Report

Thomas E. Berry Faculty Fellow Program in Integrated Waster Research and Management

The Application of Fly Ash to Treat Stormwater around Poultry Houses

Submitted to the
Oklahoma Water Resources Center
Oklahoma State University

by
Dr. Glenn O. Brown, P.E.
Regents Professor

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DEPARTMENT OF
Biosystems &
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Introduction

Non-point runoff is responsible for the pollution of 39% of the rivers, 45% of the lakes, and 51% of the estuaries in assessed water bodies in the United States (USEPA, 2002)[1]. In Oklahoma, phosphorous from urban and agricultural runoff is the greatest concern and leads to algae blooms in many streams and lakes. Zhang (2014)[2] presents specific sources and concerns with phosphorous in Oklahoma waters.

Starting July 1, 2015, the Thomas E. Berry Faculty Fellow program funded the author's efforts to extend on-going research in removal of phosphorous from urban stormwater, to agricultural sources. This report presents progress and accomplishment to date under the funding. This report describes general activities and expenditures while the appendix presents a brief technical progress report prepared by Ms. Lise Montefiore, Ph.D. candidate.

Research Activities

This research is attempting to use fly ash in an engineered stormwater filter to reduce phosphorous from stormwater at poultry houses and other agricultural sites. The author has completed multiyear research with a fly ash filter amendment in urban bioretention cells. That research was generally successful. However, it is not directly transferable to agricultural applications due to the cost of the cells. To maintain an adequate flow of stormwater, the fly ash could only be mixed at 5% by weight of the filter media. The remaining media had to be clean sand. This greatly increased the cell volume, and thus the construction cost. To address the restriction, this study has two general tasks. First, create a permeable fly ash granular media that can be used in a pure form without other materials. Then perform laboratory tests to characterize the ability of the granular media to adsorb phosphorous, which will enable the design of simple and hopefully, low-cost agricultural filters.

Fly ash

The fly ash used in this study was obtained from the Sooner Generating Station, Redrock, OK. A powdered, class C fly ash, its composition has been reported previously by Zhang, et al. (2008)[3].

Creating a granular fly ash pellet.

The fall of 2015 and spring of 2016 were dedicated to determining how to effectively turn the powered fly ash into a granular media. Fly ash is slightly cementitious. However, if mixed like

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[1] USEPA,2002. National water quality inventory: 2000 Report. *EPA 841-R-02-001*, U.S. 672 Environmental Protection Agency, Washington, DC.

[2] Zhang, H., 2014. Phosphorous and Water Quality. Oklahoma Cooperative Extension Service, Fact Sheet PSS-2917.

[3] Zhang, W., G.O. Brown, D.E. Storm, and H. Zhang, 2008. Fly ash-amended sand as filter media in bioretention cells to improve phosphorus removal. *Water Environment Research*. 80(6):507-516.

cement, it produces a gel that disintegrates into a slurry when added to water, which would be unusable for the intended application.

A series of experiments were conducted with the assistance of an undergraduate student, Nick Redmond. These experiments focused on understanding and maximizing the cementation of the fly ash. To do so, we needed to maximize hydrated water. That is, water bound in mineral crystals that will maintain the structure of the media. Figure 1 presents some of our results on the impact of curing time (the time after water is mixed with the fly ash), with the weight loss after drying at temperatures between 23 and 630 ºC. Drying at and below 105 ºC removes free and gel water. At higher temperatures, hydrated water is released. Curing time was varied from 1 to 29 days. As can be seen, the longer curing times retain greater dry weights indicating the mineralization is occurring, but is relatively slow. These and other results indicate that wetting the fly ash at low water contents, compressing and curing for a minimum of 28 days produced a solid matrix that would not dissolve in water.

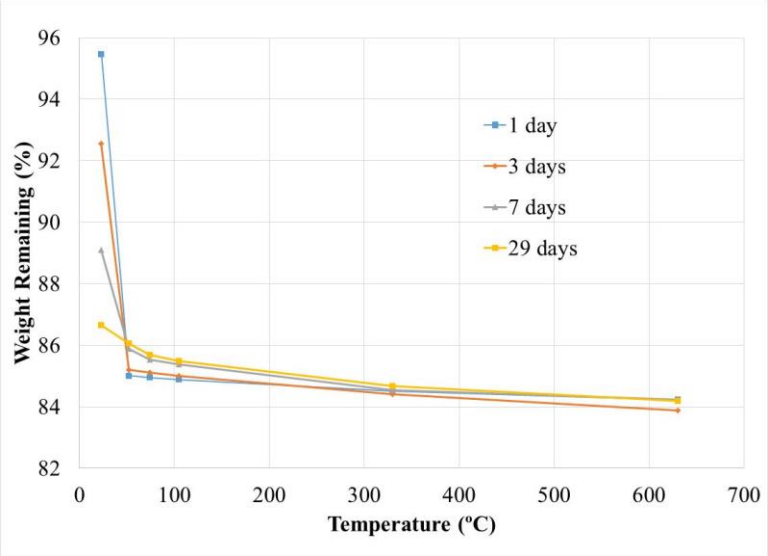

Figure 1. Cured fly ash weight loss as a function of curing time, and drying temperature.

After wetting and curing, the fly ash will be a solid block. A granular media is produced by simple crushing and sieving to the desired size. Figure 2 presents the original fly ash and two standard granular sizes.

Figure 2. Fly ash and granular pellets. Top raw fly ash, lower right, 0.25 to 0.50 inch pellets, lower left, 0.08 to 0.5 inch pellets.

Literature Review

In the fall of 2016, a new Ph.D. student, Lise Montefiore, was supported by the Fellow funding. To bring her up to speed on the subject, she performed an in-depth literature review on filter media additives. That review has produced a paper that has been submitted to *Water*.

> *Lise R.A. Montefiore, L.R.A., J.R. Vogel, and G.O. Brown, 2017.* Review of additives to improve pollutant treatment in bioretention**.** *Water* (special issue, Additives in Stormwater Filters for Enhanced Pollutant Removal. G.O. Brown editor). *In review.*

Leaching columns

Starting in the fall of 2016, and continuing in the spring and summer of 2017, the principal research activity is being conducted. A series of column experiments are being conducted to quantify the design parameters for the eventual fly ash treatment system. The appendix, prepared by Lise Montefiore, present the preliminary results of those experiments. Four columns have been completed to date. It is expected that four to eight additional columns will be required to fully characterize the phosphorous retention and to obtain transport parameters suitable for design of a prototype filter.

Conference Presentations

Soon after the start of this project, its results were integrated into the presentations made by the author. Table 1 lists professional conferences presentations by the author and Ms. Montefiore which reported in whole, or in part, the results of Berry Fellow funding.

Table 1. Presentations Reporting Berry Fellow Funding

Montefiore, L, J.R. Vogel, and G.O. Brown, 2017. Stormwater filters additives: a review and critique. *Oklahoma Clean Lakes and Watersheds Association Annual Meeting*, Stillwater, OK, April 5-6.
Montefiore, L, J.R. Vogel, and G.O. Brown, 2017. Testing and design of fly ash pellets for phosphorous removal in stormwater filters. *Oklahoma Clean Lakes and Watersheds Association Annual Meeting*, Stillwater, OK, April 5-6.
Brown, G.O., J.R. Vogel, and L. Montefiore. 2016. Additives for Stormwater Filters: What works, what doesn't, and what is still to be learned. *18th Annual EPA Region 6 Stormwater Conference*, Oklahoma City, OK, October 2-6.
Brown, G.O., and J.R. Vogel, 2016. The effectiveness of fly ash to retain phosphorous and heavy metals in stormwater filters. *18th Annual EPA Region 6 Stormwater Conference*, Oklahoma City, OK, October 2-6.
Brown, G.O., J.R. Vogel and D.E. Storm, Fly ash amended filter media to enhance phosphorous removal from stormwater *2016 EWRI World Environmental & Water Resources Congress*, West Palm Beach, May 22-26.
Brown, G.O., J.R. Vogel and D.E. Storm, 2016. Using fly ash in bioretention cells to remove phosphorous from stormwater. *2nd Biennial Great Plans LID Research and Innovation Symposium*, Omaha, NE, March 7-9.

Future Work

Laboratory experiments will continue through June of 2016. In parallel with the experiments, the lab results will be fit with *Chem Transport*, a generalized porous-media transport model developed by Dr. Magdi Selim, at Louisiana State University. Those fittings will provide the transport parameters to design the prototype filter. In addition, *Chem Transport* will be used to simulate a range of filter designs. The author has extensive experience with an earlier version of the model, and is confident that the desired results will be obtained.

Expenditures

The largest part of the Berry funding, approximately $15,000, has been expended on undergraduate and graduate salaries and benefits. Minor expenses have consisted of approximately $500 for sample analysis in the Soil Water and Forage Laboratory, and $125 for registration to the 2017 Oklahoma Clean Lakes and Watershed Conference. It is expected that the all Berry funding will be expended by the end of June, 2017.

Appendix

Thomas E. Berry Faculty Fellow Program

Column Leaching Experiments Progress

Lise Montefiore, Ph.D. Candidate

Introduction

This progress report presents an overview of experiments conducted to date. It is intended as but an experimental record and a planning document for future work. Result analysis is minimal and no conclusions can be offered at this time.

Methods

Column

Standard apparatus in the OSU Groundwater Laboratory were used in these experiments. The set-up used for most of the experiments is presented in Figure A1.

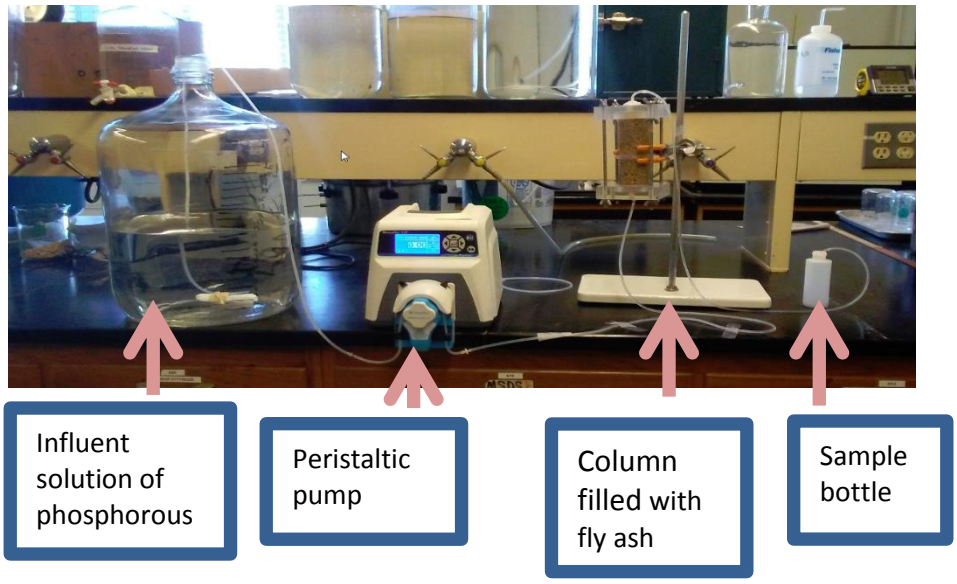

Figure A1: Experimental apparatus.

Influent solution with phosphorous is pumped through an acrylic column and collected in a sample bottle. The column was 4.13 cm in diameter, 14.87 cm in length and had an active volume of 199 cm^3.

Dry packing was used. A discrete portion of fly ash was poured in the column and pressed by the hand. This relatively delicate packing was used to prevent the pellets.

The column was operated under saturated conditions. Initially, distilled water was used saturated the column in an up-flow mode to displace the air in the pores. It was observed that the up-flow

mode wasn't enough adequate to remove air. Thus for the third and later experiments, the column was vacuum-saturated for 48 hours before leaching.

Phosphorous Solution Preparation

The phosphorous solution for the influent solution was prepared from reagent grade $Na_3PO_4(H20)_{12}$ with the following calculation

Molar mass of $Na_3PO_4(H_2O)_{12}$:
Na: 23g/mol
P: 31g/mol
O: 16g/mol
H: 1g/mol
M ($Na_3PO_4(H_20)_{12}$) = 380 g/mol

To prepare 10 mg/L of phosphorous, m= $(10*10^{-3}/31)*380$ = 123 mg. Pour 123 mg of the powder ($Na_3PO_4(H_2O)_{12}$) and add 1 l of distilled water.

To prepare a solution of 1 mg/L of phosphorous, a 4L container was used. 0.0492 g of $Na_3PO_4(H20)_{12}$ is weighted in a beaker. Then distilled water is added to the beaker and the solution is poured in a 500 mL (or directly 1 L if available) volumetric flask. The beaker is filled 4 more times with distilled water and the solution is poured to the 500 mL volumetric flask to insure that all the $Na_3PO_4(H_2O)_{12}$ is transferred. The volumetric flask is filled with distilled water until 500 mL line is reached. The volumetric flask is agitated to homogenize the solution. The mixture is poured in the 4L container. The volumetric flask is filled this time only with distilled water and poured in the 4L container. Three more liters of distilled water are added to the 4L container by using a 1L graduate cylinder. The 4L solution is poured in a bigger container which will be used to contain the influent solution during the experiment.

Sample Collection

For most of the experiments, sample bottles (Figure A1) are used.

Steps:

- Take one sample bottle. Put the output tubing in the sample bottle. Record the time.
- Fill the sample bottle for at least 7 min to have enough solution.
- Tare the second bottle sample.
- Place a 0.45 μm filter on the syringe and filter the solution collected previously. Use the second sample bottle.
- Weight the sample bottle. Record this value. Place an etiquettes and record the number (A209-XXX).
- Put a drop of H_2SO_4 in the solution filtered (use of gloves necessary). Then, put a lid and place the sample in the fridge if not analyzed in the few next hours.
- Place the remaining sample in the beaker and measure the pH and the EC.

All samples were analyzed in the Soil, Water and Forage Laboratory (SWAFL), OSU.

Calibrations
The pump was calibrated before each new experiment. The pH and EC- meter was calibrated before each the start of the experiments and every 7 days for verification.

Cleaning
All materials used were cleaned following each test and before reuse. The methodology consisted of: Rinsing 3 times with distilled water, washing 3 times with soap, rinsing 3 times with distilled water, rinsing 3 times with hydrochloric acid 5%, and rinsing 2 times distilled water.

Cleaned beakers, containers etc. are covered with paraffin to prevent contamination.

Fly ash

The fly ash was obtained from the Sooner Power Plant near Red Rock, Oklahoma. The plant's coal source is a sub-bituminous coal from the Powder River basin in Wyoming. The fly ash is class C and was formed into a block at low water content and cured for a minimum of 30 days. The block was then hammered and sieved to size. After sieving, fly ash pellets in two sizes (0.08-0.25 and 0.25-0.50 inch) were collected

Summary of Experiments
The four experiments conducted to date are summarized in the Table A1.

Table A1: Characteristics of the experiments

Parameter	**Experiment**			
	1	2	3	4
Fly ash size (inch)	0.25-0.50	0.25-0.50	0.08-0.25	0.08-0.25
Tubing	L/S 13	L/S 13	L/S 13	L/S 16
Phosphorous solution (mg/l)	1	1	1	1
Empty column (g)	888.3	888.4	900.1	896.9
Unsaturated column (g)	1027.5	1033.8	1052.4	1044.8
Saturated Column (g)	1155.3	1159.5	1170.7	1158.5
Weight of Fly ash (g)	139.2	145.4	152.4	147.9
Volume of water (ml)	127.8	125.7	118.3	113.7
End Volume (ml)	7	7	9	9
Bulk density (g/cm3)	0.698	0.729	0.764	0.742
PV	21.3	21.0	19.7	37.9
Flow, Q (cm^3/min)	6	6	6	3
Area, A (cm^2)	13.4	13.4	13.4	13.4
Seepage, V (cm/min)	0.45	0.45	0.45	0.22

Experiment 1

The experiment started on 01/20/2017. The 0.25-0.50 inch fly ash was tested with a flow of 6 ml/min. Samples were collected once a minute in an automatic sample collector. Effluent phosphorous concentration are presented in Table A2 and plotted in Figure A2. Not enough data was collected for early times. It was decided for the next experiments to collect data once a day.

Table A2: Results for Experiment 1.

Time (min) since the start of the experiment	**Concentration Phosphorous (mg/l)**	**Volume of Samples (mL)**	**pH**
16	0.45	17.83	8.78
77	0.35	17.15	8.77
137	0.31	18.49	8.79
170	0.29	17.57	8.82
197	0.32	18.85	8.81
230	0.30	18.63	8.81
257	0.30	18.85	8.85
290	0.31	18.67	8.79
317	0.31	18.35	8.86
350	0.32	18.77	8.83
317	0.33	17.74	8.84
410	0.33	18.77	8.83
437	0.34	18.30	8.84
470	0.34	18.14	8.86
497	0.35	18.87	8.82
460	0.37	18.22	8.85
557	0.38	18.31	8.86
590	0.38	18.09	8.86
617	0.41	18.16	8.85
650	0.40	17.78	8.86

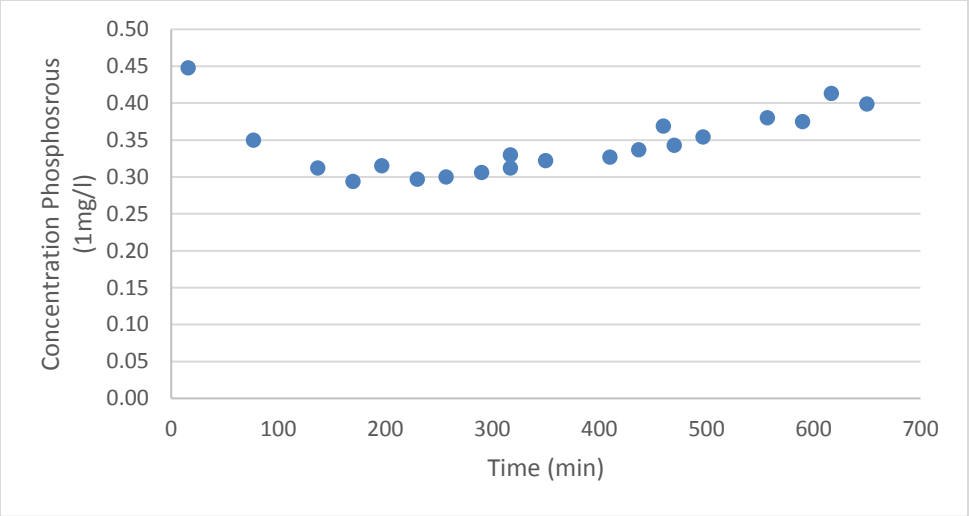

Figure A2. Experiment 1 Effluent phosphorous concentration vs time.

Experiment 2

The experience was realized on 02/02/2017. The 0.25-0.50 inch fly ash was tested. Phosphorous solution at a concentration of 1mg/l was injected at a flow of 6 ml/min. Samples were collected manually. Effluent concentrations are presented in Table A3 and Figure A3. Several leaks occurred in the tubing which might explain the variation of concentration in the graph. This experiment clearly indicated that the flow rate was too high to achieve full phosphorous retardation for this size of media.

Table A3. Results for experiment 2.

Date	Time (min)	Concentration Phosphorous (mg/l)	Volume of Samples (mL)	Pore Volume	pH	Conductivity (uS/cm)
02/02/2017	0				7.87	41.5
03/02/2017	1087	0.52	37.77	49.15	10.039	154.8
04/02/2017	2583	0.64	39.35	116.79	9.82	180.6
05/02/2017	4088	0.7	34.94	184.84	9.81	170.7
06/02/2017	5389	0.67	33.61	243.66	9.902	156.9
07/02/2017	6803	0.79	41.1864	307.60	9.686	149
08/02/2017	8386	0.63	27.03	379.17	9.573	137.13
09/02/2017	9699	0.7	43.68	438.54	9.709	159.3
10/02/2017	11388	0.77	50.49	514.91	9.832	149.3
14/02/2017	16961	0.69	47.4807	766.89	9.672	149.1
17/02/2017	21588	0.83	30.071	976.10	9.611	116.17

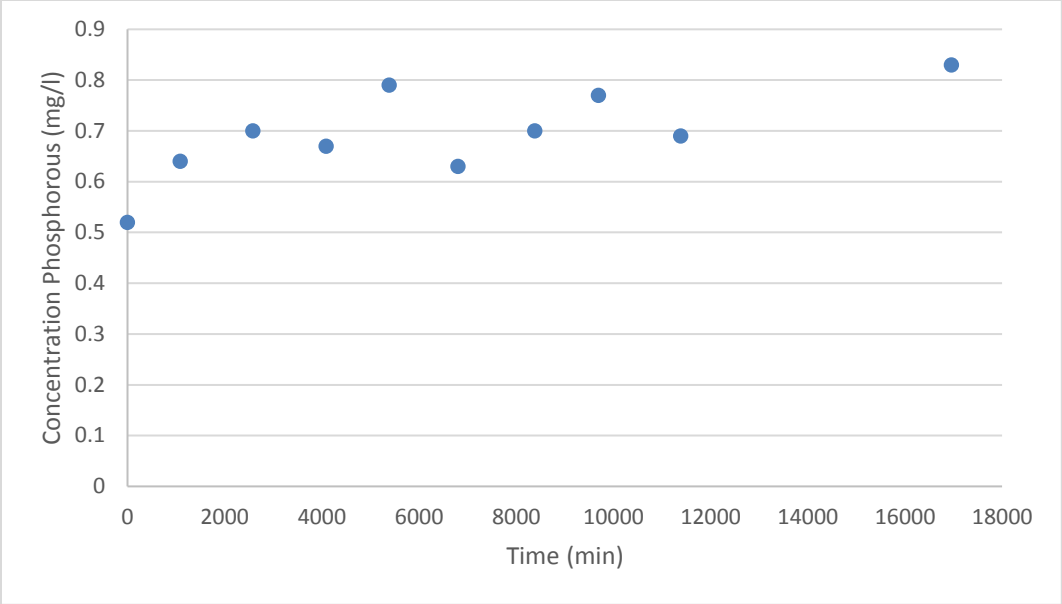

Figure A3. Experiment 2 phosphorous concentration in the effluent solution vs time.

Experiment 3

The experiment was realized on 03/14/2017. The column was filled with 0.08-0.25 inch fly ash. The column was saturated with distilled water during 48h and vacuum was applied to remove air. Tubing size was L/S 13. Then, a 1mg/l solution of phosphorous was injected with a flow of 6 ml/min. Samples were collected manually. Results are presented in Table A4 and plotted in Figure A4. A leak occurred on 03/19/2017 at 14h30. The tubing was replaced in 10 min.

Table A4. Results for Experiment 3.

							Quality control	
Date	**Hour**	**Time (min)**	**Concentration Phosphorous (mg/l)**	**Volume of Samples (mL)**	**Pore Volume**	**pH**	**Influent concentration of Phosphorous**	**Distilled water**
03/14/2017	15h34	0	0.07	24.84	0.00	8.89	0.94	<0.01
03/14/2017	16h14	40	0.13	27.67	2.03	8.96		
03/15/2017	15h28	1428	0.26	56.80	72.47	9.02	1	<0.01
03/16/2018	11h49	2649	0.37	35.62	134.43	9.54	0.97	
03/17/2019	6h10	3750	0.42	48.83	190.30	9.98	0.99	<0.01
03/18/2020	12h07	5547	0.50	45.83	281.50	10.05	0.97	
03/19/2021	12h12	6992	0.51	46.23	354.83	10.12	0.99	<0.01
03/20/2022	12h12	8955	0.36	43.79	454.44	10.15	0.96	
03/21/2023	8h42	10382	0.49	35.23	526.86	10.47	0.92	<0.01

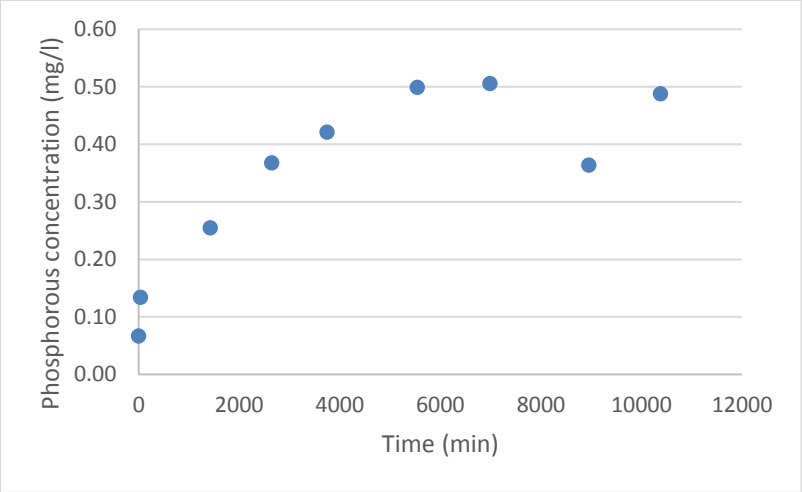

Figure A4. Experiment 3. Phosphorous concentration in the effluent solution vs time.

Experiment 4 (in progress)

The experiment was realized on 03/04/2017. The 0.08-0.25 inch fly ash was tested with a flow of 3 ml/min. The column was saturated with distilled water during 48h and vacuum was applied to remove air. Tubing size was L/S 16 to avoid leaking (tubing L/S13 is too fragile for long time experiment). Then a 1mg/l solution of phosphorous was injected with a flow of 3 ml/min. Samples were collected manually.