Steel Slag and Limestone as a Rock Filter for Eliminating Phosphorus from Domestic Wastewater: A Pilot Study in a Warm Climate

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Abstract: Phosphorus input with excessive use of fertilizers and manure as one of the main sources of nutrient pollution has increased recently in the wastewater as result of intensive farming and industrialized and densely populated areas. The novelty of the current work lies in improving a Vertical Aerated Rock Filter (VARF) using steel slag and limestone media to enhance the efficiency of a rock filter (RF) to eliminate total phosphorus (TP) from domestic wastewater. RF was designed with steel slag and limestone (calcium hydroxide) as a pilot scale called vertical aerated steel slag filter (VASSF) and optimized based on hydraulic loading rates (HLR) (0.16 to 5.44 m^3/m^3 day) and airflow rates ranging from 3 to 10 L/min. The highest removal for the design of the laboratory scale steel slag filter (LSSSF) was achieved by approximately 58%, while for the laboratory-scale limestone filter (LSLSF), it was 64%. The VASSF achieved a removal percentage at 30% of TP, biological oxygen demand (BOD; 89%), chemical oxygen demand (COD; 75%), total suspended solids (TSS; 73%), and total coliforms (TC; 96%), recorded with 7 L/min of an airflow rate and 1.04 m^3/m^3.day of hydraulic loading rate (HLR) at potential of hydrogen (pH) 7.3 and 5.09 mg/L of dissolved oxygen (DO). These findings indicated that the steel slag is higher than limestone in TP removal, because of ion exchange between phosphorus hydrolysis and the adsorption process. Moreover, in the pilot study, the removal efficiency needs more investigation to determine the best conditions for TP considering the temperature, which is unstable, and presence of other pollutants, which might negatively affect the removal efficiency under unstable conditions.

Keywords: aerated rock filter; phosphorus; optimization; removal; pilot study

1. Introduction

The aerated rock filter (ARF), which uses waste media as a filter to enhance organic pollutants removal quality before it is discharged to a river or stream, has become one of the alternative natural wastewater treatment technologies for eliminating phosphorus from wastewater [1,2]. The demand to improve the existing wastewater treatment plants is developed by using ARF technology to remove the nutrient and to comply with stricter regulation of wastewater disposal [3]. The ARF, created by Mara [4] in the UK, serves as an alternative approach to the treatment of BOD5, suspended solids (SS), ammonia, and COD. ARF has great potential to remove algae solid from lagoon effluents and becomes more ideal for secondary treatment based on the saved area; and it has good potential by replacing the lagoons and having the advantage of taking less space. Rock filters in vertical flow mostly

perform better than horizontal flow and are easy to construct [5]. The aeration inside the vertical flow filter is more accessible for maintenance and replacement because they are below the wastewater level in the filter. In the vertical flow, it also prevents the media from clogging and reduces the algae attachment on the media. According to Vymazal [6], the aeration of the bed can cause desorption and release the phosphorus. However, this can be solved by controlling the aeration rate using the minimum air flow inside the filter. Žibienė et al. [7] claimed that 95.7% of the phosphorus removal was achieved using a vertical flow filter.

The potential of steel slag waste, a byproduct of steel manufacture, to remove phosphorus from various wastewaters was demonstrated [8,9]. The combination of steel slag with a secondary treatment system can improve phosphorus removal and it can avoid the addition of chemical products [10]. Maarup et al. [11] indicated that the steel slag used in vertical aerated RF has a great impact on the removal of phosphorus in wastewater and can be well managed after use through their recycling and reuse processes.

Additionally, after treatment, the steel slag, could be used in useful applications such as steel slag cement, recycling of scrap metal, as the flux of iron and steel smelting, road engineering or backfilling materials, fertilizers and soil improvers, preparation of ceramic products such as glass-ceramics, and environmental protection applications [12,13]. Steel slag could be used as a suitable material for carbon capture to mitigate global warming [14]. Moreover, in the study of the potential of P saturated electric arc furnace, steel slag as a P fertilizer or soil modification with Medicago sativa was investigated. The study showed P efficiency for high germination rates, suggesting that steel sludge with P could be re-used as soil amendment [15]. The limitations of using steel slag are leaching of heavy metals and costly factor [16].

Previous research looked at how well a vertical flow aerated steel slag filter system combined with nitrifier bacteria removed nutrients from residential wastewater [17–21], while research into the effectiveness of steel slag using more calcium oxide and ferric oxides to remove phosphate from synthetic wastewater was conducted [22,23]. A preliminary study with simple work was conducted on the removal of TP using Pilot-Scale Vertical Aerated Steel Slag Filter based on the filter depth [11]. The current study aimed to improve a Vertical Aerated Rock Filter (VARF) to enhance the efficiency of phosphorus removal from the residential wastewater by using selected media containing Ca, Mg, and Al with the different hydraulic load level (HLR) and airflow rates. The effectiveness of VARF was tested at the pilot scale vertical aerated steel slag filter (VASSF), while the effectiveness of elimination was investigated at the lab scale with steel slag filter (LSSSF) and laboratory-scale limestone filter (LSLSF). The study also investigated the optimization of the removal technique and process.

2. Materials and Methods

At the initial stage of the experiments, the process started with the designing process and was constructed in the lab-scale filter and vertical ASSF system. A lab-scale filter was placed at the laboratory to investigate the effective filter media with limestone and steel slag while for the pilot scale, the filter was placed on site to investigate the most effective HLR and to study the effectiveness of the pilot scale under a warm climate. Influence and effluent were collected once a week and tested in the laboratory.

2.1. Wastewater Sampling and Analyses

Wastewater samples were collected from the Bukit Perdana primary clarifier wastewater treatment plant (WWTP), Batu Pahat (1°50′37.05″ N, 102°56′49.43″ E) owned by Indah Water Konsortium (IWK) (Figure 1). Wastewater samples were collected and fed into the filter using a dual-headed peristaltic pump (Cole-Parmer Masterflex L/S Model 7524-40 with the W77200-62 pump head). The filtration systems were aerated using an oil-free compressor (rocker model 167420-11-22), while the effluent was discharged by gravity from the filter outlet to the nearest river.
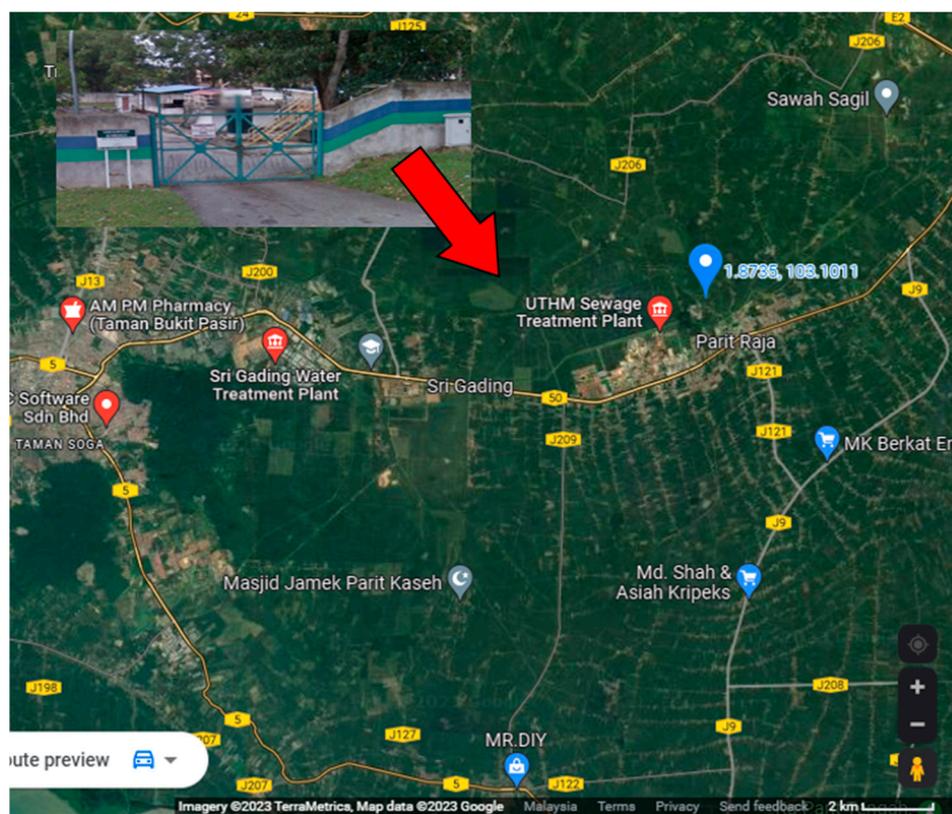
Figure 1. Sampling location.

Domestic wastewater samples were collected on a weekly basis, every Sunday at 10 a.m. (± 1 h) from WWTP. Samples were treated on site using the VARF filter and the effluent was analyzed in the laboratory, while a sample of wastewater was collected from WWTP Bukit Perdana to fill in the feeder tank in the laboratory for the lab-scale treatment filter. The factors affecting on the removal efficiency included the duration of time to take the sample, weather, apparatus, sampling method, temperature store box, and the chemicals needed to preserve the sample. The sample was kept in an ice box container to maintain the temperature at 4 °C until analysis. All samples were taken in a glass jar. pH, TSS, alkalinity, temperature, TP, COD, and BOD were determined according to APHA [24].

2.2. Laboratory-Scale Rock Filter for Phosphate Removal Study

These experiments were carried out in a laboratory and were conducted simultaneously using the limestone and steel slag filter. The pipe containers used to hold the filters were made from acrylic which was 15 cm in diameter and 39.5 cm high. The schematic diagram in Figure 2a shows that the 14 cm aerator was located at the base of the filter with influent and effluent taps. The porous plate was placed above the diffuser to protect the diffuser from being clogged and damaged due to the media. Table 1 illustrated the lab-scale characteristics and operational conditions.

2.2.1. Construction of Lab-Scale Filter

The laboratory-scale filter pipe used in this experiment was made of acrylic. The filter with 14.4 cm in diameter was fitted with 14 cm diameter coarse bubble diffuser and protected by a porous plastic plate to protect the diffuser from being clogged or damaged. The filter had an inlet tap to feed the filter with wastewater and an outlet tap to discharge treated wastewater to the drain, as shown in Figure 1b, where the sampling was taken at both outlets. Both filters had different outlet taps and it had a plastic pipe to discharge effluent to drain nearby. The wastewater supply tank was held using plastic containers with a 10 mm outlet to feed the lab-scale filter. Each filter was run together to make sure

there were no different data observed and it was receiving the same influent characteristic (Figure 2b).
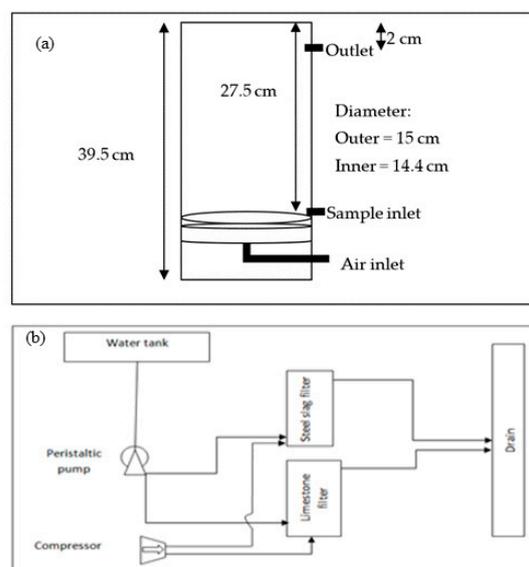
Figure 2. (**a**):Side view of the lab-scale filter. (**b**):Flow diagram of limestone and steel slag filter system layout.

Table 1. Lab-scale characteristics and operational conditions.

Parameter	Unit	Lab-Scale Filter
Total height	cm	39.5
Internal diameter	cm	14.4
Liquid depth	cm	27.5
Volume of wastewater (working volume), Q	m^3	0.0044
HLR	m^3/day	0.00264
HRT	day	1.67
Airflow	L/min	20

2.2.2. Lab-Scale Filter Media

Limestone and steel slag were selected as the filter, medium in the laboratory-scale filter, and these materials were locally available in Malaysia. Both media have great potential in removing phosphorus due to the high capacity of phosphorus adsorbent available chemically in these media [25]. The media were kindly provided via Perwaja Steel Sdn. Bhd. based in Kemaman, Terengganu. Before the media were used, they were subjected to the cleaning process before being placed into the filter. The medium was washed with tap water and then washed again with distilled water. After that, the media were dried in the oven for 24 h at 105 °C. Table 2 shows the chemical composition of both media as analyzed using the X-ray fluorescence (XRF) instrument.

2.2.3. Experimental Setup of a Lab-Scale Filter

The laboratory-scale filter experiment was conducted simultaneously for both limestone and steel slag filters. Each filter was filled with 10 to 20 mm medium aggregate, and these media were filled up to 26 cm high while wastewater was 25 cm in height, leaving a freeboard space of about 2 cm to prevent algal growth in the filter (Figure 3). These filters were left running for two weeks to allow the filter media to acclimate to wastewater before the sample was taken. After the steady state of the filters was achieved and the fraction allowed between 0 and 2.0 mm, the wastewater samples were sampled in weekly analysis

for phosphorus removal. In steady state conditions, these two types of media were equal and maintained a result, and the sampling data were analyzed for further analysis. Steady state is where there is a condition mostly indicated by the stability in effluent concentration.

Table 2. Chemical composition for both media.

Chemical Component	Concentration	
	Steel Slag	**Limestone**
CO_2	0.10%	-
CaO	31.20%	94.20%
Fe_2O_3	40.00%	0.87%
SiO_2	16.40%	2.57%
Al_2O_3	5.04%	0.79%
MgO	3.25%	0.98%
K_2O	-	0.14%
MnO	2.00%	-
TiO_2	0.53%	-
Cr_2O_3	0.32%	-
P_2O_5	0.56%	-
S	0 < LLD	-

Figure 3. Lab-scale filter.

2.2.4. Hydraulic Loading Rate (HLR) Determination

Rock filters require low HLR and long HRT to achieve efficient removal of P [26]. The HLR is very important because it can ensure a lasting performance without any problem such as clogging or overflow. It becomes an important factor in designing rock filters based on these HLR and HRT determination.

HLR is expressed as a volume of filter effluent (m^3) applied over a gross rock filter volume per day ($m^3/m^3 \cdot d$) [4]. HLR and HRT can be calculated using the following equations:

$$HLR = \frac{m^3}{m^3 day} \frac{Q_{ww}}{V} \tag{1}$$

$$HRT, 0 \; day = \frac{V_{ww}}{Q_{ww}} \tag{2}$$

where:

Q_{ww} = wastewater flow (m^3/day)
V = gross volume of the rock filter (m^3)
V_{ww} = wastewater volume (m^3)

2.3. Removal Study

The pilot-scale vertical upward-flow ARF (VARF) design developed by Maarup et al. [11] was used in this experiment. The treatment plant under study was designed with 15,800 population equivalents (PE). Figure 4a shows that the VARF flow diagram system is running. The aerator inside the VARF was protected by a porous disc to ensure that the air diffuser did not get damaged when the steel slag was placed in the VARF. The wastewater sample was taken at the primary treatment chamber by using a peristaltic pump (Cole-Parmer Masterflex L/S Model 7524-40 with W77200-62 pump head). The influent wastewater sample was filtered using a PVC strainer as shown in Figure 4b to retain the large particles that entered through the VARF to prevent the system from getting clogged. The airflow in the filter was fed to the diffuser by using oil-free Jun-Air compressor (West Air Compressor, Sydney) with airflow for 3, 5, 7, and 10 L/min and Table 3 shows the operational conditions for VARF.

Table 3. VARF operational condition.

No	Parameter	Unit	VASSF
1	Total Height	m	2.0
2	Internal Diameter	m	0.3
3	Filter Bed Depth/Liquid Depth	m	1.5
4	Media Volume, V	m^3	0.106
5	Volume of Wastewater in the filter (Working Volume)	m^3	0.063
6	$Q_{wastewater}$ (variable)	m^3/d	0.0170, 0.0276, 0.0360, 0.0339, 0.0551, 0.0721, 0.1103, 0.1442, 0.2205, 0.2884, 0.4411, 0.5768
7	Hydraulic Retention Time, θ (variable)	day	3.71, 2.29, 1.75, 1.86, 1.14, 0.87, 0.57, 0.44, 0.29, 0.22, 0.14, 0.11
8	Hydraulic loading rate, HLR (variable)	$m^3/m^3 \cdot d$	0.16, 0.26, 0.34, 0.32, 0.52, 0.68, 1.04, 1.36, 2.08, 2.72, 4.16, 5.44
9	Air Flow Rate (variable)	L/min	3, 5, 7, 10
10	Flow Rate, Q (variable)	mL/min	12, 19, 25, 24, 38, 50, 77, 100, 153, 200, 306, 401

2.4. Construction of VASSF

The VARF was constructed on site and made from 15 mm thick PVC pipe which is 30 cm in diameter and 2 m in height, as seen in Figure 3c. The filter base consists of a 25 cm diameter of fine air bubble air diffuser while the inlet and outlet water tap were placed with a 0.25 m gap between the other taps (Figure 3c) with the material used in the installation of fine bubble air diffusers in the VARF system on site.
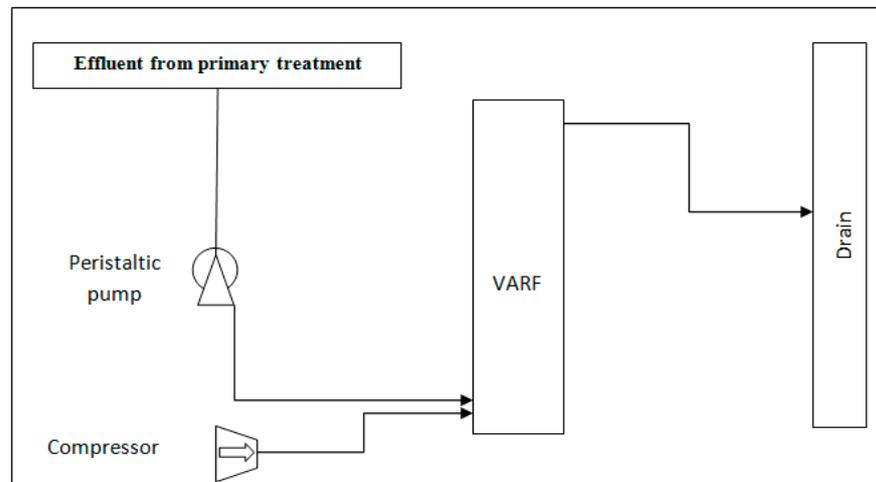
(a)
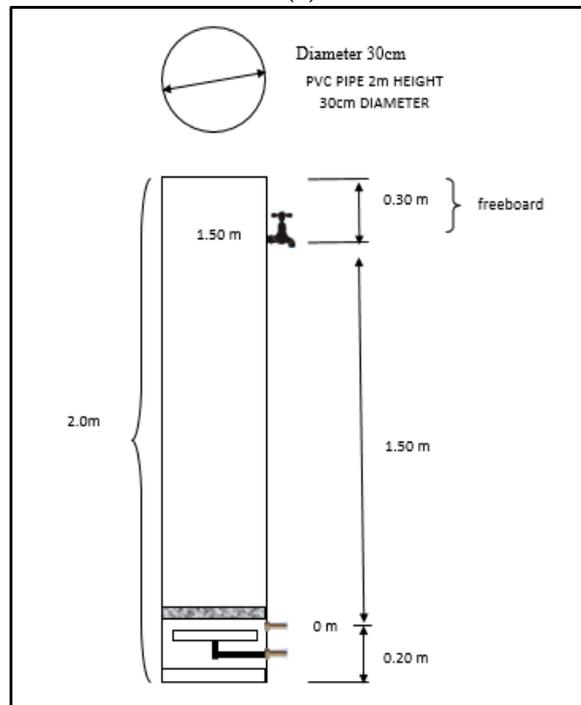
(b)
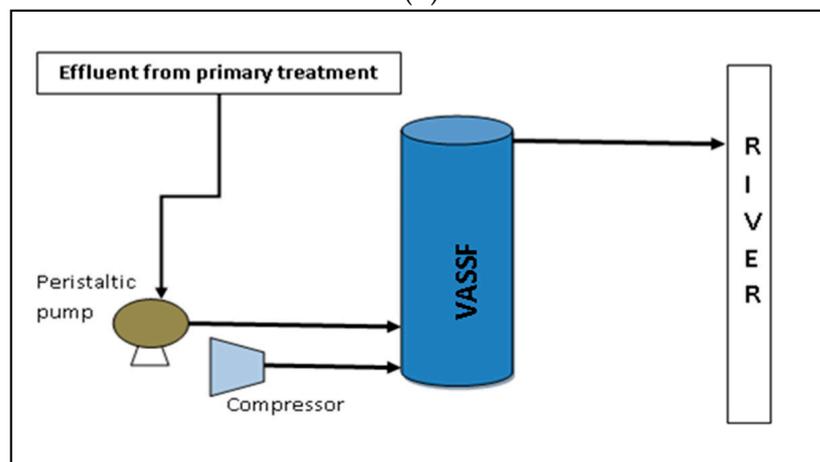
(c)

Figure 4. (**a**) VARF flow diagram system operations. (**b**) Plan and side view of VASSF system. (**c**) Layout of the optimization study.

2.4.1. Filter Media Used in VASSF

Filter media, either limestone or steel slag, showed the best potential in removing phosphorus from the domestic wastewater that has been selected as filter media. Steel slag was selected to be used as a filter medium in the pilot-scale filter to remove phosphorus from wastewater. Fresh slag samples with triplicate samples were analyzed for chemical composition by using X-ray fluorescence (XRF).

2.4.2. Experimental Setup

For these VARFs, the acclimatization period was run for two weeks until it reached steady state before the grab samples were taken. The steady state was achieved when the result data were equal, or when the result and stability in effluent concentration were maintained. Sample media were filled in the filter with 10–20 mm media aggregate and this filter was filled up to 1.6 m height while wastewater was at 1.5 m height, leaving a freeboard space about 0.30 m to prevent algal growth on the surface. While the acclimatization period was running, the VARF system was optimized for the HLR study of 0.16–5.44 m^3/m^3·d. The value of the HLR range was taken from Swanson and Williamson [27] for a warm climate of 0.06–0.34 m^3/m^3·d and the range was multiplied until the HLR failed in the VARF system. These HLR values were selected based on phosphorus removal efficiency. The selected HLR was used until the system achieved a steady state based on phosphorus removal (maintain approximately 90% phosphorus removal or achieve effluent stability), and after that, all parameters were tested weekly.

2.5. Routine Maintenance

Both systems, which were lab-scale and pilot-scale filters, required proper maintenance throughout the overall study period (Table 4). The system was maintained on a weekly basis to ensure there was no clogging in the piping and to ensure the system ran smoothly.

Table 4. Routine maintenance.

Type Maintenance	Lab Scale	Pilot Scale
Cleaning the strainer for inlet system	N.A.	Cleaning strainer
Checking and Maintenance of the Inlet and outlet piping system	N.A.	Change broken piping
Replacing the clogged pipe and water tap	N.A.	Change clogged tap
Maintenance of the peristaltic pump and compressor	Change broken pipe	Change broken piping
Remove the plant that grew on the filter media	Remove algae	Remove algae

2.6. Microstructure Analysis

In the present study, scanning electron microscopy (SEM/EDX) (Hitachi, Jeol-JSM6380LA, Tyoko, Japan) was used to find the phosphorus attachment on the steel slag surface. Both fresh and treated samples were characterized using SEM/EDX. Steel slag sample was taken out from the filter and analyzed using SEM/EDX test after being treated in the filter for a two-month period. SEM analysis enables direct observation of the surface microstructures of the composite material. It is the primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. The sample of media was used in the form of tiny stones to carry out the SEM-EDX analysis. The media containing metal salt was adhered with double-sided carbon tape before being placed on a factory sample plate. The sample was cleaned and dried, and after that, the sample was placed inside the auto fine coater. After a few minutes, the samples were run with SEM to identify the size, particle shape, energy dispersive X-ray spectroscopy (EDX spectra), and surface microstructures.

2.7. Statistical Analysis

All data for influent and effluent samples were statistically analyzed using Microsoft Excel 2010 and the Social Science Statistical Package (SPSS) to analyze the *t*-test. The *t*-test

was used to compare the mean for two different groups which is between the limestone and steel slag laboratory filter for total phosphorus removal.

3. Results and Discussion

3.1. Performance of Treatment Systems

Table 5 provides the characteristics of domestic wastewater. The results revealed that domestic wastewater contains 126 mg/L of BOD, 262.08 mg/L of COD, and 19 mg/L of TP. These concentrations were considered high for the final disposal of the wastewater and had to be subjected for the treatment process to meet the discharge criteria.

Table 5. Initial characteristics of domestic wastewater.

| Parameter	Concentration $\pm$ SD *
BOD (mg/L)	126 mg/L $\pm$ 4.00
COD (mg/L)	262.08 mg/L $\pm$ 21.00
DO	1.04 mg/L $\pm$ 0.48
pH	6.97 $\pm$ 0.03
Temperature (°C)	28.6 °C $\pm$ 0.07
TSS (mg/L)	146.7 mg/L $\pm$ 1.15
Alkalinity (mg/L)	205 mg $CaCO_3$/l $\pm$ 5.00
TP (mg/L)	19 mg/L $\pm$ 1.53
TC	1600 cfu/100 mL $\pm$ 50.00

* Standard division for triplicate sampling.

The efficiency of the filtration process is presented in Figure 5, which shows the COD removal rates for each day and contains data on influent and effluent concentrations for both the steel slag and the limestone lab-scale filter. The influent COD concentration for both lab-scale filters averaged 426.06 $\pm$ 343.5 mg/L while the effluent concentration for the lab-scale steel slag filter (LSSSF) averaged from 110.43 $\pm$ 62.5 mg L and the lab-scale limestone filter (LSLSF) averaged from 168.82 $\pm$ 180.37 mg/L. The COD removal efficiency for LSSSF varied from 34% to 94% while for LSLSF varied from 12% to 94%. The highest COD removal was found at 94% for both media. Laboratory-scale experiments showed quite satisfactory performance in organic matter removal, with almost three-quarters of the sampling data removal rates reaching more than 70% but less than 90% removal. According to Stefanakis and Tsihrintzis [28], satisfactory removal usually exceeds 90%. The final effluents for both laboratory-scale filters were consistently lower and met the allowed discharge of wastewater for the standard B limit (200 mg/L). The increase in DO by the aeration process was associated with the decrease in the value of COD from domestic wastewater. The main reason for the large variation in both the influent and effluents of two lab-scale reactors was the effect of the weather that caused dilution of the wastewater on rainy days, whereas in dry days, the wastewater was more concentrated. The higher HLR (lower flow rate) reduced the COD because it deduced with a longer contact time in the filter, the higher removal rate can be reached. The utilization of steel slag and limestone in the filter led to the elimination of COD, as they have the capacity to absorb organic and inorganic compounds from wastewater. Grab samples were taken twice a week and analyzed for COD/BOD removal. The removal of BOD was much higher in the aerated lab scale filter and most of the effluent concentration from both lab scale filters was found to meet the effluent quality for the standard B requirements of <50 mg L compared to the influent that did not meet the requirement. Since the *p*-values for the LSSSF was 0.256 and LSLSF systems was 0.531, none of the variables related to effluent quality and elimination effectiveness was statistically significant.

(**a**)

(**b**)
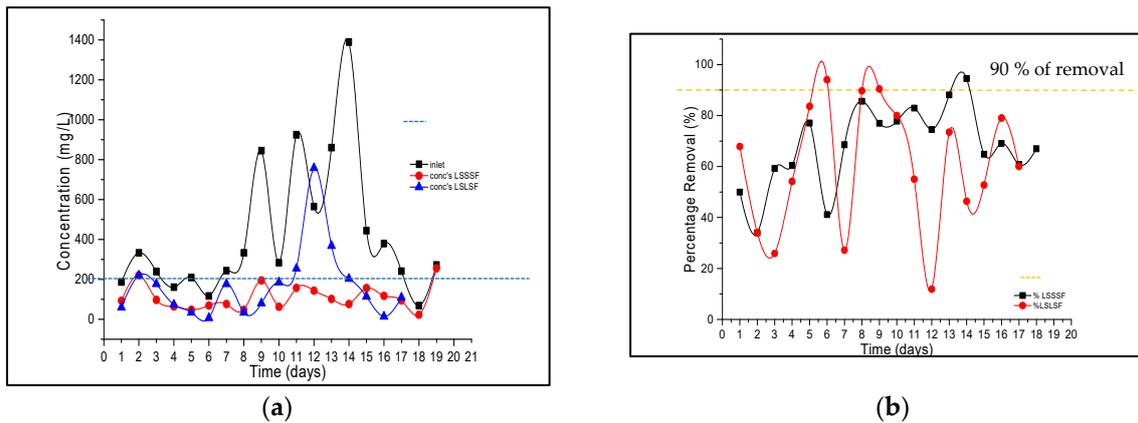
Figure 5. LSSSF and LSLSF of influent and effluent COD concentration; (**a**) Percentage removal; (**b**) Acceptable condition of sewage discharge (200 mg/L).

The influent concentration of BOD in the laboratory scale filter averaged 266.3 ± 269.7 mg/L, while for the effluent concentration for LSSSF the average was 47.59 ± 51.7 mg/L and for LSLSF the average was 78.86 ± 74.8 mg/L (Figure 6). The efficiency of the lab-scale steel slag filter (LSSSF) ranged from 33% to 99% while it varied from 15% to 95% for the laboratory-scale limestone filter (LSLSF) (Figure 5). The graph fluctuated because of the filter received different loading from the wastewater treatment plant. However, the most effective filter was steel slag compared to limestone. The highest removal of BOD from steel slag was 99%, while it was 95% by limestone. The filter aeration process improves the removal of BOD and SS [5]. LSSSF and LSLSF systems efficiently removed BOD from domestic wastewater, as it was statistically significantly different in terms of effluent efficiency and effluent quality since the *p*-values were 0.043 and 0.025.

(**A**)

(**B**)
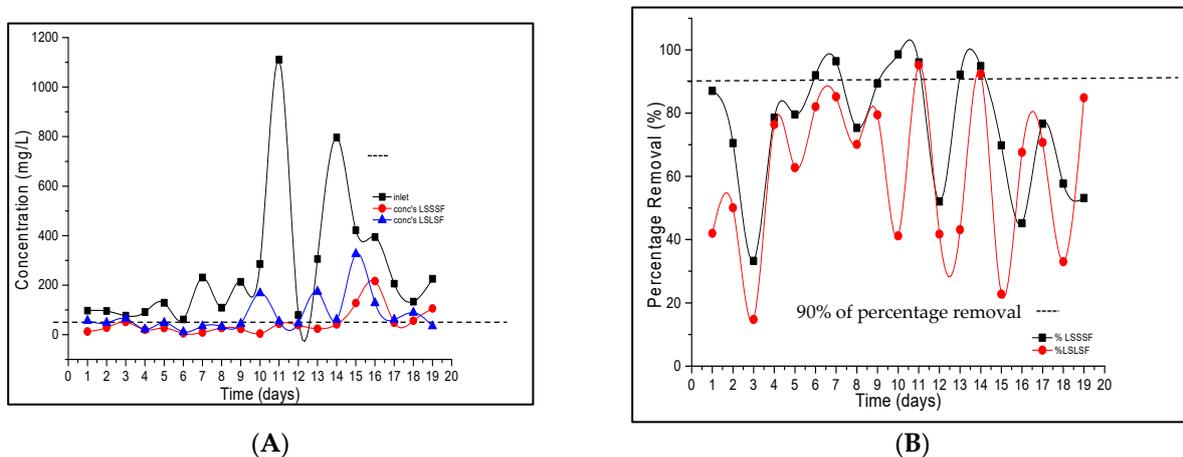
Figure 6. LSSSF and LSLSF of influent and effluent BOD concentration; (**A**) Percentage removal; (**B**) Acceptable condition of sewage discharge (50 mg/L).

pH and alkalinity are the important monitoring parameters in the ARF system as a TP removal from wastewater. pH is important in controlling the removal of phosphorus on the adsorption and desorption process. The removal of TP from wastewater depends on the adjustment of pH values [29]. pH profile and final effluent quality were statistically significant difference as the *p*-value both LSSSF and LSLSF systems were 0.009. Figure 6 shows the concentration for both steel slag and limestone media. The influent or inlet pH ranged from 6.11 to 6.46. pH increased from 6.69 to 7.68 in the steel slag filter, while it increased from 6.42 to 7.18 in limestone filter. This is because the component inside the steel slag consists of magnesium oxide, sulfur, and iron oxide while limestone consists

of calcium, where this component can increase the pH almost 10–12 when it reacts with water [30].

Figure 7 shows the alkalinity concentration for both lab-scale filters. The value of alkalinity for influent was averaged from 314.61 to 206.98 mg/L. The final effluent of both filters was lesser than the influent. The effluent from LSSSF had 169.34 ± 38.6 mg/L and 192.50 ± 113.80 mg/L from LSLSF. Because the p-value was 0.563, there were no statistically significant differences between the LSSSF and LSLSF systems. In the filter, the data were slightly lower and at a pH less than 8.3, the alkalinity was affected, indicating that less alkalinity was created [31]. Because the pH of the influent was less than 6.5, it was assumed that the pH controlled the alkalinity. pH is a good indicator of the transition from carbonate to bicarbonate alkalinity [32].


(A)　　　　　　　　　　　　　　(B)
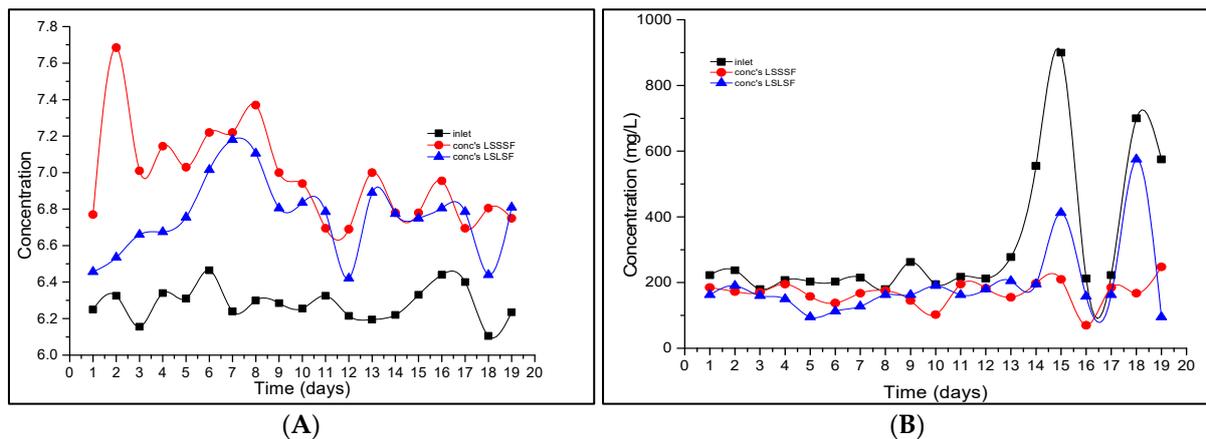
Figure 7. LSSSF and LSLSF of influent and effluent pH (**A**); alkalinity (**B**).

Ordinary domestic or municipal wastewater contains both inorganic and organic materials as suspended solids. Both consist of a biodegradable and a nonbiodegradable fraction. At the bottom of the filter, inorganic suspended materials collect [33]. The concentration of TSS influent for these experiments was averaged at approximately 612.37 ± 581.98 mg/L. The effluent of both filters (steel slag and limestone) was 54.74 ± 41.31 mg/L for LSSSF and 138.16 ± 174.01 mg/L for LSLSF (Figure 8). TSS results were not statistically significant differed as p-value was 0.053 and 0.201 for effluent quality and removal efficiency. Both filters performed well in removing the TSS, but the steel slag filter achieves more removal than limestone. The percentage of TSS removal shows that the highest removal was recorded at about 97% for LSSSF while 95% for LSLSF (Figure 7). LSSSF recorded 10 samples with more than 90% of removal while LSLSF recorded less than 5 samples with 90% of the removal. LSSSF has a capability in removing TSS compared to LSLSF because of steel slag has a porous and rough surface compared to limestone with a smooth and plain surface. The suspended solid cannot be attached to any smooth surface, leading to the solid being removed with effluent.

DO profile was recorded with the best result because the wastewater was fed with oxygen by using the aeration system. The influent concentration was 0.19 ± 0.2 mg/L. The effluent result for both media was higher in both filters. The effluent for steel slag was 3.86 ± 1.2 mg/L, while for limestone it was 3.43 ± 1.6 mg/L. Figure 9 shows that the highest concentration was recorded at 5.60 mg/L for LSSSF and LSLSF. The DO level was higher in the LSSSF and LSLSF system and there was no statistically significant difference since the p-value was 0.706. The levels of DO levels in steel slag filters were found to be higher than those of limestone due to the structure of the medium and the filter condition. According to Hamdan [34], the vertical system effectively treats high-strength effluent as a good or as further removal of biodegradable organic matter. However, more importantly, that makes the DO level higher because of the aeration process that is inducted into the

treatment system. The filter system's state is the more appropriate for providing a more favorable environment for the anaerobic process [35].
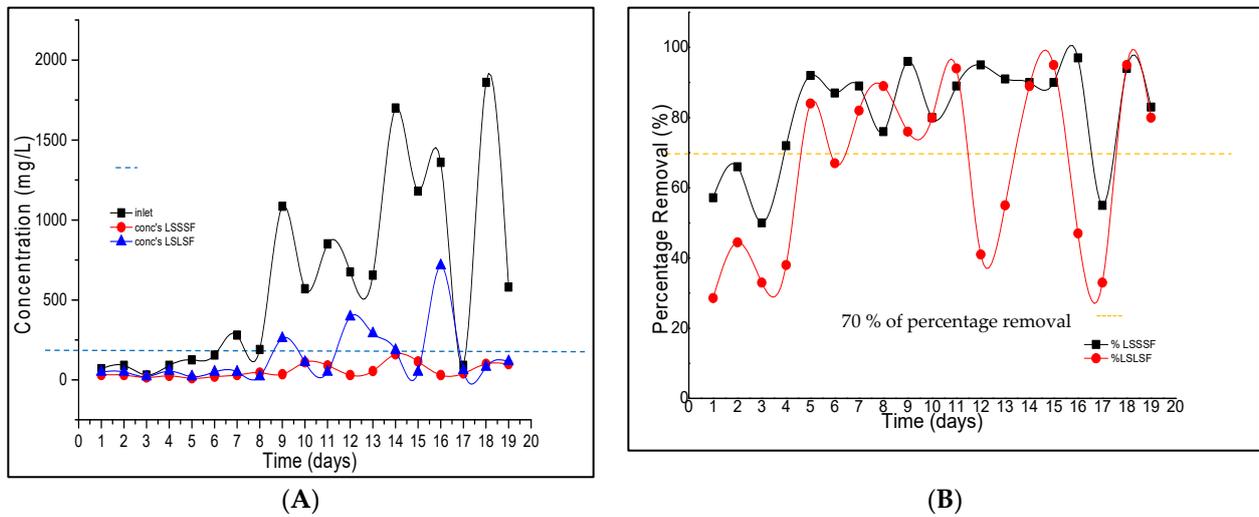
Figure 8. LSSSF and LSLSF of influent and effluent TSS concentration; (**A**) Percentage removal; (**B**) Acceptable condition 100 mg/L.
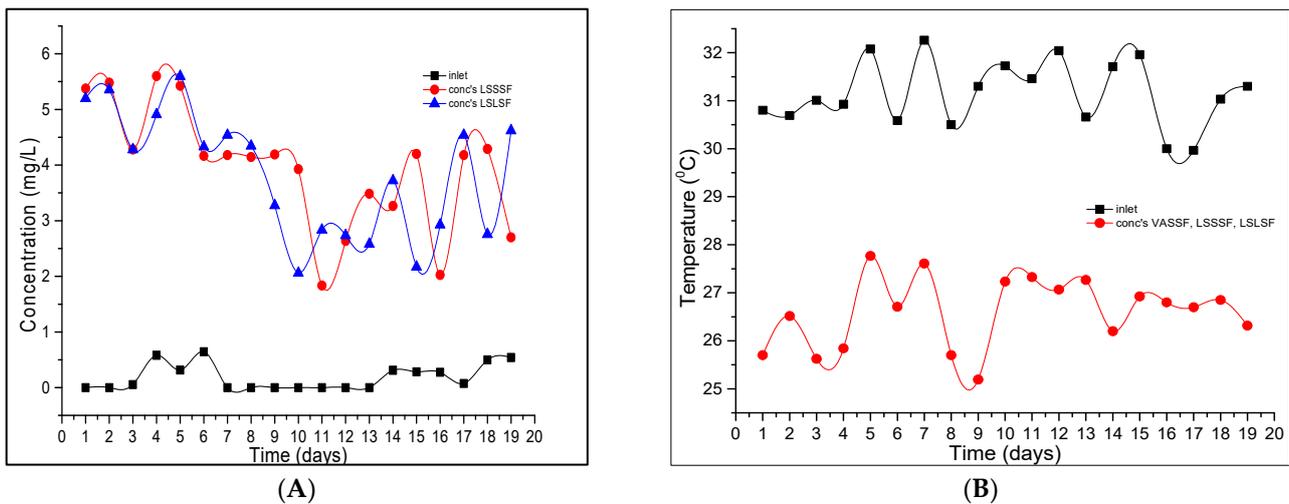

Figure 9. LSSSF and LSLSF of influent and effluent DO concentration (**A**); temperature (**B**).

Figure 9 shows the temperature profile summaries for both filter media. The ambient temperature for this experiment averaged room temperature (31.36 ± 0.7 °C) and the result obtained fluctuated due to the change of climate condition. However, an effluent temperature of 26.67 ± 0.7 °C was recorded during this experiment. The temperature was dropped because of the filter block heat from outside, and the aeration process in the filter helped to reduce the temperature in the filter system. The temperature results were not statistically significant due to differences as the *p*-value was 1.000 for both the LSSSF and LSLSF system. Temperature mainly has a great impact on phosphorus because it affects the rate of adsorption or desorption. According to Weber (1972) cited in Hamdan [34], the adsorption increases when the temperature decreases due to the vibration energies desorbing into the surface. According to Akpor [36], the optimal temperature for phosphorus removal is between 30 and 40 °C, and it is an optimal temperature condition for the biological nutrient removal activities.

Total phosphorus removal for this experiment was recorded in Figure 10. The influent amounted to 10.44 ± 2.7 mg/L during the experiment. The effluent of phosphorus was

7.89 ± 3.6 mg/L for LSSSF and 8.25 ± 3.4 mg/L for LSLSF. The highest removal of TP by LSSSF was 58%, while by LSLSF it was 64%. The data fluctuated because the filter received different loading from the wastewater treatment plant. It seems that the filter removes phosphorus less than 60% due to unfavorable environmental conditions and due to different loading, it receives from the wastewater treatment plant. The removal of phosphorus decreases because of the detachment and clogging of the medium, which causes decreased mass transfer from the liquid phase to the surface of the filter medium, decreasing the adsorption and the removal efficiency. This is because a large amount of attachment on the media slows the adsorption capacity and detaches from the media surface. In addition, the treatment plant also combined the household waste with yard waste, for example sludge treatment. From the data obtained, the influent was also recorded to be less than 10 mg/L due to the raining season, diluting the wastewater sample and making it lower than others. Domestic wastewater TP compared to the LSSSF and LSLSF system was not statistically significantly different in terms of effluent quality and effluent removal efficiency, since the *p*-values were 0.708 and 0.688, respectively. The results show that steel slag and limestone remove phosphorus nearly 60%, indicating they are still good adsorbents for phosphorus removal in wastewater treatment. Steel slag is the best material that can be used for this experiment because it is one of the waste products, abundant, and locally available compared to limestone.
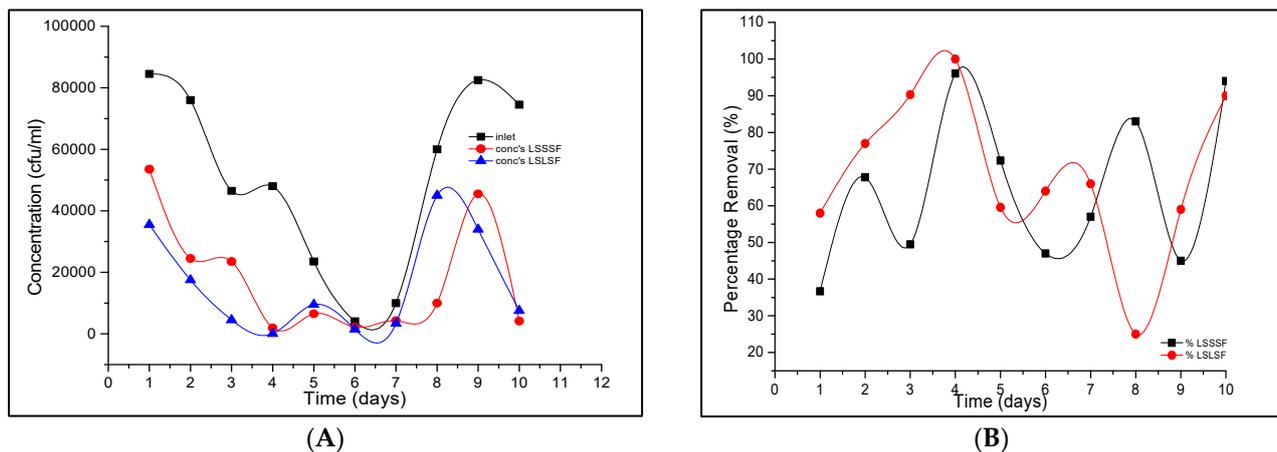

Figure 10. LSSSF and LSLSF of influent and effluent TP concentration (**A**); Percentage removal (**B**).

Figure 11 shows the TC concentration for both filters and for the influent averaged 50,949 CFU/100 mL. In the effluent, the data concentration was recorded averaged at 17,595 CFU/100 mL for steel slag, while it was 15,831 CFU/100 mL for limestone. Figure 10 shows that all the samples achieved more than 50% removal and that it was the most efficient removal for this experiment. The removal seems to not be 100% because it still has the balance of TC inside the water. The filter needs an alternative solution to eliminate 100% of TC from wastewater.

3.2. Phosphorous Removal Mechanism

The understanding of the identification of P removal in wastewater treatment by using steel slag is necessary to maximize the efficiency of P removal and to prevent pollution from the wastewater plant. Chemical composition results from XRF analysis of steel slag showed iron (Fe)—40.00%, calcium (Ca)—31.20%, silica (Si)—16.40, aluminum (Al)—5.04%, manganese (Mn)—3.25%, and other elements. The slag used in these experiments was primarily high in iron and aluminum. According to Ndegwa et al. [29], removal of phosphorus in wastewater was accomplished by the simultaneous adjustment of pH and the addition of iron, calcium, or aluminum. Steel slag is rich in Fe and calcium and plays an important role in P retention in wastewater. The presence of calcium in the steel slag facilitates P retention through precipitation and deposits Ca-P on the solid surface [37]. However, the

identification of phosphorus removal in the filter is still being investigated for future studies because it considers various factors. According to Hamdan [34], phosphorus from the slag filter is regulated by pH, temperature, and the concentration of metallic salt in the treatment system [38].
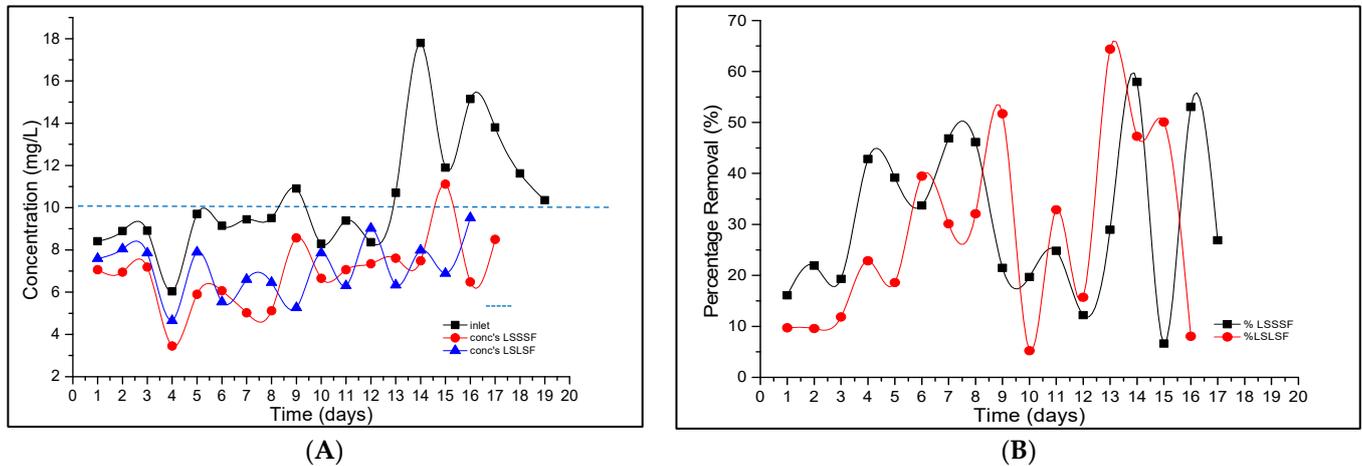
Figure 11. LSSSF and LSLSF of influent and effluent TC concentration. (**A**) Percentage removal; (**B**) Acceptable condition of saline discharge (10 mg/L).

The mineral composition of fresh steel slag in terms of its components is presented in Figure 12a. From the figure, oxygen, calcium, carbon, and silica are the highest chemistry domination. The filter systems are controlled by the interaction and reaction between oxygen, calcium, carbon, and silica.

The XRF test was used to determine the chemical composition of the fresh steel slag, and the data are presented in Table 6. The results of the XRF analyses show that the highest elemental chemistry was dominated by calcium, iron, and silica. Based on the SEM/EDX and XRF analysis, the highest chemical composition on a fresh steel slag surface was dominated by calcium, iron, and silica. The test result revealed no detection for the phosphorus on the surface of the fresh steel slag.

Table 6. Chemical composition of fresh steel slag.

Chemical Component	Concentration
CO_2	0.10%
CaO	31.20%
Fe_2O_3	40.00%
SiO_2	16.40%
Al_2O_3	5.04%
MgO	3.25%
MnO	2.00%
TiO_2	0.53%
Cr_2O_3	0.32%
P_2O_5	0.56%
S	0 < LLD

The steel slag sample taken out from the filter was analyzed using the SEM/EDX test after being treated in the filter over a two-month period. The steel slag with CaO and MgO easily produce volume expansion after hydration, and this is the main factor affecting the stability of steel slag. The composition of the steel slag with CaO has important role in

the removal process and at pH 3 to 5, reached to the optimal saturation and P-removal efficiency due to the higher amount of CaO, which might have caused higher levels of CaO dissolution, followed by Ca_2PO_4 precipitation.
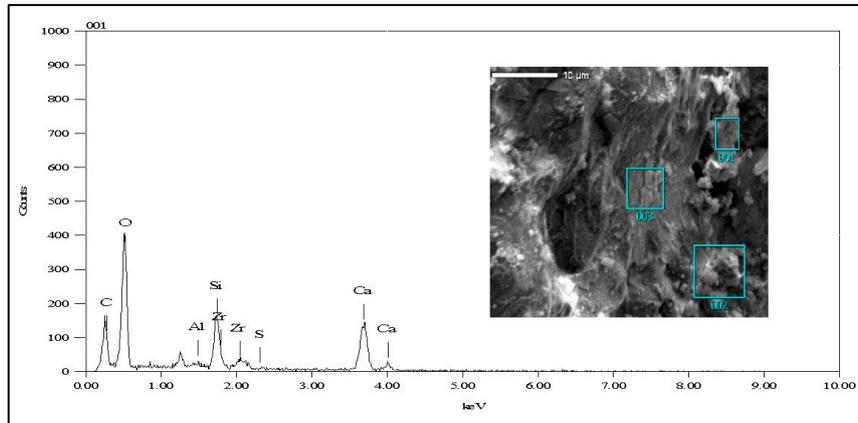
(**a**)
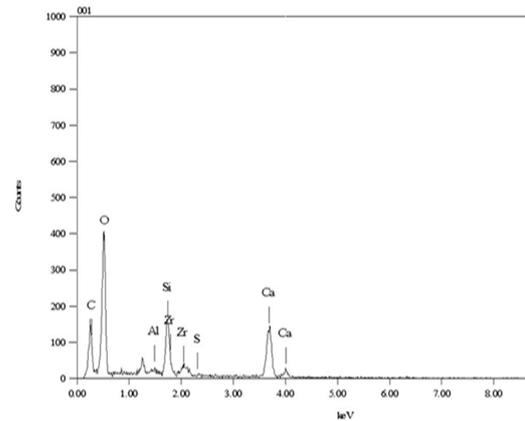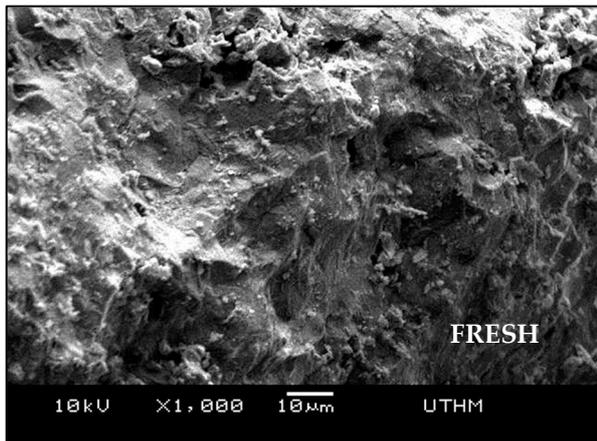
(**b**)
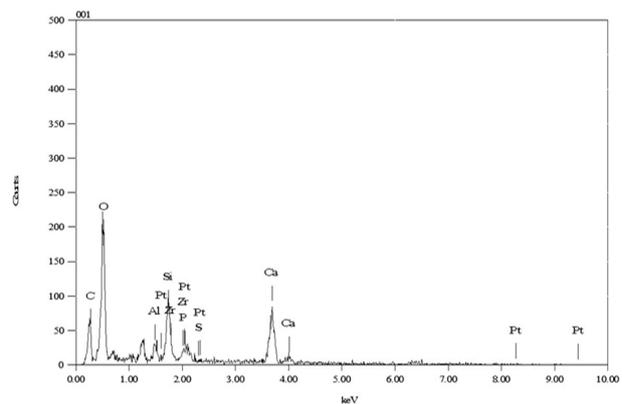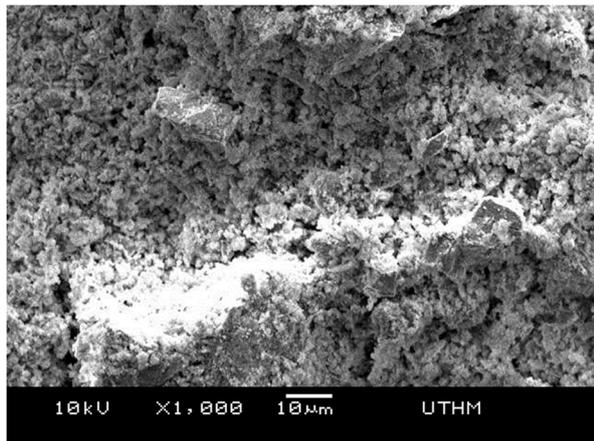
(**c**)

Figure 12. (**a**): EDX spectrum of a fresh steel slag sample. (**b**): SEM/EDX micrograph of the surface and spectrum of fresh steel slag. (**c**): SEM/EDX micrograph of surface scanned and spectrum of used steel slag over a two-month treatment period in the filter.

Figure 12b,c shows the presence of phosphorus in steel slag by using EDX mapping and by spectrum analysis of the surface sample over a two-month period of wastewater treatment. Based on Figure 11c, phosphorus was found on the surface of the steel slag

sample and was clearly seen based on the peak value in the EDX graph. In the steel slag sample, a peak value was available on the surface. It shows that the steel slag has an adsorption capacity based on finding from the EDX result. Adsorptions occur based on the mechanism key contained in the steel slag because of its richness in calcium, iron, and silica which is why this composition plays an important role in P-removal. At acidic pH, high reductive dissolution of Fe oxides leads to the release of more Fe which then reacts with phosphate and is removed efficiently from the wastewater influents. Furthermore, Ca facilitates P retention through precipitation and forming a Ca-P deposition on the solid surface [39,40].

3.3. Membrane-Based Separation Processes Using Steel Slag

Membrane-based separation technologies have developed over the last decades to provide an elegant, robust, and cost-effective treatment solution to achieve high effluent standard [41–44]. When combined with enhanced phosphorous co-precipitation such as steel slug, a great and stable phosphorous removal can be expected [45–47]. The contact angle of such modified membrane with steel slag demonstrated increased hydrophilicity and subsequently increase in water-flux and P-removal. According to the Malaysia Environmental Quality (Scheduled Waste) Regulation (2005), steel slag is classified as non-hazardous waste which can be disposed of in appropriate landfills.

4. Conclusions

The novelty of the current work is in improving a Vertical Aerated Rock Filter (VARF) using steel slag and limestone media to enhance the efficiency of a rock filter (RF) to eliminate total phosphorus (TP) from domestic wastewater. The effluent parameters that left the lab-scale system met the discharge limit for standard B throughout the monitoring period for LSSSF and LSLSF in domestic wastewater. The organic matter from the original influent was successfully removed through this system. LSSSF and LSLSF are good at removing COD, BOD, and TSS. The effluent complies with the requirement, but almost 70% of COD removal is from LSSSF. Alkalinity, pH, and DO effluent significantly met the criteria requirement standard. Both filters were good at increasing the pH value due to the action of the filter media. Influents from wastewater treatment had a zero DO and when the influent was treated in the filter, the DO became higher because of the aeration process and media surface. According to the TP result, both filters had good removal of about 58% for steel slag and 64% for limestone. As a result, the LSSSF system was more appropriate compared to LSLSF because steel slag is the best material that can be used for this experiment. The contact angle of such modified membrane with steel slag demonstrated increased hydrophilicity and subsequently an increase in water-flux and P-removal. The presence of Ca, Al, and Fe helps remove phosphorus in wastewater. In addition to that, the difference between steel slag and limestone is that the slag has a porous surface compared to limestone. This porous surface makes the adsorption of phosphorus better than that of a smooth surface. Steel slag is also a waste product, abundant and locally available compared to limestone. LSSSF is the alternative media for phosphorus. Steel slag is also a waste product, abundant and locally available compared to limestone, and could be a successful alternative medium to eliminate the phosphorus from residential wastewater in wastewater treatment plants.

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References

1. Bunce, J.T.; Ndam, E.; Ofiteru, I.D.; Moore, A.; Graham, D.W. A review of phosphorus removal technologies and their applicability to small-scale domestic wastewater treatment systems. *Front. Environ. Sci.* **2018**, *6*, 8. [CrossRef]
2. Adnan, S.H.; Abd Roni, N.; Hamidon, N.; Ismail, T.N. The efficacy of recycled concrete aggregate for removal phosphorus in synthetic wastewater with different pH value. *J. Adv. Ind. Technol. Appl.* **2020**, *1*, 24–30.
3. Carey, R.O.; Migliaccio, K.W. Contribution of wastewater treatment plant effluents to nutrient dynamics in aquatic systems: A review. *Environ. Manag.* **2009**, *44*, 205–217. [CrossRef] [PubMed]
4. Mara, D.D. *Good Practice in Water and Environmental Management: Natural Wastewater Treatment*; Chartered Institute of Water and Environmental Management: London, UK, 2007.
5. Mara, D.D.; Johnson, M.L. Aerated rock filters for enhanced ammonia and fecal coliform removal from facultative pond effluents. *J. Environ. Eng.* **2006**, *132*, 574–577. [CrossRef]
6. Vymazal, J. Removal of nutrients in various types of constructed wetlands. *Sci. Total Environ.* **2007**, *380*, 48–65. [CrossRef]
7. Žibienė, G.; Dapkienė, M.; Kazakevičienė, J.; Radzevičius, A. Phosphorus removal in a vertical flow constructed wetland using dolomite powder and chippings as filter media. *J. Water Secur.* **2015**, *1*, jws2015005. [CrossRef]
8. Ruzhitskaya, O.; Gogina, E. Methods of removal of phosphates from wastewater. *MATEC Web Conf.* **2017**, *106*, 07006. [CrossRef]
9. Wang, L.; Penn, C.; Huang, C.H.; Livingston, S.; Yan, J. Using steel slag for dissolved phosphorus removal: Insights from a designed flow-through laboratory experimental structure. *Water* **2020**, *12*, 1236. [CrossRef]
10. Zuo, M.; Renman, G.; Gustafsson, J.P.; Klysubun, W. Dual slag filters for enhanced phosphorus removal from domestic waste water: Performance and mechanisms. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7391–7400. [CrossRef]
11. Maarup, S.N.; Hamdan, R.; Othman, N. Study on the Performance of a Pilot-Scale Vertical Aerated Steel Slag Filter for Phosphorus Removal. In Proceedings of the Advancements in Marine and Freshwater Sciences UMTAS 2013, Terengganu, Malaysia, 8–10 October 2013.
12. Bing l Biao, T.; Zhen, M.; Hanchi, C.; Li Hongbo, L. Physical and Chemical Properties of Steel Slag and Utilization Technology of Steel Slag at Home and Abroad. *Earth Environ. Sci.* **2019**, *242*, 032012. [CrossRef]
13. Deus, A.C.F.; de Almeida Bertani, R.M.; Meirelles, G.C.; Soares, A.D.A.V.L.; Moreira, L.L.Q.; Büll, L.T.; Fernandes, D.M. The Comprehensive Utilization of Steel Slag in Agricultural Soils. In *Recovery and Utilization of Metallurgical Solid Waste*; Zhang, Y., Ed.; IntechOpen: London, UK, 2019. [CrossRef]
14. Tian, S.; Jiang, J.; Zhang, Z.; Manovic, V. Inherent potential of steelmaking to contribute to decarbonisation targets via industrial carbon capture and storage. *Nat. Commun.* **2018**, *9*, 4422. [CrossRef] [PubMed]
15. Bird, S.C.; Drizo, A. Investigations on phosphorus recovery and reuse as soil amendment from electric arc furnace slag filters. *J. Environ. Sci. Health Part A* **2009**, *44*, 1476–1483. [CrossRef] [PubMed]
16. Li, L.; Ling, T.; Pan, S. Environmental benefit assessment of steel slag utilization and carbonation: A systematic review. *Sci. Total Environ.* **2022**, *806*, 150280. [CrossRef] [PubMed]
17. Yao, Q.; Peng, D.C. Nitrite oxidizing bacteria (NOB) dominating in nitrifying community in full-scale biological nutrient removal wastewater treatment plants. *AMB Express* **2017**, *7*, 25. [CrossRef] [PubMed]
18. Hamdan, R.; Ibrahim, I.I.; Wan Mohamed, W.A.; Al-Gheethi, A.; Othman, N.; Mohamed, R. Optimizing the vertical flow aerated steel slag filter system with nitrifiers bacteria for the removal from domestic wastewater: A pilot study. *J. Chem. Technol. Biotechnol.* **2021**, *96*, 1067–1079. [CrossRef]
19. Pytka-Woszczylo, A.; Różańska-Boczula, M.; Gizińska-Górna, M.; Marzec, M.; Listosz, A.; Jóźwiakowsk, K. Efficiency of Filters Filled with Rockfos for Phosphorus Removal from Domestic Sewage. *Adv. Sci. Technol. Res. J.* **2022**, *16*, 176–188. [CrossRef]
20. Kasprzyk, M.; Gajewska, M. Phosphorus removal by application of natural and semi-natural materials for possible recovery according to assumptions of circular economy and closed circuit of P. *Sci. Total Environ.* **2019**, *650*, 249–256. [CrossRef]
21. Preisner, M.; Neverova-Dziopak, E.; Kowalewski, Z. An Analytical Review of Different Approaches to Wastewater Discharge Standards with Particular Emphasis on Nutrients. *Environ. Manag.* **2020**, *66*, 694–708. [CrossRef]
22. Ahmad, S.Z.N.; Hamdan, R.; Al-Gheethi, A.; Alkhadher, S.; Othman, N. Removal of phosphate from wastewater by steel slag with a high calcium oxide column filter system; efficiencies and mechanisms. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 3232–3240. [CrossRef]
23. Penn, C.; Livingston, S.; Shedekar, V.; King, K.; Williams, M. Performance of field-scale phosphorus removal structures utilizing steel slag for treatment of surface and subsurface drainage. *Water* **2020**, *12*, 443. [CrossRef]

24. Bridgewater, L.; American Public Health Association; American Water Works Association; Water Environment Federation. *Standard Methods for the Examination of Water and Waste Water*, 22nd ed.; American Public Health Association: Washington, DC, USA, 2012.

25. Zhang, H.; Zhang, X.; Bai, S.; Zhu, Y.; Gong, Y. Adsorption Removal of Phosphorus from Aqueous Solution by Steel Slag Columns. In Proceedings of the 2010 4th International Conference on Bioinformatics and Biomedical Engineering, Chengdu, China, 18–20 June 2010; pp. 1–4.

26. Chang, J.; Zhang, X.; Perfler, R.; Xu, Q.; Niu, X.; Ge, Y. Effect of Hydraulic Loading Rate on The Removal Efficiency in A Constructed Wetland in Subtropical China. *Fresenius Environ. Bull.* **2007**, *16*, 1082–1086.

27. Swanson, G.R.; Williamson, K.J. Upgrading lagoon effluents with rock filters. *J. Environ. Eng. Div.* **1980**, *106*, 1111–1129. [CrossRef]

28. Stefanakis, A.I.; Tsihrintzis, V.A. Performance of vertical flow constructed wetlands treating simulated municipal wastewater: Effect of various design parameters. *Desalination* **2009**, *248*, 753–770. [CrossRef]

29. Ndegwa, P.M.; Zhu, J.; Luo, A. Influence of temperature and time on the removal of phosphorus in swine manure during batch aeration. *J. Environ. Sci. Health Part B* **2003**, *38*, 73–87. [CrossRef] [PubMed]

30. Penn, C.J.; Bowen, J.M. *Design and Construction of Phosphorus Removal Structures for Improving Water Quality*; Springer: Berlin/Heidelberg, Germany, 2018; pp. 91–94.

31. Yihuan, D.; Andrew, W. Mechanism of Phosphorus by Recycled Crushed Aggregate. *Int. J. Environ. Res. Public Health* **2018**, *15*, 357.

32. Sunny, N.; Roy, A.; Pavithran, A.; Johnson, M.; Shafana, P.H. Inhibitors of Aerobic Treatment System and its Control Measures. *Int. Res. J. Eng. Technol.* **2021**, *8*, 4110–4115.

33. Chen, X.; Sun, X.; Xu, P.; Wang, S.; Zhou, T.; Wang, X.; Yang, C.; Lu, Q. Optimal regulation of N/P in horizontal sub-surface flow constructed wetland through quantitative phosphorus removal by steel slag fed. *Environ. Sci. Pollut. Res.* **2020**, *27*, 5779–5787. [CrossRef]

34. Hamdan, R.B. Aerated Blast Furnace Slag Filters for Enhanced Nitrogen and Phosphorus Removal from Small Wastewater Treatment Plants. Ph.D. Thesis, School of Civil Engineering, University of Leeds, Leeds, UK, 2010.

35. Chazarenz, F.; Stephane, T.; Comeau, F. Effect of Loading Rate on Performance of Constructed Wetlands Treating an Anaerobic Supernatant. *Water Sci. Technol.* **2017**, *56*, 23–29. [CrossRef]

36. Akpor, O.B.; Olaolu, T.D.; Okolie, E.C. The Effect of Temperature on Nitrate and Phosphate Uptake from Synthetic Wastewater by Selected Bacteria Species. *Br. Microbiol. Res. J.* **2013**, *4*, 328–342. [CrossRef]

37. Drizo, A.; Forget, C.; Chapuis, R.P.; Comeau, Y. Phosphorus removal by steel slag and serpentinite. *Water Res.* **2006**, *40*, 1547–1554. [CrossRef]

38. Han, C.; Wang, Z.; Yang, W.; Wu, Q.; Yang, H.; Xue, X. Effects of pH on phosphorus removal capacities of basic oxygen furnace slag. *Ecol. Eng.* **2016**, *89*, 1–6. [CrossRef]

39. Hussain, S.I.; Blowes, D.W.; Ptacek, C.J.; Olding, D. Phosphorus removal from lake water using basic oxygen furnace slag: System performance and characterization of reaction products. *Environ. Eng. Sci.* **2014**, *31*, 631–642. [CrossRef]

40. Ahmad, S.Z.N.; Al-Gheethi, A.; Hamdan, R.; Othman, N. Efficiencies and mechanisms of steel slag with ferric oxides for removing phosphate from wastewater using a column filter system. *Environ. Sci. Pollut. Res.* **2020**, *27*, 35184–35194. [CrossRef]

41. Modi, R.; Kavaiya, A.R.; Vanzara, P.B.; Raval, H.D. Membranes in Zero-Liquid-Discharge Systems for Efficient Processes toward Sustainable Environment: A Review. *J. Environ. Eng.* **2022**, *148*, 03122004. [CrossRef]

42. Raval, H.D.; Mondal, M. *Advancement in Polymer-Based Membranes for Water Remediation*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 335–379.

43. Ankoliya, D.; Mehta, B.; Raval, H. Advances in surface modification techniques of reverse osmosis membrane over the years. *Sep. Sci. Technol.* **2019**, *54*, 293–310. [CrossRef]

44. Lesjean, B.; Gnirss, R.; Adam, C.; Kraume, M.; Luck, F. Enhanced biological phosphorus removal process implemented in membrane bioreactors to improve phosphorous recovery and recycling. *Water Sci. Technol.* **2003**, *48*, 87–94. [CrossRef]

45. Raval, H.; Mehta, B.; Joshi, R.; Kumar, A. A Novel Thin Film Composite Reverse Osmosis Membrane Modified by Ionic Liquid. *Braz. J. Chem. Eng.* **2018**, *35*, 1249–1256. [CrossRef]

46. Raval, H.; Mehta, B.; Joshi, R. A novel low-fouling zeolite-polysulfone nanocomposite membrane for advanced water treatment. *Desalination Water Treat.* **2017**, *88*, 8–15. [CrossRef]

47. Lesjean, B.; Gnirssb, R.; Adam, C. Process configurations adapted to membrane bioreactors for enhanced biological phosphorous and nitrogen removal. *Desalination* **2002**, *149*, 217–224. [CrossRef]