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Conversion of CAFO Manure into a Slow-Release Fertilizer

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Introduction

The objective of this research project is to answer the following question: Which modification of a chemical treatment process for the conversion of manure from a Concentrated Animal Feeding Operation (CAFO) into a controlled-release fertilizer using a photoactive iron polysaccharide polymer will produce the best performance with regard to 1) separating solids from water; 2) binding ortho-phosphate, ammonia, and nitrate + nitrite; and 3) releasing ortho-phosphate, ammonia, and nitrate + nitrite at rates slower than the rate of release from raw manure.

Harmful Algal Blooms

The Harmful Algal Blooms (HABs) seen internationally are known to be a serious health and environmental hazard.[1] Some types of algal blooms release toxins, such as microcystin, that could cause human death or illness.[1] A major contributor to the occurrence of the HABs is known to be the presence of nutrient contaminants, specifically reactive phosphate, nitrate plus nitrite, and ammonia in the water system.[1] One of the sources of these nutrient contaminants is from excess application of manure as fertilizer to agricultural fields, which then results in runoff and contamination of groundwater resources.[2] Reducing the concentration of these contaminants in Lake Erie has mitigated the growth of HABs in the past.[1]

Concentrated Animal Feeding Operations

This recent increase of HABs is an effect suspected to be caused by the recent growth of CAFOs in the southwestern Lake Erie Basin.[3] These CAFOs are high density sites of livestock agriculture.[4] Due to this high density of animals agriculture, CAFOs produce more manure than can be applied to the soil without exceeding the nutrient capacity of the soil in many locations.[4] This issue is caused by the fact that there is not enough agricultural land near the CAFOs to use all of the manure without exceeding the soil limits. Unfortunately, the low nutrient density of the diluted CAFO manure means that it is prohibitively expensive to transport the manure elsewhere to use on more agricultural land.[5,6] If the nutrients in the manure can be concentrated, coagulated, and separated from the water, then the transportation of these solid nutrients over longer distances would be much more cost effective.[5,6,7] The removal, concentration, and reuse of nutrients is also important because there is a limited supply of rock phosphate, the primary source of phosphorous.[8,9] Rock phosphate reserves are only projected to last for another 50 to 100 years.[8] This makes it extremely important that we develop a more effective way to recycle phosphorous from other sources, such as manure.

Manure Treatment

The removal of phosphate from manure is known to be achievable by several chemical treatment methods. One method uses metallic salts, such as Ferric Chloride, to bind the phosphorous and precipitate it out of solution.[6,10] Another uses Calcium hydroxide, or lime, to create several Calcium phosphate compounds that will precipitate out of solution.[4,7,10] Yet another uses cationic polymer as a flocculant to increase the particle size of the solids in the manure such that the water can be more easily removed.[6,10,11,12] A combination of these treatment methods could be used to obtain a solid final product with the desired characteristics.

These treatment methods can also produce a product with the added benefit of being a useful fertilizer product.[5,7,8,9] The creation of a fertilizer product is difficult with metal salts because many metal compounds, such as Iron (III) phosphate, have a very low solubility product constant.[13] This means that very little of the phosphate will dissolve and become available for the plants. Some phosphorous removal techniques have issues with the loss of ammonia into the atmosphere, but there are other methods with promise for stopping the loss of ammonia.[7,14] A photoactive iron polysaccharide polymer could potentially be used to bind to ammonia and act as a flocculant.[14] By using a photoactive polymer as a treatment method, a mechanism for controlled release of the nutrients based upon photo degradation of the polymer could be designed.

Alginate Polymer Gels

Alginate is a polysaccharide polymer that contains two different residue units usually obtained from seaweed.[15,16] These residues are β-(1-4) D-mannuronic acid and α-(1-4) L-guluronic acid.[15,16] Alginate can be used to form hydrocolloid gel particles under the correct conditions.[15] These gels are currently used in many applications, including food, pharmaceuticals, chemical, and agriculture industries.[15] It is known to have the ability to trap and then release flavors, nutrients, and pharmaceutical products.[15]

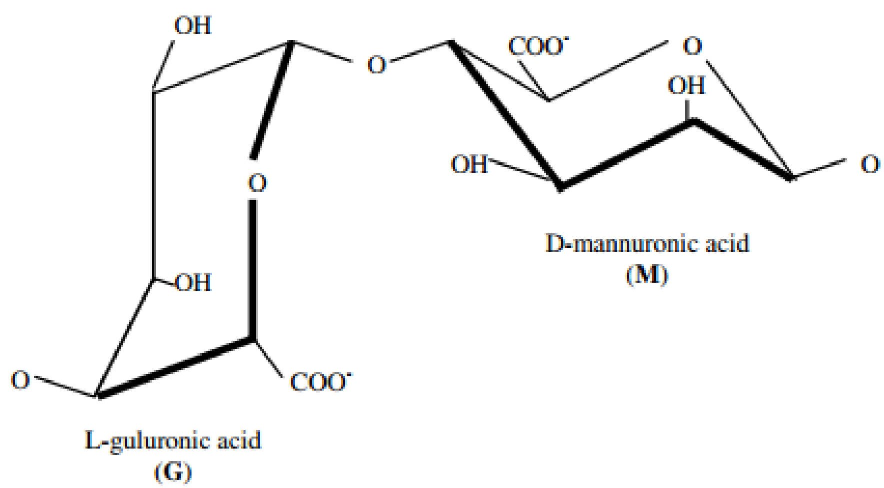

Figure 1: Structure of alginate acid residues (Burey 2008)

One way these hydrocolloid gels can be formed from alginate is through the process of Ionotropic gelation by a mechanism known as diffusion setting.[15] Ionotropic gelation is the process by which a gel is formed by the introduction of ions into the hydrocolloid solution.[15] In the case of this project the ions in question are Iron (III) ions in the form of aqueous ferric chloride. Diffusion setting is a type of ionotropic gelation which describes the diffusion of ions into a hydrocolloid solution, which results in an inhomogeneous gelation.[15] This gelation is accomplished in this project through dispersed phase formation by use of extrusion.

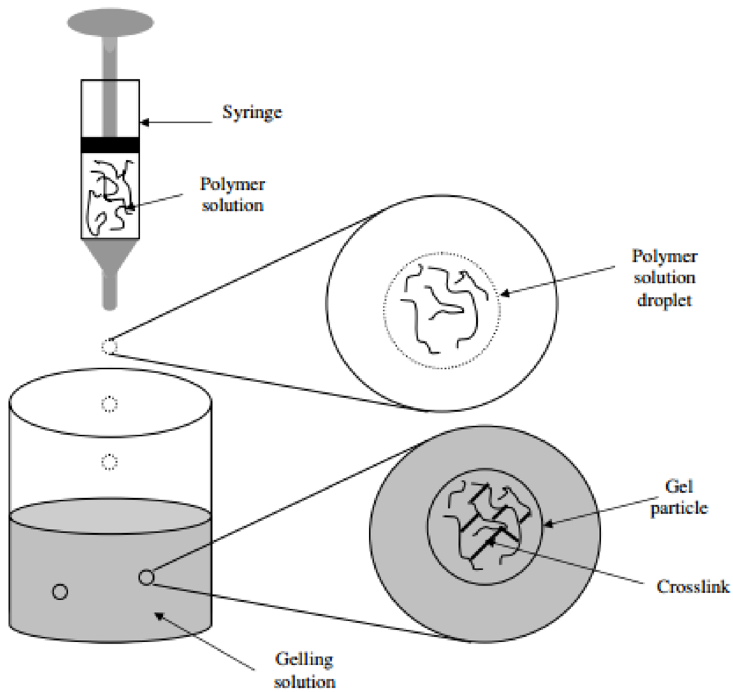

Figure 2: The process of extrusion to form gel particles (Burey 2008)

Dispersed phase formation is a method of developing individual gel particles or “beads” by forming a droplet of the hydrocolloid solution before gelation.[15] The formation of these droplets can be accomplished by several methods, such as extrusion. Extrusion is the process of forming the hydrocolloid solution droplets, by the use of a syringe. Then the droplets are allowed to fall into a gelling solution.[15] The resulting gel particles formed by extrusion have a firm outer "shell" and a soft core as a product of inhomogeneous gelation.[15] It is then likely that these gel particles can be dehydrated for transport and will retain their molecular structure.[16]

Through the use of information presented in previous research, a novel treatment process to convert CAFO manure into a controlled release fertilizer could be devised using photoactive polysaccharide polymer gels.

Methods

Treatment Process

Lab scale testing of the alginate treatment process was utilized to evaluate the effectiveness of nutrient release. These tests consisted of the treatment of twenty-five milliliters of manure obtained from a dairy CAFO with food grade sodium alginate from Modernist Pantry to create an approximately 0.01% solution of alginate.

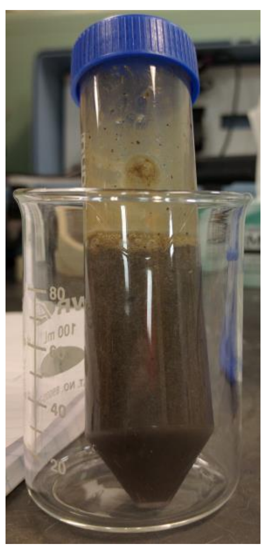

Figure 3: The 0.01% alginate manure solution.

The resulting solution is then pulled into a syringe and dripped into a solution of 5% aqueous ferric chloride. The gel beads that form are then filtered out of the ferric chloride solution using wire mesh. Some of the gel beads are then dried to compare the difference between hydrated and dehydrated release.

Figure 4: The above figure shows hydrated gel beads (left) and dehydrated gel beads (right).

The resulting gel beads were tested by use of a rain simulation procedure developed to estimate the rate of release for the nutrients to the crops over an extended period of time.

Rain Simulation

Soil was washed with purified water to remove as much nutrient content as possible. It was then ground and sieved into fine and coarse soil. Sixty grams of fine, sixty grams of coarse soil, and the gel beads were mixed into a Whatman disposable filter funnel.

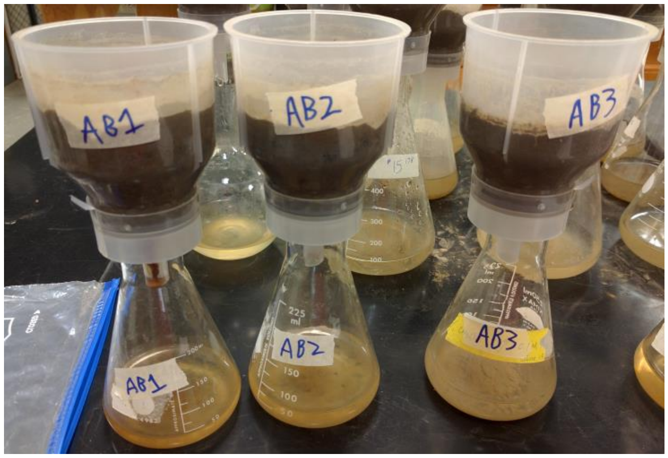

Figure 5: The above figure shows the apparatus for the rain simulation procedure.

Raw manure tests contained twenty-five milliliters of raw manure instead of the gel beads. For each rain simulation, one hundred milliliters of purified water were added to each test. The filtrate was collected in an erlenmeyer flask, syringe-filtered, and then stored in a labeled Whirlpak bag for chemical analysis. One set of rain simulations was carried out under ambient light conditions and one set was carried out under a Spectroline EA-160 ultraviolet light at 365nm, 11cm away from the samples. The light was operated at 115volts, 60Hz, and 0.20 amps.

Chemical Analysis

The filtrate from each rain simulation was analyzed for dissolved reactive ortho-phosphate, ammonia, and nitrate + nitrite using the SEAL AQ2+ Discrete Chemical Analyzer. The nitrate plus nitrite was determined using EPA Method 114-A Rev. 7 by reducing nitrate to nitrite with a cadmium column, along with N-(1-naphthyl)-ethylenediamine dihydrochloride and then taking a spectrophotometric measurement at 520nm. The dissolved reactive phosphorus was tested using EPA Method 118-A Rev. 4 by reacting with $MoO_3 \cdot H_2O$ and ascorbic acid and then taking a spectrophotometric measurement 880nm. The ammonia was tested using EPA Method

103-A Rev. 6 by reacting with alkaline phenol and sodium nitroferricyanide and then taking a spectrophotometric measurement at 650-660nm.

Results

Three 25 mL samples of raw CAFO manure were treated with .25 g of sodium alginate. They were then extruded into a solution of 5% $FeCl_3$ to form gel beads. Each of these samples of beads and a 25mL sample of raw manure were then collected. Samples AB2 and AB3 were dehydrated under room temperature and pressure, and then each sample was set up for rain simulations under ambient light conditions.

Table 1: The table below shows the dates for each rain simulation.

	AB Raw	AB1	AB2	AB3
Rain 1	3/3/2016	3/7/2016	3/7/2016	3/3/2016
Rain 2	3/4/2016	3/8/2016	3/8/2016	3/4/2016
Rain 3	3/7/2016	3/9/2016	3/9/2016	3/7/2016
Rain 4	3/8/2016	3/11/2016	3/11/2016	3/8/2016
Rain 5	3/11/2016	3/14/2016	3/14/2016	3/11/2016
Rain 6	3/14/2016	3/17/2016	3/17/2016	3/14/2016
Rain 7	3/18/2016	3/18/2016	3/21/2016	3/18/2016
Rain 8	3/21/2016	3/21/2016	3/24/2016	3/21/2016
Rain 9	3/24/2016	3/24/2016	3/28/2016	3/24/2016
Rain 10	3/28/2016	3/28/2016	4/1/2016	3/28/2016
Rain 11	4/1/2016	4/1/2016	4/6/2016	4/1/2016

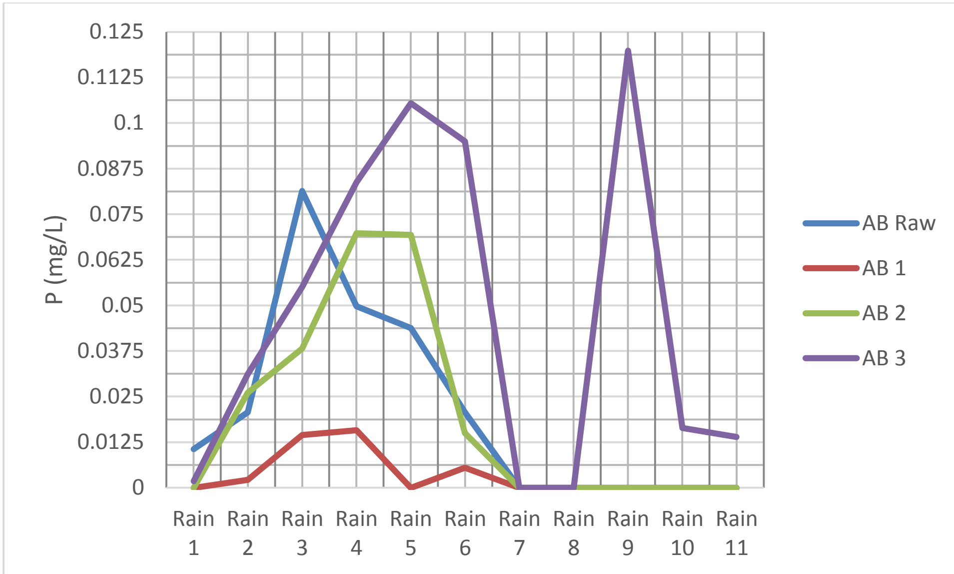

Figure 6: This figure shows the release rate of ortho-phosphate under ambient light.

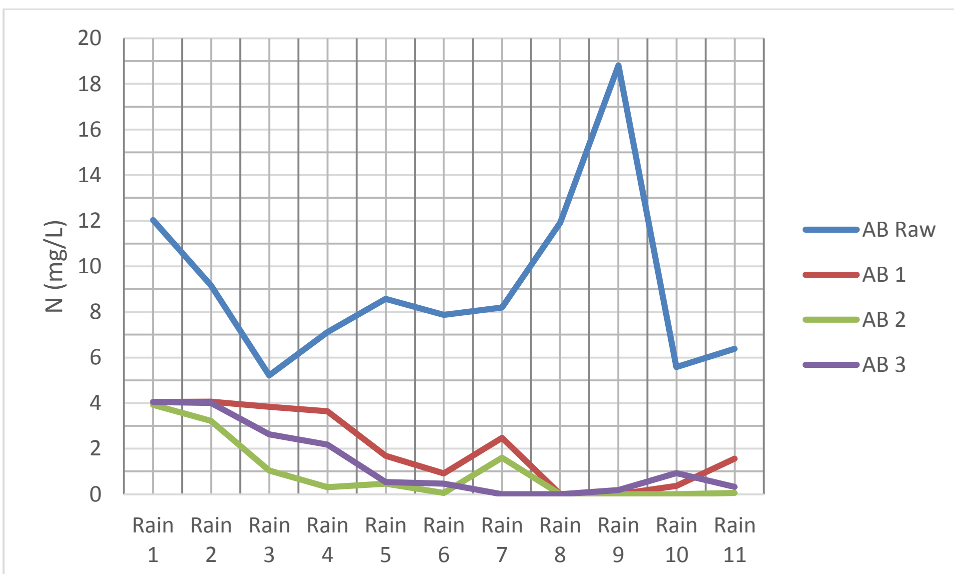

Figure 7: This figure shows the release rate of ammonia under ambient light.

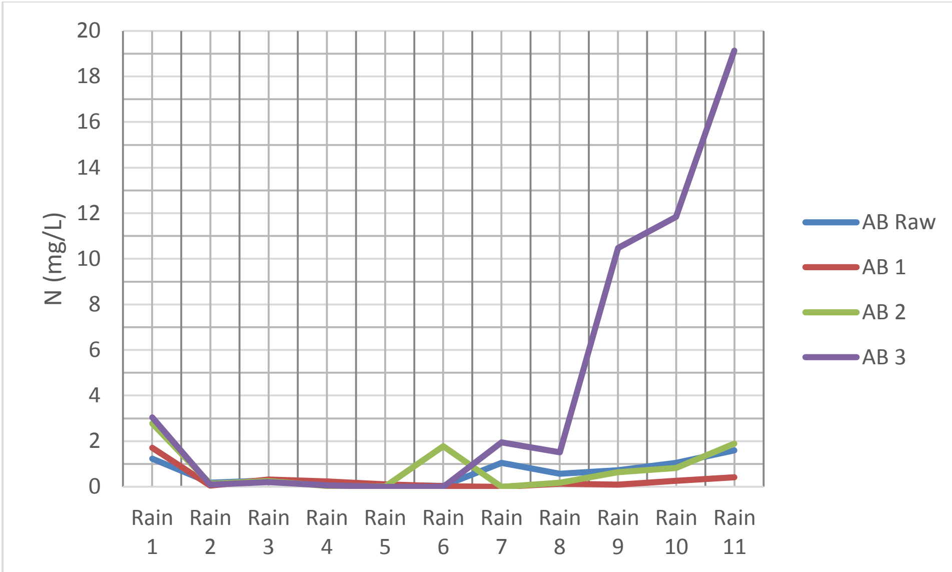

Figure 8: This figure shows the release rate of nitrate + nitrite under ambient light.

Two 25 mL samples of raw CAFO manure were treated with .25 g of sodium alginate. They were then extruded into a solution of 5% $FeCl_3$ to form gel beads. Both of these samples of beads and a 25mL sample of raw manure were then collected. Sample AB4 was dehydrated under room temperature and pressure, and then each sample was set up for rain simulations under ultraviolet light conditions.

Table 2: The table below shows the dates for each rain simulation.

	AB Raw	AB4	AB5
Rain 1	4/12/2016	4/12/2016	4/12/2016
Rain 2	4/14/2016	4/14/2016	4/14/2016
Rain 3	4/15/2016	4/15/2016	4/15/2016
Rain 4	4/18/2016	4/18/2016	4/18/2016
Rain 5	4/19/2016	4/19/2016	4/19/2016
Rain 6	4/21/2016	4/21/2016	4/21/2016
Rain 7	4/22/2016	4/22/2016	4/25/2016
Rain 8	4/25/2016	4/25/2016	4/28/2016

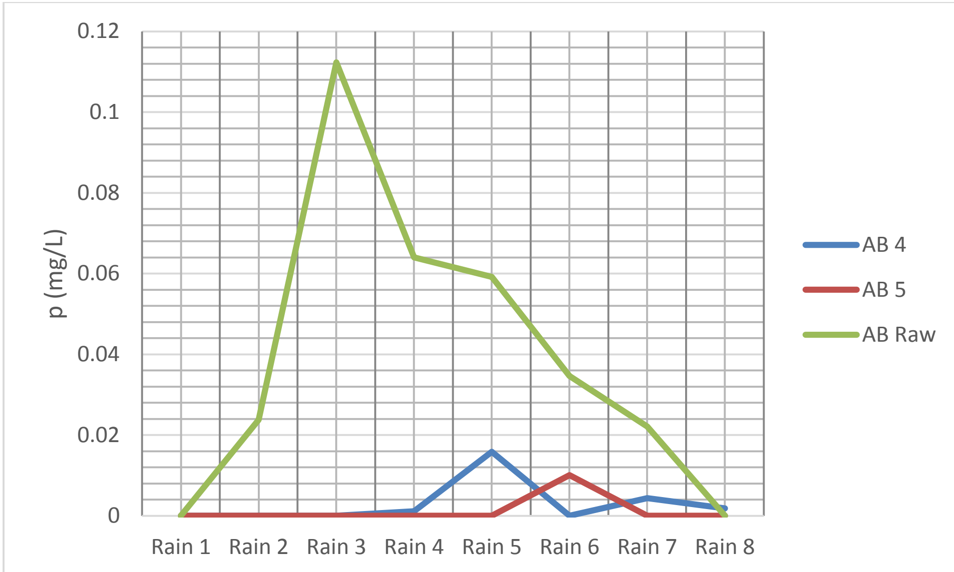

Figure 9: This figure shows the release rate of ortho-phosphate under ultraviolet light.

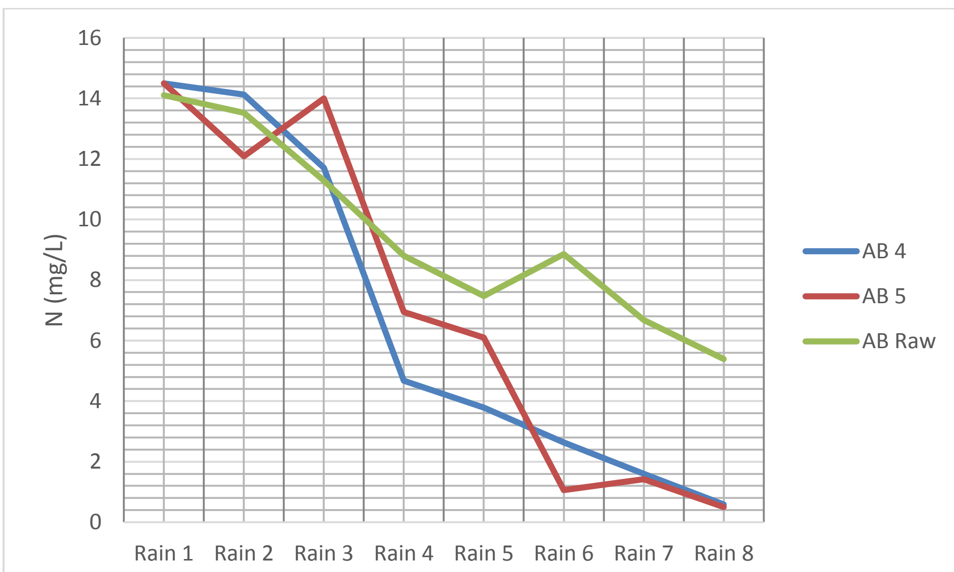

Figure 10: This figure shows the release rate of ammonia under ultraviolet light.

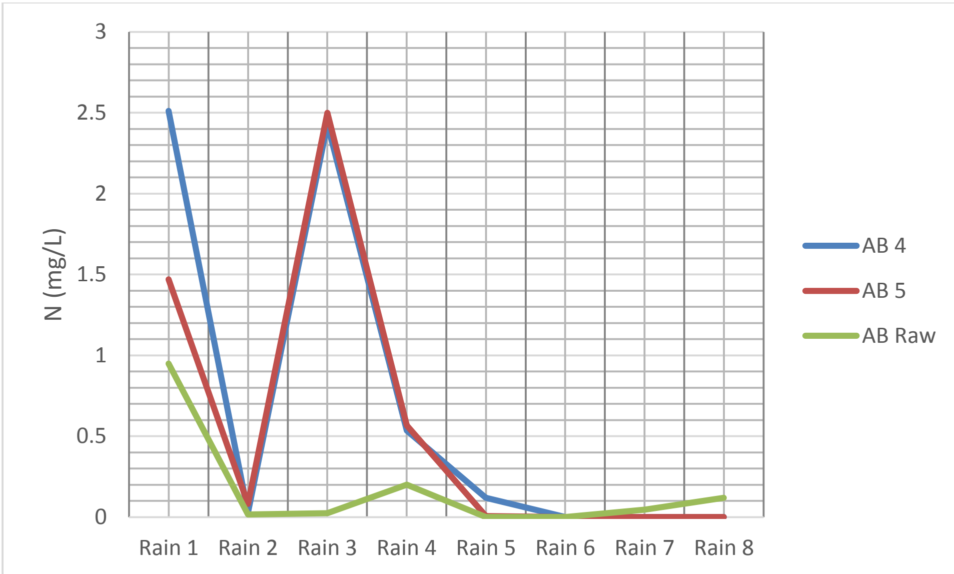

Figure 11: This figure shows the release rate of nitrate + nitrite under ultraviolet light.

Discussion/Conclusions

This study is a single test of the alginate polymer treatment once under ambient light and once under ultraviolet light. The purpose of this project was to determine if it might be possible to use alginate gel as part of a manure treatment process to capture and control to release of nutrients. It is not possible to draw significant conclusions about the exact binding and release rates of nutrients from the limited data in this study. Further research and testing is needed to determine the effectiveness of this treatment process. Given the heterogeneous nature of both the manure and the soil used high variability is expected in the results. Therefore, many replicates must be run to determine the binding effectiveness and the rates of nutrient release. However, given the limited data, there are some possible conclusions. From the limited data it appears that the alginate gels do not bind and release the ortho-phosphate or nitrate + nitrite very effectively. However, the results suggest a possible binding and slow release of ammonia.

Based on the limited data from this study, the ortho-phosphate release under ambient light conditions is sporadic and very low. There does appear to be a slight difference in the release rates for the hydrated and dehydrated beads, but the scale is so small that it is still not a statistically relevant difference. Under ultraviolet lighting the release rates for the alginate beads stays at almost zero for the entire duration of the testing. There does not appear to be a difference for the hydrated and dehydrated beads.

It appears in the limited data available that the release of ammonia under ambient light conditions shows potentially promising results. It remained lower and more consistent than the release rate from raw manure. Also there seems to be very little difference between the hydrated and dehydrated beads. In contrast, under ultraviolet light conditions the release rates are very similar to the release rates for raw manure throughout the testing. This is not desired, but is somewhat expected because of the photoactive nature of the alginate polymer gels. In similarity to the ambient light conditions, there is not much difference in the release rates between the hydrated and dehydrated beads under ultraviolet light.

Under ambient light conditions the release rate of nitrate + nitrite remains at zero until after rain 8, at which point AB3 skyrockets up to approximately 20ppm. This is confusing, but could possibly be explained by biological or chemical activity in either the manure or the soil. More experiments would need to be run to determine the source of this behavior. Under ultraviolet light the release rates of nitrate + nitrite is similar for both the hydrated and dehydrated treatments, as well as the raw manure. There is a spike in both treatments at rain 3, which is also hard to explain without further testing.

The results of this project show promise for the use of alginate gel as a treatment for conversion of manure into a slow-release fertilizer. Some promising aspects of this treatment process are the ease of filtration, the reduction of mass in the final product, and the potential of binding and releasing ammonia. The formation of larger gel beads creates a product that is more easily separated by use of wire mesh then other treatment methods which require vacuum filtration or a sand bed filter. If the dehydrated beads can be used as the final fertilizer product, the transportation cost would be significantly decreased from the cost of transporting raw manure. The results from this testing suggest little to no difference between the hydrated and dehydrated beads. Other treatment processes, such as the cationic polymer treatment used in wastewater treatment, bind and release ortho-phosphate and nitrate + nitrite, but do not capture ammonia effectively. The limited data in this preliminary testing suggests that the alginate treatment might bind and release ammonia effectively.

The next steps for this project are to conduct additional testing both with this treatment process to determine the replicability of these results, as well as varying some aspects of this process to determine which treatment process is the most effective. For example, a lower concentration of the ferric chloride gelling solution could be used to determine the effective change in release rates. This process could also be combined with other polymer treatments, such as the cationic polymer treatment, to better bind and release ortho-phosphate, ammonia, and nitrate + nitrite.

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