



CAPACITY OF BIOCHAR TRICKLING FILTER FOR TREATING WASTEWATER FROM AN CUU MARKET, HUE CITY, VIETNAM

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Abstract. The pollution caused by market wastewater has occurred for several years in Vietnam. In particular, untreated wastewater from riverside markets is often directly discharged into a river nearby, increasing loads of pollutants in the river. Every day, the An Cuu Market averagely discharges about 19 cubic metres of wastewater into the An Cuu River. However, a wastewater treatment system has not been yet built at the market due to different reasons, including the lack of investment capital. A trickling filter (TF) consisting of a fixed bed of biochar is a cost-acceptable technology for treating organic pollutants, nutrients, and suspended solids. In this study, a model of TF using biochar for An Cuu Market wastewater treatment is effectively operated with the organic loading rate varying from 188 to 550 $\text{g}_{\text{BOD}_5} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$ and the hydraulic loading rate from 532 to 1899 $\text{L} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. The biochar trickling filter shows high removal efficiencies: 97% BOD_5 , 92% COD, 97% TSS, 66% P_{Tot} , and 62% N_{Tot} .

Keywords: An Cuu Market, wastewater treatment, biochar trickling filter, Vietnam

1 Introduction

The An Cuu Market is a famous market located on the left bank of the An Cuu River in Hue city, Vietnam. In recent years, the An Cuu River has become polluted. One of the waste sources affecting the river water quality is wastewater from the market. Every day, the An Cuu Market averagely discharges about 19 cubic metres of wastewater into the river. In 2015, the discharge was 8 $\text{m}^3 \cdot \text{day}^{-1}$, carrying nutrient loads of 438 $\text{g} \cdot \text{day}^{-1}$ and 302 $\text{g} \cdot \text{day}^{-1}$ in nitrogen and phosphorus [12]. However, until now, the management board of the An Cuu Market has not been able to build a wastewater treatment system due to difficulties in capital source and land area. Therefore, seeking a suitable technology solution for treating An Cuu market's wastewater is necessary and useful.

A trickling filter (TF), also called biological trickling filter, is a traditional wastewater treatment technology, normally consisting of a fixed bed of rocks, sand, gravel, or ceramic, over which wastewater flows downward and causes a layer of microbial slime (biofilm) to grow and cover the bed of the filter material [16]. However, using these traditional filter materials often leads to several restrictions on the performance, such as clogging after a short time of application, high bulk density, low porosity, and low specific surface area. To increase the surface area of the

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sand material in the filter, it is necessary to decrease the size of sand particles. However, this leads to sooner clogging in the filter. Meanwhile, biochar has recently attracted much attention in the wastewater field thanks to its superior properties. "Biochar is a carbon-rich solid product formed by pyrolysis of bio-organic materials at temperatures less than 700 °C under anoxic conditions" [4]. Numerous studies on the application of biochar to adsorb pollutants in wastewater are reported in the literature. This material possesses a large surface area, a large pore volume, sufficient functional groups, environmental stability, and ease of preparation [4]. They indicate a high capacity of biochar filters for wastewater treatment. For example, Kaetzl et al. treat municipal wastewater and achieve a significant reduction in chemical oxygen demand (COD) (up to 90%), TOC (up to 80%), and turbidity [7]. Manyuchi et al. also report a reduction in COD, total suspended solids (TSS), TKN, and P_{Tot} (90, 89, 64, and 78%, respectively) [8]. Dalahmeh [11] reports that the performance of biochar filters for domestic wastewater treatment is better than that of sand filters. In addition, the capacity of biochar filters against the fluctuation of the organic loading rate (OLR) and the hydraulic loading rate (HLR) is also better than that of sand filters. Biochar can be used for the adsorption of heavy metals and organic substances, including the high-molecular compounds used in agriculture, medicine, and manufacturing industries. The studies using biochar for removing heavy metals from wastewater account for 46%, while those for organics account for only 39% [17].

Although biochar is advantageous for wastewater treatment applications, it has not been sufficiently studied in Vietnam. In terms of biomass from agriculture and timber, Vietnam ranks third in Southeast Asia, after Indonesia and Thailand [10]. Simultaneously, the sources of biomass in Vietnam are diverse, estimated at over 100 million tons per year, and potential biomass types are husks, leaves, bagasse, and natural forest trees [13]. Therefore, this study is carried out to test the An Cuu Market wastewater treatment capacity of a trickling filter using the commercial biochar made from sawdust as a filter material.

2 Materials and methods

2.1 Sampling and sample analysis

The An Cuu Market wastewater was sampled according to ISO 5667-10:1992 and stored in the Institute of Resources and Environment – Hue University – according to ISO 5667-3:2003. The sampling was carried out 1–2 times per month in March, May, July, September, and December 2018, and once per month in February and May 2019. Basic parameters, namely dissolved oxygen (DO), pH, COD, biochemical oxygen demand after five days (BOD_5), TSS, total nitrogen (N_{Tot}), and total phosphorous (P_{Tot}) were determined according to national and international standards [1] to control the test quality through repeatability [2].

2.2 Filter design and experimental setup

The experimental design was set up as follows (Figure 1):

1. A 20-litre reservoir containing raw wastewater is situated 1.8 metres above the ground so that wastewater can flow to a filter column at a lower height. At the bottom of the reservoir, there was a drain valve connected to an 8-mm diameter pipe for supplying wastewater into the filter column. The end of the inlet pipe was connected with a water split pipe to distribute the wastewater to the surface of the filter material.

2. The filter column was designed with a cylindrical structure, made of PVC with an inner diameter of 100 mm and a height of 1 m. Inside the column, biochar was stuffed with a height of 0.6 m. Below this layer, there is a 20-cm layer of gravel with a grain size of 10–25 mm as a drainage layer. A drainage valve is arranged at the height of 10 cm from the bottom of the column.

3. The filter column was aerated by an oxygen blower operating continuously with an aeration speed of 2.5 litres per minute and the max aeration depth of 0.5 m from the middle of the column to the top. This blower creates aerobic conditions at the top half part of the filter column and anoxic conditions at the bottom.

2.3 Filter material

The filter material used in this experiment is the commercial biochar made from sawdust. This biochar is one of the commercial products of Viet Renewable Energy Technology Joint Stock Company. The biochar characteristics are described in Table 2.

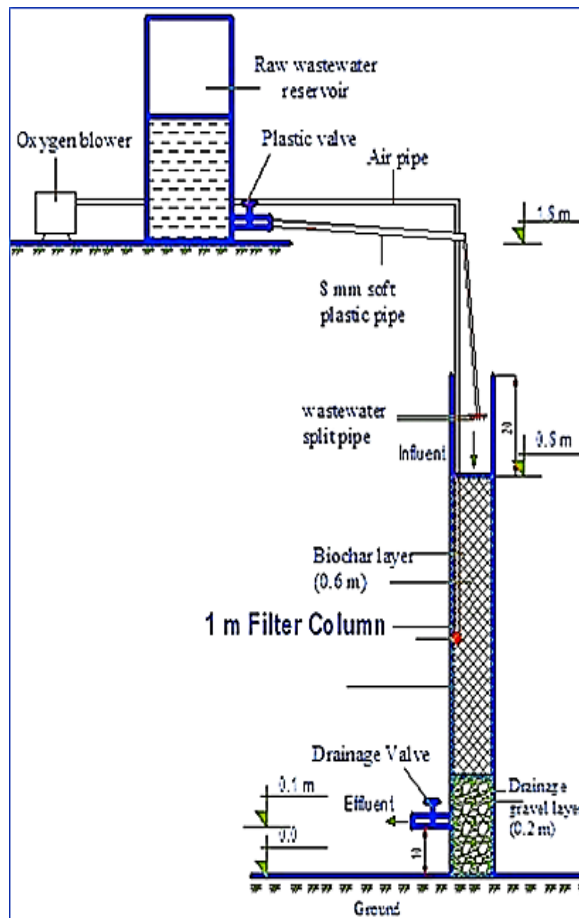


Figure 1. Schematic diagram of experimental setup for testing wastewater treatment effects with biochar filter material

Table 1. Characteristics of commercial sawdust biochar

| No. | Parameter | Unit | Value |
|-----|---------------------------|---------|--------|
| 1 | Total energy value | kcal/kg | >7000 |
| 2 | Fixed-carbon content | % | 80–95 |
| 3 | Sulphur content | % | 0–0.01 |
| 4 | Moisture content | % | <4 |
| 5 | Carbonization temperature | °C | <1000 |

Biochar production

Sawdust was pressed into a hexagonal cylinder block and pyrolyzed in a kiln at approximately 1000 °C.

Biochar filter material preparation

The commercial biochar was crushed and screened through sieves of different sizes to achieve different granular composition in mass. The uniformity coefficient is a numeric estimate of how the filter material is graded. In this study, it was calculated by dividing the d60 value (the size of screen opening where 60% of a sample passes through and 40% is retained) by d10 value (the size of screen opening where 10% of a sample passes through and 90% is retained) [11]. In this study, the uniformity coefficient is 2.5.

Biochar material disposition inside the filter column

A biochar layer with a height of 0.6 m was set into a 1 mm mesh bag and stuffed along the filter column. It comprises three sub-layers of different particle sizes: bottom layer sized 10–15 mm (39.9% mass), middle layer (4–10 mm, 49.7%), and top layer (1–4 mm, 10.4%). The drainage material layer located at the bottom of the column is 0.2 m high and made of crushed stones sized 10–25 mm.

2.4 Wastewater and biological sludge

The influent used in the experiment is wastewater from the market. The wastewater was diluted with tap water to reduce the concentration of pollutants. The tap water was settled for 24 hours to remove chlorine before use.

The biological sludge used for the experiment is activated sludge taken from an aeration tank in Phu Bai industrial zone wastewater treatment plant, Thua Thien Hue province, Vietnam. The biological sludge was fed with the studied wastewater at an organic loading rate of 0.2–0.3 mg_{BOD5}·mg_{VSS}⁻¹·d⁻¹ (VSS – Volatile Suspended Solid).

2.5 Preparation for experiment

The biochar filter column was operated with tap water in three days to enable air inside the column to escape and to monitor and control the flow, HLR, and hydraulic retention time. The working solution was prepared by mixing a quantity of activated sludge with diluted wastewater to obtain the concentration of 144 mg·L⁻¹ and 190 mg·L⁻¹ for TSS and BOD₅. The solution was then poured into the filter column and aerated continuously, resulting in a biofilm inside the column. In the following days, the filter column was operated with diluted wastewater with the BOD₅ concentration of 200 mg·L⁻¹ and the surface loading rate of 506 L·m⁻²·day⁻¹. The microbiological culture period lasted 12 days (when the output COD concentration was stable).

2.6 Operating parameters

The biochar filter column was fed with wastewater with the HLR ranging 532–1899 L·m⁻²·day⁻¹. The concentration of pollutants was reduced by diluting the wastewater, and the OLR and HLR were changed by adjusting the drain valve of the storage reservoir. The experiment was conducted with the OLR in the range of 188–550 g_{BOD5}·m⁻³·day⁻¹.

pH, TSS, BOD₅, COD, N_{Tot}, and P_{Tot} in wastewater before and after treatment were determined to evaluate the treatment effectiveness of the biochar filter. The OLR and HLR are calculated according to the following formulas

$$OLR = \frac{Q \times L_0}{1000V_{vl}}$$

$$HLR = \frac{Q}{S}$$

where Q is the wastewater flow (L·day⁻¹); L_0 is the influent concentration of organic matters (mg·L⁻¹); V_{vl} is the volume of biochar filter material (m³); S is the cross-sectional area of the filter column (m²).

3 Results and discussion

3.1 Characteristics of An Cuu Market wastewater

The characteristics of An Cuu Market wastewater do not meet the National Technical Regulation on Domestic Wastewater QCVN 14:2008/BTNMT for organic pollutants and suspended solids. The values of these parameters exceed the limit in the regulation many times (Table 2).

Table 2. Concentrations of pollutants in An Cuu market's wastewater during March 2018–May 2019. The average values shown are mean \pm standard deviation

| Parameter | Unit | 2018 | | 2019 | | QCVN 14:2008/BTNMT | |
|------------------|--------------------|-----------|-----------------------------------|------------|-----------------------------------|-----------------------|-----|
| | | Min–Max | Average | Min–Max | Average | A | B |
| | | | | | | | |
| pH | | 6.2–7.3 | 6.7 \pm 0.4 | 6.5–7.1 | 6.8 \pm 0.4 | 5–9 | 5–9 |
| DO | mg·L ⁻¹ | 2.8–3.9 | 3.5 \pm 0.4 | 2.8–3.3 | 3.1 \pm 0.4 | – | – |
| TSS | mg·L ⁻¹ | 57–190 | 124 \pm 45 | 133–220 | 177 \pm 62 | 50 | 100 |
| BOD ₅ | mg·L ⁻¹ | 180–360 | 249 \pm 67 | 128–220 | 174 \pm 65 | 30 | 50 |
| COD | mg·L ⁻¹ | 338–747 | 499 \pm 174 | 272–540 | 406 \pm 190 | – | – |
| N _{Tot} | mg·L ⁻¹ | 3.1–67.2 | 22.1 \pm 21.8 | 44.5–108.4 | 76.5 \pm 45.2 | – | – |
| P _{Tot} | mg·L ⁻¹ | 1.74–11.8 | 5.96 \pm 3.8 | 16.1–19.1 | 17.6 \pm 2.12 | – | – |

3.2 Removal of pollutants with the biochar trickling filter

The concentration of pollutants in wastewater after treatment with the biochar filter meets the limits of the National Technical Regulation on Domestic Wastewater QCVN 14:2008/BTNMT (Table 3).

Table 3. Wastewater treatment effectiveness of biochar trickling filter

| Parameter | Inflow (mg·L ⁻¹) | Effluent (mg·L ⁻¹) | Removal (%) | QCVN 14:2008/BTNMT | |
|------------------|---------------------------------|-----------------------------------|---------------------------------|--------------------|-----|
| | | | | A | B |
| BOD ₅ | 221 \pm 79 | 20 \pm 10 | 90 \pm 6 | 30 | 50 |
| COD | 457 \pm 162 | 92 \pm 39 | 79 \pm 8.9 | – | – |
| TSS | 168 \pm 60 | 24 \pm 20 | 87 \pm 8.1 | 50 | 100 |
| N _{Tot} | 43.5 \pm 28.2 | 21 \pm 16.8 | 55 \pm 8.4 | – | – |
| P _{Tot} | 7.53 \pm 5.2 | 4.38 \pm 3.2 | 41 \pm 11.9 | – | – |

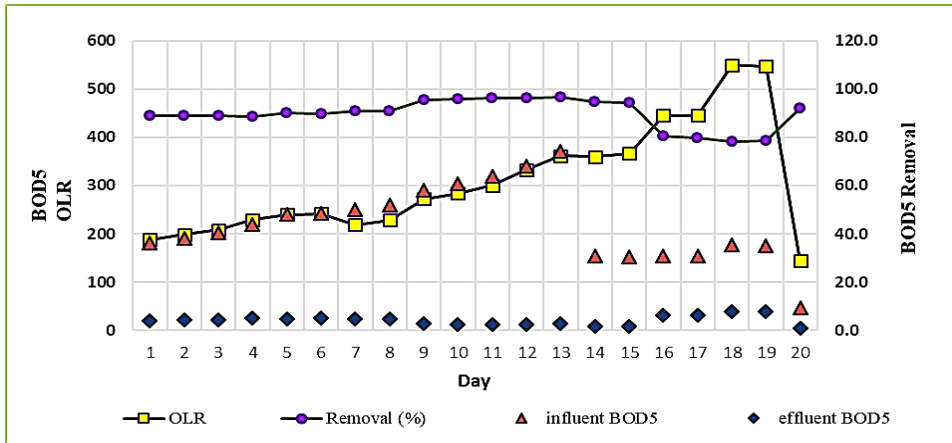
Notes: The values shown are mean \pm standard deviation, $n = 20$. Triplicate analysis was conducted for each test.

Effect of biochar filter on removal of organic matter

BOD₅ removal

At each HLR, the biochar filter is operated with a gradual increase in substrate concentration until the wastewater treatment performance decreases. Accordingly, the OLR starts from 144 to 550 g_{BOD5}·m⁻³·day⁻¹. The concentration of BOD₅ in the inflow is from 46 to 370 mg·L⁻¹. The

concentration of BOD₅ in the effluent is from 3.6 to 38 mg·L⁻¹. BOD₅ removal performance increases and reaches the maximal value of 97% at the OLR of 362 g_{BOD5}·m⁻³·day⁻¹. When the OLR increases to 445–550 g_{BOD5}·m⁻³·day⁻¹, BOD₅ removal performance decreases to 78–80%. A negative correlation between the BOD₅ removal efficiency and OLR is observed ($R = -0.567$). The performance of the biochar filter in the removal of BOD₅ varies according to the different OLRs (Figure 2).



OLR (g_{BOD5}·m⁻³·day⁻¹), BOD₅ (mg·L⁻¹)

Figure 2. BOD₅ removal performance of biochar filter varying according to the different OLRs

The BOD₅ removal performance of the biochar filter also depends on the HLR (Figure 3). With the HLR ranging from 532 to 1458 L·m⁻²·day⁻¹ (equivalent to flow velocities of 0.038–0.103 m·h⁻¹ inside the column), the BOD₅ removal performance is high (89–97%). However, when the HLR increases to 1772–1899 L·m⁻²·day⁻¹, the BOD₅ removal performance decreases clearly to less than 80%. It means that the performance of the biochar filter for the BOD₅ removal depends on both OLR and HLR.

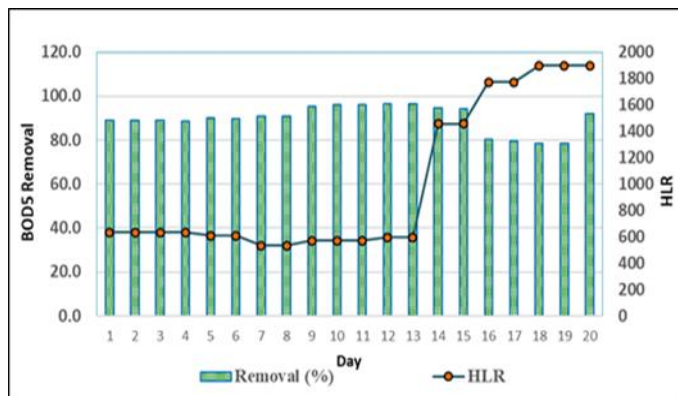


Figure 3. Performance of biochar filter in removal of BOD₅ by HLR

In addition, the removal performance in this study is higher than that of some others. Ngan et al. use sawdust and cocopeat as filter materials to treat fish-processing wastewater at an HLR ranging from 393 to 450 L·m⁻²·day⁻¹ and attain the BOD₅ removal of 89–93% [9]. Doan Van Dong uses synthetic plastic material for hospital wastewater at a low OLR of 200 g_{BOD5}·m⁻³·day⁻¹, and the BOD₅ removal performance is 88.8% [5]. Dalahmeh treats domestic wastewater on a biochar filter with a much lower HLR (32 to 128 L·m⁻²·day⁻¹) and a low OLR (38.8 to 197 g_{BOD5}·m⁻³·day⁻¹) and attains a BOD₅ removal of 93% [11].

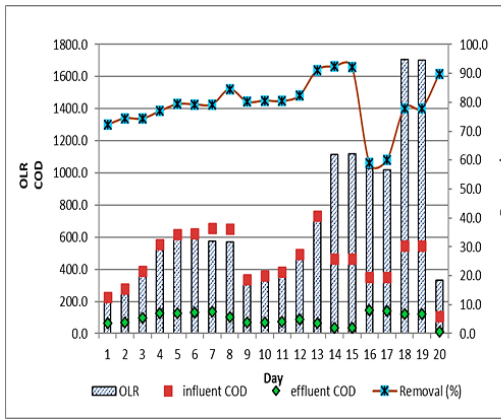
The high removal performance in this study might result from a high fixed-carbon content of the commercial biochar and its high porosity, leading to a larger specific surface area. Therefore, this structure facilitates better settling and adsorption compared with other traditional filter materials, such as sand and gravel. Thus, the biochar filter preliminary shows an operating capacity with an OLR 1.8 times higher than that in traditional trickling filters (using filter materials such as macadam, pebble, gravel, slag) to gain BOD₅ removal performance above 90%. At the same time, the biochar filter can treat wastewater with BOD₅ 1.85 times higher than the BOD₅ concentration limit of traditional trickling filters without causing an overload phenomenon and is also able to adapt to the shock of OLR from low to high and vice versa.

COD removal

The performance of the biochar filter for COD removal varies from 59 to 92% with the mean value at 80%. The correlation coefficient between BOD₅ removal efficiency and COD removal is strong ($R = 0.683$). The chart of COD removal efficiency is shown in Figure 4. Compared with another similar research, the COD treatment efficiency in this study obtains similar and somewhat higher values. For example, Bui Thi Vu et al. report the highest COD removal efficiency of 74% for the noodle production wastewater treated in an anaerobic filter with a coal slag material [15].

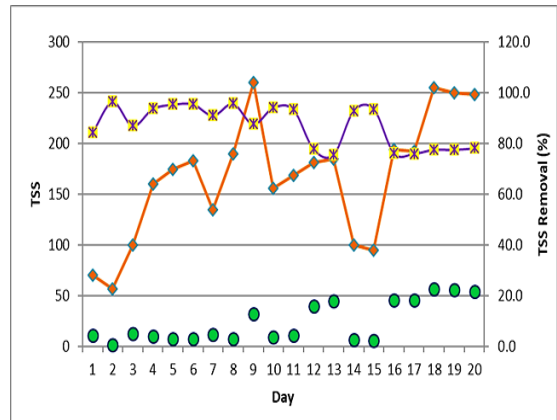
Table 4. Comparisons between biochar TF and traditional TF

| Parameter | Traditional TF | Biochar TF |
|--|----------------|------------|
| BOD ₅ concentration in inflow (mg·L ⁻¹) | ≤200 | Up to 370 |
| HLR (m ³ ·m ⁻² ·day ⁻¹) | 1–3 | 0,87–3,12 |
| OLR (g _{BOD5} ·m ⁻³ ·day ⁻¹) | 100–200 | 144–550 |
| Performance (%) | >90 | Up to 97 |



COD (mg·L⁻¹), OLR (mgCOD·m⁻³·day⁻¹)

Figure 4. COD removal performance of biochar filter varying according to different OLRs



TSS (mg·L⁻¹)

Figure 5. TSS removal performance of biochar filter

Effect of the biochar filter on removal of TSS

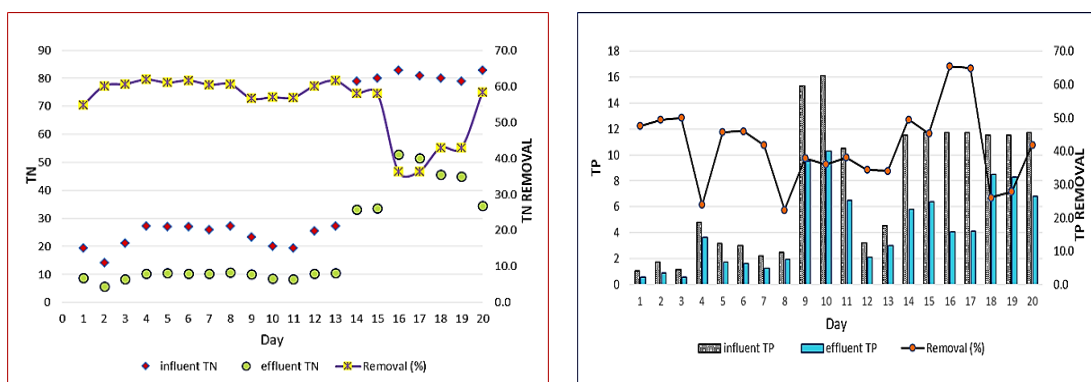
The performance of the biochar filter in TSS removal varies from 76 to 97% (Figure 5). Initially, the TSS removal efficiency varies proportionally to the TSS concentration in the inflow, but after that, it has an inverse relationship. In the period from the 3rd day to the 8th day of the experiment, when the input TSS concentration increases, the TSS removal efficiency also increases. Conversely, from the 9th day onwards, an inverse relationship is observed. When the input TSS concentration increases, the TSS removal efficiency decreases, and the decrease in the input TSS concentration leads to an increase in the TSS removal. It is because, on the 9th day, the input TSS concentration reaches the maximal value of 260 mg·L⁻¹. It is well known that the TSS concentration of the inflow for a traditional TF is normally set below 150 mg·L⁻¹ to prevent clogging [3]. However, in this study, the input TSS concentration varies from 57 to 260 mg·L⁻¹, and 70% of the values are higher than 150 mg·L⁻¹, but the TSS removal performance remains high. This is because the porosity of the filter material is relatively high at 59%. In detail, with the input TSS concentration ranging from 156 to 260 mg·L⁻¹, the TSS removal performance is 85.4%, with the output TSS concentration at 30.7 mg·L⁻¹, meeting the A level of the national technical regulation on domestic wastewater quality QCVN 14:2008/BTNMT. Besides, a negative correlation between TSS removal efficiency and flow rate through the biochar filter column is observed, with *R* being -0.58. It means that the TSS removal performance tends to decrease when the flow rate increases.

Effect of the biochar filter on removal of nutrients

Total nitrogen removal

The biochar filter eliminates 36–62% of N_{Tot} in the wastewater with the average performance of 55%. The N_{Tot} removal performance is relatively stable during the experimental period from the 2nd day to the 8th day, fluctuating slightly in the range of 60–62%, corresponding to the OLR of 188–228 $g_{BOD5} \cdot m^{-3} \cdot day^{-1}$. For the experimental series from the 9th day to the 15th day, the N_{Tot} removal performance decreases slightly and fluctuates around 57–62%, corresponding to the OLR of 272–367 $g_{BOD5} \cdot m^{-3} \cdot day^{-1}$. However, in the experimental series from the 16th day to the 19th day, the performance dropped sharply to only 36–43%. This is probably because the OLR is 1.2–2.93 times higher than that in previous experiments. In contrast, on the 20th day, when the OLR decreases to 144 $g_{BOD5} \cdot m^{-3} \cdot day^{-1}$, the N_{Tot} removal performance increases again to approximately 60% (Figure 6).

Our results are somewhat better than those reported by Dalahmeh [11]. In his study with sand as a filter, a stable N_{Tot} removal efficiency of around 50% is observed but with a much lower OLR. Also, according to Dalahmeh, a sand filter often only removes less than 5% of N_{Tot} . Thus, this shows that the N_{Tot} removal efficiency of the biochar filter can be up to 12 times higher than that of a sand filter. This is obviously an outstanding advantage of a biochar TF compared with TFs using traditional filter materials. The reason for a high N_{Tot} removal performance is that biochar has a much larger surface area and porosity than sand; thus, it facilitates the formation of higher microbial film density and longer contact time between wastewater and microorganisms. Therefore, processes such as nitrogen assimilation in biofilm and denitrification take place more inside a biochar biofilter than inside a sand biofilter, leading to a higher N_{Tot} removal efficiency. In addition, the adsorption of ammonium from wastewater by biochar also contributes to the increase in N_{Tot} removal efficiency.



N_{Tot}, P_{Tot} ($mg \cdot L^{-1}$)

Figure 6. Performance of the biochar filter in removal of N_{Tot} and P_{Tot}

Total phosphorus removal

The P_{Tot} removal efficiency of the biochar filter is from 22 to 66% with the average value of 41% and does not tend to fluctuate clearly (Figure 6). However, the pH in the effluent fluctuates from 7.65 to 8.74 and shows a moderate correlation with the P_{Tot} removal efficiency ($R = 0.554$). In practice, phosphorus can be normally removed from wastewater biologically and physicochemically. The biological method requires a direct flow of wastewater from anaerobic zones to aerobic ones. However, in this study, the wastewater flows in the opposite direction, from the aerobic zone to the anaerobic zone; therefore, the removal efficiency is insignificant. Meanwhile, phosphorus can be adsorbed by the metals present on the biochar surface, such as aluminum (Al), iron (Fe), and calcium (Ca). This adsorption process depends partly on pH. In this study, a moderate correlation between pH and P_{Tot} removal efficiency is observed, and this is possibly due to the presence of Al, Ca, and Fe on the biochar surface.

3.3 Estimated cost of biochar trickling filter for An Cuu Market wastewater treatment

The expenditure of the biochar TF comprises the cost of construction and the cost of biochar material. The former depends on the tank's volume (V), which is calculated from the following formula

$$V = \frac{Q \times L}{OLR}$$

where Q is the wastewater flow ($19 \text{ m}^3 \cdot \text{day}^{-1}$); L is the influent BOD_5 concentration ($360 \text{ g} \cdot \text{m}^{-3}$); OLR is the organic loading rate ($360 \text{ g} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$). Thus, the biochar TF's volume is 19 m^3 , corresponding to a construction cost of around 57 million VND.

The price of commercial biochar made from sawdust is normally from 12,000 to 20,000 VND/kg. The required volume of biochar is 19 m^3 (about 9.5 tons), corresponding to a price ranging from 114 to 190 million VND.

4 Conclusions

This study reveals that the capacity of biochar trickling filter for the An Cuu Market wastewater treatment is relatively satisfying. The filter can remove up to 97% of BOD_5 , 97% of TSS, 62% of N_{Tot} , and 66% of P_{Tot} . Meanwhile, the commercial biochar made from sawdust is commonly sold with a price of 12,000 to 20,000 dong per kilo. To treat An Cuu Market 's wastewater with the max BOD_5 concentration of $360 \text{ mg} \cdot \text{L}^{-1}$ and the flow of $19 \text{ m}^3 \cdot \text{day}^{-1}$, the investment cost only ranges from 114 to 190 million VND and the min area of the biochar filter surface is 13 m^2 corresponding to the HLR of $1460 \text{ L} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. This is an acceptable cost for market wastewater treatment at present. Furthermore, biochar filter materials can be reused as fertilizers or fuels. The decision-makers might choose this trickling filter for An Cuu Market's wastewater treatment.

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