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Research article

# Evaluation of fly ash pellets for phosphorus removal in a laboratory scale denitrifying bioreactor



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# ABSTRACT

Nitrate and orthophosphate from agricultural activities contribute significantly to nutrient loading in surface water bodies around the world. This study evaluated the efficacy of woodchips and fly ash pellets in tandem to remove nitrate and orthophosphate from simulated agricultural runoff in flow-through tests. The fly ash pellets had previously been developed specifically for orthophosphate removal for this type of application, and the sorption bench testing showed a good promise for flow-through testing. The lab-scale horizontal-flow bioreactor used in this study consisted of an upstream column filled with woodchips followed by a downstream column filled with fly ash pellets (3 and 1 m lengths, respectively; both 0.15 m diameter). Using influent concentrations of 12 mg/L nitrate and 5 mg/L orthophosphate, the woodchip bioreactor section was able to remove 49-85% of the nitrate concentration at three hydraulic retention times ranging from 0.67 to 4.0 h. The nitrate removal rate for woodchips ranged from 40 to 49 g N/m<sup>3</sup>/d. Higher hydraulic retention times (i.e., smaller flow rates) corresponded with greater nitrate load reduction. The fly ash pellets showed relatively stable removal efficiency of 68-75% across all retention times. Total orthophosphate adsorption by the pellets was 0.059-0.114 mg P/g which was far less than the saturated capacity (1.69 mg/g; based on previous work). The fly ash pellets also removed some nitrate and the woodchips also removed some orthophosphate, but these reductions were not significant. Overall, woodchip denitrification followed by fly ash pellet P-sorption can be an effective treatment technology for nitrate and phosphate removal in subsurface drainage.

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# 1. Introduction

The quality of any body of surface or ground water is a function of either both natural and human influences. The intensive agricultural production activities produce a large amount of contaminants, including nutrients and solids that greatly threaten the water quality in the receiving watercourses. Especially in the Midwestern United States, the pervasive use of subsurface drainage systems critically reduces the travel time for nutrient fluxes to reach a receiving water body (Rabalais et al., 2001). A recent study conducted in the Mississippi River Basin estimated that agricultural watersheds (with high subsurface drainage density) accounted for

\* Corresponding author. E-mail address: rbhatta2@illinois.edu (R. Bhattarai). 70% of the total N and P delivered to receiving waters (García et al., 2016). The nutrients transported by the Mississippi River are a main contributor to the formation of hypoxic zone in the Gulf of Mexico every summer (Rabalais et al., 2001).

There are many on-farm and edge-of-field conservation practices to control the nutrient flux from agricultural areas (Haas et al., 2017; Rudolph et al., 2015). The edge-of-field approach has been identified as an effective method to help control subsurface drainage nutrient loss (Rittenburg et al., 2015). In this method, the contaminated water has to go through a filter media (biological or chemical) chamber before entering the receiving water body. Edgeof-field practices are usually located at the outlet of the subsurface drainage tile. Well-designed systems are installed parallel to the receiving water bodies and take little to no agricultural land out of production. With nitrate being the primary contaminant transported through artificial subsurface drainage, the early focus of this



approach was to promote denitrification through the introduction of a solid carbon source. Although the nitrate removal varies by design, woodchips and other carbon containing substrates have shown great promise for promoting denitrification and have greatly reduced nitrate loads in several studies (García et al., 2016; Jaynes et al., 2008; Li et al., 2016; Robertson and Merkley, 2009; Schipper et al., 2010).

Multiple studies on the woodchip bioreactor have been conducted to determine factors influencing nitrate removal efficiency and removal rate (Hoover et al., 2016; Lepine et al., 2016; Nojiri et al., 2009; Schipper et al., 2010). The retention time is an important parameter, which strongly influences nitrate removal by limiting the water contact time with denitrifying bacteria and release of carbon source (Hoover et al., 2016; Lepine et al., 2016). At the same time, the level of dissolved oxygen and pH of the water also affects the performance of the bioreactor (Thomas et al., 1994). Meanwhile, there is increasing interest in removing orthophosphate along with nitrate because considerable loss of phosphorus (P) through the tile system has been reported (Allred, 2010; Bird and Drizo, 2010; Penn et al., 2007; Vohla et al., 2011; Westholm, 2006). In many studies, multiple materials have been reported for their ability to remove soluble P from the contaminated waters (Boujelben et al., 2008; Dobbie et al., 2009; Jayarathna et al., 2015; Kunaschk et al., 2015; Xiong et al., 2008).

Fly ash, which is an industrial waste product, was suggested as an ideal sorbent because it contains large percentages of natural minerals, such as calcium (Ca), aluminum (Al), and iron (Fe) in various forms (Li et al., 2017; Xie et al., 2015). Li et al. (2006) reported that fly ash provided an average 52% P removal ability with the pH at 7 and at room temperature. Wang et al. (2016) developed a fly ash based lanthanum oxide hybrid material and found it removed the most P under high pH (8.51–9.11) conditions. Li et al. (2017) used fly ash as the base materials to create a pellet form sorbent which was proved to have more than 90% P absorption efficiency in a batch test. This pellet form sorbent is ideal for chamber structures that could be incorporated into an edge-of-field practice and are stable enough for the hydraulic status in tile system.

While existing research has begun to address efficient and cost effective approaches for controlling contaminant release from tiled drained agricultural lands, current methods and materials are far from refined. New methods and materials need be developed to increase in the removal efficiency of the nutrients to alleviate water quality issues. Bioreactors have been proven effective in removing nitrate, but the current design needs to be modified to make it effective for orthophosphate removal as well. The goals of this study was to conduct lab scale column experiments to test the efficacy of using woodchips and fly ash pellet (FAP) developed in our earlier study (Li et al., 2017) in flow-through tests for their abilities to remove nitrate and orthophosphate (soluble P) from agricultural drainage.

# 2. Materials and methods

#### 2.1. Research site and bioreactor

Two horizontal-flow laboratory-scale column reactors were constructed in the Agricultural Engineering Sciences Building at the University of Illinois campus (Urbana, Illinois, USA) to test FAP for its capacity to remove soluble phosphorus from tile drainage water, while simultaneously examining the effect of woodchip media used for nitrate removal (Fig. 1 "A" and "B"). To allow for simultaneous experimental repetitions, each reactor consisted of two identically constructed horizontal PVC columns (0.1524 m diameter), and each configuration consisted of an upstream 3 m section filled with woodchips, and a downstream 1 m long FAP-filled section. The material was secured in the columns by PVC plates with drilled holes ( $12 \times \phi 1$  cm) covered by a non-reactive mesh at each end. Flow through the columns was regulated using a controlled drainage structure connected to a manifold, which diverted the flow equally and served as the inlet for each of the two columns. The outlet of each column consisted of a 5.08 cm diameter PVC pipe. The outlet pipe could be rotated to an angle to achieve head differences ranging from 0 to 1.5 m below the inlet water level to induce a variation in the flow rate.

The configurations were calibrated by measuring volumetric flow rates (in triplicate) from the paired column outlets while the configurations were operating at three outlet placements. Effective hydraulic conductivity ( $K_e$ ) for each column was calculated using Darcy's law (Equation (1)) as follows:

$$K_e = \frac{Q}{A} \cdot \frac{L}{\Delta H} \tag{1}$$

where  $K_e$  = effective hydraulic conductivity [L/T], Q = Flow [L<sup>3</sup>/T], A = Area [L<sup>2</sup>], L = column length [L], and  $\Delta H$  = head difference [L].

# 2.2. Bioreactor media

The coal fly ash was obtained from the Abbott Power Plant in Urbana, IL, USA. The chemical composition of this coal fly ash was 35.8% SiO<sub>2</sub>, 28.19% Al<sub>2</sub>O<sub>3</sub>, 8.6% Fe<sub>2</sub>O<sub>3</sub>, 5.3% CaO, 1.9% MgO, 2.6% Na<sub>2</sub>O, and the carbon content was 17.6% (measured as loss on ignition). The density of fly ash was  $1325 \text{ kg/m}^3$ . The other two ingredients in the pellets were fine bentonite clay with a bulk density 801.1 kg/m<sup>3</sup> and lime powder with a  $1190.24 \text{ kg/m}^3$  bulk density (Li et al., 2017). Li et al. (2017) previously tested these FAP and found the P adsorption capacity was 1.98 mg/g and equilibration time was 24 h.

The FAP used in this study was prepared by following the method outlined as in Li et al. (2017). All the dry materials (fly ash 60%, lime 30%, and clay 10% by weight) were mixed uniformly with a blender. Deionized water (15% by weight) was added to the mixture and blended again to prepare the slurry. The slurry mix was then sealed, left to stabilize for 24 h at room temperature, then converted into pellets using a commercial pelletizer (Colorado Mill Equipment-ECO-10, USA) equipped with a 10 HP, 3-phase motor. The pellets were then baked in a high-temperature furnace (Thermolyne BOX furnace, MA, USA) for a total of 7 h, raising the temperature 200 °C each hour for 5 h, then keeping it at 1000 °C for another 2 h. Once the pellets were removed from the oven, they were cooled for 6 h and then rinsed with distilled water (Li et al., 2017).

The woodchips used in the study were collected from an existing field-scale bioreactor at a university research farm at the University of Illinois (Urbana, IL). This bioreactor was established in 2015 and previous research showed a promising result for nitrate removal (Rendall, 2015). The woodchips were collected from the surface to a depth of approximately 0.61 m. Previous study at this site showed this depth was often/always fully submerged, thus a selection of aerobic and anaerobic-exposed woodchips was included. The woodchips were collected in plastic bins, and transported to the Agricultural Engineering Sciences Building on the University of Illinois campus where they were packed into the PVC columns. The columns sections were vertically compacted with a long tamping rod at 2.54 cm increments during loading and filled the columns to a height of 290 cm to achieve an approximately uniform density throughout all of the columns.



Fig. 1. Illustration of two replicated paired-column configurations using woodchips and fly ash pellets (FAP) fed by a control structure which was supplied water via a pump.

# 2.3. Characterization of materials

Gravimetric measurement of drainable porosity was undertaken by draining the columns from the bottom over a 1-h period, measuring the weight of the drained water, and then extracting the media from the columns and measuring the difference in wet and dry media weights after air drying in a fume hood for 3 d. Primary porosity was calculated as the ratio of the drainage water volume to the open bed volume of the columns and secondary porosity (porosity internal to the wood particles) was calculated as the ratio of the water loss upon media drying to the open bed volume. Total porosity was then calculated as the sum of the primary and secondary porosities. Bulk density was measured using Oertling YP4 balance.

The size of materials, based on observation, ranged from approximately 0.25 cm-10 cm for the woodchips and 0.5 cm-1.5 cm for the FAP (Fig. 2). The woodchips were of varying thickness and length, while the FAP tended to be more uniform and of pellet shape.

# 2.4. Experimental method

The column reactor was used for a series of three experiments each using a different flow rate that tested for both nitrate and orthophosphate removal efficiency of woodchips and FAP. Based on retention time recommendation of NRCS conservation practice standard of denitrifying bioreactor (Code 605) (USDA-NRCS, 2015), the flow rates were set 2.80 mL/s, 5.68 mL/s and 1.98 mL/s for test 1, 2, and 3, respectively. Subsequently, the retention times for the woodchip sections of the paired configurations were 2.9, 1.5, and 4.2 h, respectively, while the retention times for the FAP sections were 1.36, 0.67 and 1.92 h, respectively. This low-high-low flow rate sequence was set to avoid the flow rate bias on the bacterial growth on woodchips.

The water used in the study was collected from a detention pond at the Agricultural Engineering Farm (located at Urbana, IL) that collected subsurface drainage outflow. Prior to the experiment, the systems were initialized by flushing them with the pond water for three days at a flow rate of 4.6 mL/s. The flushing water was spiked with KH<sub>2</sub>PO<sub>4</sub> and KHNO<sub>3</sub> to produce an approximate 5 mg-P/L and 12 mg-N/L solution. This solution was pumped by an electric pump into the controlled drainage (Agri-Drain, Adair, Iowa) structure that served as a constant head device, and then into the manifold connecting the configurations (Fig. 1). The overflow from the constant head device spilled back into the holding tank, continuously mixing the solution.

During the experiment, water samples were collected at every 2 h interval and the water quality parameters (temperature, DO and pH) were measured in situ using a Hach Quanta multi-parameter water quality probe. The probe was calibrated according to manufacturer procedures prior to each experiment. For each sample, two 30 mL of water were collected from the control structure, the woodchip section outlet, and the FAP outlet. One sample was vacuum filtered by a 0.45- $\mu$ m filter and stored at 4 °C and analyzed for Orthophosphate according to EPA Method 365.1 (EPA, 1993a) and the other was treated with concentrated sulfuric acid (0.25 mL)



Fig. 2. The fly ash pellets (left) and woodchips (right) used in this study.

and stored at 4 °C and analyzed for Nitrate-N according to EPA Method 353.2 (EPA, 1993b). Volumetric out flowrates were measured every 4 h, and used as feedback to adjust for a consistent flow using the adjustable outlet elevation. The total experiment time was 28 h for each test.

The N removal rate were calculated to evaluate the denitrification efficiency of both chambers as shown below (Equation (2)):

$$N removal rate = \frac{Q_{day} \times \left(C_{inf} - C_{eff}\right)}{V_{act}}$$
(2)

where  $Q_{day}$  is the total flow volume passed by woodchips in a day,  $C_{inf}$  is the average influent N concentration,  $C_{eff}$  is the average effluent N concentration, and  $V_{act}$  is the active volume of woodchips.

# 3. Result and discussion

# 3.1. Materials characterization

The effective hydraulic conductivities of the two columns were not significantly different from each other (Column A and B  $3.10 \pm 0.18$  and  $3.13 \pm 0.10$  cm/s, respectively; p = 0.85). These results were comparable to those reported by Goodwin et al. (2015) where the average effective hydraulic conductivity ranged from 2.57 to 3.1 cm/s for four columns. The bulk density of woodchips in the packed columns was 200 kg/m<sup>3</sup> (5.96 kg; 0.03 m<sup>3</sup>) with a drainable porosity of 54.5% (Table 1), similar to other reports (Goodwin et al., 2015; Christianson et al., 2017). The bulk density of fly ash pellets was 1.037 g/cm<sup>3</sup>, and the drainable porosity was 75.3% in the column. Based on the bulk density and drainable porosity of the fly ash pellets, the effective volume and weight in FAP section was calculated to be 0.014 m<sup>3</sup> and 14.2 kg, respectively.

# 3.2. Orthophosphate removal

Significant reductions in orthophosphate concentration were observed as the result of passing the solution through both the woodchips and the fly ash pellets (Fig. 3A–C). The main orthophosphate removal in this system was achieved through the FAP section. The FAP section exhibited an average orthophosphate removal of 71.4%, and the removal efficiencies were not significantly different among the three tests even though the retention time varied (P removal rate of 74.7%, 68.3% and 71.2% for tests 1, 2, and 3, respectively). This result indicated that the FAP had a stable performance of trapping orthophosphate under the different flow rates and even under higher inflow P concentrations when an increase in concentration was observed exiting the woodchips (Test 3 in Fig. 3C). Phosphorus adsorption is an exchange reaction which takes place on the surface of calcium, iron, and aluminum hydroxides (Li et al., 2017). Binuclear or bridging complexes are formed between  $HPO_4^{2-}$  ions and metal oxide surfaces and  $OH_2$  and OH<sup>-</sup> are displaced (Vohla et al., 2011). Previous work demonstrated the P sorption ability of FAP, and this flow-through study further shows that FAP, which can be rich in calcium, iron or aluminum oxide, can be a proper filter material for P absorption in a tile drainage system. The performance of FAP in removing the orthophosphate in this study was better than other industry byproducts which were tested in similar experimental settings. Goodwin et al. (2015) reported a 53% P removal efficiency using steel turnings for a similar column arrangement. Hua et al. (2016) demonstrated a similar P absorption result (70% removal efficiency) by steel turnings, but this test was conducted in small scale vertical tubes and under a low flow rate, which is not practical in the field setting. King et al. (2010) reported zeolite as an absorbent that could provide 52% P removal in a similar setting. Christianson et al. (2017) demonstrated Fe-based acid mine drainage treatment residuals could remove 56–58% orthophosphate in a paired woodchips-P filter configurations on a 7.6 min retention time. These results suggest FAP is a promising material to be applied for orthophosphate removal in tile systems.

In all three tests, the woodchips also contributed to orthophosphate removal in some extent, despite their primary purpose being for nitrate removal, with average concentrations reductions ranging from 10 to 13%. There was no significant difference in the woodchip outflow average orthophosphate concentration between the three tests (Test 1, 2, and 3: 3.99, 4.04, and 4.21 mg P/L; p > 0.05). At the beginning of test 3, the first two sample's concentration (average 4.5 mg/L) which may have been due to a release of absorbed orthophosphate from woodchips during the anaerobic time between the tests (Fig. 3C, box). Two potential pathways in which woodchip could remove orthophosphate include physical attachment/sorption or bacterial assimilation. The change in bacteria metabolism could be the cause of the release of the orthophosphate.

#### 3.3. Nitrate removal

All three tests resulted in a significant reduction in nitrate concentration after water passed through the woodchip section (Fig. 3D–F). The general woodchip nitrate removal rate was stable during the entire test period in all three tests. In test 1, there was an average nitrate reduction of 70% observed after the woodchip section and an additional 2% average reduction after the FAP section. A lower nitrate removal efficiency in test 2 (average 47.5%) versus test 1 was due to the decrease in retention time (Test 1 and 2 woodchip section retention time: 2.9 vs. 1.45 h). In test 3, the retention time was 4.1 h. Nitrate was not detected in the first 2 samples, because the water leaving in the woodchip section was fully denitrified. At 10 h during test 3, the nitrate concentration stabilized at 2.3 mg N/L resulting in a nitrate removal efficiency of 80.8%. The notably lower woodchip effluent concentration at the beginning occurred because the sampling interval was shorter than the retention time (2.0 vs. 2.9 h, respectively), and it is likely the initial water had already been sufficiently denitrified. Other low effluent concentration events (at 16 h during test 1 and at 12 and 24 h during test 2) were due to refilling the water supply tank which extended the water retention time as it took around 3 h to pump water at the farm and transport it back to campus.

Similar denitrification efficiencies were observed by Goodwin et al. (2015), who reported the general denitrification efficiency was 88.8% for a 12 mg N/L inlet nitrate concentration with average 4.9 h retention time. Hua et al. (2016) also found a similar

Table 1

Bulk density and drainable porosity of fly-ash pellets and woodchip used in this paired column study.

	Bulk Density (Dry Basis) (kg/m <sup>3</sup> )	Drainable Porosity (%)	Effective volume (m <sup>3</sup> )
Pellet	1037	75.3	0.014
Woodchips	200	54.5	0.03



**Fig. 3.** Phosphate (A–C) and nitrate (D–F) concentrations for the inlet, effluent from the woodchips, and effluent from the fly ash pellet (FAP) sections for three tests operated at woodchip section hydraulic retention times of 2.9, 1.5, and 4.2 h (Tests 1, 2, and 3, respectively).

denitrification efficiency (84.4% removal efficiency) in a vertical tube test for a six-month period (retention times of 6–24 h; inlet concentration 20 mg N/L). Additionally, both Lepine et al. (2016) and Hoover et al. (2016) reported 55–65% removal efficiency in lab scale woodchip bioreactors (influent concentration and retention times: 20–80 mg/L, 6.5–55 h and 10–50 mg/L, 1.7–21.2 h, respectively).

There was a small reduction in concentration of nitrate after the FAP section in all three tests results, especially when the retention time was raised. In test 3, the nitrate concentration difference averaged 0.8 mg/L before and after the FAP section. It is likely this was due to the active composition in FAP which also possibly absorbed nitrate. In fly ash pellet, the aluminum and magnesium oxide are the active ingredients that can provide a physical and chemical absorption of nitrate when they have enough contact time (Islam and Patel, 2009). The chemical absorption reaction of aluminum and magnesium oxide with nitrate follows the equation below (Equation (3)).

$$\begin{bmatrix} Mg_{1-x}^{II}AI_{x}^{III}O\end{bmatrix}^{x} \cdot yH_{2}O + xNO_{3}^{-} \rightarrow \begin{bmatrix} Mg_{1-x}^{II}AI_{x}^{III}(OH)_{2}\end{bmatrix}^{x+} \begin{bmatrix} NO_{3}^{-}\end{bmatrix}_{x} \cdot yH_{2}O$$
(3)

This reaction involves the breaking up of electrostatic interactions as well as the hydrogen bonds between the hydroxide layers and the outgoing anion and the reformation of these bonds with the incoming  $NO_3^-$ . The only factor that could have impacted these reactions were the contact time and the pH levels in the FAP section in this test. Further results and discussion about pH are shown in section 3.3.

# 3.4. pH and DO results

The inlet water pH was very stable during each test as illustrated

in Fig. 4(a). The average pH measured at the inlet was 7.78, 7.55 and 7.68 for test 1, 2 and 3, respectively. The woodchips section consistently reduced the average pH to 6.94, 7.10 and 7.00 for the three tests, respectively. Hydrolytic acidification processed by the anaerobic heterotrophic bacteria could provide H<sup>+</sup> and decrease the pH in the woodchips section. The evidence could be found at box plot positions for woodchips sections for each test. The box plot of woodchip section in test 2 showed significant difference from the other two tests which meant the test condition strongly impacted the variation in pH in the woodchips section. In test 2, where the retention time was shorter compared to other tests, the decrease in pH was less when water passed through the woodchips section. On the contrary, when water passed through the FAP section, the water pH increased dramatically. The average pH of effluent from the FAP section were 8.75, 7.45 and 7.86 for test 1, 2 and 3, respectively. The reason for the increase in pH in this section is the lime contained in FAP added the OH<sup>-</sup> into the water as it passes and long contact time. Similar to the woodchips section, the retention time is the main factor that impacted the change in pH in FAP section as well.

Based on the size of the box in each section for all three tests, the DO didn't vary significantly during the test period (Fig. 4b). For example, in the test 1 inlet DO box, the first quartile was only 4.2% DO different from the fourth quartile, but the inlet average DO was significantly different (F = 662.2, p < 0.01) for each test which was 55.5%, 44.1% and 65.8% for test 1, test 2 and test 3, respectively. This is because the pond water conditions varied by the weather and farmland cultivation activities. For instance, the precipitation event would strongly increase the tile drainage flow and increase the pond water DO. The woodchips section was the main part that consumed the DO in water. The measured DO values in woodchip sections were 5.5%, 7.45% and 5.2% for in test 1, test 2 and test 3, respectively. About 85% DO reduction occurred in woodchips section in each test, because denitrification occurs during the



Fig. 4. Each section pH and DO result for all three tests in the box chart (the square in box represents the average and the line is the median).

anaerobic condition, and lower DO is an essential condition for the higher denitrification rate. In this study, the longer water retention time in test 3 led to a lower DO environment in the woodchips column, which helped to reduce more nitrate in this test compared to the other two tests. The DO had a slight increase after the water passed through the FAP section, and the average FAP section DO of each test reached 8.15%, 8.38% and 10.54% in test 1, test 2 and test 3, respectively.

# 3.5. The effect of retention time on nutrient removal

Total nitrate removal rates across the paired configurations were 46, 55 and 55 g N/m<sup>3</sup>/d for test 1, 2 and 3, respectively (Fig. 5A). Correspondingly, nitrate removal rates for only the woodchip section were slightly lower at 40, 49 and 41 g/m<sup>3</sup>/d. This result indicated the retention time was negatively related to the nitrate

removal rate in this study. It should be noted that the higher flow rates (lower RTs) also result in more mass loading into the bioreactor. On the contrary, the nitrate removal rate contributed by FAP for all three tests were impacted by the retention time positively (i.e., the smallest flow rate led to the most N removal at the FAP section).

Like nitrate, the P removal rate also increased when retention time decreased (Fig. 5B). The P removal rate for each test in the FAP section was 0.06, 0.11, and 0.09 mg/g which was far below the saturation absorption capacity (1.98 mg/g) of FAP reported by Li et al. (2017). Therefore, the P removal rate in FAP section was negatively related to retention time. These results indicate that these two materials might provide a stable nutrient removal under the normal tile drainage flow conditions. There is a need to further assess the effectiveness of these media for both N and P removal in the field condition in future.



Fig. 5. The nitrate and orthophosphate accumulation removal rate of both sections for all three tests (woodchip section hydraulic retention times of 2.9, 1.5, and 4.2 h, respectively).

## 4. Conclusion

In this study, a bi-column test of woodchips and FAP have been applied as bioreactor media for nutrient (nitrate and orthophosphate) reduction from a lab scale tile drainage system. The results showed that the woodchips section nitrate removal efficiency was strongly impacted by the retention time, and the shorter retention time test had less N removal efficiency. The removal efficiency ranged from 47.8 to 80.8%, but the N removal rate was higher when woodchips was subjected to the higher flow condition because of higher mass loading into the bioreactor. The FAP section also contributed to the nitrate removal, likely by chemical absorption, which removal rate raises along with the retention time, but this contribution was not significant. The total nitrate removal rates of this system are 46, 55, and 55 g N/m<sup>3</sup>/d for test 1, 2 and 3, respectively. The fly ash pellets effectively removed phosphate in the bioreactor effluent and the total phosphate adsorption was 0.059–0.114 mg P/g which was far less than the saturated capacity previously reported (1.69 mg/g by Li et al. (2017)). The total phosphate removal efficiency could be maintained at the range of 81.7-84.5% under different flow rate situations (across both columns). Both the nitrate and orthophosphate in this effluent was effectively removed by the woodchips bioreactor-FAP filter system.

Overall, the results of this study suggest that FAP can be applied as effective adsorption materials for phosphate removal in subsurface drainage. Also, this in-stream two-stage nutrient removal system is a highly promising technique and could be applied in the field. The follow-up research on FAP for phosphorus retention should be focused on their hydraulic parameters combined with applying recovery from the FAP. Likewise, more attention should be given to investigating obvious constraints such as poor saturation time, high pH of outflow, or possible desorption conditions in the field.

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