NDnano
Center for Nano Science and Technology

ND*nano* Summer Undergraduate Research
2018 Project Summary

1. Student name & home university:
Angela Abarca Perez
Universidad Popular Autónoma del Estado de Puebla

2. ND faculty name & department:
Dr. Kyle Doudrick
Department of Civil & Environmental Engineering & Earth Sciences

3. Summer project title:
Investigation of the sorption behavior of organic acids onto catalytic- and food-grade titanium dioxide nanoparticles

4. Briefly describe new skills you acquired during your summer research:
During my summer research experience I strengthened my skills on data analysis by modeling the experimental results using thermodynamic equations. Additionally, I gained new knowledge on organic and inorganic chemical structures in nanoscale, and how they interact by using chemical principles. I was also able to synthesize nanoparticles in a new way for me, by a hydrothermal method using high pressure titanium vessels.

5. Briefly share a practical application/end use of your research:
Nanomaterials have been discovered in natural aquatic systems (i.e. streams) as a result of human and industrial activities. Most of them have no regulatory standard and can potentially cause deleterious effects in aquatic life. Therefore, one way of assessing the risk associated with nanoparticles is to study and model their adsorption behavior in aquatic systems with the presence of dissolved organic matter (DOM). Since DOM consists mainly in complex molecules, simple organic acids can be used to for experimentation to provide a better understanding of the fate and transport of nanoparticles in aquatic systems. Hence, the resulting knowledge of the macro-scale sorption properties of organic acids (i.e. outcome data from batch isotherm experiments) can be used in conjunction with molecular-scale dataset to create predictive sorption models and evaluate the risk of nanoparticles in the environment.

6. 50- to 75-word abstract of your project:
In this study the adsorption of DOM- analogue organic acids (mono-carboxylic acids, di-carboxylic acids, tri-carboxylic acids, and phenols) onto the surface of TiO_2 nanoparticles (commercial Evonik P90, food-grade E171 and hydrothermally synthesized nanoparticles) with acidic pH and constant ionic strength, is being assessed in order to predict its behavior in natural environments where complex molecules such as humic acid are present.

7. References for papers, posters, or presentations of your research:
Abarca A, Schranck A, Doudrick K. Investigation of the sorption behavior of organic acids onto catalytic- and food-grade titanium dioxide nanoparticles. Poster session presented at: University of Notre dame Summer Research Symposium; 2018 July 25; Notre Dame, IN.

One-page project summary that describes problem, project goal and your activities / results:

Nanoscience and nanotechnology present potential routes towards addressing critical issues such as clean and sustainable energy, environmental protection and human health.[1] Today, nanoscale materials are being used in a variety of different areas such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic and material applications. Consequently, the use of engineered nanoparticles (ENP) is resulting in increased release of these ENP into the environment. In order to assess the risk of these ENP in natural systems, it is required to understand their transport and reactivity. For this, there is a growing interest in studying the behavior of ENP in aquatic environments. One promising way to achieve this is studying the stability of ENP in aqueous solutions as a function of pH and ionic strength as well as upon the adsorption of dissolved organic matter.[2]

Among manufactured nanomaterials, titanium dioxide (TiO_2) has become widely used because of its chemical and physical properties that can be exploited in different applications including photo catalysts, solar cells, biomaterials, memory devices and environmental catalysts.[3] Consequently, many sources of nanoscale TiO_2 could result in the entrance of this material into the environment through air, water or soil. Therefore, the fate, transport, reactivity and risk associated with manufactured TiO_2 ENP released in the environment can be assessed by evaluating TiO_2 aggregation in aquatic environments. In addition, dissolved organic matter (DOM) in the environment can significantly alter the aggregation behavior of TiO_2 ENP. DOM consists mainly of fulvic and humic substances, which attach to the surface of particles in a variety of ways.[4]

Therefore, the goal of this project is to study the adsorption of DOM-analogue organic acids (mono-carboxylic acids, di-carboxylic acids, tri-carboxylic acids, and phenols) onto the surface of TiO_2 ENP with acidic pH and constant ionic strength, in order to predict its behavior in natural environments where complex molecules such as humic acid are present.

Batch adsorption experiments were conducted using a group of organic acids with concentrations ranging from 5-100 mg/L, selected to examine a range of structural features in an electrolyte media (0.01 M of $NaClO_4$) under acidic pH and an adsorbent concentration of TiO_2 of 1 g/L. The organic acids were selected to evaluate the adsorption behavior of particular structures including increasing number of carboxylic acids and phenolic groups. In addition, different types of TiO_2 ENP (commercial Evonik P90, food-grade E171 and hydrothermally synthesized nanoparticles.[5]) were used to assess the adsorption of di-carboxyl acids onto them.

The results showed that the adsorption of organic acids at acidic pH onto TiO_2 ENP have similar behavior which can suggest that the forces involved are intermolecular forces (van der Waals forces) as in physisorption, rather than by valences forces of the chemical compounds as in chemisorption (Fig 1).

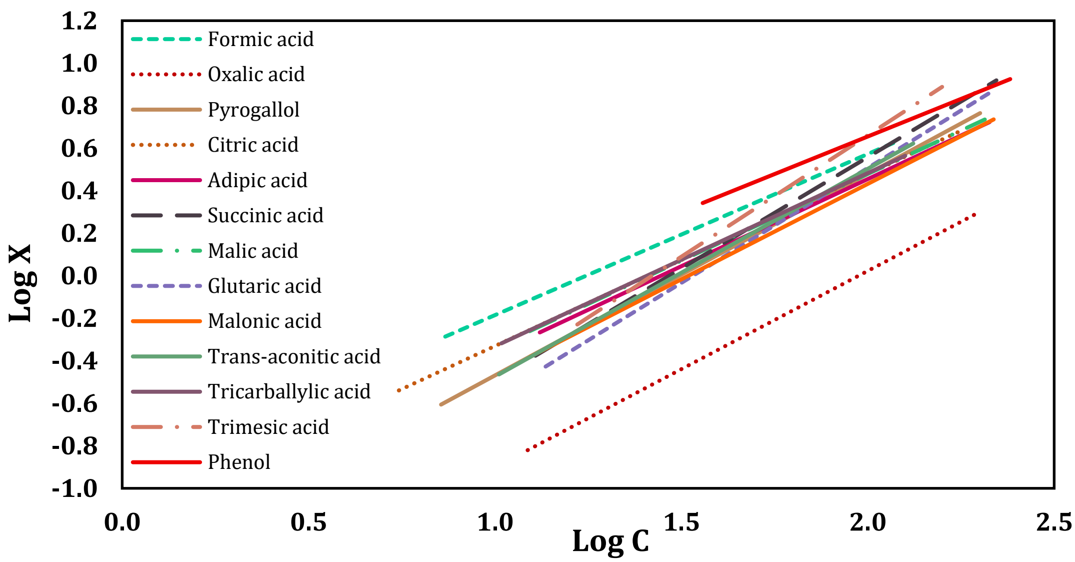

Fig. 1 Adsorption isotherms obtained by applying the Freundlich equation to the experimental data points, using mono-carboxylic, di-carboxylic, tri-carboxylic acids and phenols at concentrations ranging from 5-100 mg/L, with 1 g/L of TiO_2 ENPs.

In addition, Freundlich constants were obtained. The constant *K* can be related to the capacity or affinity of the adsorbent, while 1/*n* may be the indicator of the intensity of adsorption, or how the capacity of the adsorbent varies with equilibrium solute concentration.[1]
The results are showed in Table 1.

Functional group	Organic Acid	*1/n*	*K*	R	pH range
Di-carboxylic	Succinic acid	1.05	0.03	0.99	4.56-4.10
	Glutaric acid	1.08	0.02	0.99	3.15-2.14
	Malic acid	0.81	0.07	0.99	3.82-3.14
	Malonic acid	0.9	0.04	0.99	5.97-3.88
	Adipic acid	0.82	0.07	0.98	4.47-3.66
	Oxalic acid	0.92	0.01	0.99	6.06-5.81
Phenol	Phenol	0.89	0.05	0.97	3.64-4.62
	Pyrogallol	0.68	0.15	0.99	4.84-4.20
Mono-carboxylic	Formic acid	0.65	0.23	0.97	5.87-5.58

	Trans-Aconitic acid	0.98	0.04	0.99	4.48-3.24
Tri-carboxylic	Tricarballylic acid	0.84	0.07	0.98	3.84-3.61
	Trimesic acid	1.14	0.02	0.98	4.38-3.45
	Citric acid	0.81	0.07	0.99	4.79-3.22

Table 1. Resulting constants from Freundlich equation. Constants n and K were obtained from the linear equations of the adsorption isotherms. The values for R are the correlation coefficients for the linear relationships. Five data points were used.

Furthermore, TiO_2 ENP synthesized using a hydrothermal method showed better adsorption than E171 nanoparticles, this can be attributed to the phosphate coating that E171 has, which increases negative charges (Fig 2 and Fig 3). Additionally, E171 presents different sizes of nanoparticles which decreases surface area for adsorption.

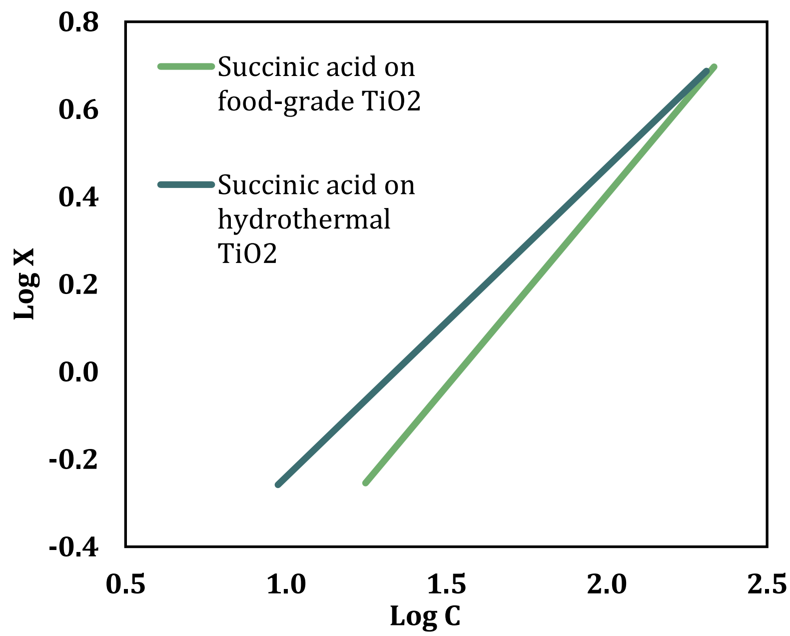

Fig. 2 Adsorption isotherms using Freundlich equation for succinic acid adsorption onto 1 g/L of food-grade E171 and hydrothermally synthesized nanoparticles.

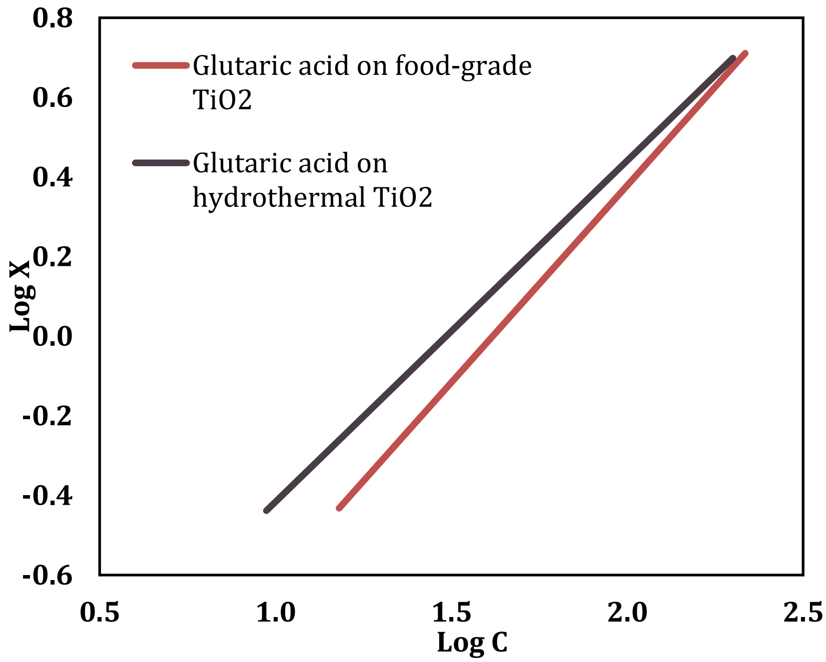

Fig. 3 dsorption isotherms using Freundlich equation for glutaric acid adsorption onto 1 g/L of food-grade E171 and hydrothermally synthesized nanoparticles.

Further studies are planned using humic and fulvic acid to model their sorption behavior and compare adsorption isotherms with simple organic acids. In addition, experiments with different pH and ionic strength will be performed to build surface complexation models. As well, experiments using different types of TiO_2 ENPs and normalized to surface area instead of concentration will be performed.

Refrences:

1. Mudunkotuwa, Imali A., Alaa Al Minshid, and Vicki H. Grassian. "ATR-FTIR spectroscopy as a tool to probe surface adsorption on nanoparticles at the liquid–solid interface in environmentally and biologically relevant media." *Analyst* 139.5 (2014): 870-881.
2. Bian, Shao-Wei, et al. "Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: influence of pH, ionic strength, size, and adsorption of humic acid." *Langmuir* 27.10 (2011): 6059-6068.
3. Pettibone, John M., et al. "Adsorption of organic acids on TiO2 nanoparticles: effects of pH, nanoparticle size, and nanoparticle aggregation." *Langmuir* 24.13 (2008): 6659-6667.
4. Hotze, Ernest M., Tanapon Phenrat, and Gregory V. Lowry. "Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment." *Journal of environmental quality* 39.6 (2010): 1909-1924.
5. Oskam, Gerko, et al. "The growth kinetics of TiO2 nanoparticles from titanium (IV) alkoxide at high water/titanium ratio." *The Journal of Physical Chemistry B* 107.8 (2003): 1734-1738.