

Electrochemical Assisted Phosphorus Precipitation of the Liquid Fraction of Dairy Manure in Microbial Electrolysis Cells: A Look into Phosphorus Removal

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Introduction

Although the United States has created numerous laws and regulations against environmental pollution, agricultural regions still have a dire contribution to aquatic pollution. Dairy farms in specific have been targeted as producers of aquatically hazardous pollution due to the phosphorus and nitrogen content contained in the manure. Phosphorus presides in two predominant forms in manure: organic matter and dissolved reactive phosphorus or orthophosphates. Orthophosphates will be able to escape the manure via dissolution into surface runoff and can be transported off the fields into rivers, lakes, or other aquatic environments. The arrival of phosphorus in aquatic environments has been seen to accelerate eutrophication of aquatic autotrophs and pose a detrimental impact to the surrounding biodiversity.

Microbial Electrolysis Cell (MEC) technology has recently been studied as an electrochemical treatment option for phosphorus ridden wastewater. An MEC will use microbes and an applied voltage to precipitate certain elements and compounds out of solution. A typical wastewater – or manure solution – treatment system will usually target phosphorus in attempts to remove as much as possible from the solution. Upon precipitation, struvite, calcium phosphate, and hydroxyapatite are the majority of products in which all can be used for fertilizer (Wang et al, 2005). A treatment via MEC technology has been shown to remove 20-40% of the total phosphorus from solution, with an applied voltage up to 1.05 V (Cusick and Logan, 2012). Although treatments exist with a removal rate of 99%, this method is much more cost effective and energy efficient.

Experimental Set-up

Six electrodes were initially constructed for each of the six differing reactors. The electrodes consisted of: titanium wire (30GA), coated wire, type 430 stainless steel 10x10 mesh (.025in, cut into 15cm x 4cm), and silver conductive epoxy adhesive. Each electrode then has approximately 240mm².

Six reactors were then constructed using simple plastic bottles with a cap containing three holes for the anode wire, cathode wire, and for access to the liquid manure for measurement. The electrodes were placed inside each reactor with the appropriate wires protruding from the cap. The exposed wires were the logical choice in connecting the circuit that was desired. Figure 1 is a representation of the reactor set-up.

Circuit construction involved the entirety of the reactors. Each reactor was connected to a DC power supply through the Cathode (+) directly followed by a series of five 1.1 Ohm resistors which were in turn connected to the Anode side (-). The control reactor was not connected to this series due to the lack of charge needed (0 V) whilst reactor 5 had a circuit that contained all five resistors. Sure enough reactors 1-4 were connected to 1-4 resistors, respectively.

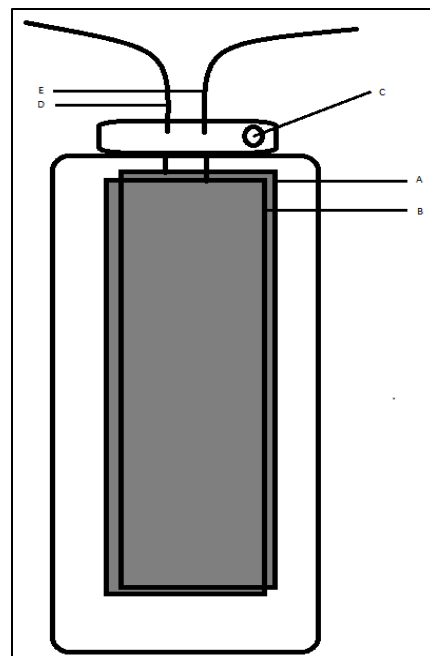


Figure 1: Reactor Configuration. A) Cathode. B) Anode. C) Extraction position. D) Cathode wire. E) Anode wire.

Before the reactors could be started, the appropriate phosphorus testing methods were to be tested and chosen. This was determined by the use of deionized water compared to tap water that would be used in dilutions. Deionized water tested better and would in turn be used in the dilutions for preparation of Hach® 843 and Hach® 845 testing kits.

The final stage of experimental construction is the addition of manure to the system. The manure was first filtered using two different sized filters (200 μ m and 50 μ m, respectively). The remaining liquid portion of dairy manure was secured inside a 10 gallon bucket and stored in a refrigerator for the entirety of the experiment.

At the end of the experiment, the reactors will be thoroughly mixed and tested for phosphorus content using the Hach® kits. The mixed manure from each reactor will then be fractionated using NaCl, NaHCO₃, NaOH, and HCl solutions, respectively. This will allow for the quantification of the different phosphorus forms in solution.

Experimental Operation

Commencement of the experiment began with the addition of 500mL of liquid dairy manure to each reactor, the connection of the circuit, and 1.0 V given off from the power supply. This is the standard condition in which the circuit will run; however, careful analysis of the reactors' individual voltage measurements indicated a higher voltage than necessary. Lowering the voltage given by the DC power supply to 0.9 V supported the desired measurement more accurately. This would give better target voltages for each reactor: 0.2 V, 0.4 V, 0.6 V, 0.8 V, and 1.0 V.

For 35 days, approximately 2mL samples of manure is to be extracted through the hole (covered by tape) on the top of each reactor, from three different locations: the top, middle, and bottom. The manure that is extracted must be replaced, in which the stored liquid dairy manure will be the best replacement. Each 2mL sample was stored in 2mL centrifuge tubes in which would provide for a good extraction location for precise handling. The samples were then extracted at 0.25mL and diluted 200x (50mL solution) with DI water. The solution would be mixed on the vortex mixer and then transferred to 10mL storage tubes, so approximately 10mL of solution was added to the 10mL tubes. Now, the Hach® kits were ready to be used; however the initial stage of kit preparation is to use 2mL of solution, when instead 1mL of solution was diluted with 1mL DI water, for an overall 400x dilution. The [ultra-low range Hach® 843] kits' procedures were carefully followed and ended with a spectrophotometer reading of the color of the solution. The results will indicate how diluted the solution should be.

After the allotted time for testing, the reactor circuit will be disconnected. The manure is mixed and extracted as one extraction per each reactor. This will then be tested using a 100x dilution and the ultra-high range Hach® 845 kit.

The fractionation procedure is a modification of Hirooka and Ichihashi (2012). 1mL of manure will be added to a 50mL 0.5 M NaCl solution, centrifuged, and consequentially filtered with a cellulose filter to release all loosely adsorbed and pore water phosphorus (Hirooka and Ichihashi, 2012). The remaining solids will then be added to 50mL of 0.5 M NaHCO₃ solution, centrifuged, and again filtered to remove redox-sensitive P bound to hydrated oxides (usually Fe) (Hirooka and Ichihashi, 2012). Then 50mL of 0.1 M NaOH solution is added to the remaining solids, centrifuged, and filtered to extract easily hydrolysable organic P compounds (non-reactive P) and the rest of P bound to Fe- and Al-oxides (Hirooka and Ichihashi, 2012). A solution of 50mL 1.0 M HCl is combined with the remaining manure solids, centrifuged, and filtered to remove apatite and other inorganic P (Hirooka and Ichihashi, 2012). A final phosphorus test will identify the amounts of each of these types of P containing compounds. One test will include a 1:10 dilution with the NaCl manure solution. The second will be a 1:5 dilution with the NaHCO₃ solution. The third will contain 2mL NaOH manure solution with 0.170mL 1.0 M HCl and 1.830mL 1.0 M NaOH. The added HCl is to keep the pH between 2 and 10, or at a sufficient level for

testing. The fourth and final test will have 2mL HCl manure solution, 0.919mL 1.0 M NaOH, and 1.081mL 1.0 M HCl

Results

The liquid dairy manure solution was analyzed and interpreted for the composition of important aspects. The total solid concentration averaged out to be 2.22% with a dissolved solids average of 0.62%. Total and dissolved volatile solids was then measured to be 0.54% and 0.16%, respectively. The ratio of total volatile solids to total solids gives 24.43% and the ratio of dissolved volatile solids to dissolved solids as 26.32%.

There can be a general trend followed for most reactors throughout the time of the trial: as time progresses the precipitation of phosphorus out of solution will decrease phosphorus concentration in solution at the top of the reactor whereas the bottom of the reactor will increase in phosphorus concentration. This general trend is not followed precisely, due to extraction contamination. Only one hole on the top of the reactor is available for extraction, so the different levels inside the reactor can be contaminated by the other levels, which could be seen to affect the overall phosphorus content. This could be the reason for experimental error.

The 1.0V reactor should precipitate the largest amount of phosphorus out of solution, compared to the control reactor which will have the least precipitated phosphorus. The 1.0V reactor is the best representation of this phenomenon due to the top concluding at 80.4 mgPO₃-P/L, the middle at 170.4 mgPO₃-P/L, and the bottom at 508 mgPO₃-P/L. Fig. 2 supports the initial claim of a correlation between higher voltage and precipitate formed. Without including the control reactor, each reactor ends with a higher concentration of phosphorus in the bottom and a lower concentration in the top, compared to the middle of each reactor. In theory, an increase in the applied voltage will produce an increase in phosphate precipitates. The suggestion of consistently increased amounts of precipitated phosphates correlated to a consistent applied voltage increase cannot be experimentally confirmed here due to the 0.4 V and 0.6 V reactors.

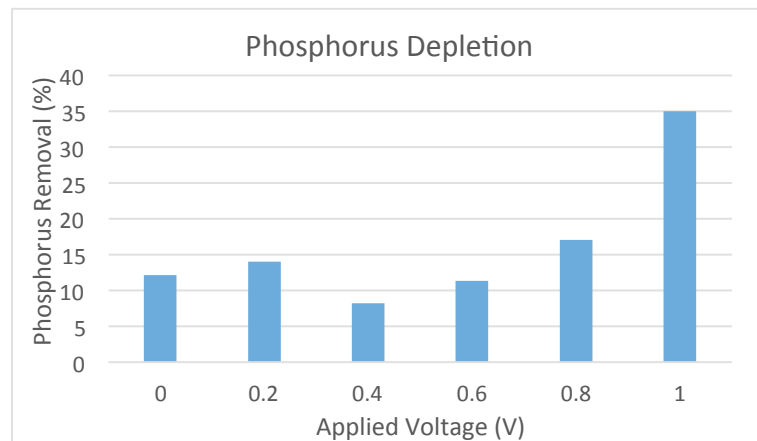


Figure 2: Reactor final phosphorus concentrations were compared to the initial concentration of 381.5 mg/L.

The assumption that a higher voltage will precipitate more phosphorus out of solution, however, can be made because of the general trend of phosphorus removal (seen in Fig. 1) and especially the 1.0 V reactor. The 1.0 V reactor precipitates almost double the amount of the 0.8 V reactor and more than double for all of the others. This could suggest 1.0 V to be the ideal voltage for precipitation, or even that an applied voltage higher than 1.0 V could be used.

Fractionation of the manure samples extracts and quantifies different phosphorus containing compounds. Roughly 98.5-99% of the phosphorus in each reactor that is loosely adsorbed or contained in pore water is removed from the NaCl solution. This is the largest source of phosphorus contained in the manure, by far. The NaHCO₃ and NaOH solutions remove roughly 0.5-1% and 0.01-0.5% of the remaining phosphorus, respectively. The HCl test removed the rest of the phosphorus and gave negative final phosphorus concentrations for each reactor besides the 1.0 V reactor. This was likely due to Chlorine ions preventing bonding and was therefore ignored.

A T-test was given to the final manure composition data in attempts to find a reactor that stood out from the others. The smallest p values indicate the largest difference between the two data sets, so it wasn't surprising to see the smallest p values relating to reactor 5. Reactor 5 therefore has data supporting its larger amount of precipitated phosphorus.

Conclusions

The removal of phosphorus from wastewater can differ greatly and scientists continue to examine these ways in hopes of an energy and cost efficient process with high results. Experimental data from earlier shows that 8-35% of the total phosphorus concentration can be removed from solution with an application of 0-1.0 V to an electrode in an MEC, with 35% coming from the highest voltage reactor. Although this study contained a set of reactors of 500mL size, it would take much larger reactors to have an effect on the eutrophication of aquatic autotrophs that is desired in the long run. Even scaled up, this process will need configurations leading to increased phosphorus removal rates; 35% is not high enough for large scale application. Experimental data, however, does show that this financially plausible set-up using 1.0 V of applied voltage could precipitate a noticeable amount of phosphorus out of solution.

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