Aggregation and Deposition Behavior of Carbon-Based Nanomaterials in Aquatic Environments

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Engineered Carbon-Based Nanomaterials

- Exponential growth in production and potential applications
- Unique properties (shape, surface charge, reactivity)
- Environmental and health impacts are not known
Aggregation and Deposition Behavior Determines Fate and Transport

- Influences rate of settling and transport
- Removal from aqueous phase
- May influence reactivity and toxicity
Complex Interactions in Aquatic Systems

Ions
Na\(^+\)
Cl\(^-\)
Ca\(^{2+}\)
Mg\(^{2+}\)

NOM, biomolecules, minerals/suspended solids

Nanomaterials
Aggregation Kinetics of Fullerene Nanoparticles
Fullerene Nanoparticles

Buckminsterfullerene $C_{60}$  \hspace{2cm} n$C_{60}$
Ordered Structure of $C_{60}$ Molecules

Buckminsterfullerene $C_{60}$  $\rightarrow$  n$C_{60}$

10 nm scale
Two Synthesis Methods

- **Sonicated C\textsubscript{60} Nanoparticles (Son-C\textsubscript{60})**
  - Fullerene (99.9% purity)
  - Dissolve fullerene in toluene
  - Sonicate with water and ethanol for 3 hr
  - Filter with 0.45 then 0.2 µm filters

- **Aqueous C\textsubscript{60} Nanoparticles (Aq-C\textsubscript{60})**
  - Stirring fullerene in deionized water for 40 days before filtration
Physical Characterization

Son-C$_{60}$

$R_H = 50.5$ nm

Aq-C$_{60}$

$R_H = 83.1$ nm
Physical Characterization

Son-C$_{60}$  
Aq-C$_{60}$
Electrophoretic Mobility (EPM) in KCl

- Negatively charged
- Aq-C$_{60}$ more negatively charged than Son-C$_{60}$
- EPM becomes less negative as KCl concentration increases
ALV Light Scattering Setup

- Dynamic light scattering to derive hydrodynamic radius
- YAG laser with wavelength of 532 nm
- Scattered light intensity measured at 90° from incident beam
Time-Resolved Dynamic Light Scattering

Initial aggregation kinetics:

\[ k_A \propto \left( \frac{dr_h(t)}{dt} \right)_{t \to 0} \]

Attachment Efficiency or Inverse Stability Ratio:

\[ \alpha = 1/W = \frac{k_A}{k_{A, \text{fast}}} \]
Aggregation Kinetics in KCl

- Classic slow and fast aggregation regimes
- Aq-C$_{60}$ are much more stable (CCC of 200 mM)
Aggregation Kinetics in KCl and CaCl$_2$

Inverse Stability Ratio, 1/W

KCl Conc. (M) vs. pH 5.5

- Son-C$_{60}$
- Aq-C$_{60}$

CaCl$_2$ Conc. (M) vs. pH 5.5

- Son-C$_{60}$
- Aq-C$_{60}$

Concentrations:
- 50 mM KCl
- 200 mM KCl
- 4.3 mM CaCl$_2$
- 6.0 mM CaCl$_2$
Increased Stability in Humic Acid with NaCl

- NaCl concentration = 650 mM
- pH 8

Chen and Elimelech, *J. Colloid Interface Sci.* **2007**, *309*, 126-134
Increased Stability in Humic Acid with NaCl and MgCl₂

- NaCl concentration = 650 mM
- pH 8

Chen and Elimelech, *J. Colloid Interface Sci.* 2007, 309, 126-134
Steric Stabilization with Humic Acid in NaCl and MgCl₂

- Electrophoretic mobility (EPM) similar with and without humic acid
- Indication of steric stabilization
Enhanced Aggregation at High CaCl$_2$ Concentrations

- CaCl$_2$ concentration = 40 mM
- pH 8
Enhanced Aggregation at High CaCl$_2$ Concentrations

- At 1 mg/L TOC, enhanced aggregation occurs above 10 mM CaCl$_2$
Humic Acid Clusters Bridge Fullerene Nanoparticles

100 mM MgCl$_2$

40 mM CaCl$_2$
Humic Acid Clusters Bridge Fullerene Nanoparticles

40 mM CaCl$_2$
Aggregation Kinetics of Multi-Walled Carbon Nanotubes (MWNTs)
MWNT Sample Preparation

- 10 mg MWNTs added to 100 mL DI water
- Sonicated for 30 minutes using ultrasonication probe
- Supernatant collected
- Re-sonicated for 5 more cycles (30 minutes each) to obtain final sample
TEM Images of Untreated and Treated MWNTs

- Tubes are bundled and long before treatment
- Sonication debundles and reduces average length
Diameter and length distributions are obtained with TEM.

- Average diameter 18 nm and average length 1.5 μm
Aggregation Kinetics with Monovalent Salt (NaCl)
Classic aggregation behavior with slow and fast regimes
Deposition Kinetics of Fullerene Nanoparticles
Aggregation and Deposition Behavior Determines Fate and Transport

Aggregation

Deposition/Attachment

Mineral Surfaces

Sediment
Quartz Crystal Microbalance (QCM)

Flow Cell:

Sauerbrey relationship:

\[ \Delta m = - \frac{C \Delta f}{n} \]

Silica coating

Quartz crystal

AC

Deposition starts

Frequency Shift (Hz)

Time (min)
Deposition Kinetics

![Graph showing deposition kinetics with frequency shift (Hz) on the y-axis and time (min) on the x-axis. The graph includes lines for 1 mM, 10 mM, and 30 mM concentrations.]
Attachment Efficiency

Deposition attachment efficiency:

\[ \alpha_D = \frac{k_D}{k_{D,\text{fast}}} \]

Favorable (fast) deposition:
Pre-adsorption of +ve charged poly-L-lysine (PLL) on silica surface.
Influence of NaCl and CaCl$_2$ on Deposition Kinetics

- Below CCC, as electrolyte concentration increases – faster deposition through charge shielding
- Towards CCC and above – significant drop in deposition rate
Simultaneous Deposition and Aggregation at Higher Ionic Strength

At 100 mM NaCl:

- Aggregate formation – lower convective-diffusive transport towards silica surface
- Bigger aggregates formed at later stages – deposition rate decreases even more

![Graph showing frequency shift over time with non-linear deposition behavior.](attachment:image.png)
Release of Deposited Nanoparticles

A – Baseline (pH 5.7)

B – Deposition at 30 mM NaCl and 0.6 mM CaCl$_2$ (both $\alpha_D \sim 1$)

C – Rinsing with respective electrolytes

D – Rinsing with 1 mM NaCl

E – Rinsing with DI water

F – Rinsing with DI water (pH 12.3)

Release at Stage F – sudden increase in surface potential of C$_{60}$ nanoparticles and silica surface
Concluding Remarks

- Electrostatic interactions control the aggregation and deposition behavior of carbon-based nanomaterials (CBNs)
- Humic substances stabilize CBNs by electrosteric repulsion
- Under solution chemistries of natural waters, CBNs are stable and thus expected to be mobile
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