

**REVERSIBLE SORPTION OF PHOSPHORUS ON ZIRCONIA
AND DESIGN OF ADSORPTION UNIT
FOR PHOSPHORUS POLLUTION ABATEMENT**

by

Tyler Matthew Roberts

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Bachelors of Chemical Engineering with Distinction

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Dawn at the Well of Inspiration

Before morning breaks at dawn
As the fading nocturnal essence exhales on the eternal lawn
For one brief, lingering magical moment
In a final ritual act of peaceful atonement
The night bequeaths on the morning grass, translucent pearls of fragile dew
To glisten and shine when dawn breaks anew

When morning breaks at last
And the eastern sky explodes on horizon vast
The golden exuberance of the reincarnated sun
Announces triumphantly the start of a long-awaited run
As the lone blue hen on the distant hill crows
Imploring the dawn to reveal what only the day knows

Build me a house with five pillars strong
Lead me to the land where the excellent belong
Where seekers seek and boldly chart tomorrow's skies
Where creators make the dreams of prophets arise
Where teachers inspire and learners acquire confident, nimble hands
To fashion for humanity's through a future woven with better strands

We will burnish the blue to a cobalt brilliance
We will polish the gold to a glorious radiance
We will make the good great, the great excellent
And the excellent... we will make transcendent
The valleys shall be exalted and the mountain spires made strong
The mangled corners will be straight as we right the shameful wrongs

And when evening comes at day's end
Before the glowing orange ball below the distant horizon descends
May we look back and see deep meaning and the great good
We have wrought on the sand of humanity where once we all stood
And so today with joy and great expectation
Let us draw water from the well of inspiration

Tunde Ogunnaike
November 23, 2017

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ABSTRACT

The ability of monoclinic zirconia to reversibly sorb phosphorus as a potential means of reducing the agricultural impact on eutrophication in the Chesapeake Bay Watershed is explored in this paper. The maximum batch adsorption capacity of zirconia was measured to be 3.19 mg P/g ZrO₂. A custom-built and automated reversible sorption experimental unit was utilized to optimize the flow rate, inflow phosphorus concentration, and zirconia mass in order to observe the entire adsorption behavior during each experiment. Reversible sorption experiments with up to four cycles showed the importance of higher ammonium hydroxide solution concentrations to promote complete desorption of phosphorus when recycling the zirconia. The ability of zirconia to selectively adsorb phosphorus from a farm water runoff sample experiment was inconclusive due to extrapolated phosphorus concentrations below detection limits and due to the fact that observed adsorption and desorption of organic matter could indicate the organic matter is competing with phosphorus for binding. A reversible sorption unit was also designed for implementation at a farm in Maryland and it predicts removal of 57.5 pounds of phosphorus each year over its lifetime of five years, with ammonium hydroxide usage and unit price being the most significant factors in overall raw material costs. If the research presented herein can promote implementation of zirconia to prevent eutrophication or provide general guidance in terms of experimental methods and data analysis, this work will have been a success.

Chapter 1

INTRODUCTION

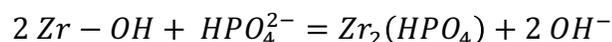
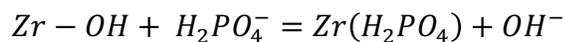
The leakage of phosphorus across land-water interfaces and transport to coastal regions has contributed to the rise in harmful algae blooms and murky waters around the world¹. Freshwater and marine ecosystems have been degraded, as these algae blooms lead to decreased biodiversity, hypoxia, and dead zones. The excess nutrients present due to these situations constitute what is defined as eutrophication. Local examples of eutrophic conditions include the Chesapeake Bay and Lake Erie, which have algae blooms that threaten the regional water supply and tourism². Agriculture is considered a major cause of eutrophication due to nutrient loadings from fertilizer use¹. Recent work at the University of Delaware seeks to improve phosphorus management in ditch-drained agroecosystems⁴. Therefore, phosphorus removal is important to conserve the natural aquatic environment and meet increasingly stringent environmental regulations^{4,5}.

Phosphorus is usually found in the form of phosphates that are in the organic form or the inorganic form. Organic phosphate is bound to plant or animal tissues and are primarily formed by biological processes while inorganic phosphate is not associated with organic material⁶. Since fertilizers generally contain inorganic phosphates known as orthophosphates, this study focuses on orthophosphate removal⁶.

Phosphorus abatement techniques that have been developed include chemical precipitation, biological treatment, coagulation, and sorption by adsorbents⁵. The latter of which is a prevalent choice due to its easy operation, low operating costs, and

selectivity when in solutions with coexisting pollutants⁵. A number of filter materials have been proposed to remove phosphorus with on-site wastewater treatment systems, but with no standard procedure and experimental parameters agreed upon, one has difficulty comparing the results⁷. Nonetheless, some of the main parameters affecting the adsorption systems are the form and amount of material, pH, initial concentration of phosphorus solution, retention time, agitation and temperature⁷. Phosphorus sorption capacity typically divides filter materials into three categories: Low (<0.5 mg P/g sorbent), moderate (0.5-1.0 mg P/g sorbent), and high (>1.0 mg P /g sorbent)⁷. Some materials such as blast furnace slag and red mud are within the high phosphorus sorption category, but their sorption is irreversible and thus the material cannot be reused. In order to potentially extend the lifetime of phosphorus sorbing materials, this study focuses on determining if monoclinic zirconia can reversibly adsorb and desorb phosphorus. Zirconium hydroxide has gained attention recently due to its ability to control phosphorus since it has a high binding affinity for phosphate ions and stability over a wide pH range⁵.

A study was conducted to study the reversible sorption properties of zirconia when it is dispersed on an inert support. E. Zong et al. showed through batch and column adsorption experiments that reversible phosphorus sorption is possible by dispersing zirconium hydroxides over graphite oxide, an inert support with high surface area⁵. The adsorption mechanism was described as follows⁵:



Results showed that phosphate adsorption was suppressed by increasing pH, which was explained due to the presence of negatively charged ions competing with the

phosphorus for adsorption. Therefore, NaOH solution was utilized to flush the phosphorus after the adsorption process and regenerate the material. Column flow through tests were also conducted and the material appeared to be recyclable due to stable adsorption-desorption behavior in 11 consecutive test cycles. Since the process of incorporating zirconia onto graphite oxide is time intensive and due to the fact that the sorption properties of pure zirconia were unknown, monoclinic zirconia was selected in this study. This study utilizes the same sorbent, so the above adsorption mechanism, influence of pH, and reversibility are expected.

Liu et al. also studied phosphorus removal through utilization of mesoporous zirconia⁸. The maximum phosphorus adsorption capacity was estimated to be 29.71 mg P/g, which classifies mesoporous zirconia as a material with high sorption capacity. Phosphorus desorption was also achieved with NaOH and the adsorption ability was shown once again to be decreased with increasing solution pH. Liu et al. suggested ion exchange and physiochemical attractions were the mechanisms by which the immobilization phosphorus probably occurred. However, the desorption properties of mesoporous zirconia were only studied in batch experiments. Therefore, the batch adsorption capacity of Liu et al. can be helpful when benchmarking the capacity of monoclinic zirconia to adsorb phosphorus.

Based on the typical application of phosphorus sorbing materials to adsorb continuous flows of contaminated water, this study emphasizes the column flow through experimental approach while first using batch experimentation to determine the capacity of zirconia to confirm its feasibility. The flow system is then characterized based on the impact of phosphorus concentration, flow rate, zirconia mass, and desorption solution concentration. Farm drainage ditch runoff solution with

phosphorus and other compounds is then sent through the flow system to determine if the reversible sorption properties of zirconia are affected by the presence of competing ions. Then, a design of a real-world reversible phosphorus sorption unit is described and its potential to mitigate eutrophication analyzed.

Chapter 2

EXPERIMENTAL METHODS

2.1 Chemicals

The chemicals utilized for the experiments desired in this paper can be found below in 1.

Table 1. Chemicals utilized for experiments

Chemical Name	Chemical Formula
Potassium Phosphate Monobasic	KH_2PO_4
Monoclinic Zirconia	ZrO_2
Ammonium Hydroxide Solution	NH_4OH
Magnesium Sulfate Anhydrous	MgSO_4
Calcium Sulfate	CaSO_4
Sodium Chloride	NaCl
Potassium Chloride	KCl
Ammonium Molybdate, 4-Hydrate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
Antimony Potassium Tartrate	$\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$
Sulfuric Acid	H_2SO_4
Ascorbic Acid	$\text{C}_6\text{H}_8\text{O}_6$

2.2 Orthophosphate Concentration Analysis

The following spectrophotometric analysis technique was followed to measure orthophosphate concentration (Murphy-Riley Molybdate Blue Method)⁹. Figure 2-1 below the procedure shows the standard reagent curve utilized for orthophosphate concentration analysis.

Reagent A Preparation

1. Dissolve 12.0 g of ammonium molybdate, 4-hydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in approximately 250 mL of deionized H_2O in a beaker. (Exact volume is not necessary here).
2. Dissolve 0.2909 g of antimony potassium tartrate $[\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot 1/2\text{H}_2\text{O}]$ in approximately 100 mL of deionized H_2O . (Exact volume is not necessary here).
3. In the chemical fume hood, very cautiously add 148 mL of concentrated H_2SO_4 to approximately 1 L of deionized H_2O in a 2-L volumetric flask. This will generate considerable heat. Add the ammonium molybdate and antimony potassium tartrate solutions to the H_2SO_4 solution in the 2-L flask. Mix thoroughly and bring to 2-L volume.
4. Reagent A is 5 N H_2SO_4 and should be treated as a strong acid. It can be stored and should be kept in a polyethylene bottle in the refrigerator, but most importantly in the dark. Be sure to allow the reagent to equilibrate to room temperature prior to use.

Reagent B Preparation

1. Reagent B must be prepared each day that this colorimetric determination is done since it does not remain stable beyond 24 h. Do not make a large batch and then store it.
2. Dissolve 0.528 g of ascorbic acid in 90 mL of Reagent A in a 100-mL volumetric flask and mix thoroughly. Bring to 100-mL volume with Reagent A. Dissolution can be scaled by volume: 0.264 g for 50 mL, 1.056 g for 200 mL.
3. Pipette into a cuvette 4.2 mL of sample and add 0.8 mL of Reagent B. Invert, let stand 20 min (30 min max), then read on the spectrophotometer set to 882 nanometers.
4. If your samples at 4.2 mL are going to be too concentrated to fall within the linear range of the standard curve, you would have to scale down the amount used.
5. Typical standards of 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 mg P/L are used (made as 4.2 mL standard solution + 0.8 mL Reagent B) with absorbances of 0.07, 0.20, 0.33, 0.45, 0.55, and 0.67. The range is typically linear to between 0.0 and 1.0 mg P/L.

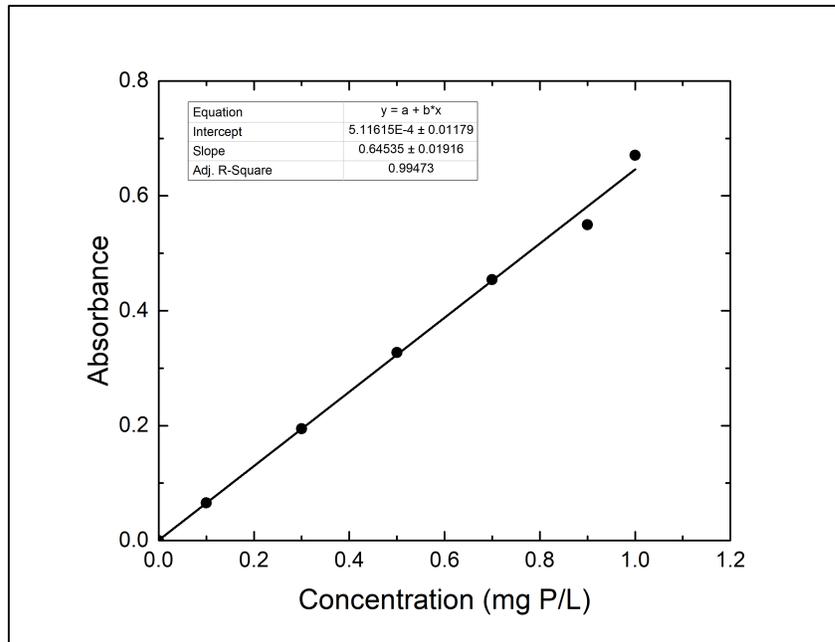


Figure 2-1. Standard calibration curve for Murphy-Riley Molybdate Blue method.

2.3 Batch Experiments

2.3.1 Counter-Ions Present

In order to determine the phosphorus adsorption capacity of zirconia and its feasibility as a phosphorus removing material, a series of batch experiments were conducted. The first batch experiment was with other ions present in solution that are typically found when phosphorus is present. The experiment consisted of 30 mL solutions with 0, 1, 10, 25, 50, or 100 mg P/L initial phosphorus concentrations, 1 g of zirconia, and a series of counter ions present. This batch experimental procedure was adapted from a Penn et al. standard batch isotherm with matrix representative of agricultural runoff¹⁰.

1. Weigh 1 g of ZrO_2 and place into 50 mL centrifuge tubes. Repeat for 18 tubes.

2. Use stock 1000 mg/L and 10 mg/L P solutions and dilute to 0, 1, 10, 25, 50, and 100 mg/L P. Note: All concentration calculations are based on the concentration of phosphorus in solution and not the concentration of phosphate ions or any other species, only purely P.
3. Add 30 mL of each solution concentration to three individual vials.
4. Add reagent grade MgSO₄, CaSO₄, NaCl, and KCl to make a matrix of 5.6, 132, 110, 10, and 17 mg/L of Mg, Ca, S, Na, and K, respectively.
5. Close centrifuge tubes and shake in end-over-end shaker for 24 hours.
6. After equilibration, centrifuge each tube at 2000 rpm in 13 minute cycles and filter solutions through a 0.45 µm filter.
7. Measure phosphorus concentration in the samples using the Murphy-Riley molybdate blue method.

2.3.2 Without Counter-Ions Present

In order to more accurately determine the experimental maximum capacity of zirconia, a similar batch experiment without counter ions was conducted, but this time with 0.04 g zirconia and 0.0, 0.1, 0.5, 1.5, 3.5, or 7.0 mg P/L solutions in order to clearly surpass the potential maximum theoretical capacities of zirconia measured in the batch experiment with counter ions present. This batch experimental procedure was also adapted from a Penn et al. standard batch isotherm with matrix representative of agricultural runoff¹⁰.

1. Weigh 0.04 g of ZrO₂ and place into 50 mL centrifuge tubes. Repeat for 12 tubes.
2. Use stock 1000 mg/L and 10 mg/L P solutions and dilute to 0.0, 0.1, 0.5, 1.5, 3.5, and 7 mg P/L.
3. Add 30 mL of each solution concentration to two individual vials.
4. Close centrifuge tubes and shake in end-over-end shaker for 24 hours.

5. Centrifuge each tube at 2000 rpm in 13 minute cycles until the solutions are clear and all zirconia is collected at the bottom.
6. Measure phosphorus concentration in the samples using the Murphy-Riley molybdate blue method and pull the solutions directly from the centrifuge tubes.

2.4 Reversible Sorption Flow Experiments

2.4.1 Physical System

The images and schematics below depict the reversible sorption flow experimental setup for the flow experiments. The equipment list provided in Table 2 describes the materials necessary to create this flow experimental setup.



Figure 2-2. Front view of reversible sorption flow experimental setup.

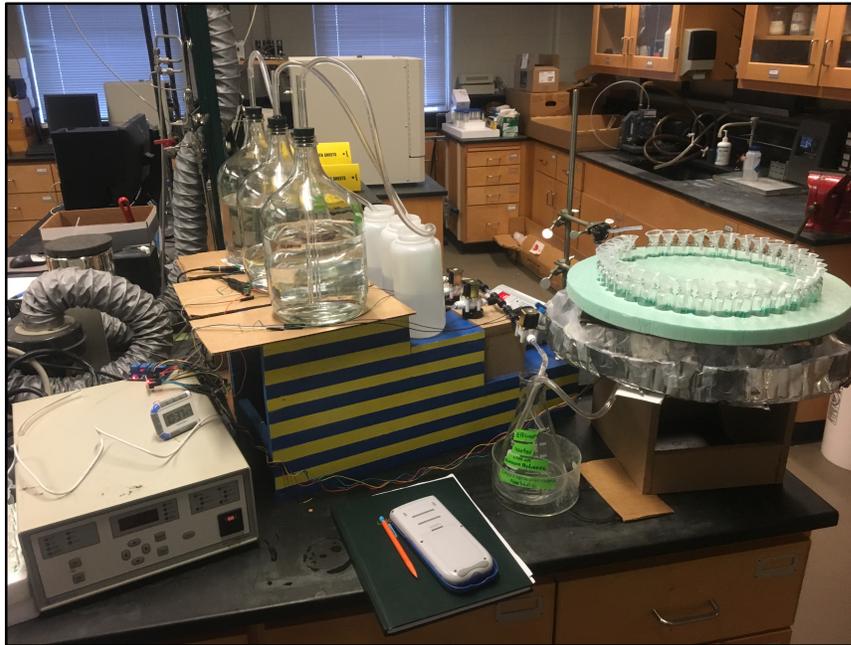


Figure 2-3. Side view of reversible sorption flow experimental setup.

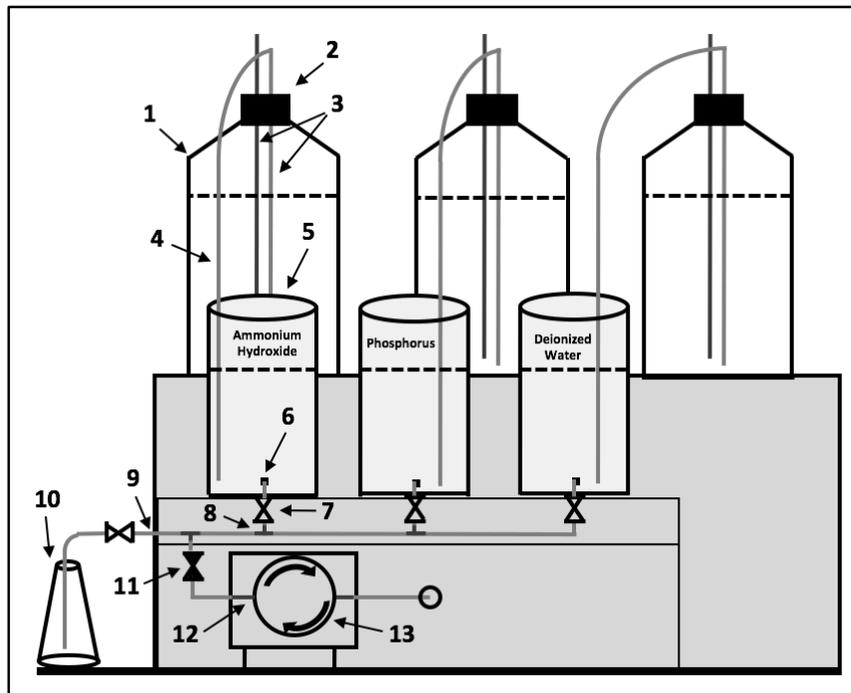


Figure 2-4. Front view schematic of reversible sorption flow experimental setup.

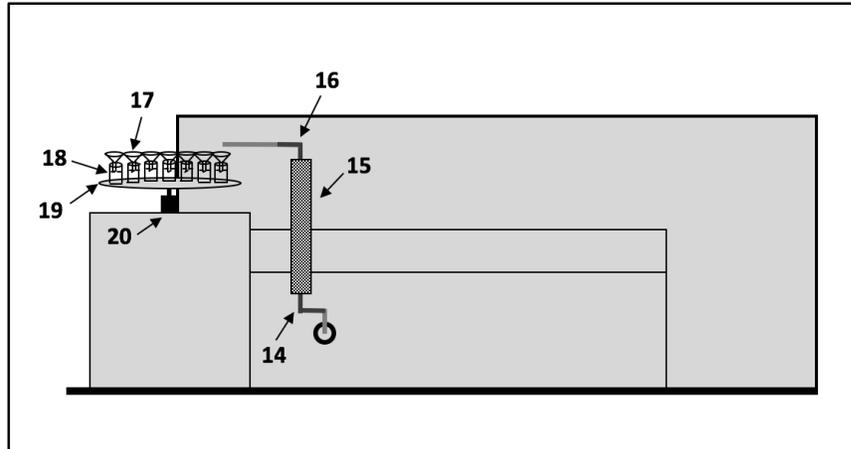


Figure 2-5. Front view schematic of reversible sorption flow experimental setup

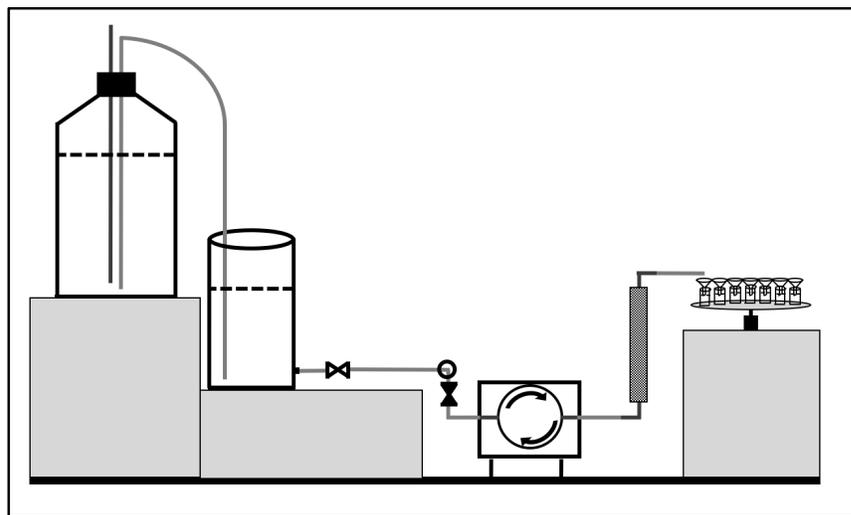


Figure 2-6. Side view schematic of reversible sorption flow experimental setup.

Table 2. Materials for reversible sorption flow experimental setup.

Material Number	Material Specifications
1	Qorpak Clear Glass Jug with Black Phenolic PolyCone Cap 128 oz
2	#6 Two Hole Rubber Stopper
3	Glass Rod, 14" Length, 1/4" ID

4	Tygon Tubing, 1/4" ID, 3/8" OD
5	Leak-Proof HDPE Wide-Mouth Bottles
6	Nylon Tube and Hose Fitting 1/4" HB x 1/8" NPT
7	DC 12V 1/4" Inlet Feed Water Solenoid Valve Quick Connect N/C Normally Closed
8	Push-to-Connect Fitting for Food and Beverage, UV-Resistant, Tee Connector, for 1/4" Tube OD, Black
9	Crack-Resistant Teflon PFA Semi-Clear Tube, 5/32" ID, 1/4" OD
10	Pyrex Narrow-Neck Heavy-Duty Glass Erlenmeyer Flask
11	Polypropylene On/Off Valve for Drinking Water, Push-to-Connect Female for 1/4" Tube OD
12	Fisherbrand Variable-Flow Peristaltic Pump (Low Flow) Tubing 3/32"
13	Fisherbrand Variable-Flow Peristaltic Pump (Low Flow)
14	Push-to-Connect Fitting for Food and Beverage, 90 Degree Elbow Reducer, for 3/8" x 1/4" Tube OD
15	Crack-Resistant Teflon PFA Semi-Clear Tube for Chemicals, Flexible, 1/4" ID, 3/8" OD
16	Push-to-Connect Fitting for Food and Beverage, 90 Degree Elbow Reducer, for 3/8" x 1/4" Tube OD
17	Mini Plastic Funnel
18	Wheaton Glass 20mL Scintillation Vials and Urea Caps
19	Turntable Wood Supports and Base
20	12V Stepper Motor

2.4.2 Automatic Control System

The Arduino control system is responsible for the automatic control valves and the turntable rotations. A schematic of the control system can be found in Figure 2-7 and the materials for the control system can be found in Table 3. The Arduino system flush code can be found in Appendix A and the Arduino system operation code can be found in Appendix B.

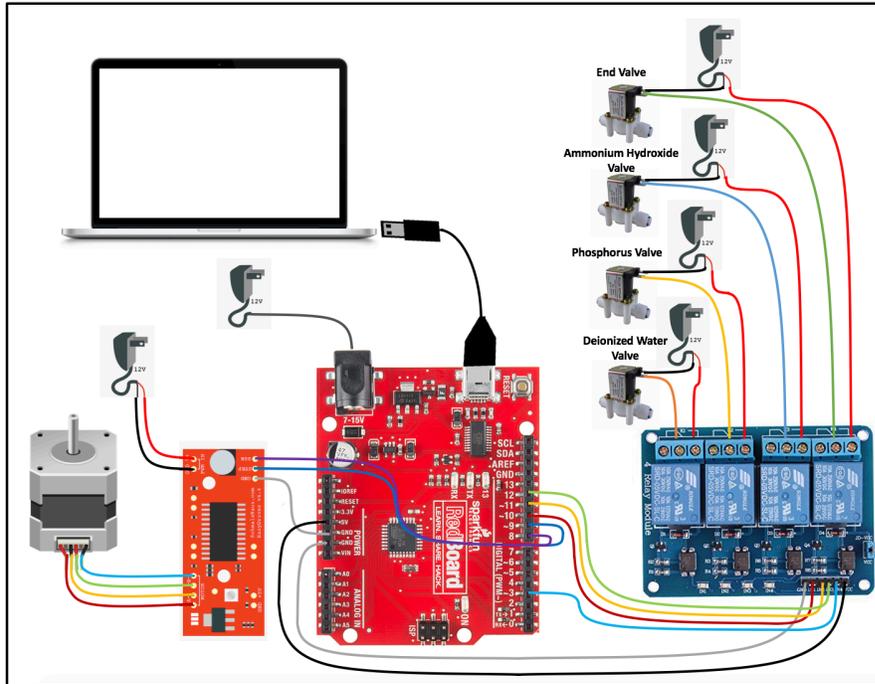


Figure 2-7. Schematic of Arduino control system.

Table 3. Materials for Arduino control system

Material Number	Material Specifications
1	SparkFun RedBoard - Programmed with Arduino
2	AC Adapter, AMASKY 12V/2A Switching Power Supply Adapter for 100V-240V AC 50/60Hz with DC Connector
3	Male to Female/Male (Depending on Setup) Breadboard DuPont Wires Jumper Cables for Arduino Raspberry Pi
4	12V Stepper Motor with Cable
5	EasyDriver - Stepper Motor Driver
6	JBtek 4 Channel DC 5V Relay Module for Arduino Raspberry Pi
7	Female Headers
8	DIGITEN DC 12V 1/4" Inlet Feed Water Solenoid Valve Quick Connect N/C Normally Closed
9	USB 2.0 A-Male to Micro B Cable

2.4.3 Phosphorus and Ammonium Hydroxide Solution Preparation

The following procedures were utilized to create phosphorus and ammonium hydroxide solutions. Since the clear glass jugs are one gallon each, it is prudent to add no more than 3.5 L of each solution to the jugs.

Phosphorus

Prepare 1000 mg P/L stock solution by diluting monopotassium phosphate in deionized water. Ensure concentration is in terms of phosphorus.

Phosphorus Molecular Weight = 30.9738 g/mol

Monopotassium Phosphate Molecular Weight = 136.086 g/mol

To prepare phosphorus solutions for flow experiments, dilute using the following equation: $C_1V_1 = C_2V_2$.

Ammonium Hydroxide

Utilize the Sigma-Aldrich Normality and Molarity Calculator to prepare a specific volume and concentration of ammonium hydroxide solution¹¹. Solution prepared from ammonium hydroxide (30% NH₃) in chemicals cabinet. In fume hood, open stock solution and pour enough into small beaker for the graduated cylinder measurement. Pour into volumetric flask and bring to volume.

2.4.4 Zirconia Particle Preparation

The following procedure outlines the method of creating 425-850 micron zirconia particles for the flow adsorption experiments. It was previously determined that powder zirconia would create too large a pressure drop for the system to operate.

1. Fill 13 mm press die to half volume with zirconia.
2. Place steel die rod in the die and place a rectangular block on top of the rod.
3. Place the die, rod, and block onto the press and bring to a pressure of 8,000 pounds for one minutes.
4. Release the pressure and remove the pellet from the die.

5. Crush the pellet into particles small enough to go through the No. 40 (850 micron) die, but not smaller enough that they pass through the No. 20 (425 micron) die.

2.4.5 Analysis of System Operation

A series of qualitative experiments were conducted to analyze how well the flow system operated and to adjust the system before conducting experiments. Red and orange Gatorade was utilized in addition to deionized water in these experiments. Figure 2-8 a) shows these solutions in the holding tanks and the bottom left of the image shows the red Gatorade flowing through the system toward the column. A lack of red color or tint to the upstream side of the tee connection indicates that there is in fact little to no mixing between solutions. Figure 2-8 b) shows the adsorption column with 0.25 g of sand, held in place by quartz wool on each side, to mimic the experimental conditions with zirconia. Red Gatorade flowed through the column for 45 minutes at about a 1 mL/min flow rate, but even after 30 minutes of the deionized water flow, some red color still existed, which is why some of the column appears red. Therefore, solution mixing when changing solutions is inevitable, despite all efforts to reduce pipe diameters. Corrections for this mixing behavior can be found in the Data Analysis Methodology section.

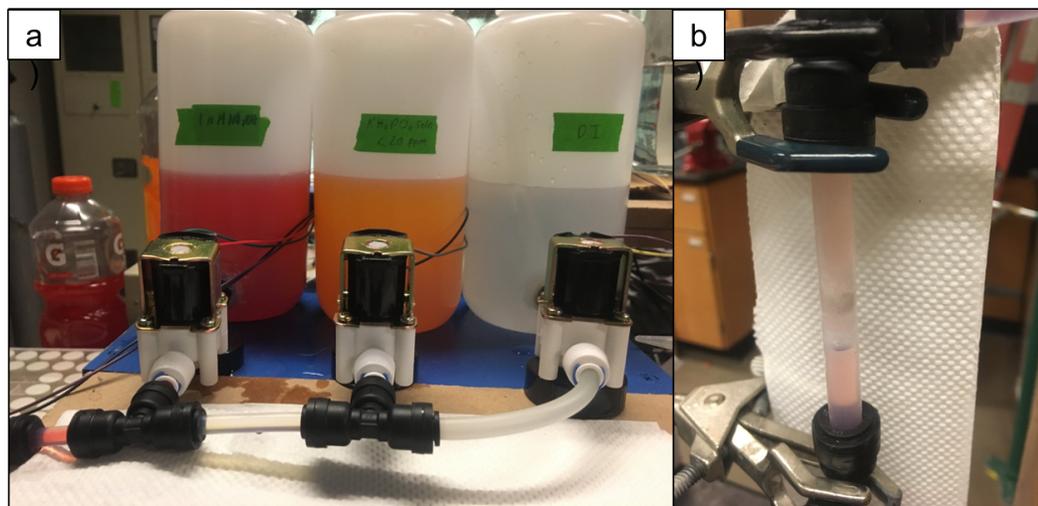


Figure 2-8. Dyed solution experiment with a) confirming no backflow mixing and b) highlighting mixing

2.4.6 Time Delay Compensation

The timing of each experiment begins when the first drop of solution has flowed through the entire flow system and drops into the first vial. To account for the time delays associated with switching solutions, the volume of the pipes from each tee connector was measured. The volume from the ammonium hydroxide tee connector to the column outlet was 14.5 mL and the volume from the phosphorus and deionized water tee connector was 16.5 mL. It was assumed that the minimal volume between the automatic valves and the tee connectors was filled with the desired solution and therefore no additional considerations needed to be made for each solution. Back-calculations from the desired flow rates were made to determine as best as possible how long the time delay would be for each solution. The time delay from the ammonium hydroxide tee connector (Eq. 1) and the phosphorus and deionized water (Eq. 2) can be calculated from the following equations:

$$\text{Short Time Delay (min)} = \frac{14.5 \text{ mL}}{\text{Flow Rate } \left(\frac{\text{mL}}{\text{min}}\right)} \quad \text{Eq. 1}$$

$$\text{Long Time Delay (min)} = \frac{16.5 \text{ mL}}{\text{Flow Rate } \left(\frac{\text{mL}}{\text{min}}\right)} \quad \text{Eq. 2}$$

2.4.7 Evaporation Compensation

1. Filled 20 mL scintillation vials with ~18 mL of DI water and the funnel attached. Weighed each vial.
2. Allowed the vials to sit on the rotation collection apparatus for 24 hours. Weighed each vial.
3. Difference between the initial and final vial weights divided by 24 hours gave the amount of water evaporated from the vials per hour: $0.005 \pm 0.001 \text{ mL/hr}$.

2.4.8 Experimental Procedure

The following is the experimental procedure utilized for all flow system experiments. PPE of safety glasses, gloves, and a lab coat are required.

1. Make desired solutions of ammonium hydroxide and phosphorus according to the solution preparation section. Put each of these solutions and one solution of deionized water into the clear glass jugs. Remove the glass jug caps and place each glass jug on the level above the holding tanks. If solutions have already been made, keep the cap of the glass jugs on and swirl for 15 seconds to ensure thorough mixing. Then, remove the cap and place the glass jugs on the level above the holding tanks.
2. Pour or pipet one 20 mL scintillation vial each of the solutions for initial concentration testing later.
3. Weigh all labeled sample vials with funnels and place onto turntable.
4. Place rubber stoppers with two glass rods and one plastic tube into the caps of each jug.

5. Connect each plastic holding tank with hose fitting to their associated control valves.
6. Use squeeze bottle to squeeze air into each glass rod that does not have a plastic tubing attached until water begins to flow through the plastic tubing and into the plastic holding tanks. Be sure not to release the bottle until you disconnect from the glass rods.
7. Attach plastic tubing to the effluent/waste line and place into Erlenmeyer flask. Ensure there is secondary containment on the Erlenmeyer flask.
8. Plug Arduino USB connection into computer and upload system flush code.
9. Place 1 cm of balled up quartz wool into one end of the adsorption column and push up with rod until about half way up the column.
10. Weigh desired mass of zirconia.
11. Pour material into adsorption column so that the quartz wool provides support.
12. Place 1 cm of balled up quartz wool into other end of the adsorption column and push down so that the material is sandwiched between two layers.
13. Connect upper and lower 90-degree elbow pieces to the adsorption column, ensuring the top piece's piping is centered on the desired first vial.
14. Ensure manual valve is set to the closed position.
15. Connect pump tubing to the lower 90-degree elbow piece and associated piping and wrap pump tubing around the pump.
16. Plug in pump and set at Speed 30. Then turn on and reduce/increase speed slowly until desired speed and rpms has been reached.
17. Disconnect Arduino USB computer connection.
18. Plug in all of the automatic valves as well as the turntable.
19. Connect the Arduino USB computer connection. The system flush code will begin.

20. Once the system flush has stopped and is waiting to start the experiment, open the manual valve and ensure its tubing is connected to the inlet side of the pump tubing.
21. Allow the desired solution to flow through the entire column and just as the first drop is about to land in the first vial, start the experiment code.
22. Plug in the power cord and you can now unplug the Arduino USB computer connection.
23. Check the system for leaks before leaving.
24. The code should execute the opening and closing of the valves and once the experiment is set to end or the maximum number of vials is about to be reached, you must step in to finish the process.
25. Once the code stops, open the manual valve, unwrap the pump tubing, and hold the column well above the turntable, so as to promote the water to drain out of the effluent valve. Once the water level goes below that of the manual valve, close the manual valve.
26. Disconnect the 90-degree elbows from the adsorption column tubing and push the steel wool and zirconia out and into a vial with a steel rod.
27. Weigh the filled vials with funnels and then close with caps.
28. Unplug all of the electrical connections.
29. Empty the effluent container.
30. Hold the plastic tubing inside the holding tanks above the level of the bottom glass rod and the solution will flow back into the tank.
31. Remove the plastic stoppers and put away.
32. Disconnect the holding tanks and prevent leakages when transferring contents back to the original glass jugs. Put caps on the glass jugs.
33. Complete data analysis.

2.5 Data Analysis Methodology

The vial solution volumes (mL) were assumed equal to the difference between the initial mass (g) of the empty vial and funnel with the final mass of the empty vial and funnel. This is due to the fact that the density of the samples was assumed to be that of water, which is typically 1 g/mL, so one gram is equal to one milliliter. The flow rates (mL/min) were calculated based on the amount of time (min) solution flowed into each vial. The concentrations without evaporation considerations of each vial were calculated using the standard curve previously discussed. The evaporation rate from each vial was calculated previously to be 0.005 mL/hr and so the evaporated volume (mL) from each vial can be calculated using Eq. 3.

$$\text{Evaporated Volume (mL)} = \left(0.005 \frac{\text{mL}}{\text{hr}}\right) \left(\frac{1 \text{ hr}}{60 \text{ min}}\right) (\text{Time Delay (min)}) \quad \text{Eq. 3}$$

The actual concentration (mg P/L) that was present in the vials before evaporation can be determined using Eq. 4.

$$\begin{aligned} &\text{Actual Concentration (mg P/L)} \\ &= \frac{(\text{Vial Volume (mL)} - \text{Evaporated Volume (mL)})(\text{Concentration (mg P/L)})}{\text{Concentration P (mg P/L)}} \quad \text{Eq. 4} \end{aligned}$$

The mass of phosphorus (mg) in each vial can be calculated using Eq. 5 and the potential maximum mass of phosphorus (mg) in each vial can be calculated by exchanging the actual concentration with the inflow solution concentration. The mass of adsorbed phosphorus (mg) is the difference between the potential mass of phosphorus and the mass of phosphorus in each vial.

$$\begin{aligned} &\text{Vial Mass of Phosphorus (mg)} \\ &= \frac{(\text{Actual Concentration (mg P/L)})(\text{Vial Volume (mL)})}{\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)} \quad \text{Eq. 5} \end{aligned}$$

The discrete phosphorus removal fraction is calculated from Eq. 6.

$$\begin{aligned} & \text{Discrete Phosphorus Removal} \\ & = 1 - \frac{\text{Actual Concentration (mg P/L)}}{\text{Inflow Solution Concentration (mg P/L)}} \end{aligned} \quad \text{Eq. 6}$$

The cumulative mass of phosphorus adsorbed is the summation of the adsorbed phosphorus masses from each of the preceding vials. This procedure is applicable for when only phosphorus solution is flowing through the column, but once deionized water starts mixing with the phosphorus solution and dilutes the outflow into the vials, the assumption is that the phosphorus will continue to be removed by the zirconia at a percentage equal to that of the last discrete phosphorus removal amount before the dilution started. This back-calculation method is used to calculate the extra adsorbed mass of phosphorus that is diluted during the deionized water flush.

When the phosphorus solution starts flowing and mixing with the deionized water, some phosphorus is typically present in the last deionized water vial. To account for this early phosphorus flow, Eq. 7 is utilized to start the initial summation of cumulative phosphorus adsorbed.

$$\text{Phosphorus Adsorbed (mg)} = \frac{(\text{Discrete P Removal})(\text{Vial Mass of P (mg)})}{(1 - \text{Discrete P Removal})} \quad \text{Eq. 7}$$

The amount of phosphorus adsorbed per amount of zirconia can be calculated using Eq. 8.

$$\begin{aligned} & \text{Phosphorus Adsorbed Per Mass Zirconia (mg P/g ZrO}_2\text{)} \\ & = \frac{\text{Cumulative Phosphorus Adsorbed (mg)}}{\text{Mass Zirconia (g)}} \end{aligned} \quad \text{Eq. 8}$$

It is assumed that any phosphorus present in the ammonium hydroxide solutions or the deionized water solutions during the system flush is desorbed

phosphorus and it can be calculated utilizing the same phosphorus adsorption methodology.

Chapter 3

ADSORPTION BATCH EXPERIMENTS

3.1 Results and Discussion

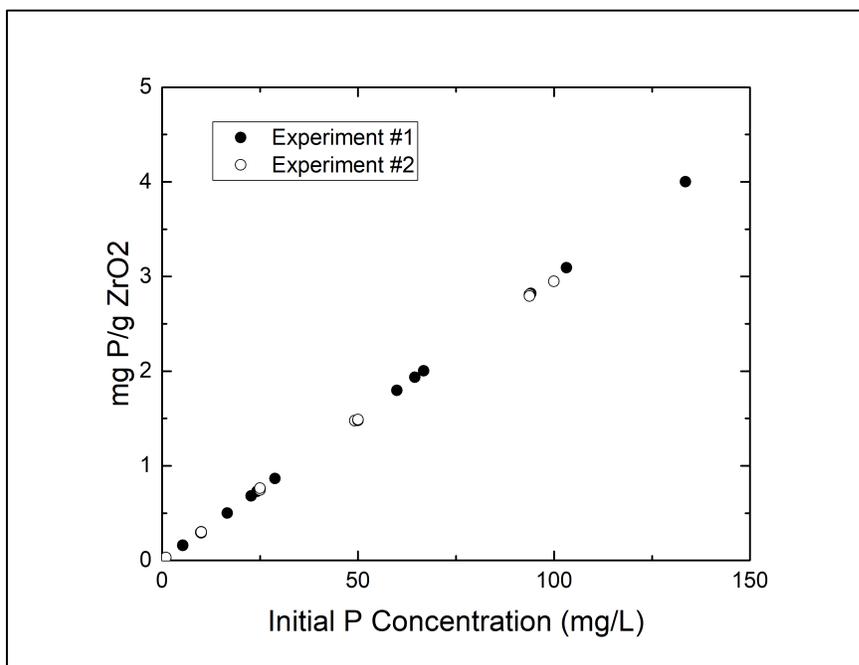


Figure 3-1. Batch isotherm zirconia with counter-ions present. Observed maximum capacities are 3.30 mg P/g ZrO₂ for Experiment #1 and 2.85 mg P/g ZrO₂ for Experiment #2.

A general linear trend of increasing adsorption capacity of phosphorus per mass of zirconia can be seen in Figure 3-1 with increasing initial phosphorus

concentration, which is expected since more phosphorus present in solution would generally allow for more phosphorus to adsorb. In the experiments with reaction concentrations below 75 mg P/L, no phosphorus was present in solution after the 24-hour shaking period. However, when zirconia was reacted with the 100 mg P/L solution, there were small amounts of measured phosphorus remaining in solution, indicating that an equilibrium maximum capacity had been reached based on the given conditions. This equilibrium capacity was calculated to be around 3.30 mg P/g ZrO₂ for Experiment #1 and 2.85 mg P/g ZrO₂ for Experiment #2. Since zirconia showed its ability to adsorb phosphorus with magnesium, calcium, sulfur, sodium, and potassium ions present in this experiment, the other ions were determined to have a negligible impact on the remaining experiments for this thesis and are not present in the ensuing experiments.

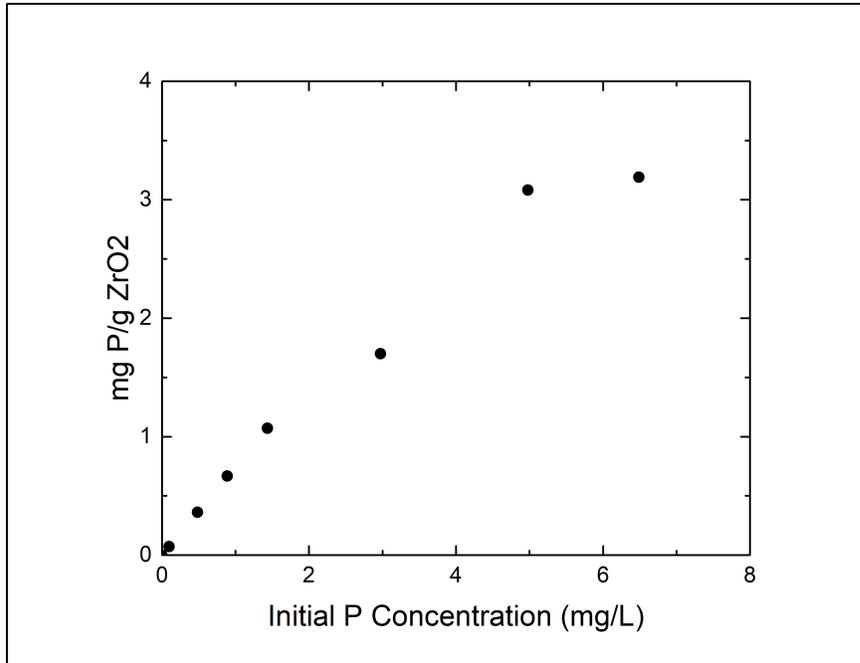


Figure 3-2. Batch isotherm zirconia without counter-ions present. Observed maximum capacity was 3.19 mg P/g ZrO₂.

The results of the next batch experiment, this time without counter ions, can be found in Figure 3-2. The maximum theoretical adsorption of 0.04 g zirconia and a 30 mL solution is 2.63 mg P/g ZrO₂ for a 3.5 mg P/L initial concentration and 5.25 mg P/g ZrO₂ for the 7.0 mg P/L initial concentration. As expected, the lower initial concentrations of phosphorus followed a linear trend on the plot, indicating all of the phosphorus had adsorbed. However, at 5 and 7 mg P/L initial concentrations, a maximum amount of phosphorus adsorption appears to be reached. The adsorption capacity value at the 7.0 mg P/L initial concentration solution was 3.19 mg P/g ZrO₂, thus showing consistency with the baseline results from the first batch experiment. With the maximum experimental adsorption capacity of zirconia identified, flow through experiments could begin, since there was now a general idea of the maximum

amount of solution at a given concentration that could be flowed through the zirconia. What remained uncertain was the adsorption capacity of zirconia with much shorter residence times than the batch experiments.

Chapter 4

SORPTION FLOW EXPERIMENTS

4.1 Results and Discussion

These experiments are only sorption experiments, meaning only a solution with phosphorus was flowed through the zirconia. The first experiment sought to determine the flow adsorption ability of zirconia. With only knowledge about the maximum capacity of zirconia (3.19 mg P/g ZrO₂), a flow rate ($Q = 0.56$ mL/min) was selected to be consistent with a range of typical runoff rates, the concentration (6.12 mg P/L) was selected to be higher than the typical 1 mg P/L concentrations in order to load more phosphorus in a reasonable amount of time, and 1.0 g of zirconia was chosen¹⁰. Figure 4-1 a) depicts the outflow concentration over time in the top plot and the flow rate over time in the bottom plot. The second experiment sought to utilize a lower flow rate (0.34 mL/min) with similar concentration (6.25 mg P/L) and double the amount of zirconia (2.0 g). Figure 4-1 b) depicts both the outflow concentration over time and the flow rates over time.

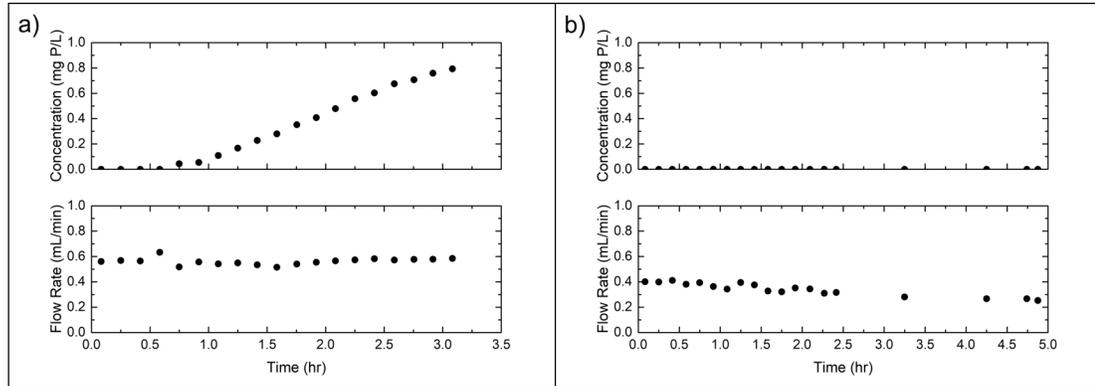


Figure 4-1. a) Experiment #1: Sorption flow. $Q = 0.56$ mL/min, $C_0 = 6.12$ mg P/L, $m = 1.0$ g ZrO_2 . b) Experiment #2: Sorption flow. $Q = 0.34$ mL/min, $C_0 = 6.25$ mg P/L, $m = 2.0$ g ZrO_2 .

It appears, in Experiment #1, that all of the phosphorus in solution was adsorbed in the first hour and then the percentage of phosphorus removal continued to decline over time. These results make sense, considering as the amount of phosphorus loading increases, it should be more difficult to add more and there will be less of a driving force for adsorption. The cumulative loading of phosphorus onto zirconia in Experiment #1 was 0.65 mg/g ZrO_2 , so only 20% of the maximum capacity was reached. The data from Experiment #2 shows that all of the phosphorus in solution was removed during the process. This result makes sense in the context of the first experiment because a lower flow rate and a larger mass of zirconia were used. Lower flow rates allow for more adsorption time and more zirconia allows for greater phosphorus adsorption. The cumulative loading of phosphorus onto zirconia in Experiment #2 was 0.31 mg/g ZrO_2 , so only 10% of the maximum capacity was reached. A more thorough analysis of the cumulative phosphorus loading in each experiment can be seen in Figure 4-2. The discrete phosphorus removal percentage as a function of cumulative phosphorus loading can be found in this plots. As expected,

with greater loading, the percentage of phosphorus in solution that is removed declines.

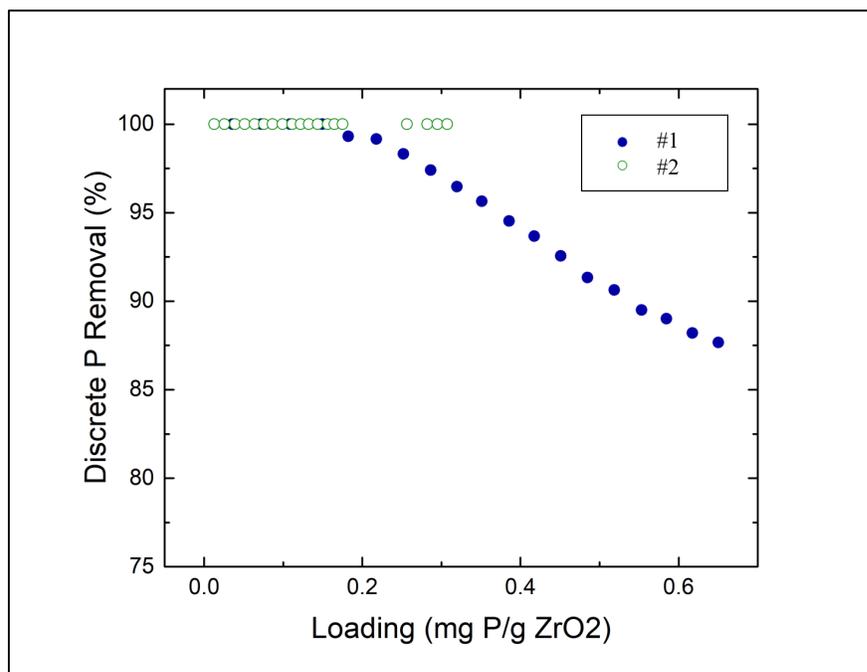


Figure 4-2. Cumulative phosphorus loading Experiments #1 and #2.

Experiments #3 and #4 attempted to expand upon the knowledge gained from the first two experiments. The two goals were to determine if adsorption was still possible at higher flow rates and at lower solution concentrations. Figure 4-3 a) shows the results of a 1.90 mL/min flow rate and Figure 4-3 b) shows the results of a 1.50 mL/min flow rate. Both experiments had a solution concentration of 1.25 mg P/L and used 1.0 g of zirconia.

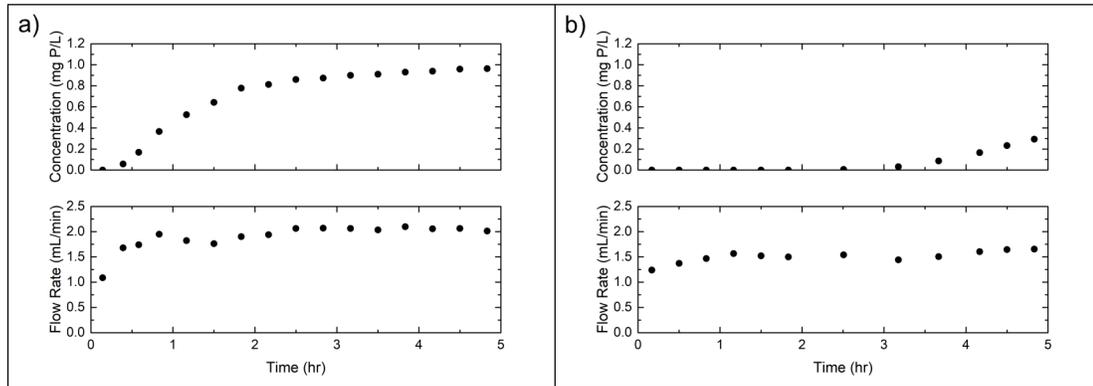


Figure 4-3. a) Experiment #3: Sorption flow. $Q = 1.90$ mL/min, $C_0 = 1.25$ mg P/L, $m = 1.0$ g ZrO_2 . b) Experiment #4: Sorption flow. $Q = 1.50$ mL/min, $C_0 = 1.25$ mg P/L, $m = 1.0$ g ZrO_2 .

It is evident from Experiment #3 that complete adsorption only occurred for the first half hour and then the outflow concentration eventually proceeded to increase at a much slower rate after two hours. These results show that adsorption is possible at higher flow rates and lower concentrations. Experiment #4 shows a similar linear profile as Experiment #3, but this does not occur until after three hours of flow. These results are somewhat inconsistent with those in Experiment #3 because complete adsorption was only obtained until 0.05 mg P was adsorbed by the zirconia while in Experiment #4, complete adsorption was observed until 0.33 mg P was adsorbed. While the reasons for this discrepancy are unknown, the establishment of adsorption ability at lower concentrations and higher flow rates is most important. The cumulative phosphorus loadings in these experiments can be found in Figure 4-4. Higher flow rates account for the much lower discrete phosphorus removal numbers with increased phosphorus loading in Experiment #3.

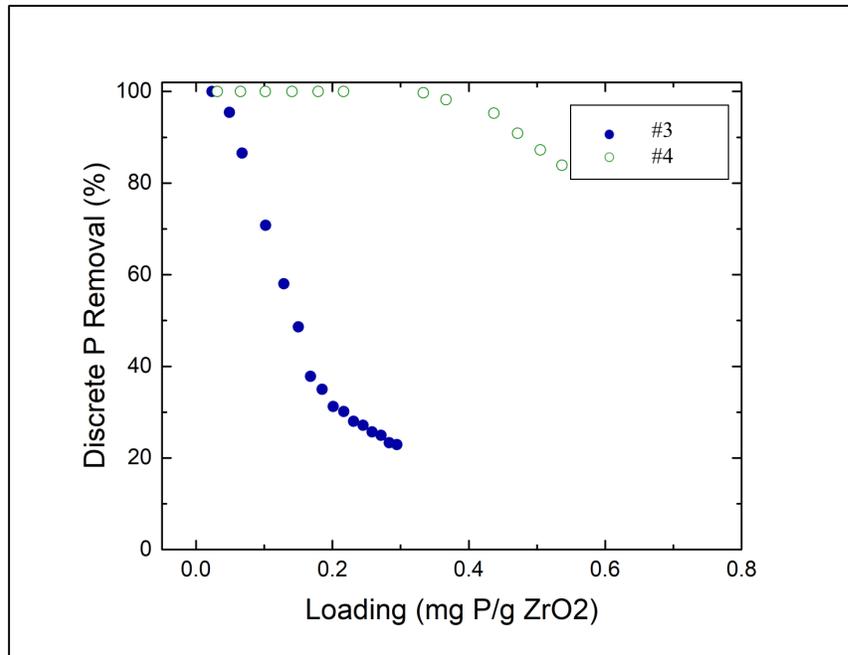


Figure 4-4. Cumulative phosphorus loading Experiments #3 and #4.

Experiment #5 sought to determine the long-time behavior of zirconia and attempted reach its maximum theoretical capacity as shown in the batch experiments. Despite a slightly declining flow rate throughout the experiment, the discrete phosphorus removal started above 30%, but approached 10% at long times. The cumulative phosphorus loading neared the maximum capacity of 3.19 mg P/g ZrO₂, but was still unable to reach the value. Adsorbing only 10% of the phosphorus through zirconia is not ideal and so future experimentation should be conducted to determine if the time spent in the higher discrete phosphorus removal regions can be optimized.

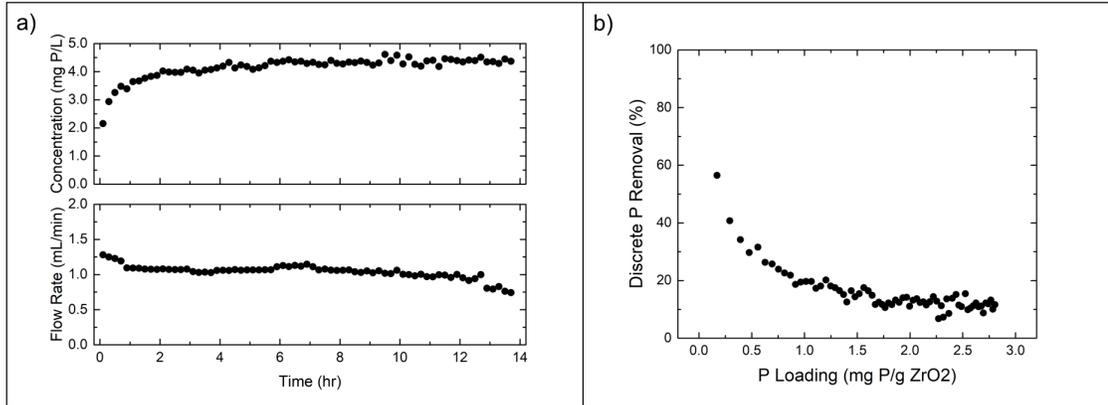


Figure 4-5. Experiment #5: Sorption flow. $Q = 1.04$ mL/min, $C_0 = 4.95$ mg P/L, $m = 0.25$ g ZrO_2 .

Experiment #6 sought to expand upon the results of Experiment #5 by cutting the flow rate by a third and keeping the other system properties constant. This change in properties led to a much higher discrete phosphorus removal throughout the course of the experiment and long-time removal percentages approaching 30% as opposed to the 10% in Experiment #5.

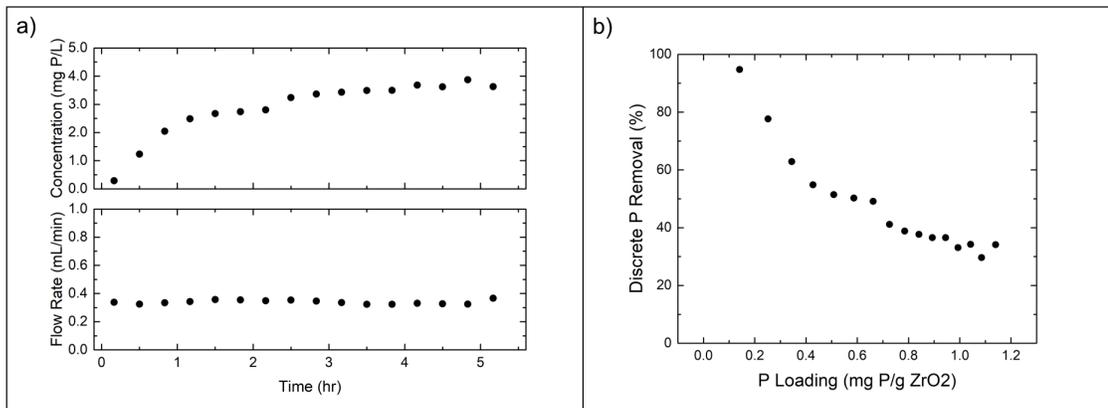


Figure 4-6. Experiment #6: Sorption flow. $Q = 0.34$ mL/min, $C_0 = 5.50$ mg P/L, $m = 0.25$ g ZrO_2 .

Chapter 5

REVERSIBLE SORPTION FLOW EXPERIMENTS

Flow experiments were conducted using the physical system and Arduino control system discussed in the Experimental Methods section. The phosphorus and ammonium hydroxide solutions, as well as the zirconia particles, were prepared as previously discussed. For these reversible sorption experiments, as opposed to simply the sorption experiments, time delay compensation was accounted for. In all experiments, evaporation was addressed, the experimental procedure was followed, and the data analysis was completed.

With the sorption experiments conducted and an idea of the adsorption flow behavior of zirconia, the reversible sorption experimental phase began. Figure 5-1 depicts the concentration profile and flow rates of Experiment #7. This experiment had a flow rate of 0.91 mL/min, solution concentration of 4.85 mg P/L, zirconia mass of 0.25 g, and an ammonium hydroxide concentration of 1 mM. The general up and down concentration profile can be explained by the initial deionized water flush, which is followed by phosphorus loading, a deionized water flush, an ammonium hydroxide rinse, and then one last deionized water flush before repeating the process for a total of three cycles. Initially, one would expect a low outflow concentration because there is some dilution from the deionized water rinse as well as a high phosphorus removal percentage. As seen in Experiment #3, once loading reaches a certain point, the zirconia tends to start adsorbing much less and this behavior can also be seen in Figure 5-1. The concentration profile continues to follow expected trends because it decreases toward zero during the deionized water rinse. Then, the

concentration profile increases sharply to account for all of the phosphorus desorbing during the ammonium hydroxide flush. Finally, the last deionized water rinse brings the concentration back down to zero before renewing the cycle.

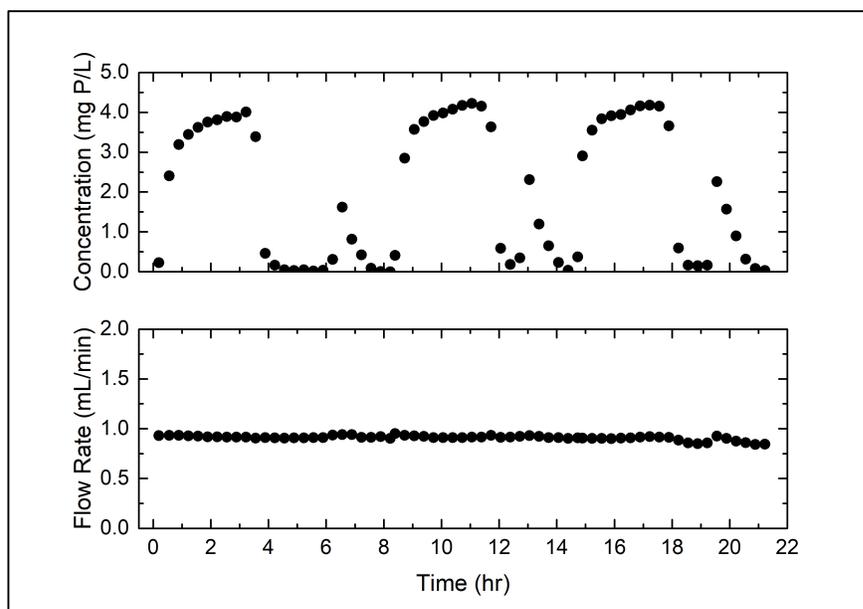


Figure 5-1. Reversible sorption flow Experiment #7. $Q = 0.91$ mL/min, $C_o = 4.85$ mg P/L, $m = 0.25$ g ZrO_2 , $C_{NH_4OH} = 1$ mM.

In order to more easily interpret and analyze the data from these flow experiments, a condensed plot of concentration as a function of time for each cycle is generated. Figure 5-2 is a condensed reversible sorption curve of the experiment discussed above. Since the area above the adsorption curve and below the inflow solution concentration provides the amount of phosphorus adsorption on the zirconia, the greater the area and adsorption. We can see from Figure 5-2 that there is slightly more area under the 1st cycle's adsorption curve, which indicates slightly more

zirconia is adsorbed in the 1st cycle than the 2nd and 3rd cycles. This condensed plot also allows one to decipher minute differences between the cycles. In this case, the 1st cycle's desorption curve is shifted to the right by about two hours and this is addressed by the fact that the deionized water rinse was allowed to continue for two more hours than the 2nd and 3rd cycles. The other main comparison the condensed plots allow us to compare the desorption of each cycle. The area under the desorption sections of the curve allow for a general idea of the amount of phosphorus that was desorbed in the process. We can see that the 1st cycle had a slightly smaller peak than the 2nd and 3rd cycles that had very similar trends. Comparing the areas under the adsorption and desorption curves for each cycle can allow for determination if all of the phosphorus that had adsorbed was also desorbed during that cycle. In these cycles, the area above the adsorption curves and 4.85 mg P/L appears to be slightly greater than the areas under the desorption curves. Therefore, we can conclude qualitatively in Experiment #7 that more phosphorus was adsorbed in the 1st cycle and less was desorbed in the 1st cycle while the behavior in the 2nd and 3rd cycles appeared relatively similar. 4 provides specific adsorption and desorption values to confirm these observed trends. The phosphorus adsorbed in the 1st cycle (0.24 mg) is greater than that adsorbed in the other cycles and the amount of phosphorus desorbed in the 1st cycle (0.06 mg) is less than that desorbed in the other cycles. It is important to note that this experiment shows the accumulation of phosphorus on the surface of zirconia, which could cause problems with recycling the material, but stronger concentrations of ammonium hydroxide will be used in some future experiments to increase desorption.

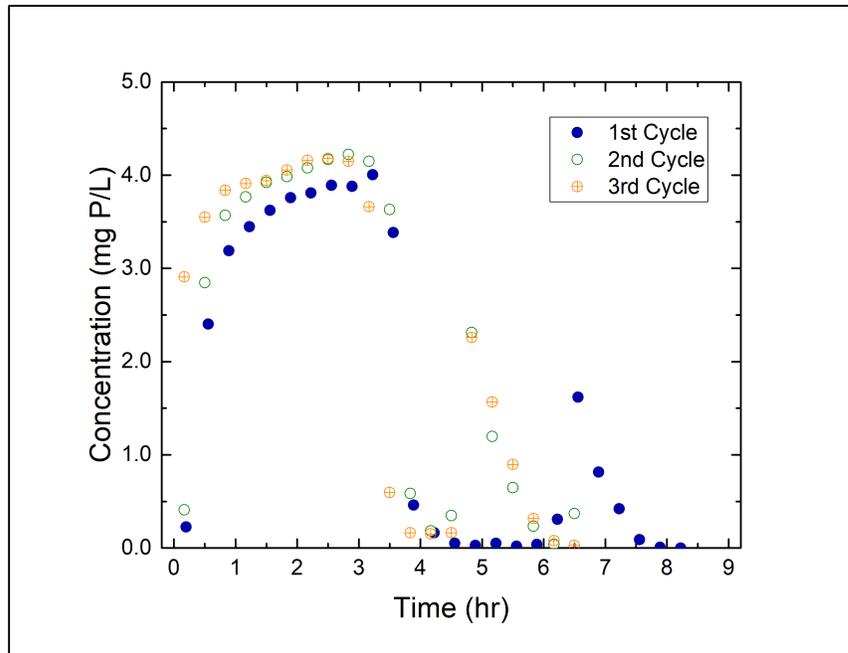


Figure 5-2. Reversible sorption flow Experiment #7 condensed.

Table 4. Experiment #7 phosphorus adsorption and desorption quantitative analysis.

	P Adsorbed (mg)	P Desorbed (mg)	Cumulative P (mg)	Loading (mg P / g ZrO₂)
1st Cycle	0.24	0.06	0.18	0.72
2nd Cycle	0.19	0.09	0.29	1.14
3rd Cycle	0.18	0.10	0.36	1.46

Experiment #8 was initially conducted to build upon the lessons in Experiment #7 and see if the same behavior was observed for higher flow rates. However, as can be seen in Figure 5-2, the flow rates continued to decline throughout each cycle. This behavior was later attributed to a pipe tubing diameter too large for the desired flow rates, but nonetheless these results should only give a qualitative description of the adsorption and desorption behavior. It appears as if the concentration profile for this experiment is opposite that of Experiment #7, since the 1st cycle has the smallest area

above its adsorption curve. However, when considering that the flow rates continued to decrease throughout each cycle, the profiles seem quite similar and appear to shift later in time as the flow rate decreases. This makes sense because lower flow rates mean it will take longer to switch between solutions. A comparison of the desorption profiles corroborates this idea, since the peaks shift to the right and grow larger with each cycle. Despite the desorption peaks being larger, they do in fact have similar desorption numbers since the total amount of desorbed phosphorus was 0.05 or 0.06 mg for each cycle.

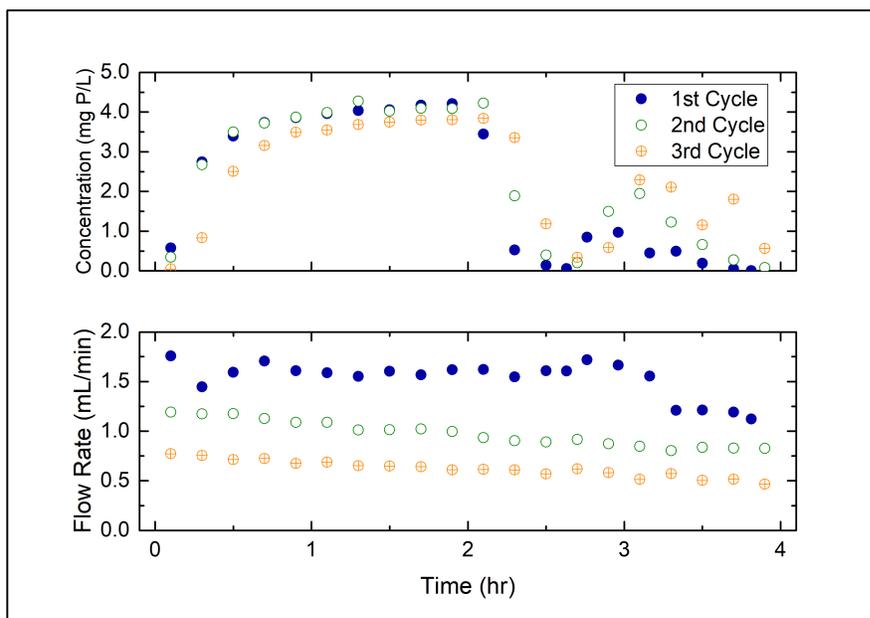


Figure 5-3. Experiment #8: Reversible sorption flow. $Q = 1.05$ mL/min, $C_o = 4.84$ mg P/L, $m = 0.25$ g ZrO_2 , $C_{NH_4OH} = 1$ mM.

The goal of Experiment #9 was to show that the adsorption and desorption behavior found in the previous experiments would be consistent at lower flow rates

and to see the impact of a higher ammonium hydroxide concentration (10 mM). The result of Experiment #9 can be found in Figure 5-4 below. The first note is that the 3rd cycle flow rate was lower than the other two cycles, for the same reason as Experiment #8, since this problem was not corrected until after this experiment. The 1st and 2nd cycle concentration profiles are almost identical and the 3rd cycle appears to adsorb slightly more phosphorus, which could have resulted from the lower flow rates. This greater adsorption can be seen in the discrete phosphorus removal versus phosphorus loading curves, which are quite similar, but the zirconia adsorption capacity was highest during the 3rd cycle, most likely due to these flower flow rates. 5 corroborates this qualitative analysis and shows that a much greater percentage of phosphorus was desorbed in these cycles than in previous experiments, thus confirming that using a higher concentration ammonium hydroxide solution will cause greater phosphate desorption.

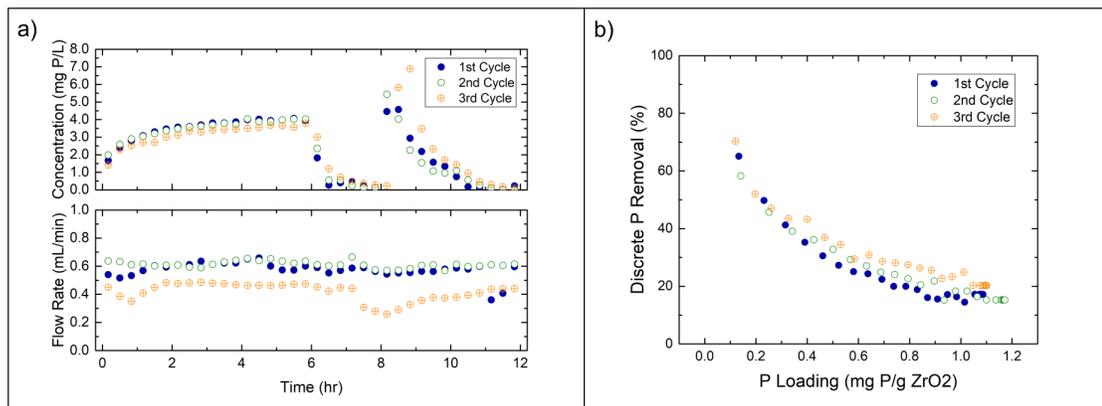


Figure 5-4. Experiment #9: Reversible sorption flow. $Q = 0.53$ mL/min, $C_0 = 4.68$ mg P/L, $m = 0.25$ g ZrO₂, $C_{\text{NH}_4\text{OH}} = 10$ mM.

Table 5. Experiment #9 phosphorus adsorption and desorption quantitative analysis.

	P Adsorbed (mg)	P Desorbed (mg)	Cumulative P (mg)	Loading (mg P / g ZrO₂)
1st Cycle	0.27	0.20	0.07	0.27
2nd Cycle	0.29	0.20	0.16	0.64
3rd Cycle	0.28	0.16	0.27	1.09

With the reversible sorption flow characteristics generally well understood after the previously discussed experiments, the recyclability of the zirconia was to be tested with an added 4th cycle to see if the same general trends were observed. Figure 5-5 is the first of these two experiments with four adsorption/desorption cycles. With the flow rate constant throughout the entire experiment, direct comparison among cycles is possible. Since the concentration profiles were nearly identical for all four cycle and the discrete phosphorus removal curves were nearly identical, the ability to recycle zirconia as a phosphorus sorbing material could be confirmed. 6 shows that the amount of phosphorus adsorbed and desorbed in each cycle was almost identical. About 60% of the phosphorus adsorbed in each cycle was desorbed, which means that some phosphorus was accumulating on the surface of the zirconia. The cumulative phosphorus loading onto the zirconia reached 1.65 mg P/g ZrO₂, which is 52% of the maximum theoretical capacity of 3.19 mg P/g ZrO₂.

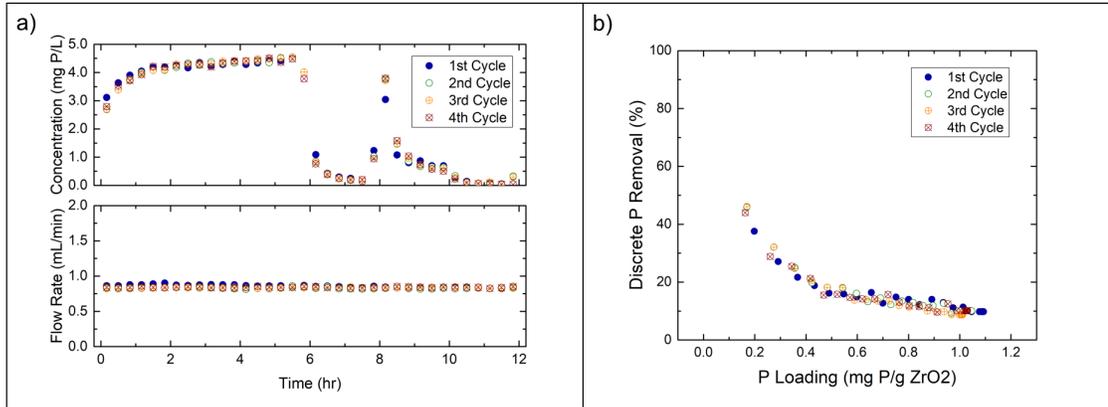


Figure 5-5. Experiment #10: Sorption flow. $Q = 0.84$ mL/min, $C_o = 4.98$ mg P/L, $m = 0.25$ g ZrO_2 , $C_{NH_4OH} = 10$ mM.

Table 6. Experiment #10 phosphorus adsorption and desorption quantitative analysis.

	P Adsorbed (mg)	P Desorbed (mg)	Cumulative P (mg)	Loading (mg P / g ZrO_2)
1st Cycle	0.27	0.15	0.12	0.49
2nd Cycle	0.26	0.16	0.23	0.90
3rd Cycle	0.25	0.16	0.32	1.27
4th Cycle	0.26	0.16	0.41	1.65

The reversible sorption experiments conducted thus far have used concentrations around 5 mg P/L, which have allowed for less time required to conduct each experiment since the maximum theoretical capacity could be reached more quickly. However, the next experiment was conducted at a more typical phosphorus concentration of 1.0 mg P/L in order to determine if adsorption was realizable with reduced concentrations and a potentially decreased driving force. Experiment #11 replicated the procedure in Experiment #10 while decreasing the inflow solution concentration to 1.06 mg P/L. As shown in the concentration profile, the outflow concentrations of phosphorus at each time point for the cycles were essentially the

same, with the 1st cycle having slightly lower concentrations of phosphate retained by the zirconia during the adsorption phase. The discrete phosphorus removal curve shows little to no differences in phosphorus desorption among these cycles, so further trials should be conducted in the future to understand this initial behavior. Nonetheless, the recyclability of zirconia when reacted with phosphorus at these lower concentrations can be seen; the data in 7 helps to quantify this statement. It appears that again, about 60% of the phosphorus adsorbed during each cycle was desorbed, which means that some phosphorus was accumulating on the surface of the zirconia. With lower input phosphorus concentrations, however, it would take much longer for the maximum phosphorus sorption capacity of zirconia to be approached, which means more experimental cycles could be used. It appears as if the ability of zirconia to adsorb phosphorus at lower initial concentrations is equal to the sorption ability at higher concentrations, which is a favorable property for a phosphorus sorbing material to have since concentrations of phosphorus in the inflow solution will typically fluctuate during operation.

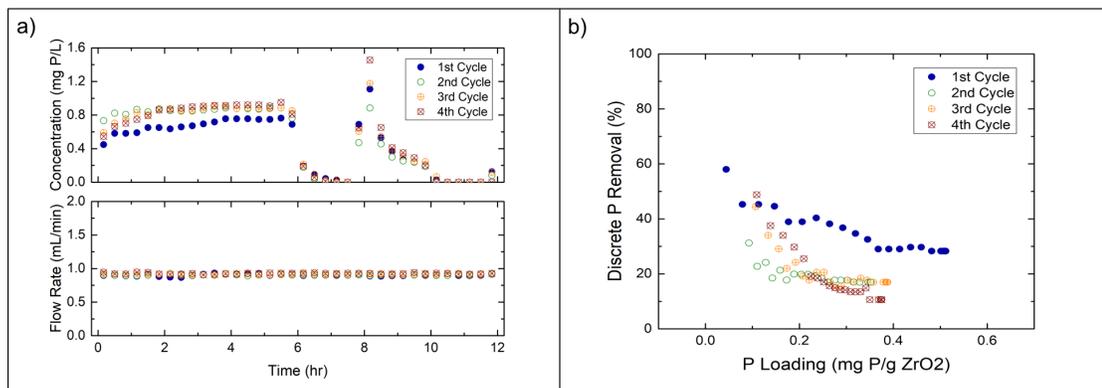


Figure 5-6. Experiment #11: Sorption flow. $Q = 0.91$ mL/min, $C_0 = 1.06$ mg P/L, $m = 0.25$ g ZrO₂, $C_{\text{NH}_4\text{OH}} = 10$ mM.

Table 7. Experiment #11 phosphorus adsorption and desorption quantitative analysis.

	P Adsorbed (mg)	P Desorbed (mg)	Cumulative P (mg)	Loading (mg P / g ZrO₂)
1st Cycle	0.13	0.06	0.07	0.27
2nd Cycle	0.09	0.05	0.10	0.42
3rd Cycle	0.10	0.07	0.14	0.55
4th Cycle	0.09	0.07	0.16	0.62

Chapter 6

REVERSIBLE SORPTION RUNOFF FLOW EXPERIMENTS

6.1 Results and Discussion

In order to determine if zirconia can be implemented to capture phosphorus from farm water runoff, we teamed up with Lauren Mosesso from the Plant and Soil Science Department at the University of Delaware. Lauren's current research interests include using stable water isotopes to characterize pathways of subsurface phosphorus loss in a ditch-drained field¹². Her studies focus on understanding the hydrology of flat, ditch drained fields in the Delmarva Peninsula, of which many have a history of manure applications at rates exceeding crop phosphorus removal. As a result, these soils are enriched with phosphorus, and the risk of dissolved phosphorus losses during runoff or shallow leaching events becomes greater. For the purposes of our studies, Lauren collected a gallon sample of water from the ditch adjacent to the field site from the UMES Research Farm located in southern Maryland, which is a part of the Chesapeake Bay Watershed, as seen in 6-1.

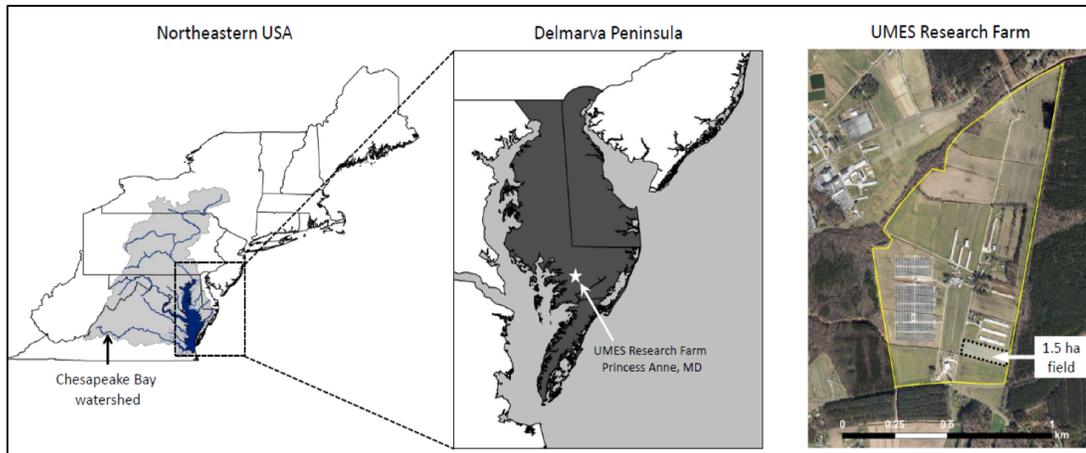


Figure 6-1. Source of phosphorus solution for reversible sorption runoff flow experiment¹².

The conditions of the reversible sorption runoff flow experiment were intended to be similar to those found in Experiment #11. The flow rate was set to around 0.90 mL/min since we were hoping to observe similar adsorption properties from previous experiments. The mass of zirconia was tripled to 0.75 g in order to provide for a longer adsorption period than was found in Experiment #11. The concentration of the ammonium hydroxide solution was increased to 50 mM in order to determine if it would lead to greater desorption in a shorter period of time. While the concentration of phosphorus in solution was unknown, it was anticipated to be around 1 mg P/L, since this is what is typically measured in drainage from the University of Maryland Research and Teaching Farm. Figure 6-2 below depicts the samples vials taken during the second 12-hour cycle of the experiment. It is important to note that the original one gallon phosphorus solution was a dark yellow color, most likely due to dissolved organic matter.

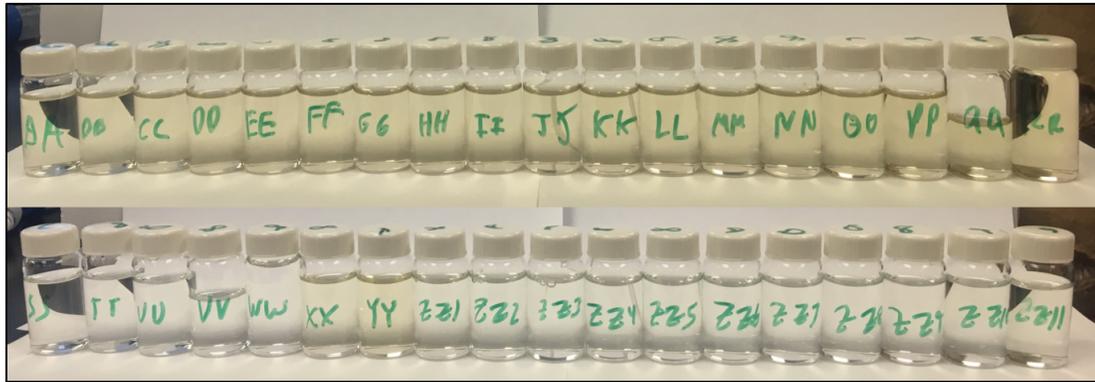


Figure 6-2. University of Maryland Research and Teaching Farm ditch water flow through sorption unit for sample vials AA to RR, with water rinse in vials SS to WW and ZZ4 to ZZ11, and ammonium hydroxide flush in vials XX to ZZ3.

The color trend found in Figure 6-2 is quite similar to the color trend observed after the molybdate blue is added to the samples to measure phosphorus concentration. For sample vials AA to RR, phosphorus solution is flowed through the zirconia. For sample vials SS to XX and ZZ6 to ZZ11, deionized water is flowed through the zirconia to flush the system. In between the two water flushes is the ammonium hydroxide flow regime. It appears that the yellow color darkens throughout the phosphorus loading phase. The yellow color appears again during the ammonium hydroxide desorption flow. The molybdate blue method was implemented on all of these sample vials, but none had measureable phosphorus concentrations except for sample vial XX. The concentration in sample vial XX was about 0.055 mg P/L. Considering this vial most likely contains most of the adsorbed phosphorus, if the flow rates and the concentration are back-calculated, it can be determined that the original phosphorus runoff solution contained about 0.003 mg P/L. If more time had allowed at the beginning of this experiment, tests would have been run on the original solution to

see if it had enough phosphorus originally to generate useable results. If the zirconia only captured 10% of the phosphorus flow through, the original phosphorus runoff solution could have had a concentration of up to 0.030 mg P/L. We attribute the lower than normal phosphorus concentrations to significant rainfall in the months leading up to the sample collection. Regardless, these phosphorus concentrations are below measureable concentrations and thus only qualitative results should be taken from this runoff flow experiment.

With the yellow color observed during the ammonium hydroxide desorption flow regime and the yellow color darkening as the phosphorus regime progressed, we can hypothesize that the zirconia was in fact not only adsorbing and desorbing any phosphorus contained in the solution, but also the dissolved organic matter. While carbon testing should be completed in the future to determine the extent of organic loading, we can qualitatively state some amount of organic matter must be adsorbed by the zirconia. Therefore, the organic matter most likely would compete with the phosphorus present in solution for binding sites, which could further limit the adsorption capacity of the zirconia. However, we are unsure of the complete extent of the organic content adsorption and there is some evidence that the formation of organic complexes could in fact increase adsorption, so this is only a preliminary hypothesis that should be examined in the future. Regardless of these results, enough information has been gathered throughout the experiments discussed in this paper to design a reversible sorption unit for phosphorus pollution abatement.

Chapter 7

REVERSIBLE SORPTION UNIT DESIGN

7.1 Design Parameters and Properties

The challenge of designing a reversible sorption unit for farm water runoff applications begins with determining the annual phosphorus loading of the unit. Based on a 2010 EPA study, 2.3 million kilograms of phosphorus a year enter the Chesapeake Bay as a result of agriculture¹⁴. To determine the phosphorus loading from an average farm, the number of farms in the Chesapeake Bay Watershed was found to be 87,000¹⁵. Therefore, 26 kilograms of phosphorus will be loaded onto the unit over the course of a year. It is important to note that this even allocation of phosphorus loading is a gross oversimplification of the phosphorus loading throughout the region, since not all entities that are considered farms would be expected to contribute to phosphorus pollution. If the average concentration of the farm water runoff is 1 mg P/L, the loading equates to 0.88 L/sec flowing through the sorption unit. It is assumed that the unit will be able to adsorb phosphorus until the maximum capacity of 3.19 mg P/g ZrO₂ is reached and that the phosphorus removal is 20%, which was typical of the experiments discussed previously. It is also assumed that the zirconia will operate effectively over five years, which is only a prediction, and the exact number will be determined through future field experiments. The ammonium hydroxide solution flush was assumed to be only necessary for 20 minutes after each maximum adsorption capacity is reached and we assume the 50 mM solution will be

able to remove all of the phosphorus adsorbed onto the zirconia in this time. The aforementioned design parameters and values can be found in Table 8.

Table 8. Design parameters and values for reversible sorption unit.

Design Parameter	Units	Value
Lifetime	yr	5
Solution Concentration	mg P/L	1.0
Maximum Capacity	mg P/g ZrO ₂	3.19
P Removal	%	20
Ammonium Hydroxide Flush Time	min	20

With the design parameters specified, the system properties can be calculated and are found in Table 9. A zirconia mass of 5.13 kg is required to adsorb all of the necessary phosphorus. It is important to note that this flow rate and mass equate to 10.3 mL/min*g ZrO₂. Previous experiments with 20% phosphorus removals have been with approximately 3.6 mL/min* g ZrO₂, so there is some uncertainty if the same sorption characteristics will be realized with this design. Nonetheless, with these parameters, it will take about 5.5 hours for the maximum capacity of the zirconia to be reached. Another important discussion is what happens in large storm events that last longer than the 5.5 hours required for the maximum capacity of zirconia to be reached. In these situations, the holding tank would most likely be sized to handle large weather events lasting more than 24 hours so that the runoff can be captured and eventually filtered in due time with the parameters discussed previously. With this allowable adsorption time, followed by a 20 minute ammonium hydroxide solution flush, between which the transition time is considered negligible, there will be about 1,502 system cycles each year. To create the 50 mM ammonium hydroxide solutions, ammonium hydroxide with 30 wt% of ammonia is added to water. The total annual

volume of ammonium hydroxide solution to flush all of the phosphorus will be about 26,000 L.

Table 9. System properties for reversible sorption unit.

System Property	Units	Value
P Capture	lb/yr	57.5
Zirconia Mass	kg	5.13
Time to Reach Maximum Capacity	hr	5.50
Flow Rate	L/sec	0.88
Cycles per Year	-	1502
Ammonium Hydroxide Solution Yearly Volume	L	26332

7.2 System Costs and Sensitivity

With the system properties calculated above, the system costs can now be approximated. Table 10 includes the raw material costs, prices, and then yearly and overall costs for the five-year project. It is important to note that these costs are from Fischer Scientific and thus could be somewhat inflated. However, actual quantities of zirconia and ammonium hydroxide are not much more than largest quantities sold on these sites, so the costs could be reasonable. It appears that since the ammonium hydroxide is an annual cost and the zirconia is a one-time cost, the influence of the ammonium hydroxide on the total cost is much more significant. We can see that we can design a reversible sorption unit for phosphorus pollution abatement that captures 57.5 pounds of phosphorus each year for only about \$11,000.

Table 10. Material costs and total five-year costs for reversible sorption unit.

Material	Price	Yearly Cost	Total Cost
Ammonium Hydroxide (~30% NH3)	\$508/25L ¹⁵	\$1,841	\$9,203
Zirconia	\$120/500g ¹⁶	\$1,231	\$1,231
			\$10,434

Once again, there are considerable uncertainties and assumptions with this design that include but are not limited to: Capital costs, permitting costs, and inflation have been ignored; the water costs for the ammonium hydroxide solutions are considered negligible and the actual phosphorus removal percentage could be higher than what has been measured in this study. In order to better understand the impact of variance among some of these parameters, a 10% of the parameter value sensitivity analysis was conducted on the initial system design. The results can be found below in Figure 7-1. An important first note is that the ammonium hydroxide flush time and ammonium hydroxide cost lines overlap each other, so only one is visible. It appears that the theoretical maximum capacity and cost of the zirconia has a minimal impact on the final system cost, which indicates that a system with more zirconia that needs to be flushed less often could be beneficial. It appears that the larger the water runoff concentration the cheaper the raw material costs due to more ammonium hydroxide flushes. The phosphorus removal percentage and the ammonium hydroxide flush time and costs also have significant impacts on the five year costs since increasing any three parameters leads to an increase in the overall system costs. Therefore, as the system design currently stands, the least expensive sorption unit will be one with more zirconia that requires fewer ammonium hydroxide flushes.

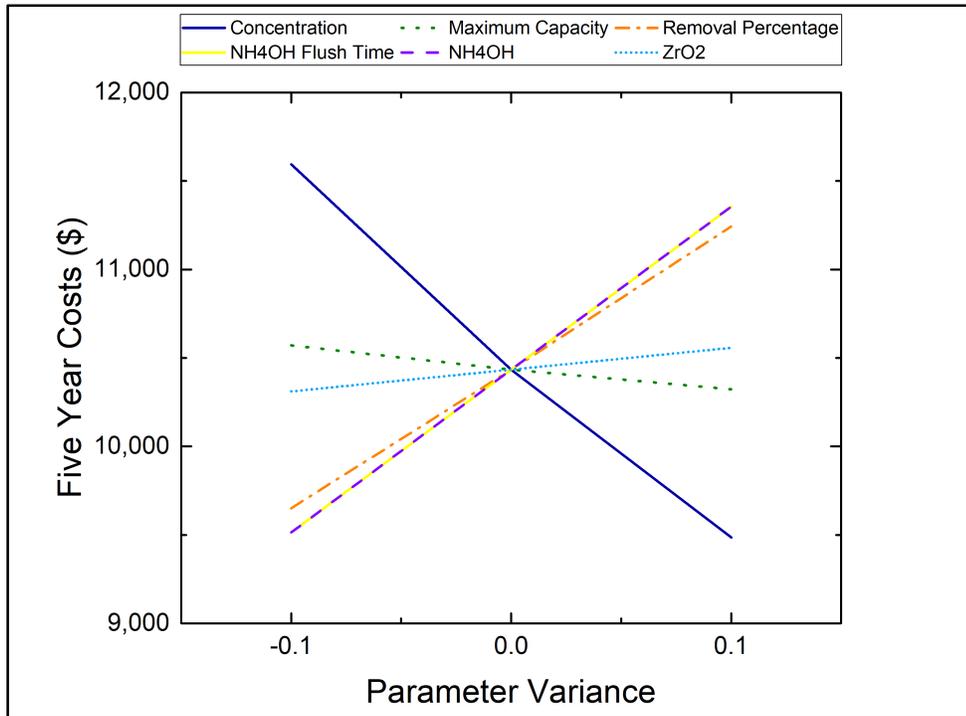


Figure 7-1. Reversible sorption unit sensitivity analysis for five year costs.

7.3 System Operation

The reversible sorption unit will work similarly to the experiments conducted in lab, except for the fact that there will be no deionized water rinses when changing solutions. Figure 7-2 depicts how the unit would be applied to a farm with phosphorus runoff. The phosphorus would enter drainage ditches at the edges of the crop fields, which would then flow into a holding tank. This notion of a holding tank is standard in chemical engineering systems, but not typical in drainage ditch discussions, so more discussions with farmers and experts should be conducted before following through on this holding tank strategy. When the sorption unit is ready to adsorb phosphorus, the pump will be turned on and the holding tank contents will flow through the sorption unit. If there is ample time or capacity to adsorb more phosphorus, the solution will be

recycled to the holding tank for another adsorption pass. If not, the outflow will be discharged to a local stream or river or the original ditch. Once the maximum capacity of the sorption unit has been reached, the pump will stop flowing from the holding tank and will begin flowing the desorbent from the ammonium hydroxide tank. The outflow from the sorption unit will be passed to the fertilizer tank, which will store the outflow fertilizer until the farmer is ready to disperse onto crops. This solution may need to be processed and pH adjusted before applying to the crops in order to ensure the health of the crops and safety of the farmers.

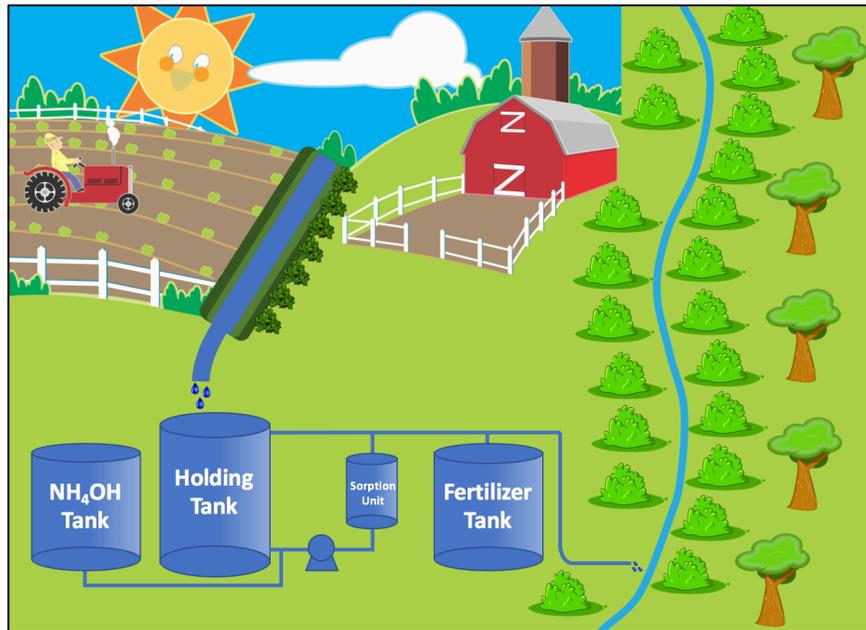


Figure 7-2. Reversible sorption unit design implementation.

Chapter 8

CONCLUSIONS AND FUTURE WORK

The studies described above have tried to further the current research in the field of phosphorus sorbing materials in order to better prevent eutrophication in waterways throughout the world, such as the Chesapeake Bay Watershed and throughout the globe. The maximum adsorption capacity of monoclinic zirconia was measured and the sorption flow experiments allowed for a greater understanding of the variables that impact adsorption. The reversible sorption experiments showed promising results in terms of the recyclability of zirconia, but the introduction of farm water runoff samples could indicate a decreased capacity due to competing ions. Further research should be done using the concentrations of competing ions typically found in agricultural runoff that was discussed previously. This research culminated in the design of a reversible sorption unit for implementation in a Chesapeake Bay Watershed farm that is able to handle the average yearly phosphorus load. Future work should aim to better understand the impact of inflow solution phosphorus concentration fluctuations and how the system would work under non steady-state conditions. It will be interesting to learn if this technology is scalable and how the reversible sorption unit would be designed for application. Incorporating other particles onto zirconia or impregnating zirconia into other materials could reduce costs and promote even greater phosphorus adsorption. Ultimately, with more time and resources, a team should be able to optimize the entire system to reversibly adsorb and desorb as much phosphorus as possible in order to prevent the effects of eutrophication.

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Appendix A

ARDUINO SYSTEM FLUSH CODE

The following code was utilized to flush each of the system solutions before beginning the experiment to ensure no air bubbles were present in solution and to mitigate mixing when switching solutions. The open-source Arduino software (IDE) can be downloaded for free online¹⁷.

[code]

```
// FLOW SYSTEM FLUSH CODE
// This code is designed to flush each of your holding tank solutions
// in order to ensure there are no air bubbles present in the tubing
// that could prevent flow. This code also flushes last with the solution
// being used first in the experiment to minimize solution mixing.

// The following code sets each of the Arduino valve pins as an output
// and sets their initial positions to closed. This runs only once
// at the beginning of the operation.
void setup() {
  pinMode(10, OUTPUT); // DI valve assigned to pin 10
  pinMode(11, OUTPUT); // P valve assigned to pin 11
  pinMode(12, OUTPUT); // B valve assigned to pin 12
  pinMode(3, OUTPUT); // End valve assigned to pin 3
  digitalWrite(10,HIGH); // DI valve set closed
  digitalWrite(11,HIGH); // P valve set closed
  digitalWrite(12,HIGH); // B valve set closed
  digitalWrite(3,HIGH); // End valve set closed
}

// The following code will loop infinitely until the system power is unplugged
// or another Arduino code is uploaded to the board. The end valve is opened to allow
// all of these waste flows to not enter the adsorption column piping. The B valve
// is opened and allowed to flow for five minutes to ensure all air bubbles are removed.
// The B valve is closed and the DI valve is opened. The DI valve is then closed
// and the P valve is opened last, since it will be flowed through the column first.
```

```

// After five minutes, the P and end valves are closed for two minutes to allow
// the manual valve to the column to be opened. One this time is up, the P valve
// is reopened to start flow onto the column. An "infinite" delay is set so that
// the loop does not repeat until power is unplugged or a new code is uploaded.
// All delay times are in milliseconds.
void loop() {
  digitalWrite(3,LOW); // End valve set open
  digitalWrite(12,LOW); // B valve set open
  delay(300000); // 5 minute flush

  digitalWrite(12,HIGH); // B valve set closed
  digitalWrite(10,LOW); // DI valve set open
  delay(300000); // 5 minute flush

  digitalWrite(10,HIGH); // DI valve set closed
  digitalWrite(11,LOW); // P valve set open
  delay(300000); // 5 minute flush

  digitalWrite(11,HIGH); // P valve set closed
  digitalWrite(3,HIGH); // End valve set closed
  delay(120000); // Delay two minutes to open manual valve to adsorption column
  digitalWrite(11,LOW); // P valve set open

  delay(600000000); // Delay until next code is implemented
}
[/code]

```

Appendix B

ARDUINO SYSTEM OPERATION CODE

The following code was utilized to run the flow system for each adsorption experiment.

[code]

```
// FLOW SYSTEM OPERATION CODE
// This code is designed to flow three different solutions through your
// adsorption column and rotate vials on the turntable to collect consistent
// data and ensure time delays are account for when switching solutions.

// This section provides an overview of the manually adjusted variables
// for the flow experiment. While initializing using "int" does not actually
// add these variables to the system and you must still implement them in the
// code manually, it is helpful to have these numbers recorded for later review.
// The numbers provided in this section are for a flow system experiment in which
// four successive experiments of P flow, DI flow, B flow, and DI flow occur.
// The turntable rotates the vials every 1,200,000 ms (20 minutes) and the
// number of P vials to be collected in each cycle is 18 (6 hours), 6 DI vials (2 hours),
// and 6 B vials (2 hours). The anticipated flow rate is 0.9 mL/min, so from
// time delay calculations, the P/DI valve must be turned open 1,100,000 ms before
// switching vials and the B valve must be turned open 966,667 ms before switching
// vials.
int t = 1; // Do not change this value since it tracks the number of rotated vials
int Num_Runs = 4; // Number of adsorption and desorption cycles
int Vial_Time = 1200000; // Length of time solution flows into a new vial
int P_Vials = 18; // Number of P vials
int DI_Vials = 6; // Number of DI vials
int B_Vials = 6; // Number of B vials
int Long_Turn_Delay = 1100000; // Time delay (P/DI) from anticipated flow rate and
system volume measurements
int Long_Valve_Delay = 100000; // Vial_Time - Long_Turn_Delay
int Short_Turn_Delay = 966667; // Time delay (B) from anticipated flow rate and
system volume measurements
int Short_Valve_Delay = 233333; // Vial_Time - Short_Turn_Delay
```

```

int Infinite_Time = 1000000000000; // Infinite time

// The following code sets each of the Arduino valve and motor pins as an output
// and sets their initial positions. This runs only once at the beginning of the operation.
void setup() {
  pinMode(10, OUTPUT); // DI valve assigned to pin 10
  pinMode(11, OUTPUT); // P valve assigned to pin 11
  pinMode(12, OUTPUT); // B valve assigned to pin 12
  pinMode(3, OUTPUT); // End valve assigned to pin 3
  digitalWrite(10,HIGH); // DI valve set closed
  digitalWrite(11,LOW); // P valve set open
  digitalWrite(12,HIGH); // B valve set closed
  digitalWrite(3,HIGH); // End valve set closed
  pinMode(8, OUTPUT); // Motor pin set
  pinMode(9, OUTPUT); // Motor pin set
  digitalWrite(8, LOW); // Motor position set
  digitalWrite(9, LOW); // Motor position set
}

// The following code will loop infinitely until the system power is unplugged
// or another Arduino code is uploaded to the board. A loop is created to run
// the number of cycles specified. The P loading loop is then created based
// on the number of P vials specified, the turntable is rotated, and the time
// delays are compensated for by opening the DI valve before rotating the last vial.
// This process is repeated for the DI, B, and DI again to wash. Then, if this is the
// last cycle, the system will close all valves except for the end valve and wait
// indefinitely. If this is not the last cycle, the system will cycle through the loop again.
// Fill in the VALUES of the variables defined above into the code, as the variable
// definitions will not work. All delay times are in milliseconds.
void loop() {
  for (int x=1; x<Num_Runs+1; x=x+1){ //Repeating code and cycling (Num_Runs)
  number of times

//P Loading Code
  for (int i=1; i<P_Vials+1; i=i+1){ //Repeating code (P_Vials) number of times
    if (i<P_Vials) {
      if (t % 4 == 0) { // Since there are 37 vials on the turntable and 1800 microsteps
        int turntable2(); // available to the stepper motor, every four microsteps,
        turntable2(); // the system is programmed to make one extra setp to compensate.
        t = t + 1;} // A rotation is logged by increasing the value of t.
      else {
        int turntable1();

```

```

    turntable1();
    t = t + 1;
    if (t == 38) { // If the value of t reaches one more than the number of vials
        t = 1;}} // on the turntable, the t value is set back to 1 to repeat the process.
else { // On the last P vial, the time delay must be accounted for
    if (t % 4 == 0) {
        int turntable22();
        turntable22();
        t = t + 1;
        delay(Long_Valve_Delay); //Time until P valve should be closed and DI valve
Opened
        digitalWrite(11,HIGH); //P valve set closed
        digitalWrite(10,LOW); //DI valve set open
        delay(Long_Turn_Delay-880);} //Time until turntable should next rotate
    else {
        int turntable11();
        turntable11();
        t = t + 1;
        if (t == 38) {
            t = 1;}
        delay(Long_Valve_Delay); //Time until P valve should be closed and DI valve
Opened
        digitalWrite(11,HIGH); //P valve set closed
        digitalWrite(10,LOW); //DI valve set open
        delay(Long_Turn_Delay-880);} //Time until turntable should next rotate

//DI Wash Code
for (int i=1; i<DI_Vials+1; i=i+1){ //Repeating code (DI_Vials) number of times
    if (i<DI_Vials) {
        if (t % 4 == 0) {
            int turntable2();
            turntable2();
            t = t + 1;}
        else {
            int turntable1();
            turntable1();
            t = t + 1;
            if (t == 38) {
                t = 1;}}}}
    else {
        if (t % 4 == 0) {
            int turntable22();
            turntable22();

```

```

    t = t + 1;
    delay(Short_Valve_Delay); //Time until DI Valve should be closed and B
Valve Opened
    digitalWrite(10,HIGH); //DI valve set closed
    digitalWrite(12,LOW); //B valve set open
    delay(Short_Turn_Delay-880);} //Time until turntable should next rotate
else {
    int turntable11();
    turntable11();
    t = t + 1;
    if (t == 38) {
        t = 1;}
    delay(Short_Valve_Delay); //Time until DI Valve should be closed and B
Valve Opened
    digitalWrite(10,HIGH); //DI valve set closed
    digitalWrite(12,LOW); //B valve set open
    delay(Short_Turn_Delay-880);} //Time until turntable should next rotate

//B Flush Code
for (int i=1; i<BI_Vials+1; i=i+1){ //Repeating Code (B_Vials) Number of Times
    if (i<BI_Vials) {
        if (t % 4 == 0) {
            int turntable2();
            turntable2();
            t = t + 1;}
        else {
            int turntable1();
            turntable1();
            t = t + 1;
            if (t == 38) {
                t = 1;}}}}
    else {
        if (t % 4 == 0) {
            int turntable22();
            turntable22();
            t = t + 1;
            delay(Long_Valve_Delay); //Time until DI Valve should be closed and B
Valve Opened
            digitalWrite(12,HIGH); //B valve set closed
            digitalWrite(10,LOW); //DI valve set open
            delay(Long_Turn_Delay-880);} //Time until turntable should next rotate
        else {
            int turntable11();

```

```

    turntable11();
    t = t + 1;
    if (t == 38) {
        t = 1;}
    delay(Long_Valve_Delay); //Time until DI Valve should be closed and B
Valve Opened
    digitalWrite(12,HIGH); //B valve set closed
    digitalWrite(10,LOW); //DI valve set open
    delay(Long_Turn_Delay-880);} //Time until turntable should next rotate

//DI Wash Code
for (int i=1; i<DI_Vials+1; i=i+1){ //Repeating Code (DI_Vials) Number of Times
    if (i<DI_Vials) {
        if (t % 4 == 0) {
            int turntable2();
            turntable2();
            t = t + 1;}
        else {
            int turntable1();
            turntable1();
            t = t + 1;
            if (t == 38) {
                t = 1;}}}}
    else {
        if (t % 4 == 0) {
            int turntable22();
            turntable22();
            t = t + 1;
            if (x<4) {
                delay(Long_Valve_Delay); //Time until DI Valve should be closed and P
Valve Opened
                digitalWrite(10,HIGH); //DI valve set closed
                digitalWrite(11,LOW); //P valve set open
                delay(Long_Turn_Delay-880);}
            else {
                delay(Long_Valve_Delay); //Time until DI Valve should be closed and P
Valve Opened
                digitalWrite(10,HIGH); //DI valve set closed
                digitalWrite(11,LOW); //P valve set open
                delay(Long_Turn_Delay-880);}
            else {
                int turntable11();
                turntable11();

```

```

        t = t + 1;
        if (t == 38) {
            t = 1;}
        if (x<4) { // If not on the last cycle, allow the time delay compensation to
continue
            delay(Long_Valve_Delay); //Time until DI Valve should be closed and P
Valve Opened
            digitalWrite(10,HIGH); //DI Valve Closed
            digitalWrite(11,LOW); //P Valve Open
            delay(Long_Turn_Delay-860);} //Time until Turntable should next rotate
        else { // If about to finish the last cycle, allow the DI valve to stay open until
last vial finished
            delay(Vial_Time); //
            digitalWrite(10,HIGH); //DI Valve Closed
            digitalWrite(3,LOW); //End Valve Open
            delay(Infinite_Time);}}}} //Delay Indefinitely
    }}

// The following sections of code tell the stepper motor to make a specified number
// of steps (43 or 44) depending on the number of vials turns. It takes 20 ms for the
// motor to make one step, so this time is multiplied by the number of microsteps and
// decreased from the time delay, since it takes time to make every turntable rotation.
void turntable1() {
    for (int i=0; i<43; i=i+1 ){
        digitalWrite(9, HIGH); // Setting motor pin to high
        delay(10); // Delaying 10 ms
        digitalWrite(9, LOW); // Setting motor pin to low
        delay(10);} // Delaying 10 ms
        delay(Vial_Time-860); // Delaying until next turntable rotation less the motor time
delay
    }
void turntable2() {
    for (int i=0; i<44; i=i+1 ){
        digitalWrite(9, HIGH);
        delay(10);
        digitalWrite(9, LOW);
        delay(10);}
        delay(Vial_Time-880);
    }
void turntable11() {
    for (int i=0; i<43; i=i+1 ){
        digitalWrite(9, HIGH);
        delay(10);

```

```
    digitalWrite(9, LOW);
    delay(10);}
}
void turntable22() {
  for (int i=0; i<44; i=i+1 ){
    digitalWrite(9, HIGH);
    delay(10);
    digitalWrite(9, LOW);
    delay(10);}
}
[/code]
```