

## **Solids Reduction Process for Agricultural Effluent – A Laboratory Feasibility Study**

### **ABSTRACT**

Process steps of flocculation, filtration and centrifugation are investigated to better utilizing existing storage capacity of agriculturally based effluents and at the same time minimize the environmental impact of agricultural operations.

As flocculant  $\text{Ca}(\text{OH})_2$  as a 20% solution,  $\text{FeCl}_3$  as a 30% solution, and  $\text{Al}_2(\text{SO}_4)_3$  as a 20% solution were used.

The solids content of the liquid manure, having a preadjusted pH of 9.5, resulted in a reduction of up to 46.8% with centrifugation.

For all flocculants, the 20%  $\text{Ca}(\text{OH})_2$  solution, the 30%  $\text{FeCl}_3$  solution, and the 20%  $\text{Al}_2(\text{SO}_4)_3$  solution resulted in a decrease of the solids content of the liquid manure.

$\text{FeCl}_3$  as flocculant reduced the solids content by 45%,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Ca}(\text{OH})_2$  as flocculant by 21.0% after the second centrifugation process. Filtration as the fourth process step reduced the solids content further by 31.6% for the  $\text{Ca}(\text{OH})_2$  flocculant, whereas for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  as flocculant and increase of the solids content by 18.2% and 2.5% respectively resulted.

The flocculant  $\text{Ca}(\text{OH})_2$  outperformed  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  by 71.2%, 65.4%, and 56.9% respectively.

A Maximum COD removal rate of 47/8% could be realized without flocculant and 70.6% COD removal rate could be utilized using  $\text{FeCl}_3$  as flocculant applying a second centrifugation process.

*Keywords: Agricultural effluent, Aluminum sulfate calcium hydroxide, centrifugation, contaminants, ferric chloride, flocculation*

### **1. INTRODUCTION**

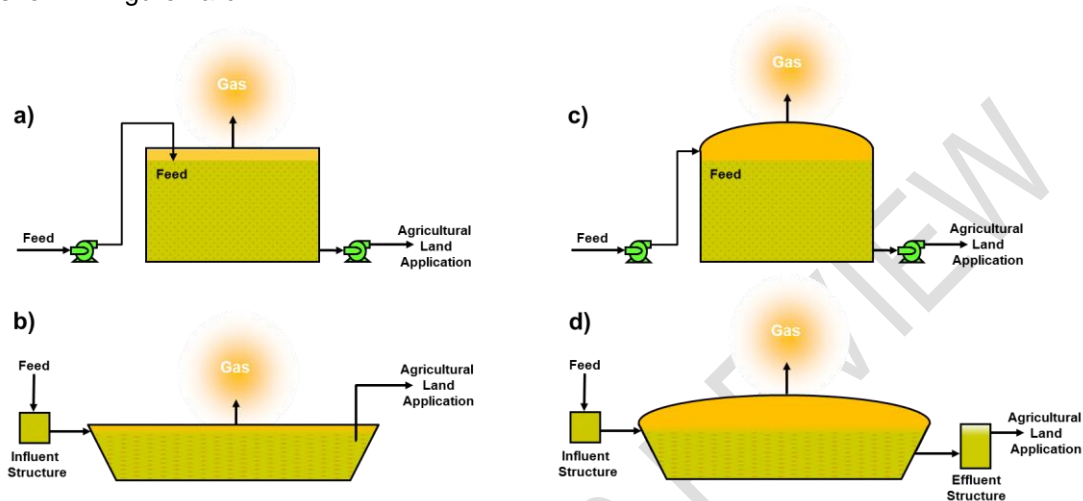
Clean water is one of the most significant challenges our world faces in the future. Life without clean water is not sustainable pertains to clean water. Water pollution affects local wildlife and us humans equally and we all should work on minimizing and perhaps eliminating waste and water pollution [1].

Sustaining the natural beauty and quality of our water bodies is today's biggest challenge with ever growing urban and suburban developments closer to existing and expanding industrial agricultural operations [2]. To compete in the agricultural market segment, farm operations have to become more mechanized and intensive and therefore use more fossil fuel, antibiotics, synthetic fertilizer and pesticide to yield high production levels and at the same time increase their environmental footprint by contaminating air, depletion soil fertility through monocultures, and contaminate water bodies [3,4].

released phosphorus from agricultural application due to overfertilization can lead to algae blooms mostly during warm summer month, eutrophication, and bacterial growth in drinking water [5,6], leading to an increase of nutrient levels in streams and lakes, changing them from oligotrophic to eutrophic [7]. All this can create dead zones in inland water bodies with

the result that valuable ecosystems of inland waterbodies are destroyed affecting negatively wildlife, human health, and the economy at the same time [8-10].

Today industrial dairy, beef, swine and poultry operations use uncovered lagoons or vessels as the primary storage for agricultural residues. [11,12]. Figure 1 shows exemplary a process sketch of such a lagoon or vessel system. The feed liquid (livestock residue) is either pumped into the storage vessel or enters the lagoon through an influent structure as shown in figure 1a-c.



**Fig. 1: Process Sketch of an Agricultural Storage System [13]**

the solids content of 1.0% to 6.0% [14,15] for most applications but can be as high as 12% if sand is used as the primary bedding material for the livestock operation. However, the pretreated manure enters the lagoon or storage vessel at around 0.5 to 2% solids content [16, 17].

Agricultural storage systems are generally not heated and operate at ambient temperatures [16] with retention times of 1 to 50 days depending on lagoon size [16, 18], but can also be up to 360 days depending on the facility management and imposed regulatory measures [19].

Mainly in spring and fall residue content (manure) in the lagoon is pumped out and land applied onto agricultural fields with spreading vessels and/or sprayer systems. During the manures storage time anaerobic fermentation occurs and a gas consisting primarily of methane gas ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and ammonia ( $\text{NH}_3$ ) is released into the atmosphere [14,15,20]. All these gases contribute to global warming. According to the United States Environmental Protection Agency (EPA)  $\text{N}_2\text{O}$  stay approximately for 114 years in the atmosphere before destroyed by a sink or chemical reaction and has a 100-year Global Warming Potential (GWP) of 298 compared to  $\text{CO}_2$  [21]. In comparison has a GPW of 28-36 [21].

Beside Green House Gas (GHG) emissions lagoon systems account for odor emissions through releasing  $\text{NH}_3$  which is converted into  $\text{N}_2\text{O}$  and contributes to Particulate Matter (PM) with a size  $25 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) [22]. This requires locating the lagoon in remote areas. Lagoon systems require relatively long retention times and a large area of land to build. In addition, they can provide seepage into the groundwater if not professionally lined [17].

To reduce air emission of agricultural storage systems a cover can be added. This allows to operate the agricultural storage system as an Anaerobic Digester (AD) system under semi plug flow operational conditions as shown in Figure 1c and 1d and convert the collected biologically produced gas it into electricity and heat that can offset the agricultural operations energy requirements.

This research project explores a concept that might allow agricultural entities to improve their operation and environmental footprint by better utilizing existing storage capacity for agriculturally based effluents by applying centrifugation, flocculation and filtration before the agricultural effluent is stored. Optimizing the storage capacity available at agricultural facilities might lead to more efficient operation, flexibility, and improvement for land applications.

## 2. MATERIAL AND METHODS

The material and methods section describes the materials, laboratory type equipment, procedures and analytical methods that were used for this research on studying an new approach on a Cleaning Process for Agricultural Effluents (CPAE).

### 2.1. Influent Materials

Cow manure was sampled from the State University of NEW York Dairy Farm operation in Morrisville, NY.

To simulate dewatering in the laboratory; a) a hand operated fruit and vegetable screw press with 3 mm holes in the dewatering screen and b) a regular T-Shirt fabric was used to simulate a screw press operation.

For simulating an industrial decanter process a Thermo Scientific Sorfall T1 laboratory centrifuge was used.

A 20% Calcium Hydroxide  $\text{Ca}(\text{OH})_2$  solution is prepared in distilled water and is used to adjust the pH of the manure as well as flocculation agent.

Iron Chloride ( $\text{FeCl}_3$ ) in a 30% solution is used as a second flocculation agent.

Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) prepared in a 20% solution is used as a third flocculation agent.

A 150 mm syringe with an drilled metal disc as support for the filter paper is used to simulate the filtration process.

Whartman No. 4 filter paper with a pore size of 20-25  $\mu\text{m}$ . for filtering the processed wastewater. The filter paper is cut to a diameter of 30 mm to fit in the 150 ml syringe.

### 2.2. Laboratory Testing Procedures

The Chemical Oxygen Demand (COD) was measured according to HACH Method 8000 [23] using HACH COD TNTplus® Spectrophotometer Vial Test with a range of 3-150.0 mg/L.

The HACH TNTplus® test vials were heat treated with a HACH DRB200t according to the HACH 8000 Test Method, followed by analyses using a HACH DR900 Spectrophotometer.

The total Solids (TS) content was measured in triplicate. Each test sample was measured using a marked and weighted 300 ml aluminum sample container. For each test approximately 200 ml to 220 ml of the prepared substrate was added to each of the three corresponding aluminum sample containers, followed by weighting of the sample containers. The containers were then placed in a  $\sim 105^\circ\text{C}$  oven to dry for 48 hours to evaporate the moisture. After drying, the sample containers were weight again to determine the dry weight measurement. The remaining solids in the sample containers represented the TS content of the substrate.

Temperature and pH measurements were conducted using a portable Milwaukee MW102 pH/temperature meter.

### 2.3. Preparation of Selected Influent Substrates

To determine the working capacity of the CPAE the collected agricultural manure was preprocessed to remove the large organic content by simulating an agricultural screw press operation. The liquid effluent of the simulated screw press operation was the used for the subsequent study of centrifugation, flocculation and filtration.

The original Manure and the pre-processed manure effluent was stored in a cold room at 5.0°C (41.0°F) until they were processed. Prior to usage the substrates were brought to room tempered 23.0°C (73.4°F) in the sampling container.

#### 2.4. Centrifugation Procedure

To simulate a industrial decanter process a laboratory centrifuge was used. For centrifugation an evaluation the material was centrifuged at 1500g for total of 6 minutes including the start-up time till the centrifuge reached 1500g and the break time till the centrifuge came to a complete stop.

#### 2.5. Filtration Procedure

For the filtration a 300 ml laboratory syringe was used that that had a drilled metal plate on the bottom as support for No. 4 Warthman filter paper with a pore size of 20-50 µm.

#### 2.6. Testing Procedure

Testing followed the procedure shown in Figure 2., which outlines the different process stages involved in evaluating the CPAE process.

The first stage evaluated TS, COD of the preprocessed agricultural manure which is used for the subsequent process stages. The second stage involves centrifugation of the preprocessed agricultural manure and measuring TS, COD of the supernatant. The third stage involves a flocculation process. After Stage 3, the sample is centrifuged again and TS, COD is measured of the supernatant. In the last stage 4, the supernatant is filtered with an 80µ filter paper, and the TS and COD is in measured of the supernatant.

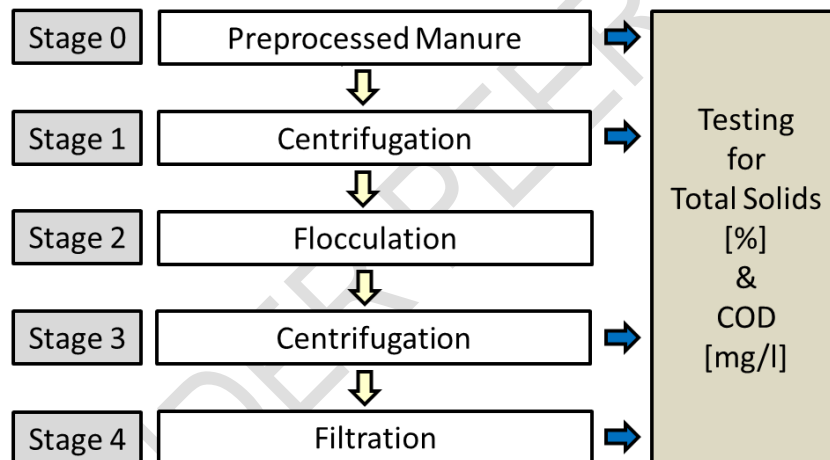


Fig. 2: Testing Procedure.

### 3. RESULTS AND DISCUSSION

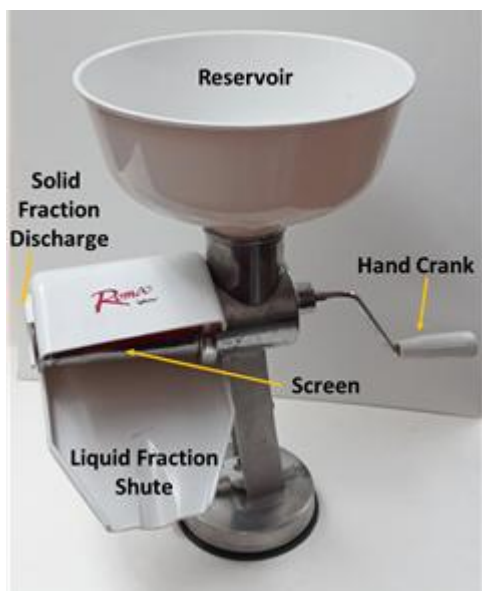
The following chapter summarizes and compares the processes and effluent qualities of the CPAE application.

For this research the initial pH of the manure was 7.5 for the first process step of centrifugation. After centrifugation the pH of the liquid manure supernatant was adjusted to a pH of 9.5 in a 500 ml beaker by using a 20% Ca(OH)<sub>2</sub> solution. After pH adjustment the flocculant Ca(OH)<sub>2</sub> as a 20% solution, FeCl<sub>3</sub> as a 30% solution, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as a 20% solution was added in the flocculation stage. After flocculation the manure supernatant was centrifuged for a second time. The supernatant from the second centrifugation was then filtered using a modified syringe to simulate a pressurized filtration process.

For all process stages pH, TS, COD for the supernatant was measured. For the solid phase the TS was measured.

### 3.1. Manure Preprocessing

The preprocessing process for the collected manure includes a separation process for the removal of large undigested organic compounds. In order to simulate an industrial mechanical separation process in the laboratory two approaches were used. First a hand operated Roma Fruit and Vegetable Screw Press (FVSP) with 2.0 mm holes in the dewatering screen, as shown in Figure 3.



**Fig. 3: Fruit and Vegetable Screw Press [24]**

The second procedure utilized a T-Shirt fabric cut into a 50 cm x 50 cm (20 in x 20in) square Dewatering Cloth (DC) in which the liquid manures is filled prior to dewatering.

The operation of the FVSP and DC is shown in Figure 4a and 4b.

The resulting liquid manure effluent and manure solid fraction from the FVSP and DC is shown in Figure 4c and 4d.

Prior to dewatering the solids content of the manure obtained from the SUNY Morrisville dairy operation was measured at consistency of  $13.2 \pm 0.2\%$ .



**Fig. 4: Laboratory Manure Dewatering, a) Laboratory Screw Press, b) T-shirt, c) Liquid Manure Effluent, d) Solid Manure Effluent [25]**

### **3.1.2. Dewatering with a Laboratory Screw Press**

For the operation of the FVSP, shown in Figure 4a, two liters of the manure was fed in the reservoir of the FVSP. Then the hand crank of the FVSP was turned and the manure was transferred with the screw into the conical screen. The pressure applied by the screw feeding the manure into the conical screen dewatered the manure. The pressed solids exit the screen plate at the end and the liquid is squeezed out through the holes in the conical screen plate.

However, at a consistency of  $13.2 \pm 0.2\%$  the FVSP was not able to dewater the manure and plugged the FVSP. Therefore, various dilutions of the manure to consistency of 12%, 10%, 7.5% and 5% were tried. A solids content of 5% of the manure gave satisfactory dewatering results in operating the FVSP.

### **3.1.2. Dewatering with a Dewatering Cloth**

For manure dewatering using a DC, the DC was used to line a two-liter bucket. One liter of the manure with an original solids content of  $13.2 \pm 0.2\%$  was poured into the DC. The DC was closed on the top and then wringed to dewater the manure pressing the liquid through the DC and leaving the solids in the DC. However, manure at a consistency of  $13.2 \pm 0.2\%$  was not able to be dewatered very well with the DC. Therefore, the same dilutions of the manure to consistencies of 12%, 10%, 7.5% and 5% were tried as for the FVSP. At a solids content of 8% the manure gave satisfactory dewatering results for using a DC

### **3.1.3. Dewatered Manure**

Final dewatering of the collected manure for the FVSP and DC as shown in Figure 3, process was done at 5% solids to keep both processes influences the same.

Dewatering with the FVSP achieved a solids content of up to  $18.11 \pm 0.2\%$  in the press ate and  $3.5 \pm 0.2\%$  in the liquid effluent. Whereas dewatering using a DC achieved a solids content of up to  $24.11 \pm 0.2\%$  and  $3.5 \pm 0.2\%$  in the liquid effluent.

Both the FVSP and DC are dewatering options for simulating laboratory dewatering. However, the DC method reaches higher dryness levels comparable to commercial dewatering devices [xx]. Therefore, the DC method was used for all subsequent approaches in providing the dewatered liquid effluent for this study.

The produced liquid manure effluent with the DC method used for this study resulted in a solids content of  $3.5\% \pm 0.2\%$  and a COD content of  $15,000 \pm 50$  mg/l.

The produced manure effluent and the original manure were stored in a cold room at  $5.0^\circ\text{C}$  ( $41.0^\circ\text{F}$ ). Before they were used they were transferred in a separate container and heated slowly during a two hour period to a room temperature of  $23.0^\circ\text{C}$  ( $73.4^\circ\text{F}$ ) by using a stirring hot plate.

### 3.2 Measurement of pH and Conductivity based on Flocculant used

Prior to performing the different process steps of centrifugation, flocculation, centrifugation and filtration a titration was performed to investigate the usage of the flocculants.

For measuring pH and conductivity 500 ml of liquid manure stored at  $5.0^\circ\text{C}$  with a  $3.5\% \pm 0.2\%$  was sampled and heated slowly to a temperature of  $23.0^\circ\text{C}$  ( $73.4^\circ\text{F}$ ) prior to performing the experiment. From the liquid manure at  $23.0^\circ\text{C}$  ( $73.4^\circ\text{F}$ ) 100 ml were sampled into a 100 ml beaker for each of the three titration experiments with the flocculants  $\text{Ca}(\text{OH})_2$  as a 20% solution,  $\text{FeCl}_3$  as a 30% solution, and  $\text{Al}_2(\text{SO}_4)_3$  as a 20% solution, prior to testing.

#### 3.3.1 Calcium Hydroxide

Figure 5 shows, that for adding a 20%  $\text{Ca}(\text{OH})_2$  solution the pH of the liquid manure increases steadily by adding the  $\text{Ca}(\text{OH})_2$  solution up to a pH of 11.77 for the addition of 5 ml. the conductivity decreased first from 18.20 mS/cm to 15.25 mS/cm at the addition of 4ml  $\text{Ca}(\text{OH})_2$  Solution at a pH of 9.63 and then increased to 18.26 mS/cm at a pH of 11.77. No discoloration of the liquid was observed after the flocs in the 100 ml beaker settled.

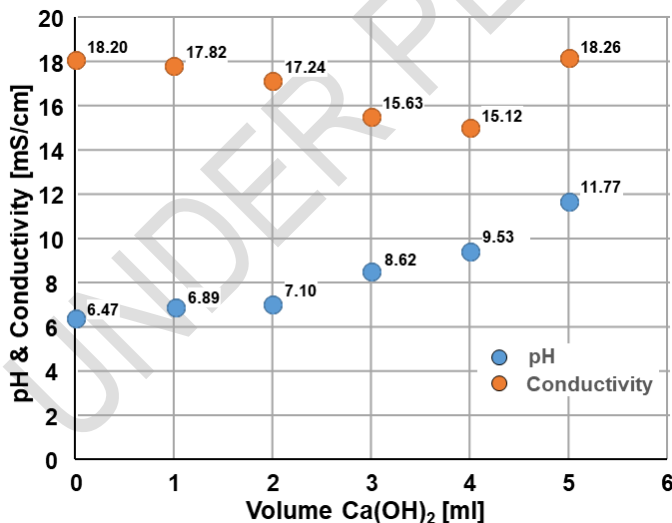


Fig. 5: Liquid manure titration with  $\text{Ca}(\text{OH})_2$

#### 3.3.1 Iron Chloride

Figure 6 shows that for adding a 30%  $\text{FeCl}_3$  solution the pH of the liquid manure decreases steadily from an initial pH of 6.68 to a pH of 3.58 for the addition of 1 ml  $\text{FeCl}_3$  solution. The conductivity decreased from 16.94 mS/cm rapidly to 6.90 mS/cm when 0.1 ml of  $\text{FeCl}_3$  solution are added, followed by a steadily increase to 11.25 mS/cm at the addition of 1ml  $\text{FeCl}_3$  solution and a resulting pH of 3.58. Flocculation started below a pH of 6.5 with good flocculation and visibility of large flocs at a pH below 6.0. at a pH below 5.5. It was noticed that the liquid after the flocs settled in the 100 ml beaker, turned into a yellowish red color, indicating an overdose of the flocculant.

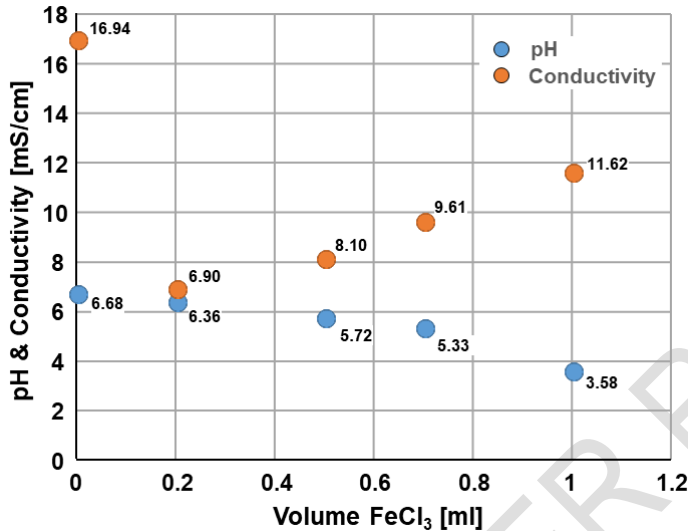
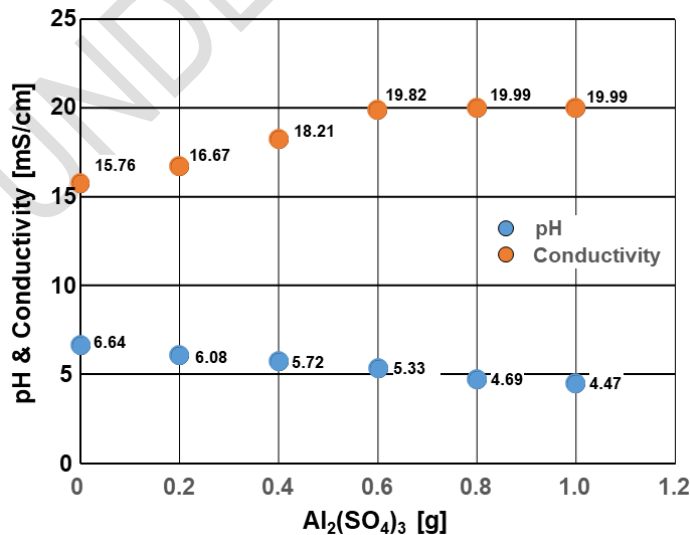


Fig. 6: Liquid manure titration with  $\text{FeCl}_3$

### 3.3.1 Ammonium Sulfate

Figure 7 shows, that for adding a 20%  $\text{Al}_2(\text{SO}_4)_3$  solution the pH of the liquid manure decreases steadily from an initial pH of 6.64 to a pH of 4.47 for the addition of 1 ml  $\text{Al}_2(\text{SO}_4)_3$  solution. The conductivity increases steadily from 15.76 mS/cm to 19.99 mS/cm when 1.0 ml  $\text{Al}_2(\text{SO}_4)_3$  solution is added. Flocculation started below a pH of 6.5 with good flocculation and visibility of large flocs at a pH below 6.0. No discoloration of the liquid was observed after the flocs in the 100 ml beaker settled.



**Fig. 7: Liquid manure titration with  $\text{Al}_2(\text{SO}_4)_3$**

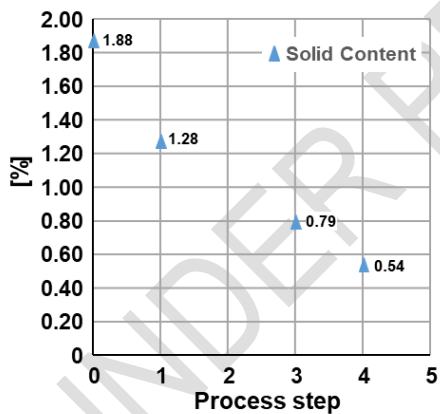
Titration of the liquid manure with the different flocculants  $\text{Ca}(\text{OH})_2$  as a 20% solution,  $\text{FeCl}_3$  as a 30% solution, and  $\text{Al}_2(\text{SO}_4)_3$  as a 20% solution showed that the liquid manure acts as a buffer and a minimum of 0.4 ml of the liquid solution for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  had to be added till flocculation occurs. For  $\text{Ca}(\text{OH})_2$  a pH above 10 and a minimum of 4ml was needed to start flocculation.

### 3.3 Measurement of Solids Content based on Flocculant used

The liquid manure stored at  $5.0^\circ\text{C}$  with a  $3.5\% \pm 0.2\%$  was diluted with tap water for better processing, and then heated slowly to a temperature of  $23.0^\circ\text{C}$  ( $73.4^\circ\text{F}$ ). Prior tests showed that a liquid manure solids content between 1.6% and 2.0% works best with the laboratory procedures in place. The final solids of the diluted manure used for the following study was 1.88%. From the diluted manure three 500 ml samples were prepared for each of the three flocculants  $\text{Ca}(\text{OH})_2$ ,  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  prior to testing the 4 process steps.

#### 3.3.1 Calcium hydroxide as Flocculant

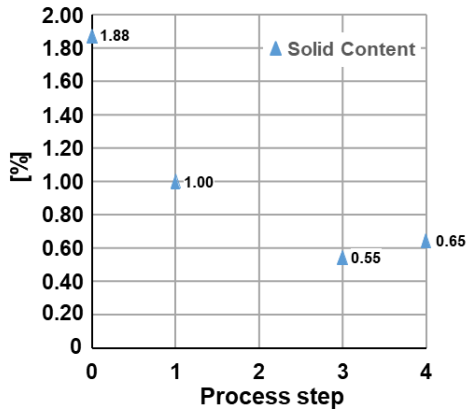
Figure 8 shows, that for  $\text{Ca}(\text{OH})_2$  as flocculant the SC in the supernatant decreased from 1.88% to 1.28% after the first centrifugation step. Adding additional  $\text{Ca}(\text{OH})_2$  solution as flocculant to the supernatant from the first process step during the second process step increased the pH to 10.5 and additional flocculation occurred. A second centrifugation in process step 3 decreased the COD in the supernatant to 0.79%. In the fourth process step the supernatant from the third process step was filtered using a syringe and a filter paper which resulted in a final SC of the supernatant of 0.64%.



**Fig. 8: Liquid manure solids content using  $\text{Ca}(\text{OH})_2$  as flocculant**

#### 3.3.2 Ferric Chloride as a Flocculant

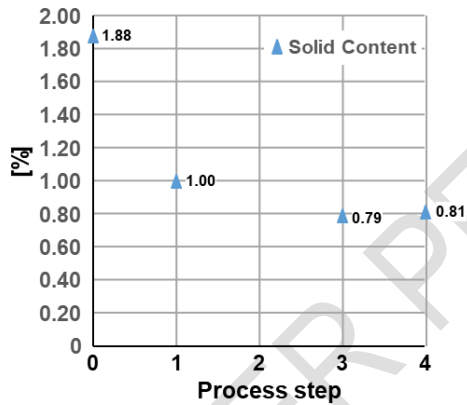
The first process step of centrifugation of the liquid manure at a pH of 9.5 resulted in a SC of 1.28% of the supernatant as shown in Figure 9. Titrating a 30%  $\text{FeCl}_3$  solution, in process step 2 as flocculant resulted in a pH of 6.1 with good visible flocculation. The second centrifugation in process step 3 decreased the SC in the supernatant 0.79%. Filtration of the supernatant from the third process step lower the SC to 0.54% in the fourth process step.



**Fig 9.: Liquid manure solids content using  $\text{FeCl}_3$  as flocculant**

### 3.3.3 Aluminum Sulfate as a Flocculant

When  $\text{Al}_2(\text{SO}_4)_3$  was titrated as a flocculant to the liquid manure in process step two a pH of 6.4 resulted and good visible flocculation occurred. Figure 10 shows, that prior to flocculation the SC was reduced from 1.88% to 1.00%. After the second centrifugation in process step 3, a SC in the supernatant of 0.55% resulted. Filtration of the supernatant from the third process step increased the SC to 0.65% in the fourth process step.



**Fig. 10: Liquid manure solids content using  $\text{Al}_2(\text{SO}_4)_3$  as flocculant**

Based on the above results, centrifugation without flocculation but pH adjustment to pH 9.5 using 20%  $\text{Ca}(\text{OH})_2$  solution, resulted in a SC range between 1.00% to 1.28% or a solids content reduction between 31.9% and 46.8%. Based on the overall SC reduction achieved after the first centrifugation process.  $\text{FeCl}_3$  as flocculant reduced the SC by 45%,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Ca}(\text{OH})_2$  as flocculant by 21.0% after the second centrifugation process. Filtration as the fourth process step reduced the SC further by 31.6% for the  $\text{Ca}(\text{OH})_2$  flocculant, whereas for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  as flocculant and increase of the SC by 18.2% and 2.5% respectively resulted.

Based on the initial SC of 1.88%  $\text{Ca}(\text{OH})_2$  outperformed  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  by 71.2%, 65.4%, and 56.9% respectively.

The increased solids content for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  could be explained with the precipitation during the flocculation process of Iron Phosphate ( $\text{FePO}_4$ ), Calcium Phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), Ammonium Sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) ( $\text{NH}_4\text{MgPO}_4$ ) from the Ammonia ( $\text{NH}_3$ ), Magnesium (Mg) and Phosphorous (P) present in the liquid manure. The precipitated  $\text{FePO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{MgPO}_4$  crystals could not be completely removed by

either the centrifugation g-force used in this study as well as the Whartman No. 4 filter paper with a pore size of 20-25  $\mu\text{m}$  which was not able to filter out the small, precipitated particles.

### 3.4. COD with different Flocculants

As shown in Figure 11, the COD of the liquid manure was 8050 mg/l at an initial SC of 1.88% prior to the individual process steps of centrifugation flocculation second centrifugation, and filtration as shown above in Figure 2.

The pH of the liquid manure was adjusted for all flocculants prior to processing to a pH of 9.5 with a 20%  $\text{Ca}(\text{OH})_2$  solution.

#### 3.4.1 Calcium Hydroxide as Flocculant

For  $\text{Ca}(\text{OH})_2$  as flocculant the COD in the supernatant decreases to 5845 mg/l after the first centrifugation step. Adding additional  $\text{Ca}(\text{OH})_2$  solution as flocculant to the supernatant from the first process step during the second process step increased the pH to 10.5 and additional flocculation occurred. A second centrifugation in process step 3 decreased the COD in the supernatant to 3345 mg/l. In the fourth process the supernatant from the third process step was filtered using a syringe and a filter paper which resulted in a final COD of the supernatant of 2670 mg/l.

#### 3.3.4 Ferric Chloride as a Flocculant

The first process step of centrifugation of the liquid manure at a pH of 9.5 resulted in a COD of 4760 mg/l of the supernatant. Titrating a 30%  $\text{FeCl}_3$  solution, in process step 2 as flocculant resulted in a pH of 6.1 with good visible flocculation. The second centrifugation in process step 3 decreased the COD in the supernatant to 2370 mg/l. Filtration of the supernatant from the third process step did not change the COD. The COD value stayed at a level of 2370 mg/l in the fourth process step.

#### 3.3.5 Aluminum Sulfate as a Flocculant

When  $\text{Al}_2(\text{SO}_4)_3$  was titrated as a flocculant to the liquid manure in process step two a pH of 6.4 resulted when good visible flocculation occurred. Prior to flocculation the COD was reduced from 850 mg/l to 4200 mg/l. After the second centrifugation in process step 3, a COD in the supernatant to 3385 mg/l resulted. Filtration of the supernatant from the third process step increased the COD to 3480 mg/l in the fourth process step.

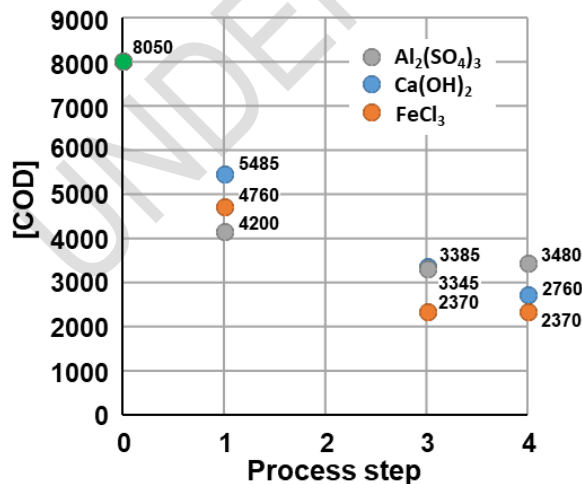


Figure 11: Chemical Oxygen Demand of supernatant after the different process steps using  $\text{Ca}(\text{OH})_2$ ,  $\text{FeCl}_3$ , and  $\text{Al}_2(\text{SO}_4)_3$  as Flocculant.

Based on the above results, centrifugation without flocculation but pH adjustment to pH 9.5 using 20%  $\text{Ca}(\text{OH})_2$  solution, resulted in a COD range between 4200 mg/l to 5485 mg/l. Based on the overall COD reduction after the first centrifugation process,  $\text{FeCl}_3$  as flocculant resulted in the highest COD reduction of 50.2%, followed by  $\text{Ca}(\text{OH})_2$  with 49.7% and 17.1% for  $\text{Al}_2(\text{SO}_4)_3$  as flocculants. Based on the initial COD of 8050 mg/l,  $\text{FeCl}_3$  outperformed  $\text{Ca}(\text{OH})_2$  and  $\text{Al}_2(\text{SO}_4)_3$  by 70.6%, 65.7%, and 56.85% respectively.

## CONCLUSION

Agricultural operations produce effluents that are stored in lagoons and vessels prior to the field application for fertilization. Over fertilization from agricultural applications can cause negative effects on water bodies such as algae bloom and eutrophication.

To minimize overfertilization agricultural effluents put on the field need to be minimized. This research project investigated process steps of flocculation, filtration and centrifugation can help to decrease the effluents quantity that is put on agricultural fields and might allow agricultural entities to improve their operation and environmental footprint by better utilizing existing storage capacity for agriculturally based effluents.

Titration of the liquid manure with the different flocculants the flocculants  $\text{Ca}(\text{OH})_2$  as a 20% solution,  $\text{FeCl}_3$  as a 30% solution, and  $\text{Al}_2(\text{SO}_4)_3$  as a 20% solution showed that the liquid manure acts as a buffer and minimum of 0.4 ml of the liquid solution for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  had to be added till flocculation occurs. For  $\text{Ca}(\text{OH})_2$  a pH above 10 and a minimum of 4ml was needed to start flocculation

The SC of the liquid manure, with a preadjusted pH of 9.5, could be reduced by up to 46.8% with centrifugation.

For all flocculants, the 20%  $\text{Ca}(\text{OH})_2$  solution, the 30%  $\text{FeCl}_3$  solution, and the 20%  $\text{Al}_2(\text{SO}_4)_3$  solution resulted in a decrease of the SC of the liquid manure.

$\text{FeCl}_3$  as flocculant reduced the SC by 45%,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Ca}(\text{OH})_2$  as flocculant by 21.0% after the second centrifugation process. Filtration as the fourth process step reduced the SC further by 31.6% for the  $\text{Ca}(\text{OH})_2$  flocculant, whereas for  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  as flocculant and increase of the SC by 18.2% and 2.5% respectively resulted.

The flocculant  $\text{Ca}(\text{OH})_2$  outperformed  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  by 71.2%, 65.4%, and 56.9% respectively. However, a high pH in the supernatant may add an additional costly process step.

Based on the results a centrifugation without flocculation can remove up to 47.8% of the COD. A Maximum COD removal rate of 70.6% using  $\text{FeCl}_3$  as flocculant could be archived with a second centrifugation process.

By applying centrifugation, flocculation and filtration to the liquid manure solids from the manure can be separated and reduce the liquid that needs to be stored and may optimizing the storage capacity available at agricultural facilities. This might lead to more efficient operation, flexibility, and improvement for land applications.

Future research should focus on combining the individual flocculants to achieve maximum COD and solids removal, explore the utilization of the liquid and solid fraction separate as fertilizer and or value added product and the associated environmental impact, as well as process cost associated with the individual process steps.

## REFERENCES

1. U.S. Environmental Protection Agency. Nutrient Pollution. Accessed May 25, 2023. Available: <https://www.epa.gov/septic/how-care-your-septic-system>
2. Dölle K, & Lex S. Application of a Sludge Blanket Reactor for Effluent Treatment: A Laboratory Study. *Journal of Energy Research and Reviews*. 2022;11(4): 19-32.
3. Gilbert N. One-third of our greenhouse gas emissions come from agriculture. *Nature*. (2012).
4. Horrigan L, Lawrence RS, walker P. How Sustainable agriculture Can Address the Environmental and human Health of Industrial Agriculture. Center for a livable Future, Johns Hopkins Bloomberg School of Public Health. *Environmental health Perspectives*. 2002;10(5):445-456.
5. Dölle K, Watkins C. Algae to Remove Phosphorous in a Trickling Filter. *Journal of Advances in Biology & Biotechnology*. 2016;11(2):1-5.
6. Dölle K, Van Bargaen M. Phosphor Removal from Waste Water using Hydrodynamic Cavitation. *British Journal of Scientific Research and Reports (JSRR)*, 2017;14(2),1-11.
7. Dölle K, Watkins C. Application of Algae as a Biomass Feedstock Source at a Waste Water Treatment Facility. *Journal of Advances in Biology & Biotechnology*, 2015;4(3):1-9.
8. Bootsma H, Young EB, Berges JA. Cladophra Abundance and Physical/chemical Conditions in the Milwaukee Region of Lake Michigan, Milwaukee Metropolitan Sewage District 2006. 10. October 2016. Available: [http://www.mmsd.com/-/media/MMSD/Documents/Water%20Quality/Reports/cladophora\\_report.pdf](http://www.mmsd.com/-/media/MMSD/Documents/Water%20Quality/Reports/cladophora_report.pdf).
9. Cost estimate of Phosphorous removal at waste water treatment plants, Ohio Environmental Protection Agency. 2013. 10 October 2016. Available:[http://epa.ohio.gov/Portals/35/wqs/nutrient\\_tag/OhioTSDNutrientRemovalCostEstimate\\_05\\_06\\_13.pdf](http://epa.ohio.gov/Portals/35/wqs/nutrient_tag/OhioTSDNutrientRemovalCostEstimate_05_06_13.pdf).
10. Dölle, K., & Lex, S. (2022). Application and Testing of a Laboratory Biotower Septic Tank System for Effluent Treatment - A Laboratory Study. *Asian Journal of Advanced Research and Reports*. 2022;16(9):8-17.
11. Dölle K, Hughes T, Kurzmänn DE. From Fossil Fuels to Renewable Biogas Production from biomass Based Feedstock- A Review of Anaerobic Digester Systems”, *Journal of Energy Research and Reviews*. 2020;5(3):1-37.
12. Safley Jr. LM, Westerman JR. Performance of a Dairy Manure Anaerobic Lagoon. *Bioresource. Technology*. 1992;42:43-52.
13. Dölle K. Process Sketch of an Agricultural Storage System. Pdf-file. 2023
14. Moeletsi ME, Tongawe MI. 2004 Methane and Nitrous Oxide Emissions from Manure Management in South Africa. *Animals* 2015; 5:193-205.
15. Leytem AB, Dungan RS, Bjorneberg DL, Koehn AC. Emissions of Ammonia, Methane, Carbon Dioxide, and Nitrous Oxide from Dairy Cattle Housing and Manure Management Systems *Journal of Environmental Quality*. 2011;9 • Volume 40(5):1383–1394.
16. Pen State Extension (2013) Covered Lagoon, Accessed 4/19/2020 <https://extension.psu.edu/covered-lagoon>
17. Environmental protection Agency Waste Water Technology fact sheet – Anaerobic Lagoons Accessed 4/19/2020 <https://www3.epa.gov/npdes/pubs/alagoons.pdf>
18. University of California, Agriculture and Natural resources (2012) Manure Treatment Anaerobic Lagoons. Accessed 4/19/2020 <https://anrcatalog.ucanr.edu/pdf/8409.pdf>
19. United States Department of Agriculture (2007) An Analyses of Energy Cost from Anaerobic Digestion Systems on U.S. Livestock Production facilities. Accessed 4/19/2020 [https://www.agmrc.org/media/cms/manuredigesters\\_FC5C31F0F7B78.pdf](https://www.agmrc.org/media/cms/manuredigesters_FC5C31F0F7B78.pdf)
20. Jun P, Bibbs M, Gaffeny K,. CH<sub>4</sub> and N<sub>2</sub>O Emissions from Livestock Manure. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Available at: Accessed, April 20<sup>th</sup>, 2020 [https://www.ipcc-nggip.iges.or.jp/public/gp/bgp/4\\_2\\_CH4\\_and\\_N2O\\_Livestock\\_Manure.pdf](https://www.ipcc-nggip.iges.or.jp/public/gp/bgp/4_2_CH4_and_N2O_Livestock_Manure.pdf)

21. United States Environmental Protection Agency (EPA). Overview of Greenhouse Gases Available at: Accessed April 18, 2020 <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>
22. Grant RH, Boehm MT. Ammonia emissions from an in-ground finisher hog manure tank. Atmospheric Environment. 2018;190:42-52.
23. HACH Method 8000: Oxygen Demand, Chemical, Available: <https://www.hach.com/dr1900-portable-spectrophotometer/product-parameter-reagent?id=18915675456>
24. Dölle K. Fruit Vegetable Screw Press. Pdf-file. 2023
25. Dölle K. Laboratory Manure Dewatering. Pdf-file. 2023

UNDER PEER REVIEW