# SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
# FINAL REPORT

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|---|---|
| **SCHOLAR NAME:** | John Moore |
| **FACULTY ADVISOR:** | Dr. William A. Phillip |
| **PROJECT PERIOD:** | May 22, 2023-July 29, 2023 |
| **PROJECT TITLE:** | Charge-Functionalized Nanofiltration Membranes Exhibit Multi-Valent Ion Rejection |
| **CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):** | **( X) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear<br>( ) Smart Storage and Distribution ( ) Transformation Solar<br>( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind** |

## MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

| RESEARCH GOALS | ACTUAL PERFORMANCE AND ACCOMPLISHMENTS | % OF GOAL COMPLETED |
|---|---|---|
| **Develop a Reproducible Protocol for Functionalizing Large Membranes** | Developed a highly reproducible protocol for charge-functionalizing membrane sheets using copper catalyzed azide-alkyne cycloaddition reactions that afforded high rejection of target solutes. Protocols for amine-isothiocyanate coupling reactions were also developed, however not detailed in the report. | 80% |
| **Quantify the Impact of Membrane Functionalization on Target Solute Transport** | Fourier-Transform Infrared Spectroscopy was used to track the progress of the reaction as the azide moiety in the membrane chemistry is converted to a triazole, which removes the azide peak at 2100 $cm^{-1}$. In addition, ion rejection experiments were done that showed high rejection of Cobalt and Lithium cations in neutral and acidic solution, while little to no rejection was observed in basic solution, showing that the pH-dependent functionality was introduced to the membrane and was the reason for the rejection phenomena. | 100% |
| **Develop Protocols for Executing the Functionalization using Inkjet Printing Technology** | Calibration of the inkjet printing interface was achieved, however printing of reactive solutions onto the membrane surface was not undertaken. | 10% |
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## RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

| CATEGORY | INFORMATION |
|---|---|
| **EXTERNAL PROPOSALS SUBMITTED** | (Sponsor, Project Title, PIs, Submission Date, Proposal Amount) |
| **EXTERNAL AWARDS RECEIVED** | (Sponsor, Project Title, PIs, Award Date, Award Amount) |
| **JOURNAL ARTICLES IN PROCESS OR PUBLISHED** | (Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)<br>- **Journal article in process based on work done this summer, title not yet decided.** |
| **BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH** | (Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) |
| **PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH** | (Event, Presentation Title, Presentation Date, Location)<br>**Summer Undergraduate Research Symposium, Charge-Functionalized Nanofiltration Membranes Exhibit Multi-Valent Ion Rejection, July 26, 2023, Jordan Hall of Science University of Notre Dame** |
| **AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT** | (Purpose, Title, Date Received) |

| | |
|---|---|
| **INTERNAL COLLABORATIONS FOSTERED** | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions )<br>- **Dr. Richard Taylor, University of Notre Dame, contacted to collaborate on synthesizing quaternary amine salt for membrane functionalization, weekly email.** |
| **EXTERNAL COLLABORATIONS FOSTERED** | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions)<br>- **Dr. John Hoffman, National Institute of Standards and Technology, contacted for training on inkjet printing technology, infrequent emails and one in person training.** |
| **WEBSITE(S) FEATURING RESEARCH PROJECT** | (URL) |
| **OTHER PRODUCTS AND SERVICES** (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups) | (Please describe each item in detail) |

## RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

**I loved the experience. I had been doing research during the school year, but that doesn't compare. Actually being able to commit 40+ hours per week to research allows for more results and more exciting conclusions, and was a pleasure to take part in. The lab personnel I worked with were both incredibly helpful and knowledgeable, and I would not have completed the work that I did if I had not had them there to bounce ideas and questions off of. I think that more meetings involving just the Slatt Fellows would be an improvement to the experience of the fellowship.**

# FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

Access to potable water is one of the biggest challenges humanity is facing in the 21st century. Membrane technology has shown promise as a means for filtering otherwise potable water and removing harmful contaminants like alkali and heavy metals. Commercially available nanofiltration (NF) membranes treat water through steric rejection, by making the pore size of the membrane smaller than the target solute. This study will explore a different route. By charge-functionalizing the membrane pore chemistry, electrostatic interactions can be utilized to reject target ions in solution.

First, a copolymer is synthesized via a free-radical polymerization between three monomers: trifluoro ethyl methacrylate, poly(ethylene glycol) methacrylate, and glycidyl methacrylate. This copolymer is then precipitated three times in hexane, then dried in a vacuum oven overnight. In order to convert the copolymer to a form that can be reacted, the copolymer is dissolved in dimethyl formamide then reacted with excess sodium azide and ammonium chloride to open the epoxide ring in the glycidyl methacrylate and attach an azide moiety. This new copolymer is precipitated three times in water, then dissolved in 2,2,2-trifluoroethanol.

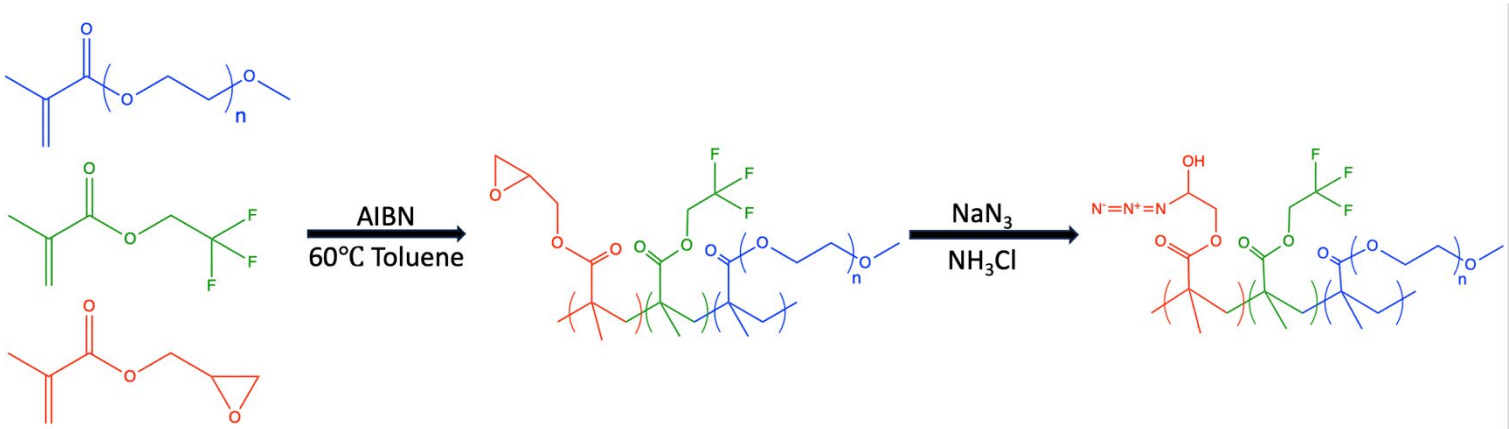



**Figure 1.** Mechanistic steps for the synthesis of the copolymer used in this study. The three monomers used are selected because of their affinity for water. Trifluoro ethyl methacrylate is hydrophobic, and will form the membrane backbone when the microphase separation occurs during casting. Both poly(ethylene glycol) methacrylate and glycidyl methacrylate are hydrophilic, and will form the pore wall during the microphase separation during casting.

Once the copolymer is synthesized, the membranes must be cast. The copolymer solution is pipetted onto a poly(vinylidene difluoride) [PVDF] substrate, then a doctor blade with a gate height of ≈63 µm is drawn back to spread out the solution. The TFE solvent is allowed to evaporate, then the membrane sheet is placed into a non-solvent bath (usually isopropyl alcohol), where the solvent and non-solvent exchange places. After the non-solvent bath, the membrane sheets are removed, allowed to dry for 90 seconds, then cut into disks.

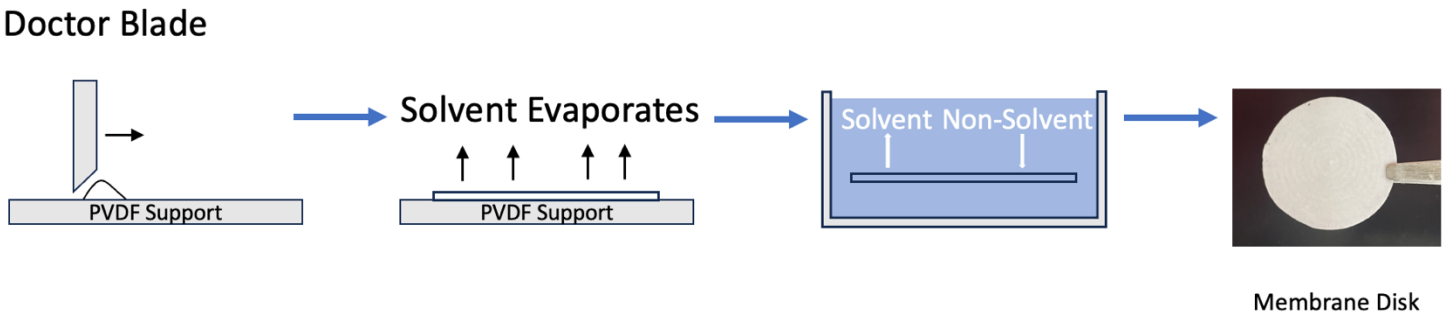



**Figure 2.** NIPS casting procedure for casting membrane disks for testing.

Membrane characterization experiments were done to quantify the pre-functionalization characteristics of the membranes. First, hydraulic permeability measurements were done to quantify the base throughput of the membrane. This is done through a dead-end stirred cell experiment with an Amicon stirred cell. The experiment is done by adding the membrane to the stirred cell with DI water, then applying 60 psi of pressure to the cell. The water will be pushed through the membrane

then collected in a scintillation vial on a scale. The mass readout of the scale is recorded every 15 seconds, then a linear regression is made whose slope will provide the hydraulic permeability of the membrane. Usable azide NF membranes will have a permeability of around 1-5 L $m^{-2}$ $h^{-1}$ $bar^{-1}$.

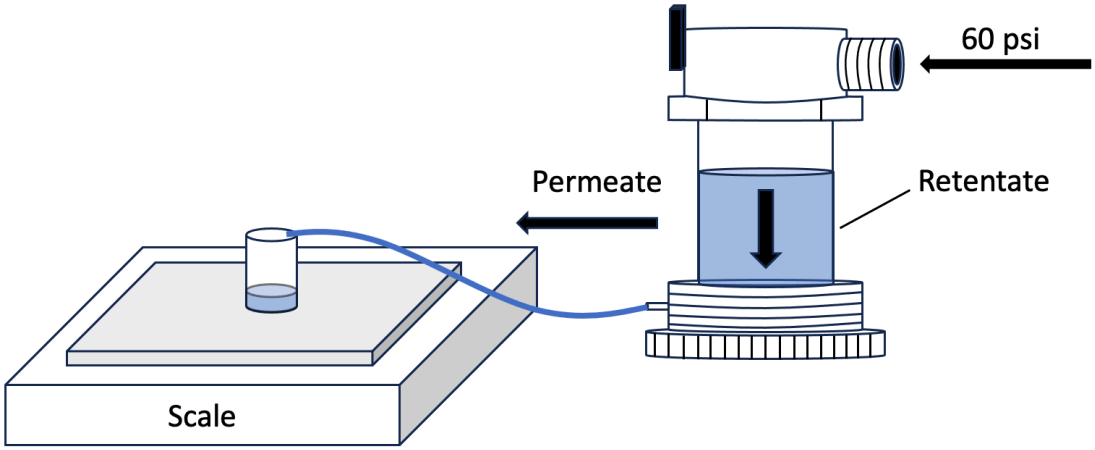
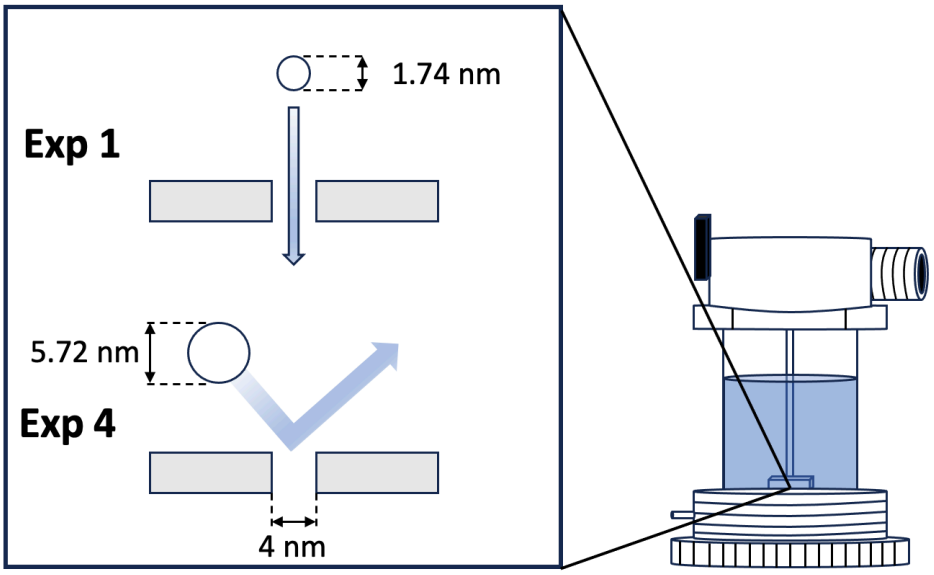
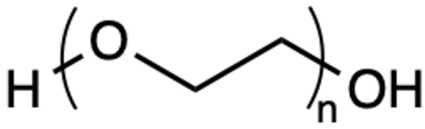



**Figure 3.** Diagram for the collection of hydraulic permeability measurements using a dead-end stirred cell experiment.

Once the obviously unusable membranes (high or extremely low permeability) are weeded out, neutral solute rejection experiments are performed to quantify the pore size of the membranes. This is done using poly(ethylene oxide) [PEO] of varying molecular weight, since it has a definable molecular diameter. These experiments are done in a similar manner to how permeabilities are collected, by adding the PEO solution to a stirred cell and pushing it through the membrane under pressure.




**Poly(ethylene oxide)**

| Experiment | PEO MW (g/mol) | Diameter (nm) |
|---|---|---|
| 1 | 1200 | 1.74 |
| 2 | 2150 | 2.40 |
| 3 | 4150 | 3.47 |
| 4 | 10,200 | 5.72 |

**Figure 4.** Diagram for the performance of neutral solute rejection experiments to determine the pore size of the membranes.

Both the permeate and retentate solutions are collected, then analyzed for carbon concentration using a Shimadzu TOC-L total organic carbon analyzer, and from there, rejection can be calculated, and an estimated pore size can be extrapolated.

Once the membranes are characterized, functionalization reactions can be performed using Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) “click” reactions. Since there is already an azide moiety grafted to the pore wall chemistry, any functional group can be introduced as long as it has an alkyne-terminated substituent. In this study, the alkyne-terminated

primary amine propargylamine is explored, because it is protonated, and therefore positively charged, at neutral and acidic pH.

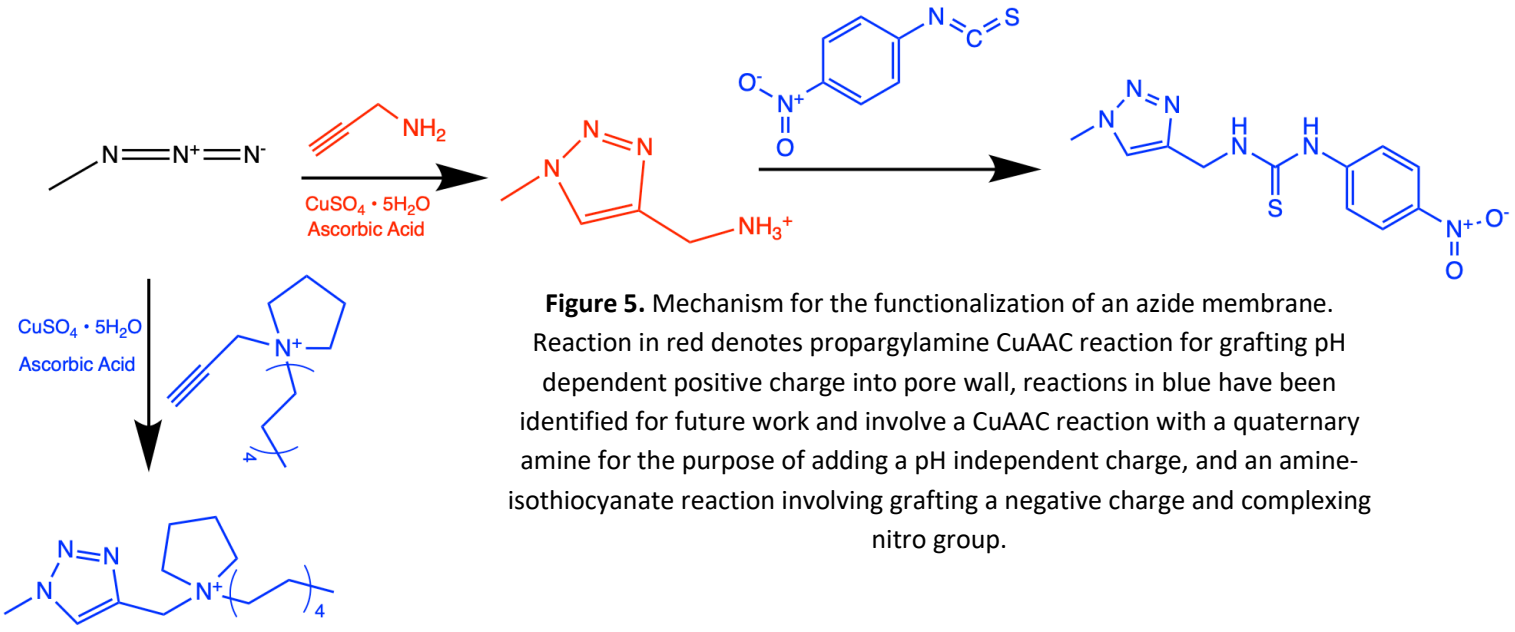



**Figure 5.** Mechanism for the functionalization of an azide membrane. Reaction in red denotes propargylamine CuAAC reaction for grafting pH dependent positive charge into pore wall, reactions in blue have been identified for future work and involve a CuAAC reaction with a quaternary amine for the purpose of adding a pH independent charge, and an amine-isothiocyanate reaction involving grafting a negative charge and complexing nitro group.

The progress of the reaction is tracked using Fourier Transform Infrared Spectroscopy (FT-IR). There is a distinct azide peak that is present in the parent membrane around 2100 $cm^{-1}$, and as the reaction progresses this peak will slowly disappear. The utilities of the CuAAC reaction include its speed and regioselectivity, which allows for tracking to be extremely clear.

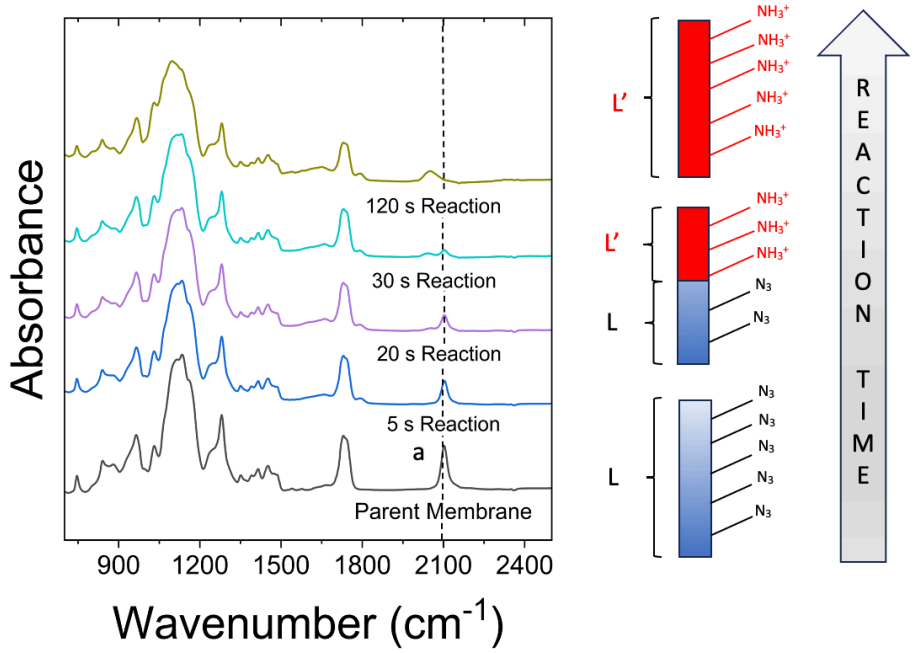



**Figure 6.** Fourier Transform Infrared Spectroscopy diagram showing the progression of the CuAAC functionalization reaction.

Once functionalization is complete, the membranes are transferred to DI water. Before any testing or use can be done, a 15 mM ethylenediaminetetraacetic acid (EDTA) solution must be passed through them using a stirred cell apparatus. The EDTA readily forms water soluble complexes with any copper that is caught in the membrane structure.

The efficacy of the membrane functionalization hinges on its ability to perform ion rejection. Ion rejection experiments are performed using a stirred cell apparatus, but instead of DI water, a dilute solution of a salt is used. Both the permeate and retentate solutions are collected and analyzed using a conductivity meter. Since the ions in solution are electrolytic, they will exhibit different conductivity measurements based on their concentrations in solution. The conductivity of increasing concentrations of the salt solution is taken to construct a calibration curve, which will allow for a direct conversion from conductivity to concentration, allowing for the construction of a rejection curve.

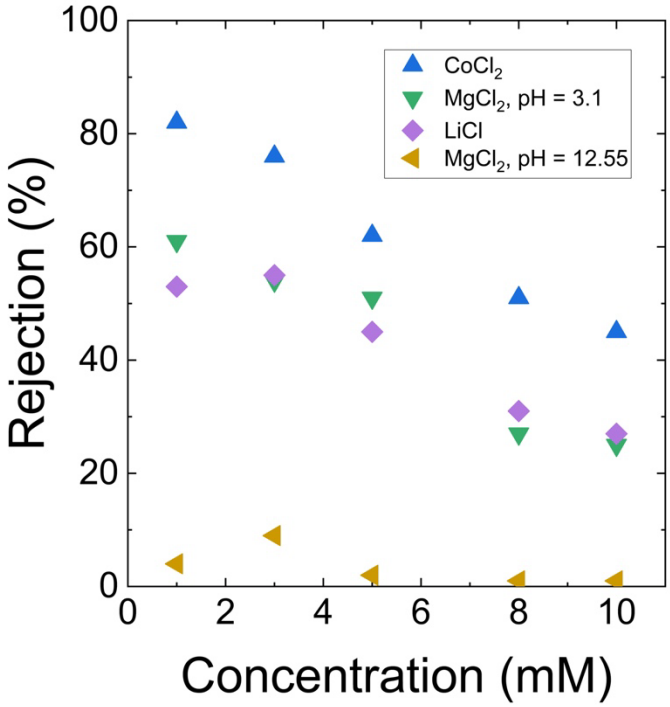



**Figure 7.** Ion rejection curves illustrating the rejection properties of propargylamine functionalized membranes. $CoCl_2$ illustrates the highest rejection because of its adsorption properties, which aid in rejection, while a basic solution of any salt will show no rejection because the primary amine will be deprotonated and no electrostatic interactions will occur.