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The characteristics and effect of grain-slag media for the treatment of phosphorus in a biological aerated filter (BAF)

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ABSTRACT

Haydite and grain-slag, a new type of filter media made of grain slag, were used as filter media for biological aerated filter (BAF) to treat synthetic wastewater in parallel. The aim of this study was to compare the phosphorus removal performance of two BAF reactors at the different influent pH values, hydraulic retention time (HRT), and phosphorus load rates. It demonstrated that the BAF packed with grain-slag showed higher phosphate removal efficiency than with haydite. The removal of phosphate by the grain-slag BAF was in the range of 75.21–84.98%; 63.10–70.44%; 40.49–48.02%; and 26.10–33.11%, respectively, under the HRT of 12, 8, 5, and 1 h. The results obtained from the study of phosphate removal rate vs. pH values indicated that grain-slag BAF could remove phosphorus effectively by biologically induced chemical precipitation and the sediments do not affect the effluent turbidity.

Keywords: Grain-slag media; Biologically induced; Chemical precipitation; Phosphorus removal

1. Introduction

With increasing pressure and changes in water discharge legislation since the 1970s, phosphorus (P) has become a concerned pollutant due to eutrophication and deterioration of watercourses, if phosphorus (P) is discharged into water bodies such as lakes, rivers, and creeks in excessive amounts. Phosphorus removal from wastewater has been widely studied during the past decades. The conventional technologies for P-removal from wastewater are: physical processes (settling and filtration), chemical precipitation (with aluminum, iron, and calcium salts), and biological processes that rely on the biomass growth (bacteria, algae, and plants) or intracellular bacterial polyphosphates accumulation [1]. Low-cost and low-maintenance extensive treatment processes based on P-retention in biological aerated filter (BAFs) containing reactive media have been developed and showed promising results [2]. The application of low-cost and easily available materials has been widely investigated during recent years, such as fly ash [3], blast furnace slag [3,4], and iron oxide tailings [5]. Grain slag is a type of granular residue which is produced by water quenching and allegro cooling in the process of steelmaking. At the recent times, grain slag dumped as waste material by majority of steel mills not only occupy large amount of cultivated land, but also contaminate environment [6]. The development and utilization of grain slag are still in the early stage. Due to similar mineral contents, grain slag wastes were selected to replace a part of clay in our research to produce a new filter material grain slag. In our previous study, grain-slag filters employed in an

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upflow lab-scale BAF were investigated for synthetic wastewater treatment [7]. The results indicated that under ammonia nitrogen load rates varying from 0.49 to 1.21 kg NH_3-N· $(m^3\,d)^{-1}$, the overall NH_3-N reductions of the BAF supported by grain slag and haydite averaged 84.30 and 80.87%, respectively, suggesting that the grain-slag system had a remarkable superiority to the haydite employed as support.

The objective of this work was to test the feasibility of the grain-slag BAF for the removal of phosphorous. The characteristics of grain slag such as total porosity, total surface area, pore size distribution, apparent and bulk density, crystal structures, and chemical composition were examined and analyzed. The solution pH, contact time, and initial phosphate concentration of grain slag and haydite were evaluated in batch experiments using orthophosphate solution. Subsequently, two BAFs with different granular mediums were conducted with the synthetic wastewater in parallel. The P-removal performance of two BAF reactors at the different influent pH values, hydraulic retention time (HRT), and phosphorus load rates were investigated.

2. Materials and methods

2.1. Materials

Grain-slag particles were composed of waste material—grain slag, clay, and starch with a mass ratio of 3:2:1; Grain slag was taken from Laiwu Iron & Steel Co., Ltd, Shandong Province of China and clay was obtained from Jinan Waste Treatment Plant. Haydites were made only from clay. Grain slag and haydite were prepared as follows: first, raw materials were mixed in a muller and transported into a rotational disk; meanwhile tap water was added to prepare powdered materials into particles with a similar diameter. And then, semi-manufactured grain-slag media were diverted to the front of a rotary kiln for desiccation and heated at a high temperature of 1,150℃. Finally, filter media were obtained and cooled off after screen separation.

2.2. Reactor description

Lab-scale BAF reactors were made of Plexiglas with a diameter of 0.15 m and are shown in Fig. 1. The reactors had an upflow configuration, a height of 2.3 m and contained 0.2 m of supporting layer in 1.5 m of media. The volume of reactor was 0.265 L. One reactor was packed with grain slag and the other was packed with haydite. Parameters were determined according to the Filter Material for Water Treatment (CJ/T 43-2005) standard including particle diameter and density. The pore characteristics of filter materials were detected by mercury intrusion porosimetry (ASAP2020). As shown in Table 1, Grain slags were superior to haydites in many ways, including higher total porosity, larger total surface area, and lower density. According to the investigation of Kent et al. [8], these characteristics were essential for filter materials which were suitable for BAF media.

The biofilter was backwashed periodically in order to remove the accumulated suspended solid and the excess biomass produced. We carried out backwashing every

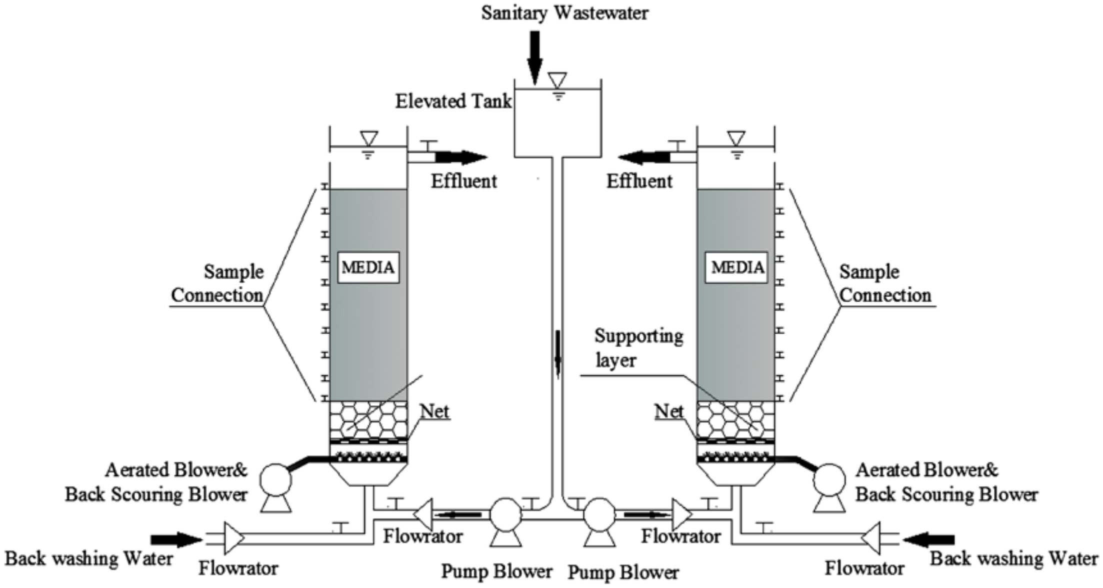


Fig. 1. Experimental schematic view of lab-scale BAF system.

24 h. The backwash sequence included air scour, followed by air scour and water backwash, at last water scour. The backwash air and water superficial velocities were both 10 L $(m^2 s)^{-1}$. Backwash conditions are as follows: in the first step, after shutting off the feeding to the reactor, air was introduced for 3 min at the bottom of the filter. In the second step, clean water and air were kept entering the filter for 5 min. Then in the third step, airflow was stopped and clean water was kept for 7–8 min.

2.3. Wastewater characteristics

Throughout the experimental period, the BAF was fed with synthetic wastewater at ammonia nitrogen loading rates ranging from 0.76 to 0.78 kg NH_3-N·$(m^3 d)^{-1}$ and chemical oxygen demand (COD) ranging from 3.55 to 3.62 kg COD·$(m^3 d)^{-1}$. Synthetic concentrated water containing ammonium chloride, bicarbonate, and starch served as main sources of nitrogen, inorganic and organic carbon, respectively, as well as other nutrients (Table 2). The concentrated substrate solution was diluted with tap water to meet the demanded concentration before entering the reactor.

2.4. Analytical methods

The composition of filter materials were analyzed according to the method of Kent et al. [8]. During the operation of BAFs, influent and effluent samples were taken regularly and the concentrations of total phosphorus (TP), COD, ammonia nitrogen, turbidity, colour, and calcium ion were analyzed according to standard methods [9,10]. Probes were used to measure the temperature, pH, and dissolved oxygen concentrations during the experimental period. Ports, at intervals of 0.15 m from the base of the columns, allowed samples to be drawn at specific intervals so that substrate removal profiles could be examined. Generally, samples were drawn at the end of the filter run, but occasionally samples were also taken immediately after backwashing to examine the recovery of effluent quality.

2.5. Batch phosphate sorption experiments

To investigate the relationship between solution pH and P-removal varied with time, different solution pH (initial values ranging from 4.02 to 10.36) and phosphate removal as a function with time were examined in a series of experiments using the same initial phosphate concentration of 20 mg L^{-1}, and the solutions were adjusted to the desired pH levels by using 0.1 mol/L HCl or NaOH solution. 5 g grain slag

Table 1
The comparison of elemental property between grain slag and haydite

Filter material	pH	Particle diameter (mm)	Particle density (kg m^{-3})	Bulk density (kg m^{-3})	Total porosity (%)	Biofilm (g g^{-1})	Total surface area ($m^2 g^{-1}$)
Grain slag	9.5	3–5	2202.60	1256.80	35.17	0.032	9.98
Haydite	7.1	3–5	2262.40	1524.93	29.59	0.021	0.73

Table 2
The synthetic wastewater composition

Constituents	Concentration ($mg\,L^{-1}$)	Constituents	Concentration ($mg\,L^{-1}$)
Starch	150–180	$MgCl_2 \cdot 6H_2O$	5
Peptone	10	$FeCl_3 \cdot 6H_2O$	5
$Na_2HPO_4 \cdot 12H_2O$	15–20	$NaHCO_3$	100–500
NH_4CO_3	10	NaCl	5
$CaCl_2$	5	Sanitary waste (%)	10%
NH_4Cl	100–150		

or 5 g haydite was put in each 250 mL Erlenmeyer glass flasks containing 100 mL of different P solution, and shaken at 150 rpm and 25℃. At different time intervals, the pH and phosphate concentration of the solution were measured.

2.6. Operating conditions

The BAF test was divided into four stages. During each test stage, the operating conditions of two BAFs were identical, which were summarized as follows:

- Stage one, 30 days: The temperature of the mixed liquid was controlled at 20–25℃, Dissolved Oxygen (DO) above 4 $mg\,L^{-1}$, pH 6.2–6.8, and HRT 12 h.
- Stage two, 30 days: The temperature of the mixed liquid was controlled at 20–25℃, DO above 4 $mg\,L^{-1}$, pH 6.2–6.8, and HRT 8 h.
- Stage three, 30 days: The temperature of the mixed liquid was controlled at 20–25℃, DO above 4 $mg\,L^{-1}$, pH 6.2–6.8, and HRT 5 h.
- Stage four, 30 days: The temperature of the mixed liquid was controlled at 20–25℃, DO above 4 $mg\,L^{-1}$, pH 6.2–6.8, and HRT 1 h.

2.7. Start-up of BAFs

Seed sludge was inoculated from Jinan City Wastewater Treatment Plant. The two BAFs were operated under the same conditions and backwashed once in every 24 h, then steady state was reached after 7-weeks' operation.

3. Results and discussion

3.1. Chemical characteristics of the materials

The chemical composition of the materials for this study is presented in Table 3. The grain slag was rich in calcium (Ca) oxides, representing 50.77% (Table 3). Ca is known to play an important role in P-retention by soils and sediments [11,12]. The presence of Ca facilitates P-retention via precipitation, and formation of Ca–P deposition on the solids surfaces [13]. Depending on the pH and the solution composition of Ca and P ($H_2PO_4^-$ or HPO_4^{2-}), several Ca–P may form: amorphous calcium phosphate, octacalcium phosphate, dicalcium phosphate, dicalcium phosphate dihydrate, tricalcium phosphate, and hydroxyapatite [14,15].

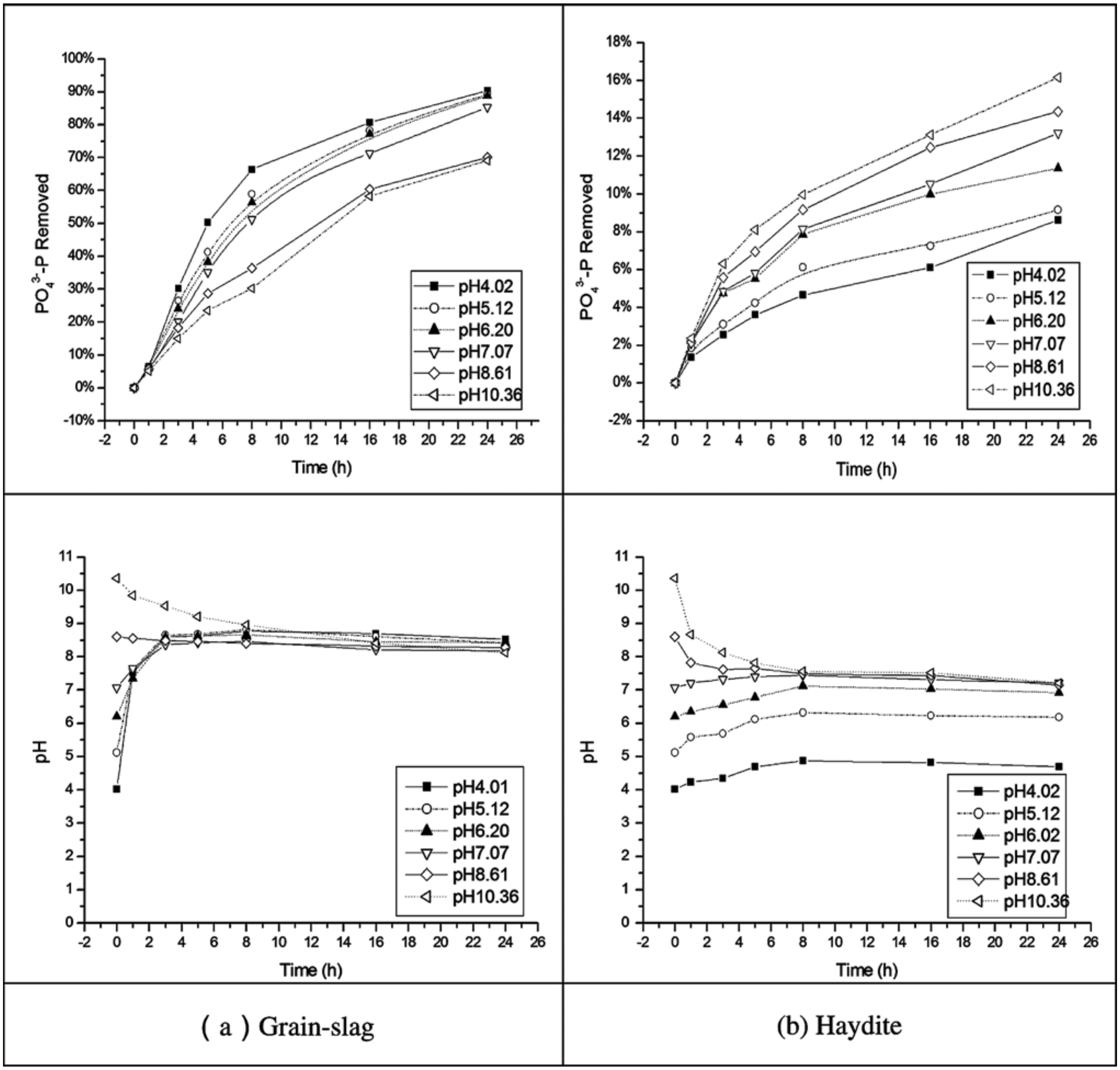
Si and Ca oxides constituted 69.20 and 2.55% of the haydite, respectively (Table 3). The haydite was high in Si, however, it was previously reported that Si has little efficiency for P-retention [16].

3.2. Solution pH and P-removal varied with time

To investigate the relationship between solution pH and P-removal varied with time, six solutions with the same initial phosphate concentration (20 $mg\,L^{-1}$) and different initial solution pH values, in range of 4.02–10.36, were detected at different time intervals for grain slag and haydite, respectively. Phosphate removal rates and pH changes of grain slag and haydite with time are presented in Fig. 2. It was found that solution pH plays a critical role in the rate and mechanism of the removal of phosphate. The solution

Table 3
The chemical composition of the filter materials

Filter materials	SiO_2 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Loss (%)
Grain-slag	30.15	50.77	7.3	0.96	5.16	1.25
Haydite	69.20	2.55	2.63	5.80	16.70	0.53



(a) Grain-slag

(b) Haydite

Fig. 2. Phosphate removal rates and pH changes with time by grain slag and haydite.

pH with grain slag changed dramatically and remained close to the neutral level with time, and was stable around pH of 8.5 in 8 h. But the solution pH with haydite also keeps stable around it. The adsorption process, in which grain slag was used, started in the acidic range and was followed by an increase in pH. The increase in pH was considered to be due to the grain-slag dissolution, when some of the grain-slag compound as iron, hydroxide, and oxide hydroxide were released to the solution. The decrease in pH in basic range for grain slag can be explained that the removal of phosphate was accompanied by a decrease in the Ca^{2+} ion concentration and pH value [17].

Fig. 2 shows the P-removal rate of grain slag was higher than haydite. The P-removal of the grain slag tended to decrease with increase in initial pH above neutral. It is known that high pH and high Ca^{2+} concentration are advantageous for calcium phosphate precipitation. The influence of initial pH on P-removal by grain slag was significant at beginning, and with solution pH close to a stable value, the pH was eliminated. The influence of initial pH on phosphate removal by haydite was significant, especially in the terminal. Based on the chemical composition of the grain slag and haydite and the appropriate solution pH, it was believed that Ca content primarily contributed to P immobilization in grain slag. The mechanism of calcium contents in phosphate immobilization may be the formation of calcium phosphate precipitation by the reaction of dissolved Ca^{2+} with the phosphate in solution.

3.3. TP reduction in two BAFs

Two BAFs were monitored for 6 months after the start-up of the biofilters. Throughout the experiment, DO was maintained above $4\,mg\,L^{-1}$ and water temperature was kept between 20 and 25°C. Organic loading rates varied from 3.55 to $3.62\,kg\,COD{\cdot}(m^3\,d)^{-1}$ and ammonia nitrogen loading rate from 0.76 to $0.78\,kg\,NH_3\text{-}N{\cdot}(m^3\,d)^{-1}$. Four HRTs, 12, 8, 5, and 1 h were adopted, coincided with hydraulic loadings 0.125, 0.1875, 0.300, and $1.5\,m^3\,(m^2\,h)^{-1}$, respectively. The changing trends of TP of the influent and effluent are shown in Fig. 3.

In terms of removing TP, grain-slag BAF showed higher TP removal compared with haydite BAF, as shown in Fig. 3. The TP removals of grain slag and haydite BAFs were 26.11–84.98% (on average, 57.10%) and 3.47–38.11% (on average, 19.85%), respectively. The results indicated that there might be precipitation of calcium phosphate produced in grain-slag BAF during the process. As shown in Fig. 3, grain-slag BAF had excellent removal on the TP when HRT was longer than 5 h, and manifested a decrease of TP removal while HRT was at 5 and 1 h.

The TP in the effluent ranged from 1.20 to $2.79\,mg\,L^{-1}$ with an average of $1.94\,mg\,L^{-1}$ for grain-slag BAF. TP removals of grain-slag BAFs varied from 63.10 to 84.98% (on average, 74.30%), when HRT was longer than 5 h. When HRT was 5 and 1 h, the effluent of grain-slag BAF had TP concentrations of 3.83–$6.00\,mg\,L^{-1}$ (on average, $4.77\,mg\,L^{-1}$). TP removal grain-slag BAFs varied from 26.10 to 48.02% with an average of 37.36%. According to the study of Carlsson [18], calcium phosphate precipitation occurred in all the systems at sufficiently high concentrations of calcium and phosphate at neutral pH. The wastewater in this study did not contain so much high phosphate concentrations, and thus no precipitation was produced in grain-slag BAF. But as shown in Fig. 3, once HRT was longer than 5 h, the TP removal improve from 11.44 to 27.12% in average for haydite BAF. On the other hand, in grain-slag BAF the TP removal

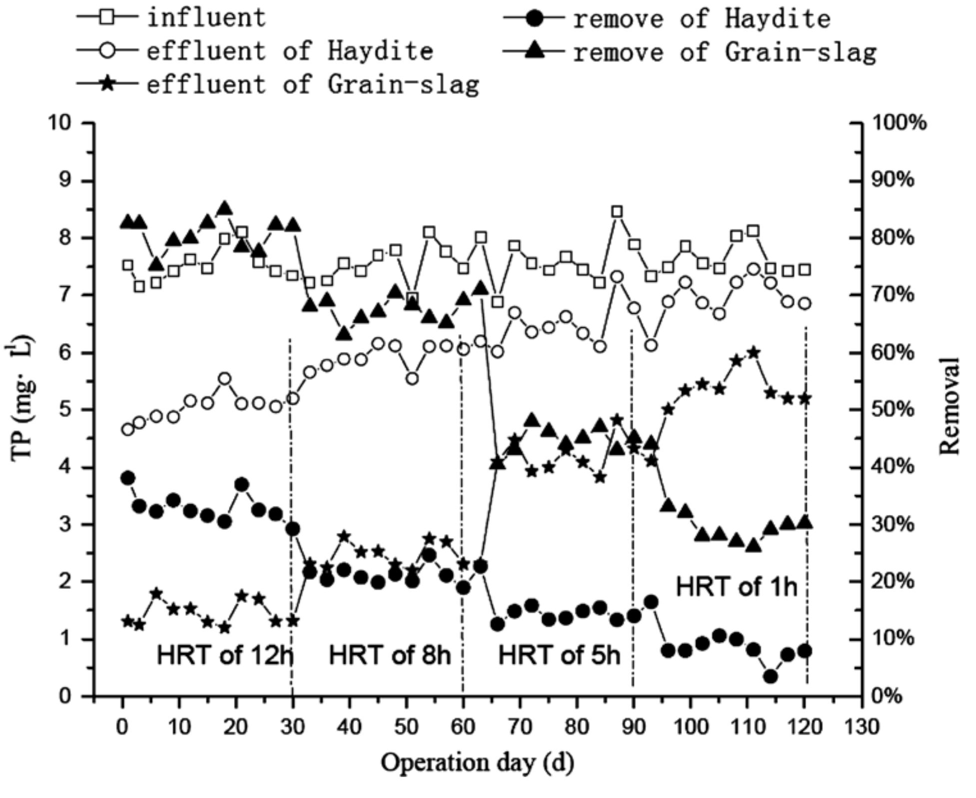


Fig. 3. TP concentrations and removals in influent and effluent of BAFs.

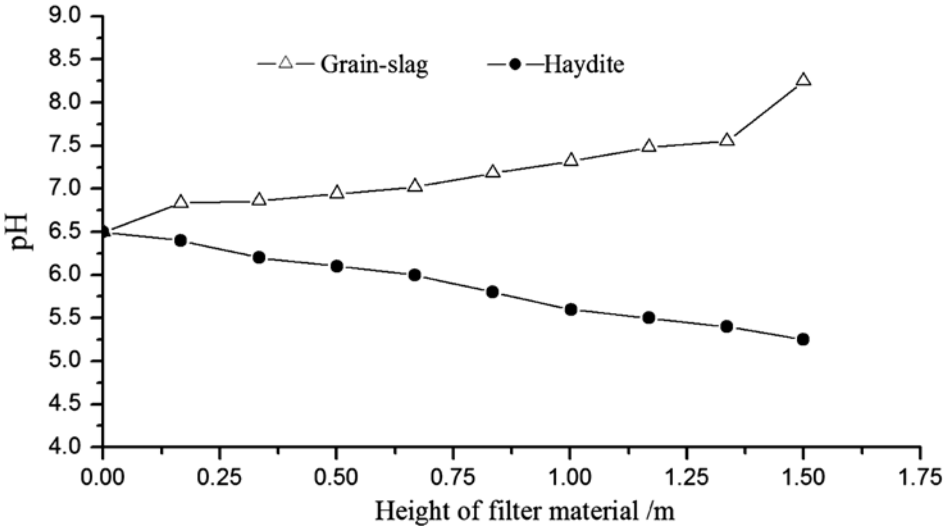


Fig. 4. Comparison of pH values in axial distribution with between grain-slag BAF and haydite BAF.

reached an average of 37.36 and 74.30%, respectively. This result confirmed that TP in grain-slag effluent could be removed by producing calcium phosphate precipitation at longer HRT.

3.4. Influent and effluent pH in two BAFs

To investigate pH value in axial distribution of two BAFs, the pH value of influent water was kept at 6.50. The operational results are shown in Fig. 4. According to operation result, the pH value increased

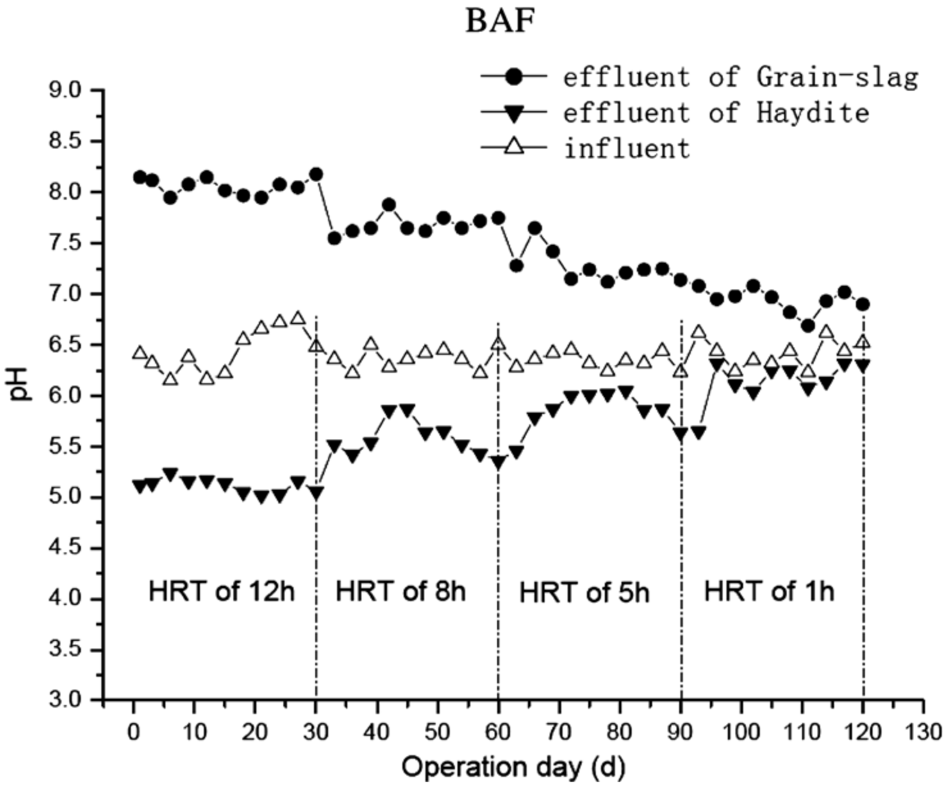


Fig. 5. pH value in influent and effluent of BAFs.

rapidly from 6.50 to 8.25 with the height of filter media in the grain-slag BAF, while the pH value decreased from 6.50 to 5.25 in the haydite BAF. The results also indicated that grain slag can remove $CaCO_3$ into the wastewater to buffer pH value.

The influent and effluent pH of two BAFs are shown in Fig. 5. Effluent pH of grain-slag BAF was constant and higher, mainly due to its buffer ability to neutralize H^+ produced during NH_3-N nitrification. The effluent pH of haydite BAF was lower than that of grain-slag BAF, resulting from H^+ accumulation during the process of NH_3-N nitrification. This result also confirmed that grain slag can remove $CaCO_3$ into the wastewater to buffer pH value and could remove phosphorus effectively by biologically induced chemical precipitation.

4. Conclusion

The solution pH with grain slag changed dramatically and remained close to the neutral level with time, and was stable around pH of 8.5 in 8 h. But the solution pH with haydite also was stable around it. Based on the chemical composition of the grain slag and haydite and the appropriate solution pH, it was believed that content primarily contributed to P immobilization in grain slag. The results of two BAFs experiments indicated the feasibility of the grain slag as filter media for phosphorous removal from wastewater. And, the BAF packed with grain slag presented higher phosphate removal efficiency than that with haydite. The TP removals of grain slag and haydite BAFs were 26.11–84.98% (on average, 57.10%) and 3.47–38.11% (on average, 19.85%), respectively. TP in grain-slag BAF effluent could be removed by producing calcium phosphate precipitation at longer HRT. Due to the low cost, the grain-slag BAF possess the potential to be utilized for cost-effective phosphorus removal and wastewater treatment.

Acknowledgments

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