Removing Total Nitrogen from Wastewater Using Biochar and Activated Carbon

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ABSTRACT

This article details an effort to lower the levels of total nitrogen in domestic wastewater by using biochar and activated biochar as a sorbent. Date palm fibers were used to prepare two varieties of bio-adsorbates using different temperatures and compositions. The first biochar was chemically activated to form chemical activated carbon. The second type was prepared by slow pyrolysis. An arrangement of four-column reactors was made. Chemically activated biochar makes up the entire first-column reactor. Sand and chemically activated biochar make up the second-column reactor (25% of the volume is activated biochar). Pyrolysis Biochar is the sole material used to fill the third-column reactor. Sand and pyrolysis biochar make up the fourth-column reactor (25% of the volume is pyrolysis biochar). All kinds of treatments were used to treat the influence in a static environment. A higher sorption removal efficiency for nitrogen resulted from chemically activated carbon (65–81 %) then from pyrolysis biochar (60–80%) then from chemically activated carbon with sand (54-76%) and finally from biochar with sand (53–75 %). Improving sorption effects likely depends on altering or activating biochar's surface chemistry during modification. Adding sand to pyrolysis biochar and the activated carbon decreased the cost but pure media showed better removal for nitrogen.

Keywords: *Wastewater treatment; Nitrogen removal; Activated carbon; Biochar; Biofilters.*

1. Introduction

Household wastewater always contains organic compounds, sediments, microbes, heavy metals, and nutrients. For a long time now, these materials have been a major environmental and health concern [1]. Among the most pressing environmental issues, the loss of marine habitats has far-reaching and urgent consequences. The term "eutrophication" describes the process by which waters become more fertile for plant life, which in turn lowers water quality and disrupts the water's biological balance. This is one of the disadvantages of dumping wastewater into waterways. In most freshwater bodies of water, such as rivers, reservoirs, and lakes, nitrogen is the scarcest nutrient. The eutrophication process is accelerated by nitrogen imports that are induced by humans.

Several strategies have been devised to remove total nitrogen (TN) from wastewater to lessen the ecological damage it causes. Adsorption, chemical precipitation, chemical reduction, ion exchange, activated charcoal, and other physical-chemical methods have been widely used to remove TN from wastewater. Using a variety of metals through adsorption and precipitation is the main method for nitrogen removal [2] [3][4].

One of the most exciting developments in odor control treatment methods is the bio-trickling filter (BTF). Microorganisms that break down odorants form a biofilm that is adhered to an inert packing material, such as lava rock, open-pore foam, and random or organized plastic rings. Water and nutrient-rich solution are trickling over the packing media as an odorant-laden stream moves through the packed bed, delivering the odorants to the biofilm [5].

From reduced operational costs and environmental impact to high efficiency and robustness, BTFs display all the benefits of biotechnologies compared to traditional physical and chemical approaches [6].

In these types of bioreactors, the immobilization, growth, and activity of the microorganisms responsible for treatment depend on the packing materials that are chosen. There is a close relationship between the contaminant's hydrodynamics, bioavailability for degradation, and the packing material's physicochemical characteristics [7].

2. Aim and Research Significance

The purpose of this study is studying the use of chemically activated carbon (CAC) technology and biochar (BI) fabricated from date palm fiber residue in

the removal of TN, studying the efficiency of TN removal if sand was added to the CAC and the BI. Also studying the effect of activating BI in the removal of TN.

3. Experimental Program
The installation of the pilot plant for this investigation took place at the Qaha wastewater treatment plant, Qalyobia Governorate, Egypt. The prototype plant operated continuously for a duration of nine weeks, five days a week (from Sunday to Thursday), working around the clock for 24 hours each day.

2.1 Media preparation
2.1.1   Sand.
Fine sand was sourced from Markaz Kafr Shukr, a nearby building supply store. The sand was passed through a filter with a 2 mm mesh size to remove any large particles or impurities. Following that, it was rinsed with tap water to remove any remaining dissolved organic substances and extremely fine particles.

2.1.2   Pyrolysis Biochar (BI).
Solid waste fibers from a date palm tree in Benha, Elqaluibia, were used for preparing BI. Date palm fibers were dried in the oven at 105°C for 24 hours. BI was synthesized in the lab through a slow pyrolysis process. The date palm fiber material was then heated in crucibles with an aluminum foil lid to create Pyrolysis biochar, which effectively reduced the quantity of oxygen that could enter. To allow the developed gases to escape, a small hole was drilled into the foil using a needle. The crucibles were placed in a muffle furnace. It was programmed to gradually go from room temperature to the final pyrolysis temperature of 550°C, with rate of 17°C/min, and then stay at that temperature for another 1.5 hours. The charcoal was given time to cool down in the furnace before being transferred to the separator for 15 minutes. At last, two separate batches of Pyrolysis biochar were prepared in the same time.

2.1.3   Chemically activated carbon (CAC).
Date palm fibers were steeped in a 5% sulfuric acid (H_2SO_4) solution for 24 hours to liberate the cellulose and trace components. The dust settles to the bottom of the acidic solution and is poured out. The samples were rinsed in distilled water for many times to remove acid before being dried.

The activation process began with 50g of date palm fibers particles mixed with 100 ml of a 30% phosphoric acid (H_3PO_4) solution that had just been prepared. A temperature of 600 °C was maintained for a duration of two hours. Once cooled to room temperature, the sample was rinsed multiple times with distilled water to remove acid until the pH reached 5-7.

2.2 Characteristics of Media
Table 1 lists some of the basic physical properties of the BI and CAC that be used in the experiment. The following characteristics of the media have been determined:
1- **Media** Yield (%) =ma/mb*100% where:
ma is the weight of the sample after preparation.
mb is the weight of the sample before preparation.
2- Ash content: The samples were burned to a constant weight in a muffle furnace at 750 °C for six hours, at which point the ash content was determined.
3- Specific Surface Area: was determined using Blaine method.
4- pH-value: the pH was determined by mixing BI or CAC with distilled water (1 g: 20 mL).

Table 1- CAC & BI physical and chemical properties.

property	BI	CAC
Yield (%)	19.34 ± 0.81	16.88 ± 0.53
Ash content (%)	8.62 ± 1.03	9.06 ± 0.76
Specific Surface Area (m²/g)	253 ± 9.5	500 ± 24
pH	6.5 ± 0.24	6.9 ± 0.45

2.3 Treatment Media preparation
There were four treatments; one with 8% BI (weight ratio) and another with only BI. Pure CAC was used in the third, whereas 8% CAC was used in the forth. Reasons for the selection of the BI to sand ratio include practical considerations (8% by weight is equal to 25% by volume), adherence to values found in the literature, and previous experience using biochar in artificial wetlands. Figure 1 shows the pilot's preparation.

2.4 Packing of media
The media was packed using a glass column with an internal diameter of 70 mm, as seen in Figure 2. Crushed stone that had been thoroughly rinsed with flowing water was used as an underdrainage layer at the base. Two sheets of plastic mesh were stacked on top of each other to prevent the media from mixing up. The glass column was filled to a height of 150 mm with bio media, which could be a mixture of sand and BI, a mixture of sand and CAC, pure BI, or pure CAC. Before adding a 20 mm layer of crushed stones, two layers of plastic mesh were used to keep the biochar from floating. To make sure the wastewater was spread out equally across the surface, this was done before the experiment. Figure 2 shows schematic diagram of the column design.

Figure 1- schematic diagram of the pilot.
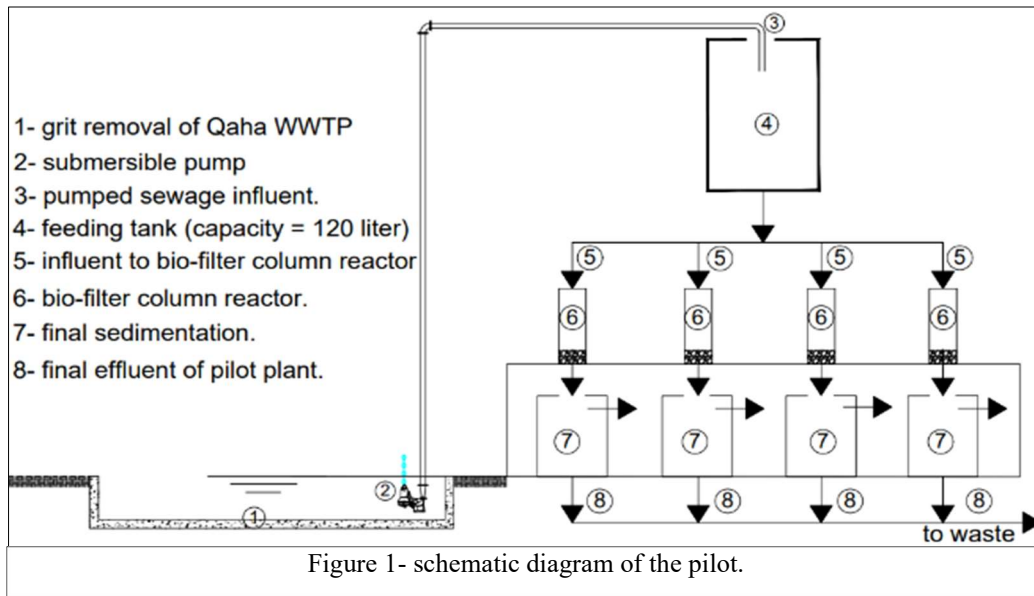
2.5 Loading of the columns

The Qaha wastewater treatment plant (WWTP) in Qaha City, Alqaluobia, Egypt, was the site of the pilot's construction. Every day, the pilot was fed fresh raw wastewater from the plant's grit removal outlet for period of 9 weeks starting in June 2022. After being stored in the feeding tank, the RWW was fed into the column through the indicated valves at an estimated hydraulic loading rate. The average daily loading for each column was 7,000 ml of wastewater, resulting in

Figure 2- schematic diagram of the column.

a daily hydraulic loading rate (HLR) of 1.875 m^3/m^2. From Sunday through Thursday, the system was loaded, and then on Friday and Saturday, it was left to breathe. Every week, three 50 mL bottles were used to collect plant effluent and influent samples for analysis. In addition, 50 mL vials were utilized to collect three samples of the pilot effluent (from the sedimentation tank used in the pilot) weekly for analysis. HLR increased from week 4 to week 6. Which caused flooding incidents in the system. With an average daily loading of 9100 ml (a 30% increase), each column was filled with wastewater, resulting in a daily HLR of 2.37 m^3/m^2. The goal was to simulate the increase in the hydraulic loading that would result from a downpour of unprecedented intensity. Similarly, samples were taken and examined following the identical protocol for the initial three weeks. Over the last three weeks, the system has been studied its behavior by returning to the initial loading of 7,000 ml of wastewater every day.
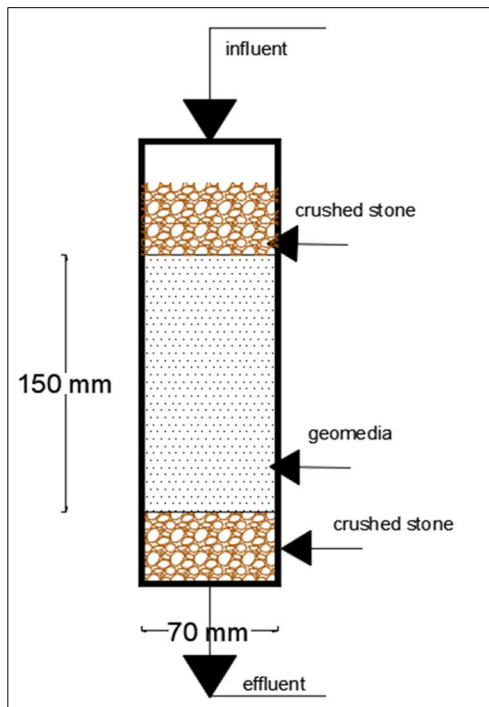
2.6 Measuring of TN

TN in an aqueous sample was determined by digestion (according to EN ISO 25663) with potassium sulfate-containing sulfuric acid, in the presence of a catalyst organic nitrogen compounds that be converted into ammonium sulfate. Kjeldahl's nitrogen is determined photometrically according to the indophenol method.

4. Results and Discussion

TN concentration in the influent wastewater to the model was in the range 37.63 - 44.77 mg N/l. This experiment shows that comprehensive nitrogen removal could be quite effective. CAC without sand demonstrated the highest removal efficiency.

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However, all treatments demonstrated resistance to flooding episodes and system stability after the floods ended.

Figure 3 illustrates the TN concentration in the influent (raw wastewater enters the wastewater treatment plant) and the effluent from each treatment.

Table 2 and Figure 4 show the total nitrogen removal efficiencies and the removal efficiencies of each media under various loading conditions.
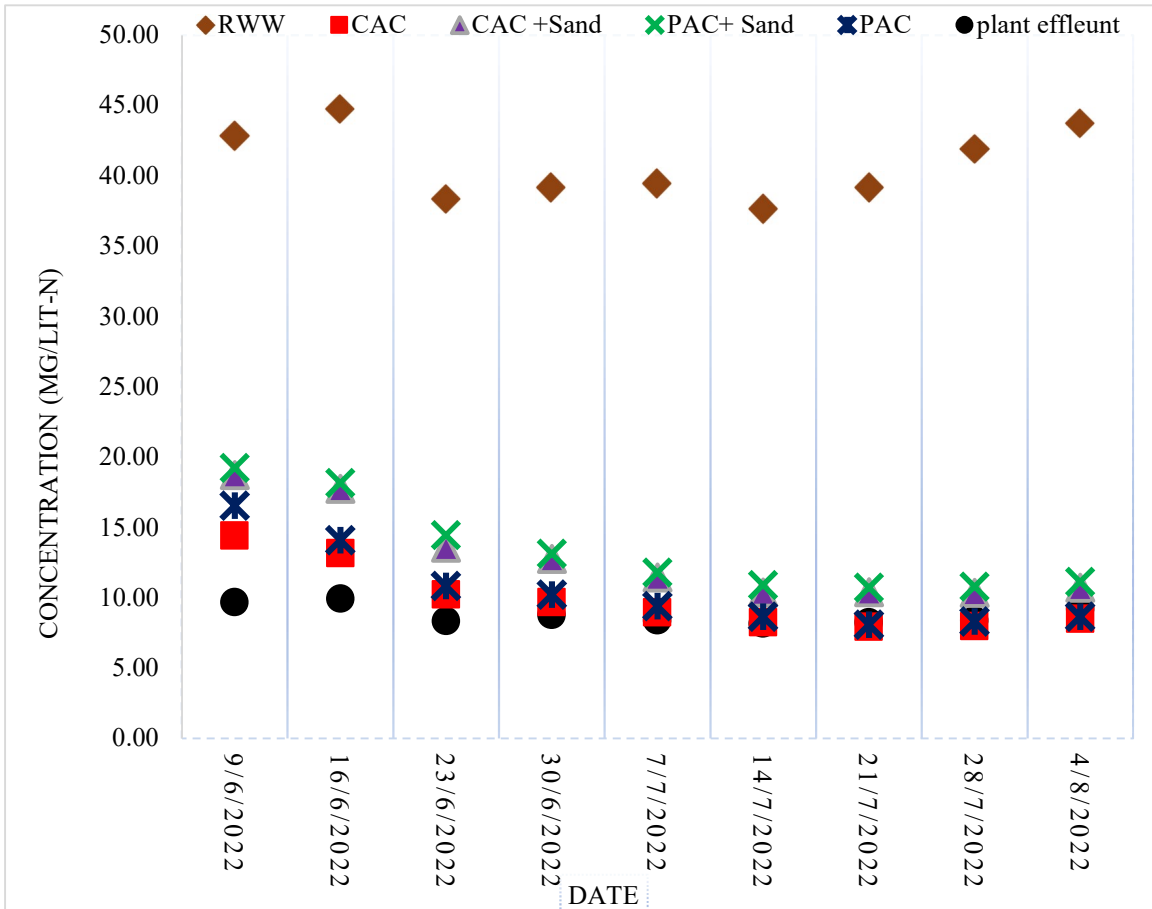

Figure 3- TN concentrations in mg/l of the influent and effluent from each treatment.
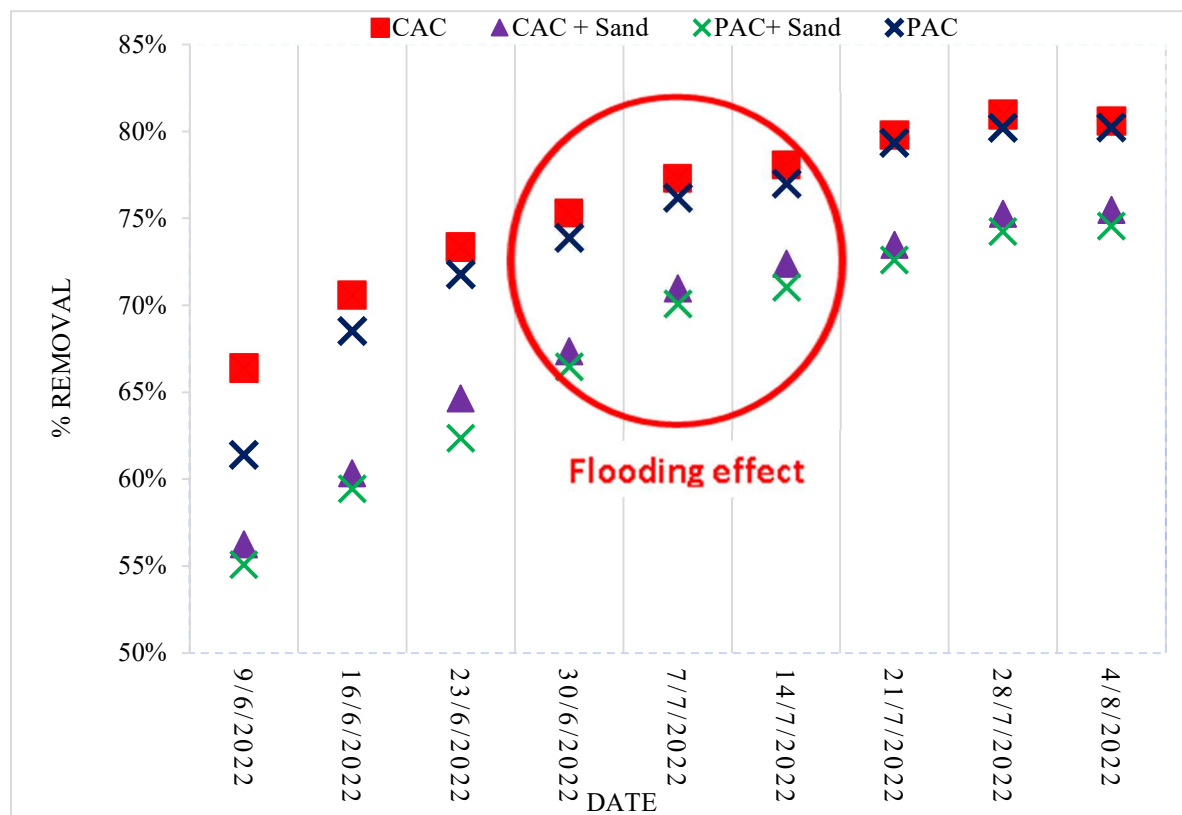
Figure 4- TN removal efficiency of the influent and effluent from each treatment

Table 2- TN removal efficiency in the four pilot reactors.

	CAC	CAC+ sand	BI+ sand	BI
9-Jun	66%	56%	55%	61%
16-Jun	71%	60%	59%	69%
23-Jun	73%	65%	62%	72%
30-Jun	75%	67%	67%	74%
7-Jul	77%	71%	70%	76%
14-Jul	78%	72%	71%	77%
21-Jul	80%	73%	73%	79%
28-Jul	81%	75%	74%	80%
4-Aug	81%	75%	75%	80%

4.1 Characteristics of media

The biochar adsorption process for nitrate involves several removal mechanisms, including physical adsorption through pores, electrostatic attraction through binding sites, chemical sorption through a chemical reaction with binding sites, and surface precipitation through salts[8]. Therefore, it was required to look into a few of the CAC and BI characteristics.

1- Media Yield: Due to dehydration and temperature-induced biomass fractionation into components such as cellulose, hemicellulose, and lignin, the yield for both BI and CAC was very low[9]. More precisely, the decrease in biochar production at higher temperatures is caused by condensation polymerization[10].

2- Condensation polymerization takes center stage as pyrolysis temperature rises. Agriculture waste residues' macromolecular components did not fully decompose at low temperatures; instead, just a small percentage of their weak chemical bonds were broken. Crop waste dehydrates and loses hydration water before 250 °C, and between 200 and 300 °C, hemicellulose decomposes. In this case, crop waste may yield very small volumes of tar and gas, which are composed of many microscopic molecules. Then, between 300 and 380 degrees' Celsius cellulose breaks down, and between 200 and 500 degrees' Celsius lignin breaks down. The high polymer components' molecular bonds break at higher temperatures, releasing more volatile substances[10].

3- Compared to BI, the specific surface area of CAC is greater. The final activation temperature and the chemical impregnation ratio are significant process variables that impact the surface area. The activation process stimulates the formation of already-existing pores and creates new ones when the activation temperature is raised, increasing the surface areas[11]. When the proper impregnation ratio was applied, the activating agent (H_3PO_4) produced new pores, according to the results of earlier experiments. The rise in surface area and pore volume with the impregnation ratio suggests that the gaps left by phosphoric acid are the cause of the porosity produced by acid and water washing[12].

4- According to the results of batch experiments, the pH range of 6–10 was optimal for the use of activated carbon to remove phosphate from aqueous solutions[13] [14]. The procedure employed in this experiment is within the ideal pH range, as shown in Table 3.

4.2 Effluent pH

The pH of the influent ranged from 7.6 to 8.2. The effluent from CAC has pH values ranging from 7.0 to 9.0, CAC + sand from 7.1 to 8.8, BI+ sand from 7.4 to 9.8, and BI from 7.5 to 9.8 as shown in figure 4, all of which indicate significant alkalinity.

The findings showed that the BI had a higher average pH value than the CAC. We can deduce that adding sand causes the pH to drop. This finding is consistent with the findings of [15] [16], which reported that the pH of effluent from a dairy lagoon rose following biochar filtration. The higher pH of the effluent is most likely caused by the higher pH of the filter material. Additionally, the addition of the alkaline biochar increased the pH of the solution due to the formation of $Ca_3(PO_4)^2$ in the higher pH environment, which would have facilitated phosphate precipitation[17].

Table 3- pH value of the influent and effluent from each treatment.

Date	RWW	BI		CAC		BI + Sand		CAC + Sand	
		Mean	SD[*]	Mean	SD	Mean	SD	Mean	SD
9-Jun	7.4	7.8	0.25	7.9	0.39	7.8	0.12	7.5	0.19
16-Jun	7.8	8.3	0.29	7.6	0.29	8.1	0.25	8.5	0.19
23-Jun	7.2	8.4	0.15	7.8	0.14	7.6	0.10	8.5	0.33
30-Jun	7.5	8.3	0.25	8.0	0.20	8.3	0.47	7.8	0.25
7-Jul	7.6	8.6	0.30	7.8	0.33	8.5	0.40	7.6	0.25
14-Jul	8.3	9.5	0.33	8.6	0.36	9.4	0.44	8.4	0.27
21-Jul	7.4	7.9	0.27	7.3	0.27	7.7	0.24	8.0	0.18
28-Jul	7.2	8.2	0.29	7.5	0.32	8.2	0.39	7.3	0.24
4-Aug	7.8	8.2	0.12	7.9	0.20	7.8	0.21	8.3	0.41

SD[*]: standard deviation.

4.3 Effect of Different Media on Removal of TN

Table 3 illustrates the total nitrogen removal efficiencies and depicts the removal efficiencies of each media under different loading circumstances. CAC was the best medium for TN removal (65–81 %) then BI (60–80%) then CAC with sand (54- 76%) then BI with sand (53–75 %). These results for nitrogen removal by biofiltration agreed with the reported values in the literature. Clough et al (2013)[18] reviewed the impacts of biochar on soil N and discussed various potential explanations for the observed reductions in N leaching in soils supplemented with biochar. These included the adsorption of NH_4-N, NO_3-N, and Org-N compounds, as well as changes in microbial N cycling brought on by the biochar. The observed reductions in N leaching reported here are consistent with several other investigations of a similar nature. Fornes et al (2015)[17] discovered that, in columns supplemented with sycamore biochar and inorganic fertilizer, dairy slurry, and dairy manure, respectively, mineral N

reductions of 44, 48, and 67% were seen. The high pH of the utilized biochar may contribute to an increase in predicted N emissions, which can be partially explained by ammonia volatilization. In comparison to biochar treatments with lower soil pH values. Schomberg et al (2012) [19] discovered that biochar derived from feedstocks and pyrolysis conditions that raised soil pH above 7 had noticeably higher $NH_3–N$ losses soon after fertilizer application. A portion of the decline in NH_3-N + NH_4-N leaching may also be explained by this. One of these elements alone is unable to account for the N outcomes found in this investigation. As a result, it's possible that multiple mechanisms worked together. The results of N leaching and retention imply that variations in N cycling were caused by nutrient sorption as well as the physical makeup of biochar.

4.4 Flooding Effect on TN Removal

From week 4 to week 6, there were significant flooding occurrences that affected the treatments. To determine the system's stability under flooding conditions, the system's performance following the flooding incident was assessed. Lucas and Greenway (2011) [20] found that bio-retention mesocosm performance improved after significant rain events.

In this study, it was observed that the effectiveness of TN removal wasn't affected.

5. Conclusions

In the current work, two types of adsorbents were prepared from date palm fiber (BI and CAC) to study the possibility of TN removal from wastewater. Also, the two types of were mixed with sand to study the possibility of reducing the cost. Also, the flooding effect was simulated to study its effect on the media and on the removal efficiency. Based on the experimental test results in simulated pilot of BTF, the following conclusions were concluded:

1. CAC was more efficient in removing TN from wastewater than other treatments.
2. TN removal for AC was (65–81 %) for BI (60–80%) for CAC with sand (54- 76%) for BI with sand (53–75 %).
3. Adding sand to biochar decreases TN removal.
4. Adding sand to activated biochar decreases TN removal.
5. all types of media were resistant to simulated hydraulic, nitrogen overloading events.
6. The findings reported carry significant ramifications for agricultural waste usage and wastewater treatment methods that rely on the use of activated carbon and biochar applications.

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