NSF Nanoscale Science and Engineering Grantees Conference, Dec 16-18, 2003
Grant #: BES-0210865

The Role of Nano-Scale Colloids in Particle Aggregation and Trace Metal Scavenging in Aquatic Systems

NSF NIRT Grant BES-0210865

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Recent observations have demonstrated that nano-scale fibrils rich in acid polysaccharides form a major component of the population of colloidal particles in aquatic systems. These nanoparticles form a matrix for the formation of larger aggregates and can scavenge metal ions from the surrounding water. A better understanding of the structure and properties of these fibrils is crucial for understanding their role in aquatic systems and in predicting the properties of larger aggregates formed from them. This project is concerned with increasing our understanding of the role that extra-cellular polysaccharides play in the formation of aggregates and transport of trace metals and pollutants in aquatic systems (Fig. 1). The project combines both experimental and modeling approaches [1,2].

A major goal of the project is modeling the dynamics of idealized chains interacting with their environment and with other particles. The overall aim of the modeling part of this project is to use the information obtained in the laboratory to model the interactions between fibrils and inorganic colloidal particles. The relative strength of fibril-fibril, fibril-colloid and colloid-colloid interactions helps determine the structure and properties (such as fractal dimension, settling speed) of macroscopic marine aggregates. Modeling interactions between fibrils and inorganic particles in aqueous environments is made easier because we need consider only Brownian motion.

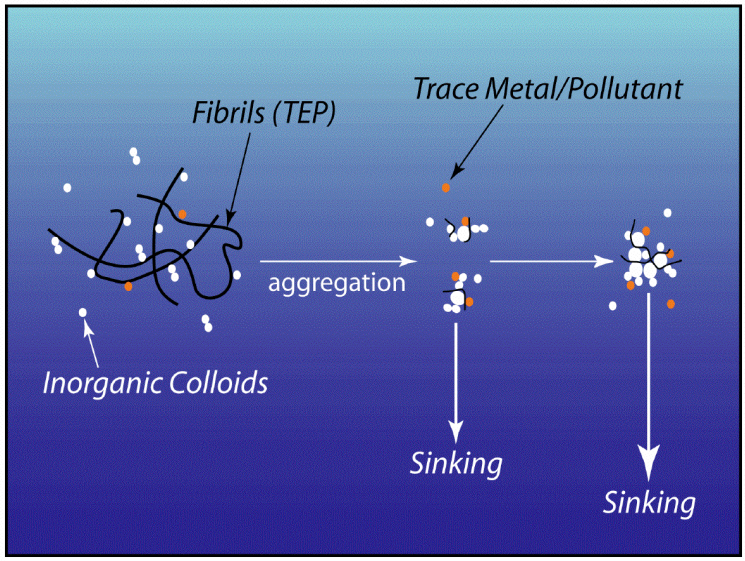

Fig. 1. Diagram representing the major routes of the formation of large scale aggregates from the aggregation of fibrils and colloidal particles.

The modeling effort during the first year of this project has concentrated on developing and testing various algorithms for the computer codes. The core of the computer code [3] we eventually decided to use was developed originally by Prof. Serge Stoll, University of Geneva,

Switzerland and is being extended and modified to simulate the situations we are considering here. The core code represents polymer chains using a "beads on a necklace" model and colloids as spherical particles (Fig. 2). We have ported the code to run on Linux machines using the GNU Fortran compiler, which has led to a dramatic improvement in performance – additional performance increases are expected by porting to the Intel Fortran compiler. In addition, we are developing a series of visualization programs using Matlab that can be used in conjunction with the Fortran code.

Currently, we are extending the code by incorporating periodic boundary conditions (the code currently uses reflective boundary conditions) and improving the efficiencies of the algorithms being used. The next stages of model development will include altering the algorithms that move fibrils to include the effects of different persistence lengths and incorporating variable charge densities along the polymers. The structures obtained from these simulations will be compared with those obtained from the laboratory results so allowing us to concentrate on particular areas of model development.

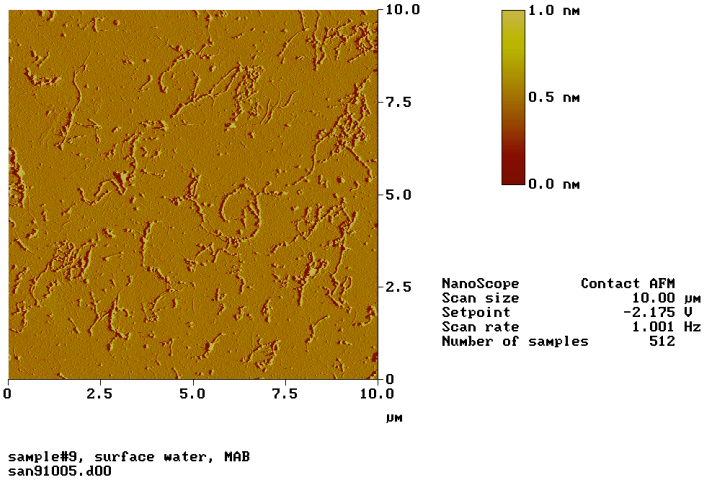

Fig. 2. Atomic Force Microscopy (AFM) image of fibrils and small nano-colloids from the Middle Atlantic Bight with an architecture like "perls on a neckless" [4].

Experiments are underway at TAMUG to extract and purify polysaccharide-rich extra-cellular polymeric substances (EPS) from marine phytoplankton (*e.g.*, *Emiliania huxlei*, *Synechococcus cf elongates*) and bacteria (*e.g.*, *Sagitulla stellata*, *Roseobacter gallaeciensis*) using repeated alcohol precipitation, centrifugation, and enzymatic digestion procedures [5]. The progress of these experiments is monitored by using dissolved organic carbon, carbohydrate and protein analysis, Gas Chromatography-Mass Spectrometry (GC-MS) and Transmission Electron Microscopy (TEM) techniques. Sufficient quantities of EPS were extracted for the laboratory experiments of the collaborating institutions. In addition, Gel Electrophoresis methods are used to improve purity and physicochemical properties (*e.g.*, size, amphiphilicity and stickiness, metal binding strength). Calibration experiments with a flocculator are under way. The information gained during these flocculation experiments can then be compared to the spectroscopic techniques used by the collaborating institutions, and will allow us to further enhance our computer simulations of the coagulation and/or flocculation process, which is in progress as well, even though we are still searching for a post-doc in this area.

The investigation of the aggregation process between small colloidal particles and natural organic fibrils requires first the use of objects that have well defined morphology. Therefore, we have focused our attention on the synthesis of particles that will be used to calibrate future aggregation experiments. In particular, the Northwestern group is testing various recipes to produce mono-disperse (uniformly sized) colloidal suspensions of Fe (down to 10 nm size) and Mn oxides that will be reacted with a variety of extra-cellular polysaccharides. We have prepared hematite particles following classical recipes [6], as well as hydrothermal routes using

microwave oven promoted reactions [7] - by modifying the time of the experiment the size of the particles can be regulated. Currently, we are directing our efforts to the use of sol-gel synthesis methods that should allow us to obtain a more reproducible size. The particles produced are characterized by transmission electron microscopy (TEM), and by photon correlation spectroscopy (PCS) to assess whether they are mono-disperse. In addition, we use X-ray absorption spectroscopy (XAS) to probe the average local environment of Fe and the size of particles [8]. These syntheses are key for a sound interpretation of the scattering and XAS data that will be collected later on. In addition, we have set up a potentiometric titration system that provides us with the ability to determine the surface charges and proton distribution on both colloidal particles and polymeric substances. Currently, we are performing various trials to downsize titrations to small volumes so that we can perform titrations on small aliquots of the EPS material prepared by the TAMUG Group.

One objective of our project is to use a combination of electron microscopy, small angle x-ray scattering (SAXS), and XAS to document better the formation of flocs in natural systems. So far we have been able to synthesize hematite particles that have an average mean hydrated diameter of about 12 nm. Preliminary cryo-TEM observations showed that the particles were relatively mono-dispersed and selected area electron diffraction confirmed the hematite structure. These particles were studied by XAFS to determine if different aqueous environments would lead to specific spectral signatures. The principal goal of this approach is to use XAFS as a local probe for determining whether metal contaminants in the environment will preferably bind to the organic matrix or the inorganic colloids. The next steps of our experimental plan are to characterize organic fibrils isolated from biological cultures by cryo-TEM so that we can observe their conformation in water, as well as to start SAXS experiments to characterize the fractal nature of the aggregates formed and the dynamics of the aggregation process.

References

[1] For further information about this project link to **<http://halodule.marsci.uga.edu/Research/nano.html>** or email **<adrian@plankton.marsci.uga.edu; jf-gaillard@northwestern.edu; aal@duke.edu; santschi@tamug.edu; hungc@tamug.tamu.edu>**

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