

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Eva Homberger
FACULTY ADVISOR:	Dr. Peter Burns
PROJECT PERIOD:	January – May 2023 (Spring Semester 2023)
PROJECT TITLE:	Batch Sorption of U ₆₀ Nanocluster to Muscovite in the Presence of Electrolytes
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input type="checkbox"/> Energy Conversion and Efficiency <input checked="" type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> 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
Isotherm Experiment for Sodium (Na⁺)	Fully completed with good ICP data. Percent removal plots were created for elements of interest to distinguish sorption behavior, and isotherm plots have a form that is typical for sorption behavior, close to a Langmuir curve.	100%
Isotherm Experiment for Strontium (Sr⁺²)	Like with sodium, fully completed with good ICP data. Percent removal plots were created for elements of interest to distinguish sorption behavior, and the isotherm plots have a form that is typical for sorption behavior, close to a Langmuir curve. The strontium showed much stronger interaction with the uranium and appeared to contribute to much higher removal.	100%
Controls	Several sets of controls were completed to try to distinguish the roles of individual components within the reaction. However, more controls should be completed to determine baseline levels of removal (if any) due to leaching from the sample holder as well as additional controls for each U ₆₀ concentration and pH of interest, since recent studies indicate that the stability of U ₆₀ depends on the U ₆₀ concentration and pH.	70%
Isotherm Experiments for Potassium (K⁺) and Calcium (Ca⁺²)	These experiments are being put on hold for the time being since the scope of the project is quite large. Choosing to focus on just one monovalent and one divalent cation will allow faster and more focused progress.	0% (nixed)
Kinetics Experiments	The system to complete the kinetics experiment has been designed, which includes a water bath and jacketed flask to maintain constant temperature. However, given the time span necessary to collect data from the entire duration of sorption (at least two weeks), kinetics have been postponed for now.	10%

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)
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)
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)
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
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?

This research experience definitely met my expectations. I really valued the opportunity to have more leadership on a project and appreciated being able to be a part of the entire process, including experiment design, decision-making, budgeting, sharing results at group meetings, and data analysis. Working with graduate students, especially my mentor for this project, Justin Daniels, allowed me to learn new practical skills and good practices for scientific work. Lab personnel, including graduate students and the OWLs, were very helpful and able to provide assistance when needed. I also appreciated being able to discuss my work with my faculty advisor, Dr. Burns, and benefited from his insight. My only suggestion for something that could have been done to allow me to achieve more results would be if I was allowed to work in the lab without supervision, as this would have allowed me to perform more lab work on my own time. However, I understand that this is not always possible for undergraduates given the safety protocols of the actinide research lab.

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.)

Motivation

Nuclear energy presents a carbon-free and scalable solution to the looming energy crisis, but proper waste treatment is necessary to ensure that nuclear energy is sustainable in the long-term. The motivation for this project stems from the looming issue of the Hanford Site in Washington State, a decommissioned nuclear production complex that now has become a massive national liability due to the scale of hazardous waste and contamination present at the site. Waste at Hanford is stored in tanks, several of which are leaking. The potential for uranium mobility in the environment of course poses a threat to safety, particularly if the waste reaches groundwater. Furthermore, evidence suggests that clusters, such as U_{60} , are likely forming in this leaking waste.¹ As a result, it is critical to acquire a deeper understanding of the behavior of U_{60} , especially regarding sorption.

Hypothesis

Muscovite, the sorbent material in this study, is a mica with the chemical formula $KAl_2(Si_3Al)O_{10}(OH,F)_2$.² It possesses several properties which make it ideal for this research including a point of zero charge (PZC) of 5.5 and its ability to cleave near perfectly, which is optimal for imaging of sorbed materials post-treatment. U_{60} is a uranyl peroxide cage cluster, with the crystalline composition $Li_{44}K_{16}[(UO_2)(O_2)(OH)]_{60} \cdot 255H_2O$.³

The immediate goal of this project is to assess the impact of various conditions (cation, pH, concentration) on the sorption of U_{60} to muscovite. I hypothesize that introduction of cations into a system containing U_{60} and muscovite will enhance sorption of uranium-bearing phases to the muscovite surface.

Reasoning for this hypothesis stems from the knowledge that the pH levels selected for this study are well above the PZC for muscovite. Thus, the surface of the muscovite is negatively charged, as is the anionic U_{60} cluster. As both species are negative, charge-based repulsion will impede direct sorption of the U_{60} cluster to the muscovite surface. Introduction of alkali and

alkaline earth metals may then provide the necessary charge barrier to improve interactions between U_{60} clusters and the muscovite surface.

Methods & Materials

The main objective for this semester was to complete isotherms for the sodium (Na^+) and strontium (Sr^{+2}) cations. Isotherm plots are developed by repeating batch sorption experiments at varying concentrations of the adsorbate, in this case U_{60} . For this study, reactions were completed for the two cations (Na^+ and Sr^{+2}) at four pHs (8, 9, 10, and 11) at seven concentrations of U_{60} (5, 10, 25, 50, 100, 250, and 500 ppm). In total, there were 112 batch sorption experiments, 56 for each cation. Na^+ was added at a concentration of 5 mM and Sr^{+2} was added at a concentration of 0.5 mM, to account for its increased charge. For each reaction, a constant mass of muscovite was added (10 mg). The samples were set on a shaker device (see Fig. 1) and allowed to equilibrate for 15 days. At the end of this time period, aliquots were removed from the samples using a $0.2 \mu m$ filter, intended to remove any muscovite or aggregated U_{60} particles, and then diluted with nitric acid. These aliquots were then analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). This technique provided the final equilibrium concentration of elements within the samples. Comparison with initial measurements revealed the changes (sorption capacity and percent removal) that occurred over the two-week time frame.

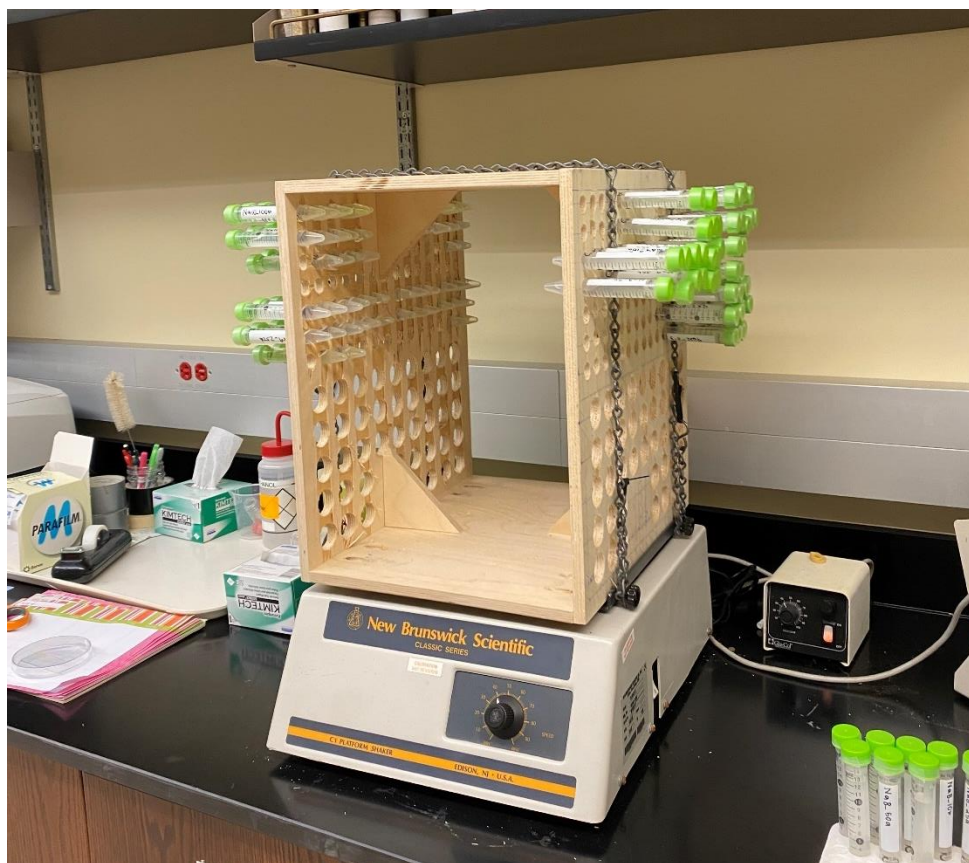


Figure 1: Shaker device for holding batch sorption reactions.

Several controls were also completed in a similar fashion to examine the individual reactions between different components. For example, a reaction with just muscovite and water was performed to see what electrolytes may come off of the mineral when in water. Reactions with electrolytes (both Na^+ and Sr^{+2}), muscovite, and water (no U_{60}) revealed how much electrolyte removal from solution can be expected without any clusters. Lastly, a reaction with muscovite and U_{60} helped determine how much “pure” sorption (i.e. no aggregation) can be anticipated without electrolytes present. More controls of these types should be performed to consider the effects of pH and especially a wider range of U_{60} concentrations.

Other techniques used this past semester include Electrospray Ionization Mass Spectrometry (ESI-MS) and Scanning Electron Microscopy (SEM). The ESI was used as a “fingerprinting” technique to ascertain that U_{60} clusters were present in the solution of the reactions after two weeks. SEM was used to characterize the muscovite sample and assess its size and uniformity. Prior work on this project has also made use of Dynamic Light Scattering (DLS) to determine particle sizes (specifically to identify

clusters versus aggregated clusters) in the reactions, as well as Powder X-Ray Diffraction (PXRD) to characterize the muscovite sample. Future work will likely make use of Atomic Force Microscopy (AFM) in order to perform in-situ analysis of the sorption process.

Results

The data from ICP analysis showed uranium removal took place in almost all batch sorption experiments. Data from ICP was organized into isotherm graphs, which plot sorption capacity as a function of equilibrium U₆₀ concentration. Sorption capacity is the ratio of sorbed material to sorbent, in this case the ratio of milligrams of U₆₀ removed to grams of muscovite in the mixture. Equilibrium concentration is the concentration of U₆₀ measured at the time of sampling, represented in ppm. These variables and units are typical for sorption analysis. Isotherms for sodium at the four studied pHs are shown in Fig. 2.

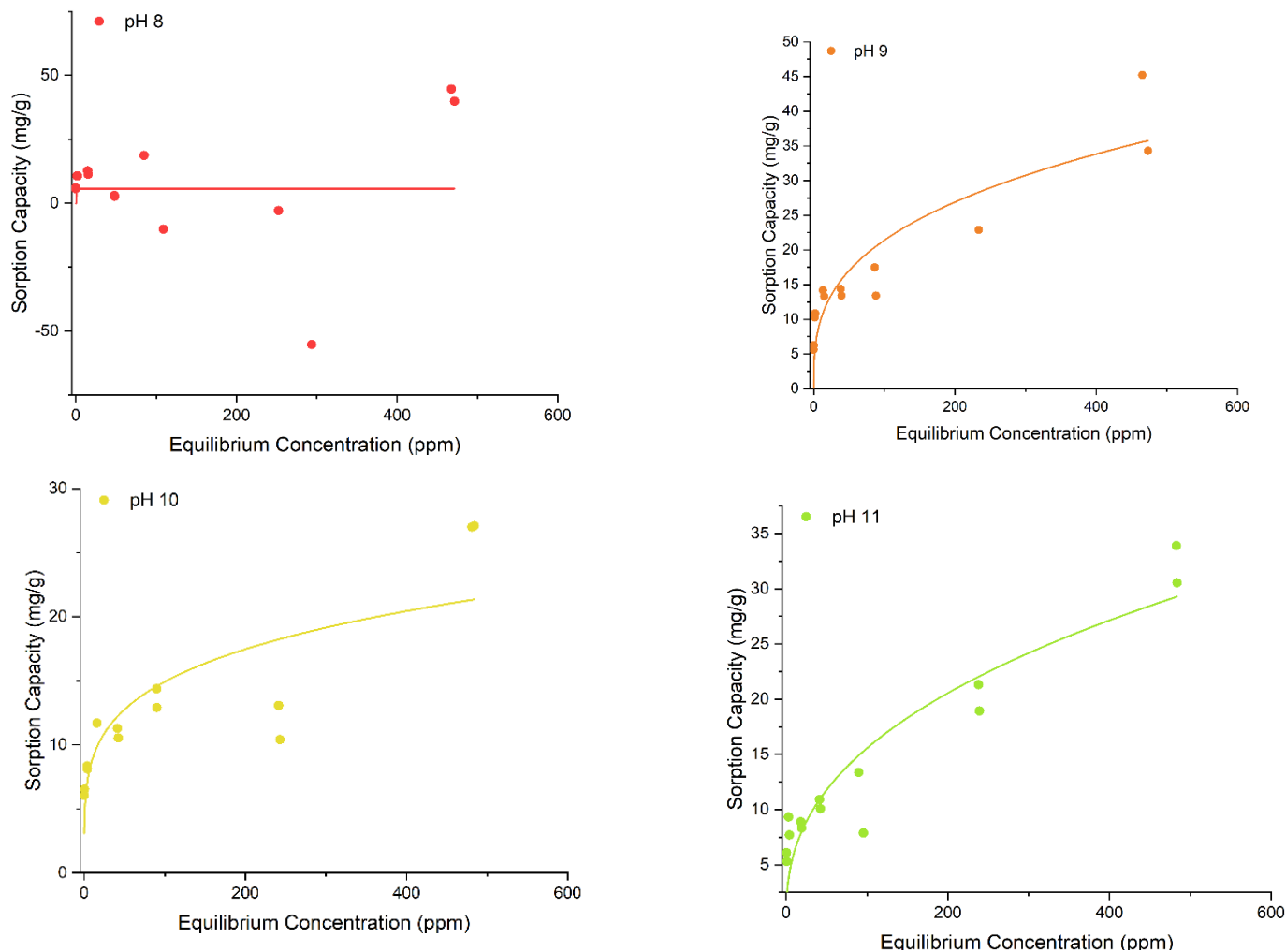


Figure 2: Isotherm curves for sodium at four different pHs. The data is fit with a Langmuir curve.

From Fig. 2, it is shown that sorption capacity generally increases as equilibrium concentration increase. This is expected for sorption experiments. The sorption capacity at which the plot levels out at represents q_{max} the maximum sorption capacity of the system; beyond this the muscovite can no longer support any further sorbed U₆₀.

Notably, while pHs 9, 10, and 11 show consistent trends of non-linear increasing sorption capacity, pH 8 does not follow this trend. Furthermore, the suggestion that there is negative sorption capacity is indication that something has gone awry. Recent studies have found that U₆₀, at low pHs and especially at low concentrations, tends to break down and speciate. Thus, it appears that pH 8 is too low to support the presence of U₆₀ clusters. As the presence of U₆₀ clusters is critical to the hypothesis and goals of this study, going forward pH 8 will be eliminated from consideration.

The curves fitted to the data represented in Fig. 2 are Langmuir curves, fitted using the general adsorption isotherm equation of Eq. (1),⁴ where q is the amount of U_{60} (presumed to be) sorbed, q_{max} is the maximum sorption capacity of the muscovite, C is concentration of U_{60} present in solution at equilibrium, and k is the equilibrium constant. Note the assumption that all uranium is in cluster form.

$$q = \frac{q_{max}KC}{1 + KC} \quad (1)$$

The data from the higher three pHs fit this model reasonably well, with R values between 0.67 and 0.84. The main objective of fitting the data with the Langmuir curve is to determine the q_{max} value for the reactions, since this quantifies the maximum amount of U_{60} that is able to be sorbed onto muscovite. These values for q_{max} , K , and R^2 values are summarized in Table 1. Further investigation is necessary to confirm the accuracy of these values, though the preliminary results suggest that the sorption capacity is highest at pH 9. Fig. 3 combines data from Fig. 2 into a singular plot for easier comparison between the four pHs for sodium. Note the unusual behavior of pH 8.

Table 1: Results of Langmuir curve fit for sodium isotherms.

pH	Maximum Sorption Capacity, q_{max} [mg/g]	Error	Equilibrium Constant, K [ppm ⁻¹]	Error	R ² Value
8	5.722	15.946	748.606	6.397E16	-0.0129
9	328607.354	4077730000	1.420E-5	0.176	0.807
10	156337.420	2086450000	3.358E-5	0.448	0.670
11	87751.220	279760000	2.795E-5	0.0891	0.844

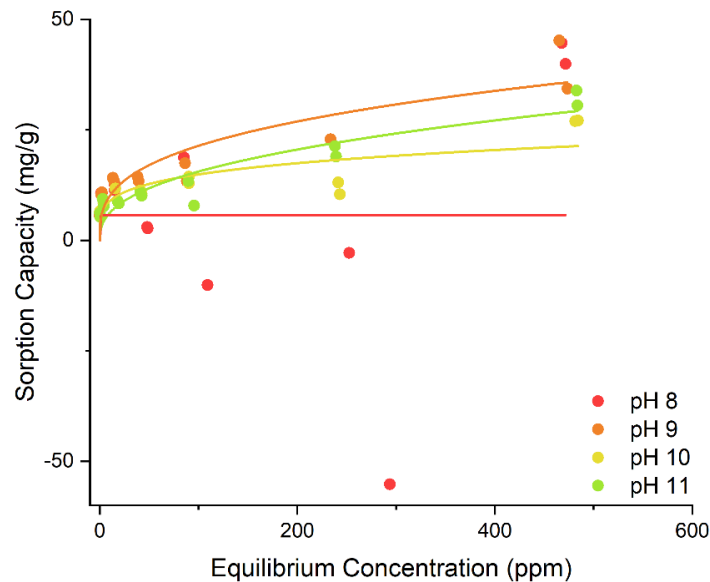


Figure 3: Isotherms for sodium including results from all four pHs.

The same isotherm experiments were repeated for strontium. After two weeks of equilibrating, it was immediately visually apparent that the behavior of the contents had changed significantly. Both sodium and strontium sample exhibited a uniform yellow, hazy appearance when initially reacted. However, once removed from the shaker, most strontium samples demonstrated the separation depicted in Fig. 4. The solution at the top of the reactor was remarkably clear, while at the bottom the solid collected in a sludge-like state. This differed from the appearance of the equilibrated sodium reactions, which maintained a yellow hue throughout the entirety of the reaction period. Even without more in-depth analysis, it was clear that strontium showed a much greater ability to induce aggregation of U_{60} clusters than sodium did. This was anticipated because

strontium is divalent as opposed to sodium being monovalent, through in these reactions strontium was still made to be 10 times more dilute than sodium.



Figure 4: Strontium (pH 8, 250 ppm U_{60}) reaction after two weeks of equilibration. It is visually apparent that separation has occurred due to the distinction between clear solution and solid.

To support the visual observations, ICP analysis was performed on the strontium samples, yielding the results shown in Fig. 5. Strontium in general showed much higher sorption capacities than sodium, with the highest sorption capacities exhibited at pH 8 and 10. This suggests that strontium is more effective than sodium at removing U_{60} from solution, whether by sorption or aggregation. The equilibrium concentrations were also much lower than those exhibited for sodium, which further indicates the strong interaction between strontium and U_{60} .

As was the case with the sodium isotherms, the isotherm plot of pH 8 appears significantly different than the other pHs, forming an “S” shaped sorption curve. The unusual behavior again may be attributed to the breakdown of U_{60} at such a low pH, particularly at the lower concentrations of U_{60} .

Again, the data was fit with the Langmuir adsorption isotherm equation with reasonable success. The values for q_{max} , K , and R^2 are summarized in Table 2. In support of the plots for pH 8 and 10, the sorption capacities for these pHs are quite high. It seems that the value for pH 9 may need to be investigated further based on comparison with the other pH results.

Table 2: Results of Langmuir curve fit for strontium isotherms.

pH	Maximum Sorption Capacity, q_{max} [mg/g]	Error	Equilibrium Constant, K [ppm ⁻¹]	Error	R ² Value
8	636.985	358.629	0.00216	0.110	0.781
9	1059870.531	10132900000	0.000257	2.461	0.616
10	620.174	156.712	1.960	-	0.584
11	510.102	1041.191	0.445	1.411	0.613

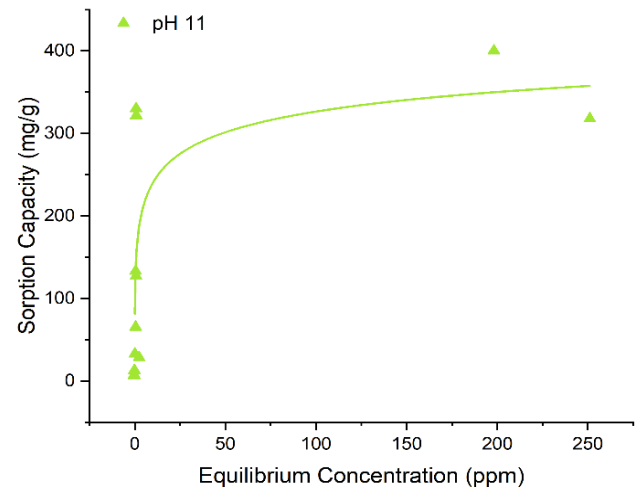
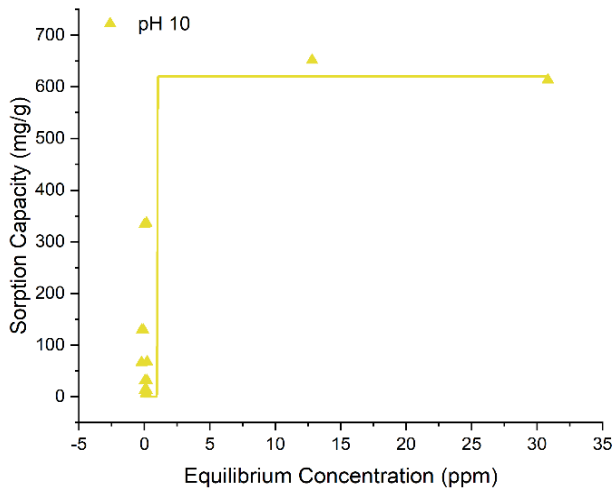
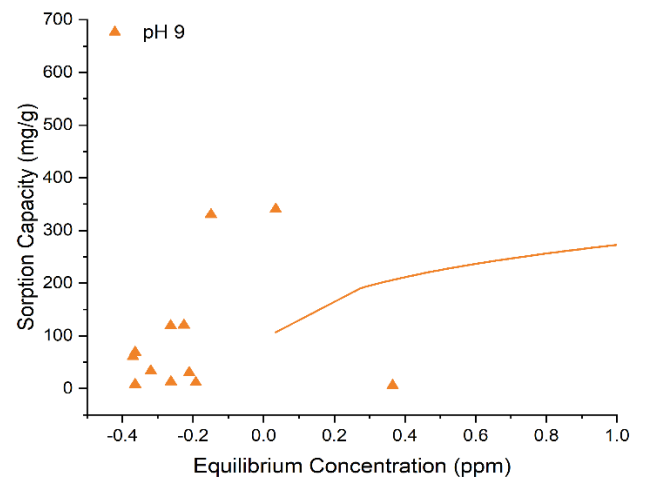
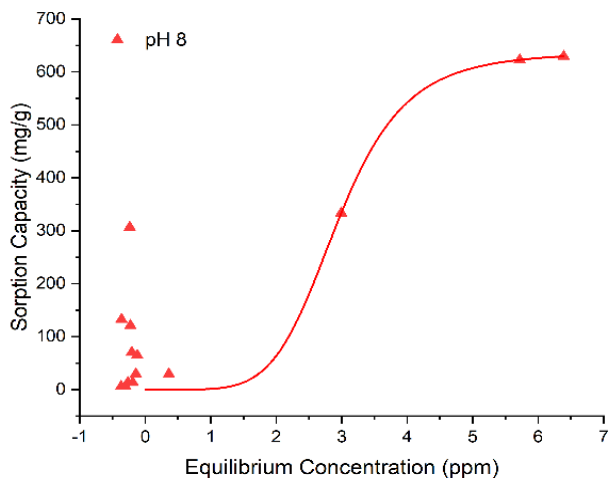


Figure 5: Isotherm curves for strontium at four different pHs. The data is fit with a Langmuir curve.

All four pHs of strontium sorption isotherm experiments are shown together in Fig. 6 to provide easier comparison. Note again the much higher sorption capacities than were shown for sodium in Fig. 3.

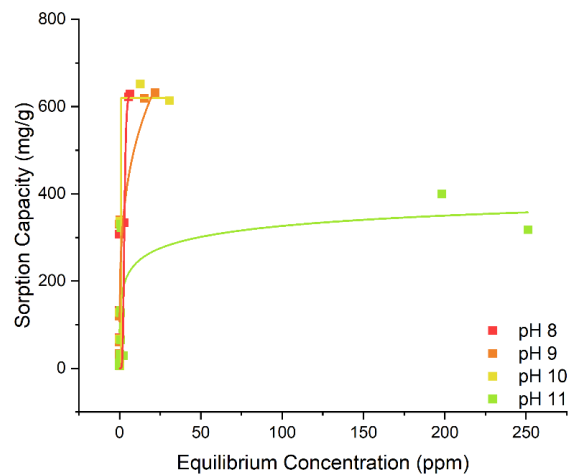


Figure 6: Isotherms for strontium including results from all four pHs.

Part of the hypothesis for this study was the role of electrolytes in the sorption process. As such, ICP analysis was also used to determine the amounts of electrolyte left in solution at the end of the two-week equilibration period. Based on initial added amounts of sodium, the percent of sodium removed from the system is shown in Fig. 7 as a function of initial U_{60} concentration. Here, removal means taken out of solution.

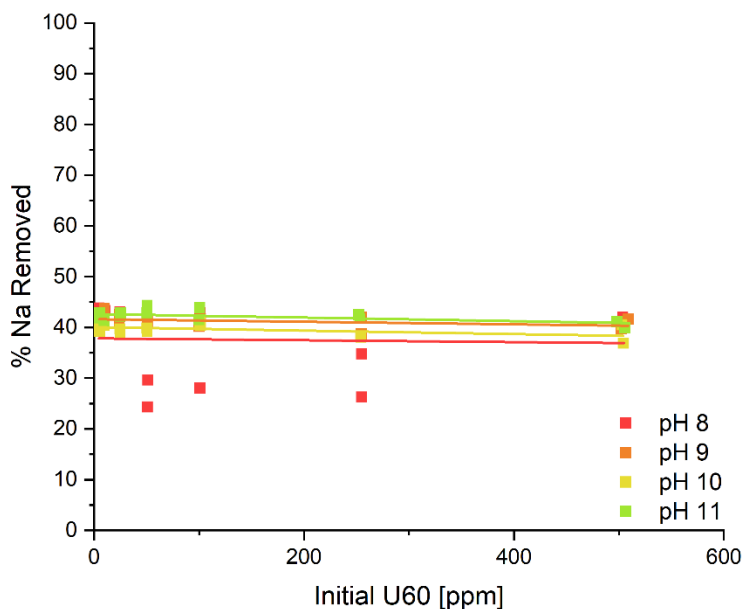


Figure 7: Percent of sodium cation removed from solution for all four pHs.

The percent of sodium removed shows relatively little difference between the varying initial concentrations of U_{60} , remaining fairly constant around 40% removal. This does not align with the increasing sorption capacity values seen in Fig. 3. Thus, this indicates that while sodium may have played some role in the removal of U_{60} from solution, it may not be as influential to the sorption process as hypothesized.

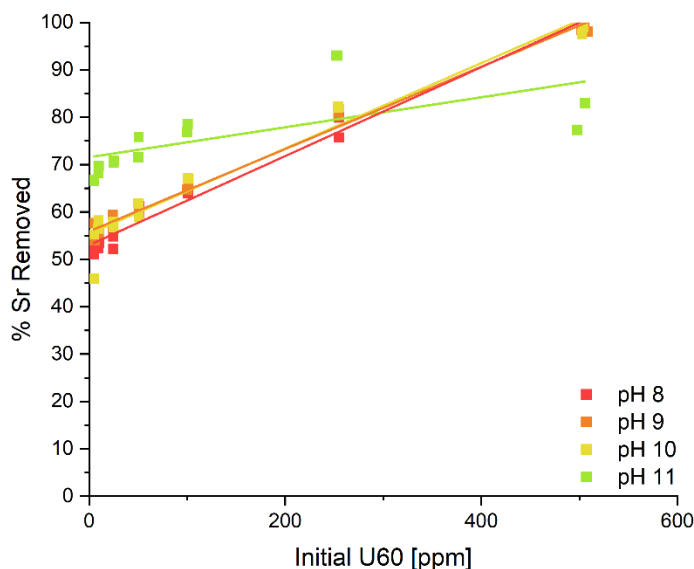


Figure 8: Percent of sodium cation removed from solution for all four pHs.

On the other hand, Fig. 8 shows the percent removal of strontium from solution as a function of initial U_{60} concentration. This plot shows a strong positive linear correlation, with up to nearly 100% removal of the cation. This matches well with the

increasing sorption capacities shown in Fig. 6. Thus, this plot suggests that the removal of strontium is linked closely with the removal of U_{60} , and therefore may play a critical role in reducing the mobility of uranium.

Fig. 9 shows the difference in removal of the two cations for each pH. Again, it is apparent that sodium shows little change in removal while strontium shows a consistent linear trend.

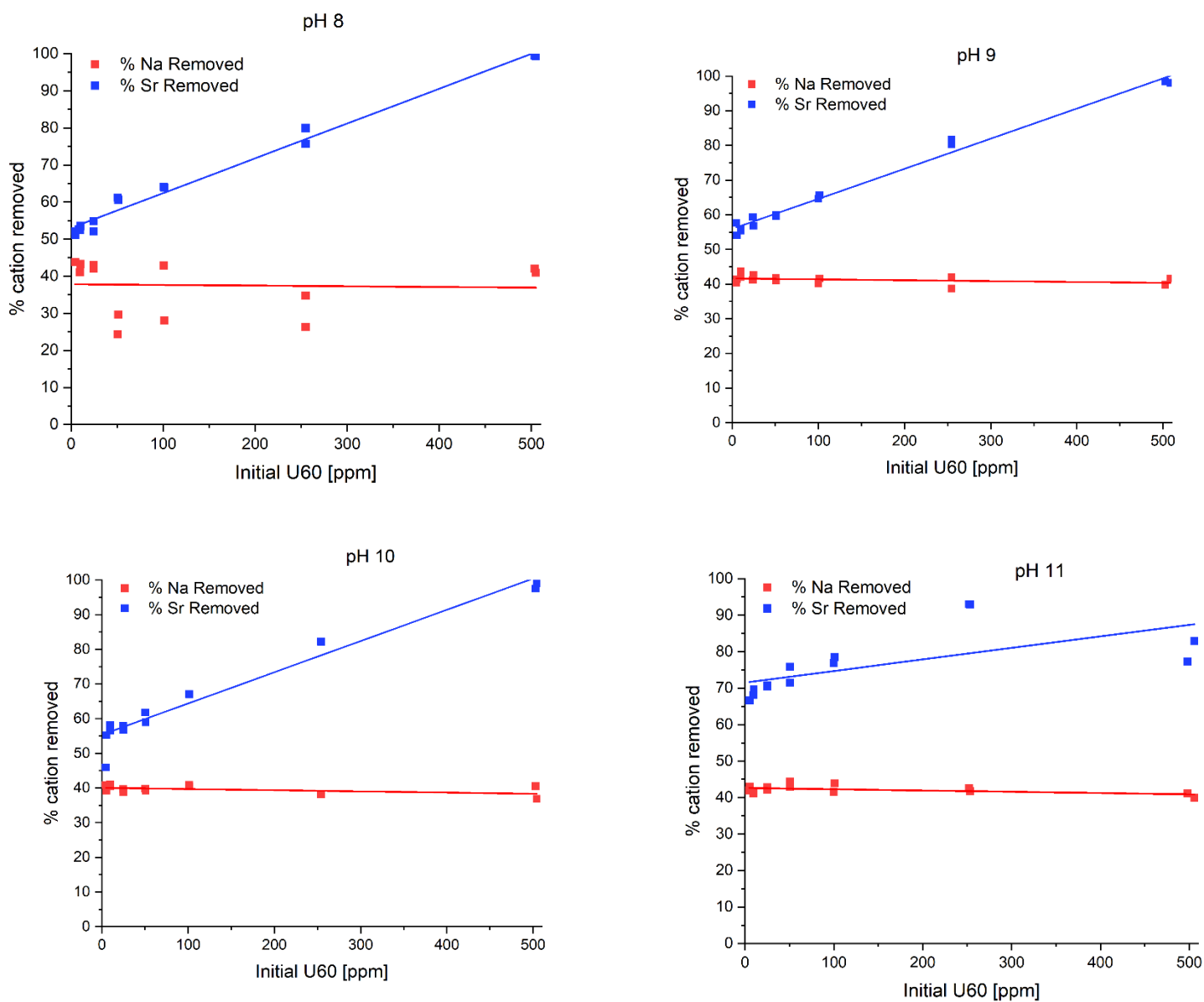


Figure 9: Comparison of cation removal (sodium and strontium) for each pH as a function of initial U_{60} concentration.

Conclusions & Future Directions

Significant progress on this project has been made over the course of the past few months, and several key discoveries will guide future work on this project.

First, after beginning implementation of the initially proposed plan, it became clear that the scope of this study is quite large (especially for an undergraduate project). Working with a graduate student in the Burns lab (Justin Daniels) made this more manageable. Still, there are many different variables to consider, with variations in concentrations of three different reactants, varying pH levels, and different types of cations. Considerable time needed to be dedicated simply to identifying appropriate experimental procedures and quantities. Furthermore, since the time period over which sorption occurs is two weeks at a minimum, time is another factor that complicates what can be accomplished in a few months. With these considerations in

mind, it was decided to postpone experiments involving calcium and potassium (which were initially proposed) to make the scope of the project more reasonable. Additionally, when performing kinetics experiments in the future, limiting the experiments to one or two ideal cation-pH-muscovite systems identified from the isotherms will also help make the project scope more reasonable.

Another important issue encountered is the difficulty in distinguishing between sorption and aggregation. The isotherm results show consistent and promising high uranium removal. However, saying with certainty that this removal is due to sorption, or aggregation, or both, is a challenging matter. Additionally, whether the uranium in the reaction is held in U_{60} clusters or has broken down into other species is another question that remains unclear. Conducting additional controls, integrating ESI as a fingerprinting technique into the experimental process, as well as eventually performing AFM may all be important strategies in determining these key results. Another key strategy may be to conduct desorption experiments, using ESI, DLS, and Small-Angle X-Ray Scattering (SAXS) to determine the contents of desorbed material.

Additionally, after recognizing the unexpected results for both cations at pH 8 and after consulting with another Burns graduate student regarding her ongoing work, it was discovered that U_{60} tends to break down at low pHs and low concentrations. As such, continuing to conduct experiments at pH 8 will not be useful at supporting or rejecting the proposed hypothesis. Going forward, either shifting the pH range higher (e.g. to pHs 9, 9.5, 10, and 10.5) or simply eliminating pH 8 will help streamline the study.

Another consideration, based on an unpublished study from a graduate student in Dr. Amy Hixon's group, is that aggregation is dependent on salt to cluster ratio. Thus, in order to keep the aggregation of U_{60} consistent across varying concentrations of the cluster, it will be necessary to vary salt concentration as well. This may be useful in distinguishing between the effects of sorption and aggregation.

Finally, based on feedback from Dr. Burns, deeper analysis into the character of the muscovite sample which this study has used is necessary to propose possible sorption mechanisms as well as gain an idea of the ideal expected sorption capacity for U_{60} and muscovite. This includes further PXRD analysis of the muscovite sample, as the current PXRD results suggest an amorphous character which would counter the baseline assumption of crystalline muscovite.

With these lessons and considerations in mind, future work includes (1) further controls to support the proposition that sorption, not just aggregation, is taking place in the isotherm experiments, (2) kinetics experiments to identify the time-dependence of the sorption process, (3) further analysis and characterization of the muscovite sample, (4) utilizing AFM to gain insight into the interactions and possible sorption mechanisms between clusters, aggregates, and muscovite, and (5) possibly revising the isotherm experiments to match an adjusted pH range and include a constant salt to cluster ratio.

References

- ¹ Peterson, R.; Buck, E.; Chun, J.; Daniel, R.; Herting, D.; Ilton, E.; Lumetta, G.; Clark, S. Review of the Scientific Understanding of Radioactive Waste at the U.S. DOE Hanford Site. *Environ. Sci. Technol.* [Online] 2018, 52 (2), 381-396. DOI: 10.1021/acs.est.7b04077 (accessed May 9, 2023).
- ² Muscovite Mineral Data. *Webmineral*. http://webmineral.com/data/Muscovite.shtml#.ZFqa_HbMK3A (accessed May 9, 2023).
- ³ Olds, T.A.; Dembowski, M.; Wang, X.; Hoffman, C.; Alam, T. M.; Hickam, S.; Pellegrini, K. L.; He, J.; Burns, P. C. Single-Crystal Time-of-Flight Neutron Diffraction and Magic-Angle-Spinning NMR Spectroscopy Resolve the Structure and 1H and 7Li Dynamics of the Uranyl Peroxide Nanocluster U_{60} . *Inorg. Chem.* 2017, 56 (16), 9676-9683.
- ⁴ Kalam, S.; Abu-Khamsin, S.; Kamal, M.; Patil, S. Surfactant Adsorption Isotherms: A Review. *ACS Omega*. 2021, 6, 32342-32348.