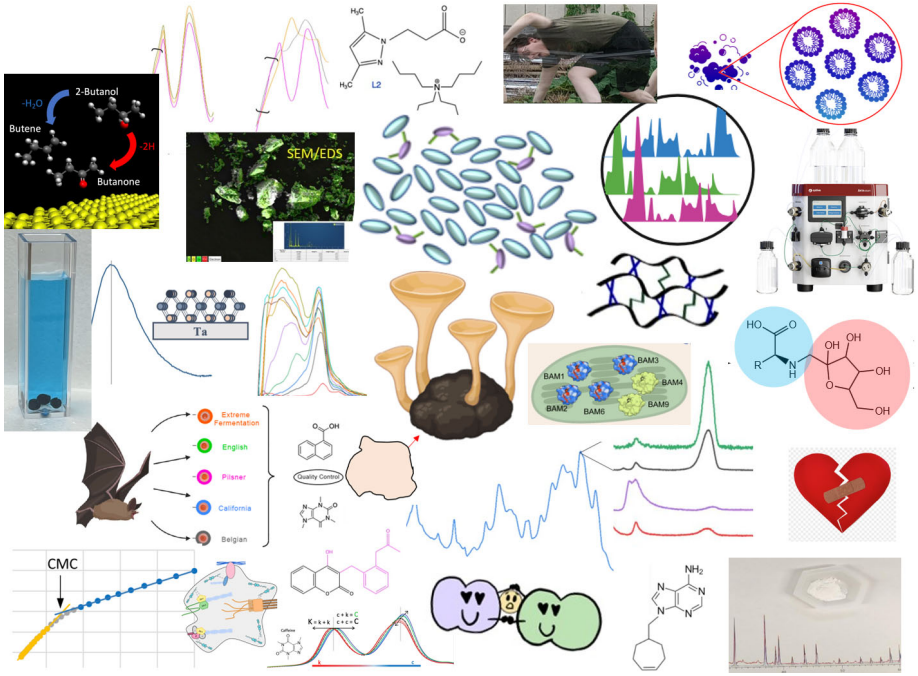
JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY



48TH ANNUAL SPRING UNDERGRADUATE RESEARCH SYMPOSIUM

THURSDAY APRIL 18, 2024

ORAL SESSION I: 10:00AM – 12:00PM (KING 259)
ORAL SESSION II: 1:00 – 2:30 PM (KING 259)

FRIDAY APRIL 19, 2024

POSTER SESSION: 1:00 – 3:00 PM (PCB LOBBY)
SPECIAL ANNOUNCEMENTS: 3:30PM (KING 159)
KEYNOTE ADDRESS: 3:35 – 4:35 PM (KING 159)

48th Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium

Keynote Speaker

Ashley Head, PhD
(JMU Class of 2005)
Staff Scientist
Brookhaven National Laboratory
Upton, NY

Ashley Head is a staff scientist at Brookhaven National Laboratory. She earned her Bachelor of Science degree with a minor in mathematics from James Madison University in 2005. Her JMU research efforts focused on synthesizing lanthanide complexes with phosphine ligands with Dr. Donna Amenta and Dr. John Gilje. She worked for a year in milk packaging quality control laboratory at HP Hood in Winchester, VA while applying for graduate schools. Ashley then attended the University of Arizona where she earned her doctorate degree in physical inorganic chemistry from Dr. Dennis Lichtenberger. One of her research assistant positions in graduate school was in a small X-ray spectroscopy facility where she learned to help other scientists perform advanced spectroscopy experiments and to maintain high tech equipment. For a postdoctoral research position, Ashley moved to Sweden for two years to work in a larger scientific user facility at Lund University and the MAX IV synchrotron facility. In this position, Ashley studied the mechanisms of depositing atomically thin layers of metal oxides. Returning to the States, Ashley did a second postdoc at Lawrence Berkeley National Laboratory where she used X-ray spectroscopies to study the interaction of nerve agent simulants with gas mask filter components.

In 2018, Ashley joined the staff at the Center for Functional Nanomaterials, a Department of Energy Nanoscale Science Research Center at Brookhaven Lab. She manages X-ray and IR spectroscopy equipment and helps scientists from around the US and beyond conduct experiments to study surface reactions in situ. She is also a manager in a DOE project to revitalize the US nanoscience infrastructure. Ashley conducts her own research in heterogeneous catalysis, focusing on understanding surface reactions on metal oxides and in confined spaces of materials. Ashley also develops ways to advance X-ray spectroscopy. For these efforts, she was selected as the James Madison University College of Science and Mathematics Alumna of the Year in 2018.

Aside from her love of science, Ashley enjoys hiking, cooking, and gardening. She and her husband also have a house filled with kid-friendly(ish) science experiments for their two young daughters.

Past Keynote Speakers Each year we feature a keynote speaker for the Department's annual Spring Undergraduate Research Symposium. We are honored to have had speakers who are alumni of the department and are willing to come back and share with our students their experiences of "life after JMU". We thank each of these speakers and look forward to future alumni participation in Spring Symposium.

Year	JMU Class	Speaker	Affiliation
2024	2005	**Dr. Ashley Head**	*Brookhaven National Laboratory*
2023	1994	**Dr. Kevin Bennett**	*Hood College*
2022	1994	**Dr. Timothy W. Graul**	*Pfizer Inc.*
2021	2005	**Dr. Christian Zeigler**	*Vertex Pharmaceuticals*
2019	1995	**Dr. Lisa M. Christianson (M.D.)**	*University of Virginia School of Medicine*
2018	2002	**Dr. William Gemmill**	*Eminess Technologies, Inc.*
2017	2004	**Dr. Zeric Hulvey**	*United States Department of Energy*
2016	2007	**Dr. Reid Gadziala**	*Cleveland Clinic*
2015	1994	**Dr. Michael Leopold**	*University of Richmond*
2014	1996	**Dr. Dana McGraw Dattelbaum**	*Los Alamos National Laboratory*
2013	1999	**Dr. Christy Vestal Martin**	*Vorbeck Materials*
2012	1994 N/A	**Dr. Melissa C. Rhoten** **Dr. Orde Q. Monro**	*Longwood University* *University of KwaZulu-Natal*
2011	1992	**Dr. Morgan S. Sibbald**	*The Sherwin-Williams Company*
2010	1988	**Dr. Kevin Morris**	*Carthage College*
2009	1988	**Dr. Chris E. Holmes**	*The University of Vermont College of Medicine*
2008	1995	**Dr. Jonathan Dattlebaum**	*University of Richmond*
2007	1987	**Dr. Elizabeth Perry (M.D.)**	*Signature Healthcare, Inc.*
2006	1967	**Dr. Carolyn Abitbol (M.D.)**	*University of Miami (FL) School of Medicine*
2005	1975 1976	**Dr. Daniel Downey** **Dr. Gary Rice**	*James Madison University* *College of William and Mary*
2004	1987	**Dr. James (Dusty) Baber**	*National Institutes of Health*
2003	1984	**Dr. Fred King**	*West Virginia University*
2002	1977	**Dr. Roger Bertholf**	*University of Florida School of Medicine*
2001	1979	**Mrs. Katheryn Lam**	*International Business Machines*
1999	1987	**Dr. Jose Madalengoitia**	*University of Vermont*
1997	1986	**Dr. Fred R. Kinder**	*Novartis Research Institute*
1996	1976	**Dr. Terry O. Trask**	*DuPont Chemicals*
1995	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*
1994	1990	**Dr. Michele A. Kelly**	*University of Maryland Baltimore County*
1993	1985	**Dr. Cynthia K. Fallon**	*DuPont Chemicals*
1992	1983	**Dr. Laurie Locascio**	*National Institute of Standards and Technology*
1991	1983	**Dr. Noreen Naiman**	*North Carolina School of Science and Mathematics*
1990	1982	**Dr. Matthew T. Stershic**	*Atomchem North Amercia*
1989	1982	**Dr. Michael Kinter**	*Cleveland Clinic Lerner Research Institure*
1988	N/A	**Dr. Thomas J. Meyer**	*Los Alamos National Laboratory*
1987	1980	**Dr. Steven Davis**	*Naval Research Laboratory*
1986	1980	**Dr. Steven A. Hackney**	*Michigan Technological University*
1983	1978	**Dr. Richard B. Lam**	
1982	1975	**Dr. Daniel Downey**	*West Virginia University*
1981	1959	**Mr. Ronald E. Ney**	*Environmental Protection Agency*
1980	N/A	**Dr. Stanley G. Sunderwirth**	*Metropolitan State College (Denver, CO)*
1979	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*

Oral Session I: Thursday April 18, 2024 *(King 259)*		
10:00 am	Ava J. Galgano, Dr. Ashleigh E. Baber, and Dr. Petra Reinke (UVA)	Effect of Thermal Annealing and Ion Sputtering on WSe_2 Adsorption Sites
10:15 am	Patrick Randolph and Dr. Thomas Devore	Altering Acetate's Chemical Shift and Relaxation Time Based of Viscosity and Counter Cation
10:30 am	Nina A. Metzger and Dr. Yanjie Zhang	Specific Ion Effects: Hofmeister Cation Effects on the Fluorescence of Coumarin and Derivatives
10:45 am	Stephanie N. Ouderkirk, Kamrin D. Shultz, Dr. Nathan T. Wright, and Dr. Callie J. Miller	Measuring Cellular Mechanics Using Image Analysis Techniques to Provide Evidence for a Molecular Pathway Involving Obscurin
11:00 am	Heidi J. Arenas, Dr. Yanjie Zhang, and Dr. Gina MacDonald	Effects of Combined Chaotropic, Kosmotropic, Anions and Cations on Caffeine Aggregation using ATR-FTIR
11:15 am	Xander M. Dirom and Dr. Gretchen M. Peters	Impact of Crosslinker Length on the Properties of PVA-BA Gels
11:30 am	Gabriella Newsome and Dr. Isaiah Sumner	The Vibrational Spectra of Glycerol-boric Acid Complexes
11:45 am	Angelina V. Lo Presti, Dylan M. Virts, and Dr. Christine A. Hughey	Laboratory-scale Model of the Maillard Reaction in a Single Malt, Single Hop (SMaSH) Beer

Oral Session II: Thursday April 18, 2024 *(King 259)*		
1:00 pm	Kamrin D. Shultz, Stephanie N. Ouderkirk, Dr. Callie J. Miller, Dr. Kristopher E. Kubow, and Dr. Nathan T. Wright	Understanding the Effect of Obscurin on Cellular Architecture and Dynamics
1:15 pm	Madeleine Benes, Roujon Aranowzari, Clay P. Page, Isabel I. Romov, and Dr. Nathan T. Wright	Prevention of Protease-Induced Degradation of Desmoplakin via Small Molecule Binding
1:30 pm	Angela Kayll, Harrison Tarbox, Andrew Pulido, Dr. Joseph Provost, and Dr. Christopher E. Berndsen	Solution Structure of the hMDH2-hCS Metabolon
1:45 pm	Zachary Ryan and Dr. Oleksandr Kokhan	A Modular, Affordable, 3D-Printed FPLC
2:00 pm	Ashley E. Clements, Alexa G. Lee, Dr. Navid J. Ayon, Dr. Cody E. Earp, Raveena Gupta, Dr. Fatma A. Butun, David Dainko, Dr. Matthew T. Robey, Manead Khin, Dr. Lina Mardiana, Dr. Alexandra Longcake, Dr. Manuel E. Rangel Grimaldo, Dr. Michael J. Hall, Dr. Michael R. Probert, Dr. Joanna E. Burdette, Dr. Nancy P. Keller, Dr. Huzefa A. Raja, Dr. Nicholas H. Oberlies, Dr. Neil L. Kelleher, and Dr. Lindsay K. Caesar	Bioactivity-driven Metabologenomics Identifies Antiproliferative Stemphone Analogs and Their Biosynthetic Gene Cluster
2:15 pm	Eric J. Shepard, Tengis Tamir, and Dr. Debra Mohler	A Novel Synthetic Strategy for Antisense Oligonucleotide Analogs

(Student presenters underlined)

Poster Session: Friday April 19, 2024, 1:00 – 3:00 pm *(PCB lobby)*	
Isabella M. Daniel, Zachary H. Shelor, Dr. Donna S. Amenta, and Dr. John W. Gilje	Synthesis of N-Pyrazolyl and N-Benzotriazolyl Derivatives as Chelating Ligands for Ruthenium Complexes
Haley Frankovich, Lyssa A. Garber, Ava J. Galgano, Charles L. Grant, Erin D. Schell, John Yoo, Clayton J. Rogers, Dr. Ashleigh E. Baber, and Dr. Kendra Letchworth-Weaver	Computationally Enhanced Experimental Investigation of Reactivity of Isomeric Butanol on TiO_2/Au(111)
Juan M. Garcia, Maxwell J. Tyree, and Dr. Christine A. Hughey	Quality Control for Untargeted Metabolomics in Single Malt, Single Hop (SMaSH) Beers Brewed with Five Genetically Different Yeast Strains
Shyleigh A. Good, Mary M. Sessoms, Frances E. Homan, Lyn G. Haugh, Ashley E. Clements, Alexa G. Lee and Dr. Lindsay K. Caesar	Induction of Natural Products by Fungal-Fungal Co-Cultures
Evelyn Haugh, Alexa Lee, Ashley Clements, and Dr. Lindsay Caesar	Ecological Inspired Co-cultures of Anti-fungal Bacteria to Combat White-Nose Syndrome
Joseph C. Loiselet, Erin D. Schell, John Yoo, Ava J. Galgano, and Dr. Ashleigh E. Baber	Enhancing the Selectivity of Acetaldehyde Formation Using Copper-based Metal Catalysts
Seth W. Mars, Kayla H. Moore, Dr. Gretchen M. Peters, and Dr. Brycelyn M. Boardman	A Tale of Tails: A Spectroscopic Investigation of the Primary and Secondary Interactions of Polyol Plasticizers in Molecular and Polymeric Systems.
Sam Mason and Dr. Thomas DeVore	Synthesis and Water Absorption of Metal Carbonates, $Na_2Cu(CO_3)_2$ $3H_2O$, $Zn_5(CO_3)_2(OH)_6$, and $Na_2Zn_3(CO_3)_4$ $3H_2O$
Joshua Sambo, Eric Rhoades, Josie Swanton, Antonio Harvey, and Dr. Kevin Caran	Synthesis and Characterization of Bicephalic Biscationic Amphiphiles with Potential for Zeolite Templating
Sara Scanlan, MacKenzie Freeze, Dr. Jonathan Monroe, and Dr. Christopher Berndsen	A Colorimetric Assay to Determine Substrate Specificity of Beta-Amylases
Erin D. Schell, Joseph C. Loiselet, Ava J. Galgano, and Dr. Ashleigh E. Baber	Understanding CO Binding Trends for CO_2 Reduction Catalyst Optimization
Miranda Shackelford and Dr. Gina MacDonald	Using Infrared Spectroscopy to Monitor Protein Unfolding with Hoffmeister Salts Over Time Without the Addition of Heat
Josie M. Swanton, Eric A. Rhoades, Joshua S. Sambo, Antonio K. Harvey, and Dr. Kevin L. Caran	Synthesis and Critical Micelle Concentration (CMC) of Biscationic Amphiphiles with Various Carbon Chain Lengths
Ryan E. Tonetti, Jessie M. Hallers, and Dr. Thomas DeVore	Synthesis and Characterization of Nickel-Cobalt Mixed Metal Tutton Salts
Aliyah N. Walker, Jessie M. Hallers, Jacquelyn E. McBride, and Dr. Barbara A. Reisner	Embedding Metal Organic Frameworks (MOFs) in Chitosan Beads for Dye

(Student presenters underlined)

Special Announcements: Friday April 19, 2024 *(King 159)*	
3:30pm	Announcement of Chemistry and Biochemistry Student Award Winners

Keynote Address: Friday April 19, 2024 *(King 159)*		
3:35 - 4:35 pm	Ashley Head, PhD JMU Class of 2005	Navigating Through Science User Facilities After Leaving JMU

Keynote Address

Friday, April 19, 2024 at 3:35 pm
King 159

Navigating Through Science User Facilities After Leaving JMU

Ashley Head, PhD
(JMU Class of 2005)
Staff Scientist
Brookhaven National Laboratory
Upton, NY

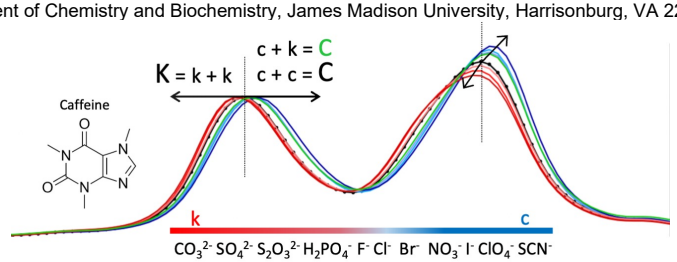
The U.S. Department of Energy has national laboratories around the country to lead science solutions to the nation's energy problems. Scientific user facilities are a core part of this leadership. I will discuss my journey from James Madison University to one of these user facilities at Brookhaven National Laboratory. My pathway includes some gap years and a road paved by X-rays. Spectroscopy instrumentation is the vehicle that has led me down this road. I will discuss pit stops at inorganic synthesis, depositions of thin metal oxide films, nerve agents, and heterogenous catalysis. Meeting scientific locals and tourists has been one of the most rewarding parts of the journey. Spectrometer customization and tinkering remains a consistent hobby. I hope to share some lessons learned along the way to inspire a new set of undergraduates just beginning their own science roadtrip.

STUDENT ABSTRACTS

(Student presenters underlined)

Effects of Combined Chaotropic, Kosmotropic Anions and Cations on Caffeine Aggregation Using ATR-FTIR

Heidi Arenas, Dr. Yanjie Zhang, and Dr.Gina MacDonald
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807



The Hofmeister series ranks ions based on their ability to destabilize (salting-in) and stabilize (salting-out) proteins. It is important to understand the behavior of ions in aqueous solutions. In this study, caffeine was used as a model compound to study mixed ion interactions with solute molecules. We studied cations, anions, and the combined effects of different kosmotropic and chaotropic salts on caffeine vibrations in both deuterium oxide (D_2O) and water (H_2O) using attenuated total reflection-fourier-transform infrared (ATR-FTIR). Different combinations of salts, and some singular salts were studied to determine the influence of ions on caffeine aggregation. Our results show that combinations of chaotropic salts (NaSCN, NaI, NaBr,) additively shift the vibrations at ~1650 and ~1750 cm^{-1} to lower wavenumber indicating less aggregation and increased solvation. The combination of kosmotropic salts (Na_2SO_4, NaH_2PO_4) also additively shifts the vibrations, but to higher wavenumbers indicating increased aggregation and decreased solvation. Infrared studies of caffeine in a combination of salts show that the effects of chaotropic ions dominate over the influence of kosmotropic ions. Bromide and chloride salts with a series of cations were also studied but showed smaller effects on caffeine aggregation.

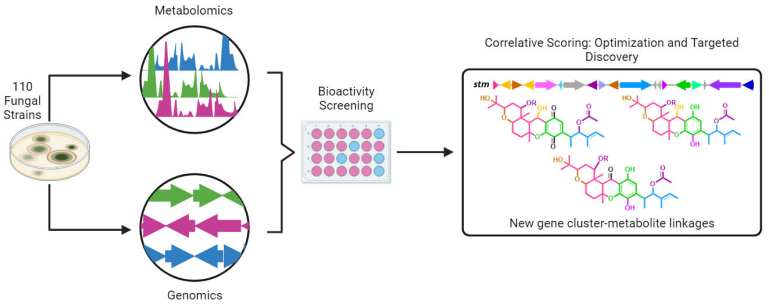
Prevention of Protease-Induced Degradation of Desmoplakin via Small Molecule Binding

Madeleine Benes, Roujon Aranowzari, Clay P. Page, Isabel I. Romov, and Dr.Nathan T. Wright
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807

Mutations in the desmosomal protein desmoplakin (DSP) underlie about 5% of Arrhythmogenic Cardiomyopathy (AC) cases. Recent data from our lab show that some disease-linked DSP mutations are hypersensitive to calpain, an endogenous calcium-dependent protease. The resulting loss of DSP destabilizes the desmosome and leads to weakened cell-cell adhesion, which is correlated with fibrofatty infiltration in AC. Our lab has probed the molecular mechanism of this DSP degradation, showing that DSP mutant hypersensitivity to calpain is dependent upon the exposure of a usually occluded cleavage site on the DSP surface. Mutant DSP remains folded globally, but exhibits increased local dynamics and solvent accessibility around this site. As proof of concept of this mechanism, the addition of a secondary stabilizing mutation once again occludes the DSP calpain cleavage site and rescues DSP levels. Here, we present evidence that small molecules can also stabilize DSP levels in the presence of calpain. We screened ~2500 FDA-approved drugs for those that inhibited both trypsin and calpain-dependent degradation of DSP but did not inhibit BSA degradation. Of these compounds, 5-10 specifically inhibit DSP degradation regardless of the DSP mutation. This represents the first step of identifying ways to reverse the molecular underpinnings of this kind of AC, instead of simply identifying them.

Bioactivity-driven metabologenomics identifies antiproliferative stemphone analogs and their biosynthetic gene cluster

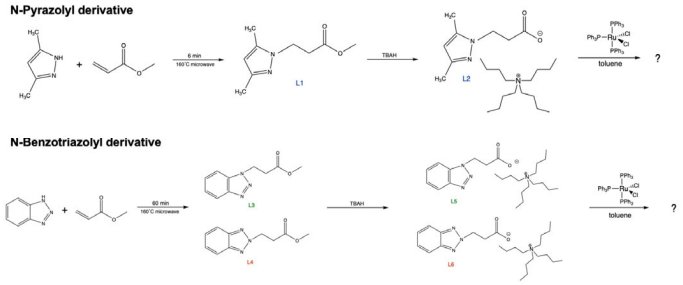
Ashley E. Clements[1], Alexa G. Lee[1], Dr. Navid J. Ayon[2], Dr. Cody E. Earp[3], Raveena Gupta[2], Dr. Fatma A. Butun[2], David Dainko[2], Dr. Matthew T. Robey[4], Manead Khin[5], Dr. Lina Mardiana[6], Dr. Alexandra Longcake[6], Dr. Manuel E. Rangel Grimaldo[3], Dr. Michael J. Hall[6], Dr. Michael R. Probert[6], Dr. Joanna E. Burdette[5], Dr. Nancy P. Keller[7], Dr. Huzefa A. Raja[3], Dr. Nicholas H. Oberlies[3], Dr. Neil L. Kelleher[4], and Lindsay K. Caesar[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]Department of Chemistry, Northwestern University, Evanston, IL 60208
[3]Department of Chemistry and Biochemistry, University of North Carolina at Greensboro, Greensboro, NC
[4]Department of Molecular Biosciences, Northwestern University, Evanston, IL 60208
[5]College of Pharmacy, Pharmaceutical Science, University of Illinois Chicago
[6]Chemistry, School of Natural and Environmental Sciences, Newcastle University, UK
[7]Department of Medical Microbiology and Immunology, University of Wisconsin-Madison, Madison, WI



Secondary metabolites (natural products) have made substantial contributions as both pharmaceuticals and agrochemicals. Fungi in particular biosynthesize chemically diverse secondary metabolites with a wide range of biological activities. Natural product scientists have increasingly turned towards bioinformatics approaches, combining metabolomics and genomics to target secondary metabolites and their biosynthetic machinery. We recently applied an integrated metabologenomics workflow to 110 fungi and identified more than 230 high-confidence linkages between metabolites and their biosynthetic pathways. In this study, we introduce a bioactivity-driven metabologenomics workflow that combines quantitative chemical information, antiproliferative bioactivity data, and genome sequences to prioritize the discovery of bioactive secondary metabolites and their biosynthetic pathways. Using this platform, we isolated and characterized three new stemphone analogs, 19-acetylstemphones G, B and E, that demonstrated antiproliferative activity in the range of 3-5 μM against human melanoma (MDA-MB-435) and ovarian cancer (OVACR3) cell lines. We proposed a rational biosynthetic pathway for these compounds, highlighting the potential of using biological activity as a filter for the analysis of integrated -Omics datasets. We also observed the difference in the expression of these metabolites by the fungi due to differences in growth conditions, and interconversion of 19-acetylstemphone E to 19-acetylstemphone B, and finally to 19-acetylstemphone G, indicating that 19-acetylstemphone G is the most stable of the three analogues. This work successfully demonstrates how the incorporation of biochemometrics as a third dimension into the metabologenomics workflow can help prioritize the discovery of metabolites with medicinal applications.

Synthesis of N-Pyrazolyl and N-Benzotriazolyl Derivatives as Chelating Ligands for Ruthenium Complexes

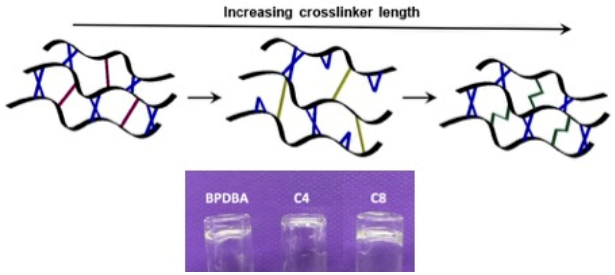
Isabella M. Daniel, Zachary H. Shelor, Dr. Donna S. Amenta, and Dr. John W. Gilje
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807



In this study we are preparing and studying 2,4-dimethylpyrazolynethylproponoate (L1), the symmetric (L3) and asymmetric (L4) isomers of N-benzotriazolylmethylproponoate, and their corresponding carboxylates. These are potentially hemilabile ligands that can coordinate to a metal through a heterocyclic nitrogen and/or an oxygen in the ester or carboxylate moiety. The solvent-free, catalyst-free Michael addition of 3,5-dimethylpyrazole with methyl acrylate resulted in the formation of an ester (L1) with high yields. L1 was allowed to react with tetrabutylammonium hydroxide (TBAH) to form the carboxylate anion (L2) of the ester as a viscous liquid. L2 was characterized using NMR and IR spectroscopy. L2 was allowed to react with $RuCl_2(PPh_3)_3$ and the products were investigated with ^{31}P NMR spectroscopy. These data indicate that the reaction yielded multiple products, which have yet to be separated and individually characterized. Under similar conditions, the Michael addition of benzotriazole with methyl acrylate yielded two isomeric esters (L3 and L4) which were separated by elution chromatography. Reactions of L4 with $RuCl_2(PPh_3)_3$ yielded a red/orange precipitate assigned to a ruthenium complex in which the ligand binds in a bidentate fashion. ^{31}P NMR studies indicate that the complex transitions into a bridged structure in solution. When treated with TBAH, both L3 and L4 formed the corresponding carboxylates (L5 and L6). Treatment of these anions and the precursor esters with $RuCl_2(PPh_3)_3$ is currently being investigated.

Impact of Crosslinker Length on the Properties of PVA-BA Gels

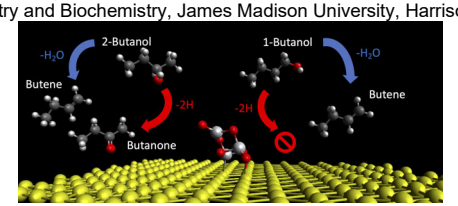
Xander M. Dirom and Dr. Gretchen M. Peters
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807



The applications of gels are wide-ranging and diverse. Because of this, developing ways to easily control and optimize the properties of gels is of great interest. Recently, we reported a tunable organogel formed with polyvinyl alcohol (PVA) and mixtures of boric acid (BA) and 1,4-benzenediboronic acid (1,4-BDBA). We found that using mixtures of crosslinkers yielded stiffer and more stable materials than those with either crosslinker alone. We rationalized that these improved properties were the result of a cooperative crosslinking phenomenon in which 1,4-BDBA decreases the distance between polymer chains, thus enabling BA to form crosslinks with PVA and stiffening the gel. To probe this theory, we designed and synthesized a library of diboronic acid crosslinkers of varying linker length. Of these crosslinkers, all were found to form gels with PVA alone. In combination with BA, we found that increasing the linker length resulted in materials with higher critical gelation concentrations (CGCs) and lower storage moduli (G′). This is consistent with our proposed cooperative crosslinking mechanism. Interestingly, at moderately long chain lengths, we observed a decrease in CGC and an increase in viscosity and material stiffness (i.e., higher G′). We attribute this to an increased flexibility between the diboronic acids units. We are currently investigating the impacts of linker length and flexibility on the morphology and stability of PVA-BA gels.

Computationally Enhanced Experimental Investigation of Reactivity of Isomeric Butanol on TiO_2/ Au (111)

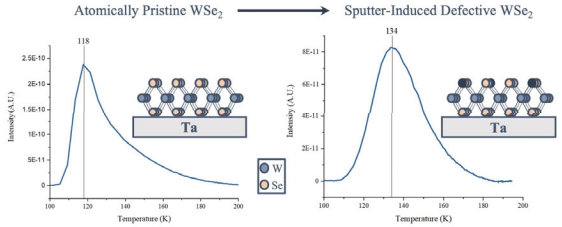
Haley Frankovich, Lyssa A. Garber, Ava J. Galgano, Charles L. Grant, Erin D. Schell, John Yoo, Clayton J. Rogers, Dr. Ashleigh E. Baber, and Dr. Kendra Letchworth-Weaver
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807



Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon-neutral cycle. Biobutanol has low volatility and multiple transportation options which make it an attractive alternative fuel. Understanding the fundamental thermal catalysis processes of butanol over heterogeneous model catalysts can aid in the design of more efficient catalysts. To better understand the processes in play, temperature-programmed desorption (TPD), atomic force microscopy (AFM), density functional theory (DFT), and high-performance computing are used to investigate its reaction. This study aimed to examine the reactivity of different isomers of butanol, namely 1-butanol, 2-butanol, and isobutanol, when exposed to a TiO2/Au(111) surface. TPD was used to detect products, with 1-butanol showing little reactivity and elimination products, 2-butanol showing oxidation and elimination, and isobutanol yielding all products. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. AFM highlighted the morphology of the surface and shows the Au(111) crystal has ~0.13ML and 0.27ML of TiO2 with predominantly 1D wire like nanoparticles. Higher coverages of TiO2 result in more particles distributed across the surface indicating that the reactivity was influenced by butanol proximity to TiO2 nanoparticles rather than differences in size or shape. DFT calculations to investigate energetic trends and provide an atomic-scale understanding of the structure of butanol adsorbed on the surface are ongoing.

Effect of Thermal Annealing and Ion Sputtering on WSe_2 Adsorption Sites

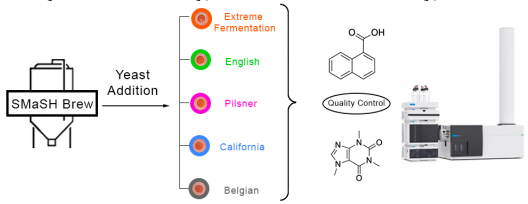
Ava J. Galgano[1], Dr. Petra Reinke[2], and Dr. Ashleigh E. Baber[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA
[2]Department of Materials Science and Engineering, University of Virginia; Charlottesville, VA



Transition metal dichalcogenides (TMDs) are two dimensional (2D) materials gaining attention as catalysts for CO_2 hydrogenation and the hydrogen evolution reaction due to their unique properties at low dimensions. Defects, or surface irregularities, of the atomic structure of TMDs are suggested active sites; however, the link between defects, electronic structure, and catalytic activity is unknown, which limits the ability to control the reactivity of the 2D TMDs. To better understand the fundamental nature of defects on TMDs, a promising material, WSe_2, was studied using temperature programmed desorption (TPD). The surface of WSe_2 was cleaved via mechanical exfoliation and the sample was mounted on a tantalum (Ta) sample holder. The WSe_2/Ta sample was gently annealed and sputtered under ultrahigh vacuum (UHV) conditions to increase the defect inventory of the surface. Results shown here highlight the adsorption and reactivity of methanol as a probe molecule using UHV-TPD on WSe_2/Ta. Upon annealing the sample to 673 K, the desorption of methanol also shifted to higher temperatures (> 150 K) on both WSe_2/Ta and during control experiments on the Ta sample holder. The shift to higher desorption temperatures for both the sample and sample holder indicated that the change in adsorption site is related Ta sites, and that annealing to 673 K induces the potential alloying of WSe_2 with Ta. To test this hypothesis, a clean WSe_2 surface was gently sputtered via Ar^+ bombardment to induce defects without thermal annealing. A resulting shift in the low temperature desorption peaks for methanol/WSe_2 (120-140 K) as sputter energy increased indicated that ion bombardment increased the defect inventory of WSe_2 without alloying. Future microscopy studies will link the geometric changes induced by sputtering WSe2 to the shift in methanol binding energies, lending insight into the structure/stability relationships of TMD defects.

Quality Control for Untargeted Metabolomics in Single Malt, Single Hop (SMaSH) Beers Brewed with Five Genetically Different Yeast Strains

Juan M. Garcia, Maxwell J. Tyree, and Dr. Christine A. Hughey
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA



Beer is a complex mixture made of thousands of compounds. Most of the compounds present are unidentified. Since it is not feasible to identify all compounds, metabolomic tools are used to extract compounds of potential interest. Here a single malt, single hop (SMaSH) pale ale was fermented with five genetically distinct yeasts strains: Belgian Saison, California ale, Czech pilsner lager, English ale, and Extreme fermentation. Samples were systematically collected throughout brewing and fermentation. The 89 samples collected were randomized for analysis by reverse phase liquid chromatography coupled to a quadrupole time of flight mass spectrometer (LC q-TOF MS). Each sample was analyzed in triplicate in both positive and negative ion electrospray (ESI) modes. All samples were spiked with caffeine and naphthoic acid to monitor retention time and response (both MS and UV) reproducibility. Large untargeted studies, such as this one, require robust quality control measures to ensure that high quality data is collected over weeks and/or months. Data collected thus far indicates that retention time reproducibility and mass accuracy are very high. MS and UV response fell within acceptable limits (<10% RSD) until recently. Because of the internal standards, we were able to immediately identify a problem and are now working to resolve it. Once the data set is collected, Mass Profiler Professional (MPP) will be employed to discern similarities and differences in compounds across the five genetically different yeast strains. MS/MS spectra will be used in a molecular networking workflow within the Global Natural Product Search (GNPS) to facilitate compound identification.

Induction of Natural Products by Fungal-Fungal Co-Cultures

Shyleigh A. Good, Mary M. Sessoms, Frances E. Homan, Lyn G. Haugh, Ashley E. Clements, Alexa G. Lee and Dr. Lindsay K. Caesar
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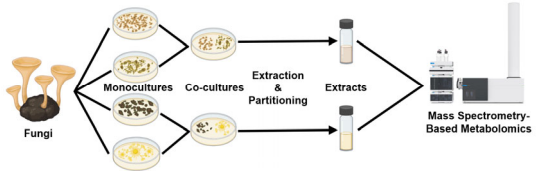

Secondary metabolites (natural products) from bacteria, fungi, and plants have had major impacts on human society, producing many commercially-used small molecule pharmaceuticals and agrochemicals. Fungi biosynthesize a plethora of chemically and structurally diverse secondary metabolites, many of which have found use as drugs, pigments, dyes, antioxidants, and other consumer products. Despite the promise of fungal secondary metabolites, the majority of fungal biosynthetic pathways remain silent under laboratory conditions, and their associated secondary metabolites are not produced unless induced by an external stressor. Co-culturing, a technique that involves growing two different fungal strains on the same media, induces stress on fungi by limiting space and nutrients for growth. The competition between fungi for resources can result in the expression of silent biosynthetic pathways that form new secondary metabolites. Nine fungal strains were isolated and grown from soil collected at 38°26'0" N 78°51'41" W in Harrisonburg, VA, on January 23, 2023. Of the 36 soil fungal-fungal co-cultures, ten of them were pursued for further study due to noticeable interactions between fungi detected by visual changes in the appearance of the fungi in the co-culture as compared to the monoculture. The nine soil fungi were also co-cultured with a cave fungus collected from Grand Caverns in Grottoes, VA. Co-culturing fungi from two different ecological niches, such as a cave fungus from an extreme environment with soil fungi from a moderate environment, may induce novel secondary metabolites. Of the nine cave fungal-soil fungal co-cultures, four of them were identified for further study. Target co-cultures were prepared for chemical analysis by growing them on rice, extracting them in $CHCl_3$, and eliminating sugars and fats using liquid-liquid partitioning. The resulting extracts were dried by N_2. Future work includes analyzing these extracts by UHPLC-MS to identify novel compounds using untargeted mass spectrometry-based metabolomics and MS^2-based molecular networking.

Ecological Inspired Co-cultures of Anti-fungal Bacteria to Combat White-Nose Syndrome

Evelyn Haugh[1], Alexa Lee[1], Ashley Clements[1], Diana Northup[2], Paris Salazar-Hamm[2] and Dr. Lindsay Caesar[1]
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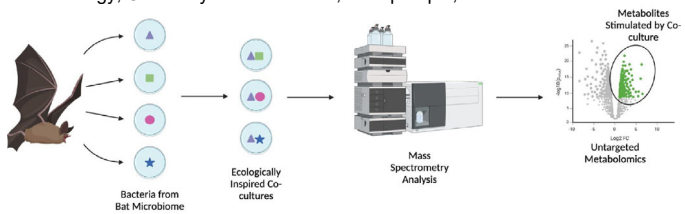

Bats play a crucial role in global biodiversity and support diverse ecosystems. Unfortunately, the fungal pathogen *Pseudogymnoascus destructans,* the causative agent of White-Nose Syndrome (WNS), is sweeping across the US, killing over 7 million bats in the last decade. Already two of the 47 North American bat species are endangered (4%), and another ten (21%) are affected by WNS with varying severity. Previous efforts surveyed >1000 bacterial isolates from bats captured in and around WNS-free caves in New Mexico and Arizona and found ~100 strains with anti-*P. destructans* activity, suggesting that bats' natural microbiome may provide some protection from infection. Preliminary studies on 18 strains that exhibit antifungal behavior against *P. destructans* were performed and a suite of putative antifungal molecules were identified for purification efforts. Unfortunately, upon arrival at James Madison University, the strains of interest no longer produced the target antifungal metabolites under standard culture conditions. To more accurately mimic the ecological niche in which these bacteria originate, we are now working to produce ecologically-inspired co-cultures with bacteria isolated from the same bat species to induce expression of biosynthetic pathways that may produce these target metabolites. Following growth of co-cultures, untargeted mass spectrometry-based metabolomics will be used to evaluate expression of the target antifungals and identify additional up-regulated metabolites induced by co-culture experiments.

Solution Structure of the hMDH2-hCS Metabolon

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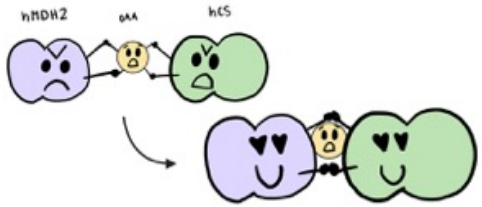

The tricarboxylic (TCA) acid cycle is a process that occurs in mitochondria which produces energy for cellular function. One multi-enzyme complex that regulates metabolic flux in the TCA cycle is the malate dehydrogenase (MDH)-citrate synthase (CS) complex. Overexpression of MDH has been found in a variety of cancers, and high concentrations of MDH have been used as a possible cancer prognosis. Mitochondrial human malate dehydrogenase 2 (hMDH2) mutations have also been suggested to cause early-onset severe encephalopathy, which is a condition characterized by refractory seizures, neurodevelopmental impairment, and poor prognosis. While there are several predicted structures of the MDH-CS complex, they are inconsistent and lack enough information to be insightful due to variations in crosslinking and docking models. The lack of a known structure prevents us from understanding the channeling of oxaloacetate between the two enzymes and the regulation of this process. We aim to describe the structure of the hMDH2-hCS complex using small-angle X-ray scattering (SAXS) to identify a potential structural model leading to the characterization of the biochemical functions of this complex. We aim to empirically support a hypothetical model to provide more information about how the complex functions. hMDH2 and hCS were expressed in E. coli and purified separately before being cross-linked to form a stable complex. Structural analysis of hMDH2, hCS, and hMDH2-hCS was completed using size exclusion chromatography (SEC) coupled to SAXS and high-throughput (HT) SAXS. Modeling was performed using DENSS and HADDOCK. SAXS data on hMDH2 and hCS alone is consistent with existing structural data and models. We are fitting and refining existing models based on biochemical studies to our SAXS data. The refined model based on the SAXS data will be useful for describing substrate channeling for this metabolon, which will provide insights into potential therapeutic targets that are linked to human disease.

Laboratory-scale Model of the Maillard Reaction in a Single Malt, Single Hop (SMaSH) Beer

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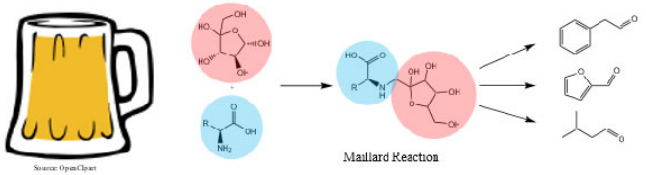

The Maillard reaction, a non-enzymatic browning reaction that produces flavor, is hypothesized to occur during brewing of a single malt, single hop (SMaSH) beer due to the presence of amino acids, sugar, and heat. During mashing, in which malt is added to water and sugars, amino acids, and flavor compounds are extracted, Maillard reaction intermediates, specifically Amadori rearrangement products (ARPs), are also extracted. These compounds originate from the malt and result in the formation of Strecker aldehydes and other flavor compounds. Thus, ARPs can influence the flavor of the final beer. Previous work suggests that brewing conditions may lead new, additional ARPs to form in wort from free amino acids and sugars. A method was developed to track the reaction by quantifying amino acids, sugars, ARPs, and volatile flavor compounds in a laboratory-scale simulation of brewing. Specifically, a 2:1 ratio of maltose to amino acid (either leucine, Leu, or phenylalanine, Phe) was added to water and heated for 60 minutes at 90°C followed by 45 minutes at 105°C. Amino acids and their respective ARPs were quantified using HILIC positive-ion LC/MS-QqQ-MS. MS/MS experiments were performed on ARPs using q-TOF MS, and fragmentation patterns of ARPs were confirmed by matching to the literature. Maltose was quantified using a similar method in negative ion mode, and volatile flavor compounds were quantified with headspace solid phase microextraction (HS-SPME) GC/MS. In both Leu and Phe systems, ARPs increased significantly after 60 minutes of heating. Accordingly, Phe decreased throughout the reaction while Leu remained relatively constant. In the Leu system, maltose also decreased during the reaction. In both systems, flavor compounds nonanal and decenal increased. The Phe system also saw the production of ethyl acetate and phenylacetaldehyde. This work demonstrates that ARPs can indeed be formed at mashing and boiling temperatures.

Enhancing the Selectivity of Acetaldehyde Formation Using Copper-based Metal Catalysts

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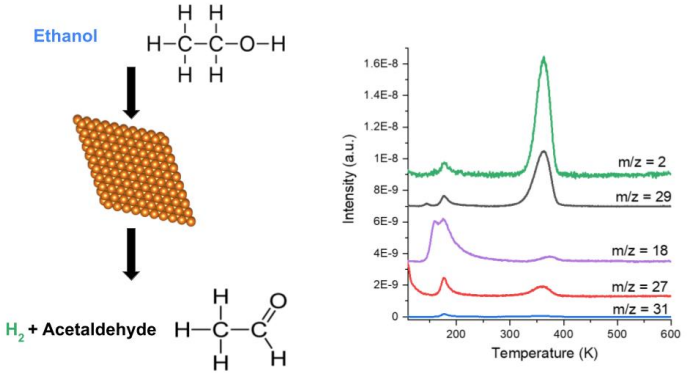

Many metals and their oxides have proven to be efficient catalysts for small alcohol reactions under ultrahigh vacuum (UHV) conditions. Ethanol is a common reagent found in industrial reactions due to its oxidation reaction producing acetaldehyde and hydrogen, both of which hold markets worth several billions of dollars. Reactivities of flat, roughened, and surface oxidized Cu(111) (CuOx/Cu(111)) surfaces were studied using temperature programmed desorption (TPD). The different Cu(111) surfaces were compared to determine which could most efficiently complete ethanol oxidation while limiting the dehydration reaction, which forms ethylene and water.

A Tale of Tails: A Spectroscopic Investigation of the Primary and Secondary Interactions of Polyol Plasticizers in Molecular and Polymeric Systems

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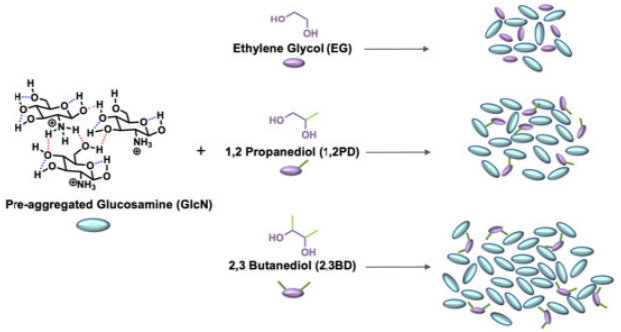

The use of bioplastics as modern alternatives to petroleum-based plastics has been a large source of interest and research in the past decade. The properties of these biomaterials are commonly developed by combining a biopolymer, such as chitosan, with a plasticizer, such as glycerol (Glyc). Previous studies with glucosamine (GlcN), the repeat unit of chitosan, and glycerol indicated the importance of a specific glycerol binding motif on GlcN aggregation. Glyc has the capability of 1,2 or 1,3-OH primary binding, with an additional OH functionality for secondary binding interactions. In order to effectively understand the impact of primary binding on the aggregation and disaggregation of GlcN, ethylene glycol and (1,3)-propanediol were used to probe 1,2 and 1,3 binding specificity, respectively. Secondary interactions were then further investigated using polyol plasticizers with varying alkyl tail lengths, while keeping the primary binding mode constant. Intermolecular interactions between all diols and GlcN were spectroscopically analyzed using dynamic light scattering (DLS), attenuated total-reflectance infrared spectroscopy (ATR-IR), and nuclear magnetic resonance (NMR). Based on these results, we found that both primary and secondary plasticizer-GlcN interactions are critical for hydrogen-bonding with GlcN, disrupting intramolecular GlcN interactions and promoting GlcN-GlcN aggregation. Ethylene glycol and 1,3-propanediol readily bind to GlcN, only methylated derivatives (1,2-propanediol, 1,3-butanediol, and 2-methyl-1,3-propanediol) impact GlcN intramolecular hydrogen-bonding and self-assembly. We have further correlated these spectroscopic observations with GlcN to variations in material and mechanical properties of plasticized chitosan films.

Synthesis and water absorption of metal carbonates, $Na_2Cu(CO_3)_2\ 3H_2O$, $Zn_5(CO_3)_2(OH)_6$, and $Na_2Zn_3(CO_3)_4\ 3H_2O$

Sam Mason and Dr. Thomas Devore
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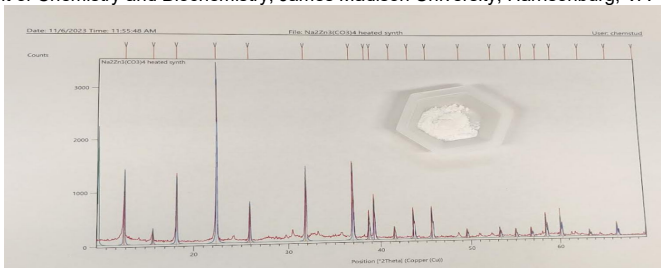

Multiple metal carbonates were synthesized and characterized with a focus on their ability to release and absorb water when heated. These metal carbonates were synthesized through precipitation after the combination of a sodium carbonate and a metal salt hydrate, with the specific compound forming being dependent on the ratio between reactants, synthesis was also investigated at several different temperatures. After synthesis characterization was found through a combination of infrared spectroscopy (IR), powder x-ray diffraction (PXRD), and differential scanning calorimetry (DCS). Multiple weight analysis trials were also performed on the samples to analyze the amount of water that was lost through heating and gained when left in humid conditions. This research shows the synthesis characterization and water absorbing properties of multiple metal carbonates.

Specific Ion Effects: Hofmeister Cation Effects on the Fluorescence of Coumarin and Derivatives

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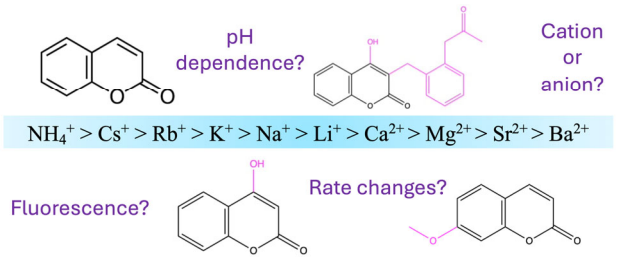

The Hofmeister series as it relates to the fluorescence of coumarin and its derivatives is investigated in this study. Coumarin was chosen as a model drug due to its hydrophobic and hydrophilic areas allowing ions to interact in contrasting ways. Coumarin has various derivatives including Warfarin, 7-Methoxycoumarin, and 4-Hydroxycoumarin that possess varying properties from their core structure. Hofmeister cations in chloride salts demonstrated fluorescent enhancing, or an increase in fluorescent intensity in coumarin. Hofmeister cations in bromide salts quenched the fluorescence of coumarin, the opposite of chloride salts. Experiments on mixed salts indicated varying fluorescence enhancing or quenching properties depending on the salts mixed. Coumarin derivatives demonstrated varying enhancing or quenching based on functional group interactions with ions. Further, protonation states in warfarin and 4-hydroxycoumarin greatly affected their fluorescent quenching patterns. Different buffers and pH experiments provide contrasting results from the parent molecule. The results of these fluorescent studies will be presented.

The Vibrational Spectra of Glycerol-boric Acid Complexes

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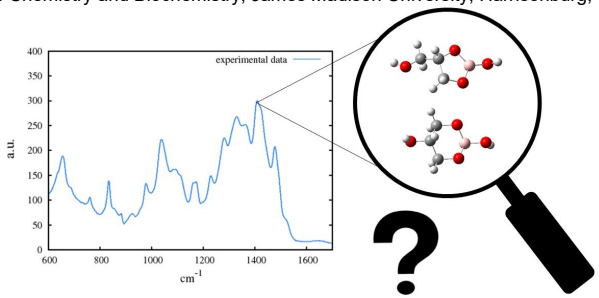

Chitosan, a polysaccharide of linked D-glucosamine units, is found in crustacean exoskeletons and fungi and is a promising biopolymer with potential as a biodegradable plastic for food packaging, as well as nontoxic material for a range of biomedical applications. Generally, small molecule plasticizers, such as glycerol, are added to chitosan films to plasticize and improve the material properties. Manipulating the binding motif of glycerol would change hydrogen-bonding interactions between glycerol and chitosan repeat units and thus alter glycerol's ability to function as a plasticizer. Experimentally this was done using boric acid to bind to glycerol, effectively reducing the available sites for plasticization. However, the vibrational spectra of glycerol and boric acid complexes are not well characterized, making it difficult to gain an atomic-level understanding of the interactions between chitosan and these modified plasticizers. Therefore, we use computational chemistry to better understand the vibrational spectra of these complexes. We simulate vibrational spectra using the M06-2x/6-311+G(2d,p) level of theory. Additionally, the vibrational spectra of different ratios of glucosamine, the repeat unit of chitosan, and glycerol-boric acid complexes were used in these processes and compared to experimental results. Our computational results are in good agreement to experimental spectra and can be used to gain a detailed understanding of the types of interactions formed in chitosan/glycerol bioplastics. Additionally, other polyols are currently under investigation for their ability to plasticize chitosan.

Measuring Cellular Mechanics Using Image Analysis Techniques to Provide Evidence for a Molecular Pathway Involving Obscurin

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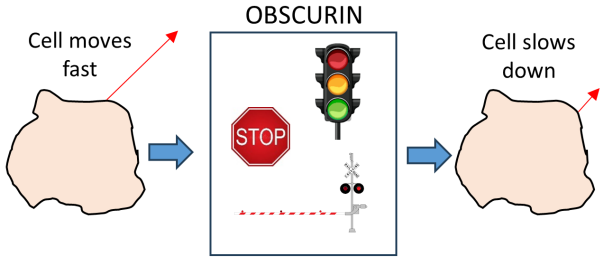

Obscurin is a large cytoskeletal protein found in epithelial and muscle cells. When obscurin is knocked down or out, the cell undergoes an epithelial tomesenchymal transition (EMT), a process associated with cancer development. This is accompanied by faster cell migration. The molecular mechanism of how obscurin inhibits migration is thought to be through a global activation of the RhoA/ROCK pathway. However, we find that the C-terminus of obscurin partially colocalizes at the membrane, which is not where RhoA is located. Here we begin probing the cellular significance and mechanism of this unexpected localization pattern. Adding extra obscurin to MDCK epithelial cells hinders motility. However, the addition of the ROCK inhibitor, Y-27632, does not rescue motility, suggesting that obscurin partially controls motility through another pathway. BioID and colocalization experiments suggest obscurin interacts with multiple adhesion junctions. Actin staining shows that obscurin-containing cells lose their central stress fibers in a phenotype reminiscent of ROCK inhibition. Relatedly, disruption of the actin cytoskeleton normally flattens cells, but the presence of obscurin
rescues the wild-type phenotype. These findings collectively suggest that obscurin indirectly modulates the cytoskeleton by engaging in non-RhoA motility pathways, likely at the cell membrane.

Altering Acetate's Chemical Shift and Relaxation Time Based of Viscosity and Counter Cation

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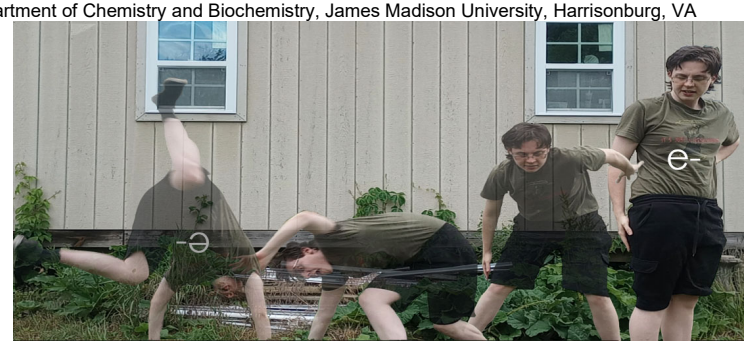

The acetate ion is a common organic ion that cannot exist in a solid state without a positive metal ion associated with it. When dissolved in solution the metal ion alters some of acetate's properties from interactions between the ions. This study analyzed what effect altering the metal ion and the concentration of acetate in solution had on the chemical shift and T_1 relaxation time of the solutions measured using NMR. The samples were analyzed on a 400 MHz NMR in single tubes for compounds dissolved in D_2O, and in coaxial tubes for compounds dissolved in water. The ions used with acetate were all 2+ ions, and a concentration series was performed on magnesium acetate in the coaxial tube. Relaxation time and chemical shift were drastically shortened and moved downfield respectively by using paramagnetic instead of diamagnetic ions. Diamagnetic ions had slightly different chemical shifts and the relaxation times loosely following the trend of atomic radius. Decreasing ion concentrations increased the relaxation time and moved the chemical shift downfield. The main take away from this research is that T_1 is inversely proportional to viscosity and as pH decreases the T_1 takes increasing character from the conjugate acid.

A Modular, Affordable, 3D-Printed FPLC

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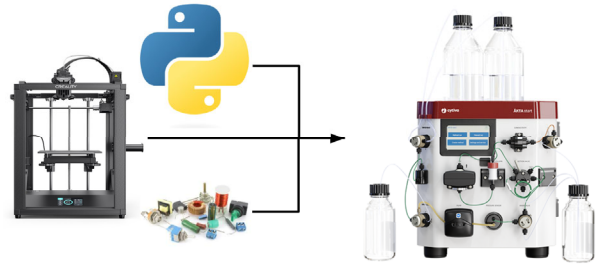

Liquid chromatography systems are prohibitively expensive for undergraduate education and research, typically priced in the tens of thousands of dollars. To more broadly introduce liquid chromatography to education and research, this work describes a modular liquid chromatography system, designed for biochemistry teaching labs, composed of detectors and supporting components. The entire assembly is powered using a standardized ATX power supply, avoiding complex and expensive custom power supplies. Weak signals from various detectors are amplified using a modular op amp, capable of amplifying up to 4 signals at once. A UV detector, composed of a 3D-printed flow cell with glass coverslip windows, a UV LED, and a UV photodiode that does not require focusing lenses and mirrors is available. Additionally, a conductivity detector is in development, which will provide information about salt concentrations during the run. Fluid flow is provided by a 3D-printed peristaltic pump, and a fraction collector and pressure sensor are under development. Data collected throughout the chromatography run is collected and averaged by the Arduino and is sent to a Python-based control program on a user's computer. This control program can display real-time run data, save and view runs, and control pump speed. 3D models are available online through Tinkercad, a free and easy-to-learn online modeling program. Ultimately, we aim to introduce this work into undergraduate teaching labs.

Synthesis and Characterization of Bicephalic Biscationic Amphiphiles with Potential for Zeolite Templating

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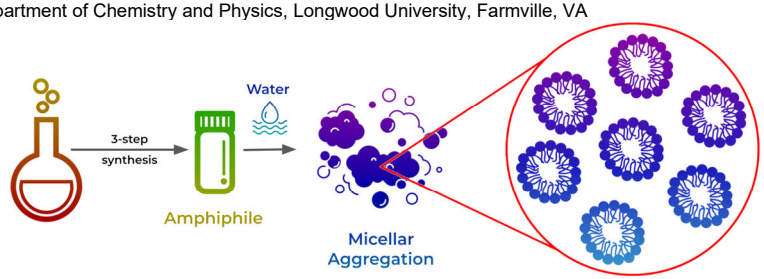

Zeolites are porous, crystalline materials usually made of aluminum, silicon, and oxygen. They have been historically utilized in the petrochemical industry for oil refining. Zeolites exhibit exceptional abilities in environmental remediation and as efficient catalysts, which can be largely attributed to the size and shape of the pores within their structure. Pore size and shape are heavily influenced by the synthesis of the zeolite. This study focuses on aqueous micellar suspensions derived from various synthetic amphiphiles and their ability to act as soft templates for zeolite formation. Each amphiphile, made via a 3-step synthesis, has two carbon linear hydrophobic alkoxy chains and two hydrophilic cationic headgroups of varying composition. Studies include amphiphile synthesis, colloidal examination of the aqueous micellar suspensions, and zeolite templating using these novel amphiphiles.

A Colorimetric Assay to Determine Substrate Specificity of Beta-Amylases

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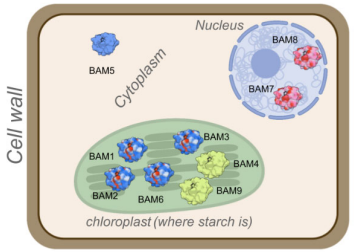

Starch is the primary form of energy storage for plants. During the day, starch is synthesized, stored, and then broken down in the chloroplast during the night to form usable sugar in the form of maltose. Among the enzymes that catalyze this degradation are β-amylases, which cleave two glucose units from the reducing end of a polyglucan chain, forming β-maltose. The Arabidopsis β-amylase (BAM) gene family is commonly used as a model system to study amylases. β-amylase (BAM) proteins are diverse in both structure and function, and collectively contribute to a number of cellular processes including gene expression and starch metabolism in plants. There are five catalytically active BAMs in Arabidopsis that are expressed under different conditions and are localized either in the chloroplast or the cytoplasm, although their specific functions are unclear. The goal of this project is to examine the substrate specificity and selectivity of β-amylases found in Arabidopsis as a means to understand their broader roles in the physiology of the plant. In order to quantify the generation of new reducing sugars, the bicinchoninic acid (BCA) assay was used, which is a colorimetric assay that operates by the reduction of copper ions and the formation of a colored copper-bicinchoninate complex. Data was collected for the activity of several β-amylases from Arabidopsis and compared them to a well characterized ortholog found in sweet potatoes (Ipomoea batatas BAM5). Kinetic data was collected for various substrates, including soluble starch, maltodextrin, and the individual components of soluble starch: amylopectin and amylose. Future directions include expanding the tested substrates, and collecting kinetic data for other catalytically active BAMs, ultimately leading to a comprehensive understanding of the way different Arabidopsis β-amylases interact with substrates and function within the plant.

Understanding CO Binding Trends for CO_2 Reduction Catalyst Optimization

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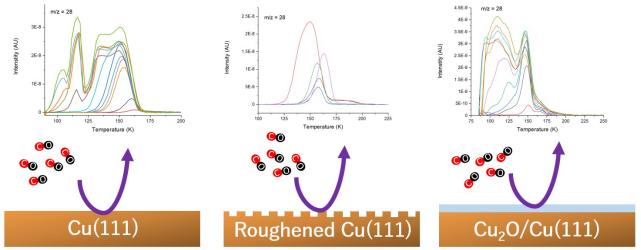

In the past century, there has been a drastic increase of anthropogenic carbon dioxide (CO_2) in the Earth's atmosphere. The excess of this greenhouse gas has dramatic negative effects on the environment such as extreme weather patterns, poor air quality, and a rise in global temperatures. Studying the thermodynamics of the formation of CO_2 is a crucial component to combat this obstacle. Cu-based catalysts are the industrial standard for the reduction of CO_2. One mechanism for CO_2 reduction first produces CO as an intermediate, however the binding of CO to metal sites inhibits further CO_2 reduction. Therefore, CO binding must be minimized to promote the efficient reduction of CO_2. This is a detailed study of the adsorption and reaction of CO to CO_2 on a Cu(111) surface with the goal of identifying and minimizing CO adsorption sites. Clean and sputtered Cu(111), as well as oxidized Cu_2O/Cu(111) samples were prepared under ultrahigh vacuum (UHV) conditions and exposed to varying pressures of CO. Temperature programmed desorption experiments were done on each of the prepared samples. Defects imposed by sputtering formed higher energy CO adsorption sites, whereas oxidized surfaces decrease the stability of CO binding. Therefore the oxidized Cu(111) surfaces play an important role in minimizing CO poisoning on Cu catalysts.

Using Infrared Spectroscopy to Monitor Protein Unfolding with Hoffmeister Salts Over Time Without the Addition of Heat

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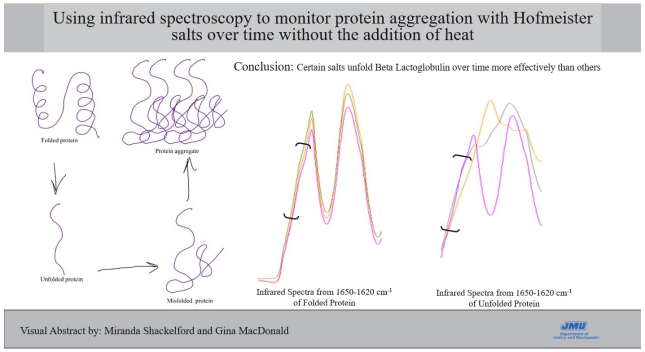

Protein aggregation has been widely studied because of the impact's proteins have on living organisms. Understanding how these proteins unfold under different conditions can help understand the protein unfolding that occurs in certain neurological diseases. Often in these studies protein unfolding is studied under heated conditions, however since most people are under standard conditions, it is imperative that protein unfolding is understood without the addition of heat. Infrared spectroscopy is commonly utilized to observe protein behavior over time due to its effectiveness to identify known unfolded peak structure. This experiment uses 40 mg/mL Beta- Lactoglobulin (BLG) in 20 mM HEPES buffer with 500mM $NaNO_3$, 500mM $NaSO_4$, 500mM NaCl, and 500mM $NaClO_4$ to understand how time impacts the protein with salt solutions. In this study, it was found that after fourteen weeks the following aggregated greatest to least: 40 mg/mL BLG in 20 mM HEPES, 40 mg/mL BLG and 500mM NaCl, 40 mg/mL BLG and 500mM $NaNO_3$, 40 mg/mL BLG and 500mM $NaClO_4$, and 40 mg/mL BLG and 500mM $NaSO_4$. Due to the known effects of the Hofmeister series, these results need further investigation to fully understand how these salts impact BLG without the addition of heat.

A Novel Synthetic Strategy for Antisense Oligonucleotide Analogs

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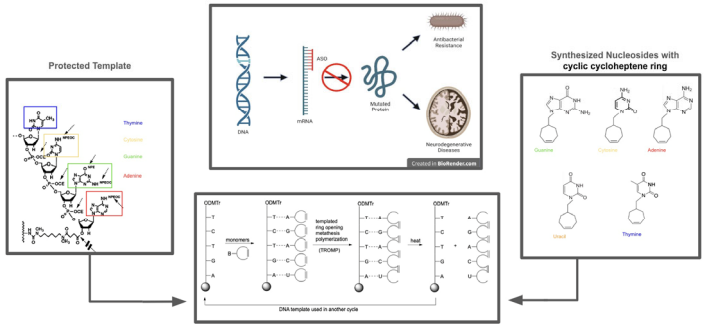

Antisense oligonucleotide analogs (ASOs) are short, modified RNA molecules that have the ability to bind messenger RNA (mRNA) and prevent protein transcription through various mechanisms. ASO technology has the potential to prevent or reduce the severity of numerous diseases by limiting harmful protein production. In vivo, ASOs often face degradation, membrane impermeability, RNase activity, and non-specific activities. In an effort to address these challenges, we propose to produce more stable ASO analogs via a novel synthetic strategy from nucleoside analogs. The synthesis and characterization of the Adenine, Cytosine, Thymine, and Uracil derivatives have all been achieved, while the characterization of the Guanine derivative is still ongoing. In order to polymerize the nucleic acid derivatives into the ASO analog, a reusable oligonucleotide template on a solid support is needed. Therefore, out current work is focused on modifying the protecting group strategy by which oligonucleotide strands are synthesized on the solid support.

Understanding the effect of Obscurin on cellular architecture and dynamics

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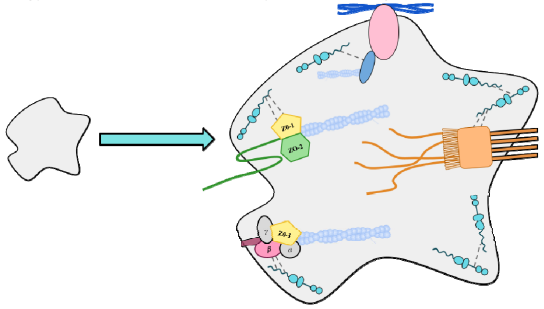

Obscurin is a large cytoskeletal protein found in epithelial and muscle cells. It is the second most mutated protein in breast and colorectal cancers and is significantly downregulated in pancreatic cancer. Obscurin activates ROCK via RhoA, which in turn activates actomyosin contractility, F-actin polymerization, and modulates cellular motility and migration. Obscurin knockdown leads to an epithelial to mesenchymal transition (EMT), a hallmark of cancer progression. Here, we extend these findings to show that the C-terminus of Obscurin A localizes near the cell membrane in MDCK cells. At the cell membrane, the presence of this part of Obscurin A both colocalizes with membrane-junction proteins and prevents stress fiber formation, but does not seem to prevent F-actin polymerization. These changes to the cytoskeleton and membrane system are associated with slower cell migration. In these same cells, Obscurin A is under >5 pN of tension force, and changes in cell architecture, through both drugs and physical distortions, decrease this tension. Together, the fact that Obscurin is under tension, alters cellular mechanics, and alters both cytoskeleton and the cell membrane suggest Obscurin is a mechanosensor.

Synthesis and Critical Micelle Concentration (CMC) of Biscationic Amphiphiles with Various Carbon Chain Lengths

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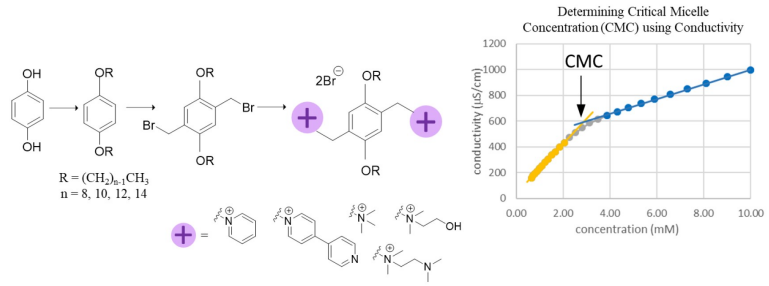

Five series of cationic amphiphiles were prepared and their structure-property relationships were investigated. The synthesized amphiphiles each contain an aromatic core with two cationic headgroups, and two alkoxy tails of varying length. For each of four chain lengths, hydroquinone was subjected to a Williamson Ether Synthesis to produce a diether with two linear chains. Two bromomethyl groups were subsequently installed via electrophilic aromatic substitution. Each dibromide served as a common intermediate to produce 5 different series of amphiphiles with varying cationic head groups. Aqueous critical micelle concentration (CMC) values were measured using a conductivity probe for two of the head group series. This allowed comparison of colloidal properties with varying chain length and head group identity. There is an inverse logarithmic relationship between CMC and hydrophobic chain length for each series tested. 1H and 13C NMR were taken to confirm structural identity. These amphiphiles can be used in various applications such as serving as antimicrobial agents or as templates for zeolite formation.

Synthesis and Characterization of Nickel-Cobalt Mixed Metal Tutton Salts

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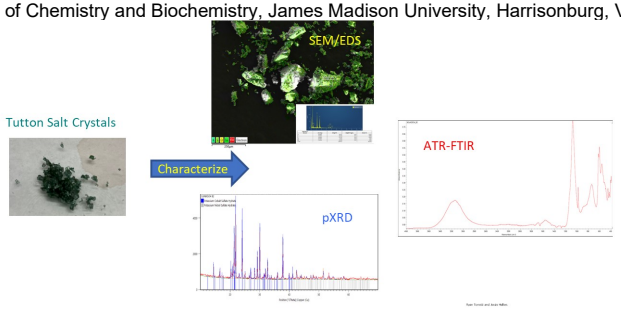

Tutton salts have applications in heat recovery and optical lenses. There has been recent interest to fine-tune these applications using mixed metal Tutton Salts. In this research, we synthesized mixed Nickel-Cobalt Tutton Salts through isothermal evaporation of water. We characterized the crystals through Powder X-Ray Diffraction (PXRD), Fourier-transform infrared spectroscopy (FTIR), Differential scanning calorimetry, and Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDS). Batches of crystals were taken at different stages of crystal growth and separately characterized. It was found that at early stages of crystal growth, Nickel-rich Tutton Salts precipitate out of the solution first with Cobalt-rich Tutton Salts precipitating out of the solution when most of the water has evaporated.

Embedding Metal Organic Frameworks (MOFs) in Chitosan Beads for Dye

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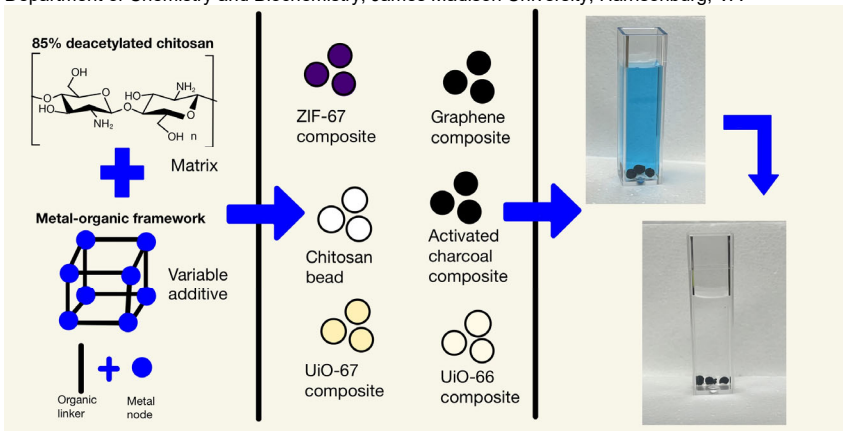

The goal of this research is to prepare zeolitic imidazole framework (ZIF) and metal organic framework (MOF) chitosan composites to improve the removal of contaminants from aqueous solutions. MOFs and ZIFs are porous, crystalline materials composed of metal ions and organic linkers. Chitosan is a polysaccharide derived from chitin. When combined with acetic acid and polyacrylic acid (PAA), chitosan and MOFs/ZIFs form functional composites that can be used to uptake dyes. The concentration of chitosan, amount of additives, and ratios of additives were explored to produce viable composite beads. The adsorption capacity of composites including UiO-66, UiO-67, ZIF-67, graphene, and activated charcoal was studied. UV-Vis's spectroscopy was used to measure the uptake of the cationic dye, malachite green. Powder X-Ray diffraction (PXRD) was used to show that the additives were incorporated in the chitosan composites. This research will compare the rate and amount of dye uptake by the various composites.

2024 Department of Chemistry and Biochemistry Student Award Winners

Amenta Award	Shyleigh Good
R.D. Cool Award	Eric J. Shephard
J.W. Chappell Scholarship (May 2023)	Lynnea S. H. Gedney
Palocsay Award in Undergraduate Research	Patrick T. Randolph
Service Award	Lauren Slaber
J. W. Chappell Award	Lynnea Geddney
American Institute of Chemists	Hayden Chewning
Degesch America Award	Steph Ouderkirk
ACS Award	Nina Metzger
Casali Scholarship (May 2023)	Angelina V. LoPresti
Dean's Award (Chemistry)	Ava Galgano
Dean's Award (Biophysical Chemistry)	Ross Hilfiker
CRC First Year Student Award	Emily M. Euler
NOBCChE Dr. Iona Black Award	Juan M. Garcia
Inclusive Excellence Award	Gabby Newsome
Goldwater Scholar	Patrick Randolph
Outstanding Student Researcher Award	*to be announced*

Divisional Awards

ACS Analytical Award	Ashley Clements
ACS Biochemistry & Chemical Biology Award	Zach Ryan
ACS Environmental Award	Samantha Forbes
ACS Inorganic Award	Shyleigh Good
ACS Organic Award	Ava Galgano
ACS Physical Award	Angelina LoPresti

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- RUI : PHY-1614475, MCB-1817448, AST-1814594, MCB-1607024, MCB-1616467, MCB-2322867

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