Phosphorus Removal in Vertical Flow Reed Beds using Baked Clay Balls as an Alternative Media

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Abstract
Phosphorous (P) entering into the water bodies through point and non-point sources is a causal agent for eutrophication. Nature Based Solutions (NBS) like Constructed Wetlands (CW) are cost effective methods for treating the grey waters in order to protect the water bodies from risk of eutrophication. The P removal efficiency of Constructed Wetlands (CW) can be improved by adding new substrate having potential P removal efficiency. The study was conducted to determine the phosphorus removal from wastewater using Baked Clay Ball (BCB) media in Vertical Flow Reed Beds (VFRB). The BCB was prepared with a mixture of river clay and saw dust. The field and lab-scale experimentation were set and operated in batch feeding mode using institutional wastewater for four months. The VFRBs were filled with BCB and planted with locally available reed grass (Phragmites karka). The hydraulic retention period in VFRB was 48 hours. Prime goal of the experiment was to investigate the Phosphorus (P) removal efficiency of the VRFBs apart from other conventional wastewater quality parameters. The concentration of phosphorus of the institutional wastewater was in the range of 27.3 mg/l to 16.3 mg/l. The average phosphorus removal efficiency of the VFRB 1 and 2 filled with BCB was 93.47%, while the average P removal efficiency of gravel filled VFRB 2 and 3 was 68.20%. Thus the experiment reflected that the BCB is a better media than the gravel for P removal. Therefore, the BCB may be used at a field scale to remove P from wastewater in constructed wetlands. Further, there is scope to develop new substrate materials focusing on its P retention capacity, long lasting performance and cost of the substrate to be applied in real treatment situations.

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Introduction

Constructed Wetlands (CW) are eco-technology based methods for wastewater treatment. The vegetation, substrate, biofilm and microorganisms of CWs work in co-action to remove a various pollutants from the wastewater. CWs have gained popularity across the world. These systems are widely applied to treat municipal sewage, dairy effluents, agricultural run off and land fill leachates. Among the four major classes of CWs the vertical flow constructed wetlands (VFCW) are chiefly being used for its smaller size and oxygen diffusing properties. Phosphorus contamination exists in aqueous wastes of many domestic and agriculture wastewaters. Phosphorus is a nutrient used by many industries and can be found in many products (a variety of cleaners) used by humans. Therefore, it is one of the main contaminants found in wastewaters. Phosphorus (P) and Nitrogen (N) are major point and non-point sources of pollution causing eutrophication of water bodies. P tends to attract towards soil and sediments of the receiving water bodies, so it gets accumulated in the system over time. It causes excessive growth of algae and cyanobacteria, leading to blooms, hypoxia, and a foul-smelling environment in the water bodies under hot climatic conditions. CWs can be used as a potential wastewater treatment technology in urban, peri-urban and rural areas. The enhanced P removal efficiencies of the CWs can address the eutrophication problems. CWs have been evaluated for removal of phosphorus (P) nitrogen (N) from wastewater. The filter media of the CWs show P removal due to its sorption capacities, P removals have been evaluated in CWs with sand, soil, marble and calcite. The most commonly used substrate in CW is gravel. Still the studies have suggested that gravel is not a good choice for P removal. To achieve substantial phosphorus removal it is necessary to select materials with high P adsorption capacity. The adsorption process has been tested for dyes also. The focus of the present study was to investigate the efficiency of vertical flow reed beds (VFRBs) for P removal using artificial baked clay balls and natural gravel. The present study focused on investigating the efficiency of vertical flow reed beds (VFRBs) for P removal using artificial baked clay balls and natural gravel. There are methods like membrane separation and ion exchange to remove P from wastewater. Still, in the coming future, the nature-based, phyto-mediated processes will gain momentum in the research and development of new technologies for P removal from wastewater. The natural substrate materials can be used in CW without processing. Still, synthetic materials have shown promising results in removing various pollutants like hazardous organic pollutants.

Materials and Methods

In order to study the performance of two different types (Baked Clay Balls and Gravel) of filter media for phosphorus reduction in wastewater, an onsite mesocosm level VFRBs were used.

Site Description And Experimental Design

The experimental set-up was installed near the open sewage drain of Central University of South Bihar, Patna. In the present study, four VFRB were designed, round plastic containers (depth 100 cm, diameter 34 cm) of 65.6 litres was used to prepare the tankage of VFRBs. Two (VFRB-1 and VFRB-2) systems were filled with baked clay ball (BCB) and other two was filled with gravel (VFRB-3 and VFRB-4). All the CWs were planted with common reed (Phragmites karka) available in the region collected from the banks of river Ganga and cultivated in nursery. Phragmites has shown promising pollution reduction in other experiments conduction in subtropical Indian climatic conditions.

Fig. 1. Schematic representation of VFRB experimentation
The VFRBs were loaded with 12 litres of wastewater emanating from the University campus in batch mode at the interval of two days with the help of a dosing bucket. The bottom of the container was fitted with a tap to collect the treated water from the outlet. The hydraulic retention time (HRT) was kept 48 hours by allowing the wastewater to remain in the VFRBs for two days. The long open sewage grain itself worked as a sedimentation basin. Five plants of *Phragmites* species were planted at the top of container of an average root length of 62.4 ±5.55 cm and shoot length of 74.3±4.38 cm (figure 1). The dense stand of the vegetation was stored in a month time. During that period the wastewater was applied to the VFRB on a periodic basis. After one month, the wastewater was loaded with the specified HRT at two days.

**Media Selection And Preparation**

In this experimental setup, two media types were selected to be tested for P removal. Two VFRB cells/containers were filled up to the depth of 60 cm by locally available river bed gravel (figure 2) and other two with BCB. These VFRBs were separate experiments not connected in series. The experimental design used two replicates VFRBs to validate the results. The gravel size was kept at 20 mm with 40% porosity. Another media (BCB) was artificially prepared in the laboratory. The constituents of BCB were Ganga river clay (that is rich in Ca) and saw mill dust. The clay used in present study has been primarily dominated by mica, kaolinite, chlorite, smectite and vermiculite. Dough of river clay and saw mill dust (6:1) was prepared with adequate amount of distilled water. Small balls of 20 mm size were prepared from the dough. BCBs (figure 2) were first solar dried for three days, and then it was baked in muffle furnace in the laboratory at 900ºC for five hours. The baking at high temperature caused burning of the saw mill dust particles resulting into a porous BCB. The prepared BCB was then cooled down at room temperature. It was soaked in the distilled water overnight and then solar dried after cooling.

**Performance Monitoring**

Samples were collected in 1 litre plastic bottle on weekly basis from the inlet and outlet of the VFRBs, for the purpose of analysis. The collected samples were stored at 4ºC for further analysis in laboratory. A pre-calibrated electronic desktop pH-meter was used for the analysis of pH collected samples. The proportions of total suspended solids (TSS) were estimated by passing 50 ml sample through pre-weighted glass fiber filter papers using the filtration assembly. Final weight of the filter paper was taken after heating it at 103°C. TSS (mg/L) was calculated using the formula below.

\[ \text{TSS (mg/L)} = \frac{((A-B) \times 1000)}{\text{Sample Volume(ml)}} \]
(A = final weight of filter paper with dried residue, mg, and, B = pre-weight of filter, mg)

The analysed wastewater quality parameters with standard methods are presented in table 1. The pollution reduction efficiency for Phosphorus, BOD and TSS was estimated for all the VFRBs by comparing the inlet and outlet concentration of wastewater quality parameters as mention in the formula.\(^\text{26}\)

\[
\text{Pollutant reduction efficiency (\%) = } \frac{(C_i - C_o)}{C_i} \times 100
\]

\(C_i = \text{concentration of pollutant at inlet in mg/L,}
\]

\(C_o = \text{concentration of pollutant at outlet in mg/L}\)

**Table 1: Methods used for analysing the samples**

| S.No. | Parameters   | Method                                                                 |
|-------|--------------|------------------------------------------------------------------------|
| 1.    | pH           | Portable pH meter                                                      |
| 2.    | TSS          | Method 2540 D, APHA, 21st Edition, 2005                                |
| 3.    | BOD\(_5\)    | Method 5210 B, APHA, 21st Edition, 2005                                |
| 4.    | Total Phosphorus | Method 4500 P, APHA, 21st Edition, 2005                                |

**Fig. 3: Box plot showing the average TSS concentration at inlet and outlet of VFRBs**

**Fig. 4: Box plot showing % TSS removal by VFRB experiments**
Fig. 5: Box plot showing the average concentration of phosphorus at inlet and outlet of VFRBs

Fig. 6: Box plot showing % Phosphorus removal by VFRB experiments

Fig. 7: Box plot showing the average concentration of BOD5 at inlet and outlet of VFRBs
Results
The pH of the institutional wastewater at the inlet during the entire experimental period was in the range of 6.80 - 7.69. The pH at the outlet in VFRB-1, 2, 3 and 4 was in the range of 6.54 - 7.58, 6.81 - 7.43, 6.78 - 7.53 and 6.77 - 7.44, respectively. The mean pH at the inlet was recorded as 7.35 ± 0.24 and the mean pH at the outlet of VFRB-1, 2, 3, 4 was 7.14 ± 0.26, 7.12 ± 0.16, 7.22 ± 0.20, 7.23 ± 0.18. P removal with different types of slag experimented at the near-neutral range of pH that demonstrated good results in P reduction.27 Constructed Wetlands are efficient in theremoval of Total Suspended Solids (TSS),28 sedimentation is one of the key processes involved in the retention of TSS associated with P. The settling of the suspended particles by the action of gravity into the bottom and filter media in CW is termed as sedimentation. In the present study mean TSS (mg/L) in the inlet wastewater was 923.48 ± 138.72. The mean TSS (mg/L) at the outlet of VFRB-1 was 356.79 ± 93.45; VFRB-2, 341.03 ± 83.46; VFRB -3, 306.79 ± 61.26 and VFRB – 4, 301.68 ± 61.06 (figure 3). Mean TSS removal as recorded in VFRB-1 was 61.5 ± 6.84%; VFRB-2, 63.1 ± 5.78%; VFRB-3, 66.5 ± 5.95% and VFRB-4, 66.8 ± 7.29% (figure 4). The mean P in the inlet wastewater was 22 ± 3.42 mg/L. The P at the outlet of the VFRB-1 and VFRB-2 was in the range of 0.9 - 3.1 mg/L and 1.1 - 2.9 mg/L, respectively. The mean P concentration at the outlet of VFRB-1 was 1.7 ± 0.59 mg/L and at the outlet of VFRB-2 was 1.7 ± 0.57 mg/L (figure 5). The mean P removal from VFRB-1 and VFRB-2 was 92.3 ± 2.28% and 92.4 ± 2.24% (figure 6). In the gravel bed, VFRB-3 and 4, P concentrations at the outlet was 4.6 mg/l to 10.1 mg/l and 4.9 mg/l to 9.2 mg/l, respectively (figure 5). The mean P concentration at the outlet of the VFRB-3 and VFRB-4 was 6.6 ± 1.5 mg/l and 6.6 ± 1.48 mg/l with a P removal efficiency of 69.6 ± 6.8% and 69.2 ± 7.1%, respectively. The results evidenced that the BCB efficiency in P removal is better than the gravel (figure 6). The BOD₅ at the inlet was in the range of 113.7 mg/l – 146 mg/l. The BOD₅ removal efficiency in VFRB-1, VFRB-2 was recorded as 59.2 ± 3.4% and
62.5±3.19%, respectively. In the gravel bed VFRB-3 and VFRB-4, the BOD5 removal was 67.1±4.79% and 69.8±5.74%, respectively.

Discussion
Phosphorus is a major pollutant causing eutrophication, so, it's removal from wastewater using natural systems is attracting research interests. Even the low concentrations of P (< 10 mg/l) are sufficient to trigger algal blooms.29 TP content in the untreated wastewater was fluctuated between 16.3 mg/l to 27.3 mg/l. The reasons for TP at the inlet were wastewater from hostel kitchens, laboratories, and floor cleaning, bathing and washing. Studies have reported that CWs have been used for removal of P from grey waters. It has been established that the P removal in CWs are due to plant uptake, wetlands soil, microbes, precipitation in standing waters and retention in the media (Figure 9). However, the media plays a substantial role in P removal.30 In the present study P removal efficiency was estimated in the range between 87.2% - 95.7% in BCB filled VFRBs. The main phosphorus removal mechanisms are adsorption and precipitation reactions with Ca, Al, and Fe.31 For domestic wastewater treatment in Turkey, the TP removal efficiency for gravel was reported only 4% in vertical subsurface flow constructed wetlands.32 In another study, a low P removal (20%) was reported using gravel in CWs.29 In a before and after treatment study it was reported that the blast furnace slag (98% removal) show similar results as BCB at a low (3mg/l) TP concentration.33 Newer substrates like fragmented limestone demonstrated an average P removal of 67% that is lower than the BCB in a mesocosm level study.34 The fly as ceramics also has equal potential (90% P removal) for P removal as BCB in the present study.35

Conclusion
VFRBs filled with gravel and BCB, planted with Phragmites were tested for P removal at the mesocosm level. The highest TP removal was recorded in VFRB-1 (92.4%) > VFRB-2 (92.3%) > VFRB-3 (69.6%) > VFRB-4 (69.2%) in the present experimental work. The VFRB-1 and 2 exhibited the highest P removal that was filled with the BCB substrates made up of clay and saw mill dust, making it porous, providing active surface activity of P. Based on the study, it is recommended that BCB can serve as better substrate for P removal in vertical flow constructed wetlands. Further, there is scope to develop new substrate materials focusing on its P retention capacity, long lasting performance and cost of the substrate to be applied in real treatment situations.

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Conflict Of Interest
The authors do not have any conflict of interest.

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