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# Removal and Reuse of Phosphorus as a Fertilizer from CAFO Runoff

Kristin Moore

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**Removal and Reuse of Phosphorus as Fertilizer from CAFO Runoff**

**WERC 2019**

**Task # 5**

**Woo Pig Poocie!**



**Ralph E. Martin Department of Chemical Engineering  
University of Arkansas**

**Removal and Reuse of Phosphorus as Fertilizer from CAFO Runoff**

**WERC 2019**

**Task #5**

March 25, 2019

**Woo Pig Poovie!**

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## **EXECUTIVE SUMMARY**

Eutrophication is the process in which nutrient saturated waters promote algal blooms on the surface of the water. This limits the amount of dissolved oxygen content in the water, effectively limiting the range of species that can survive in a body of water.

Concentrated animal feeding operations (CAFO) can contribute to this issue. The animals in a CAFO produce large amounts of nutrient-rich waste streams that can enter natural waterways if not properly managed and increase the problem of eutrophication. The ability to treat these waste streams and recover the excess nutrients would allow for not only the reduction of nutrient leaching and runoff but would help create sustainable phosphorus practice. Phosphorus is vital in terms of food production, and there is no replacement for phosphorus for plants or humans. As the population continues to increase, food demand will as well. This means that at any point that phosphorus can be recovered, it should be.

To recover phosphorus effectively from waste water sources, reverse osmosis, anion exchange, or adsorption are all viable options. Woo Pig Poole researched these options for recovering phosphorus, and adsorption was found to be the most promising from standpoints of low maintenance and cost effectiveness. Multiple adsorption materials were ranked based on appropriate performance of cost, particle size, adsorption qualities, and the effects of application of the material. Water treatment residuals, WTR (i.e. spent alum from a drinking water treatment plant), was determined to be the most effective adsorbent. WTR, a waste product, is 80% water as it exits the water treatment plant. It must be pelletized and dried before use as an adsorbent.

Pelletized and dried WTR was utilized in a full-scale facility treating 62 GPM of feed using two 11,000 gallons packed columns with associated equipment. If the cost of pelletizing and drying the WTR is included, an alternative strategy for implementation on individual farms is for several farmers to form a cooperative, which would allow the minimization of the \$1,460,000 fixed capital cost and the \$504,000 cost of manufacturing of the drying pelletizing facility. This would allow for the maximum amount of WTR to be treated increasing the revenue of the operation to \$731,500. The cooperative would have an operation of 10 years with a net present value of \$5,000.

Experimental results using WTR packed columns have shown non-detectable levels of phosphorus in the effluent. The produced phosphorus saturated WTR could be land applied to reduce the level of nutrients in runoff from fields, making a safer agriculture operation.

## 1.0 INTRODUCTION AND DISCUSSION OF TASK

Phosphorus polluted waterways have severe ecological impacts. When waterways have an excess amount of phosphorus, eutrophication can occur, which is the process of algal blooms covering the surface of the water<sup>1</sup>. Algal blooms have at least two detrimental effects (1) sunlight is inhibited from reaching the plant life below the water surface and (2) dissolved oxygen content is reduced, suffocating other forms of aquatic life. Phosphorus levels must remain lower than 0.1 ppm<sup>2</sup>, and values above 0.037 ppm<sup>3</sup> can increase the threat of eutrophication. Phosphorus is also a finite resource. This creates a necessity to reuse unnecessary waste.

Concentrated animal feeding operations (CAFOs) have a unique role in the issue of phosphorus pollution. A CAFO is defined as an animal feeding operation with more than 2,500 swine over 55 pounds, 1,000 beef cattle, 700 dairy cows, 125,000 broiler chickens, or 82,000 laying hens on a site for more than 45 days a year<sup>4</sup>. The task statement indicates that phosphorus pollution from CAFOs is most severe in the eastern US. The most densely populated CAFOs, especially swine CAFOs, are in the eastern US, specifically North Carolina. North Carolina is the second highest swine producer<sup>5</sup>, and recently has had the most trouble with nutrient leaching from heavy rainfall. The high concentration of swine CAFOs in North Carolina, leads for this study to be the effective treatment of waste runoff produced from a swine CAFO.

In most swine CAFOs, the animals are housed indoors, and the waste is flushed from the building. The floors of swine pens are usually grated, where the waste passes through the floor, and into pipes which flow into holding lagoons. These lagoons are required to be lined with natural clay or other liner to ensure that the waste does not leach into the ground and thus, into the nearby water systems. The diluted waste is open to the air, and then the slurry is sprayed onto fields. The ratio that nutrients are used by the crops or grasses being grown is less than that of the waste that is being applied to the field. Plants utilize a nitrogen (N) to phosphorus (P) ratio of 8:1, while the manure that is being applied contains a ratio of 4:1<sup>6</sup>. This excess phosphorus builds up in the soil until it is disrupted by heavy rainfall and gets washed into a waterway. However, the ability to treat this runoff stream is complicated with heavy water flow, low nutrient concentrations, and location of a system to treat multiple field's runoff. These limiting factors point to treat the most concentrated source of water-soluble phosphorus -- the lagoon water.

Treating the lagoon water would not only reduce the amount of phosphorus in the lagoon system but would also lower the amount of phosphorus that is applied to the fields in the future. This would then reduce the chance of eutrophication of waters, as the runoff water has a lesser content of water-soluble phosphates.

The premise of the task states that 20 liters of water with an orthophosphate concentration of 20 ppm are to be treated by removing and recovering the phosphorus with a moisture content of less than 25%. The process needs to be easily scalable to treat the high volume of runoff from a CAFO. This runoff described in the task can be defined as the excess lagoon water that is applied to the crops.

## **2.0 CURRENT METHODS**

An important process that treats the entirety of CAFO swine waste is the Super Soils system developed by researchers at North Carolina State University. This process first separates the solids, then treats the liquid waste. The liquid waste goes through nitrification/denitrification, phosphorus removal, and the pH spike from the addition of calcium hydroxide kills pathogens. This process is effective, but the cost of implementing it is more than four times greater than that of the lagoon system<sup>2</sup>. Other methods of treating CAFO waste primarily deal with solid waste. While most of the nutrients are in solid waste, this does not solve the problem of nutrient pollution. The only place that nutrients can leach into waterways would be from lagoons that hold the waste sludge and liquid waste. Studies to recover nutrients from runoff have not been conducted to a scale that would apply to a large farming production.

To reduce the eutrophication effect from excess phosphorus, there are three common removal methods: chemical precipitation, adsorption, and biological removal<sup>7</sup>. Precipitation uses aluminum, iron, magnesium, or calcium to react with phosphorus. To be effective, precipitation needs to occur with phosphorus at higher concentrations than what is available in waterways<sup>2</sup>. Adsorption uses industrial waste, metal oxide induced clays, and bio-waste materials. This is more promising because it involves the reuse of materials that are usually landfilled, introducing a green approach. Biological removal focuses on the use of microorganisms to digest the phosphorus, and then these microorganisms are removed from the system and are land applied or landfilled. The bacteria that digest the phosphorus have an efficiency that is sensitive to the conditions of their environment which can cause fluctuating results.

### **3.0 POSSIBLE TREATMENT METHODS**

With the fundamental notion that the technology must be readily applied to a system requiring low cost, low maintenance, and to have a useable final product, this means many characteristics limit the application of technology to treat a farm-scale system.

#### **3.1 Reverse Osmosis**

For precipitation to be more effective, reverse osmosis (RO) is a technology that could be used to increase the low phosphate concentration to a higher concentration. This could be implemented to create more applicable fertilizers, such as monoammonium phosphate (MAP), diammonium phosphate (DAP), or merely a calcium phosphate. However, calcium phosphate's maximum concentration in a soluble form is roughly 20 ppm, and if that threshold is passed, it will naturally begin to precipitate out of solution. This means that during the RO process, calcium phosphate would precipitate in the membrane housing, causing fouling issues, and other adverse effects to the membranes. Another downside of the RO process would be the energy costs required<sup>8</sup>, and the large amount of maintenance which would be intensive for a residual nutrient collector.

#### **3.2 Anion Exchange**

Anion exchange is another possible option for large scale phosphorus removal. Resins use a strong positive charge to selectively attract the negative charge of the phosphate ion that exists in the water stream. However, most cation resins have a low affinity for attracting phosphates, and if any other anion is present, it will be more attracted to the resin<sup>9</sup>. For a bench scale with a solution of only orthophosphates it could be an ideal solution, yet, in terms of scalability, it is unreasonable to conclude that phosphates are the only anion in a natural water stream<sup>10</sup>. Another difficulty with the use of anion exchange resins is the complexity of the chemical operation that would be required to achieve a usable fertilizer. Resins would have to be back washed to remove the phosphates, then, this phosphate rich solution would have to be reacted into a usable fertilizer form. Having a complex system of chemical reactions would make application unrealistic in an agricultural production.



### **3.3 Adsorption**

The most promising option is an adsorbent material that has a high affinity for phosphates and can be land applied as a long-term fertilizer. Having a material that, post adsorption, would not require a chemical reaction would be the simplest solution. An added benefit is that phosphates are not the only nutrient that is available in the runoff, and it may not be the only nutrient adsorbed by the adsorption material. This would only add value to the potential of adsorbent material to be used as fertilizer, or even as a simple soil additive.

## **4.0 ADSORPTION MATERIALS AND METHODS OF TESTING**

To select the optimum choice of which adsorbent material (ADSM) would be best for nutrient recovery from excess nutrients in a runoff stream, many aspects must be accommodated. These include: adsorption potential, rate of adsorption, potential as fertilizer, cost, and particle size. These qualities will be tested, and the results will be compared to find the most holistic solution to nutrient recovery from excess nutrient runoff. Given the number of characteristics being analyzed, there is an expansive list of ADSMs, which includes: finely ground limestone, pelletized dolomitic limestone, granular activated carbon, a mixture of the finely ground limestone and activated carbon, water treatment residuals, iron saturated red mud, fly ash, dry flue gas desulfurization by-product, and biochar. Each sub category will be ranked from high to low, then all the results will be summed, allowing the highest scoring ADSM to be the most effective overall.

### **4.1 Background of Materials**

Finely ground white limestone (LA) is an attractive adsorbent because it has been tested as a good ADSM for phosphates and showed promise<sup>11</sup>. Limestone contains calcium carbonate ( $\text{CaCO}_3$ ), which can react with phosphates to produce calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ).

Pelletized dolomitic limestone (LB) is mainly composed of  $\text{CaCO}_3$  and allows for a long-term pH adjustment to the soil. This limestone also contains magnesium carbonate, which would potentially provide another key nutrient for crop growth<sup>12</sup>.

Granular Activated Carbon is commonly used as an ADSM because of its porous nature. This increased surface area is caused by creation of a complex micropore structure<sup>13</sup>. The activated carbon used in this study was bituminous coal granular activated carbon (BGAC).

Water treatment residuals (WTR) are produced from drinking water treatment plants. The residual is created from alum,  $\text{Al}_2(\text{SO}_4)_3$ , being used as a flocculating agent, in which the product of the floc is separated from water, and then normally landfilled<sup>14</sup>. Unlike the other materials, the WTR used in this study was not ready for immediate use. The WTR needed to be pelletized and dried for increased adsorption potential. A potato ricer from a cooking store was chosen to pelletize the WTR for its simplicity and availability. This potato ricer was very effective in creating the pellets, as shown in Figure 4.1-1 and 4.1-2.



Figure 4.1-1: WTR before pelletizing.

Figure 4.1-2: Pelletized WTR.

After being pelletized, the WTR pellets had to be dried. This was done with a heat gun, and a sieve tray. The drying of the pellets required no longer than 10 minutes per tray. The dried pellets can be seen in Figure 4.1-3.



Figure 4.1-3: Pelletized and Dried WTR

Similar to the WTRs, the iron saturated red mud (ISRM) is a by-product of a local manufacturing process. It is the result of the production of steel belts, whose waste stream is in

high content of ferrous iron. An ionic polymer is then used as a flocculating agent for metal hydroxides, the resulting floc is separated from the water and landfilled<sup>14</sup>.

Fly ash is a byproduct of coal used in electric power generating plants. The mineral impurities in the coal elutriated out of the combustion chamber with exhaust gases and solidify into fly ash. The one being tested is a high-calcium fly ash with a low carbon content. Fly ash is also commonly used as a concrete additive, which causes it to harden when introduced to small amounts of water.

Flue gas desulfurization (FGD) is a process used to remove SO<sub>2</sub> from power plant emission streams via injection of a calcium sorbent<sup>15</sup>. This creates a product that can be dried, producing a dry flue gas desulfurization product (DFGD). In this study, DFGD by-product was gathered from the Southwest Arkansas’ John W. Turk Power Plant.

Biochar is created from the pyrolysis of biomass. This biomass can be from any sort of waste, which means availability would not be limited to a region. Biochar also has the benefit of carbon sequestration, as it essentially removes carbons that could be going into the atmosphere and puts them into the soil.

#### 4.2 Cost Analysis

Cost scorings were determined via per ton costs of materials. Some of the materials, WTR, ISRM, Fly Ash, and DFGD, are waste products from various industries. This means that there is no purchase cost to buy these materials and are represented by a dash in their corresponding section.

Table 4.2: Cost of Adsorbent per ton

	LA	LB	BGAC	WTR	ISRM	Fly Ash	DFGD	Biochar
Cost (\$/ton)	40 <sup>16</sup>	10.50 <sup>17</sup>	300 <sup>18</sup>	-	-	-	-	180 <sup>19</sup>
<b>Score</b>	<b>6</b>	<b>7</b>	<b>4</b>	<b>8</b>	<b>8</b>	<b>8</b>	<b>8</b>	<b>5</b>

#### 4.3 Particle Size of Adsorbent Materials

Particle size for Fly Ash, DFGD, and Biochar were measured with a camera fitted microscope, and the images were analyzed with ImageJ software. For LA, BGAC, WTR, and ISRM, particle size was measured via sieve trays.

#### 4.4 Adsorption Potential Testing

To find the maximum adsorption potential of the different materials, a known amount of adsorbent was added to a vial with 20mL of orthophosphate solution. The orthophosphate solution was prepared using diluted phosphoric acid. The amount of ADSM tested was determined based on initial testing. A ratio of 1:5000, 1:2500, 1:1250, and 1:500 of grams orthophosphate to grams adsorbent was chosen to test LA and biochar. For the WTR and ISRM, 1:500, 1:250, 1:125, and 1:75 were tested. The fly ash and DFGD were tested at the lowest ratios, 1:100, 1:75, 1:50, 1:25. The WTR was tested again at the same ratios as DFGD and fly ash after it was pelletized. The vials were then left on a VWR Signature Rocking Platform Shaker for 48 hours to be sure the solutions had all reached equilibrium. The concentration of the orthophosphate solution was measured before the experiment, and then after so the amount of phosphate adsorbed could be calculated. The measuring device used for phosphates were the Hanna Low Range Phosphate Colorimeter - Checker® (0.00-2.50ppm) and the Hanna High Range Phosphate Colorimeter - Checker® (0.0-30.0ppm). The low range kit uses the Ascorbic Acid method to induce a color change, while the high range uses the Heteropolymolybdenum Blue method.

To correlate the adsorption potential of each ADSM, the Langmuir isotherm model was used. The Langmuir isotherm was chosen because it models monolayer adsorption. The form used is as follows:

$$q_i = q_{\max} \left( \frac{k_A P_{\text{SOL}}}{1 + k_A P_{\text{SOL}}} \right) \quad (1)$$

Where:

$q_i$  : The amount of phosphate adsorbed per gram of adsorbent material (ADSM) [g P/g ADSM]

$P_{\text{SOL}}$  : The equilibrium phosphate concentration [PPM, g/m<sup>3</sup>]

$k_A$  : The affinity of phosphate to the ADSM [m<sup>3</sup>/g]

$q_{\max}$  : The maximum amount of phosphate that can be adsorbed onto the ADSM [g P/g ADSM]

Equation 1 can be rearranged so  $q_{\max}$  can be found via the graph of  $\frac{P_{\text{SOL}}}{q_i}$  vs  $P_{\text{SOL}}$ :

$$\frac{P_{\text{SOL}}}{q_i} = \left( \frac{1}{q_{\max}} \right) P_{\text{SOL}} + \frac{1}{k_A q_{\max}} ; \text{ Where } \left( \frac{1}{q_{\max}} \right) \text{ is the slope.} \quad (2)$$

#### 4.5 Kinetic Testing

Kinetic tests were conducted at the same conditions as the equilibrium tests to ensure that the equilibrium adsorption value used in the equations of the kinetic models was accurate. The experiments were set up, so a sample could be taken at various time intervals over a span of 5 hours (5, 10, 15, 30, 45, 60, 75, 90, 120, 180, 240, 300 minutes). The solutions were prepared where one common mass of adsorbent was used via the phosphate to ADSM ratio, and 20 mL of 20 ppm orthophosphate solution was added to each vial. These vials were then loaded onto a VWR Incubating Mini Shaker. The phosphate was measured prior the start of the experiment to ensure that the amount of phosphates adsorbed could be calculated.

Once data has been collected, it must be modeled to find the rate constant  $k$ . To model the data in first order or second order two new variables need to be found.

$q_e$ : amount phosphate adsorbed at equilibrium [g/kg]

$q_t$ : amount phosphate adsorbed at time  $t$  [g/kg]

To model after first-order:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

And since at  $t = 0$  then  $q_t = 0$ , the following equation can be found:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (4)$$

If  $\log(q_e - q_t)$  vs.  $t$  is graphed, then slope =  $-\frac{k_1}{2.303} t$ , and the rate constant can be found.

The same kinetic data can then be modeled onto a second-order graph, to allow the comparison of calculated data vs theoretical to ensure the accuracy of the model. This is done by using the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Applying the same conditions as for first order, where when  $t=0$  then  $q_t=0$ :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

If  $\frac{t}{q_t}$  vs  $t$ , the slope is  $\frac{1}{q_e}$ , and the intercept is  $\frac{1}{k_2 q_e^2}$ . Since the slope in this line is supposed to be

equal to the actual  $q_e$  value found during equilibrium testing, this allows for the second order model to be checked. The theoretical  $q_e$  and experimental  $q_e$  had a factor of difference of at least

ten for all ADSMs and the different ratios used. This meant that the kinetics would be judged based off the first order model.

#### 4.6 Environmental Impact

Environmental impact was tested and concluded from the amount of heavy metals that are present in the samples. To find these values, samples were subjected to HNO<sub>3</sub> acidic solution and microwave digestion, the solution was then reacted with H<sub>2</sub>O<sub>2</sub> to eliminate any organics in the solution. The samples were then run via inductively coupled plasma via Thermo Fisher's iCAP™ TQs ICP-MS which measures for trace metals. The trace metals that were the most important are those which are found in the Clean Water Act: Lead, Selenium, Arsenic, Zinc, Copper, Chromium, and Nickel. These values were found in mg/kg of ADSM.

### 5.0 EXPERIMENTAL RESULTS AND DISCUSSION

#### 5.1 Particle Size Results

Particle size of LB was inconclusive, because once the pellets were introduced to water, the pellets dissolved and became a slurry of finer ground materials. When the new slurry was dried to measure the different particles, it would re-associate into clumps of various sizes which led to the inconclusive results of particle size. ISRM particles weren't uniform and were sieved via weight percent. Particle size scoring was based on the idea that the larger particles would allow for better flow through a packed bed column.

Table 5.1: Particle Sizes of Adsorbent Materials

	LA	LB	BGAC	WTR	ISRM	Fly Ash	DFGD	Biochar
Particle Size (mm)	.074	*	0.55-0.75	2.45-2.60	30% 4-6 27% 2-4 43% <2	0.002	0.002	0.003
<b>Score</b>	<b>5</b>	<b>1</b>	<b>6</b>	<b>8</b>	<b>7</b>	<b>3</b>	<b>3</b>	<b>4</b>

## 5.2 Equilibrium Test Results

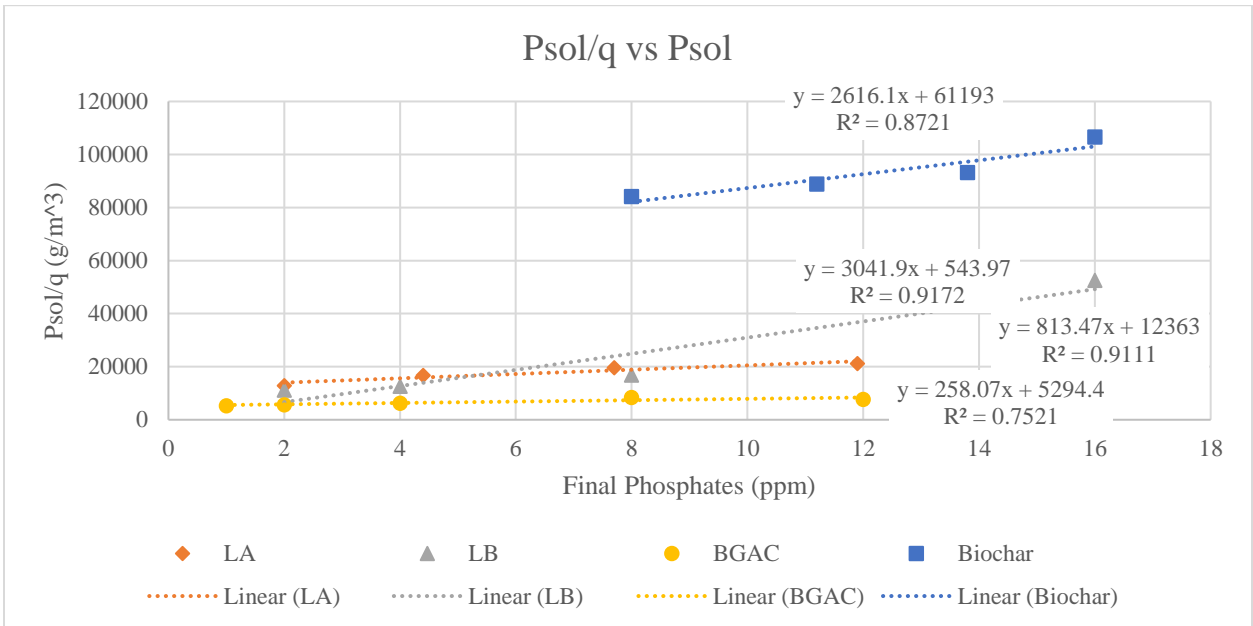


Figure 5.2-1: The equilibrium graphs of LA, LB, BGAC, Biochar.

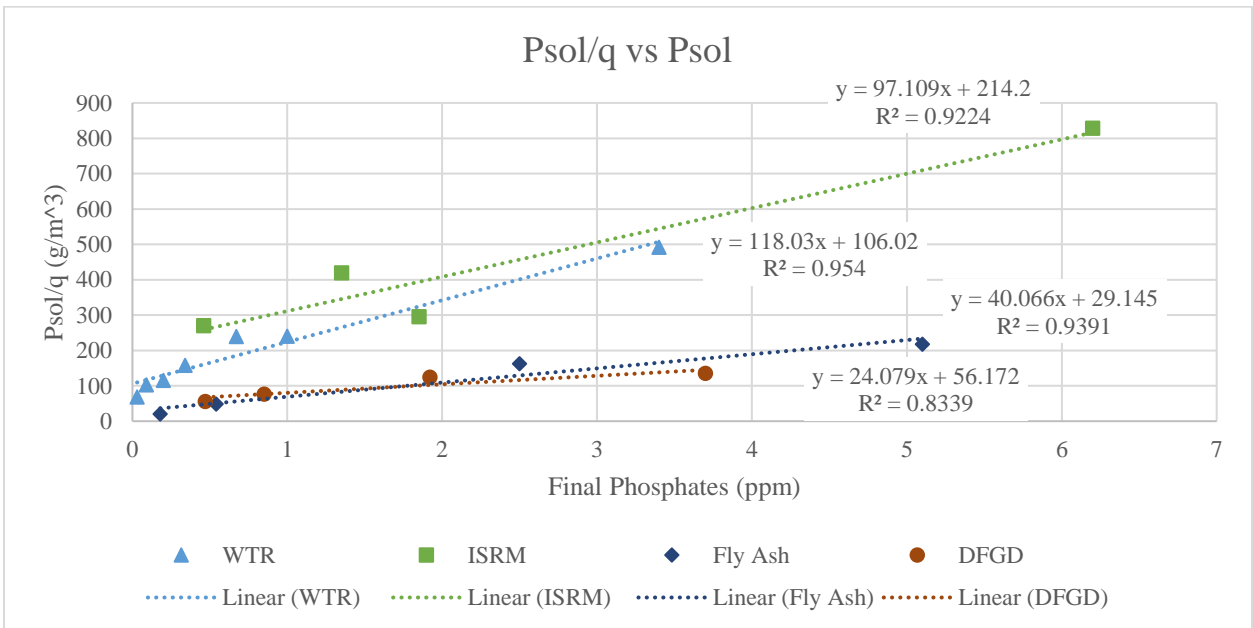


Figure 5.2-2: The equilibrium graphs of WTR, ISRM, Fly Ash, and DFGD.

Table 5.2: The maximum adsorption potential of each material.

Adsorbent Material	Slope ( $\frac{1}{q_{max}}$ )	$Q_{max}$ (g P / kg ADSM)	Score
LA	813.47	1.229	3
LB	3041.9	.329	1
BAGC	258.07	3.875	4
Biochar	2616.1	.382	2
WTR	118.03	8.472	5
ISRM	97.109	10.298	6
Fly Ash	40.066	24.496	7
DFGD	24.079	41.53	8

From the equilibrium testing, LA, LB, and Biochar were eliminated from further testing because the low maximum phosphate adsorption potential. BAGC was eliminated at this point of testing because of the lower than expected adsorption potential, causing the scale-up costs to be significantly larger than the other materials. This allowed for materials which would have a longer lifetime as an adsorption material to be further tested.

### 5.3 Kinetic Test Results

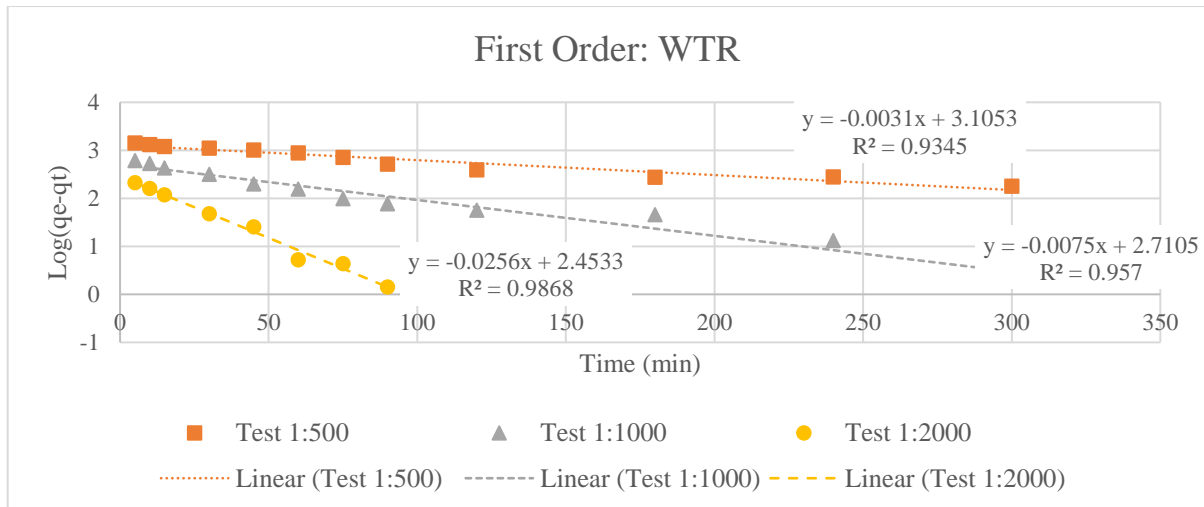


Figure 5.3-1: First Order for WTR.



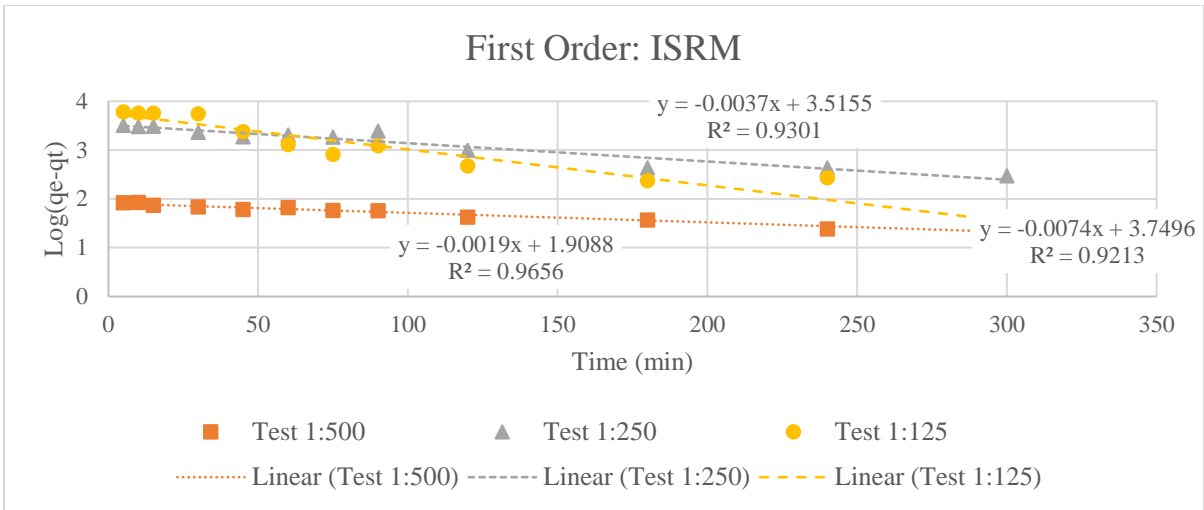


Figure 5.3-2: First Order for ISRM.

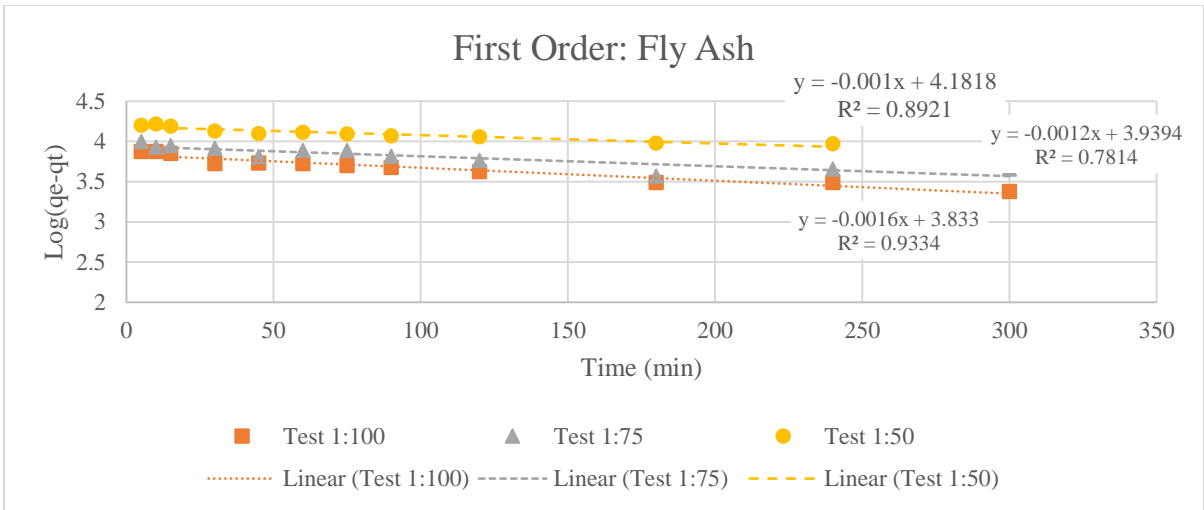


Figure 5.3-3: First Order for Fly Ash.

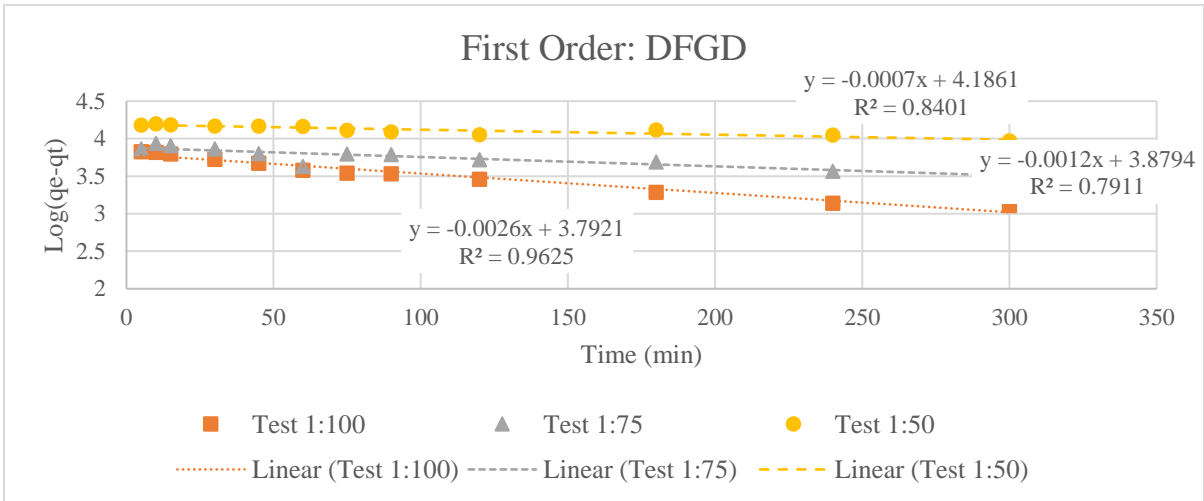


Figure 5.3-4: First Order for DFGD.

The first order model finds that slope =  $-\frac{k1}{2.303}$ ; therefore, the rate constant k can be taken from the average of the slopes for each ADSM. However, each line of fit has a different slope given the change in concentration of ADSM used in the kinetic trial. This points to the relationship between varying the amount of ADSM and the kinetic rate, and since ideal adsorption takes place in a packed column, the ratio of ADSM would be infinite compared to that of the nutrient rich water. Since adsorption would happen too quickly to be able to test a highly saturated ADSM, the R<sup>2</sup> value will be the deciding factor of the kinetic test. The R<sup>2</sup> value shows the consistency of adsorption for each ADSM, with the variation of time t and the variation in the amount of ADSM used.

Table 5.3: The average R<sup>2</sup> for each ADSM.

Adsorbent Material	Avg. R <sup>2</sup> Value	Score
<b>WTR</b>	.96	<b>4</b>
<b>ISRM</b>	.94	<b>3</b>
<b>Fly Ash</b>	.87	<b>2</b>
<b>DFGD</b>	.86	<b>1</b>

WTR has the largest R<sup>2</sup> values, which shows the consistency of adsorption through various amounts of ADSM used giving it the highest score.

#### 5.4 Environmental Impact Test Results

Table 5.4: The amount of each CWA element in adsorbent samples (mg/kg ADSM).

	Lead	Selenium	Arsenic	Zinc	Copper	Chromium	Nickel	Score
<b>DFGD</b>	9.575	4.040	6.535	47.220	47.108	30.545	18.7	<b>1</b>
<b>Fly Ash</b>	9.747	3.121	5.898	40.439	52.216	25.769	18.4	<b>2</b>
<b>ISRM</b>	2.585	0.541	6.757	28100	730.1	66.329	10.3	<b>3</b>
<b>WTR</b>	2.535	0.463	5.555	24400	1260	39.550	6.28	<b>4</b>

From the table, DFGD has the highest composition of potentially toxic metals. The arsenic and nickel are the most alarming because those metals have the smallest allowance of application as regulated by the CWA. WTR has the lowest compositions in these two categories, along with selenium and lead, giving it the highest score.

## 5.5 Final Ranking of Adsorbent Materials

The ADSMs can be ranked finally based on the scores received in all previous categories discussed.

Table 5.5: Scoring Chart, \*cells marked with an asterisk had already been eliminated as discussed in sections above.

<b>Adsorbent Material</b>	<b>Cost</b>	<b>Particle Size</b>	<b>Adsorption Potential</b>	<b>Kinetics</b>	<b>Environmental Impact</b>	<b>Total</b>
<b>LA</b>	6	5	3	*	*	<b>14</b>
<b>Dolomitic Limestone</b>	7	1	1	*	*	<b>9</b>
<b>Activated Carbon</b>	4	6	4	*	*	<b>14</b>
<b>WTR</b>	8	8	5	4	4	<b>29</b>
<b>ISRM</b>	8	7	6	3	3	<b>27</b>
<b>Fly Ash</b>	8	3	7	1	2	<b>21</b>
<b>DFGD</b>	8	3	8	2	1	<b>22</b>
<b>Biochar</b>	5	4	2	*	*	<b>11</b>

Through all the sections, WTR scored the highest overall, making it the ideal ADSM. The benefit of WTR being a waste stream would help the reduction of land filled material, introducing a green approach. Having to pelletize and dry the WTR allows for uniform pellets to be created which allows for good flow through a packed bed column. The adsorption potential for WTR, and the consistency of the adsorption kinetics show that WTR will be an effective ADSM. The reduced numbers of heavy metals show the lasting effect of application of the phosphorus rich WTR as a soil additive should not have adverse effects. These things together allowed for the scaling of a full-scale operation, and the testing of a bench scale system to model the full-scale apparatus.

## 6.0 FARM-SCALE INDUSTRIAL DESIGN

The farm-scale design is based off the average North Carolina swine CAFO with 4,603 feeder-to-finish swine<sup>20</sup>. From the Clemson University Swine Training Manual<sup>10</sup>, a flowrate was estimated for the average NC CAFO manure and wasted water, and flushing water.

Table 6.0: Flowrate Totals

Manure and Wasted Water	Flushing Water	Total Flowrate
7,537 gallons/day	81,889 gallons/day	62 gallons/min

The addition of these two streams yields a flow of 62 GPM into the swine lagoon. One note to make is that the manure and wasted water stream will contain some solids. These solids will fall to the bottom of the lagoon and the liquid volume at the top of the lagoon will be slightly lower than expected.

To determine the size of the packed columns needed for the full scale, the equilibrium maximum loading capacity of water treatment residuals of 8.47 mg phosphates adsorbed per kg of adsorbent was used. The system was designed to treat swine lagoon surface water for 30 days at 20 ppm orthophosphates. Once the water is treated through this system, the clean water should be at a concentration of 0.03 ppm phosphates or lower. This clean water can be recycled into the lagoon to reduce the amount of overall phosphates in the lagoon, used as flushing water, or undergo further treatment to be used as drinking water for the swine.

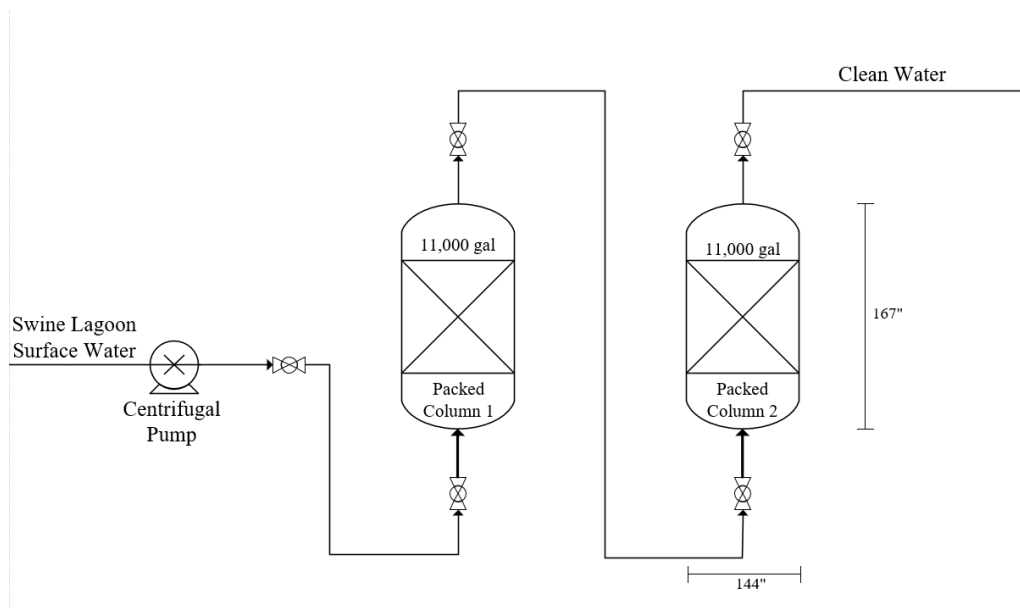


Figure 6.0-1: Full Scale Industrial Design

The amount of water treatment residuals needed per month is about 53,000 lbs. dry weight (due to tank sizes the amount used will be 54,100 lbs.). This will equate to a little over one truckload of dry WTR per month. Water treatment residuals are approximately 80% moisture upon production at a water treatment facility, which equates to about 264,000 lbs. (132 tons) wet weight WTR needed for the average NC swine CAFO per month. For the first month, double the amount of WTR will be needed to fill the two 11,000-gallon columns (54,100 lbs. of WTR to fill one 11,000-gallon polyethylene column). After the first month, only one column will become loaded and need to be emptied and replaced per month. The Beaver Water District in Fayetteville, AR treats about 55 MGD of water and produces about 7,800 tons of wet WTR annually. Using these numbers for the water treatment facilities in Raleigh, NC that treat about 67 MGD<sup>21</sup>, approximately 9,500 tons of wet WTR would be available for the surrounding area of CAFOs.

For the water treatment facility to benefit from the removal of the normally landfilled WTR, most of it would need to be used by CAFOs. One average sized CAFO could not use the full 9,500 tons available in the Raleigh area, but if several farms were using the same supply it could easily be done. The supply from Raleigh's water treatment facilities could provide six average sized CAFOs with WTR. These six farms could create an agricultural cooperative for WTR, that would create a more economic pelletizing and drying operation. This drying facility shown below in Figure 6.0-2 would be at a location near the water treatment facility to minimize costs of transporting the wet weight. The agricultural cooperative would pelletize and dry about 38 tons of wet WTR per day (5 days a week, 8 hours a day). The pelletized and dried WTR would then be loaded onto a truck and transported to the CAFO in need of new adsorbent material. Since the CAFOs will only need the new adsorbent material once a month, the excess made will be stored in hoppers awaiting need. Each CAFO would take exactly the amount of WTR needed per month (to pack a column) and would then return the phosphate loaded WTR to the cooperative at the end of the month. The cooperative would oversee the sale of the phosphate loaded WTR not needed by the CAFOs themselves as a soil additive.

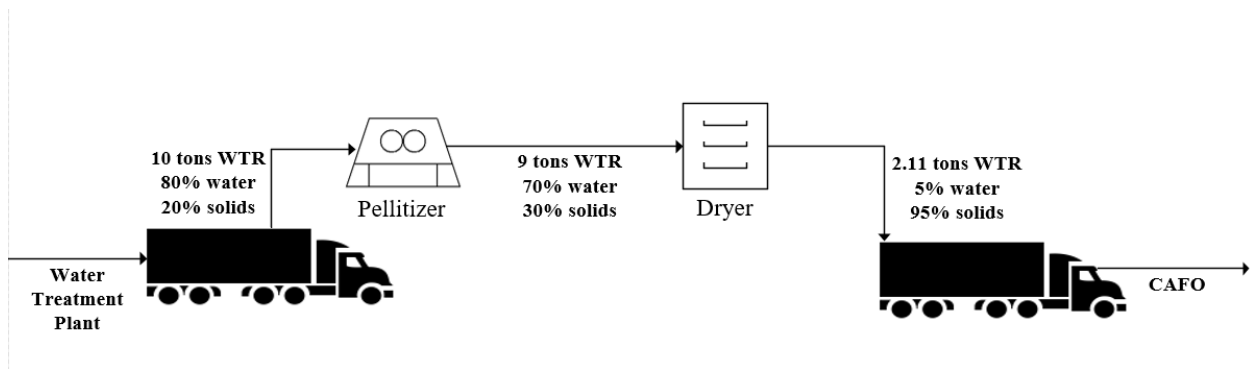


Figure 6.0-2: Adsorbent Preparation Facility (NOTE: The dryer will be a belt style and not a tray dryer as shown.)

## 7.0 BENCH SCALE APPARATUS

### 7.1 Packed Bed Column Design & Procedure

The bench scale is based directly off the full-scale design. This allows for the residence time to be the same for both processes ensuring the removal of the maximum phosphates possible. To determine the amount of WTR needed in a packed column, the basis of time was chosen. During the competition, 20 L of water will be treated in 12 hours. This means the volumetric flowrate of water needs to be roughly 28 mL/min. To have the same residence time as the full-scale system, 75 minutes, there needs to be a volume of 2,100 mL for the fluid to pass through. The void fraction of the pelletized WTR is 0.43, therefore, this gives the total volume of column needed to be 4,884 mL or 298 in<sup>3</sup>. Using 2-inch diameter piping, this gives a height of 96 inches. This height will be split between two columns and can be seen in the Figure 7.1 below.

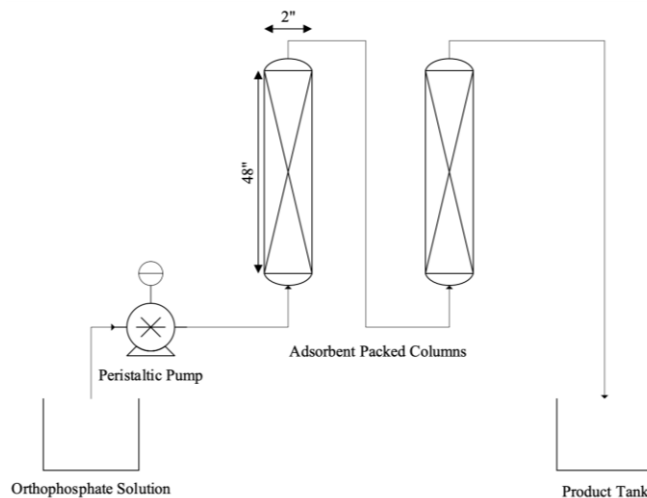


Figure 7.1: Bench-Scale Design.

The columns in the bench scale model were tested with orthophosphate solution through the bottom of the column, which allows for any air that is in the column to exit out the top. This should allow the fluid to only come into contact with the WTR pellets.

The peristaltic pump used for the bench scale is controlled with a variable speed drive, allowing the flow rate to be adjusted to that of the specific trial. This also ensures that the flowrate through the column stays constant through the entirety of the bench scale test.

To begin the preparation of the column, the pelletized WTR must be loaded into the column. This is done slowly to ensure the packing is as tight as possible to avoid channeling once flow is introduced. While packing, water is introduced to help settle the WTR in the column. Once the column is completely packed, it is sealed, and connected to the pump. Water is run through the system until the pump has been calibrated to the correct flowrate of 28 mL/min. After the pump is on the correct setting, the orthophosphate solution is introduced.

### **7.2 Packed Bed Column Testing Results**

One trial was run on the bench-scale packed bed column described in section 7.1, allowing for a little over 20 L of 20 ppm orthophosphate solution to pass through the system. For the entire test, the exit stream remained below a detectable level (0.01 ppm), which was the measurable limit of the hand-held device previously described. A total of 20.16 L was run through the system, allowing for a total phosphorus adsorbed during this time to be 402.3 mg.

## **8.0 ECONOMIC ANALYSIS**

For the economic analysis of this process, a basis was chosen to apply to a swine farm in North Carolina since the problem of phosphorus runoff is most abundant. With a file of all the registered feeder to finish swine facilities in North Carolina, the average number of swine per farm is 4,600. A farm in Sampson County, N.C. has exactly 4,600 swine registered, so that farm was chosen as the location for transportation costs.

Table 8.1: Cost Analysis

<b>Fixed Capital Investment</b>	<b>Cost of Manufacturing</b>	<b>Revenue</b>	<b>Net Present Value After 10 Years</b>
\$1,460,000	\$504,000	\$731,500	\$5,000

This cost would decrease if the owner were to take part in an agricultural cooperative that would effectively cut the cost of added labor, the pelletizer/dryer, land, and utilities attributed to the pelletizer/dryer by however many CAFOs were involved in the cooperative.

The economic benefits of using this system include saving money by recycling water, tipping fees from the water treatment company for taking water treatment residuals, and the sale of the water treatment residuals post adsorption as a soil additive. Most CAFOs already recycle lagoon water, so the monetary benefit is minimal with this system compared to current operation procedures. The tipping fees, which is the cost to dump waste into a landfill, from the Beaver Water District are \$60/ton residuals. An average of 9,500 tons per year would be estimated for the Raleigh, NC water treatment plants resulting in a yearly revenue of \$570,000 for the total cooperative facility. The nutrient saturated WTR would need to be further researched in terms of nutrient availability. It would have a theoretical ratio of 6-4-0. This ratio can be sold for \$15 per 32 pounds<sup>22</sup>. The bulk sale of this fertilizer will not be equal to specialty sale price, so a price of \$85/ton is used as the 10-year breakeven point. However, this is low in cost compared to the translation of other fertilizers up to bulk sizes, where MAP, DAP, and Potash all sell for \$400+ per ton<sup>23</sup>. At 1,900 tons of WTR per year total for six average sized CAFOs, the revenue is \$161,500/year from the sale of phosphate saturated WTR. The total revenue for the use of this phosphorus removal system is about \$731,500 per year per cooperative facility, or \$122,000 per year per CAFO.

## **9.0 ENVIRONMENTAL REGULATIONS AND CONCERNS**

One of the most significant issues when using recycled materials is that the composition of these materials changes, not only from location to location (such as gathering WTR from Fayetteville, AR, as compared to Little Rock, AR) but also from time to time. For instance, WTR is mainly composed of alum which is aluminum sulfate but is used to remove other materials out of the water. If the water is saturated with various chemicals, then this could have adverse effects on the application of the phosphate saturated WTR.

It was noted that water treatment residuals are composed mostly of Aluminum (approximately 15%). While Aluminum is not regulated by the CWA it can still cause harm to plants when soil pH is below 5. Due to soil pH being above 5 for optimum crop growth, this was deemed not an issue. Other elemental components of WTR include Magnesium, Phosphorus,



Scandium, Vanadium, Manganese, Iron, Cobalt, Gallium, Yttrium, Indium, Rhenium, Thallium, Bismuth, and Boron. Some of these heavy metals have the potential to increase plant toxicity. Most of the components are at low concentrations in the WTR, but more research should be done to determine the exact effects of land application of WTR in relation to plant toxicity. If toxic soil were to become an issue due to land application, a possible solution is bioremediation (the addition of microorganisms)<sup>24</sup>. However, using the ICP data that was previously mentioned, the following application limits can be calculated:

Table 9.1: Application limit of WTR (ton/acre/yr)

<b>Element</b>	<b>WTR (tons/acre/yr)</b>
Lead	2,570
Selenium	3,420
Arsenic	162
Zinc	4,940
Copper	4,450
Chromium	1,190
Nickel	620

While these application limits are high compared to the estimated 330 tons of phosphorus saturated WTR that would be produced at one average CAFO, the possibility of these materials building up in the soil would need to be researched further. However, the notion that WTR is used as an adsorption material has the benefit of the doubt in not allowing these materials to leech into a natural system.

The other application of the treated water stream is the potential possibility of bacteria, viruses, or microorganisms that might be present. This is something that has just become a concern from the EPA and could create some limiting factors in production. However, a fix would be UV treatment, ozone treatment, or a process like these. Even though this would require further treatment, it is possible that the economic benefit of treating this water for drinking water use would outweigh the cost of installing such a system.

## **10.0 CONCLUSIONS AND RECOMMENDATIONS**

Throughout the research conducted, WTR was the most economical and promising way to adsorb phosphates from water at such low concentrations. One thing to note is that depending on the region, the composition of the WTR could alter. WTR is made up of a coagulant called Alum and whatever solids are collected from the bottom of the water source - usually a lake. Since the chemical composition could change based on region, an ICP test should be conducted to determine the composition of the WTR that would be land applied to make sure it is in accordance with the Clean Water Act limits.

The adsorption properties could also change based on the changing composition of the WTR. Adsorption experiments should be conducted for the specific water treatment site in which the residuals are being produced.

While the task at hand was to remove 20 ppm phosphates from 20 Liters of water, the WTR should also function well in removing other unwanted concentrations of nutrients from the lagoon runoff water. Due to its adsorbent properties, once the WTR is used in a CAFO setting, the effectiveness of removing solely phosphorus could easily decrease. Experiments should be conducted using lagoon water specifically with the WTR to determine the effect of other concentrations on the adsorbent properties.

## **11.0 ACKNOWLEDGEMENTS**

The authors would like to thank the following individuals for their help and guidance: Dr. Michael Ackerson, Dr. Roy Penney, and Mr. James Barron for their advising; Dr. Andrew Sharpley from the Crop, Soil, and Environmental Sciences Department and Dr. Mark Healy from the College of Engineering and Informatics, National University of Ireland, Galway for providing the first set of samples of ISRM, Fly Ash, WTR, and DFGD; Dr. Tammy Lutz-Rechtin for safety assistance; Mr. J.M. Rice from North Carolina State University; Dr. Clinton Williams from the USDA; Dr. Lauren Greenlee from the Department of Chemical Engineering; Dr. Julie Stenken from the Department of Chemistry and Biochemistry; Mr. Jerry Genz from the Fayetteville Biosolids Management Site; Mr. Darryl Fendley from the Beaver Water District; Dr. Shannon Servoss from the Department of Chemical Engineering for lab equipment; Dr. Bob Beitle from the Department of Chemical Engineering; and Mr. John Moore.

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Civil Engineering,  
NUI Galway.

March 22, 2019.

RE: WERC 2019 – Removal and reuse of phosphorus as fertiliser from CAFO runoff.

Dear Team Members,

Thank you for the opportunity to review your submission. I think that it is an excellent piece of work and has been carefully executed. I particularly liked your approach to the selection of the media: the rating system you develop to take cognisance of the various physical-chemical properties of the media, and other factors such as cost and potential environmental impact, is very logical. Well done!

As you know, I reviewed a previous iteration of this report, so I am happy that, in most instances, my comments have been addressed. Therefore, my comments below are relatively minor.

- Formatting of the submission:  
The submission is, in general, very well organised. Good background is given to the topic, followed by discussion of the merits and demerits of existing treatment methods for CAFO wastewaters. This is then followed by discussion of the potential adsorption materials that were used in the report. I would suggest that you organise your ms into formal sections, which will be familiar to readers of academic papers and reports: Introduction, Materials and Methods (what you did in the study), Results and Discussion, and Conclusion. Therefore, consider current placement of Section 4.2 (Cost analysis) and Section 7.1 (Packed bed column design and procedure).
- Interpretation of results  
The interpretation of the results is very good. There are some minor issues, though. For example, you need to consider Section 5.3 (Kinetic test results). The idea of these studies is to see how long it takes for the media to adsorb a chemical (phosphorus, in this instance). Therefore, the best performing medium is the one that requires the shortest period of interaction to produce best results. The text in this section doesn't imply that this was considered.
- Environmental impact  
I like the section very much. However, I have some issues: it is currently unclear from the text (Section 9) whether you are proposing to land apply the P saturated WTR. If



this is the case, I would imagine that the P content of the residuals, and not the metal content, would limit the rate of application. In addition, if any medium is being considered for use in a filter, its ability to release metals into solution would be of most interest. While I think that the investigation of the metal content of the media is certainly valid, it really only gives half the picture: how it will perform in a filter may be not necessarily related to its native metal concentration.

- Field design

The field design section is well presented. There is an implication in the text (in Section 6) that the final effluent from a filter will have a P concentration below 0.03 ppm until saturation occurs. In reality, this would not be the case: as the P “saturation front” moves through the filter (i.e. as it becomes progressively more saturated), the exit P concentration will gradually increase until the exit concentration becomes equal to the inlet concentration.

Once again, congratulations on an excellent project. It was a pleasure to read it. I wish you every best for the competition and for the future.

Sincerely,

---

Dr Mark Healy  
Senior Lecturer in Civil Engineering,  
NUI Galway.

Email: [mark.healy@nuigalway.ie](mailto:mark.healy@nuigalway.ie)

March 22, 2019

Ms. Hannah Young  
Department of Chemical Engineering  
University of Arkansas  
Fayetteville, AR 72701

**RE: Removal and Reuse of Phosphorus as Fertilizer from CAFO Runoff by Water Treatment Residuals**

Dear Ms. Hannah Young,

Below is my review of your project.

**General Comments**

Overall, I was very impressed with the skills displayed by the student team. They exhibited a good knowledge of material chemistry and how it relates to nutrients and byproducts used in this study. The report was for the most part well written and most of my comments, which are detailed below, relate more to the basis for the project design and the knowledge of the drivers that affect phosphorus (P) removal and reuse from waste streams. The report would benefit from some simple restructuring to group methods in one section and result in separate section. This would help the reader (always a plus) and the flow of information. This restructuring could also help with clarity of presenting how the water is actually treated. It is confusing and seems a little conflicting as to whether it will be treated at source; i.e., lagoon water, or as field runoff. The restructuring already mentioned might help clarify the vision and pilot outcomes.

Some of the misconceptions of factors influencing eutrophication, CAFO permitting, and waste management stem from the Project Task, which was poorly designed and justified by New Mexico State University Faculty. Thus, many of my concerns relate to the inadequacies of the Task and should not reflect on the Teams performance. These concerns are;

1. Even in the arid regions of the U.S., it is unlikely that the manure produced in a CAFO is used for irrigation to supply water to the crop. Most likely it supplies a portion of the water but application rates are based on at least the nitrogen crop needs and usually limited even more due to soil P runoff concerns.
2. Liquid manure applications by CAFO's are to be made in accordance to Nutrient Management plans, which are designed to prevent runoff of manure. That is the basis of the storm water exemption for CAFOs.
3. The 20 ppm orthophosphate concentration noted in the Project Task is also concerning. This concentration is too high to represent rainfall induced field runoff water and too low to represent

liquid manure from the barns or the external holding ponds or lagoons even after rain water is added.

#### Audit Comments

**Economics:** The cost of construction and operation of the designed structures was justified in a clear and appropriate manner. Perhaps the economic assessment might consider costs based on the size of farm, i.e., number of hogs per farm. This can get complicated though as animal age will have a direct bearing on manure production. The bigger the pigs get the more they defecate. Cost comparison might also be made based on an individual farm or cooperative of several farm. As you correctly note, cost will be directly related to the availability of the source residual being used. This could vary regionally.


**Health:** There was no reference to any health impact on animal or plants to which the residual might be ultimately applied, thereby influencing the human food chain supply. Ecosystem health would also be another consideration. However, the main health risk would likely be from a component (i.e., metal contaminant) of the source residual used.

**Legal:** The main legal issues would center on the permitting process of land application of the treated residuals. This will vary depending on the source material. For example, there are currently strict guidelines/regulation on the application of water treatment residuals in Arkansas. These are based on health risks and the risks of contaminant transfer to waters of the U.S. Compliance with legal issues or regulations will vary from State to State, with some being more restrictive than others and in some cases more restrictive than a neighboring State. Compliance with regulations will have to be a major consideration in the development of any commercialized process.

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Sincerely,

  
Andrew Sharpley

Distinguished Professor, 2017 President of the Soil Science Society of America



March 24, 2019

Woo Pig Pooie Team  
Department of Chemical Engineering  
University of Arkansas, Fayetteville Arkansas

Task #5 - Removal and reuse of phosphorus as fertilizer from CAFO runoff

Thank you for the opportunity to review your paper and submit my comments. I hold a Class 3 waste water license and have six years' experience in water treatment residuals land application and biosolids fertilizer production. That scope of work includes permitting, compliance, sampling, application techniques, equipment purchase and maintenance for the City of Fayetteville. I also have worked in the EPA and OSHA compliance field for many years. I am a member of the Water Environment Federation and committee chairperson for the Arkansas Water Works and Water Environment Association.

The paper contains excellent research and attention to many details. The topics with less detail are discussed and an explanation or narrative is provided. It is obvious the team understands and demonstrated the potential of WTR to act as an ADSM for their prescribed application.

A few observations and comments:

Beneficial reuse of currently landfilled materials will become a greater focus in the future as landfills reach capacity. The result will be rising tipping fees, and eventually landfill operators selecting the materials allowed to be landfilled. I feel you may have burdened your economic analysis by not considering that increased revenue over the stated time frame.

More detail about the capital investment and cost of manufacturing would further demonstrate the value of your proposal. Again, I feel you may have burdened your economic analysis in the cost of manufacturing.

The phosphorous rich WTR will be sold and land applied as a fertilizer or soil amendment; either on the CAFO land or to area land owners. Would it be safe to assume the regulating agency will require permitting to land apply the WTR? The common "cradle to grave" responsibility of the generator; and in this case the applicator; could complicate the sale and application of the phosphorus rich WTR.

Section 10.0 covers my remaining thoughts concerning full-scale real-world application. Although you accomplished your task, the consideration of testing the actual waste stream compared to the 20ppm phosphate laden water is simply proper due diligence for the next phase of a very intriguing concept.

The body of work in your paper is exceptional. Very well done.

Sincerely;

Jerry Genz  
Lead Operator - Jacobs  
Fayetteville Biosolids Management Site

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March 13, 2018

Project Woo Pig Pooie Phosphorus as a Fertilizer Team  
Ralph E. Martin Department of Chemical Engineering  
University of Arkansas  
Fayetteville, AR

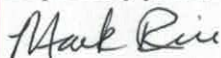
RE: Evaluation of Task 5; Removal and Reuse of Phosphorus as a Fertilizer from CAFO  
Runoff, WERC 2019

As requested I have reviewed your research paper on phosphorus removal from CAFO wastewater to  
reduce impacts to natural waterways and am pleased to offer the following observations;

1. You indicated that you were still working on the references, but be sure that they are numbered sequentially  
as they appear in the text.
2. Make sure your references are reliable, NC is not the top swine producer, although it has the top two swine  
producing counties (Duplin and Sampson Counties). Iowa has three times as many pig and market value.  
USDA, Ag Statistics would be a more reliable reference than National Geographics.  
([https://www.nass.usda.gov/Publications/Highlights/2014/Hog\\_and\\_Pig\\_Farming/index.php#industry](https://www.nass.usda.gov/Publications/Highlights/2014/Hog_and_Pig_Farming/index.php#industry)).
3. Be sure your references are as current as possible. The Clemson University Swine Training Manual that is  
referenced in based on waste characteristic data from 1998. Unfortunately, in this situation I am not aware  
of a more current source of data. Before I would recommend that a producer (or group of producers) invest  
in a system it would be prudent to perform the economic feasibility with current data from the farm.
4. The treatment options presented in the paper are well thought out and presented for consideration as is the  
methodology for selection.
5. I appreciate the systems approach undertaken here to incorporate waste and byproducts from multiple sectors  
of agriculture and municipal sources into a product that has as much value as a soil amendment.

In summary, you have done an admirable amount of work studying the alternative treatment and recovery  
options, and the solution you propose appears to be well thought out, easily implemented and minimizes  
cost/return. Your solution addresses technical, economic, health and environmental issues and is worth of  
further consideration, as you acknowledge, under site specific conditions.

Respectfully yours,



Mark Rice

Director, Animal and Poultry Waste Management Center, NCSU