

NASA KSC/Intern Research Paper – 7/30/15

Nutrient Recovery of Plant Leachates Under Thermal, Biological, and Photocatalytic Pretreatments

Student Name: Les Wong
Academic Level: Junior
Academic Major: Chemical Engineering
Academic Institution: The City College of New York

Mentor Name: Griffin Lunn
Job Title: Senior Engineer
Org Code/Branch or Division: ESC-870
Directorate: KSC-UB-A

Abstract

Nutrient recovery has always been a problem for long distance and long-term space missions. To allow humans to man these missions, a steady source of oxygen, water, and food are necessary for survival beyond Earth's atmosphere. Plants are currently an area of interest since they are capable of providing all three resources for life sustainability. We are currently interested in nutrient recovery for future plant growth and simple aqueous leachate extractions can recover some of the nutrients. However, leaching plants also removes water-soluble organic plant wastes, which inhibits plant growth if not separated properly. To combat the issues with waste and maximize nutrient recovery, we are attempting to pre-treat the plant matter using biological, thermal, and photocatalytic methods before subjecting the solution with variable-strength acid digestion. For the biological method, the inoculums: mixed heterotrophic/nitrifying bioreactor effluent and *Trichoderma vessei* are used in an attempt to liberate more nutrients from the plant matter. For the thermal method, plants are subjected to varying temperatures at different retention times to determine nutrient recovery. Lastly, the photocatalytic method utilizes TiO₂'s oxidizing abilities under specific pHs and retention times to reduce organic wastes and improve nutrient gains. A final acid digestion serves to liberate nutrients even further in order to maximize recovery. So far, we have tested ideal acid digestion variables for practicality and performance in our experiments. We found that a low retention time of 10 minutes and a high acid concentration of 0.1 and 1 M HCl were the most effective at nutrient recovery. For space travel purposes, 0.1 M currently looks like a viable acid digestion to use since it is relatively effective and sustainable from a mass and energy balance if acid recovery can be performed on waste brines. Biological pretreatments do not look to be too effective and the thermal and photocatalytic methods may be preferred since they show a potential to recover more than 70% of the nutrients.

Introduction

Humans require a reliable source of oxygen, food, and water in order to perform the necessary metabolic processes for survival. For humans on Earth, this is not usually an issue since the planet supplies the resources we need. However, for the purposes of space exploration and off-planet research, these resources become increasingly scarce, therefore astronauts are required to transport large amounts of food and water on lengthy missions. Cost becomes an issue, as it is very expensive to supply and resupply (>\$10,000 per kilogram) so a reliable means to recycle waste products can help reallocate budget funds to increase productivity and advancement. Research is currently being done at NASA's Kennedy Space Center to find efficient methods for various recycling processes. The current focus is with plants since they are a great source of oxygen, food, and water. By recycling plant waste matter in conjunction with water treatment processes; progress can be made to solve the issue of self-sustainability for space exploration by preventing plant nutrients from ending up in the waste stream, which "opens" the loop. Currently, the idea for treating both plant and water waste involves using the photocatalytic properties of titanium dioxide to oxidize organic wastes and liberate nutrients. When exposed to

ultraviolet radiation, TiO₂ can split water by photolysis creating a hydroxyl radical. The hydroxyl radical is a good oxidizer and may be able to help break down the organic wastes in our plant and water feeds that will ideally be separable from the vital nutrients we wish to recover (N, K, Ca, Mg, P, S; among others).

So far, previous research at the Kennedy Space Center aimed to recycle nutrients from unused plant matter in order to grow new plants under a hydroponic system. By soaking plant waste in water, soluble nutrients would be readily expelled into a leachate solution. The leachate solutions, however, contained toxic organic compounds that inhibit plant growth so separation would be needed to remove these while keeping the nutrient rich substances for future hydroponic plant growth. The process for extracting nutrients from, these organics involves a biological aerobic treatment that indicated that at least half the nutrients required for plant growth were recovered. It is a step towards reducing transportation costs but efficiency can still be increased. One of the main issues with this is oxidizing waste products require a long residence time of 86 days and reducing this time is necessary to help close the loop.⁶ Further research concluded that compared to direct leachate usage, growth of plants was twice as effective. Nitrogen fixation and recovery was still a problem and the plants' denitrifying behavior was still prevalent in their tests. They managed to narrow the residence time to a range of 1 day to 8 days, while recovering a comparable percentage of nutrients.⁷

The effects of anaerobic reactors were also examined and compared to aerobic ones. Using three bioreactors, an anaerobic digester, yeast reactor, and a nitrification reactor, leachates were processed through in an attempt to recover valuable nutrients using this alternate method. The anaerobic reactor helped change the organic biomass into carbon dioxide and other readily usable nutrients. The yeast reactor attempted to sequester carbon into the biomass and flowed to the nitrification reactor to convert ammonia to nitrates. The entire process required 8 days and while nutrient gains were overall pretty good, the nitrate recovery was worse than aerobic systems.⁸ By measuring masses and carbon dioxide generation, they found that a 10 day minimum residence time is ideal for maximum production and conversion of nutrients.⁹ However 10 days is still a long time and is not efficient enough to meet the demands needed for purposes in space due to large investments in volumes and retained mass. This may indicate that using microorganisms in a biological reactor may not be the most efficient method of obtaining nutrients and a design change will be necessary to reduce the residence time and see results sooner. This research, does however, show that the process is effective at degrading both soluble and insoluble wastes, which is key to extracting nutrients. Overall, the aerobic systems were preferred over the anaerobic ones.

Further research considered the solutions for recycling wastewater to maintain sustainability on long space missions via urine recycling, nitrogenous compounds that are required for plant growths could be recovered. There were several designs to solve this issue, one of which was the urea hydrolysis bioreactor that converted urea to ammonia. The process seemed to be the most effective thus far and removed all urea and reduced TOC by 95%, and serves to

use plant waste nutrients in a cycle. The Combined Nitrification-Denitrification Bioreactor converted ammonia to nitrites and then to nitrates using the bacteria *Nitrosomonas*. The reactor process is simple and removes all the urea while maintaining high TOC removal. However, nitrate generation is low and many factors can change the resulting product into something unwanted. The nitrate-nitrification bioreactor aims to convert ammonia directly to nitrates, which would help prevent denitrification and unwanted byproducts. The usefulness of utilizing urea conversion methods serves to link it with plant nutrient recycling. While creating water through the treatment process, the wastes may be further converted to something plants can use to help close the nutrient loop. The nitrate-nitrification bioreactor may be useful in preventing a photocatalytic oxidation using TiO_2 from denitrifying and increasing the yields of nitrates instead of nitrites.¹⁰ Another research area they studied included ion exchange methods that could essentially filter out unwanted items for plant loops. Doing so could potentially circumvent the need to pretreat wastewater with toxic compounds thus improving its usefulness and safety. Combining the process with a chlor-alkali process (brine electrolysis) would then degrade toxic brines. The ion exchange methods were very effective with the respective chelating resins and removed nearly 100% of the targeted magnesium and calcium. Sulfate and phosphate removals were not as efficient and selective but the process as a whole can be used for specific needs. By closing the water loop, the plant loop could be closed as well, so more research needs to be done to help extract the wanted compounds from the unwanted.¹¹

There have been attempts to utilize titanium dioxide as a possible solution for wastewater treatment. Wastewater contains a large amount of ammonia and ammonium so removing that is vital for safe drinking. Under natural conditions, nitrification would normally do this via the nitrogen cycle but it is slow and unstable. In the confinements of outer space, natural nitrification may be impractical so the efficiency of titanium dioxide was researched. To test the efficiency, a cylindrical container acted as a reactor, housing a 450W UV lamp in the center to induce the photocatalytic properties of TiO_2 . Surrounding the UV lamp was a layer of water, constantly pumped in to minimize the lamp's heating effects and maintaining a temperature of 25-31 degrees Celsius. Surrounding the water layer would be the reactants, in this case, a slurry of TiO_2 and ammonia/ammonium. This batch reactor was to be continuously stirred via magnetic stirrer. In this experiment, TiO_2 concentration and pH were variables and varied amounts of NaOH and H_2SO_4 were added to the slurry to manipulate pH. As TiO_2 concentration increased from 0.1 g/L to 3 g/L, the conversion of ammonia to nitrite and nitrate increased. At higher TiO_2 concentrations, the reaction favored the formation of nitrates rather than nitrites. This experiment was performed at pH 10.2, a 6 hour residence time, and ammonia concentration of .0001 M. The second factor tested was pH, holding TiO_2 concentration to be a constant 3 g/L and everything else the same. It was found that low pH favored nitrates and high pH favored nitrites.¹ Other research showed that a pH of 3-4 was ideal for removing other organic wastes thus reinforcing this theory. There also seemed to be a limit to the concentration of TiO_2 since high concentrations could decrease UV penetration due to the opacity.²

For our purposes, this research is a good start to determining how plant waste nutrients can be recycled. Plant wastes contain ammonia, which can be converted into nitrates that act as a more ideal fertilizing agent. By oxidizing ammonia, we can effectively push for the generation of nitrates to be recycled into new plants instead of being “burnt off” by competing methods. This research shows that the oxidation process depends greatly on TiO_2 concentration and pH so these should be one of the few variables that we will test on plant waste oxidation. Since plant wastes will be incorporated into the slurry, other organic wastes such as cellulose will be present and we will need to test whether or not it can be broken down via oxidation. Nitrates will form from nitrites through the addition of water or oxygen so this might increase the nitrate yield further.

There have also been attempts to use TiO_2 to remove plant toxins. Plants produce these phytotoxins as organic wastes and can negatively affect plant growth. The photocatalytic properties of TiO_2 were used to oxidize the organic wastes in hydroponic systems so a recycling of nutrients could occur without poisoning the next generation of plants. Plant samples were dried and crushed for testing under UV light in a suspension of TiO_2 . The results of the experiment showed that UV light coupled with TiO_2 caused a 90% decrease in TOC, yielding success in the oxidation of organic wastes. Without UV light, TOC only decreased by 30%. Phytotoxins were also believed to be oxidized to near completion because asparagus plant growth was significantly higher when the previous generation’s plant matter was treated with TiO_2 and UV light.³ This experiment done by Sunada’s research team seems to mirror our goals. The results he obtained looks to be useful in recycling a nutrient-rich broth back into successive generations of plants with minimal risk to growth. It looks to have a multitude of uses; in addition to oxidizing wastes, TiO_2 is hypothesized to also kill harmful bacteria that may also be the cause of growth inhibition. The separation of nutrients and wastes also look to be relatively simple and is feasible in space since the materials needed are very accessible and can provide the solution to a closed nutrient loop.

The degradation of cellulose is another issue that arises when attempting to break down plant organics. Using photocatalytic oxidation, cellulose degraded into 5-HMF (dehydrated sugar). It was found that TiO_2 was mainly responsible for the degradation and with a residence time of 2 hours, the conversion of cellulose (100g/L) to 5-HMF (3.87 g/L) seems to be relatively ineffective. As a result, the oxidative effects on cellulose are questionable for our purposes. For our purposes, the degradation of cellulose is a difficult issue to handle and it does not look like TiO_2 photocatalytic treatments would do much in that regard. Cellulose may not be a large issue since it does not have a positive or negative effect on future plant growth. It may be possible to just leave the cellulose if separation becomes too inefficient.⁴ However, even slight breakdown of the cellulose matrix can recover recalcitrant nutrients.

TiO_2 has also been used to treat paper factory wastes. In waste paper, starches and lignins are considered abundant toxins and do not contribute to the health of the environment so degrading them to something harmless is ideal. By measuring TOC, it can be determined whether or not the oxidative treatments on paper effluents are effective. Using a batch reactor, an

aqueous solution with the paper waste and catalyst were added and mixed for 60 minutes with varying pH tests. It was found that pH of 11 was the most effective in TOC and toxicity degradation with an 80% and 94% decrease respectively. Hydrogen peroxide addition was found to help decrease TOC levels but made toxicity removal even worse. As a result, we should probably test hydrogen peroxide's effects since it has the potential to help increase the efficiency of our reactions. The issue remains that hydrogen peroxide is not readily accessible in the confinements of outer space so this may not be a feasible alternative to water. Otherwise, this paper reinforces the idea that TiO₂ oxidation is an efficient process in degrading organic wastes into something usable as fertilizers. The most optimal pH will need to be determined since different pH ranges seem to be best at handling certain organic wastes.⁵

The use of photocatalytic oxidation seems to be a promising solution to removing unnecessary organic waste in a plant's nutrient broth. Previous research on the topic gives us a decent picture of the effectiveness of this technique and may help recover more nutrients for recycling. Testing will need to be done to determine whether or not this is a feasible solution for self-sustainability in space travel.

Materials and Methods

*Determining an Acid Digestion**

The first step of this experiment was to optimize an acid digestion treatment. By obtaining the best degradation by acid, we could maximize our nutrient gain and reduce the organic waste mass. In order to do so, 9 treatment factorials of final acid concentrations (0 M, 0.01 M, 0.1 M HCl) and residence times (10 minutes, 2 hours, 24 hours) acted as the variables for manipulation. In a VOA vial, 1 gram of Wiley Mill (Model 3383-L60, Thomas Scientific) ground pepper plant matter was mixed with 9 mL of nanopure water (18 MΩ). The vial is considered to have a volume of 9 mL and the addition of 1 mL of 0, 0.1, and 1 M HCl would dilute the mixture to the final concentrations needed. The 1 mL of acid would also serve to rinse any large plant matter particles that lingered on the homogenizer. A small magnetic stir bar was placed into each vial and the resulting vial was transferred to the 2mag Mix 15 ECO stir plate at 1200 rpm.

The resulting sample would be tested via ICP (iCap 6500, Thermo Scientific) against a 100% acid digestion to determine a baseline for a complete maximum reading of the amount of nutrients in the sample. To obtain a baseline, the dried plant matter would need to be completely liquefied using acid for ICP testing. 0.5 grams of the dried plant matter would be added to 70% nitric acid at 95C for 2 hours. Once the solution is cooled, 2.5 mL of 30% hydrogen peroxide was added for the reaction to occur. Afterwards, the solution would be heated at 95C for 50 minutes, cooled, and diluted to 50 mL with nanopure water. The resulting solution would be quenched through a 0.45 um syringe filter before testing via ICP.

	0 M HCl	.1 M HCl	1 M HCl
10 min	Ion Recovery %	Ion Recovery %	Ion Recovery %
2 hours	Ion Recovery %	Ion Recovery %	Ion Recovery %
24 hours	Ion Recovery %	Ion Recovery %	Ion Recovery %

Fig 1. 3x3 factorial to test for optimal acid digestion to use in the treatment process in order to reduce the number of trials for the whole experiment

Quenching the Sample

After allowing the vials to stir for the allotted time, the quenching process could begin. The samples were promptly removed and transferred to a 15 mL centrifuge tube. Five milliliters of nanopure water were used to rinse the vial and transfer as much of the solution as possible to the centrifuge tube. The stir bar was retrieved as well in this step. Afterwards, the sample in the centrifuge tube was centrifuged at 4000 rpm for 10 minutes (Allegra X-14R Centrifuge, Beckman Coulter), separating the sample into two layers: an organic solid waste pellet layer and an aqueous leachate layer. The resulting supernatant was decanted into a 50 mL volumetric flask and then diluted to 50 mL using GenPure water (18.2 M Ω). Following that, the supernatant in the volumetric flask was filtered using a 22 μ m syringe and filter attachment into a 50 mL centrifuge tube. The resulting sample was analyzed using ICP to determine the elemental recovery percentage. We determined the optimal acid treatment using the results from the ICP and the acid digestion process would utilize those variables during treatment. A control would use a 0 M acid digestion for comparison during the treatment step. This optimization process would be done once to narrow down the acid digestion factorials for use during the pretreatment and treatment stages.

Pretreatment and Treatment

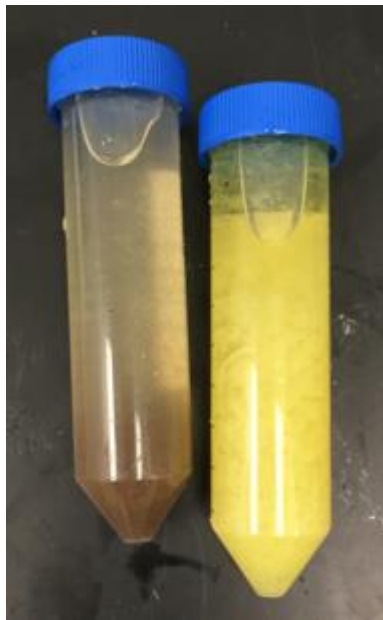
When the acid digestion factorials were optimized, the actual testing could begin. Our goal was to subject the samples to three different pretreatment types: biological, thermal, and photocatalytic before treating them with the appropriate acid digestion types that were previously downselected.

The biological test used three different inoculums: nanopure water (control), mixed bioreactor effluent (containing heterotrophic and nitrifying communities), and *Trichoderma* (wood fungus for cellulose degradation) in an attempt to help liberate more nutrients from the plant matter. In a VOA vial, 1 gram of ground plant matter was homogenized with 8 mL of nanopure water. 1 mL of the chosen inoculum was added immediately after. Afterwards, the treatment process would subject the samples to three retention times (6, 24, 168 hours) for a total of 9 factorial combinations. The acid digestion chosen prior was used after to help further degrade the plant matter. Lastly, the quenching process above was used to filter out the leachate

for analysis. While the samples underwent mixing, the decision of capping or uncapping determined whether the samples underwent anaerobic and aerobic treatments respectively. This distinguishing of samples would add another 9 to our factorial

	Sterilized Water	Mixed Bioreactor Eff.	Trichoderma
6 hours	% Ion Recovery	% Ion Recovery	% Ion Recovery
24 hours	% Ion Recovery	% Ion Recovery	% Ion Recovery
168 hours	% Ion Recovery	% Ion Recovery	% Ion Recovery

Fig 2. A 3x3 factorial depicting the 9 biological tests performed to determine ion recovery effectiveness



Picture 1: Centrifuge tubes containing the mixed

For the thermal test, there was no preprocessing. A 1-gram sample of ground plant matter was placed into the VOA vial and transferred to a heated stir plate or Muffle furnace (Carbolite, Barloworld Scientific) for the treatment process. The variables include three temperatures (90C, 180C, 360C) with three different retention times (1, 2, 24 hours). The resulting sample would be analyzed.

	90C	180C	360C
1 hour	% Ion Recovery	% Ion Recovery	% Ion Recovery
2 hours	% Ion Recovery	% Ion Recovery	% Ion Recovery

24 hours	% Ion Recovery	% Ion Recovery	% Ion Recovery
----------	----------------	----------------	----------------

Fig 3. A 3x3 factorial depicting the thermal runs performed during the plant leachate experiment.

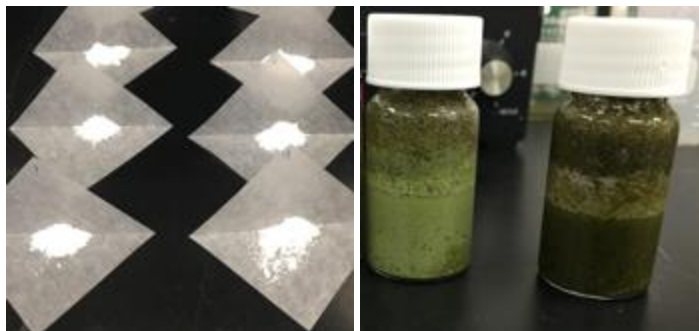


Picture 2: Resulting plant masses after thermal

The photocatalytic test used TiO_2 as a catalyst for organic waste oxidation. For the pretreatment, a dilute 1% stock solution (100 mg) of TiO_2 was combined with 9 mL of nanopure water and a 1 gram ground plant sample in a VOA vial. The resulting solution was homogenized before subjecting it to the treatment, a factorial combination of three retention times (.5, 2, 8 hours) and three pHs (4, 7, 10). A 10th control test was also tested with no TiO_2 and no deliberate pH manipulation for comparison. Appropriate acid treatment was then be added and the mixture was be quenched for analysis via the ICP.

	pH 4	pH 7	pH 10
.5 hours	Ion Recovery %	Ion Recovery %	Ion Recovery %
2 hours	Ion Recovery %	Ion Recovery %	Ion Recovery %
8 hours	Ion Recovery %	Ion Recovery %	Ion Recovery %

Fig 4. A 3x3 factorial depicting the photocatalytic runs performed to determine the ion recoveries of this pretreatment.



Picture 3: 100 mg sets of TiO_2

Picture 4:

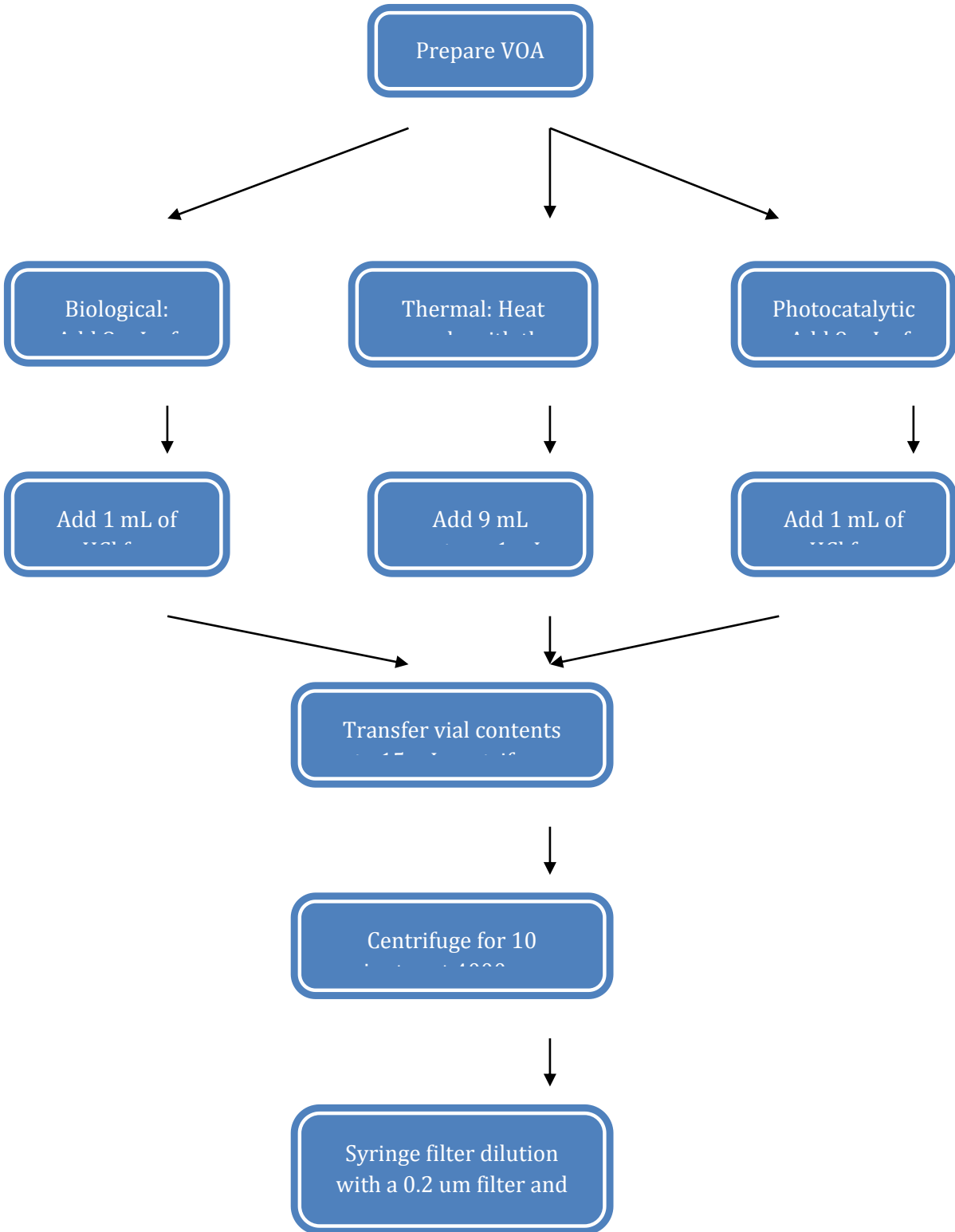


Fig 5. The flowchart summarizes the procedural steps for the plant leachate experiment. The steps branch out to three pretreatment steps before undergoing an acid digestion. The samples all receive the same quenching process.

Results

Through our experimentation, we found that an acid digestion of 1 M HCl increases the nutrient recovery by 10-20% for most elements when compared against a 0 M HCl digestion. Since the percent increase from 0 M to 1 M was not too significant, it may be more optimal to use 0.1 M HCl for space travel where concentrated acid may be too difficult or unsafe to procure. However, 1 M HCl is responsible for extracting a significant portion of calcium, a much-needed nutrient to maintain plant health. With our acid digestion tests, we managed to recover around 60-70% of the nutrients from organic waste.

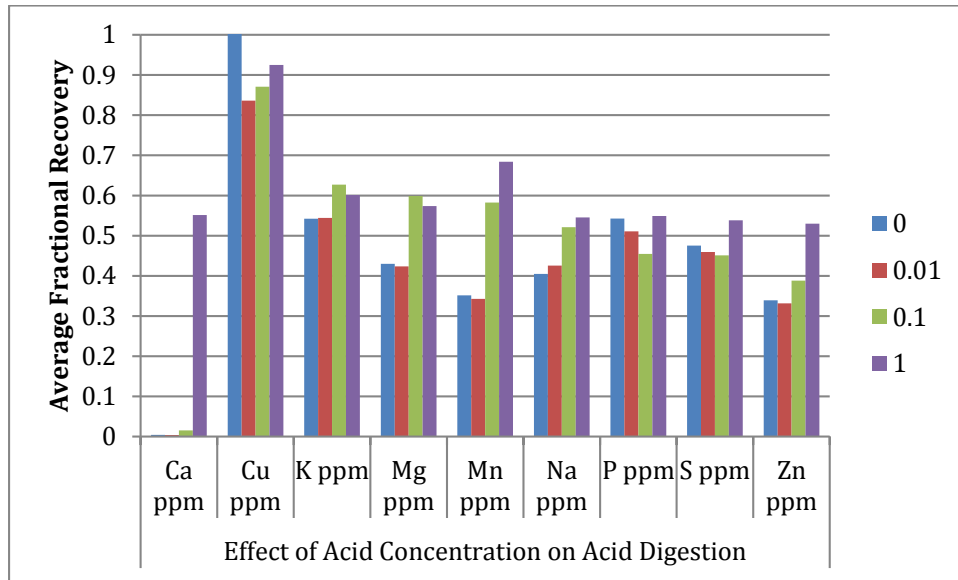


Table 1: Displays average fractional recovery of the different ions for the acid digestion organized by the retention times. Legend units are in hours.

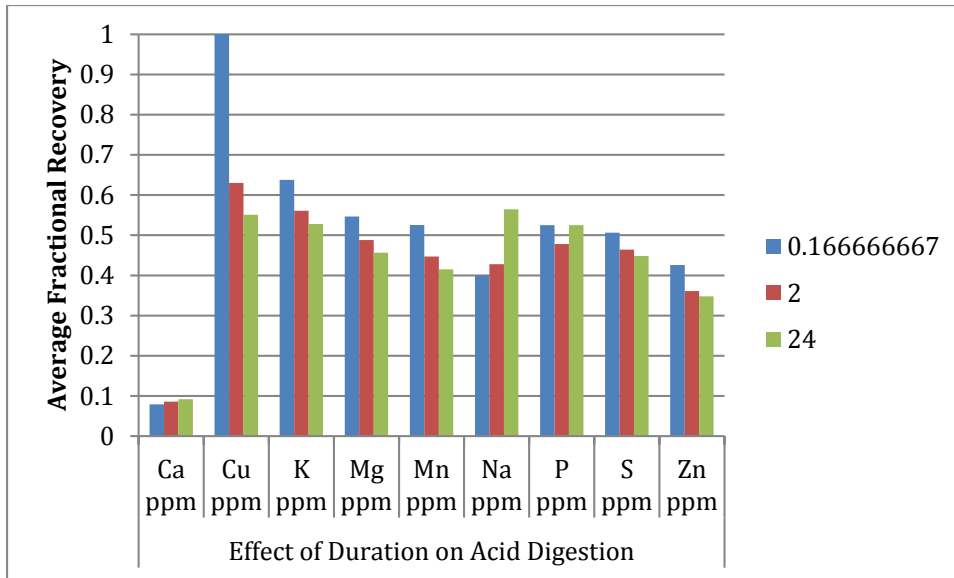


Table 2: Displays the average fractional recovery of the acid digestion organized by HCl concentration. Legend units are in molarity (M).

Our tests on an anaerobic biological were overall ineffective. For the anaerobic biological pretreatments, we found that the different inoculum types had similar fractional recoveries for nutrients. As a result, the presence of oxygen will probably be a factor in inoculum performance. Biological duration looks to be a factor in nutrient recovery since longer retention times have a slight increase in nutritional recovery. However, when comparing a 6 hour residence time with a 1 week residence time, there is only a 10% recovery increase, which may not be worth such a long duration. The acid digestion step greatly increases nutrient recovery with as much as a 20% increase overall in performance. Phosphorus was well over the 100% recovery for all runs indicating a fault in the ICP machine. Other nutrients look to be relatively accurate but look to be hitting a ceiling near 70%

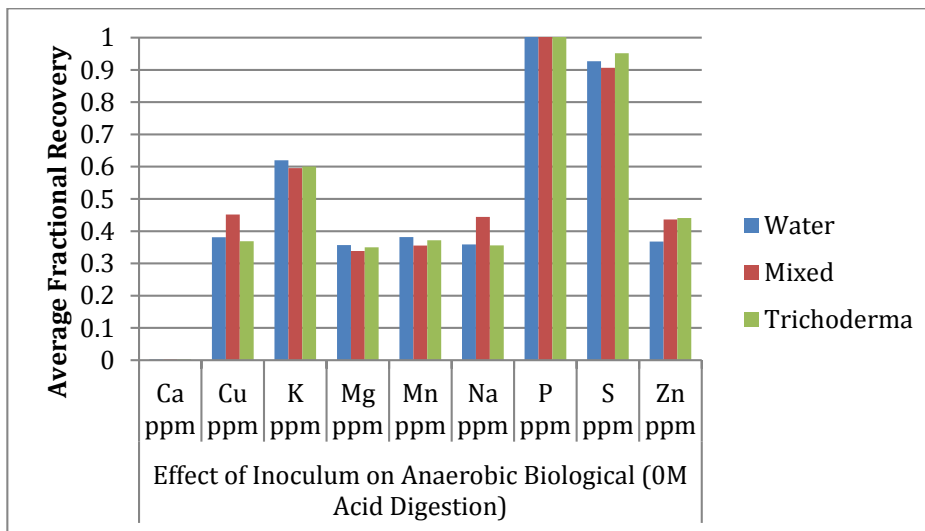


Table 3: Displays nutrient gains with varying biological inoculums with a 0 M acid digestion. Inoculums do not have an effect on nutrient gains in an anaerobic environment.

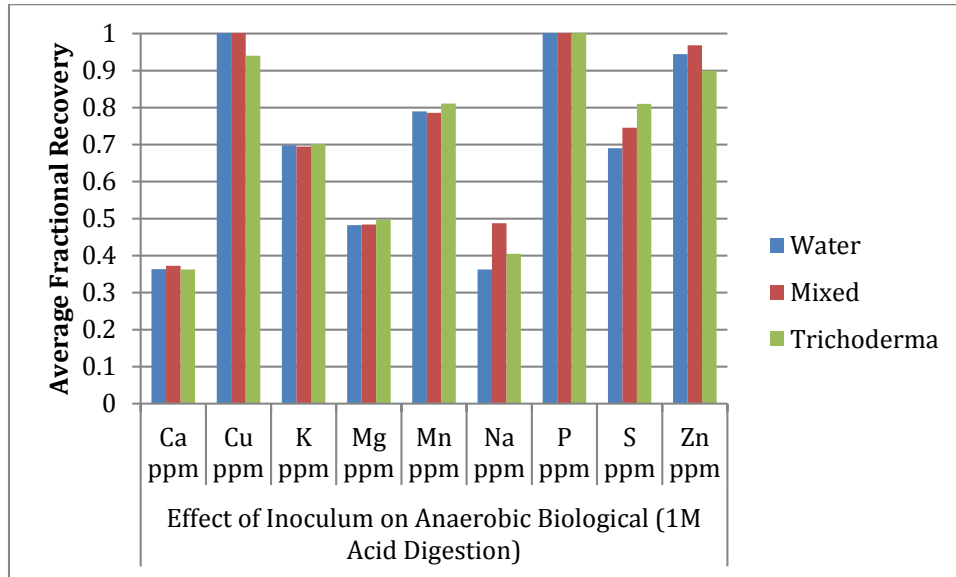


Table 4: Displays nutrient gains with varying biological inoculums with a 1 M acid digestion. Reinforces the fact that inoculums do not affect nutritional gains in an anaerobic environment.

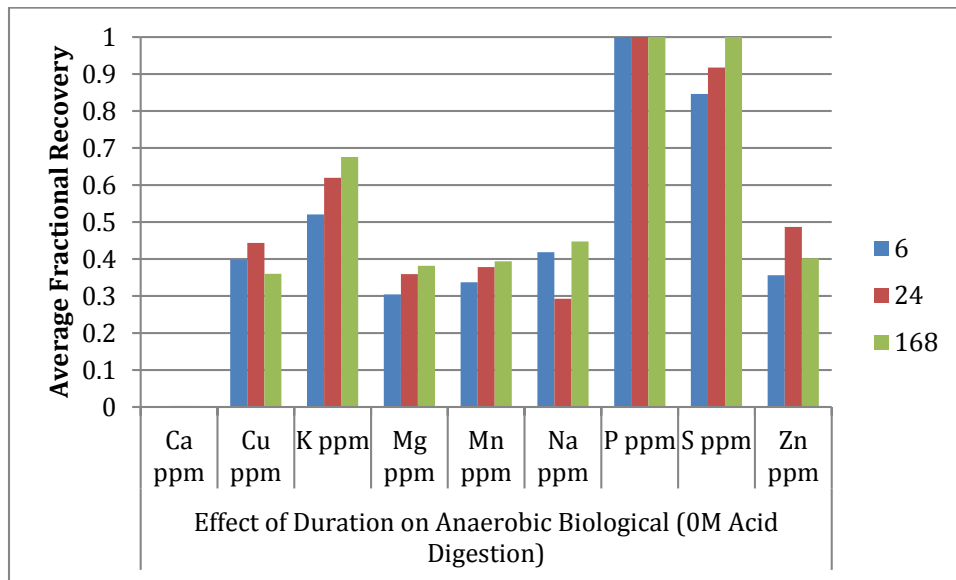


Table 5: Displays nutrient gains based on residence times. One week samples did slightly better overall but not a far reaching difference from 6 hours. Legend units are in hours.

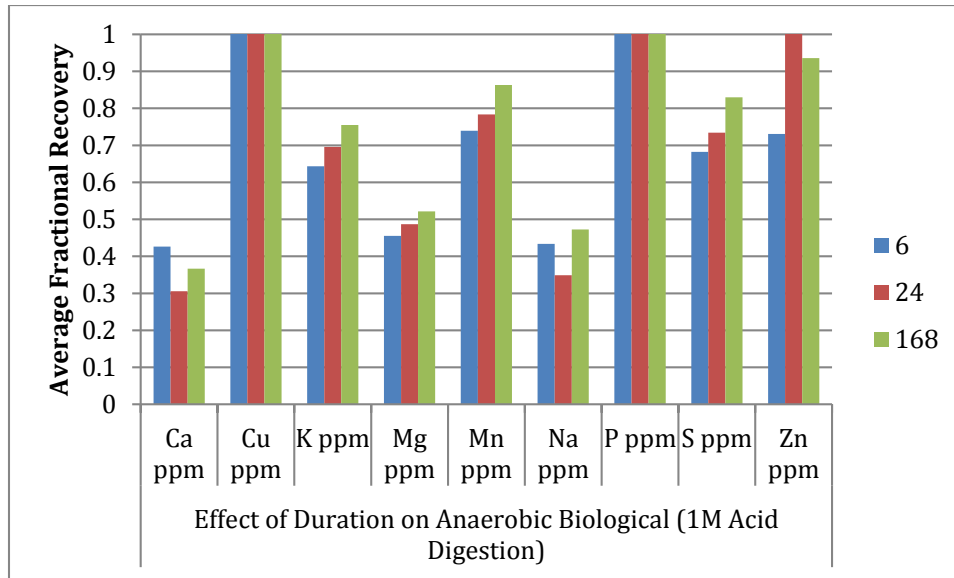


Table 6: Displays nutrient gain based on residence time with a 1 M HCl acid digestion. Recovery greatly improved overall. Legend units are in hours.

The thermal pretreatments looked to work decently well. Generally, as duration increased, more nutrients were liberated and a higher temperature did not make too much of a significant change compared to lower temperatures. There was on average, a 7% increase in nutrient recovery when comparing 90C to 360C. In the confinements of space, it is optimal to conserve energy and preserve safety with lower temperatures so a lower temperature may be more practical. The pellet sizes dramatically decreased as temperature increased which shows promise in the removal of cellulose and other unwanted waste products but does not contribute to an overall nutrient gain. It is suspected that the high temperature heating may have carried some of the ions out of the crucible, thus a procedural change would be needed. Acid digestion showed yet another 20% average increase in the nutrient recovery. Certain ions such as potassium and manganese managed to have an 80-90% gain. With longer heating and an acid digestion, 60% of calcium was liberated as well, a significant increase from the near 0 recovery previously.

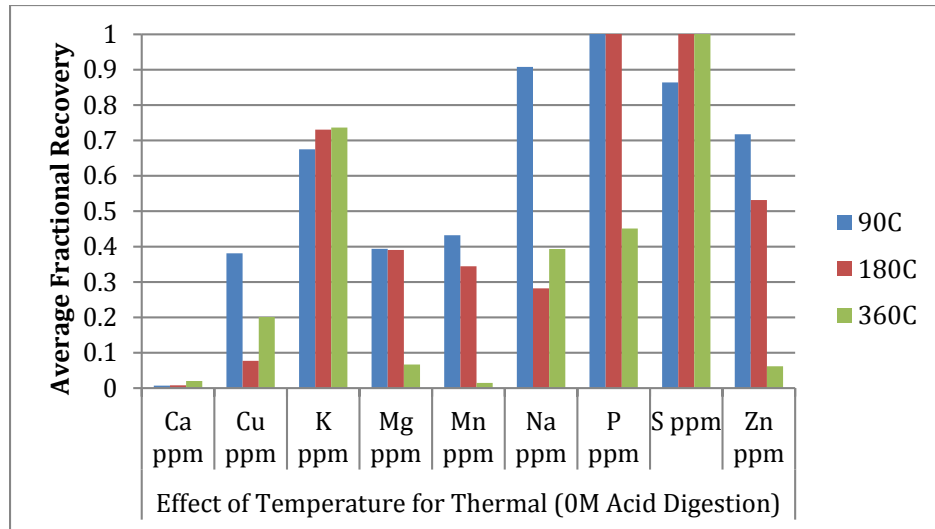


Table 7: Displays nutrient recoveries with respect to temperatures in a 0M acid digestion. Higher temperatures were not necessarily favored to recover nutrients.

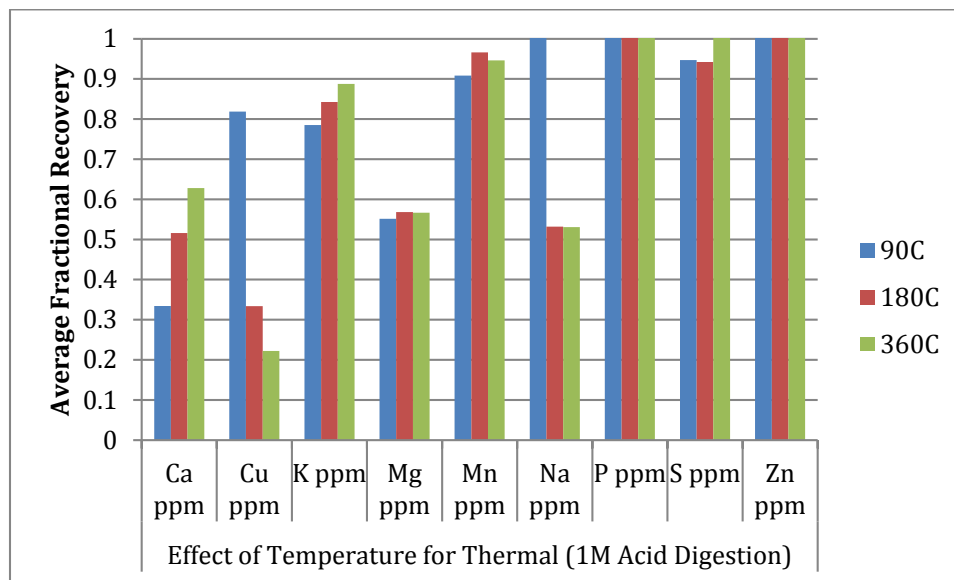


Table 8: Displays nutrient recoveries in a 1M acid digestion. Recoveries were drastically improved with the help of an acid digestion.

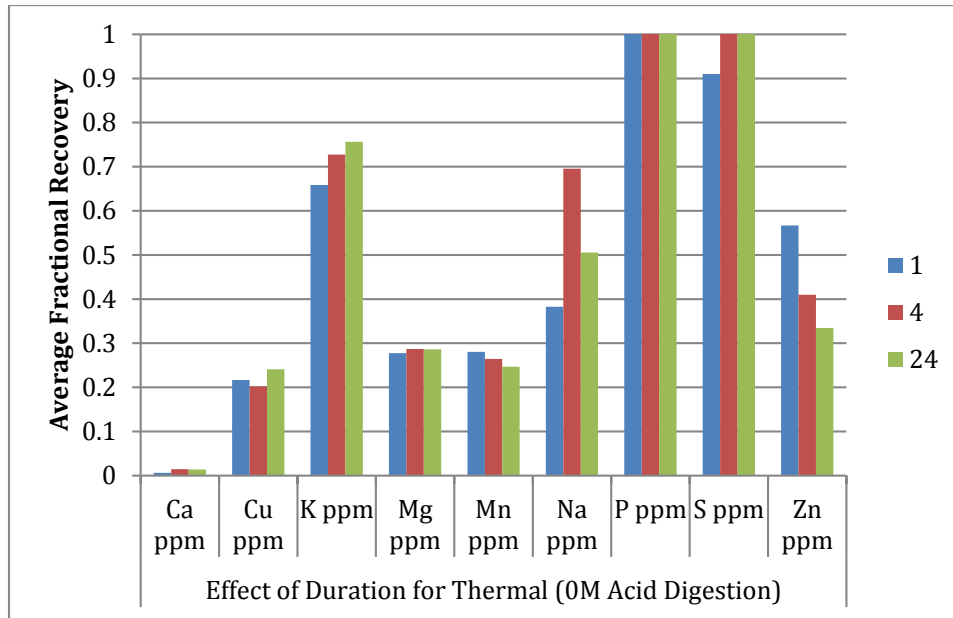


Table 9: Displays duration effects for nutrient recovery. There was not too much of a difference between 1 hour and 24 hour treatments. Legend units are in hours.

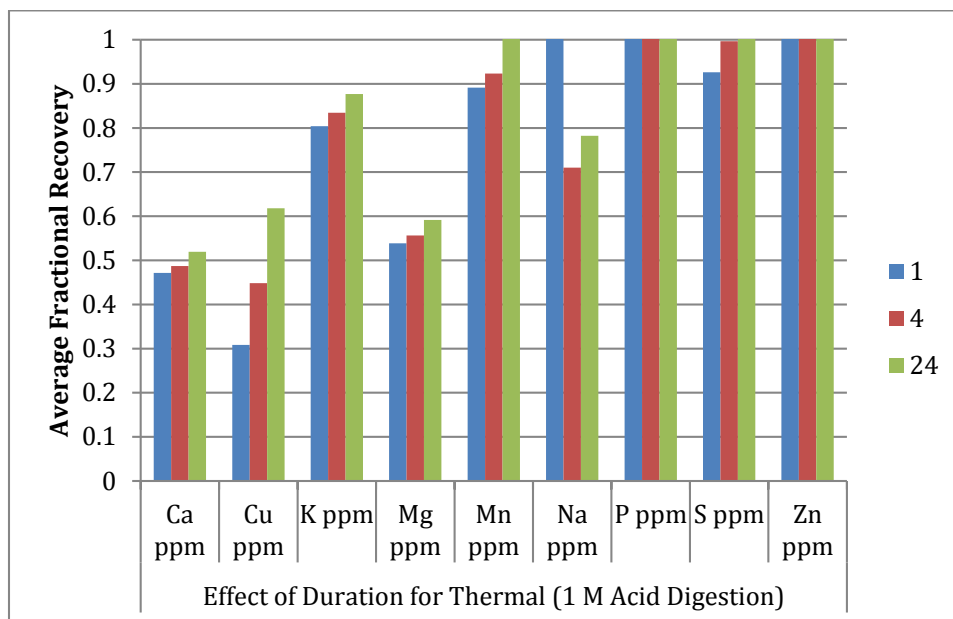


Table 10: Displays duration effects for nutrient recovery under 1 M acid digestion. Recoveries were all drastically improved.

The photocatalytic runs show promise in the liberation of nutrients. Even without an acid digestion, the recovery rates were hitting the 70% ceiling that was experienced with the anaerobic biological tests and the 1 M acid digestion. Magnesium and manganese were the exception and received only a 40% recovery. Results for the 1 M acid digestion will be needed to determine if the photocatalytic treatments can overcome the 70% ceiling, which are predicted to do. Lower pHs are favored in the nutrient recovery for certain ions, which is consistent with past experimentation. Duration does not look to make too much of a difference in nutrient recovery. A control without titanium dioxide was used to compare the effectiveness of using a photocatalyst. With photocatalyst, there is a 10% increase on certain ions when compared to using no photocatalyst. Zinc has a massive increase with photocatalyst and potassium looks to have a 10% increase when comparing the control to pH 4. Since the use of photocatalyst does not seem to make large significant changes, it may be viable to just use UV light to liberate the nutrients. The issues with the ICP on phosphorus are still present.

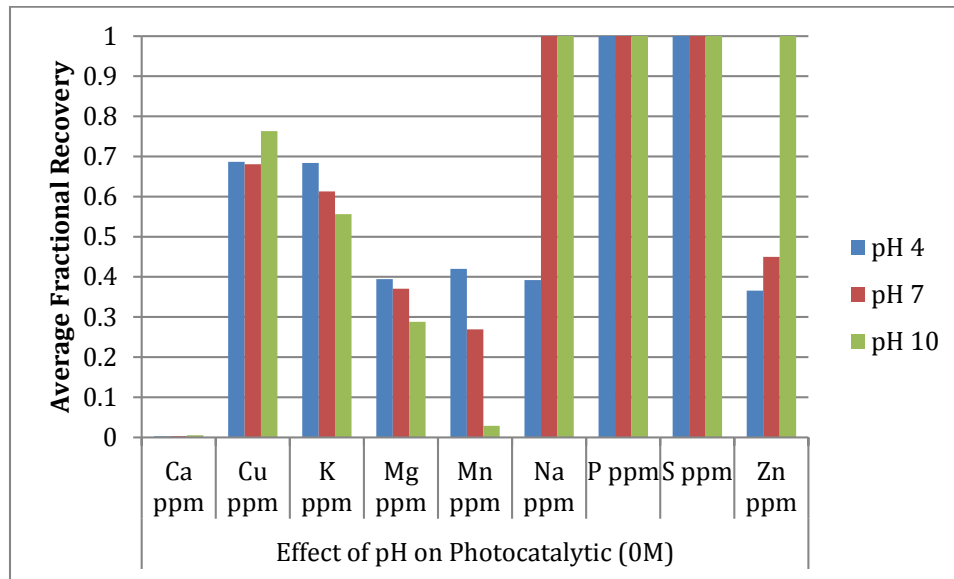


Table 11: Displays recovery percentages based on pH on the photocatalytic tests. Lower pHs are favored for slightly better recovery rates.

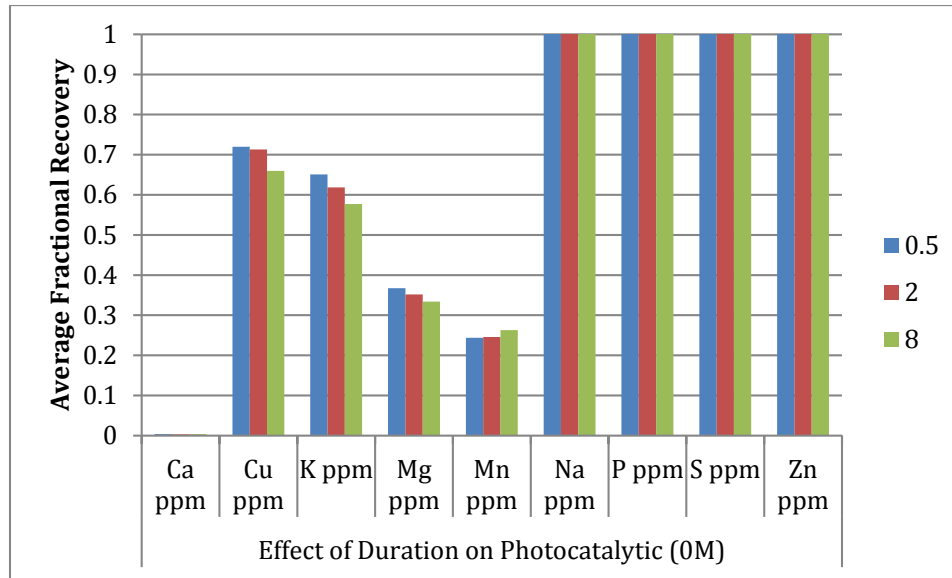


Table 11: Displays recovery percentages based on residence times on photocatalytic tests. Shorter time periods are slightly better but overall do not make too much of a difference.

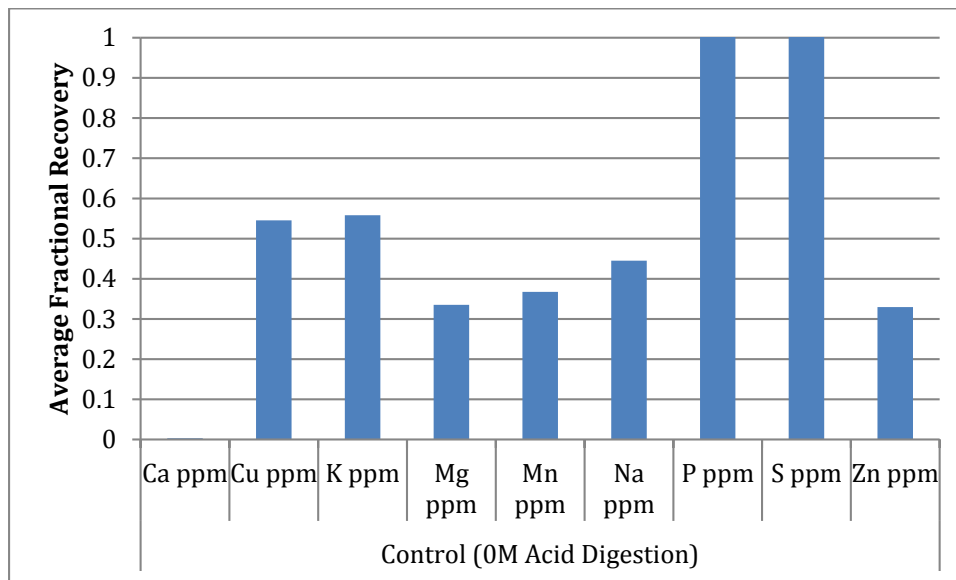


Table 12: Displays the nutrient gains with a sample with just UV light exposure, no TiO₂ photocatalyst, natural pH (~5.20) for 8 hours.

When compared via pretreatments, thermal treatments look to be consistently better than the rest. Photocatalytic tests are comparable to the thermal treatments and do slightly better than with just an acid digestion. Data has not been obtained for aerobic biological so the information for that is misleading. Anaerobic biological tests do not look to be as effective as the rest. The data reiterates that an acid digestion increases nutrient recovery rates considerably.

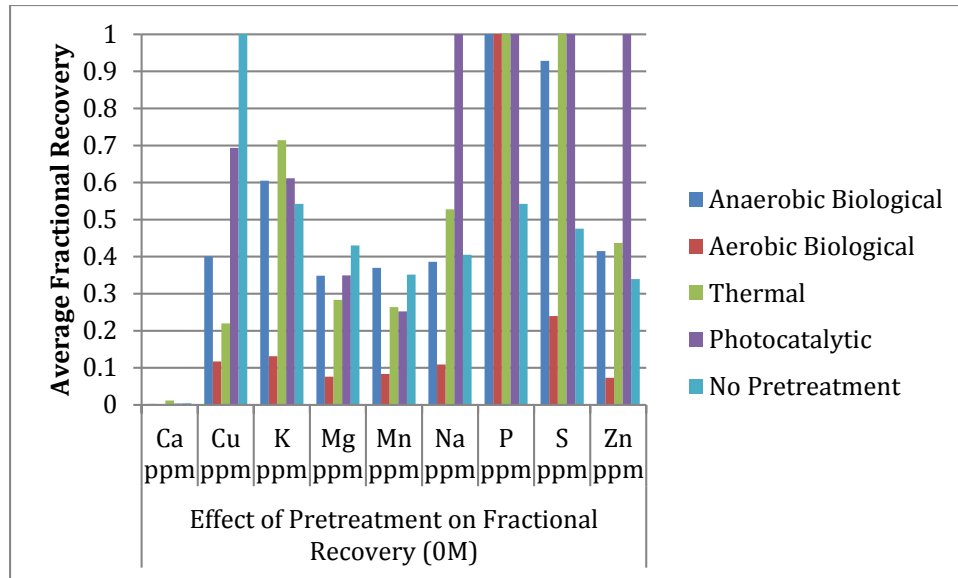


Table 13: Compares average fractional recoveries for the different pretreatments with a 0M acid digestion.

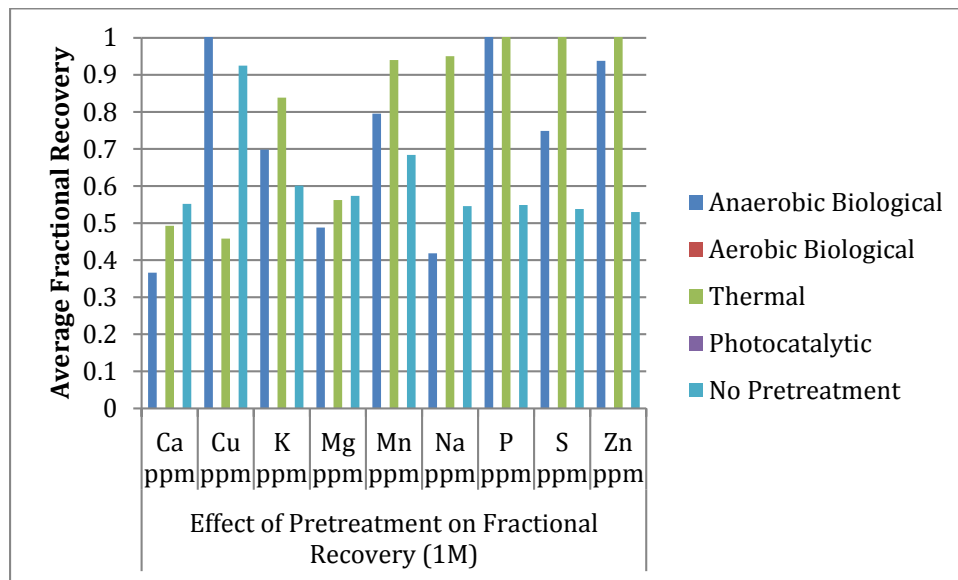


Table 14: Compares average fractional recoveries for the different pretreatments with a 1M acid digestion

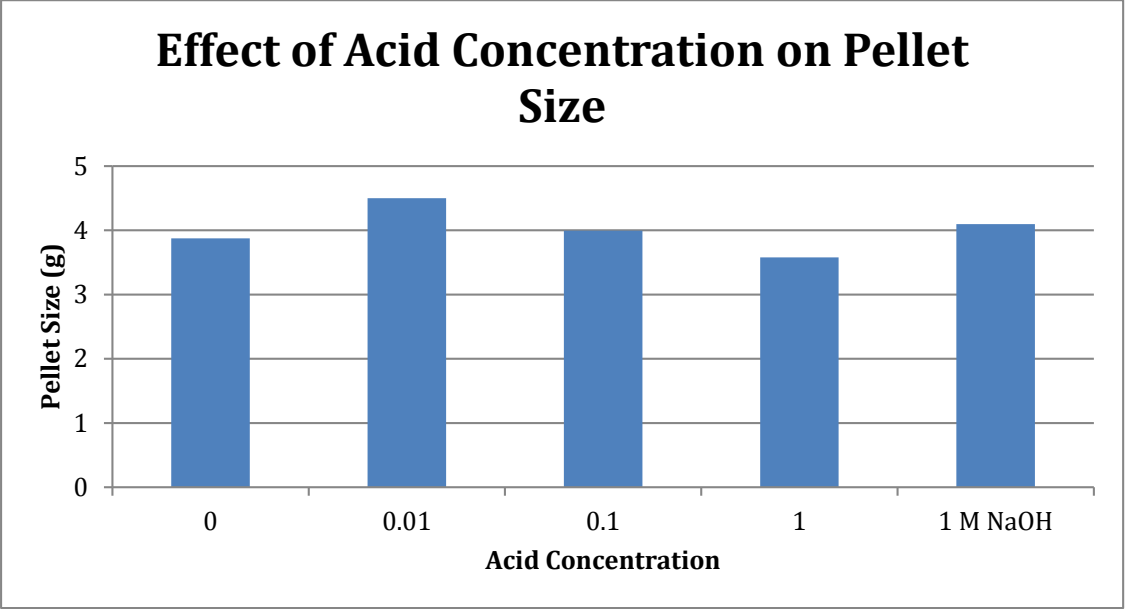
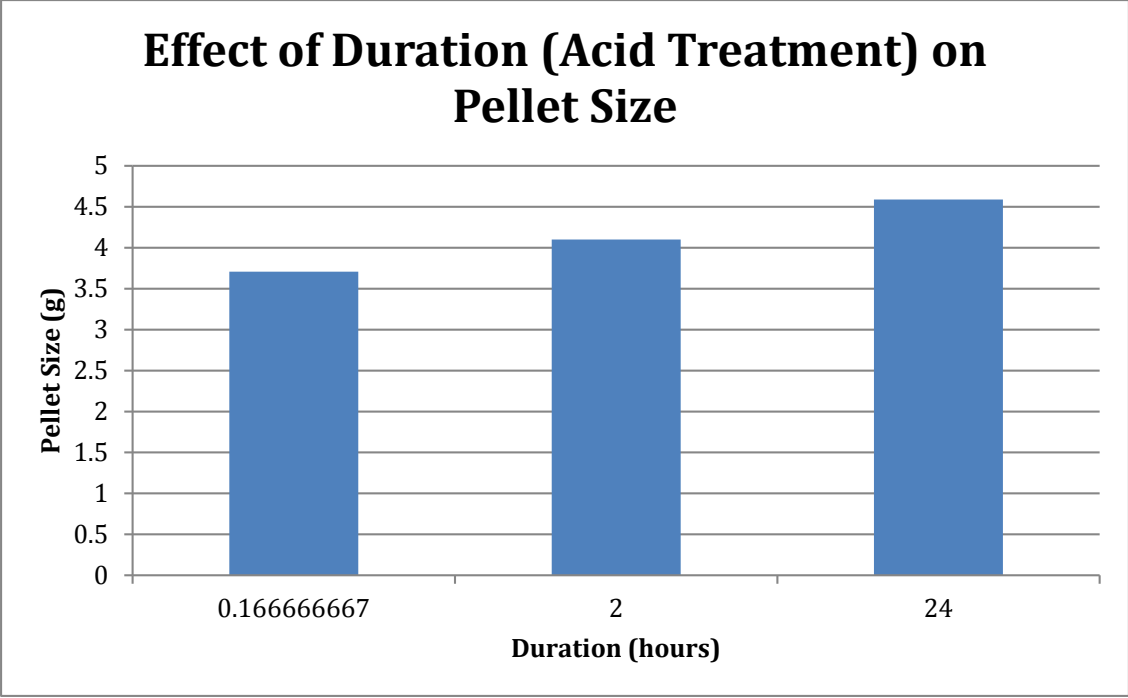


Table 15, 16: Displays acid concentration and durations of the acid digestions on pellet size. Longer durations result in larger pellet masses and larger acid concentrations generally decrease the acid size.

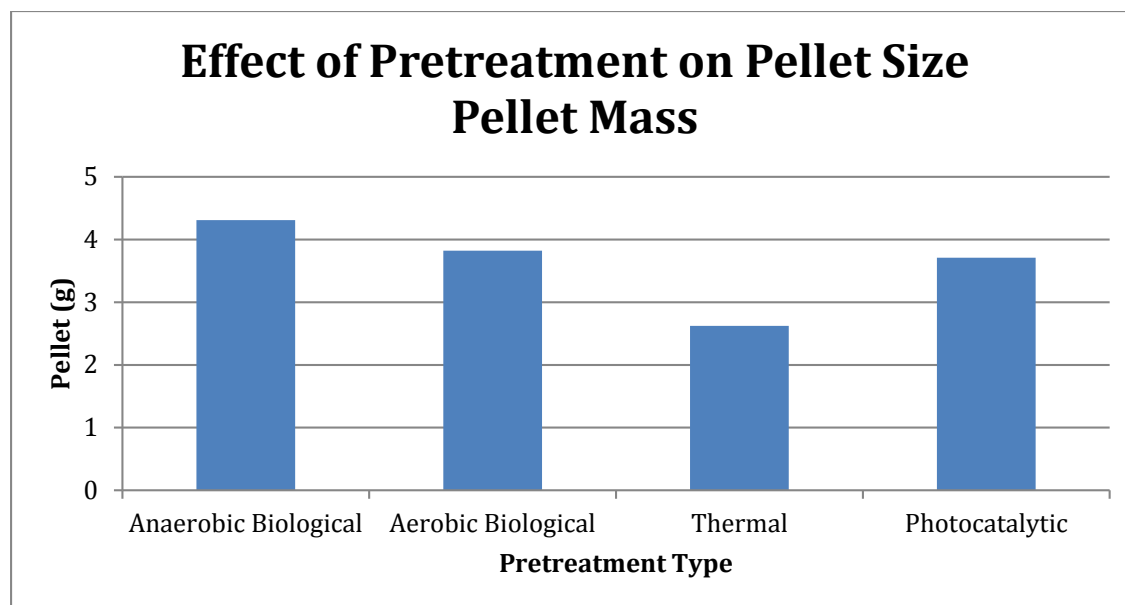


Table 17: Displays average pellet sizes as a result of pretreatment tests.

Discussion/Recommendations/Conclusion

A 1M acid digestion has a significant improvement over a simple water leach, with at least a 20% increase in nutrient recovery. However, to obtain a 1M final acid concentration, a 10M HCl acid stock was used and diluted with the samples. 10M HCl is difficult to synthesize, recover, and handle in the confinements of space and a 0.1 M final acid digestion may be preferable for safety and efficiency. However, a crucial nutrient, calcium only seems to be liberated when the final acid digestion is at 1M so alternate means to recover calcium will be needed if a 0.1M acid digestion is used. A pure 1M acid digestion is inhibited by a ceiling experienced at 60% recovery for all nutrients except copper, regardless of residence time or acid strength.

This observation was also seen with the anaerobic biological pretreatment, which experienced caps at around 70-75% recovery for calcium, potassium, magnesium, and sulfur even with a 1M acid digestion. Thermal treatments with a 1M acid digestion did not experience as much of a cap with potassium, manganese, phosphorus, sulfur, and zinc exceeding the previous 70% ceiling. However, magnesium and calcium still suffer low recovery rates. The majority of the photocatalytic treatments also experience a 70% recovery ceiling with the exception of sodium, phosphorus, sulfur, and zinc at a 0M acid digestion. This 70% ceiling may be caused by solubility problems within the samples. The supernatant may be saturated with ions and no more nutrients can leach out of the pellet due to the pellet's size. It may be necessary to perform multiple leach steps in order to maximize the recovery of any lingering ions within the pellet. A complete acid digestion of the pellet using nitric acid may be necessary to test whether there are any more nutrients trapped. Doing so will also find the full mass balance, which will help determine if there are procedure flaws. If solubility is indeed the case, further testing may

require using less plant mass for a larger dilution. With that, the pellet may be able to leach out more nutrients at a higher saturation point. Performing a series of pretreatments may also be helpful to maximize nutrient recovery. A biological followed by a photocatalytic, then a thermal pretreatment may help maximize recovery rates and reduce the pellet size.

Pretreatment methods could also be improved in order to maximize our nutrient recovery. Residence time does not look to be a large factor in all the pretreatments, so minimizing residence time can make the process simpler and knock off factorials that we need to test. It was also observed that longer retention times had larger pellet sizes, so pellet swelling and nutrient reabsorption may become an issue. The aerobic biological pretreatment methods should be improved since oxygenating the vials via cap removal solidified and dried out the mixture. The drying effect caused the stirring to stop and the recoveries were not optimal. An oxygen feed with vial caps on may be necessary for the aerobic biological pretreatments to prevent the drying effect and maintain proper distribution with stirring. A larger stir bar may help in this instance as well. Although residence times did not have an effect on the other pretreatments, it might be necessary to extend the duration of the biological samples for the inoculums to take effect. One week may not be enough for *Trichoderma* to fully break down the organic matter.

The thermal methods could also be improved on. At 360C, pellet sizes decreased dramatically and went as low as 0.5 grams in mass compared to the average 3 grams from the other treatments. However, the nutrient recoveries of the 360C thermal methods were not comparably better than the other thermal treatments, which had much larger pellet sizes. This disparity may be caused by ions being carried out of the crucible during the heating process. A cover on the crucible may help prevent this possibility and tests would need to be done to validate the claim.

Photocatalytic samples were observably opaque. The plant matter and water mixture were a densely dark green color and the addition of titanium dioxide only bleached the color to be a lighter green. The vials were nearly an inch in diameter and the penetrative power of the ultraviolet light may have been too weak to fully catalyze the TiO₂. A narrower vial or a stronger UV lamp may be necessary to optimize the exposure of the sample. Potentially, more TiO₂ could be used to perhaps increase the oxidation capabilities. A more dilute sample using less plant matter may be more transparent and allow more light through for the oxidation to occur. Similar to the aerobic biological methods, an oxygen feed may be necessary to improve performance.

Through our testing, it is observed that pretreatments help increase nutritional gain if it is used in conjunction with an acid digestion. Therefore, pretreatment methods will need to be studied and improved in order to maximize and achieve a 90-95% recovery rate for all nutrients. A simple acid digestion even at 1M is not practical enough to retain the nutrients needed for long-term space travel. Thermal and photocatalytic methods look to be the most promising of the pretreatments and focus should be placed on those pretreatments.

Acknowledgements

I would like to thank Griffin Lunn, Raymond Wheeler, and Gary Stutte for their assistance and guidance with the plant leachate study. The knowledge, resources, and mentorship have been an invaluable contribution to this project being possible. Extended thanks to Griffin Lunn for editing this report, guidance in the laboratory, and assistance in planning the experiment details. I would also like to thank LaShelle Spencer for laboratory equipment assistance and data analysis via the ICP and Janelle Coutts for assistance with the titanium dioxide handling during the photocatalytic experiment.

References

1. Zhu, Xingdong, Sunny R. Castleberry, Mark A. Nanny, and Elizabeth C. Butler. "Effects of PH and Catalyst Concentration on Photocatalytic Oxidation of Aqueous Ammonia and Nitrite in Titanium Dioxide Suspensions." *Environmental Science & Technology Environ. Sci. Technol.* 39.10 (2005): 3784-791. Web.
2. Zou, Shuai-Wen, Choon-Wai How, and J. Paul Chen. "Photocatalytic Treatment of Wastewater Contaminated with Organic Waste and Copper Ions from the Semiconductor Industry." *Industrial & Engineering Chemistry Research Ind. Eng. Chem. Res.* 46.20 (2007): 6566-571. Web.
3. Sunada, Kayano, et al. "Detoxification of Phytotoxic Compounds by TiO₂ Photocatalysis in a Recycling Hydroponic Cultivation System of Asparagus." *Journal of Agricultural and Food Chemistry J. Agric. Food Chem.* 56.12 (2008): 4819-824. Web.
4. Fan, Hongxian, Gang Li, Fang Yang, Lei Yang, and Songmei Zhang. "Photodegradation of Cellulose under UV Light Catalysed by TiO₂." *Journal of Chemical Technology & Biotechnology J. Chem. Technol. Biotechnol.* 86.8 (2011): 1107-112. Web.
5. Catalkaya, Ebru Cokay, and Fikret Kargi. "Advanced Oxidation Treatment of Pulp Mill Effluent for TOC and Toxicity Removals." *Journal of Environmental Management* 87.3 (2008): 396-404. Web.
6. Garland, J.L., C.L. Mackowiak, R.F. Strayer, and B.W. Finger. "Integration of Waste Processing and Biomass Production Systems as Part of the KSC Breadboard Project." *Advances in Space Research* 20.10 (1997): 1821-826. Web.
7. Mackowiak, C. L., et al., "Recycling crop residues for use in recirculating hydroponic crop production." NASA KSC, 1996.
8. Strayer, R.F., B.W. Finger, and M.P. Alazraki. "Evaluation of an Anaerobic Digestion System for Processing CELSS Crop Residues for Resource Recovery." *Advances in Space Research* 20.10 (1997): 2009-015. Web.
9. Strayer, R.F., B.W. Finger, and M.P. Alazraki. "Effects of Bioreactor Retention Time on Aerobic Microbial Decomposition of CELSS Crop Residues." *Advances in Space Research* 20.10 (1997): 2023-028. Web.

10. Lunn, G. M., "Strategies for stabilizing nitrogenous compounds in ECLSS wastewater: Top-down system design and unit operation selection with focus on bio-regenerative processes for short and long term scenarios." NASA KSC, 2012.
11. Lunn, G. M., et.al., "A novel ion exchange system to purify mixed ISS waste water brines for chemical production and enhanced water recovery." NASA KSC, 2012