UMSAEP UM-UWC Linkage Report

Maria Fidalgo, May 2017

Transformations of Graphene and C-dots in Natural Waters: implications for their fate, transport and toxicity in the environment

UM PI:

- Dr. Maria M Fidalgo, Associate Professor, Department of Civil and Environmental Engineering, University of Missouri, Columbia, fidalgom@missouri.edu

UWC Collaborators:

- Dr. Leslie Petrik, Associate Professor, Environmental and Nano Science Group, Department of Chemistry, University of Western Cape, lpetrik@uwc.ac.za
- Dr. Edmund Pool, Medical and BioScience Programme, Faculty of Natural Science, University of Western Cape, epool@uwc.ac.za

1. Summary of proposed work:

The goal of this project is to contribute towards the understanding of the physical and chemical transformations emerging carbon-based nanomaterials (CNM) suffer in natural waters and the implications for the fate and toxicity of these materials in the environment.

Carbon nanomaterials are particularly interesting due to their properties and therefore are being applied to an increasing number of final products; however, little is known about the transformations and final fate that they would undergo in natural waters, as well about their potential impact and toxicity to organisms. In this project, an interdisciplinary team of researchers partnered to address this issue.

The specific objectives are:

i. To describe and predict the stability and aggregation dynamics of these CNMs in water suspensions and to understand the role of natural organic matter and water chemistry in the

dispersion- aggregation processes for CNMs.

ii. To assess toxicity of CNMs.

iii. To develop and hold a workshop on Environmental Implications of Nanomaterials at the University of Western Cape. This activity aims to transfer MU expertise in the field to UWC, as well as to strengthen of research team in preparation for future collaborative proposal submissions for external funding and it was scheduled during my visit to UWC.

Experimental work on the synthesis and characterization of nanomaterials were conducted at MU and UWC; aggregation and deposition studies under different relevant aquatic chemistry were completed at MU; toxicology research was performed at UWC.

Pre-visit activities:

The collaborative work started well before my visit to UWC. The PIs met several times over skype and planned the first steps.

Graduate students in my group synthesized the nanomaterials to be investigated. Those included two types of carbon nanodots, with different surface functional groups, and graphene oxide nanosheets. Although the chemical composition of the particles is similar (all based on carbon), their surface chemistry and shape are substantially different and therefore we expect them to show different behavior regarding their transport in the environment and their toxicity.

Samples were sent to Dr. Pool at UWC for the toxicity assessment, while students in my group worked in the characterization of the physical and chemical properties of the material and the investigation of their colloidal stability under natural water conditions. The latter involves determining if the nanomaterials will stay suspended as small particles in rivers, lakes or groundwater, or if they will cluster together (aggregate) to form a larger particle that can settle and be removed from the water.

The outcome of the experimental work by Dr. Pool's graduate students showed no toxicity for the nanomaterials at relevant concentrations but they observed effects on the immune system functions. A proposal was submitted (all faculty in this UMSAEP project are co-investigators) to the National Research Foundation in May 2016, entitled: "The development of rapid biomarker assays to monitor the toxicity of the graphene and carbon dots groups of nanoparticle toxicity". The proposal was awarded, which included support for 2 MS and 2 PhD students.

The collaborative work at MU has already produced several conference presentations and one

peer-review article *("Effect of natural water chemistry on aggregation and photoluminiscence behavior of carbon dots", M. Bayati, J. Dai, A. Zambrana, C. Rees, M. Fidalgo de Cortalezzi, Journal of Environmental Science, (2017) in press*). A second manuscript is in its advanced stages and will be submitted soon for publication.

Visit activities:

My visit to the University of the Western Cape took place from March 29th to April 14th. During those days, I had the chance to meet numerous researchers from Chemical and Biomedical Sciences, as well as discuss in more depth the current findings and future direction for this collaborative work.

As part of the project, a workshop was offered for a group of students at UWC in the Nanoscience Program. The program is a postgraduate (Masters) degree and it is very interdisciplinary, attracting students from Physics, Chemistry and Biological Sciences. Through this short course that I had the opportunity to teach, students were introduced to the engineering aspects of nanotechnology, with focus on the application for water treatment and the fate and transport of nanomaterials in natural waters, which largely determines their environmental impact. The workshop included traditional lectures and a laboratory, practical component.

The lectures took place during the first week, and the laboratory experiments and modeling of nanoparticle interactions were conducted during the second week of my visit. The schedule of the workshop is presented below:

Lectures:

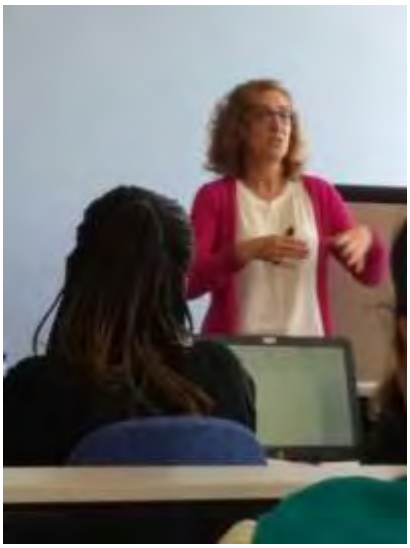
Day 1: Nanomaterials and colloids, natural and engineered nanoparticles in air and water; Nanoparticles: synthesis and materials: metals, metal oxides, carbon based, others.

Day 2: Colloidal systems: definition and morphology of colloids; centrifugation and sedimentation; brownian motion; particle sizing.

Day 3: Electrical Properties of Interfaces: charge at interfaces, electrical double layer, electrokinetics; interactions between colloidal particles: Van der Waals interactions, DLVO theory, kinetics of aggregation, non-DLVO interactions, aggregate structures, fractal aggregates.

Day 4: Particle deposition and transport: deposition onto ideal collectors, particle transport in porous media, mechanisms; soft particles; implications for the environment: removal in water treatment systems, nanomaterials for water treatment; toxicity – estimation of environmentally

relevant concentrations.



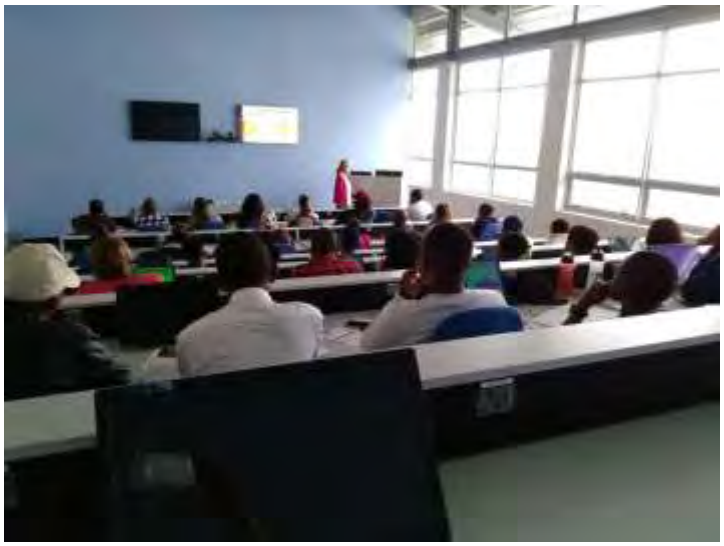


Figure 1. Workshop lecture (Dr. M. Fidalgo) at the University of the Western Cape.

The practical aspects of the workshop took place the second week, Monday, Tuesday and Wednesday. On the first day, the students synthesized nanomaterials. The laboratories were well equipped and Dr Petrik had secured all needed reactants. A group of advanced graduate students in Dr Petrik's group kindly assisted during the practice session. The students fabricated silver nanoparticles, carbon dots, and alumoxane nanoparticles. On the second day, the students started working on the characterization of the synthesized particles. Although a full characterization of the materials was beyond the scope of this workshop, the students were able to corroborate some of the characteristics and expected properties of the fabricated particles. On day 3, students continued measuring some properties, while they were introduced to the modeling of particle interactions, applying to their own materials the theory learnt during the first week of the workshop.

Outcomes:

The experience at UWC has been very rewarding both at a professional and personal level. I enjoyed the research discussion with South African researchers; sometimes because the topics highly overlapped my research interests and in many other cases because I was able to learn a lot about the potential impact of my research outside my current field of work. I identified many interests in common and specific ideas on how we can continue and grow new areas of

collaborative work that will greatly benefit both institutions.

Teaching UWC students was also an enriching experience. The classroom can be a perfect setting to understand and embrace diversity; as different cultures take singular approaches to explaining and communicating science. In a lecture, the teacher needs to adapt to the student expectations, as well as the students need to adapt to an unusual personality and teaching style. I was struck by the students' desire to learn and curiosity. It was a pleasure talking to them after class, their joyful personalities and their drive to advance their education.

Finally, the trip was very successful at the personal level. I was able to appreciate the natural beauty, the rich culture and the friendliness of the people of South Africa.

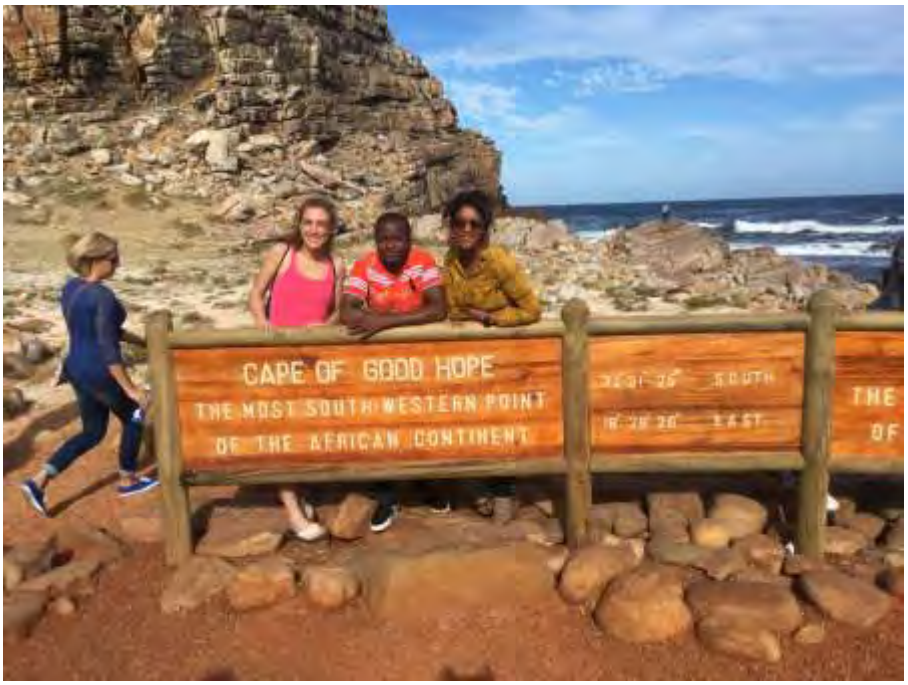


Figure 2. Visiting the Cape of Good Hope with UWC students Comas Uche and Monshia Zimri.