NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2021 Project Summary

1. Student name & home university: Alexander M. Pérez Reyes, University of Puerto Rico Mayagüez Campus

2. ND faculty name & department: Dr. Alexander W. Dowling and Dr. William A. Phillip, Department of Biomolecular and Chemical Engineering

3. Summer project title: Data-Enabled Optimization for Printing Chemical Patterns on Nanostructured Membranes

4. Briefly describe new skills you acquired during your summer research:

Throughout this summer research experience many skills in programming, mathematical modeling and research were developed. Advanced techniques and methodologies for Object Oriented Programming (OOP) using Python were acquired. The use of classes, data classes, methods and package structure as well as Version Control best practices (VCS), was explored. [1]Within this programming environment practical ways for creating numerical mathematical models for complex problems were thoroughly studied. Advanced concepts in mathematics and statistics were also touched upon enabling me to learn about non-linear regression, multi-objective optimization and kinetic modeling for Chemical systems. [2]Researching habits were also developed Throughout the experience.

5. Briefly share a practical application/end use of your research:

With data-enabled optimization the design of reactive inks that produce the chemical patterning on membranes, in other words, functionalize the membrane, can be accelerated, cutting down time and resource.[3][4] This can be upscaled to systems with fit for purpose filtering in a water treatment application were targeted chemical properties of the desired compounds to be filtered are imprinted on the membranes. a multi-stage system with different functionalized membranes for these compounds can then be implemented to achieve this fit to purpose filtering. [5]

6. 50- to 75-word abstract of your project:

Modeling Kinetics of the Copper (II)-Catalyzed Azide-Alkyne Cycloaddition(CuAAC) Reactions using numerical methods and python code combined with experimental data to produce a model capable of reproducing behaviors observed in the laboratory with minimal errors, enabling the computational optimization for the design of reactive inks. [6] [7]

7. References for papers, posters, or presentations of your research:

[1] D. Phillips, *Python 3 Object-Oriented Programming (python 3.8)*, vol. 84. 2018.
[2] "Yonathan Bard Nonlinear Parameter Estimation 1973.pdf." .
[3] F. Gao, A. Hunter, S. Qu, J. R. Hoffman, P. Gao, and W. A. Phillip, "Interfacial Junctions Control Electrolyte Transport through Charge-Patterned Membranes," *ACS Nano*, 2019, doi: 10.1021/acsnano.9b00780.
[4] E. A. Eugene, W. A. Phillip, and A. W. Dowling, "Data science-enabled molecular-to-systems engineering for sustainable water treatment," *Curr. Opin. Chem. Eng.*, vol. 26, pp. 122–130, 2019, doi: 10.1016/j.coche.2019.10.002.
[5] Y. Zhang, N. E. Almodovar-Arbelo, J. L. Weidman, D. S. Corti, B. W. Boudouris, and W. A. Phillip, "Fit-for-purpose block polymer membranes molecularly engineered for water treatment," *npj Clean Water*, vol. 1, no. 1, pp. 1–14, 2018, doi: 10.1038/s41545-018-0002-1.
[6] E. V. Shtamm, A. P. Purmal, and Y. I. Skurlatov, "Mechanism of catalytic ascorbic acid oxidation system Cu2+–ascorbic acid–O2," *Int. J. Chem. Kinet.*, vol. 11, no. 5, pp. 461–494, 1979, doi: 10.1002/kin.550110503.
[7] C. Intermediate, "Direct Evidence of a Dinuclear," vol. 340, no. I, pp. 457–461, 2010.
[8] J. R. Hoffman and W. A. Phillip, "Dual-Functional Nanofiltration Membranes Exhibit Multifaceted Ion Rejection and Antifouling Performance," *ACS Appl. Mater. Interfaces*, vol. 12, no. 17, pp. 19944–19954, 2020, doi: 10.1021/acsami.0c03075.
[9] J. R. Hoffman, A. D. Mikes, F. Gao, and W. A. Phillip, "Controlled Postassembly Functionalization of Mesoporous Copolymer Membranes Informed by Fourier Transform Infrared Spectroscopy," *ACS Appl. Polym. Mater.*, vol. 1, no. 8, pp. 2120–2130, 2019, doi: 10.1021/acsapm.9b00419.

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

Reactive Inks allow for the functionalization of membranes that make up fit to purpose filtration systems. The functionalization of the membrane requires the deposition of a reactive ink on the membrane of which as schematic can be seen in Figure 1. [8][5][9] My summer project focused on developing a python code to model Copper (II) Catalyzed Azide-Alkyne Cycloaddition reactions. [6] Specifically a model for the kinetics of the Alkyne reactions concentration profiles of each species in the reaction mechanism over time. Model predictions by themselves are not good at capturing the observed behaviors of the concentrations from experimental data. Therefore, fitting the model predictions with the experimental data is necessary to obtain a good model. The kinetic model proposed for this set of reactions lacks literature values for the backward reaction rates. Previous work on the model provided data for the first part of the reaction mechanisms backward reaction rates, k_{b1}, k_{b2}, k_{i1}. However, all the reaction rates k_{b1}, k_{b2}, k_{i1}, k_2, k_4 and k_6 from Figure 2 need to be estimated by fitting the model to see how they vary together. New experimental data for the Alkyne reactions was gathered in the laboratory to aid in producing fits for the new model. Timeseries Cu^{2+} conversion percentages gathered from UV-spectroscopy as well as Timeseries pH measurements were gathered in the lab at different concentration ratios. The chemicals used were Cu(II) SO_45H_2O (Copper sulfate pentahydrate) Ascorbic Acid and 3-Dymethylamino 1-propyne(DMA). After gathering the data, the pre-existing Python Framework was updated to load and process it. The rate laws for the reactions in Figure 2 were derived and coded. With pH data for the alkyne reactions, the model could be initialized but for Cu^{2+} data a new initialization model was needed to determine initial conditions since pH measurements play a key role in the modeling process and cannot be gathered simultaneously with the UV-spectroscopy data. This mathematical model developed was tested with numerical methods and was able to accurately calculate the initial pH for the initial conditions of each experiment seen in Graph 1. The final equation for initial pH can calculate the initial conditions for a mixture of N number of weak acids/bases.

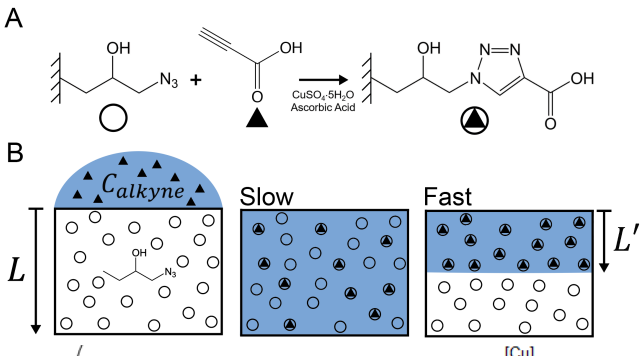


Figure 1: Schematic of the Functionalization of a Nanostructured Membrane

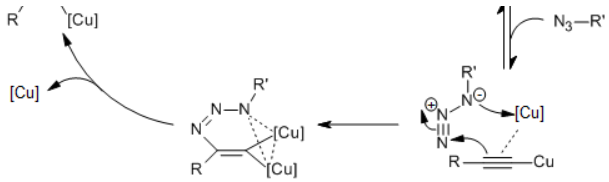


Figure 3: Copper (II) Catalyzed Azide-Alkyne Cycloaddition Reaction Mechanism

$$DH_2 \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} DH^- + H^+$$

$$DH^- + Cu^{2+} \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} CuDH^+$$

$$CuDH^+ + Cu^{2+} \rightarrow 2\,Cu^+ + D + H^+$$

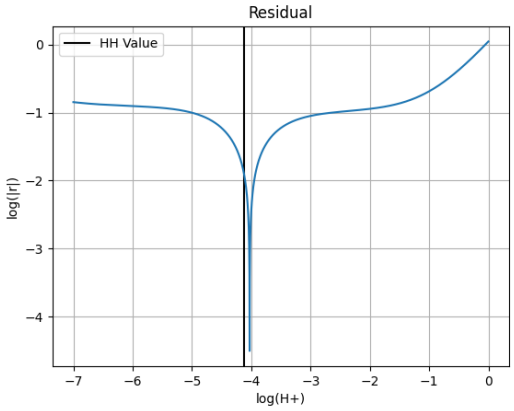
$$R{\equiv}H + Cu^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MCuPIC \underset{k_4}{\overset{k_3}{\rightleftharpoons}} R{\equiv}Cu + H^+$$

$$R{\equiv}Cu + Cu^+ \underset{k_6}{\overset{k_5}{\rightleftharpoons}} DNCuAC$$

Figure 2: Copper(II)-Ascorbic-Acid-Alkyne Reactions

$$[H^+] = \sum_{i=1}^{n} -[A_i^-]_0 + \frac{[HA_i]_0 + [A_i^-]_0}{\left(1 + \frac{[H^+]}{K_{a_i}}\right)}$$

Further work went into testing and developing the new model, by adding single, sequential and simultaneous regressions. Preliminary fitting of the newly gathered data for the alkyne model with sequential fitting is however inconclusive. Identifiability issues exist with the current model were some of the species in the mechanism are reacting, this shown in the simulation results as numerical integration noise. Further research must go into other possible intermediary reactions that inform the model as to how H^+, Cu^{2+} and Cu^+ are generated and consumed. Current ongoing work being realized towards implementing these proposed intermediary reactions as well as to add other functionalities to the code that will allow for further analysis of the fitted data.



Graph 1: Residuals for the initial conditions model pointing towards a numerical solution with near zero residual