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Performance of Porous Substrates for Domestic Wastewater Treatment under Prolonged Hydraulic Retention Time

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Abstract

Physicochemical characteristics of porous substrates (longan biochar, corn biochar, and pumice) including specific surface area (SSA), pore volume (Vp), and cation exchange capacity (CEC) were determined. Longan biochar had the highest SSA, Vp, and CEC, followed by corn biochar and pumice. Then, columns filled with each of these 3 substrates together with gravel as a control treatment, were evaluated to compare wastewater treatment efficiency under different hydraulic retention times (HRTs). Each system had been acclimatized with wastewater for 8 weeks. Then, influent and effluent were analyzed at 1, 3, 5, and 7 day intervals. Water analysis revealed that biochar-based systems showed higher dissolved oxygen (DO) development and greater removal of biochemical oxygen demand (BOD_5), total suspended solids (TSS), ammonium (NH_4-N), total Kjeldahl nitrogen (TKN), and nitrate (NO_3-N) than pumice and gravel-based systems. Prolongation of HRT significantly increased NO_3-N removal and slightly increased BOD_5 and TSS removal. Both BOD_5 and TSS removal in biochar-based systems after 1 day HRT was about 93–94% while they significantly increased with HRT extension to a high of 97–98%. Furthermore, NO_3-N removal in biochar-based systems increased from 47–48% after 1 day HRT to 80% after 5–7 days HRT. In addition, NH_4-N and TKN removal was influenced by both substrate and HRT with significant interaction between these two factors. Longan biochar-based systems, in particular eliminated almost 90% of both NH_4-N and TKN and the removal efficiency improved significantly after HRT was extended. Meanwhile, both NH_4-N and TKN removal were only 20–30% in the gravel-based systems and 50-60% in pumice-based system. The study suggests that longan biochar is the most effective substrate. Longer HRTs were also found to increase the efficiency of removing organic matter and nitrogen.

Keywords: Filter media; Hydraulic retention times; Nitrogen removal; Substrates; Wastewater treatment

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Introduction

Excess nitrogen discharged from households or agricultural areas can cause eutrophication in the water column and stimulate growth of algae, leading to a decline of dissolved oxygen in water. In order to protect aquatic life, wastewater needs to be treated before draining. Constructed wetlands (CWs) are alternative wastewater treatment systems which are low-cost investments, eco-friendly, and have high pollutant removal efficiency [1–2]. The systems remove nutrients and pollutants through several processes including microbial degradation, microbial N transformation, sedimentation, and nutrients uptake by plants. Substrates are the main elements of CWs functioning as filters, plant support, and microbial habitats. Soil, sand, gravel, and rock are conventionally used as substrates in CWs [2], but their potential to remove pollutants could be limited due to clogging and O_2 limitation [3–4]. Thus, substrate selection for CWs is an important step in setting up a system. A previous study recommended a porous substrate to be used in the treatment system, such as zeolite which lowers chemical oxygen demand (COD), NH_4-N, and NO_3-N more than conventional substrates such as sand [5].

Biochar is carbon-rich material pyrolyzed from organic material, mostly from agricultural waste, in anoxic conditions at high temperatures (300–700 ºC). It has been used for various purposes, for example, soil amendment [6], or pollutant adsorption [7]. Because of its physical structure with high porosity, high surface area, and cation exchange ability, biochar has been selected to be used in CWs as a pollutant filter [8]. Previous studies found biochar pyrolyzed from bamboo, oak tree, and *Miscanthus* have high potential to reduce biochemical oxygen demand (BOD_5), total suspended solids (TSS), nitrogen, and phosphorus in CWs [9–11]. Nonetheless, biochar characteristics and wastewater treatment efficiency vary depending on biochar derivation [12]. Longan and corn are popular economic crops in northern Thailand earning high income for farmers. However, agricultural waste such as longan branches and corn cobs are burnt after harvest which can cause air pollution. Biochar production is one solution that reduces dust emission caused by the burning of agricultural waste and commercially provides extra income for local people. Previous studies reported that biochar produced from longan branches and corn cobs can enhance growth of longan and wheat after being used for soil amendment [13–14]. In terms of wastewater treatment, few studies on the application of corn cob biochar in CWs have been reported [15–16]. By comparison, studies using longan biochar as a filter and plant support have been initiated by Jampeetong and Janyasupab [17]. The plant structure of longan and corn are obviously different (woody and non-woody plants), so pollutant removal capacity of these two kinds of biochar are presumed to be different due to the influence of physico-chemical characteristics. Pumice (volcanic rock) is another porous material which is also multi-functional. It was reported to be used as construction material [18]. For pollutant removal, it performed well in phosphorus removal and showed high COD reduction after water treatment [19–20].

Hydraulic retention time (HRT) is another factor influencing performance of wastewater treatment systems. Systems filled with conventional substrates such as gravel, rock, and sand showed increasing of pollutant removal with extension of HRT [21–23]. In the case of biochar and pumice, their porous structure and high surface area are hypothesized to purify wastewater in a shorter time than non-porous substrates. Therefore, this study measured physicochemical characteristics of porous substrates (longan biochar, corn biochar, and pumice), including specific surface area (SSA), pore volume (Vp), and cation exchange capacity (CEC) which affect organic matter filtration capacity and N elimination from wastewater [24]. Then, columns filled with the three different porous substrates were designed to evaluate their efficiency for wastewater treatment compared with a non-porous substrate (gravel) as a control treatment under different HRTs (1, 3, 5, and 7 days). The results are expected to be useful for material selection for filtration in CWs.

Materials and methods

1) Substrate preparation

Substrates used in this experiment included gravel (ø = 10–15 mm), longan biochar (ø = 3–5 mm), corn biochar (ø = 3–5 mm), and pumice (ø = 10–20 mm). Longan biochar and corn biochar were prepared at Warm Heart Foundation, Phrao District, Chiang Mai Province, Thailand. Longan branches and corn cobs were pyrolyzed in the absence of oxygen at 450 ºC for 2 h before the materials were crushed. Before use, both kinds of biochar were sieved through a 1.5 mm net to eliminate ashes. Then, they were soaked in buckets filled with tap water. The water was drained and renewed once a day for two weeks to reduce biochar toxic contaminants [25].

2) Physicochemical characterization of porous substrates

Fifty milligrams of longan biochar, corn biochar, and pumice samples were crushed into 1 mm particles, transferred into Quantachrome Autosorb-1 (Quantachrome Instrument Corp.), degassed at 120 ºC, and their N_2 adsorption was measured at 77 K. The volume of adsorbed N_2 was used for calculation of specific surface area (SSA) and pore volume (Vp) according to Brunauer-Emmett-Teller (BET) [26] and Barrett-Joyner-Halenda (BJH) [27], respectively. For CEC measurement, the samples were saturated in 1 N NH_4OAc and analyzed for exchangeable cation content according to Chapman [28].

3) Experimental design and operation

The columns (ø =15 cm, height 55 cm) were created from polyvinyl chloride (PVC) pipes (Figure 1). They were filled with four different substrates, including longan biochar, corn biochar, pumice, and gravel as a control treatment (four replicates for each substrate-filled column, totalling 16 columns). In the gravel and pumice-based systems, each substrate was filled into the column to a height of 50 cm. The bottoms of the longan biochar and corn biochar- based systems were first filled with gravel (ø =10–15 mm) to a height of 10 cm, then the 40 cm above were filled with either longan or corn biochar (Figure 1b). Domestic wastewater was collected from the Wastewater Treatment Unit, Chiang Mai University, Chiang Mai, Thailand. The columns were fully filled with wastewater to reach similar water levels (50 cm). The volume of wastewater in the gravel, longan biochar, and corn biochar-based systems was 3.7 L while the wastewater volume in pumice-based systems was 5.2 L. The higher porosity of pumice allowed the system to receive a larger wastewater volume to reach the same water level in the column. The columns were acclimatized for 8 weeks to develop biofilm. Then, the wastewater in each column was drained out and renewed. To determine the effect of HRT on performance of each system, the experiment was divided into 4 phases (four replicates per phase). In each phase, wastewater was treated under different HRTs. In the first phase (HRT = 1d), three replicates of the wastewater were sampled to measure water quality indicators before filling the cylinders from the top and allowing the water to sit for a day. Then, effluent from each column was sampled at the bottom for water analysis and completely drained out, yielding four replicates per substrate (Figure 1a).

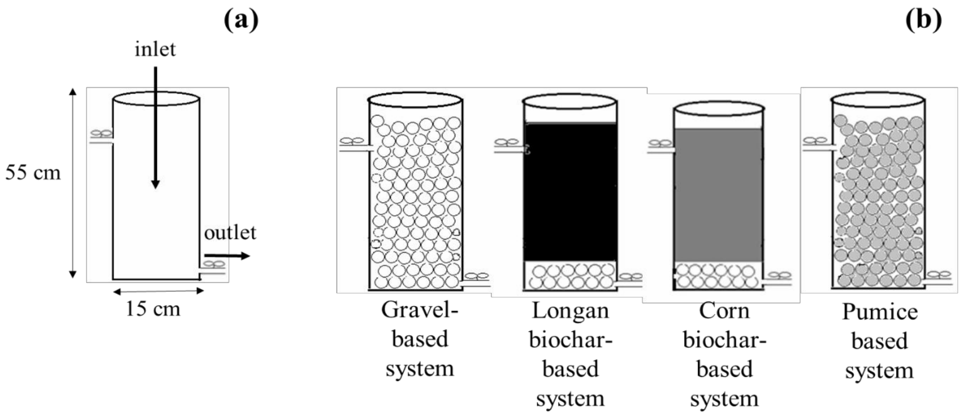

Figure 1 (a) Schematic presentation of column characteristics and water feeding and draining direction and (b) the experimental set-up of four systems filled with different substrates.

The procedure was repeated three more times to yield four replicates for HRT = 1d (totalling 4 repetitive sampling). Prior re-start each replicate, the substrate was let standing without wastewater for 1 day. In the second, third, and fourth phases, wastewater was sampled three times to measure water quality indicators and refilled into the cylinders as in the first phase but was left in the systems for 3, 5, and 7 days intervals, respectively. The procedure was repeated three more times to yield four replicates for each phase. The experiment was conducted totally 16 weeks. Mean organic loading rate (OLR) of the gravel, longan biochar, and corn biochar-based systems at 1, 3, 5, and 7 days HRT were 0.0249, 0.0096, 0.0053, and 0.0043 kg m^{-3} d^{-1} while OLR of pumice-based system were 0.0350, 0.0135, 0.0075, and 0.0060 kg m^{-3} d^{-1}. Mean nitrogen loading rate (NLR) of gravel, longan biochar, and corn biochar-based systems at 1, 3, 5, and 7 days HRT were 0.0075, 0.0032, 0.0022, and 0.0015 kg m^{-3} d^{-1} while NLR of pumice system were 0.0105, 0.0045, 0.0030, and 0.0022 kg m^{-3} d^{-1}.

4) Water analysis

Quality parameters of influent and effluent were analyzed as follows; (i) DO and BOD_5 by an azide modification method (4500-O C) [29], (ii) total suspended solid (TSS) by filtering samples through a GF-C (Whatman® Glass Microfiber Filters; Ø = 47 mm) (2540 D) [29], (iii) ammonium (NH_4-N) by the modified Salicylate method (Quikchem Method no. 10-107-06-3B; Lachat Instruments, Milwaukee, WI, USA), (iv) total Kjeldahl nitrogen (TKN) by the Kjeldahl method [30], (v) nitrate (NO_3-N) by the UV-method [31] using a UV-VIS spectrophotometer (Lambda 25 version 2.85.04, USA), (vi) pH and temperature using a multi-parameter analyzer (CyberScan PC 300, Eutech Instruments Pte Ltd., Singapore).

5) Media adsorption

Mineral content (N, K, Ca, and Mg) accumulated in each porous substrate was determined at the beginning and the end of the experiment in order to assess their adsorption ability. Approximately 500 mg of each sample (n=2) collected at the middle of the column was dried using a hot air oven (Memmert, UM 500, Germany) at 60 ºC for 48 h. Then, the samples were digested with H_2SO_4 and HNO_3 solution under high temperature (220–360 ºC). Concentrations of N were measured by the Kjeldahl method [30], while K, Ca, and Mg concentrations were analyzed using atomic absorption spectrometry (AAS) (SpectrAA, Varian, Australia) according to Robinson [32].

6) Data analysis

The removal percentages of BOD_5, TSS, NH_4-N, TKN, and NO_3-N in each system were calculated using the formula in Eq. 1.

$$\%Removal = (C_i - C_e) * 100/C_i \qquad (Eq.1)$$

where; C_i is influent concentration and C_e is effluent concentration. The data was analysed by one-way and two-way analysis of variance (ANOVA) using software Past326b [33]. Tukey Honestly Significant Differences (HSD) post hoc procedure at the 5% significance level was performed to identify significant differences between treatments.

Results

1) Physicochemical characteristics of biochars and pumice

The highest SSA, Vp, and CEC were found in longan biochar (Table 1). The SSA of longan biochar was 2 and 7 times greater than those of corn biochar and pumice. Similarly, Vp of longan biochar was 1.6 and 3.4 times compared higher than those of corn biochar and pumice. CEC in longan biochar was 1.5 and 6 times higher than in corn biochar and pumice.

2) Water analysis

The pH and temperature in the influent and effluent varied slightly between 6.8–7.2 and 27–30 ºC, respectively (Table 2). However, DO concentrations were influenced solely by substrates ($p<0.001$). They increased from 0 to 2.3–2.7 mg L^{-1} in the longan biochar and corn biochar-based systems while DO concentrations in the pumice-based system were 1.6–1.7 mg L^{-1}, but DO concentrations in the gravel-based system were only 1.2–1.4 mg L^{-1} (Table 2–3).

Table 1 Specific surface area (SSA), pore volume (Vp) and cation exchange capacity (CEC) of longan biochar, corn biochar and pumice used in this study

Substrates	Specific surface area (m^2 g^{-1})	Pore volume (cc g^{-1})	Cation exchange capacity (cmol kg^{-1})
Longan biochar	162.56	0.1429	13.06
Corn biochar	77.02	0.0887	8.49
Pumice	23.07	0.0426	2.22

Table 2 Influent and effluent measurements (mean ± SE) of DO, pH, temperature, BOD_5, TSS, NH_4-N, TKN and NO_3-N in different substrate-based columns at 1, 3, 5, and 7 days HRT

	HRT (days)	Influent	Effluent			
			Gravel- based system (control)	Longan biochar-based system	Corn biochar-based system	Pumice-based system
DO (mg L^{-1})	1	0.0 ± 0.0	1.4 ± 0.1	2.5 ± 0.2	2.6 ± 0.2	1.7 ± 0.1
	3	0.0 ± 0.0	1.2 ± 0.4	2.3 ± 0.2	2.7 ± 0.2	1.6 ± 0.1
	5	0.0 ± 0.0	1.3 ± 0.1	2.4 ± 0.2	2.6 ± 0.1	1.7 ± 0.1
	7	0.0 ± 0.0	1.2 ± 0.2	2.5 ± 0.1	2.7 ± 0.1	1.7 ± 0.2
pH	1	6.9 ± 0.3	6.9 ± 0.1	7.2 ± 0.0	7.1 ± 0.1	6.9 ± 0.1
	3	7.1 ± 0.1	6.9 ± 0.0	7.0 ± 0.0	7.0 ± 0.0	7.0 ± 0.0
	5	7.1 ± 0.0	7.0 ± 0.0	7.1 ± 0.0	6.9 ± 0.0	7.0 ± 0.0
	7	7.1 ± 0.1	6.9 ± 0.0	7.0 ± 0.0	6.8 ± 0.0	7.0 ± 0.0
Temperature (ºC)	1	29.2±0.3	28.5±0.1	28.4±0.1	28.5±0.1	28.3±0.1
	3	28.8±0.2	28.5±0.1	28.4±0.1	28.5±0.1	28.3±0.1
	5	29.4±0.5	29.4±0.3	29.2±0.3	29.5±0.3	29.9±0.1
	7	28.5±0.1	26.9±0.2	26.9±0.2	27.1±0.2	27.3±0.2
BOD_5 (mg L^{-1})	1	66.0 ± 13.7	7.5 ± 0.9	3.3 ± 0.8	4.9 ± 0.3	8.0 ± 1.3
	3	76.6 ± 6.4	6.1 ± 1.2	2.5 ± 0.5	2.5 ± 0.8	4.0 ± 0.7
	5	70.8 ± 10.7	3.7 ± 0.6	1.5 ± 0.3	1.5 ± 0.5	4.0 ± 0.4
	7	79.2 ± 8.5	3.3 ± 0.8	1.4 ± 0.3	1.9 ± 0.3	4.0 ± 0.8

Table 2 Influent and effluent measurements (mean ± SE) of DO, pH, BOD_5, TSS, NH_4-N, TKN and NO_3-N in different substrate-based columns at 1, 3, 5, and 7 days HRT (*continued*)

	HRT (days)	**Influent**	**Effluent**			
			Gravel- based system (control)	**Longan biochar- based system**	**Corn biochar-based system**	**Pumice-based system**
TSS (mg L^{-1})	1	94.5 ± 18.1	12.8 ± 1.2	5.3 ± 2.8	5.8 ± 2.2	9.4 ± 2.0
	3	97.0 ± 10.4	9.1 ± 1.5	5.1 ± 1.5	5.3 ± 1.3	7.9 ± 1.2
	5	81.7 ± 3.3	3.3 ± 1.1	1.8 ± 0.9	1.4 ± 0.6	5.1 ± 0.9
	7	91.5 ± 8.7	3.8 ± 1.0	1.9 ± 0.9	1.8 ± 1.0	4.3 ± 0.9
NH_4-N (mg L^{-1})	1	14.0 ± 1.1	10.6 ± 2.1	1.4 ± 0.4	2.5 ± 1.1	6.7 ± 1.8
	3	19.1 ± 1.1	18.0 ± 2.2	1.0 ± 0.2	2.2 ± 0.4	9.3 ± 1.4
	5	19.3 ± 0.5	15.3 ± 2.2	0.5 ± 0.1	1.6 ± 0.3	9.7 ± 1.0
	7	21.3 ± 0.4	16.9 ± 1.1	1.1 ± 0.3	2.3 ± 0.1	10.6 ± 0.7
TKN (mg L^{-1})	1	17.3 ± 0.6	11.3 ± 1.0	1.8 ± 0.7	2.9 ± 0.9	7.7 ± 1.9
	3	23.4 ± 1.3	15.4 ± 2.0	1.2 ± 0.1	2.5 ± 0.5	10.3 ± 1.4
	5	26.6 ± 2.5	18.4 ± 2.4	1.2 ± 0.3	2.4 ± 0.7	12.2 ± 1.4
	7	26.8 ± 1.8	19.2 ± 2.5	1.5 ± 0.3	2.8 ± 0.5	12.5 ± 0.5
NO_3-N (mg L^{-1})	1	2.5 ± 0.3	1.6 ± 0.6	1.4 ± 0.3	1.3 ± 0.2	1.7 ± 0.3
	3	1.8 ± 0.2	1.0 ± 0.2	0.6 ± 0.4	0.6 ± 0.4	0.9 ± 0.6
	5	1.9 ± 0.1	0.8 ± 0.0	0.4 ± 0.3	0.4 ± 0.1	0.8 ± 0.1
	7	1.8 ± 0.1	0.9 ± 0.0	0.3 ± 0.0	0.3 ± 0.1	0.7 ± 0.1

Note: Mean and standard error were calculated based on 12 replicates of influent samples and 16 replicates of effluent samples from each column

BOD_5 and TSS removal were affected by both substrate and HRT, but there was no interaction between these two factors (Table 3). BOD_5 and TSS removal in the biochar-based systems were significantly higher than in gravel and pumice-based systems (Table 4). Furthermore, BOD_5 and TSS removal efficiency in all four substrates increased with longer HRT (Table 5). BOD_5 and TSS elimination were maximized at 98% after 5 days and 7 days HRT, respectively (Table 4–5, Figure 2).

Substrate and HRT affected NH_4-N and TKN removal with a significant interaction (Table 3). The longan biochar-based system showed the highest removal percentages (89–97%), followed by corn biochar-based system (82–91%). NH_4-N and TKN removal in the pumice-based system was 50–52% and 53–56%, respectively, while removal in the gravel-based system was only 20–23% and 28–34%, respectively (Table 4). However, increasing of HRT increased removal percentages of NH_4-N and TKN in both longan and corn biochar-based systems (Table 5). Furthermore, the NH_4-N removal efficiency was maximized at 97% in longan biochar-based system after 5 days HRT (Table 4, 5; Figure 3a, 3b). NO_3-N removal in the longan biochar-based system was similar to the corn biochar-based system. They removed nearly 48% after 1 day HRT but substantially increased to 68–72% after 3 days HRT, while the removal after 5 days HRT was as high as 80% (Table 5). In contrast, in the gravel and pumice-based systems, approximately 35% of NO_3-N was eliminated after 1 day HRT, increasing moderately to 51–62% after extending HRT to 5 and 7 days (Table 5; Figure 3c).

Table 3 Results of two-way ANOVA statistics (F-ratio) of DO concentration (mg L^{-1}) and removal efficiencies (%) of BOD_5, TSS, NH_4-N, TKN, and NO_3-N

	Main effects		Interaction
	Substrate	**HRT**	**Substrate x HRT**
DO	186.6***	1.3	0.7
BOD_5 removal	12.9***	24.8***	1.2
TSS removal	8.5***	14.8***	0.8
NH_4-N removal	1,414***	2.8*	2.0*
TKN removal	1,827.8***	4.4**	2.8**
NO_3-N removal	31.0***	35.9***	1.2

Note: * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$

Table 4 Results of one-way ANOVA statistics on DO concentration and removal efficiency of BOD_5, TSS, NH_4-N, TKN, and NO_3-N (mean ± SE, n = 16) of different substrates. Different letter superscripts between columns indicate significant differences between treatments

	HRTs (d)	Substrates				F-ratio
		Gravel	**Longan biochar**	**Corn biochar**	**Pumice**	
DO (mg L^{-1})	1	$1.4±0.1^{a}$	$2.5±0.1^{b}$	$2.6±0.1^{b}$	$1.7±0.0^{a}$	41.8***
	3	$1.2±0.2^{a}$	$2.3±0.1^{b}$	$2.7±0.1^{b}$	$1.6±0.0^{a}$	28.4***
	5	$1.3±0.0^{a}$	$2.4±0.1^{c}$	$2.6±0.1^{c}$	$1.7±0.1^{b}$	81.2***
	7	$1.2±0.1^{a}$	$2.5±0.0^{c}$	$2.7±0.1^{c}$	$1.7±0.1^{b}$	101.2***
BOD_5 removal (%)	1	$89.8±1.7^{a}$	$95.0±0.6^{b}$	$92.9±1.4^{ab}$	$88.6±1.6^{a}$	4.8**
	3	$93.0±1.5^{a}$	$96.4±0.6^{b}$	$96.0±0.6^{b}$	$95.1±0.8^{ab}$	2.4
	5	$94.8±0.7^{a}$	$97.4±0.6^{b}$	$97.1±0.6^{b}$	$94.4±1.0^{a}$	4.2**
	7	$96.8±0.7^{ab}$	$98.2±0.3^{b}$	$97.7±0.3^{b}$	$94.8±0.9^{a}$	6.1**
TSS removal (%)	1	$86.4±3.4^{a}$	$94.4±1.5^{b}$	$93.8±1.5^{b}$	$90.1±2.7^{ab}$	2.3
	3	90.6±1.5	94.7±1.3	94.5±1.3	91.8±1.3	1.9
	5	$95.7±0.6^{ab}$	$97.8±0.5^{b}$	$98.3±0.6^{b}$	$94.1±1.3^{a}$	5.2**
	7	$96.3±0.9^{ab}$	$97.9±0.7^{b}$	$98.0±0.9^{b}$	$95.3±0.9^{a}$	2.4
NH_4-N removal (%)	1	$22.3±3.4^{a}$	89.7±1.3d	$82.3±1.6^{c}$	$51.5±2.6^{b}$	178.7***
	3	$22.9±3.0^{a}$	$94.6±0.5^{d}$	$88.4±0.9^{c}$	$50.7±2.5^{b}$	284.9***
	5	$20.9±2.4^{a}$	$97.0±0.3^{d}$	$91.5±0.4^{c}$	$50.1±1.4^{b}$	584.4***
	7	$20.8±1.5^{a}$	$95.0±0.4^{d}$	$89.1±0.5^{c}$	$50.2±1.0^{b}$	1,445.0***
TKN removal (%)	1	$32.8±1.7^{a}$	$89.1±1.0^{d}$	$83.3±1.4^{c}$	$55.9±2.5^{b}$	218.0***
	3	$33.8±1.8^{a}$	$94.8±0.4^{d}$	$89.4±0.8^{c}$	$55.7±1.4^{b}$	555.5***
	5	$31.0±2.0^{a}$	$95.5±0.3^{d}$	$91.1±0.9^{c}$	$54.2±1.4^{b}$	559.8***
	7	$28.3±2.1^{a}$	$93.9±0.3^{d}$	$89.1±0.6^{c}$	$53.5±1.4^{b}$	652.7***
NO_3-N removal (%)	1	36.6±1.2	47.0±7.5	48.1±1.8	33.3±5.7	2.7
	3	$44.0±5.5^{a}$	$68.1±7.1^{ab}$	$71.8±6.7^{b}$	$49.4±5.3^{ab}$	4.7*
	5	$51.6±2.4^{a}$	$79.2±2.5^{b}$	$80.6±3.2^{b}$	$58.6±3.0^{a}$	26.0***
	7	$55.6±1.7^{a}$	$82.3±1.6^{b}$	$84.5±1.9^{b}$	$61.8±2.5^{a}$	55.1***

Note: * $P < 0.05$, ** $P <0.01$, *** $P <0.001$

Table 5 Results of one-way ANOVA statistics on DO concentration and removal efficiency of BOD_5, TSS, NH_4-N, TKN, and NO_3-N of each substrate under different HRTs (mean ± SE, n = 16). Different letter superscripts between columns indicate significant differences between treatments

	Substrates	HRTs				F-ratio
		1 day	3 days	5 days	7 days	
DO (mg L^{-1})	gravel	1.4±0.1	1.2±0.2	1.3±0.0	1.2±0.1	0.6
	longan biochar	2.5±0.1	2.3±0.1	2.4±0.1	2.5±0.0	1.4
	corn biochar	2.6±0.1	2.7±0.1	2.6±0.1	2.7±0.1	0.6
	pumice	1.7±0.0	1.6±0.0	1.7±0.1	1.7±0.1	0.9
BOD_5 removal (%)	gravel	89.8±1.7^{a}	93.0±1.5^{ab}	94.8±0.7^{b}	96.8±0.7^{b}	6.4**
	longan biochar	95.0±0.6^{a}	96.4±0.6^{ab}	97.4±0.6^{b}	98.2±0.3^{b}	7.3***
	corn biochar	92.9±1.4^{a}	96.0±0.6^{b}	97.1±0.6^{b}	97.7±0.3^{b}	6.0**
	pumice	88.6±1.6^{a}	95.0±0.8^{b}	94.4±1.0^{b}	94.8±0.9^{b}	8.6***
TSS removal (%)	gravel	86.4±3.4^{a}	90.6±1.5^{ab}	95.7±0.6^{b}	96.3±0.9^{b}	6.5**
	longan biochar	94.4±1.5^{a}	94.7±1.3^{a}	97.8±0.5^{b}	97.9±0.7^{b}	3.4*
	corn biochar	93.8±1.5^{a}	94.5±1.3^{ab}	98.3±0.6^{b}	98.0±0.9^{b}	4.5**
	pumice	90.1±2.7^{a}	91.8±1.3^{ab}	94.1±1.3^{ab}	95.6±0.9^{b}	1.9
NH_4-N removal (%)	gravel	22.3±3.4	22.9±3.0	20.9±2.4	20.8±1.5	0.2
	longan biochar	89.7±1.3^{a}	94.6±0.5^{b}	97.0±0.3^{b}	95.0±0.4^{b}	17.0***
	corn biochar	82.3±1.6^{a}	88.4±0.9^{b}	91.5±0.4^{b}	89.1±0.5^{b}	13.7***
	pumice	51.5±2.6	50.7±2.5	50.1±1.4	50.2±1.0	0.1
TKN removal (%)	gravel	32.8±1.7	33.8±1.8	31.0±2.0	28.3±2.1	1.5
	longan biochar	89.1±1.0^{a}	94.8±0.4^{b}	95.5±0.3^{b}	93.9±0.3^{b}	25.0***
	corn biochar	83.3±1.4^{a}	89.4±0.8^{b}	91.1±0.9^{b}	89.1±0.6^{b}	12.9***
	pumice	55.9±2.5	55.7±1.4	54.2±1.4	53.5±1.4	0.5
NO_3-N removal (%)	gravel	36.6±1.2^{a}	44.0±5.5^{ab}	51.6±2.4^{b}	55.6±1.7^{b}	7.1**
	longan biochar	47.0±7.5^{a}	68.1±7.1^{ab}	79.2±2.5^{b}	82.3±1.6^{b}	8.1**
	corn biochar	48.1±1.8^{a}	71.8±6.7^{b}	80.6±3.2^{b}	84.5±1.9^{b}	13.2**
	pumice	33.3±5.7^{a}	49.4±5.3^{ab}	58.6±3.0^{b}	61.8±2.5^{b}	8.2**

Note: * P < 0.05, **P < 0.01, *** P <0.001

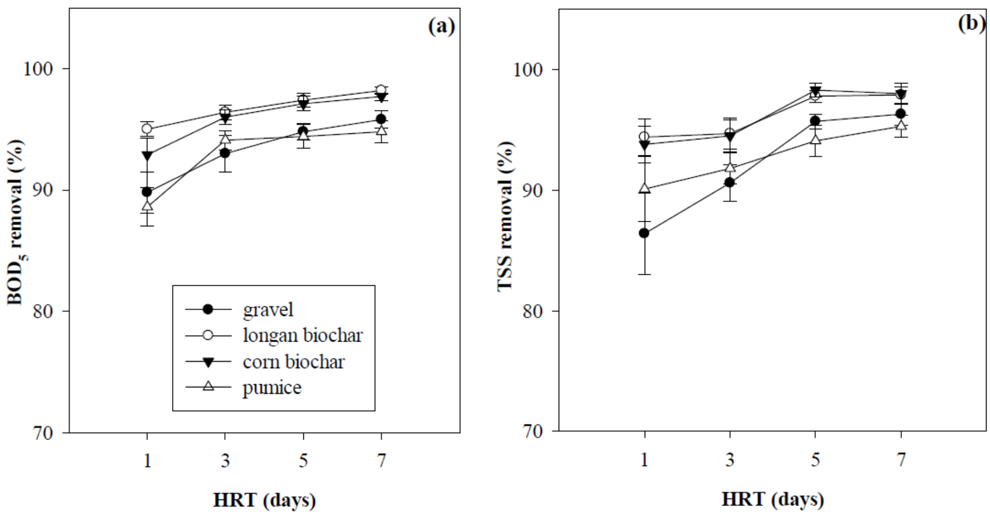

Figure 2 Removal percentages of (a) biochemical oxygen demand (BOD_5) and (b) total suspended solids (TSS) in the systems filled with longan biochar, corn biochar, and pumice compared with control treatment (gravel) at 1, 3, 5, and 7 days HRT.

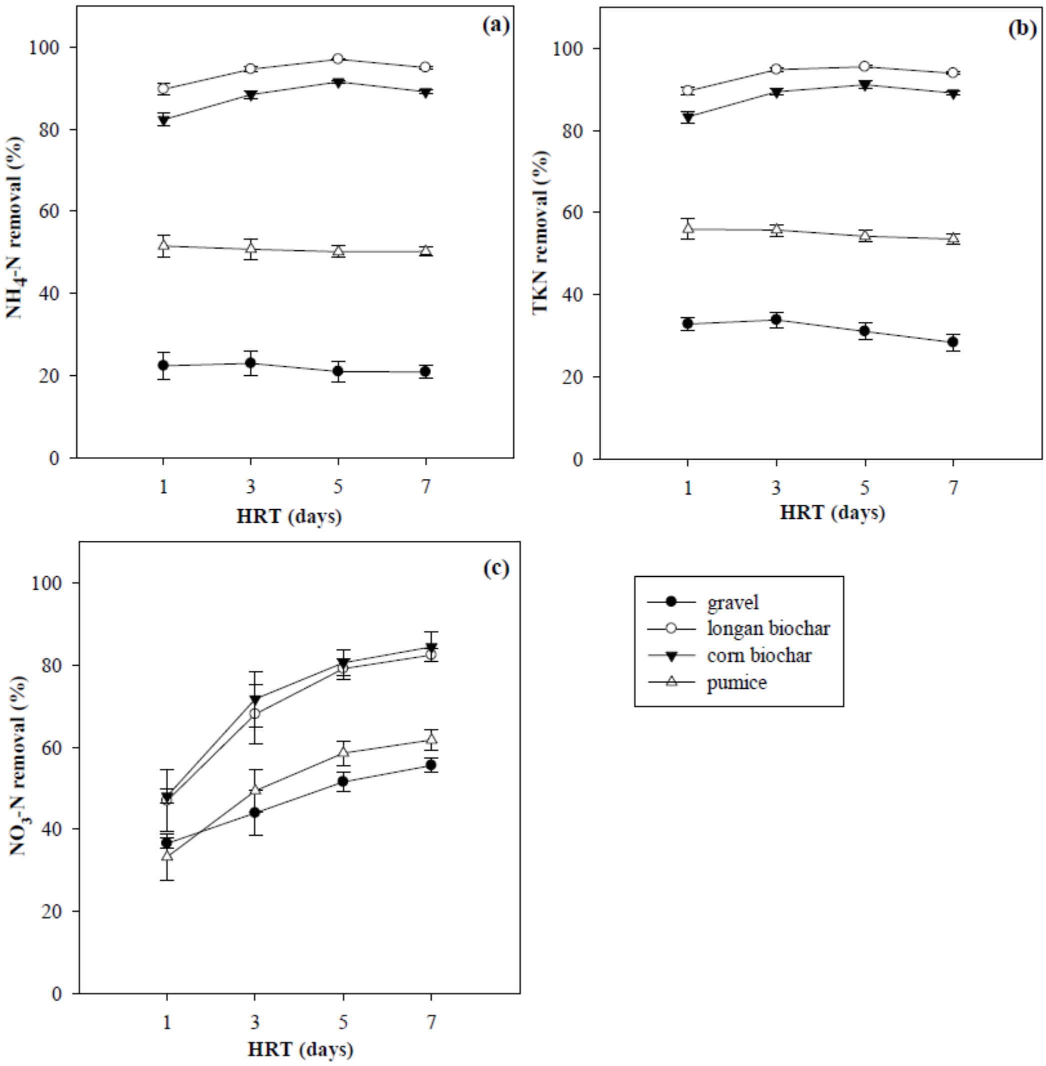

Figure 3 Removal percentages of (a) ammonium (NH_4-N), (b) total kjeldahl Nitrogen (TKN), and (c) nitrate (NO_3-N) in the systems filled with longan biochar, corn biochar, and pumice compared with control treatment (gravel) at 1, 3, 5, and 7 days HRT.

3) Media adsorption

At the end of the experiment, N accumulation in longan biochar, corn biochar, and pumice increased. In contrast, K in longan biochar and corn biochar was reduced approximately 3–3.6 g kg^{-1}, but K concentration in pumice was rather stable. Furthermore, longan biochar released Ca as high as 8.8 g kg^{-1}, while corn biochar and pumice released 1.6–3 g kg^{-1}. However, very little Mg was released from all three porous substrates (only 0.3–0.6 g kg^{-1}) (Table 6).

Table 6 Mineral concentrations (g kg^{-1}) of duplicated porous substrates (mean±SE) before using and at the end of the experiment

	N		K		Ca		Mg	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Longan biochar	5.9±0.2	6.3±0.2	4.8±0.0	1.8±0.2	34.3±1.6	25.5±0.0	2.2±0.4	1.6±0.0
Corn biochar	4.8±0.2	5.0±0.1	4.6±0.0	1.0±0.1	4.9±0.0	2.3±0.4	1.1±0.0	0.7±0.1
Pumice	1.9±0.0	2.0±0.0	2.4±0.1	2.3±0.0	5.0±0.1	3.4±0.2	1.0±0.0	0.7±0.0

Discussion

Overall, substrates influenced the removal of BOD_5, TSS, NH_4-N, TKN, and NO_3-N and interactions between substrates and HRT on NH_4-N and TKN removal were observed. From this study, BOD_5, TSS, and NO_3-N removal among the four systems increased with increasing retention time particularly in the porous substrates system. Normally, TSS was removed through sedimentation and filtration mechanisms [34]. The high SSA and Vp of longan biochar and corn biochar enhance suspended solids attachment on their surface as well as embedment in their pores. A study by de Rozari et al. [35] showed that TSS removal in biochar-added systems was higher than in a system wholly filled with gravel. Furthermore, removal of suspended solid contaminants also influences BOD_5 reduction which was found to be more effective in biochar-based systems [15]. BOD_5 and TSS are generally removed substantially during the first period of HRT (1–2 days) by filtration and sedimentation of solid contaminants [34]. Subsequently, slight increases of removal percentages with extended time could be influenced by microbial activity on organic matter degradation [36]. After effective filtration, longan and corn biochar-based systems continue to degrade organic solids which could achieve BOD_5 and TSS elimination within 5 days. However, the trend of increasing organic matter elimination along with increasing HRT could be different from our result depending on the strength of wastewater. Higher masses of suspended solid, such as TSS in livestock or strong domestic wastewater, may need more time to be filtrated and degraded. The study by Manyuchi et al. [37] in which influent TSS was as high as 450 mg L^{-1}, a biochar-added system could remove only 40% after 1 day HRT which can cause low BOD_5 reduction. Meanwhile, TSS removal increased to 90% after 5 days HRT [37]. To achieve BOD_5 and TSS elimination, the system may need more time to degrade organic solids. In longan biochar and corn biochar-based systems, DO concentrations tend to be higher than in gravel and pumice-based systems. It was probably due to the high pore volume of these substrates which enhances more atmospheric air diffusion and preservation [38]. A study by Chand et al. [39] showed a higher DO concentration in a biochar-added system than in a system fully filled with gravel.

It is well known that NH_4-N removal depends on DO concentrations, microorganism presenting in media and adsorption ability of filter media. Generally, NH_4-N removal can be more efficient when high DO concentrations support nitrifying activity [40]. More simply SSA is a property of media that affects NH_4-N removal by enhancing DO regeneration and growth of nitrifying bacteria [41]. Liu et al. [24] showed that when zeolite, which has a high SSA, was used as a filter medium in a constructed wetland, bacteria abundance was high, resulting in fast nitrification and higher NH_4-N removal rates compared with constructed wetlands filled with quartz sand, biological ceramsite or volcanic rock, which had lower SSAs. In this study, because of the high SSA of both longan and corn biochar, the biochar-based systems significantly increased DO concentrations and had higher NH_4-N removal efficiency than the pumice and gravel-based systems. In addition, the CEC of biochar, especially longan biochar, enhanced NH_4-N adsorption with concurrent release of other cations accumulated in the biochar [42]. In our study, K^+, Ca^{2+}, and Mg^{2+} accumulation in longan and corn biochar decreased probably through ion release along with the increase of N accumulation due to their adsorption ability. Unfortunately, we did not investigate the microbial community and nitrifying activity, so it is hard to determine whether adsorption ability or nitrifying activity plays a main role on NH_4-N removal. We found that NH_4-N removal efficiency was significantly increased when extending HRT from 1 to 3 days and it was maximized at 5 days, as high as 97% and 91% in the longan and corn biochar-based system, respectively. Xing et al. [43] showed that NH_4-N in biochar-added systems was substantially removed (approximately 80%) within 24–48 hours and then NH_4-N removal slightly increased along with HRT. In comparison, in the pumice-based system where SSA and CEC were significantly lower than biochar, approximately 50% of NH_4-N was removed. Gravel had a non-porous structure with low SSA and lacked of adsorption ability [15, 44]. In the gravel-based system, approximately 20% of NH_4-N was eliminated and elimination was not significantly increased even as time increased. Similarly, DO levels in gravel and pumice-based systems also did not significant differ across HRTs. The potentially long periods of system operation needed to increase NH_4-N removal rates in systems filled with these kinds of filter media could be a cause for concern. Akratos and Tsihrintzis [45] reported that CWs filled with gravel under 6 days HRT removed only 30% of NH_4-N, while the removal efficiency was approximately 50% at an HRT of 20 days. TKN removal was influenced by both substrate and HRT. It was most effective in the longan biochar-based system, followed by the corn biochar-based system as a result of favorable physicochemical characteristics of biochar and sufficient DO concentrations to support NH_4-N removal. The low SSA of pumice and lower DO concentrations than in the two biochar-based systems can lower nitrifying activity. Without cation exchange ability, TKN in the gravel-based system could scarcely be nitrified so that removal was only 30%. Similarly, NO_3-N removal was influenced by both substrates and HRT. NO_3-N is mainly removed by denitrification, which was basically occurs under anoxic conditions [46]. However, higher NO_3-N removal efficiency in spite of the increase of DO in the two biochars-based systems was probably influenced by the presence of carbon and aerobic denitrifying bacteria in them [47]. The high SSA of biochars enhanced attachment and accelerated growth of aerobic denitrifiers, which accept electron from carbon to reduce NO_3-N [48]. However, the low SSA of pumice was speculated to be inefficient in supporting denitrifiers causing insignificantly different NO_3-N removal compared with the gravel-based system. NO_3-N removal increased concurrently with HRT extension to 5 days especially in the biochar-based systems where it might be attributed to longer contact of wastewater with denitrifiers. Zhang et al. [49] found the increase of NO_3-N removal percentages with prolonged HRT as well.

From the study, longan biochar was the most effective substrate for organic matter and nitrogen removal due to its favorable physicochemical characteristics of SSA, Vp, and CEC. Pollutant removal also increased with HRT extension. Hence, it is promising to apply longan biochar as a filter media in CWs. However, more relevant research concerning practical application of biochar in CWs in relation to various types of wastewaters and system design as well as its interaction with the macrophytes and potential for bioremediation are needed in the future.

Conclusion

Biochar has better performance in domestic wastewater treatment than pumice and gravel. Its high porous structure can substantially reduce both BOD_5 and TSS, at 95%, within a day. Furthermore, longan biochar has the most effective NH_4-N and TKN removal (89–97%) as it has the highest SSA and CEC. Hence, longan biochar is a good candidate for use as an alternative filter in CWs. The extension of HRT also significantly increased pollutant removal efficiency.

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