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Developing A Novel Alum Sludge-Based Floating Treatment Wetland for Natural Water Restoration

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Abstract: Novel alum sludge-based floating treatment wetland (FTW) was developed to enhance the purification performances of natural water bodies, i.e., rivers, lakes, and ponds. Polyurethane was applied to foam the lightweight alum sludge based-substrate (PU-AL) of FTW through the response surface method. Three FTWs configurations were created for a half-year lab-scale operation, and the PU-AL FTW presents the greatest purification performance in the removal rate of chemical oxygen demand (COD) of 62.58 ± 6.65%, total nitrogen (TN) of 53.31 ± 4.65%, and total phosphorus (TP) of 45.39 ± 4.69%. PU-AL substrate could enhance the nutrient removal performance of existing FTW by providing a proper media for microbial and plants' growth. This study provides a good solution and showcase not only from a natural water restoration point of view but also from the waterworks sludge management view for a better understanding of FTWs and good applications in engineering practice.

Keywords: circular economy; constructed wetlands; natural based solutions; organic foaming materials; substrates; waterworks residues

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1. Introduction

Eutrophication of natural water bodies, i.e., rivers, lakes, and ponds, has become one of the primary worldwide environmental concerns in recent years [1]. Anthropogenic and excess nitrogen (N) and phosphorus (P) in the natural water bodies are the main reasons to cause harmful algae blooming and with severe consequences for the ecological environment as well as the local economy [2]. Meanwhile, various pollutants (e.g., nutrients, metals, sediment, hydrocarbons, organics, pesticides, pathogens) from different sources are transported by urban runoff to natural waters [3]. Although numerous corresponding solutions have been taken to tackle this issue, the current situation is still grim due to the lack of low-cost and effective strategies for the evolution of eutrophication in many regions [4,5]. Some traditional methods such as physical, chemical, and biological treatment methods were messily developed to alleviate the eutrophication. Indeed, it is still difficult to overcome the high operation costs as well as the unstable treatment performance, while some of them may even cause secondary pollution for the natural water bodies [6]. Thus, developing an efficient, cost-effective, and environmental-friendly solution to remove various contaminants from natural water remains a challenge, as the types and concentrations of contaminants from different source are complex and variable.

Since the 1990s, a number of natural-based solutions such as floating treatment wetlands (FTWs) have been developed and applied to natural water restoration [7]. FTWs, also known as ecological floating beds or artificial floating islands, are economical and sustainable green structures to restore contaminated water bodies. FTWs do not require additional land area for treatment, as they fit within the footprint of an existing natural water body and also do not require earth moving activities during installation. They are constructed by buoyant mats and aquatic plants floating freely on the water surface or the current [8]. Nowadays, they have been widely used as in situ green facilities on lakes, rivers, reservoirs, and ponds for purifying the increased pollution loadings entering the urban watersheds. Moreover, a well-constructed floating bed has a good sewage purification function as well as aesthetic landscape value [9]. Therefore, it is often used as an eco-friendly facility with both landscape and water ecological management functions, such as constructing river and lake buffer zones. Hydrophytes play a crucial role in the structure and function of aquatic ecosystems, while purification occurs as water flows through the dense network of roots suspended in the water, providing opportunities for pollutants to be removed via filtration, sedimentation, plant uptake, and adsorption to biofilms in the root zone [10]. The well-developed roots can provide a place for the growth and reproduction of microorganisms to further improve the ability of the ecological floating beds to degrade pollutants. A variety of FTWs designs has been implemented, traditionally consisting of a buoyant structure constructed of various synthetic (e.g., polyethylene foam, foam-injected plastic pipe) and natural (e.g., bamboo, coco coir) materials in which emerging macrophytes are installed. However, numerous disadvantages including the limited purification efficiency and low biomass growth rate on the hydrophytes roots hinder its further engineering applications [11].

Nowadays, there is increasing interest in constructing the FTWs with various substrates to further enhance their contaminant removal performance. In the literature, various substrates such as rice straw, light ceramsite, reed straw, modified oyster shell, and corn flakes have been well-investigated [12–15]. For instance, an integrated floating wetland with modified corn flakes (IFB-CF) has been developed and has shown a remarkable removal efficiency on COD, TP, and TN at low temperatures, with treatment efficiency of 66%, 68%, and 50%, respectively [15]. Additionally, reed biochar substrate (RBS) derived from reed straw (RS) was evaluated for effluent treatment. This new substrate had a P adsorption capacity of 0.39 mg/g and an average TN removal efficiency of 57.6% [13]. Adding rice straw as substrate in FTWs under low-temperature conditions could improve the nitrogen removal rate. The average removal rates of TN, NO^{3-}, and NH^{4+} were 78.2%, 62.1%, and 81.2%, respectively [12]. The results showed that the artificial substrates could enhance the purification ability of floating beds. Nevertheless, these materials are always difficult to retrieve and assemble due to their various geographical location. Further, the heavy weight of some substrates also hinders the transportation as well as floating and moving abilities on the water surface. Moreover, some traditional substrates may also cause clogging of substrates, which could affect the roots growth and thus the purification efficiency. Therefore, the low-cost and environmentally sustainable FTWs' substrates were still urgently needed for real practical applications.

The artificial substrates of FTWs should be lightweight, highly porous, and resistant to compression. Meanwhile, the substrate should be environmentally safe and steady in water bodies to avoid secondary pollution by disintegration or elements leaking. Alum sludge is one kind of waterworks residues where aluminum sulfate is used as the coagulant. It is an inevitable by-product in towns, cities, and metropolises during drinking-water purification [16]. In China, the annual quantity of waterworks residue generation was about 1.5–2.4 million tons [17], while the amount will increase as the population grows. A survey indicates that the global expense of inorganic coagulants used for water/wastewater treatment in 2018 was almost 1.37 billion dollars, and this is predicted to reach 1.84 billion dollars by 2023 [18]. Furthermore, alum sludge is currently classified as a non-hazardous solid waste, with landfilling as the major disposal route worldwide [19].

The high disposal cost of the large quantity of alum sludge significantly increases the operation cost of drinking water treatment plants, and limited land resources also promotes waterworks residues, making it necessary to seek innovative sustainable ways of disposal. Indeed, metal elements such as Al, Fe, and Mg from the coagulants are retained in the alum sludge, making it possible to be reused in various environmental purposes. Significantly, aluminum has an excellent ability to adsorb and chelate some substances such as phosphorus and heavy metals [16].

Although there is an increasing number of publications on intensified FTWs in recent years, many design and operation aspects related to system performance still demand more research in order to better understand the relationships between macrophytes and other pollutant removal mechanisms and to thereby improve their treatment efficiency. This study aimed to expand the current knowledge on the potential engagement of alum sludge and organic foaming agents (polyurethane) as lightweight yet high-porosity substrates into FTWs for natural water restoration, with particular emphasis on the simultaneous enhancement of COD, TN, and TP removal.

2. Materials and Methods

2.1. Raw Materials

Alum sludge was obtained from Qujiang Drinking Water Treatment Plant, Xi'an, China. The physical characteristics of collected alum sludge were as follows: moisture content 78%; aluminum content (in terms of Al_2O_3) 47.11%. After collection, it was oven-dried to a constant weight and thereafter ground and sieved through 0.3 mm mesh. The raw materials used in the synthesis of the polyurethane were purchased from Changzhou Polymer Material Technology Co., Ltd., Changzhou, China, including: polyether polyol (3630), polyether polyol (330N); isocyanate (PM200); a levelling agent (silicone oil (L580)) to ensure slow rebound and even foaming; and a catalyst (triethylenediamine (A33) and stannous octanoate (T9)) to facilitate the reaction.

2.2. Synthesis of Floating Treatment Wetland Substrate

As shown in Figure 1, the novel substrate for floating beds was synthesized by integrating alum sludge with organic foaming materials, i.e., polyurethane, through response surface method. The ratio of raw polymer material, the mass of alum sludge, and the mass of water were selected as key influencing factors in the synthesis of the substrate, while density and strength were used as response values for response surface analysis. The factors as well as the levels of analysis for the experimental design response surface methodology are shown in Supplementary Materials (Table S1), and the response surface analysis scheme and experimental results are shown in Table S2.

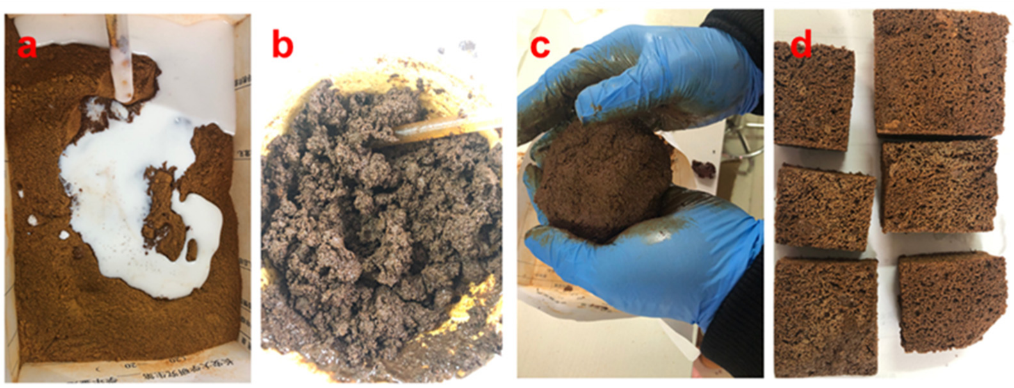


Figure 1. Synthesis of novel alum sludge-based FTWs substrate. (**a**) alum sludge mixed with organic foaming materials; (**b**) stirring and forming; (**c**) granulation; (**d**) natural drying.

The results of the experimental ANOVA are shown in Table S3. The effect of the three factors on density and water absorption is determined by the F-value, which increases when the factor affects the response value significantly [20]. It can be concluded from Table S3 that the order of significance of factors is: B > A > C. Therefore, the mass of alum sludge had the most significant effect on the density and pressure of the substrate. In addition, the *p*-value was used to determine the effect of each factor on the model, and it could be under 0.05 when a factor has a significant effect on the corresponding response value. On the contrary, the effect is not substantial. As shown in Table S3, both models are significant ($p < 0.05$), which indicates that the results of this experiment correlated with the simulation requirements. The p-values of Factor A and B for both R1 and R2 were less than 0.05, indicating that both the synthesis materials ratio and alum sludge mass have significant effects on density and pressure. The final result also means that the model simulated by Design-Expert is suitable for the response surface method with density and intensity as response values.

The response surfaces of the parameters of the resulting substrate with significant influence factor interactions are shown in Figure S1. The various parameters of the substrate were optimized with Design-Expert. By considering the lower density and higher strength of floating bed substrate. The final solution for the substrate was chosen to have a density range of 0.4–0.5 g/cm^3, and maximum pressure is 0.93 for A, 300.00 for B, and 5.00 for C, which was able to obtain a substrate with the density of 0.497 g/cm^3 and pressure of 1542.01 Pa in theory. Three parallel experiments were carried out according to the optimized ratio, and the substrate with 0.473 g/cm^3 and 1529.34 Pa was finally obtained. Therefore, the optimum formulation for the novel alum sludge based-substrate (PU-AL) has a polyether-polyol-to-isocyanate ratio of 0.93 (polyether polyol 45 g; isocyanate 50 g), alum sludge 300 g, water 5 g, silicone oil (L580) 0.3 g, triethylenediamine (A33) 0.7 g, and stannous octanoate (T9) 0.55 g.

2.3. Characterization of PU-AL

The specific surface area and pore volume were calculated according to the BET specific surface formula, and the S_{BET} = 3.496 m^2/g, pore volume = 0.003 cm^3/g, and average pore size = 3.541 nm. Figure 2 illustrates the FTIR spectra of PU-AL and raw alum sludge. The absorption bands for both materials occur at 3441.70, 1651.78, 1411.59, 1034.07, 534.78, and 470.85 cm^{-1}. The absorption bands of $Al(OH)_3$ appear at 3441.70, 1651.78, and 534.78 cm^{-1} and correspond with the OH stretching of $Al(OH)_3$, bending vibration of water molecules chemically associated with $Al(OH)_3$, as well as AlO stretching vibration, respectively. The absorption bands of silica appear at 1034.07 and 470.85 cm^{-1}, attributed to the asymmetric stretching vibration of SiOSi and bending vibration of OSiO, respectively. The absorption band of carbonate appeared at 1411.59 cm^{-1} [21,22]. It can be determined that the functional groups of PU-AL are similar to the alum sludge, which include hydroxy groups associated with Al and silicon-oxygen bonds. These functional groups are mainly derived from the sediment in the alum sludge and coagulant applied during the water treatment process. However, the absorption peaks of PU-AL are lower than that of the raw sludge. The main reason might be the coverage of alum sludge by polyurethane generated during the foaming process.

The SEM of PU-AL substrate and alum sludge in magnifications of 100× and 500× are shown in Figure 3. Compared to the raw sludge, the surface of the PU-AL is relatively smooth due to the polyurethane coating. In addition, the substrate is more porous, making it more convenient to provide places for microorganisms' attachment and growth. Overall, these characteristics of PU-AL illustrate the feasibility of its use in sewage treatment and its potential as a substrate in FTWs.

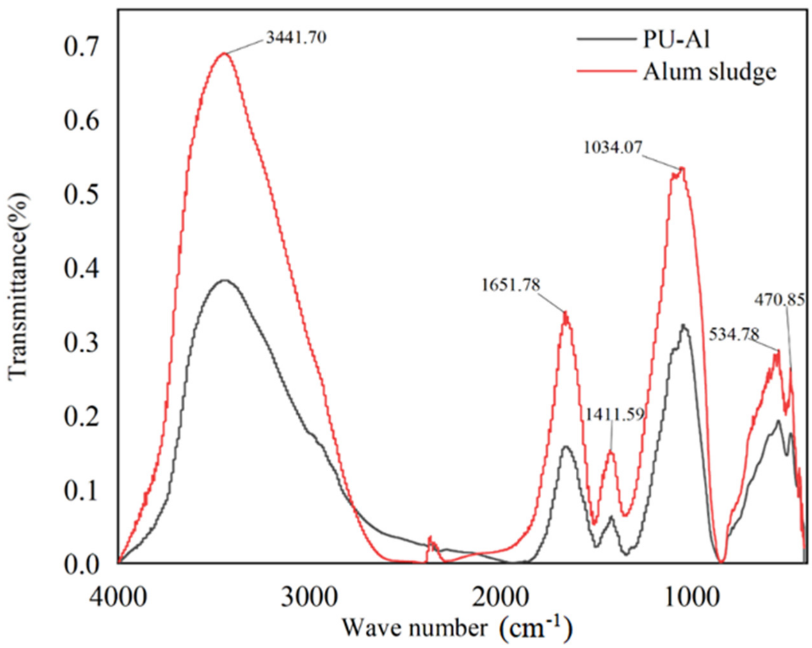


Figure 2. FTIR of PU-AL and alum sludge.

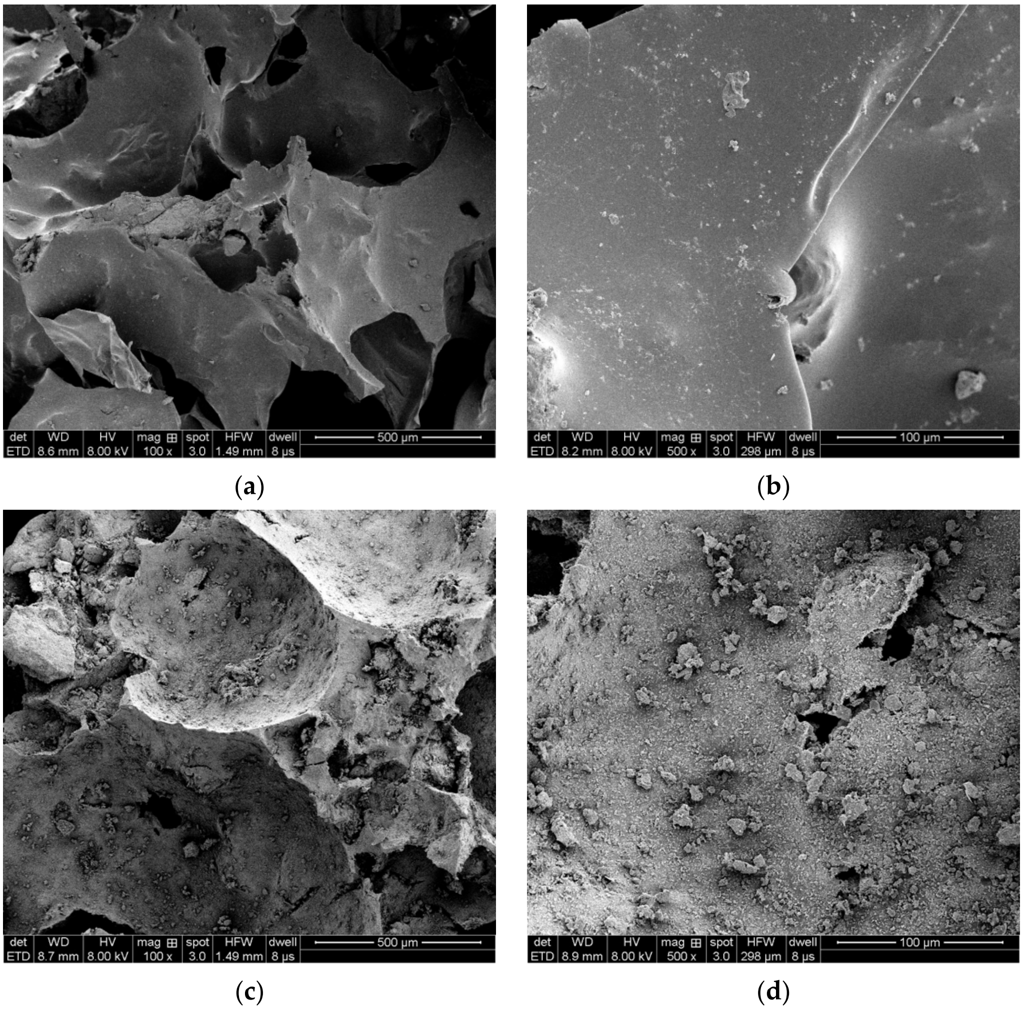


Figure 3. SEM of PU-AL and alum sludge. (**a**) PU-AL for 100×; (**b**) PU-AL for 500×; (**c**) Alum sludge for 100×; (**d**) Alum sludge for 500×.

2.4. Experimental Setup

As illustrated in Figure 4, three sets of FTWs were assembled. The natural water body was simulated by three identical rectangular acrylic tanks, which were 33 cm × 25 cm × 25 cm (L × W × H) with a total volume of 20.6 L. Three FTWs were constructed in same cylindrical mesh frames with an inner diameter of 16 cm and a height of 17 cm. The first FTW was filled with PU-AL, and the second FTW used common polyurethane sponge as its floating beds, while the third FTW was a blank floating bed (without substrate) that served as control. Thereafter, *Scindapsus aureus* were planted on each FTW with the same density. Aeration devices were installed 10 cm below the water level in each of the three tanks, and a light was installed above the floating beds to simulate natural light conditions.

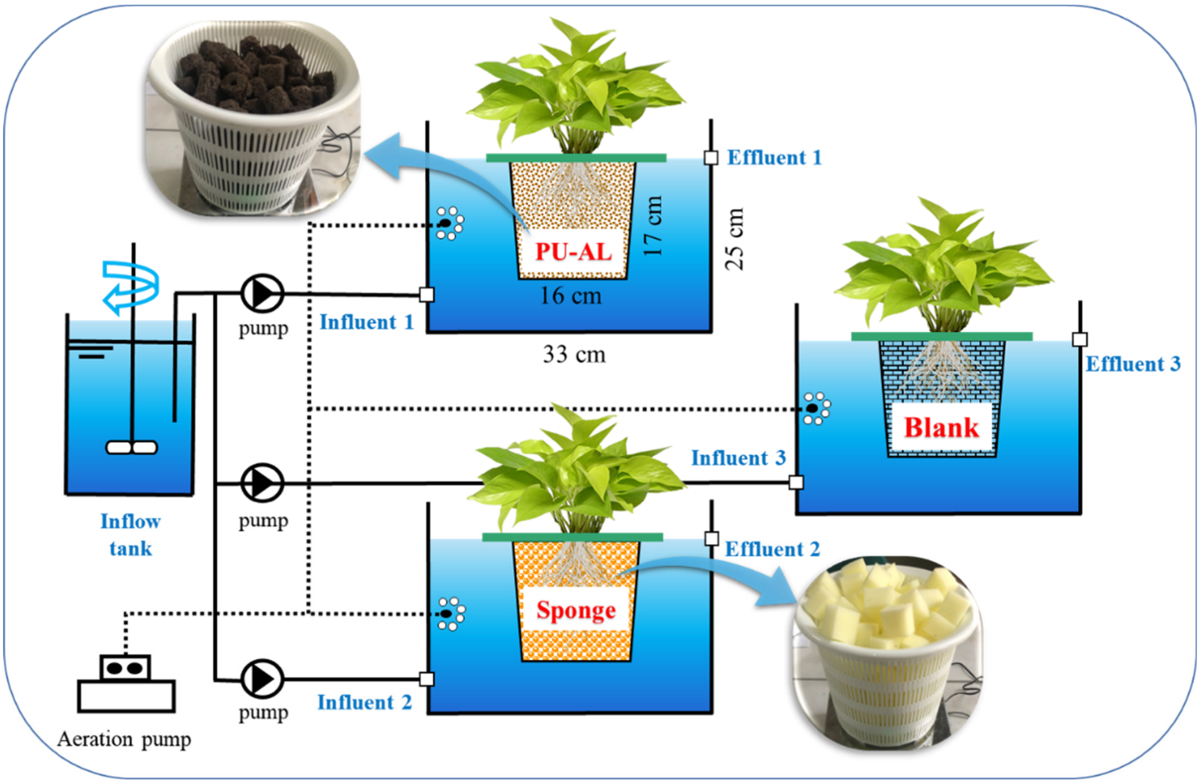


Figure 4. Configuration of the experimental system.

To simulate the natural pond (lake) and river states, the whole experiment was divided into two phases, i.e., batch and continuous flow conditions, and each phase lasted for 75 days. Before the investigation, a one-week activated sludge inoculation was carried out. During batch phase, each tank was filled with the synthetic wastewater. The hydraulic retention time of this stage was 48 h, while an intermittent (two hours per day) aeration strategy was offered during this period. In addition, lighting to simulate the natural light was provided during the daytime (from 8 a.m. to 7 p.m.). After 75 days batch operation, three FTWs were changed to continuous flow states. A peristaltic pump was conducted, and the inlet flow rate was 0.38 L/h. Hydraulic retention time, aeration strategy, and lighting time remained the same with the batch phase.

The physical operating conditions of three FTWs during the two phases of stable operation are shown in Table 1. It can be seen that the temperature was in a range of 15–20 °C. The pH value was a weak alkaline environment, which was suitable for the growth of microorganisms and aquatic plants. Due to the aeration strategy, DO levels (0.4–8.0 mg/L) in the water fluctuated throughout the operating phase. It also provides an aerobic–anaerobic alternate for microorganisms' growth.

Table 1. FTWs operation conditions.

FTWs	Phases	Temperature (°C)	pH	DO (mg/L)
PU-AL	Stage 1	15.8–20.4	7.13–7.26	0.35–7.46
	Stage 2	16.8–17.6	7.36–7.56	0.46–8.52
Sponge	Stage 1	15.8–20.4	7.22–7.33	0.34–7.46
	Stage 2	16.8–17.6	7.41–7.65	0.46–8.21
Blank	Stage 1	15.8–20.4	7.24–7.29	0.39–7.30
	Stage 2	16.8–17.6	7.48–7.56	0.47–8.65

2.5. Analytical Methods

Synthetic wastewater was prepared using tap water and analytical reagents: sodium acetate (CH_3COONa) for COD, ammonium chloride (NH_4Cl) for NH^{4+}-N, potassium dihydrogen phosphate (KH_2PO_4) for TP, and magnesium sulphate ($MgSO_4$) to supplement the inorganic elements. Furthermore, trace element solution (1 mL/L) was added to promote the growth of aquatic plants and microorganisms. The trace element solution consisted of $C_{10}H_{14}N_2O_8Na_2$ (61 μg/L), $FeSO_4{\cdot}7H_2O$ (6 μg/L), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.1 μg/L), $ZnSO_4{\cdot}7H_2O$ (22 μg/L), $CuSO_4{\cdot}5H_2O$ (1.8 μg/L), $CaCl_2{\cdot}2H_2O$ (8.2 μg/L), $MnCl_2{\cdot}4H_2O$ (5.1 μg/L), and $CoCl_2{\cdot}6H_2O$ (1.6 μg/L). The influent concentrations of COD, TN, and TP were 70.58 ± 8.16 mg/L, 10.96 ± 0.96 mg/L, and 2.12 ± 0.2 mg/L, respectively. The experiment was conducted under ambient conditions. Temperature, dissolved oxygen (DO), pH, COD, TP, and TN were analyzed according to standard methods (State Environmental Protection Administration of China, 2002). Chemical indicators were measured by an ultraviolet–visible spectrophotometer (HACH, DR-6000, US). Data were obtained through three replicate trials to ensure accuracy. The concentrations of total bacteria, nitrifying bacteria, denitrifying bacteria, and biomass weight were analyzed by 16S ribosomal DNA identification. The removal rates (R) of COD, TN, and TP in three FTWs were calculated by the following equation:

$$R = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

where, R is the removal rate, and C_{in} and C_{out} are the influent and effluent concentration (mg L^{-1}), respectively.

3. Results and Discussion

3.1. Pollutants Removal Performance

The COD, TN, and TP removal efficiency of the three FTWs during the two phases of operation are shown in Figure 5. It can be seen that the influent COD was between 60 and 80 mg/L with slight variation. The three FTWs had a slightly increasing potential for COD removal in both phases. During the first phase, the COD removal efficiency of the PU-AL-FTW and sponge FTW were 62.08 ± 4.9% and 63.21 ± 6.1%, respectively, and it was twice higher than the blank FTW (33.34 ± 5.6%). This phenomenon was similar to the research conclusion of Shen et al. [23], which combined aluminum-based drinking-water treatment residual (DWTR) as a substrate in traditional FTW. The result of the 135-day experiment showed that the COD removal efficiency increased from 35% to 88% under aeration. This result also indicates that the substrate of FTWs plays a crucial role in removing COD from the effluent.

During the second stage of operation, the COD removal efficiency of the three FTWs was almost identical to the first stage at 63.08 ± 8.4%, 63.55 ± 5.6%, and 33.30 ± 3.3% for PU-AL-FTW, sponge FTW, and blank FTW, respectively. This phenomenon illustrated that the change in operating method did not significantly improve the COD removal of the FTWs. The main reason for this might be the slight water disturbance and that the surplus aeration conditions provided throughout the experiment did not allow for a great enhancement to the system. It is also evident that the efficiency in COD removal between the PU-AL-FTW and sponge FTW in both phases of operation was similar and reached over 60%. This phenomenon proved that the PU-AL substrate has a similar structure to the sponge due to the foaming step in the preparation process and high porosity. This particular structure can facilitate the growth of plants and the attachment as well as the growth and reproduction of microorganisms due to the biosafety of raw sludge [24,25]. Therefore, the practical application of PU-AL in FTWs has been further demonstrated to be feasible.

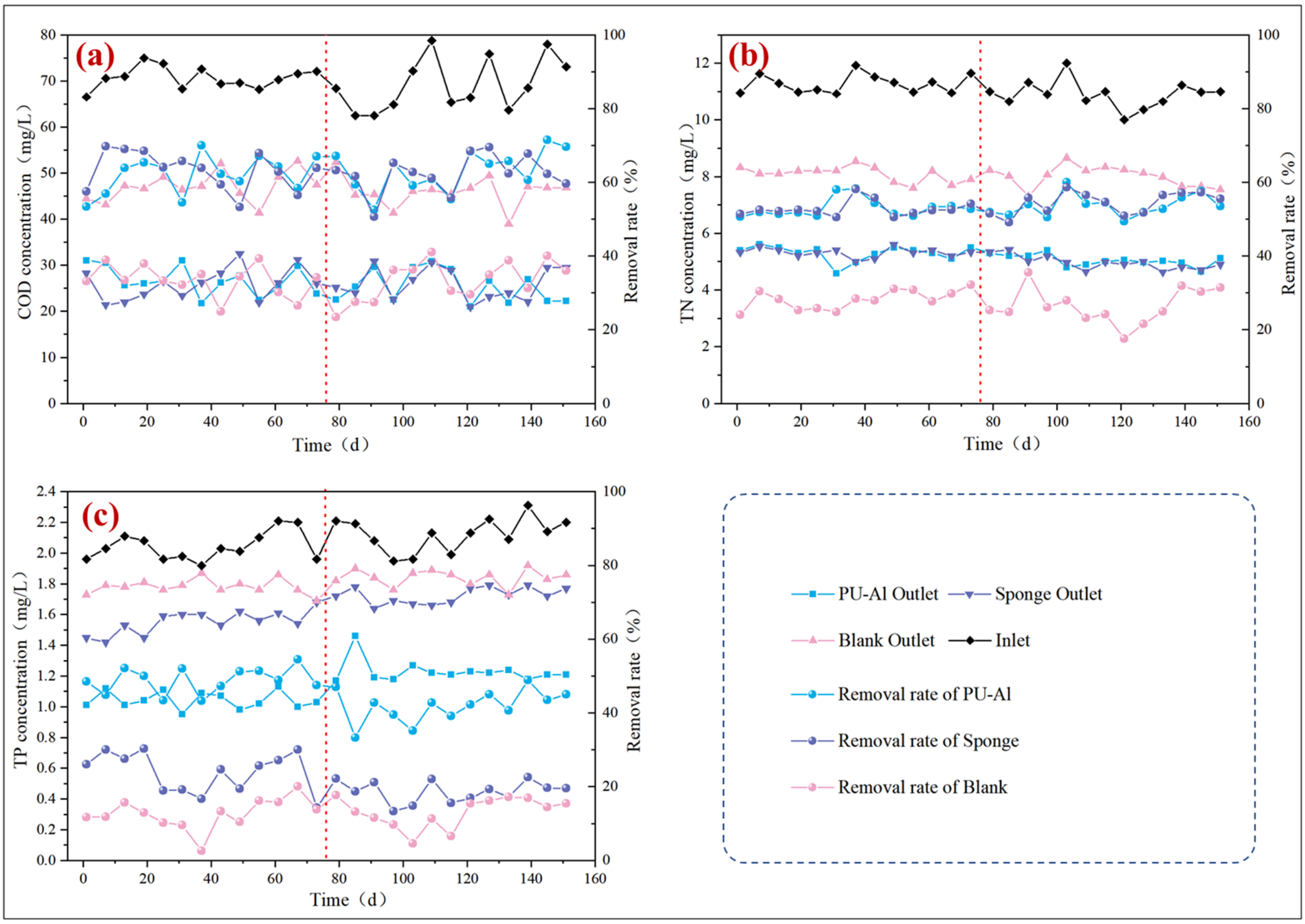


Figure 5. Pollutants removal performance in three FTWs. (**a**) COD removal performance; (**b**) TN removal performance; (**c**) TP removal performance.

As shown in Figure 5, the removal of TN is similar between the PU-AL and sponge FTWs under adequate aeration, which achieved 52.99 ± 5.3% and 52.79 ± 5.3% in stage 1 and 53.63 ± 4.0% and 54.41 ± 4.2% in stage 2, respectively. The efficiencies were much higher than the blank (stage 1: 28.19 ± 3.0%; stage 2: 26.51 ± 9.0%). This is because only a small number of micro-organisms were present in the blank due to the small amount of space available for them to attach, which caused the removal of TN in water to rely on the plants' uptake and utilization of nitrogenous nutrients. It is well-documented that plants' uptake of nitrogenous nutrients is relatively weak [26]. On the contrary, the FTWs filled with substrates can provide a place for the nitrifying and denitrifying bacteria in the water column to attach and grow due to the loose and porous structure of the substrate, thus achieving a higher TN removal rate. Furthermore, FTWs with substrates have high removal efficiency in both stages during the operation, indicating that the FTWs can maintain a stable TN removal effect under adequate aeration conditions in different water environments.

In addition, during the second stage, the TN removal rate increased in the PU-AL and sponge FTWs compared to the first stage. In contrast, the blank showed a slight decrease. The main reason is that the PU-AL and polyurethane sponge provided a specific environment for plant growth, so the plants in these two floating wetlands grew faster and had denser root systems than those in the blank. The increased number of plants strengthened the plants' ability to fix nitrogen in the water column [27]. Hence, the FTWs filled with substrates increased the TN removal rate. On the contrary, the lack of substrate support restricted the growth of plants in the blank. Within the experiment, the leaf yellowing or even falling off and the decomposition of the fallen leaves into the water column will release a certain amount of pollutants, thus affecting the effluent water quality and decreasing the removal rate.

Similarly, some researchers also incorporated different substrates into FTWs. For instance, Cao et al. [12] added rice straw as the substrate to the floating wetland to enhance its nitrogen removal capacity at low temperatures. The average removal rates of TN, NO_3^-, and NH_4^+ were increased to 78.2%, 62.1%, and 81.2%, respectively. Furthermore, Song et al. [28] evaluated the influence of stereo-elastic packing on nitrogen removal in FTWs. In their experiment, the stereo-elastic was used as additional bio-carriers and was demonstrated to enhance maximum TN removal efficiency by 65.8%. Overall, PU-AL in FTWs also played a crucial role in removing TN during the water treatment process.

The TP removal results for three FTWs during the two phases of operation are shown in Figure 5 as well. The influent TP concentrations were maintained at 1.9–2.3 mg/L throughout the experiment.

As indicated in Figure 5, three floating wetlands displayed different effects on P removal. The PU-AL-FTW was the most effective TP removal, with average rates of 48.84 ± 2.4% in stage 1 and 41.93 ± 7.0% in stage 2; the sponge FTW was lower at 23.83 ± 6.4% and 18.69 ± 3.8% in two stages. Furthermore, the blank had the least effectiveness at only 12.63 ± 3.5% and 13.10 ± 4.1%, respectively. This phenomenon is because the PU-AL was made of alum sludge, with a high P absorption effect due to its unique composition [16]. The PU-AL retained P absorption characteristics of the sludge, which fully demonstrated the superiority of the PU-AL-FTW for the TP removal from wastewater. The result confirmed that the substrate is vital in removing TP in FTWs, which is much better than plants alone. Researchers have also carried out similar studies, such as adding modified oyster shells for the efficient P removal composite into FTWs [14,29]. These studies effectively improved the TP removal rate of the FTW and were consistent with this experiment, which set a credible illustration of the role PU-AL in water treatment.

The overall pollutants removal rates for the three FTWs throughout the experiment are shown in Figure 6. The average removal efficiencies of COD and TN for PU-AL and sponge FTWs were 62.58 ± 6.65% and 53.31 ± 4.65% and 63.38 ± 5.85% and 53.60 ± 4.75%, respectively. It is clear that there was little difference in the removal of COD and TN between the two FTWs, but compared to the blank, which was only 33.32 ± 4.45% and 27.35 ± 5.97% for COD and TN removal, both showed significant advantages. This result indicates that adding substrates to traditional plant-based FTW can significantly improve water purification. In addition, in terms of TP removal, it can be observed that the PU-AL-FTW (45.39 ± 4.69%) had a much higher removal rate of TP than others (21.26 ± 5.10% for the sponge FTW and 12.87 ± 3.81% for the blank), indicating that the PU-AL has a clear superiority for the removal of TP.

At the same time, the removal efficiency of pollutants was almost identical between two different stages after changing the operating mode, which indicates that changing the operational status had little effect on the operating effectiveness of the FTWs. It also shows that the FTWs can be applied in different hydraulic conditions. In addition, as the whole experiment was under adequate aeration conditions, resulting in rapid consumption of NH_4^+-N in the water, the removal rate of NH_4^+-N in all three FTWs was 100%.

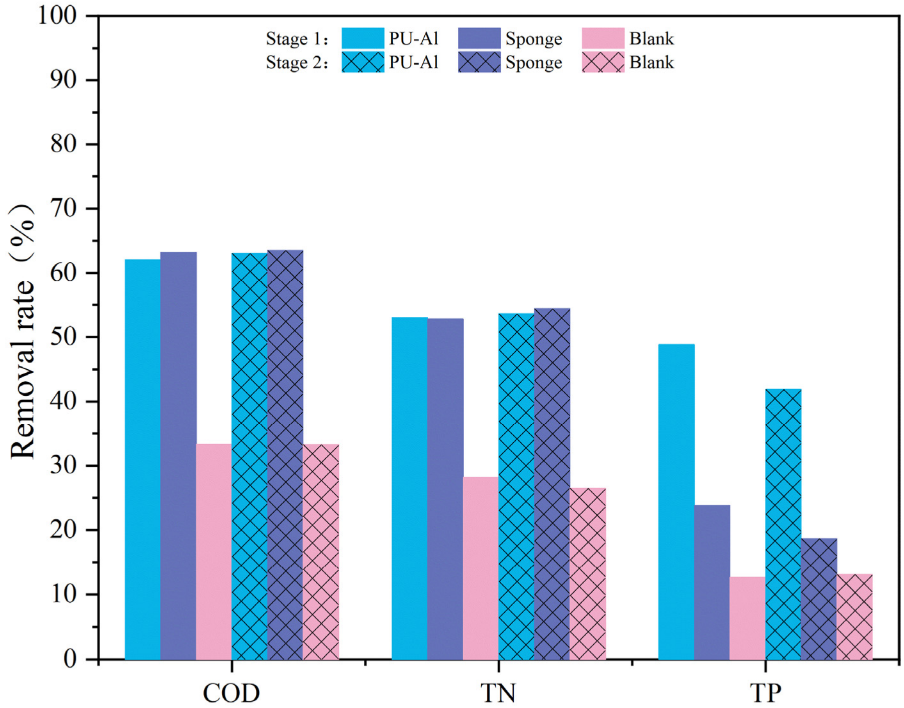


Figure 6. Overall removal performance.

Compared with the FTWs made with other artificial substrates, the PU-AL also has a clear advantage in removing pollutants and higher intensity. For example, Hu et al. [30] used dredged lake sludge and other ingredients as raw materials with the optimum mixing ratio (sludge: 72.5%, BOF slag: 12.5%, expanded perlite: 15%) and obtained a final substrate with solid compressive strength of 1.55 MPa and flexural strength of 0.24 MPa. The removal efficiency of TN and TP reached 36.3% and 35.7%, respectively. The PU-AL displayed significant advantages in removing all these pollutants. In addition, the PU-AL is much lighter than the substrates made from the same materials. Zhao et al. [31] obtained an artificial ceramsite filter material by shaping alum sludge into a ball, air-drying, and firing under 600 °C. Although the ceramsite provided better pollutants purification (78.2%, 46.7%, and 53.2% for the removal efficiency of COD, TN, and TP, respectively) than the PU-AL, it is easier to clog the reactor and increases the cost of filling and transport due to its smaller size and greater density. The PU-AL substrate obtained in this experiment avoids these problems because of its low density.

3.2. Growth Characteristics of Hydrophytes

Aquatic plants play a crucial role in floating wetlands and are one of the key factors influencing the water purification capacity of the system. The influence of plants on FTWs is mainly reflected in the following aspects: (1) Floating bed plants can rely on their purification effect by absorbing nutrients from the water column and thus purifying the effluent; (2) on the other hand, the roots of plants provide a place for the growth of the microorganisms, and they transport oxygen into the water column through photosynthesis; and (3) plants can regulate the climate, promote ecological cycles, and create good landscapes [32]. Figure 7 presents the growth states of the plants after 150 days' operation in three FTWs. It can be seen from the figure that the plant growth of the three FTWs differed under the same influent and operation conditions. Compared with the hydrophyte showing signs of slight yellowing and even loss of leaves in the plant floating bed, the plants in the PU-AL and polyurethane sponge floating beds grew well and had dense, fat leaves. Overall, the roots of the plants in FTWs were able to pierce the PU-AL and the polyurethane sponge directly, firmly rooting themselves in both substrates.

PU-Al **Sponge** **Blank**

Figure 7. Comparison of plants' growth states in three FTWs.

Comparing the growth of plants in the three FTWs, all plants have a particular effect on the fixation of nutrients such as N and P in the water. In addition, the growth of plants in the PU-AL and polyurethane floating wetlands indicated that adding substrates to FTWs could facilitate plant growth. In addition, the intricate entanglement of roots in systems showed that both substrates had a supportive effect on the development of the plants. This phenomenon also showed that the PU-AL produced in this experiment has the primary conditions to be used as a substrate for floating wetlands, proving the feasibility of using it as a new substrate for FTWs.

3.3. Microbial Growth Condition on Substrate

At the end of the experiment, the microorganisms attached to substrates were subjected to high-throughput sequencing of 16S rDNA. Figure 8 presents the Venn diagram of the PU-AL and polyurethane sponge (E1 for PU-AL, E2 for sponge) that 1108 OTUs were shared among the two different substrates, accounting for 60.48% of the total OTU, indicating that the microbial communities on the two substrates were very similar. This phenomenon illustrated the similarity of the two substrates in terms of their structural composition and effect on microbial growth, reinforcing the safety and availability of PU-AL for FTWs substrates.

To further identify the diversity of microbial communities, microorganism sequences were assigned to phylum and class levels. Figure 9 illustrates the relative abundance of microorganisms on substrates at the phylum level. After six months' operation, various microorganisms grew stably on both floating wetland substrates. The relative abundances of bacterial phyla had no significant difference between the two systems. According to the results, the relative abundance of *Proteobacteria* was highest, accounting for 46% and 58% in two substrates, respectively, followed by Planctomycetes, Bacteroidetes, and Acidobacteria. The relative abundance of these four phyla accounted for almost 80% on both substrates, while the rest of the phyla were not present in a high percentage. The Proteobacteria phylum is widely distributed in nature and is particularly common in wastewater treatment facilities, where it can stimulate denitrification in different water conditions [33]. A large number of Proteobacteria bacteria were detected in both reactors, indicating that the denitrification in ecological floating beds was mainly through the action of microorganisms. The Bacteroidetes phylum is generally used in the biochemical treatment of industrial wastewater to degrade organic matter such as cellulose and proteins [34]. Bacteroidetes have also been found to participate in the autotrophic denitrification process [13], which could improve the nitrogen removal effect of the floating beds. Similarly, the Acidobacteria phylum was confirmed to effectively remove the nitrate from wastewater by denitrification and degrade organic matter [35,36]. In addition, the Planctomycetes phylum was widespread and became the second-largest community in the system. Some bacteria in the Planctomycetes phylum can perform anaerobic ammonium oxidizing [37,38]. Therefore, the addition of substrates to the floating treatment wetlands had the potential to promote the anaerobic ammonia-oxidation process. Compared to the amount of Planctomycetes on both substrates, the PU-AL (14%) was more abundant than the polyurethane sponge (10%), which indicated that the PU-AL was more favorable to the growth of Planctomycetes than other substrates, increasing the possibility of the anaerobic ammonia oxidation in the system. Interestingly, in this study, the number of the Bacteroidetes phylum bacteria on the PU-AL was much more than the polyurethane sponge, 11% and 6%, respectively. The reason for this is that the PU-AL substrate has higher phosphorus adsorption capacity, and the phosphorus adsorbed on the surface of the substrate provides favorable conditions for the growth of phosphate-accumulating organisms (PAOs). Numerous papers have illustrated that most PAOs known nowadays were classified in the phyla Proteobacteria and Bacteroidetes [39,40], which explains the above phenomenon well. At the same time, the effect of the PU-AL floating bed on TP removal was further enhanced by the fact that the PU-AL substrate had more associated bacteria attached to its surface.

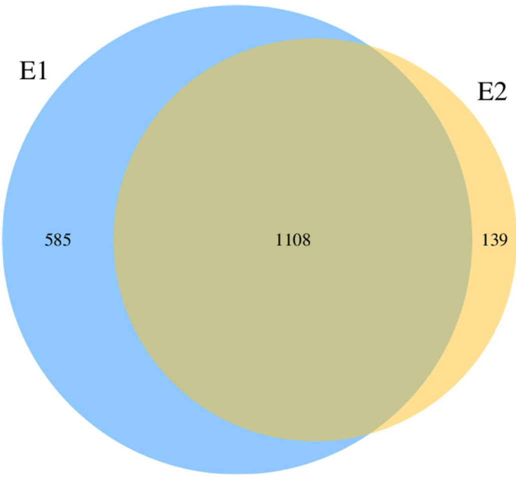


Figure 8. Venn diagram based on the OTUs of the substrates.

The composition and number of microorganisms grown on the two substrates were identical at the phylum level. Therefore, at the class level, they should also be similar. As is evident from Figure 10 that at the class level, the main classes were Alphaproteobacteria, Gammaproteobacteria, Planctomycetia, Betaproteobacteria, Sphingobacteriia and Deltaproteobacteria, accounted for 62% and 67% of total sequences in both systems, respectively. The classes Alphaproteobacteria and Betaproteobacteria were reported to include ammonia-oxidizing and nitrite-oxidizing bacteria, and they are all involved in removing ammonia nitrogen from the wastewater [33]. Gammaproteobacteria, which comprises numerous anaerobic bacteria, is mainly used to remove nitrates and nitrites during water treatment [41]. In addition, Betaproteobacteria is an essential group of bacteria that removes nitrogen and phosphorus and shows advantages for organic biodegradation [42]. The above three significant classes assigned to Proteobacteria in both rectors played vital roles in nitrogen removal during the sewage treatment. In summary, the microorganisms detected on the substrates make the TN removal by the two substrate-filled FTWs much higher than that of the purely plant-based FTW.

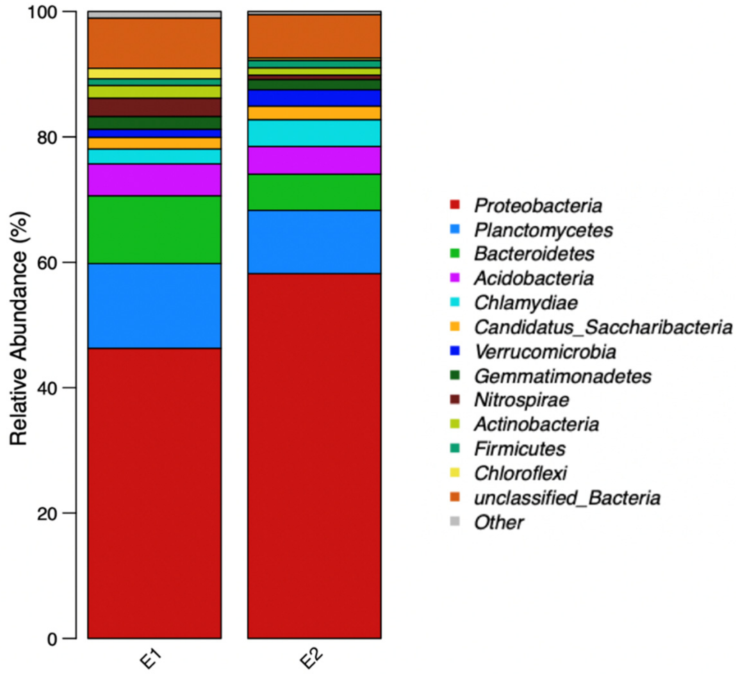
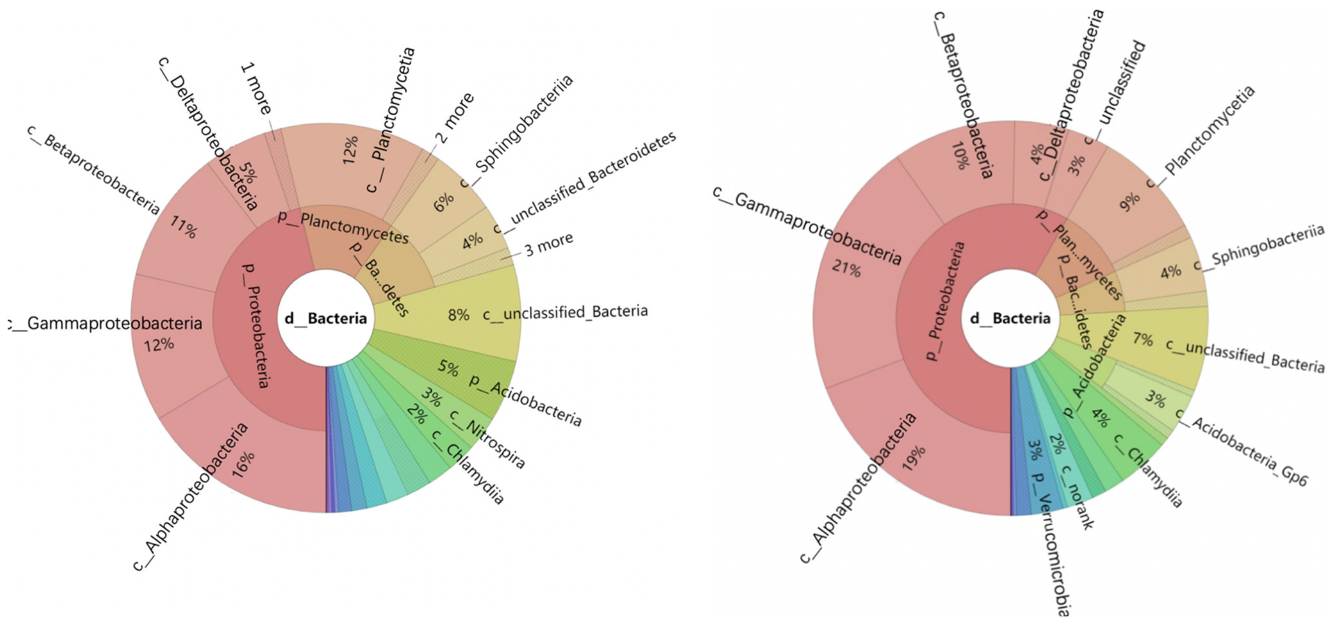


Figure 9. Microbial relative abundance on substrates at the phylum level.



E1 **E2**

Figure 10. Taxonomic classification of community structure at the class level.

Overall, the experiment proved that the PU-AL is a promising new substrate for water purification due to its loose and porous structure, which can provide sufficient space for the growth and reproduction of microorganisms. Furthermore, compared with traditional FTW substrates, the PU-AL is relatively light, stable, and effective in practical applications.

4. Perspective

FTWs have attained tremendous popularity for natural water restoration. However, traditional FTWs function establishment in nutrient removal from lakes, ponds, and rivers is still a challenge. The novel PU-AL substrate synthesized from the largely available waterworks residues presents a huge potential in engineering applications also due to its low cost and environmentally sustainable nature. Furthermore, this study also provides a win-win solution on drinking-water treatment plant sludge management and natural water restoration simultaneously. Meanwhile, the organic foaming agent used in the novel PU-AL substrate is economical and easily available. In comparison, the current price of gravel is almost USD 100–150 per cubic meter, while the only cost of organic foaming materials is almost USD 20 per cubic meter [43]. It indicates novel PU-AL FTWs have easy access, low price, good hydrophobicity, high stability, and environmentally friendly characteristics. Moreover, the applications of novel PU-AL FTWs to purify eutrophic natural water have higher feasibility, superiority, and practicability.

5. Conclusions

Compared to traditional FTWs, the novel developed PU-AL FTW simultaneously achieved higher TN and TP removal efficiencies, with average pollutant removal of 53.31 ± 4.65% for TN and 45.39 ± 4.69% for TP, respectively, while their removal rate in the blank trial was 27.35 ± 5.97% for TN and 12.87 ± 3.81% for TP. The integration of substrates with FTWs could improve the pollutant removal as well as the plants' growth environment. Overall, the presented study provides definitive evidence for PU-AL substrates' significant pollutant removal performance in FTWs in a natural water setting. It provides a good solution and showcase not only from a scientific research point of view but also from a practical application view for a better understanding of FTWs and good application of FTWs in engineering practice. To our knowledge, this is the first study that carried out a long-term trial to explore the effects of using alum sludge and polyurethane-based substrates on natural water restoration. Still, the study also possesses some limitations and open questions for the future studies, including plant species, various natural waterbodies, and large-scale investigation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14152433/s1, Table S1: Parameters of materials; Table S2: RSM designed experiments and results; Table S3: ANOVA for response quadratic model; Figure S1: Interactive effect of alum sludge mass and polyether polyol to isocyanate ratio.

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References

1. David, V.; Tortajada, S.; Savoye, N.; Breret, M.; Lachaussée, N.; Philippine, O.; Robin, F.-X.; Dupuy, C. Impact of human activities on the spatio-seasonal dynamics of plankton diversity in drained marshes and consequences on eutrophication. *Water Res.* **2020**, *170*, 115287.
2. Zeng, J.; Yin, B.; Wang, Y.; Huai, B. Significantly decreasing harmful algal blooms in China seas in the early 21st century. *Mar. Pollut. Bull.* **2019**, *139*, 270–274.
3. Wang, W.H.; Wang, Y.; Sun, L.Q.; Zheng, Y.C.; Zhao, J.C. Research and application status of ecological floating bed in eutrophic landscape water restoration. *Sci. Total Environ.* **2020**, *704*, 135434.
4. Guan, Q.; Feng, L.; Hou, X.; Schurgers, G.; Zheng, Y.; Tang, J. Eutrophication changes in fifty large lakes on the Yangtze Plain of China derived from MERIS and OLCI observations. *Remote Sens. Environ.* **2020**, *246*, 111890.
5. Hu, M.; Ma, R.; Xiong, J.; Wang, M.; Cao, Z.; Xue, K. Eutrophication state in the Eastern China based on Landsat 35-year observations. *Remote Sens. Environ.* **2022**, *277*, 113057.
6. Fan, R.; Zhu, D.; Deng, L. Causes of eutrophication and progress of integrated management technology in lake. *J. Water Resour. Water Eng.* **2010**, *21*, 48–52.
7. Colares, G.S.; Dell'Osbel, N.; Wiesel, P.G.; Oliveira, G.A.; Lemos, P.H.Z.; da Silva, F.P.; Lutterbeck, C.A.; Kist, L.T.; Machado, E.L. Floating treatment wetlands: A review and bibliometric analysis. *Sci. Total Environ.* **2020**, *714*, 136776.
8. Pavlineri, N.; Skoulikidis, N.T.; Tsihrintzis, V.A. Constructed Floating Wetlands: A review of research, design, operation and management aspects, and data meta-analysis. *Chem. Eng. J.* **2017**, *308*, 1120–1132.
9. Dai, Q.; Han, X.; Huang, H.; Zhou, D.; Cao, W. Present situation and development of ecological floating beds. *Technol. Water Treat.* **2014**, *40*, 7–11.
10. Samal, K.; Kar, S.; Trivedi, S. Ecological floating bed (EFB) for decontamination of polluted water bodies: Design, mechanism and performance. *J. Environ. Manag.* **2019**, *251*, 109550.
11. Cao, W.; Zhang, Y. Removal of nitrogen (N) from hypereutrophic waters by ecological floating beds (EFBs) with various substrates. *Ecol. Eng.* **2014**, *62*, 148–152.
12. Cao, W.; Wang, Y.; Sun, L.; Jiang, J.; Zhang, Y. Removal of nitrogenous compounds from polluted river water by floating constructed wetlands using rice straw and ceramsite as substrates under low temperature conditions. *Ecol. Eng.* **2016**, *88*, 77–81.
13. Huang, Z.; Kong, F.; Li, Y.; Xu, G.; Yuan, R.; Wang, S. Advanced treatment of effluent from municipal wastewater treatment plant by strengthened ecological floating bed. *Bioresour. Technol.* **2020**, *309*, 123358.
14. Pu, C.; Cao, Y.; Qian, C.; Fang, F.; Zhang, K.; Yan, R.; Wang, W.; Yang, M. Study on purification performance of modified oyster shell for low phosphorus concentration water. *Environ. Pollut. Control.* **2019**, *41*, 312–316.
15. Zhang, H.; Liu, H.; Cao, W. Nutrient removal effect and characteristics of integrated floating beds at low temperature. *Environ. Res.* **2022**, *204*, 112139.
16. Zhao, Y.; Yang, Y.; Akintunde, B.; Zhao, X.; Hu, Y.; Lordwin, K.; Liu, R. Overview of Development of Alum Sludge-based Constructed Wetland for Wastewater Treatment. *China Water Wastewater* **2015**, *31*, 124–130.
17. Li, Z.F.; Jiang, N.; Wu, F.F.; Zhou, Z. Experimental investigation of phosphorus adsorption capacity of the waterworks sludges from five cities in China. *Ecol. Eng.* **2013**, *53*, 165–172.
18. Shrestha, S.; Kulandaivelu, J.; Sharma, K.; Jiang, G.; Yuan, Z. Effects of dosing iron- and alum-containing waterworks sludge on sulfide and phosphate removal in a pilot sewer. *Chem. Eng. J.* **2020**, *387*, 124073.
19. Ahmed, F.R.; Muhammad, M.A.; Ibrahim, R.K. Effect of alum sludge on concrete strength and two way shear capacity of flat slabs. *Structures* **2022**, *40*, 991–1001.
20. Zhao, B.; Fang, Y.; Wu, K.; Wang, J. Optimization design and validation of algae powder-penicillin residue/low density polyethylene composites formulation by response surface methodology. *Acta Mater. Compos. Sin.* **2020**, *37*, 1894–1903.
21. Tantawy, M.A. Characterization and pozzolanic properties of calcined alum sludge. *Mater. Res. Bull.* **2015**, *61*, 415–421.
22. Shamaki, M.; Adu-Amankwah, S.; Black, L. Reuse of UK alum water treatment sludge in cement-based materials. *Constr. Build. Mater.* **2021**, *275*, 122047.
23. Shen, C.; Zhao, Y.Q.; Liu, R.B.; Morgan, D.; Wei, T. Enhancing wastewater remediation by drinking water treatment residual-augmented floating treatment wetlands. *Sci. Total Environ.* **2019**, *673*, 230–236.
24. Ahmad, T.; Ahmad, K.; Alam, M. Sustainable management of water treatment sludge through 3'R' concept. *J. Clean. Prod.* **2016**, *124*, 1–13.
25. Yuan, N.N.; Wang, C.H.; Pei, Y.S. Bacterial toxicity assessment of drinking water treatment residue (DWTR) and lake sediment amended with DWTR. *J. Environ. Manag.* **2016**, *182*, 21–28.
26. Su, X.; Yuan, J.; Dong, W.; Sun, F.; Wang, M.; Dong, Z.; Li, W.; Du, C. Organic and nitrogenous pollutants removal paths in vegetation activated sludge process (V-ASP) for decentralized wastewater treatment by using stable isotope technique. *Bioresour. Technol.* **2021**, *330*, 124959.
27. Lu, H.L.; Ku, C.R.; Chang, Y.H. Water quality improvement with artificial floating islands. *Ecol. Eng.* **2015**, *74*, 371–375.
28. Song, J.; Li, Q.; Dzakpasu, M.; Wang, X.C.C.; Chang, N.N. Integrating stereo-elastic packing into ecological floating bed for enhanced denitrification in landscape water. *Bioresour. Technol.* **2020**, *299*, 122601.
29. Liu, Y.; Lv, J.; Singh, R.P. Removal of low-concentration phosphorus by efficient phosphorus removal composite-based ecological floating beds. *J. Water Supply Res. Technol.-Aqua* **2019**, *68*, 782–792.

30. Hu, G.-J.; Zhou, M.; Hou, H.-B.; Zhu, X.; Zhang, W.-H. An ecological floating-bed made from dredged lake sludge for purification of eutrophic water. *Ecol. Eng.* **2010**, *36*, 1448–1458.
31. Zhao, X.H.; Zhao, X.Y.; Chen, C.; Zhang, H.D.; Wang, L.Q. Ecological floating bed for decontamination of eutrophic water bodies: Using alum sludge ceramsite. *J. Environ. Manag.* **2022**, *311*, 114845.
32. Yeh, N.; Yeh, P.; Chang, Y.-H. Artificial floating islands for environmental improvement. *Renew. Sustain. Energy Rev.* **2015**, *47*, 616–622.
33. Deng, C.; Huang, L.; Liang, Y.; Xiang, H.; Jiang, J.; Wang, Q.; Hou, J.; Chen, Y. Response of microbes to biochar strengthen nitrogen removal in subsurface flow constructed wetlands: Microbial community structure and metabolite characteristics. *Sci. Total Environ.* **2019**, *694*, 133687.
34. Li, E. Biological denitrifying processes and microbial communities analysis in a sequencing batch reactor treating NF concentrate from coking wastewater. *Chin. J. Environ. Eng.* **2019**, *13*, 2461–2467.
35. Lai, X.; Zhao, Y.; Pan, F.; Yang, B.; Wang, H.; Wang, S.; He, F. Enhanced optimal removal of nitrogen and organics from intermittently aerated vertical flow constructed wetlands: Relative COD/N ratios and microbial responses. *Chemosphere* **2020**, *244*, 125556.
36. Li, P.; Wang, C.; Liu, G.; Luo, X.; Rauan, A.; Zhang, C.; Li, T.; Yu, H.; Dong, S.; Gao, Q. A hydroponic plants and biofilm combined treatment system efficiently purified wastewater from cold flowing water aquaculture. *Sci. Total Environ.* **2022**, *821*, 153534.
37. Zhu, T.; Gao, J.; Huang, Z.; Shang, N.; Gao, J.; Zhang, J.; Cai, M. Comparison of performance of two large-scale vertical-flow constructed wetlands treating wastewater treatment plant tail-water: Contaminants removal and associated microbial community. *J. Environ. Manag.* **2021**, *278*, 111564.
38. Wei, Y.; Wang, Y.; Ma, Q.; Li, Q.; Li, C.; Li, X.; Xia, J.; Lu, Y.; Yu, J.; Xininigen. Effects of silt particles, ammonia nitrogen and water content on structural and functional differentiation of Plantomycetes communities. *Microbiol. China* **2020**, *47*, 2732–2745.
39. Li, H.; Zhong, Y.; Huang, H.; Tan, Z.; Sun, Y.; Liu, H. Simultaneous nitrogen and phosphorus removal by interactions between phosphate accumulating organisms (PAOs) and denitrifying phosphate accumulating organisms (DPAOs) in a sequencing batch reactor. *Sci. Total Environ.* **2020**, *744*, 140852.
40. She, C.; Lin, H.; Su, Y.; Zhang, Y.; Lin, W.; Lan, R. Diversity and community characteristics of organic phosphate-mineralizing bacteria in the sea area between Minjiang Estuary to Pingtan. *Chin. J. Appl. Ecol.* **2021**, *32*, 1863–1872.
41. Zhao, T.; Qiao, K.; Wang, L.; Zhang, W.; Zhu, J.; Tang, Y.; Hu, B.; Wang, X.; Yang, J.; Jing, Z. Measurements of Bacterial Community and Biodiversity from Activated Sludge for a Wastewater Treatment Containing Starch. *Environ. Sci.* **2020**, *41*, 321–329.
42. Jing, S.; Li, Y.; Yu, L.; Yang, W.; Zhu, H.; Li, W. Denitrification efficiency of the special moving-bed biofilm reactor (SMBBR) process for domestic sewage treatment and its microbial diversity. *Chin. J. Appl. Environ. Biol.* **2019**, *25*, 206–214.
43. Wang, Y.; Cai, Z.; Sheng, S.; Pan, F.; Chen, F.; Fu, J. Comprehensive evaluation of substrate materials for contaminants removal in constructed wetlands. *Sci. Total Environ.* **2020**, *701*, 134736.