_d/r_d^{SL} \sim 0.1)$ and of comparable value at low IS (below 10 mM). Interestingly, at higher IS, the ratio $r_{\rm d}/r_{\rm d}^{\rm SL}$ for the CdSe QD decreases (likely due to considerable particle aggregation), whereas r_d/r_d^{SL} for the CdTe QD exhibits an increase (due to a reduction in the steric stabilization imparted by the PAA coating). These phenomena are further explained below by comparing the output parameters measured by QCM-D (*i.e.*, frequency and dissipation).

4.3.4 Deposition behavior of ENPs: Interpretation of $-D_{3_{slope}}/f_{3_{slope}}$ ratio.

Fundamental differences between the deposition behavior of the polystyrene latex particles (governed by classical DLVO interactions) and that of the QDs (governed by steric forces imparted by surface coatings) can also be interpreted by considering the ratio of ΔD_3 to Δf_3 . The ratio of $-\Delta D_3/\Delta f_3$ is commonly employed as an indication of the rigidity of homogeneously adsorbed films, and it has, for instance, been useful to study the conformation of a pluronic polymer brush on surfaces of varying hydrophobicity²⁹.

Here, we present the ratio $-D_{3_slope}/f_{3_slope}$ (equivalent to $-\Delta D_3/\Delta f_3$ during the initial deposition phase) for polystyrene latex particles (Figure 4.5a) and QDs (Figure 4.5b) as a function of IS. For both *c*PL and *s*PL, the values of the ratio $-D_{3_slope}/f_{3_slope}$ are below 10⁻⁷ indicating that Sauerbrey's equation will yield an adequate estimation of the deposited mass at all conditions. The fact that the $-D_{3_slope}/f_{3_slope}$ appears constant within the studied range of IS also suggests that both polystyrene particles form a layer that is equally rigid regardless of the salt concentration.

For the polymer-coated QDs (Figure 4.5b), the experimental ratios of $-D_{3_slope}/f_{3_slope}$ are generally near or above 1×10^{-7} s⁻¹ (limit proposed by Q-Sense³²), but still below the limit of 4×10^{-7} s⁻¹ suggested by Reviakine et al²⁹. This

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indeed suggests that although the deposition behavior of the QDs is within the limits of Sauerbrey interpretation, more energy is dissipated compared to the latex particles. Thus, based on the measured values of $-D_3 \frac{1}{\text{slope}}/f_3$ slope, the latex particles are more rigidly deposited than the polymer-coated QDs on the alumina surface. Interestingly, for the CdTe QD, which is the only particle displaying an increased deposition with increasing IS, the value of $-D_3 \frac{1}{\text{slope}}/f_3$ slope decreases almost by a factor of 10 between 0.1 and 10 mM, and then increases above this IS (Figure 5a). The particular behavior of this QD can be attributed to the unique polyelectrolyte coating on the particle surface. As the IS increases from 0.1 to 10 mM, collapse of the PAA coating can result in more rigid deposition of the QD on the alumina surface which is reflected as a decrease in the ratio $-D_3$ slope/ f_3 slope. The conformation of the PAA (e.g., loops, trains, and tails) is associated with the amount of bound water, and the ratio $-\Delta D_3/\Delta f_3$ can also be interpreted as a relative estimate of the water entrapped^{56,57}. For instance, Kontturi et al.⁵⁶ used the ratio - $\Delta D_{\rm n}/\Delta f_{\rm n}$ to determine whether the valence of the electrolyte added to the solution had a strong effect on the water entrapped on cationic starch adsorbed on cellulose and bare SiO₂. Likewise, Saarinen et al.⁵⁷ reported that high dissipation values reflect thick adsorbed layers of polyelectrolyte with extended conformation of loops and tails, whereas low dissipation values were indicative of thin and rigid layers.

The ratio $-D_{3_slope}/f_{3_slope}$ can also be used to understand the colloidal stability of ENPs upon deposition. Tellechea et al.⁵⁸ reported that the magnitude of the ratio - $\Delta D_n/\Delta f_n$ is linked to the size of individual particles attached to the surface. These

researchers encountered that for liposomes and virus particles of spherical morphology and well-defined sizes (*i.e.*, 30, 80 and 120 nm), the ratio $-\Delta D_n/\Delta f_n$ increases with particle size. In this study, all the ENPs exhibit an increase in $-D_{3_slope}/f_{3_slope}$ upon an increase in particle size (Table 4.1). For instance, the ratios for both polystyrene latex particles exhibit large error bars at the highest IS (Figure 4.5a) and the ratios of the QDs also increase above 10 mM IS (Figure 4.5b).



Figure 4.5(a) $-D_{3_slope}/f_{3_slope}$ for *c*PL, *s*PL and (b) for CdTe and CdSe QDs as function of ionic strength in simple electrolyte (KCl at pH 5). The dashed line represents the limit of applicability for the Sauerbrey model according to Q-Sense³² and the dotted line represents the limit proposed by Reviakine et al.²⁹ Data represent the mean ± standard deviation.

4.3.5 Deposition of the ENPs onto DOM-coated surfaces.

In the second part of this study, we investigated the influence of DOM on the deposition kinetics of QDs and the polystyrene latex nanoparticles. Figure 4.6 illustrates the effects of water chemistry and collector surface chemistry on the deposition kinetics of ENPs. A comparison of the $-f_{3_slope}$ values in the presence and absence of the different DOM reveals a dramatic reduction in the ENP deposition rates. Our results are in agreement with previous studies where the presence of DOM significantly increased the mobility of ENPs^{20,21,59}. For instance, Franchi and O'Melia²¹ observed reduced retention of sulfate latex particles in glass bead packed columns in the presence of SRHA. Likewise, in column transport studies with sandy soil, adsorption of humic acid onto the surface of 122 nm hematite particles decreased particle retention by approximately 2 orders of magnitude⁵⁹. Similarly, in our laboratory, we observed a significant decrease in the deposition of carboxymethylcellulose-coated nZVI particles onto SiO₂ in the presence of fulvic acids and rhamnolipid²⁰.

Adsorbed layers of organic matter alter the collector surface charge from positive to negative (Table4.2). Here, the deposition of the latex nanoparticles and the QDs are significantly impacted by the presence of SRHA, even at the highest IS (100 mM) examined. The addition of rhamnolipid at a comparable concentration has a lessened effect for the *c*PL and CdTe QD at high IS. Overall, the obtained results are in qualitative agreement with other studies where the deposition of ENPs onto surfaces pre-coated with DOM has been examined using the QCM^{23,24}. Chen and

Elimelech²³ showed that the deposition rate of fullerenes in monovalent salt (NaCl at pH 5.5) was significantly hindered (up to 1 order of magnitude) on surfaces coated with SRHA and alginates. Jiang et al.²⁴ studied the deposition behavior of ZnO nanoparticles in NaCl (pH 7.8) onto SRHA-coated surfaces with similar results. In both studies, the hindered particle deposition was attributed to the additional electrostatic contribution exerted by the SRHA and alginate coatings (as both the nanoparticles and collectors were more negatively charged), yet it was suggested that steric repulsion also played an important role.

Analysis of the $-D_{3_slope}/f_{3_slope}$ ratio for experiments conducted using DOMcoated alumina reveal some larger values of the ratio than those obtained on bare Al₂O₃ (Figure 4.7). This is indicative of an even more hydrated interface between the particles and DOM-coated surface. These observations are in agreement with a previous QCM-D study where the adsorption onto Al₂O₃ of a humic acid (extracted from Yellow River sediment)has been studied at pH 5⁶⁰.Under certain conditions assessed in this study for the deposition of ENPs onto DOM-coated surfaces, the $-D_{3_slope}/f_{3_slope}$ ratios are exceptionally high, *i.e.*, above the Sauerbrey limits. In such circumstances, the acquired frequency shifts are not necessarily proportional to the deposited mass, and a combination of QCM and optical techniques (ellipsometry, reflectometry) is required for a more accurate analysis of nanoparticle deposition^{29,56}.

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Figure 4.6 Deposition rates $(-f_{3_slope})$ of the ENPs over a range of ionic strength (pH 5) onto DOM pre-coated Al₂O₃ (*i.e.*, SRHA, rhamnolipid) and bare Al₂O₃ (data from Figure 4.1 is shown here for comparison). The different solution chemistries are represented with full symbols for KCl supplemented with 2 mg/L SRHA, half full symbols for KCl with 2 mg/L rhamnolipid, and open symbols for simple KCl. Data represent the mean \pm standard deviation.



Figure 4.7 The bars represent the ratios– D_{3_slope}/f_{3_slope} onto DOM pre-coated Al₂O₃ surfaces with 2 mg/L of SRHA (light gray) or rhamnolipid (dark gray). Selected data from Figure 4.2 (deposition on bare Al₂O₃) are plotted again for comparison (white bars). In all cases, the bars represent the mean \pm standard deviation. The dashed line represents the limit of applicability of the Sauerbrey model according to Q-Sense³², and the dotted line the limit proposed by Reviakine et al.²⁹

4.4 Environmental Implications

A clear understanding of the principles controlling ENP deposition is needed to predict their transport and fate in subsurface environments and in water filtration processes. This study shows how QCM-D can be used to increase our knowledge of the roles that particle and collector surface coatings and water chemistry play in the transport and fate of ENPs in natural and engineered aquatic environments. The initial deposition rate of the studied ENPs is affected by changes in the solution chemistry (*e.g.*, IS, presence of DOM), although this behavior is highly dependent on the surface coating of the ENP.

This study focused on the initial particle deposition behavior of selected ENPs onto particle-free collector surfaces. Careful inspection of the QCM-D measurements (*e.g.*, Figure 4.5) reveals that the ENP deposition rates (values of f_{3_slope}) decrease with time as available sites for deposition are filled. For all ENPs, the maximum particle deposition rate is observed within the first ~1 minute of the QCM-D experiment and decreases rapidly with time due to "blocking" of the collector surface by previously deposited particles^{61,62}. This time-dependent change in the ENP deposition rate will also be affected by the nature of the surface and particle coatings as well as water chemistry. Indeed, the data in Figure 4.8 show that the rate of decrease of the ENP deposition rates (*i.e.*, the shape of the decay curve) varies for the different ENPs. Additional studies aimed at better understanding the variability in ENP deposition behavior with time under

different environmental conditions will provide important insight into their potential fate in granular aquatic environments.



Figure 4.8 Time-dependent change in the ENP deposition rates $(-f_{3_slope})$ onto Al₂O₃ at different IS. In most cases, the maximum deposition rate is observed within the first minute of the experiment and decreases rapidly with time due to "blocking" by previously deposited particles.

Our results demonstrate that certain ENP surface coatings (i.e., polymers or polyelectrolytes) hinder deposition of QDs onto Al₂O₃.Moreover, our data indicate that DOM coatings (either SRHA or rhamnolipids) cause charge reversal of the Al₂O₃collector surface and add an additional barrier which further decrease the retention of all ENPs examined. Consequently, since DOM are abundant in nature, and because several ENPs (in addition to QDs) are stabilized with polymeric coatings, positively charged patches present on the surface of collector grains in the natural subsurface or in granular filters may not necessarily present favorable sites for ENP deposition^{10,27}. Hence, predictions of ENP transport potential in natural or engineered aquatic environments that are based on data collected in the absence of DOM may considerably underestimate ENP mobility. Moreover, future studies should explore other types of DOM (*i.e.*, extracellular products) since specific interactions between different DOM and surface-modified ENPs or collector surfaces might occur¹⁶. These transformations will result in variations in the physicochemical properties of particles and collectors, and can significantly impact ENP transport and fate in aquatic environments.

4.5 References

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Chapter 5: Effect of Surface Modifiers and Aggregate Size on the Transport and Deposition of Engineered Nanoparticles

Connecting text: In the previous chapters, the transport and deposition behavior of cadmium-based QDs was assessed by means of packed-bed columns with granular materials and a QCM-D. However, environmental and health concerns have motivated the development of cadmium free QDs, and silicon nanocrystals (Si-NC) are an attractive alternative to replace them. In this chapter, we have used a combined approach to study the deposition kinetics as a function of solution chemistry of Si-NCs suspended in monovalent (K^+) and divalent salt (Ca^{2+}) solutions.

The results of this research are included in the following manuscript which will be submitted to *Environmental Engineering Science* by September 1, 2013: Quevedo I.R.; Olsson A.L.J., Veinot J.G.C., Tufenkji N., *Effect of Surface Modifiers and Aggregate Size on the Transport and Deposition of Engineered Nanoparticles*

5.1 Introduction

The unique physical and optical properties of engineered nanoparticles (ENPs) have been explored in diverse fields, such as, biomedical applications, solar cells, or electronic devices^{1,2}. To target specific needs, ENPs are commonly coated with different organic molecules (*i.e.*, surfactants, polymers, or polyelectrolytes)^{3,4}. For instance, TiO₂ nanoparticles stabilized with polyacrylic acid are conjugated with antibodies and used for molecular recognition⁵. Amphiphilic polymers render quantum dots water-dispersible and ready for use in biological sensing and intracellular labeling². Likewise, polymeric coatings (e.g., carboxymethyl cellulose, polyvinylpyrrolidone and guar gum) improve the stability of reactive zerovalent iron nanoparticles (NZVI) and the capability of bimetallic FePd nanoparticles to degrade chlorinated hydrocarbons⁶⁻⁹. However, an increasing number of products containing surface modified ENPs¹⁰ will likely result in their incidence in the environment¹¹, and since different ENPs have exhibited toxic effects¹, understanding their transport and fate is crucial for assessing their contamination potential¹².

In general, the mobility of ENPs has been studied using water saturated columns packed with granular materials (*e.g.*, quartz sand) representative of aquifers or engineered (deep-bed) filtration systems¹². In column transport experiments, the extent of ENP retention is evaluated by monitoring the influent and effluent particle concentrations, and the results are commonly interpreted using clean-bed colloid filtration theory¹³. Several studies of ENP transport in packed columns report an enhanced mobility of surface modified ENPs due to the

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electrosteric stabilization imparted by the polymers or polyelectrolytes used to coat them^{4,6-8,14-17}. Nonetheless, generalization to the myriad of surface modified ENPs introduced into the market every year¹⁰ is complex, since the afforded level of electrosteric stability is associated to the properties of the molecules used (*i.e.*, molecular weight, adsorbed mass, density, extended layer thickness)⁴. Thus, a better mechanistic understanding of the role surface modifiers play is required to more accurately predict the transport and fate of ENPs in natural and engineered aquatic environments.

The quartz crystal microbalance with dissipation monitoring (QCM-D) is useful in the evaluation of the deposition behavior of ENP son model soil surfaces $(e.g., SiO_2, Fe_2O_3 \text{ or } Al_2O_3)^{8,18-24}$. Briefly, as particles deposit onto the QCM sensor, an increase in mass on the collector surface results in a measurable decrease in the crystal's resonance frequency (*i.e.*, negative frequency shifts)²⁵. Additionally, dissipative energy losses, induced by the deposited mass, are measured in terms of oscillation decay time. Whereas the applicability of QCM-D as a mass sensor to assess the deposition kinetics of ENPs is well known $^{8,18-24}$, it was only recently shown that the ratio of the two QCM-D output parameters (dissipation/frequency) can be used to better understand the conformation of the surface coatings on deposited particles²³. Namely, the ratio dissipation/frequency revealed if the conformation of a polyelectrolyte (*i.e.*, polyacrylic-acid derivative) used to coat a CdTe QD was extended or compressed upon deposition onto alumina surfaces.

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In general, nanoparticle deposition kinetics are strongly dependent on the water chemistry (e.g., electrolyte species, ionic strength, and pH) as well as collector and particle surface properties¹². However, changes in water chemistry often lead to particle aggregation, which can be challenging to interpret 12,26. For instance, the retention of particle aggregates in packed granular matrices may increase due to deposition in the secondary energy minimum of the particlecollector interaction energy profile7,27,28 or physical straining in pore spaces that are too small to allow passage of the aggregates^{14,29}. Likewise, in QCM-D experiments, the deposition of aggregated ENPs might not always be straightforward to interpret using the conventional approach of mass loading^{19,21,22,30}. For instance, positive frequency shifts associated to large particles or ENP-aggregates attached to the sensor via weak bridges have been reported^{19,30}, and this atypical response appears to be linked to the size of the particle aggregate³⁰. Hence, laboratory studies to assess the transport and deposition of ENPs in packed-bed columns and QCM-D require an appropriate physicochemical characterization to adequately interpret the results.

In this study, we have systematically evaluated and compared the deposition behavior of silicon nanocrystals (Si-NCs) as a model surface-modified ENP, using: (*i*) laboratory-scale columns packed with quartz sand, and (*ii*) QCM-D with SiO₂ coated crystals (as a model sand surface). Both techniques were used to determine the deposition kinetics of surface modified Si-NCs over a broad range of environmentally relevant solution chemistries, including variations in ionic strength (IS) and ion valence (K⁺, Ca²⁺). The model Si-NCs were modified with carboxylic acids having different chain lengths, as an increase in carbon chain length has been found to improve their colloidal stability in aqueous suspensions³¹. Various techniques were also used to characterize the physicochemical properties of the Si-NCs over the range of water chemistries examined, including laser Doppler velocimetry to evaluate particle electrophoretic mobility, and dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and scanning ion occlusion sensing (SIOS) to evaluate particle and aggregate sizes.

5.2 Experimental

5.2.1 Preparation of Si-NCs suspensions

Si-NCs were prepared and functionalized with carboxylic acids of different alkylchain lengths: propionic acid (C₃), heptanoic acid (C₇) and undecanoic acid (C₁₁) and dispersed in deionized water (DI) as described elsewhere^{24,25}. Si-NC stock suspensions were diluted to a working concentration of 20 mg/L or 200 mg/L in electrolytes of varying IS (1–100 mM KCl or 1–3 mM CaCl₂) for transport experiments in packed bed columns or the QCM-D, respectively. Suspensions were adjusted to pH 5 (using HCl), and equilibrated for 2 hrs at 9°C and then at room temperature for 30 minutes prior to each experiment. All chemicals used to prepare solutions were of analytical grade.

5.2.2 Electrokinetic characterization of Si-NCs in electrolyte

Laser Doppler velocimetry (ZetaSizer Nano, Malvern) was used to evaluate the electrophoretic mobility (EPM) of Si-NCs within the range of IS. EPM measurements were repeated using at least three different samples (prepared on different days) using disposable capillary cells at 20 ± 0.2 °C. The electrical field (*E*) was adjusted between 5 and 10 ± 0.1 V/m. For comparative purposes, measured EPMs were converted to zeta potentials using the Henry equation and the expression for the retardation effect proposed by Ohshima²⁶.

5.2.3 Sizing of Si-NCs in electrolyte

Dynamic light scattering (DLS) (ZetaSizer Nano, Malvern) and nanoparticle trajectory analysis (NTA) (LM10-HS Nanoparticle Analysis System, Nanosight) were used to determine the hydrodynamic diameters of the Si-NCs suspended in electrolyte. DLS measurements (number mean) were determined with Si-NC suspensions prepared in electrolyte prior to each transport experiment. For NTA measurements, the mean square displacements of single particles were determined by tracking the scattered light, followed by analysis using the software (Nanosight v.2.2.), and where each data point represents the average for at least 150 counted particles. At selected conditions, qNano (IZON Science) was used to confirm the size of the Si-NCs in electrolyte. qNano is a Coulter-type sensor that allows single particle measurements as colloidal particles are driven through pores of known size²⁷. Membranes with different pore sizes (*i.e.*, NP₁₀₀, NP₂₀₀, and NP₄₀₀) were mounted on the instrument and the translocation of Si-NCs through the stretched

pores was detected as a result of changes in the background current²⁷. Previous calibration with polystyrene latex beads of known sizes allowed the determination of the size of Si-NCs used in this study. In all cases, results are presented as the mean of size measurements conducted in triplicate.

5.2.4 Transport experiments in packed-bed columns.

Experiments were conducted with 1 cm (internal diameter) glass chromatography columns (10/20, Amersham Biosciences, Piscataway, NJ) packed with high purity quartz sand to allow careful control of the experimental system. Prior to use, the sand was sieved with Nylon sieves (U.S. standard mesh sizes 50 and 70, 300 and $212 \,\mu\text{m}$ openings, respectively) to obtain a sand sample having an average grain diameter (d_c) of 256 µm. The sand was cleaned according to the procedure described previously²⁰. Before each transport experiment, the required mass of sand was soaked in electrolyte for at least 16 hrs. To ensure uniform packing, sand was wet packed into the glass column using gentle vibration yielding a packed-bed porosity (ε) of 0.38. The final height of the packed bed was 4 ± 0.2 cm. To condition the packed columns, 10 pore volumes (PVs) of background electrolyte (*i.e.*, KCl or CaCl₂) were pumped at a constant approach velocity of 1.06×10^{-4} m/s prior to the injection of Si-NCs. In all experiments, 8 mL of each Si-NC suspension (equivalent to 6.6 PVs) were injected into the packed column. The effluent concentrations (C) of fluorescent Si-NCs (*i.e.*, C_7 and C_{11}) were monitored in real time with a spectrofluorometer (Fluoromax-4, Jobin-Yvon Horiba) (EX/EM settings were: 350/603 for the C7, and 350/611 for C11). The

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effluent concentration of the non-fluorescent Si-NC (C₃) was monitored with a UV-visible spectrophotometer (Hewlett Packard 8453) (at a wavelength of 250 nm) and, under selected conditions, confirmed by ICP-OES (see Supplementary Information). The concentrations of the influent suspensions (C_0) were the same as those used for characterization of the particles. The absorbance or fluorescence of the injected suspensions was determined by bypassing the column apparatus. Si-NC transport experiments were conducted over a wide range of solution IS, using both monovalent (KCl) and divalent salts (CaCl₂) and conducted in duplicate for each condition.

5.2.5 Confirming the measured Si-NC (C₃) elution by ICP-OES.

Particle samples of Si-NC (C₃) exiting the UV-visible flow cell were collected in 0.5 mL aliquots. The aliquots were digested (DigiPrep Jr., SCP SCIENCE) for 1.5 hours at 95°C in closed polypropylene vials using 500 μ L of HF (Fisher Scientific, Trace Metal Grade) and completed to a volume of 3 mL. These samples were analyzed using an ICP-OES (Thermo TraceScan) at a wavelength of 251.6 nm equipped with a HF sample introduction system (SCP SCIENCE). A four point NIST traceable (SCP SCIENCE) calibration curve with concentrations ranging from 0.1 to 10 mg/L and a correlation coefficient of 0.9998 was used to determine the concentration in sample sets. In order to further compensate for instrument drift, the standard bracketing technique was used after every fifth sample.

5.2.6 Interpretation of transport experiments in packed-bed columns

The results from sand-packed column experiments were quantitatively compared by determining the particle attachment efficiency (α) using colloid filtration theory (CFT)¹³ as follows:

$$\alpha = -\frac{2}{3} \frac{d_{\rm c}}{(1-\varepsilon)L\eta_0} \ln\left(\frac{C}{C_0}\right)$$
(5.1)

where dc is the average diameter of the sand grains, ε is the porosity of the porous medium, and *L* is the packed column length. The value of *C*/*C*₀ represents the normalized column effluent particle concentration obtained from each particle breakthrough curve by averaging values measured between 1.8 and 2 pore volumes. Values of η_0 for each experimental condition were determined using the correlation developed byTufenkji and Elimelech ³⁵.

5.2.7 Deposition of Si-NCs onto SiO₂ measured by QCM-D.

Deposition rates of Si-NCs onto SiO₂-coated sensors (QSX–303, Q-Sense AB, Gothenburg, Sweden) were determined using a QCM-D (E4, Q-Sense AB). When the 5 MHz AT-cut crystals are mounted in the QCM-D flow modules, the injected flow is parallel to the flat SiO₂ surface. Si-NC deposition experiments were repeated using at least three different samples prepared on different days and conducted as follows: a peristaltic pump (Reglo-Digital IPC-N 4, Ismatec) was used to first inject DI water (50 μ L/min) to obtain a stable baseline. Next, the background electrolyte solution of interest was injected into the flow module,

followed by a Si-NC suspension in the same electrolyte solution for at least 20 min. After each experiment, the crystals, QCM-D chambers, and tubing were rinsed with 20 mL of 2% Hellmanex (Fisher Scientific) and 30 mL of DI. The crystals were further cleaned by soaking in 2% Hellmanex overnight, rinsed with DI, dried under N_2 and then exposed to UV/ozone treatment for 10 min prior to any additional measurement.

5.2.8 Interpretation of QCM-D deposition experiments.

The QCM-D is commonly referred to as a mass sensor because changes in the resonance frequency $(-\Delta f)$ of a quartz crystal are proportional to the deposited mass (Δm) per unit area, and dissipative energy losses of the adsorbed film (dissipation shift, ΔD). In the case of rigid films ($\Delta D \sim 0$), frequency shifts ($-\Delta f_n$) are proportional to the deposited mass (Δm), as described by the Sauerbrey relationship²⁵:

$$-\Delta f_{\rm n} = \frac{C}{n} \Delta m \tag{5.2}$$

In eq. 5.2, *C* is the mass sensitivity constant, equal to 17.7 Hz·ng/cm² for a 5 MHz crystal and *n* is the resonance overtone number (n=3, 5, 7, 9, 11, 13). Note that the frequency shift obtained from QCM-D (Q-Sense) is normalized by the overtone number (*i.e.*, $\Delta f_{(n)} = \Delta f_n/n$). Therefore, when the Sauerbrey relation²⁵ is valid, the rate at which frequency shift changes during a given time period (- $f_{(n)_slope}$, eq. 5.3) describes the rate at which mass is deposited on the SiO₂ surface (*r*_d):

$$r_{\rm d} = -f_{(n)_\rm slope} \cdot C = -\frac{d\Delta f_n}{dt} \cdot C$$
(5.3)

As further discussed in the manuscript, this is a valid assumption if the normalized frequency shifts at all the overtones are negative (*i.e.*, $\Delta f_{(3)}$, $\Delta f_{(5)}$, ..., $\Delta f_{(13)} \leq 0$). Conversely, positive frequency shifts at high overtones (*n*) are a clear indication of a "coupled resonance" type response, which is linked to the bond strength between particles and collector, but cannot be interpreted as deposited mass^{30,36}.

5.3 Results and Discussion

5.3.1 Characterization of capped Si-NCs in electrolyte.

The electrophoretic mobility (EPM) and size of the studied Si-NCs were assessed prior to each transport and deposition experiment in the presence of monovalent (KCl) and divalent (CaCl₂) salts (Table 5.1). All the Si-NCs studied are negatively charged under the experimental conditions (pH 5, solution IS), likely due to the presence of carboxyl groups in the surface cappings (C₃, C₇, C₁₁). As the IS increases, compression of the electrical double layer results in lower EPM values^{37,38}. Between 1 and 100 mM KCl, more important variations in the EPM values are observed for Si-NCs capped with C₃ (*i.e.*, EPM varies between -2.3 and -0.3 μ m·cm/V·s), as compared to particles capped with the longest chain length, namely C₁₁ (where EPM only varies between -1.1 and -0.7 μ m·cm/V·s). Variations in the electrokinetic properties of surface-modified ENPs as a function of IS are commonly associated with the properties of the capping ligands at the 148 particle surface⁴. Whereas large variations in the EPM values might indicate poorly capped particles (*i.e.*, C₃, C₇), low variations are likely related to "soft" particles, where surface cappings are homogenously adsorbed (*i.e.*, C_{11})³¹.

In divalent salt (CaCl₂), the variations in the measured EPM over the range of IS are more significant than in monovalent salt regardless of the chain length used. The EPM changes from -2.0 to $-0.7 \ \mu m \cdot cm/V \cdot s$ for the C₃, from -1.3 to $-0.4 \ \mu m \cdot cm/V \cdot s$ for the C₇ and from -0.9 to $-0.03 \ \mu m \cdot cm/V \cdot s$ for the C₁₁ when the IS increases from 0.3 to 3mM CaCl₂.Moreover, all the Si-NCs reach (or nearly reach) their point of zero charge (PZC) at 3 mM IS CaCl₂. In Table 5.1, EPM measurements are converted to zeta potential and these values are used later in this manuscript to interpret the deposition results within the context of DLVO theory of colloidal stability³⁹.

Table 5.1. Electrokinetic properties and particle size of Si-NCs as a function of solution IS in KCl or CaCl₂ at pH 5 determined using different techniques. Data represents the mean diameter \pm standard deviation (d_p).

electrolyte	ionic strength	Si-NC	electrophoretic mobility	zeta potential	particle size (d_p)		
					DLS	NTA	SIOS
	(mM)		(µm.cm/V.s)	(mV)	(nm)	(nm)	(nm)
KCI	1		-23+01	-42 + 2	86 + 56	72 + 4	
	10		-2.0 ± 0.1	-72 1 2	478 ± 151	12 1 4	
	30	C.	-12 ± 0.2	-17 + 2	578 + 221	253 + 33	
	50	- 3	-0.9 ± 0.1	-13 ± 2	979 ± 460	245 ± 189	766 ± 43
	100		-0.7 ± 0.1	-10 ± 1	703 ± 261	278 ± 245	862 ± 53
KCI	1		-1.8 ± 0.2	-37 ± 5	48 ± 14	97 ± 47	
	10		-1.6 ± 0.1	-25 ± 1	135 ± 36		
	30	C ₇	-0.6 ± 0.1	-8 ± 2	847 ± 185	179 ± 42	
	50		-0.7 ± 0.2	-9 ± 2	949 ± 308	163 ± 85	140 ± 20
	100		-0.7 ± 0.1	-11 ± 2	761 ± 146	362 ± 174	150 ± 10
KCI	1		-1.1 ± 0.1	-20 ± 1	92 ± 35	98 ± 34	
	10		-1.1 ± 0.3	-18 ± 4	70 ± 40		
	30	C ₁₁	-1.0 ± 0.5	-15 ± 8	69 ± 12	96 ± 10	
	50		-0.9 ± 0.3	-14 ± 5	85 ± 25	92 ± 68	140 ± 16
	100		-0.7 ± 0.2	-10 ± 3	122 ± 23	174 ± 86	155 ± 8
CaCl ₂	0.3		-2.0 ± 0.1	-37 ± 3	117 ± 10	140 ± 6	
	1.5	C ₃	-1.2 ± 0.1	-18 ± 2	1125 ± 339	278 ± 32	
	3		-0.7 ± 0.1	-11 ± 2	1066 ± 125	268 ± 70	
CaCl ₂	03		-13+04	-18 + 6	31 + 9	62 + 13	
	1.5	C7	-0.4 ± 0.2	-5 ± 3	810 ± 273	135 ± 5	
	3	,	-0.6 ± 0.1	-9 ± 1	1246 ± 393	265 ± 41	
CaCla	0.3		-09+01	-13 + 1	97 + 10	89 + 35	
	1.5	С.,	-05 + 05	-7 + 7	481 + 224	162 ± 45	
00012	3	~11	0.0 ± 0.3 0.0 ± 0.7	0 ± 10	930 ± 671	102 ± 40 202 ± 41	

Particle size plays an important role in the transport, fate, and bioavailability of ENPs in aquatic environments. Hence, to interpret the observed transport and deposition behavior of the Si-NCs, an appropriate selection of size characterization methods is required²⁶. It has been shown that the length of the ligand chain significantly influences the colloidal stability (*i.e.*, aggregation) of Si-NCs in polar solvents. Clark et al.³¹ determined that the size of the "as synthesized" capped Si-NCs used here was on the order of 3 nm, and after dispersion in DI, Si-NCs capped with C₃ and C₇ experienced aggregation. In Table 5.1, the mean diameters (d_p) for each Si-NC suspended in monovalent (KCl) and divalent electrolytes (CaCl₂) using three different methods (i.e., DLS, NTA, and SIOS) are shown. DLS measurements show that the d_p of Si-NCs capped with C₃ and C₇ increases by one order of magnitude within the range of IS investigated (1-100 mM KCl). In contrast, the particle coated with C_{11} is more stable over the range of IS. NTA measurements generally confirm the trends observed by DLS whereby Si-NCs capped with C_3 and C_7 exhibit larger d_p as compared to those capped with C_{11} . Nonetheless, the mean hydrodynamic diameters obtained by NTA are typically smaller than those obtained by DLS (except for C_{11} suspended in KCl), and these discrepancies are likely due to the interpretation of particle size with each technique. Whereas DLS measurements are influenced by the presence of small amounts of aggregates or dust particles (*i.e.*, scattered light intensity is proportional to d_p^{6}), NTA tracks individual particles and the presence of a few aggregates in suspension is not expected to bias the results as strongly as in DLS²⁶. However, because the resolution of NTA is limited by the refractive index of the material and
larger particles or aggregates (~1 µm) are not tracked by this technique⁴⁰, the use of a third method is of interest to support the characterization of the Si-NCs^{26,41}. SIOS is a recently introduced non-light scattering technique which promises to improve the size assessment of polydisperse samples based on the Coulter principle³⁴. In SIOS, particles suspended in electrolyte pass through membranes with size tunable pores when a fixed electrical potential is applied. Changes in the ionic current as a result of particles traversing the pores are defined as "blockades" and their amplitude can be related to the size of the particle passing through³⁴. In Table 5.1, mean sizes determined by SIOS at 100 mM KCl reveal significant aggregation for the particle coated with C₃ ($d_p \sim 862$ nm), and smaller sizes for C₇ ($d_p \sim 150$ nm) and C₁₁ ($d_p \sim 155$ nm).Figure 5.1shows a comparison of Si-NC size distributions measured at 100 mM KCl using the three methods (DLS, NTA and SIOS) that may help to clarify the differences in the mean size of the suspensions (Table 5.1).



Figure 5.1 Particle size distributions determined by DLS, NTA and SIOS of Si-NCs capped with (a) C₃, (b) C₇ and (c) C₁₁ in 100 mM KCl at pH 5.

In Figures 5.1a and 5.1b, Si-NCs capped with C₃ and C₇ exhibit broad size distributions and consequently, the mean sizes obtained are expected to be biased by the limitations mentioned above for the DLS and NTA techniques^{26,40}. The particles capped with C₁₁ (Figure 5.1c) clearly exhibit normal distributions with comparable mean sizes for the ensemble of characterization techniques corroborating their stability in aqueous suspensions. These results are in agreement with previous studies^{34,41} where sizes determined by SIOS have been compared with different characterization techniques; namely DLS, NTA, and transmission electron microscopy (TEM) measurements. Whereas the aggregation exhibited by Si-NCs capped with C₃ and C₇ is likely the result of lower electrostatic double layer repulsion at the high salt concentration (100 mM IS)^{37,38}, the enhanced colloidal stability exhibited by C₁₁ is likely due to non-

DLS size measurements conducted with Si-NCs suspended in CaCl₂ electrolyte (Table 5.1) reveal that considerable particle aggregation occurs, regardless of the chain length of the capping ligand (Table 5.1). For instance, the presence of 1.5 mM CaCl₂ seems to be sufficient to reach the critical coagulation concentration (CCC), which is supported by the large standard deviations observed at this IS. Notably, NTA measurements do not appear to track the aggregates⁴⁰, and due to the low conductivity of the particle suspensions, SIOS is not feasible at the studied range of IS. The results obtained here are consistent with previous studies where considerable aggregation of carboxyl-modified ENPs was observed, even in the presence of low concentrations of divalent salt^{14,16,42}.

5.3.2 Transport of capped Si-NCs in saturated sand packed columns.

Figure 5.2 shows representative particle breakthrough curves for experiments conducted with Si-NCs suspended in KCl. For all three Si-NCs, the measurements show a decrease in the column effluent particle concentration with increasing solution IS. However, the capping ligand with the longest chain (C₁₁) seems to improve the mobility of Si-NCs up to a moderate salt concentration (30 mM IS). For instance, in experiments conducted at 30 mM KCl, the particles capped with C₁₁ exhibit lower retention (~24%) as compared to those capped with C₃ (~38%), and C₇ (~56%). Yet, at 100 mM KCl, more than 50% of all the Si-NCs are retained. Figure 5.3 summarizes the calculated attachment efficiencies (α) for the surface modified Si-NCs when suspended in monovalent or divalent electrolytes. For the sake of clarity, the α values were determined using only the d_p obtained by DLS measurements (Table 5.1).



Figure 5.2 Representative breakthrough curves for transport experiments conducted with Si-NCs suspended in KCl at pH 5 in columns packed with clean quartz sand. The column diameter is 1 cm and the fluid approach velocity is 1.06×10^{-4} m/s.



Figure 5.3. Attachment efficiencies (α) calculated using eq 1 for Si-NCs capped with: (\Box) C₃, (\circ) C₇, and (\diamond) C₁₁ suspended in electrolyte over the range of IS (pH 5). Experiments were conducted using columns packed with clean quartz sand, and Si-NCs were suspended in (a) KCl (open symbols) or (b) CaCl₂ (full symbols).Dashed lines are included as eye guides, and error bars represent standard deviations.

When suspended in KCl (Figure 5.3a), the α values for the Si-NCs increase significantly over the range of IS (α values varied from 0.003 to 0.51 for the C₃; from 0.002 to 0.59 for the C₇; and from 0.01 to 0.24 for C₁₁). Notably, α does not reach the theoretical mass-transfer limited value (~1) even at the maximum IS (100 mM) for any of the Si-NCs investigated. Based on the physicochemical characterization of the Si-NCs (Table 5.1) the EPM values decrease with increasing KCl concentration and, consequently, the Si-NCs experience less electrostatic repulsion as they approach the sand grain surface, thereby leading to an increase in particle deposition³⁹.

To determine the influence of divalent cations on the transport and deposition behavior of the Si-NCs, column experiments were also carried out with Si-NCs suspended in CaCl₂ electrolyte. Unlike experiments conducted in KCl, all the particles exhibit limited transport at low IS of the divalent salt solution (1.5— 3 mM IS CaCl₂) (Figure 5.4). These trends are likely linked to the ability of divalent cations (such as Ca^{2+}) to complex with negatively charged groups on the Si-NC surface thereby decreasing the surface potential and the stability of the particle suspension (Table 5.1) as reported by Zhang, et al.⁴³. The drastic increase in α at 1.5 mM IS CaCl₂ (Figure 5.3b) and the high α values (>1) at 3 mM IS CaCl₂ suggest that the particles are retained by a mechanism of physical straining in the packed column^{14,35}. Physical straining occurs when ENPs aggregate to sizes that are larger than the pore spaces in the granular matrix. This hypothesis is supported by the physical properties of the particles (significant aggregation occurs at this IS, Table 5.1), and the porous medium; namely the transport experiments were conducted in fine silica sand ($d_c = 256 \mu m$) and the angularity of the sand grains is high (roundness factor ~ 0.67), which increases the likelihood of physical straining^{7,14,27,44}.



Figure 5.4. Representative breakthrough curves for transport experiments conducted with Si-NCs suspended in CaCl₂ at pH 5 in columns packed with clean quartz sand. The column diameter is 1 cm and the fluid approach velocity is 1.06×10^{-4} m/s.

To better understand the mechanisms governing the particle deposition behavior in monovalent salt solution, interaction energy profiles between the particles and the grain surface were calculated using classical DLVO theory^{37,38}. Within the context of classical DLVO theory (which does not take into account the contribution of steric forces), solution chemistry and particle (or aggregate) size have important effects on the height of the repulsive energy barrier (Φ_{max}), as well as on the depth of the secondary energy well ($\Phi_{2^{\circ}\text{min}}$)⁴⁵. Hence, in Table 5.2, Φ_{max} and $\Phi_{2^{\circ}\text{min}}$ are presented for each capped Si-NC as a function of IS. The total interaction potentials were calculated as the sum of van der Waals forces (VDW) and electrical double layer interactions (EDL) using the linear superposition approximation and assuming the system can be approximated by a sphere-plate geometry¹².

electrolyte	ionic strength (mM)	Si-NC	Φ_{max}	$\Phi_{2^\circ\text{min}}$
KCI	1 10 30 100	C ₃	108 100 76 NB	0.0 2.2 8.4
KCI	1 10 30 100	C ₇	45 29 NB NB	0.0 0.6
KCI	1 10 30 100	C ₁₁	33 7 NB NB	0.0 0.0

Table 5.2. Calculated classical DLVO interaction energy parameters (Φ_{max} and $\Phi_{2^{\circ}\text{min}}$) reported in units of $k_{\text{B}}T$ for the Si-NCs interacting with quartz sand.

To calculate the retarded VDW forces, a Hamaker constant of 1.92×10^{-20} J was selected for the nanoparticle–water–quartz system (*Senden and Drummond*, 1995), whereas for EDL interactions, constant-potential values were calculated using the zeta potential of the Si-NCs (Table 5.1) and the quartz sand in place of their respective surface potentials. The values of zeta potential used for the quartz sand were taken from Redman *et al.* (2004) (as they were obtained at comparable solution chemistries as those used in this study). The DLS measured particle sizes of the Si-NCs (d_p , Table 5.1) were used in the DLVO calculations. *NB:* No energy barrier predicted.

In Table 5.2, the calculated height of the interaction energy barrier $(\Phi_{\rm max})$ for the three Si-NCs generally decreases as the IS increases. Likewise, each Si-NC exhibits greater retention in the sand-packed column with increasing salt concentration (Figure 5.3). Based on these simple, idealized classical DLVO calculations, the Si-NCs capped with the longest alkyl chains (C_{11}) are expected to deposit to a greater extent onto the sand surface than the C_7 , and the C_7 are in turn expected to deposit more than the C₃, for which greater energy barriers are predicted at any given IS. However, this is not always the case; e.g., in 10 mM KCl, where $\alpha C_3 > \alpha C_7 > \alpha C_{11}$. This observation can be attributed to three main factors: (i) the particle capped with C_3 forms fairly large aggregates and may thus deposit in a secondary energy well ($\Phi_{2^{\circ}min}$) at a separation distance greater than that of the energy barrier⁴⁵ (Table 5.2), (*ii*) the larger C_3 and C_7 aggregates may be retained by physical straining, and (*iii*) the deposition of the Si-NCs capped with longer alkyl chains (C_7 and C_{11}) is hindered by a repulsive steric force (which is not accounted for in the DLVO calculations). Interestingly, in 30 mM KCl, $\alpha C_7 >$ $\alpha C_3 > \alpha C_{11}$. At this IS, DLVO calculations predict no energy barrier for the C₇ particle, yet the attachment efficiency does not reach the mass transport limited rate (~1) suggesting that the longer alkyl chain at the particle surface may be exerting some steric repulsion upon approach to the sand surface. The lower energy barriers predicted for the particle capped with C_{11} do not correlate with the low attachment efficiencies (α) measured in the transport experiments. These results suggest that the longest alkyl-chain (C_{11}) exerts significant steric repulsion thereby hindering particle deposition on the quartz sand 3,4 .

Certain surface modifiers (e.g., polymers, polyelectrolytes, surfactants) are known to inhibit the attachment of nanoparticles on sand or model silica surfaces as compared to their bare counterparts^{4,14,16}. However, some studies have demonstrated that the stabilizing effects exerted by surface coatings are not always concordant^{7,46}. Saleh et al.⁷ used packed column experiments to study the transport of zerovalent iron nanoparticles (nZVI) capped with different surface modifiers. Whereas low molecular weight surfactants (sodium dodecyl benzene sulfonate) did not effectively enhance the mobility of nZVI, particles modified with high molecular weight polymers exhibited greater mobility due to electrosteric stabilizing effects. In another study, the transport of silver nanoparticles coated with different molecules (citrate, polyvinylpyrrolidone, and gum arabic) was studied in columns packed with glass beads⁴⁶. These authors observed an enhanced attachment of silver nanoparticles to glass surfaces when the hydrophobicity of the particle coatings and surfaces increased, despite the electrosteric repulsion afforded by the surface modifier. The results of our column study with the 3 Si-NCs suggest that the longest alkyl chain exerts considerable electrosteric repulsion upon approach to the sand surface; this mechanism also impairs the deposition of the C_7 particle, but not to the same extent. Overall, the data show that a complex interplay of DLVO and non-DLVO forces and physicochemical processes contribute to the transport and deposition behavior of the surface-modified Si-NCs.

5.3.3 Deposition of Si-NCs in QCM-D.

In the second part of this study, SiO₂ coated sensors mounted in a QCM-D were used as model collectors representing the surface of the quartz sand grains used in the column experiments. Values of the Si-NC deposition rate (r_d) when suspended in KCl or CaCl₂ were determined from initial changes in frequency shifts ($\Delta f_{(n)}$) as a function of time (eq. 5.3) and are reported in Figures 5.5a and 5.5b, respectively. The data are presented in terms of mass units (*i.e.*, ng/cm²·min) using the Sauerbrey relation (eq. 5.2) and frequency responses from the third overtone (*i.e.*, $\Delta f_{(3)}$). Moreover, useful insights into the Si-NC deposition behavior can be obtained by comparing the output parameters assessed by QCM-D; namely, frequency ($\Delta f_{(3)}$) and dissipation shifts ($\Delta D_{(3)}$)^{23,47}. Hence, in Figure 5.5c, the ratio $-\Delta D_{(3)_slope}$ to $\Delta f_{(3)_slope}$ (equivalent to $\Delta D_{(3)}$ and $\Delta f_{(3)}$, during the initial phase of deposition). ENPs coated with polymers and aggregated ENP systems dissipated more energy than non-coated particles and stable colloidal suspensions resulting in higher - $D_{3_slope}/f_{(3)_slope}$ ratios ²³.

In experiments conducted in KCl, the Si-NCs capped with the longer alkyl chain lengths (C₇, C₁₁) exhibit very little deposition onto the SiO₂ surface in the QCM-D, whereas the C₃ particle deposition rate (r_d) increases with increasing salt concentration up to 30 mM IS (Figure 5.5a). Similarly, in Figure 5.5c, the ratio - $D_{(3)_slope}/f_{(3)_slope}$ tends to decrease for all the Si-NCs, which suggests that the particles are more rigidly deposited onto the SiO₂ surface at the highest salt concentration. The ratio - $D_{(3)_slope}/f_{(3)_slope}$ also reveals that the particles capped

with longer alkyl-chain cappings (C₇ and C₁₁) dissipate more energy (higher - $D_{(3)_slope}/f_{(3)_slope}$) and are consequently more loosely attached to the quartz sensor, as compared to the particles with C₃. Hence, the deposition kinetics (r_d) of Si-NCs capped with the shortest alkyl chain capping (C₃) is more sensitive to changes in IS and these particles are also more strongly bound to the SiO₂ surface (lower - $D_{(3) slope}/f_{(3) slope}$).

Interestingly, when comparing the deposition behavior of the Si-NCs using the two different experimental systems (QCM-D and packed columns), a different trend in deposition behavior is observed. In the packed column (Figure 5.3a), the C₇ particle experienced greater retention than the C₃ and C₁₁ (at 30 and 100 mM KCl). This observation can be attributed to the important contribution of physical straining in the retention of the aggregated Si-NCs in the packed granular matrix; this mechanism is absent in the QCM-D where particles deposit onto a flat surface. Such differences in deposition behavior can also be observed in CaCl₂ experiments (Figures 5.3b, and 5.5b, respectively). All the Si-NCs reach the theoretical maximum deposition rate at 1.5 mM CaCl₂ in the packed columns (α =1); however, they exhibit much lower deposition rates in the QCM-D when suspended in the same electrolyte.

In agreement with these results, other QCM-D studies have reported that when particle aggregation is highly favorable, a lessened convective-diffusive transport of aggregated particles to the surface can result in lower measured r_d values^{16,18,23}. To test this hypothesis, experimental deposition rates (r_d) were normalized with respect to the theoretical particle deposition rate (r_d^{SL}) under the assumption of pure convective-diffusive transport¹² (Figure 5.5). At high solution IS, Si-NC normalized deposition rates (r_d/r_d^{SL}) should approach unity $(\sim 1)^{23,24}$. Yet, in experiments conducted with highly aggregated Si-NCs (100 mM KCl and at 1.5 mM CaCl₂, Table 5.1), we observe, that in disagreement with the proposed hypothesis, the measured deposition rates (r_d) are considerably lower than the theoretical deposition rates (r_d^{SL}) .



Figure 5.5. Normalized retention presented as a ratio of the experimental deposition rate (r_d) to the theoretical particle deposition rate (r_d^{SL}) for QCM experiments conducted in (a) KCl (open symbols) and (b) CaCl₂ (closed symbols). In all the cases, r_d was determined from 3_{rd} overtone measurements and r_d^{SL} was estimated using the Smoluchowski-Levich approximation^{12,24} with parameters determined from DLS measurements (Table 5.1). In all the cases data represent the mean \pm standard deviation.(c) The ratio $-\Delta D_{3_slope}/\Delta f_{(3_slope}$ for all the Si-NCs as a function of IS in KCl. The dashed line represents the limit of applicability for the Sauerbrey model according to Q-Sense. In all the cases, data represent the mean \pm standard deviation.

The interpretation of aggregated nanoparticle systems using QCM-D has proven to be challenging^{21,22,30}, and in some cases, positive frequency shifts have been reported, which are counterintuitive to the principle of QCM-D as a sensitive mass sensor^{19,30}. Positive frequency shifts can be explained in the context of "coupled resonance theory"⁴⁸. In brief, changes in frequency (*i.e.*, $\Delta f_{(n)}$) can be either negative or positive depending on how well the particle couples to the oscillation of the sensor surface during the measurement. Whereas firmly coupled particles decrease the crystal resonance frequency as per conventional massloading theory (*i.e.*, inertial loading), weakly coupled particles possess a resonance of their own that, depending on the bond stiffness, might increase the crystal resonance frequency (*i.e.*, elastic loading)³⁰. The latter case has been shown to occur when micron-sized particles deposit on a QCM sensor^{19,36,49}, and in some instances, a transition from inertial loading (negative frequency shifts) at low overtones (n) to elastic loading (positive frequency shifts) at high overtones(n)can be observed along with a maximum in the dissipation factor $(\Delta D_n)^{30,36}$.In Figure 5.6a and 5.6b, we have plotted the frequency $(\Delta f_{(n)})$ and dissipation (ΔD_n) response, at different overtones (n) for Si-NCs capped with C_{11} in CaCl₂. The results can be compared with the particle size distributions and d_p values obtained using DLS (Figure 5.6c).



Figure 5.6 (a) Normalized frequency shifts $(\Delta f_{(n)})$ and (b) Dissipation shifts (ΔD_n) from experiments conducted with Si-NCs capped with C₁₁ in CaCl2 at different overtones (n = 3, 5, 7, 9, 11, 13). The dotted line in (a) indicates a "coupled resonance" response. (c) Particle size distributions for suspended Si-NCs and mean hydrodynamic diameters (d_p) from DLS measurements.

At the lowest IS (0.3 mM CaCl₂), Si-NCs capped with C_{11} are monodispersed ($d_p \sim 97$ nm), and in terms of frequency shifts, all the overtones (n = 3, 5, 7, 9, 11, 13) exhibit proportional and "negative" responses, in agreement with Sauerbrey loading³⁶. As the IS increases to 1.5 mM CaCl₂, the Si-NCs in electrolyte experience aggregation and the distributions become more polydisperse ($d_p = 481 \pm 224$ nm). At this condition, values of frequency ($\Delta f_{(n)}$) and dissipation (ΔD_n) both decrease in comparison to those measured at lower IS, but since the frequency shifts are negative over the entire range of overtones (n=3-13), this observation is likely due to a decrease in convective-diffusive transport^{18,23,24}. At 3 mM CaCl₂, the deposition of the polydispersed Si-NCs (d_p = 930 ± 671 nm) results in mostly positive frequency shifts (Figure 5.6a). At this IS, higher overtones (n = 7, 9, 11, 13) become positive as per "elastic loading", whereas lower overtones (n = 3 and 5) remain negative or close to zero as per "inertial loading". Also, we observe an increase in dissipation (ΔD_n) when compared to the lower IS of 1.5 mM (Figure 5.6b). As mentioned above, this is a clear indication that the traditional "Sauerbrey-type" response can gradually transition to a "coupled resonance-type" response as particle aggregation occurs. Applying this same analysis to all the experiments conducted in our study (Table 5.3), we note that this transition from elastic to inertial loading is likely linked to the mean size of the particle aggregates, where a critical average size $(d_p \sim 700)$ nm) appears to be the limit for this specific system.

			Size			QCM-D					Size			QCM-D				
Si-NC	electrolyte	ionic strength		d _p			r _d		Coupled Resonance?	electrolyte	ionic strength		d _p			r _d		Coupled Resonance?
		(mM)	(nm	ı)	(ng/c	m²	.min)	$\Delta f_{(n)} > 0$		(mM)	(nm	ı)	(ng/c	m²	.min)	$\Delta f_{(n)} > 0$
C ₃	KCI	1	86	±	56	3	±	1	no		0.3	117	±	10	186	±	129	no
		10	478	±	151	88	±	2	no	CaCl ₂	1.5	1125	±	339	42	±	28	yes
		30	578	±	221	91	±	9	no		3	1066	±	125	14	±	3	yes
		100	703	±	261	79	±	9	yes									
C ₇	KCI	1	48	±	14	2	±	3	no		0.3	31	±	9	305	±	15	no
		10	135	±	36	1	±	0	no	CaCl ₂	1.5	810	±	273	18	±	16	yes
		30	847	±	185	5	±	3	no		3	1246	±	393	2	±	1	yes
		100	761	±	146	6	±	1	yes									
C ₁₁	KCI	1	92	±	35	0	±	0	no		0.3	97	±	10	15	±	16	no
		10	70	±	40	20	±	27	no	CaCl ₂	1.5	481	±	224	2	±	1	no
		30	69	±	12	30	±	23	no		3	930	±	671	1	±	2	yes
		100	122	±	23	10	±	6	no									

Table 5.3. Comparison of particle size (dp - DLS) and the deposition rates of Si-NCs calculated from QCM-D (rd) experiments

The deposition rates of Si-NCs calculated from QCM-D (r_d) experiments were obtained from frequency shifts obtained from the third overtone (n = 3). In the last column, frequency shifts ($\Delta f_{(n)}$) obtained at different overtones (n = 3, 5, 7, 11, 13) were compared and when positive responses were observed (*i.e.*, coupled resonance) it has been indicated.

5.4 Conclusions

Two experimental techniques, namely column transport studies and QCM-D, were used to investigate the deposition behavior of Si-NCs onto sand surfaces and provided useful insights into the role of particle surface cappings (carboxylic acids of different alkyl-chain lengths) and aggregate size on ENP deposition kinetics. Experiments conducted with packed columns show that the mobility of Si-NCs varies as the alkyl-chain length increases. The deposition behavior of particles coated with shorter chain lengths (C_3 C_7) appears to be controlled by electrostatic mechanisms, namely retention in primary energy minimum and upon aggregation, in a secondary energy well. Physical straining also contributes to the extent of retention of the aggregated C₃ and C₇ Si-NC suspensions in higher IS KCl and in CaCl₂. Yet, the deposition behavior of Si-NCs capped with the longest alkyl chain (C_{11}) is controlled by electrosteric interactions. QCM-D provides further insight on nanoparticle deposition behavior, whereby the ratio of the two output parameters (frequency and dissipation) indicates how rigidly the nanoparticles are bound to the SiO₂ surface. However, based on the obtained results, interpretation of ENP deposition behavior by QCM-D is limited by the presence of large aggregates ($d_p \sim 700$ nm), which give rise to non-Sauerbrey behavior. Future studies of nanoparticle deposition using QCM-D should consider the response of all the overtones (n) to adequately determine whether the acquired frequency shifts are proportional to the deposited mass. The current combined approach can be a useful method for investigating ENP-surface interaction phenomena in an effort to increase our knowledge of the roles that particle and

collector surface coatings and water chemistry play in the transport and fate of ENPs in natural and engineered aquatic environments.

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The goal of this thesis was to experimentally evaluate the mobility of surfacemodified QDs in systems representative of the natural soil matrix and engineered granular filtration processes. Two experimental approaches commonly used to evaluate the transport and deposition of ENPs were used here; namely columns packed with granular materials and a QCM-D. The QDs used were stabilized with different surface coatings (*e.g.*, polymers, polyelectrolytes, and carboxylic acids) to make them water dispersible and prevent their aggregation. Hence, to better understand the role of surface modifiers on QD surfaces, polystyrene latex nanospheres were also used as model functionalized ENPs.

In Chapter 2, well-controlled column transport experiments were conducted with two commercial carboxylated QDs and carboxylated polystyrene latex in two different granular matrices, namely quartz sand and loamy sand. This investigation was conducted to identify the role of constitutional heterogeneities of the natural soil matrix in the mobility of ENPs. The results obtained indicated that in quartz sand, regardless of the surface coating used to stabilize the QDs or the polystyrene latex particle, the three ENPs exhibited comparable mobility in the quartz sand. Yet, in experiments conducted in loamy sand obtained from a farm near Quebec City, Canada, a variable transport potential was observed for each studied ENP. In particular, this study showed that differences in the binding affinities of surface-modified ENPs for specific soil constituents can play a key role in their environmental fate.

Different studies have demonstrated how quartz crystal microbalance (QCM-D) technology can be useful to examine the deposition and release of ENPs onto surfaces representative of the minearologies encountered in aquatic environments. Coated QCM-D sensors are considered to represent the surface of an aquifer or filter grain that may be encountered by ENPs. Hence, in Chapters 3 and 4, QCM-D was used to examine the deposition kinetics of carboxylated QDs onto SiO₂, Al₂O₃, and natural organic matter coated surfaces over a broad range of solution chemistries.

In Chapter 3, experiments onto SiO₂ surfaces were conducted with a carboxyl terminated CdTe/CdS QD over a wide range of solution chemistries; namely monovalent (KCl) and divalent salts (CaCl₂) and different pH values. In the presence of CaCl₂, the CdTe QD exhibited significantly higher deposition rates; as compared to experiments in KCl. Solution pH also influenced the deposition behavior, as lower pH resulted in an increase in the deposition rates. The rate of QD release from the surface following a change in solution chemistry was also monitored using QCM-D by injection of DI water. The release rates were considerably lower when QDs were deposited in the presence of CaCl₂. In experiments conducted above the critical coagulation concentration, the deposition rates (*i.e.*, Smoluchowski–Levich approximation) these variations were attributed to a decrease in the convective-diffusive transport of the QDs to the SiO₂ surface.

The deposition of QDs and model polystyrene particles onto bare Al₂O₃ surfaces was studied in Chapter 4. Experiments conducted with QCM-D revealed that polymers or polyelectrolytes used to coat QDs decreased the deposition rates by at least one order of magnitude as compared to model polystyrene latex nanoparticles. Adsorption of NOM on the surface of the collector or particle surfaces significantly decreased the retention in all the cases. The ratio of the two QCM-D output parameters, frequency and dissipation, revealed key structural information of the ENP-collector interface; namely, on bare Al₂O₃, the latex particles were rigidly attached as compared to the more loosely attached QDs.

In addition to the experiments conducted with Cd-based QDs, in Chapter 5, the transport and deposition behavior of Si-based QDs capped with organic acids of varying alkyl-chain length (*i.e.*, propionic, heptanoic, and undecanoic acid) was evaluated using water saturated sand packed columns and a QCM-D equipped with SiO₂ coated sensors. Experiments were conducted over a broad range of solution IS, and cation type (*i.e.*, K⁺, and Ca²⁺). In experiments conducted in K⁺, the results obtained in sand columns and QCM-D were comparable; an increase in IS resulted in less repulsive interactions between the Si-NCs and quartz (*i.e.*, SiO₂) surfaces, thereby enhancing the nanoparticle deposition rates. Yet, differences in deposition between each type of surface capping were more pronounced in QCM-D experiments than in sand columns. In contrast, in experiments conducted in Ca²⁺, particle aggregation resulted in an increase in particle retention in sand packed columns, whereas in QCM-D experiments a drastic decrease in the deposition rates was observed. Although QCM-D

experiments might be more suitable than column experiments to gain a mechanistic understanding of the deposition behavior of ENPs, it was determined that QCM-D studies may be limited to adequately assess the mass of aggregated ENPs.

To date, a majority of the published ENP transport and deposition studies have involved bare or non-functionalized particles. However, most ENPs (including QDs) are manufactured with surface coatings or may acquire natural coatings once released into the environment due to adsorption of NOM. This study is thus important to improve our understanding and adequately predict the fate of ENPs in natural aquatic systems. Moreover, because the environmental assessment of ENPs is complex, as trace amounts of particles will be dispersed in highly heterogeneous matrixes, studies conducted with packed-bed columns and QCM-D are useful laboratory methods for investigating nanoparticle-surface interactions. Such studies increase our knowledge of the roles that particle and collector surface coatings and water chemistry play in the transport and fate of ENPs in natural and engineered aquatic environments.