water

MDPI

Article

Seasonal Variation of Nutrient Removal in a Full-Scale Artificial Aerated Hybrid Constructed Wetland

Jun Zhai *, Jun Xiao, Md. Hasibur Rahaman, Yasinta John and Jingsong Xiao

Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, Chongqing University, Chongqing 400045, China; hasib.esrm@gmail.com (J.X.); hasib_esrm@hotmail.com (M.H.R.); john_yasinta@yahoo.com (Y.J.); 1261173372@qq.com (J.X.)

* Correspondence: zhaijun@cqu.edu.cn or zhaijun99@126.com; Tel.: +86-23-6512-0810

Academic Editor: Hans Brix

Received: 11 September 2016; Accepted: 10 November 2016; Published: 24 November 2016

Abstract: To improve nutrient removal, a full-scale hybrid constructed wetland (CW) consisting of pre-treatment units, vertical-baffled flow wetlands (VBFWs), and horizontal subsurface flow wetlands (HSFWs) was installed in August 2014 to treat sewage wastewater. Artificial aeration (AA) was applied continuously in the VBFW stage to improve the aerobic condition in the hybrid CW. Water samples were collected and analyzed twice a month between the period of August 2015 and July 2016. The results suggest that this new hybrid CW can achieve a satisfactory reduction of chemical oxygen demand (COD), ammonium nitrogen (NH_4^+-N), total nitrogen (TN), and total phosphorus (TP) with average removal rates of 85% ± 10% (35% ± 19 g/m^2 per day), 76% ± 18% (7% ± 2 g/m^2 per day), 65% ± 13% (8% ± 2 g/m^2 per day), and 65% ± 21% (1 g/m^2 per day), respectively. AA significantly improved the aerobic condition throughout the experimental period, and the positive influence of AA on nitrogen removal was found to be higher during summer that during winter. A significant positive correlation between water temperature and nutrient removal ($p < 0.01$) was observed in the system. Overall, this study demonstrates the application of AA in a full-scale hybrid CW with satisfactory nutrient removal rates. The hybrid CW system with artificial aeration can serve as a reference for future applications areas where land availability is limited.

Keywords: aeration; horizontal subsurface flow wetland; hybrid constructed wetland; nutrient removal; seasonal variations; vertical-baffled flow wetland

1. Introduction

Constructed wetland (CW) is an engineered ecosystem which is considered an alternative cost-effective wastewater treatment technology [1,2]. This system possesses complex physical, chemical, and biological processes similar to natural wetlands and is widely used to treat different types of wastewater [3–5]. CWs performances are frequently reported to be satisfactory (over 80%) for suspended solids (SS) and organic matter [6]; however, for nutrient removal, high variations in removal rates are often observed. Previous studies reported that total nitrogen (TN) and total phosphorus (TP) removal efficiencies are reported to be varied between 40%–55% and 40%–60%, respectively, in different CWs [6–8], suggesting the need to improve nutrient removal in order to obtain more reliable treatment performances.

Nitrogen removal in CWs occurs through nitrification–denitrification, plant uptake, substrate adsorption, sediment storage, and ammonia volatilization [1,8,9]. However, ammonification (dissolved organic nitrogen (DON)→NH_4^+-N) followed by coupled nitrification (NH_4^+-N→NO_2^--N→NO_3^--N), and canonical denitrification (NO_3^--N→NO_2^--N→NO→N_2O→N_2) are the major nitrogen removal pathways in CWs [1,5], which are reported to be approximately 47%–62% of total nitrogen removal [9].

On the contrary, microbial degradation of phosphorus removal in CWs was frequently reported to be insignificant [4,10]. Filter media with high phosphorus binding capacity is a suitable strategy to maximize phosphorus removal [2,11] in CWs. Even though a wide range of substrates have already been tested for phosphorus removal [2,4], further investigations are still necessary to obtain sustainable, cost-effective, and locally available media for CWs [2,4,12].

Microbial nitrification is usually considered as the rate limiting step of nitrogen removal in CWs [5,13]. Lack of dissolved oxygen (DO) in wastewater limits this microbial process [13]. Although nitrification can occur at low DO levels, the reaction rate is considerably less when DO levels fall below 2 mg/L [6]. Plants in CWs can supply oxygen in the rhizospheres and enhance nitrification processes [13,14]. However, a number of studies suggested that root oxygen release is far less than the amount needed to support the nitrification process [6,15]. The combination of various wetlands in a staged manner, such as subsurface vertical flow (VF) followed by horizontal flow (HF) CWs, referred to as hybrid CWs, are also used for better nitrogen removal [8]. In the hybrid systems, various wetlands are combined to simulate both aerobic (VF stage) and anaerobic (HF stage) conditions, which are necessary for the microbial nitrification–denitrification processes [8,16–18]. Nonetheless, nitrogen removal efficiency can vary with season in both traditional and hybrid CWs, because nitrification is generally considered as the most temperature-sensitive steps [19] and becomes inhibited below 10 °C [9,14].

In such a context, innovative designs of CWs are necessary to optimize nutrient removal efficiencies throughout the year [10]. Different approaches have been applied to improve nutrient and organic removal efficiencies in CWs through different operational and design strategies such as effluent recirculation, tower hybrid CW, drop aeration, baffled subsurface tidal, flow direction reciprocation, earthworm integration, bioaugmentation, and circular-flow corridor wetlands [1,3]. Artificial aeration (AA) is an alternative strategy which has been proposed and applied in different CWs to create an aerobic environment [20]. Previous studies reported that AA in CWs can improve nutrient removal compared to the non-aerated systems [2,5]. AA appeared to improve environmental conditions for microbial nitrification and phosphorus removal in the winter season as well [10,13]. It provides an elevated oxidization of Fe^{2+} to Fe^{3+}, which enhances the chemical precipitation of phosphorus [6]. Furthermore, AA improves the resistance of CWs to the fluctuating influent loads [13] and intensifies mineralization of solids to prevent clogging of the system, and thus increases the lifespan of CWs [13,21]. Studies on AA in CWs have been conducted mostly in short-term laboratory-scale and pilot scale experiments, but very few experiments focused on long-term full-scale systems or its integration in hybrid CWs [7,13,22]. Moreover, seasonal variations of nutrient removal in aerated full-scale hybrid systems still remain unclear.

In the present study, we investigated nutrient removal performances of a new type of hybrid CW receiving sewage wastewater. The studied hybrid system was comprised of pre-treatment units (a septic tank (ST), a contacting oxidation tank (OT), and a cross-flow sedimentation tank (CST)), a continuously aerated vertical baffled flow wetland (VBFW), a horizontal subsurface flow wetland (HSFW), and a clean water pond (CWP). AA was applied in the OT unit and a half portion of the VBFW unit. The original VBFW + HSFW design was developed by our research team and applied in many full-scale systems since 2007 [17]. We studied the performances of aerated hybrid CWs especially for nutrient removal over a period of a year.

2. Materials and Methods

2.1. Study Site

The study was conducted at the RunXi Township sewage treatment plant, a full-scale artificially aerated hybrid CW located in Chongqing City, Southwest China. The plant has been operating since August 2014, with a design capacity of treating 300 m^3/day of sewage collected from a community of approximately 3000 people. The hybrid system consists of three pre-treatment units—a ST (78 m^3), a OT (75 m^3), and a CST (22 m^3)—two main treatment units—a micro-aerated VBFW (MA-VBFW, 128 m^2) and a HFCW (394 m^2)—and a post-treatment unit of clean water pond (CWP, 20 m^3). Moreover, a sludge drying bed (21 m^3) was also installed to collect and dewater sludge from the ST unit. The VBFW consists of 2 beds, each bed with 4 sections (for example, for Bed 1, sections are VF1, VF2, VF3, and VF4). Each section is 4 m in length (L), 4 m in width (W), and 1.5 m in height (H). The HSFW consists of 2 beds of the same size. Each bed has 3 equal sections (L × W × H; 7.5 m × 7 m × 0.8 m)—HF1, HF2, and HF3. Between every two sections of a HSFW bed, a shallow cascaded natural aeration ditch (NAD, 7 m) of plastic material was constructed. The schematic diagram of the studied full-scale hybrid system is presented in Figure 1. The average raw wastewater inflow rate during the study period was 150 m^3/day. The average hydraulic retention times (HRT) for each treatment stage are approximately 12.4, 11.8, 4.2, 15.4, 17.5, and 2.2 h for the ST, OT, CST, VBFW, HSFW, and CWP, respectively, and approximately 63 h for the total treatment plant. AA was applied in the OT and the last half portion of VBFW (VF3 and VF4) units using a blowing machine with an average air flow of 1.2 m^3/min, which was separated equally between two selected treatment stages. In each aerated section of VBFW, 20 parallel perforated tubes (420 cm in length, 32 mm in diameter, PE) with pores (4 mm in diameter) were placed at the bottom (approximately 130 cm in depth) with an average airflow of 0.54 m/h. Gravel (8~30 mm in diameter) was used as the filter media with *Cyperus alternifolius* as a macrophyte in the VBFW and HSFW beds. The porosities of both VBFW and HSFW beds are approximately 50%. Considering the clogging problem and the wetland life span, water backwash pipes were installed at the bottom of the VBFW beds. More detailed information about the similar type of hybrid CWs (VBFW + HSFW) without AA can be found in previous research papers [16,17].

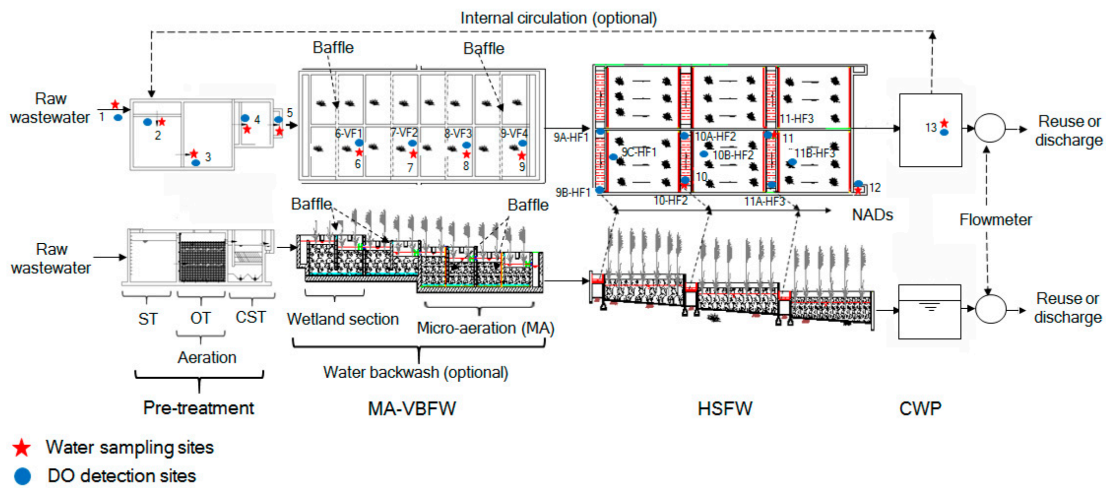

Figure 1. Schematic diagram of the studied full-scale hybrid system along with the sampling sites.

2.2. Sampling and Physiochemical Analysis

Water samples were collected twice a month from August 2015 to July 2016 of the 13 water sampling points installed along the flow route of the investigated hybrid system (Figure 1). However, for the dissolved oxygen (DO) analysis, data were collected twice a month from 20 sampling points marked separately as shown in Figure 1. Water samples were collected directly with a glassy sampling device. The samples for water temperature (WT), electrical conductivity (EC), DO, turbidity, and pH were analyzed in the field with portable sensors as described in previous studies [16,17]. All collected water samples were stored in a cooler at 4 °C, transported to the laboratory at Chongqing University for analyzing the chemical oxygen demand (COD), TN, NH_4^+-N, nitrate–nitrogen (NO_3^--N), nitrite–nitrogen (NO_2^--N), and total phosphorus (TP) according to the Chinese National Standard methods [23]. All samples were analyzed in triplicate.

2.3. Statistical Analysis

A one-way analysis of variance (ANOVA) with Fisher's least significant difference (LSD) post hoc (α = 0.05) tests were used to determine the significant differences between warm and cold seasons treatment performances. The Pearson correlation coefficients at the 95% confidence level were analyzed between the water quality parameters and environmental indicators for cold and warm periods. All calculations were carried out using Origin 8.0 software.

3. Results and Discussion

3.1. Overall Performance

The average concentration of various water quality parameters at different treatment stages of the studied hybrid system over a period of one year are summarized in Table 1. The entire full-scale AA hybrid CW achieved a satisfactory overall performance for the removal of COD, NH_4^+-N, TN, and TP with average efficiencies of 85% $\pm$ 10%, 76% $\pm$ 18%, 65% $\pm$ 13%, and 65% $\pm$ 21%, respectively. The pre-treatment stages of the hybrid CW contributed an average of 75%, 72%, 45%, and 52% in the total removal efficiency of COD, NH_4^+-N, TN, and TP, respectively. In general, among three pre-treatment stages, the OT unit showed maximum pollutants removal capacity mainly due to the AA. However, during CW treatment stages, the MA-VBFW showed better carbon and nitrogen removals, whereas TP removal was maximum in HSFW. Our results showed that maximum pollutants reduction occurred during the pre-treatment stages, whereas the MA-VBFW and HSFW contributed to further removal of pollutants. The average removed COD, NH_4^+-N, TN, and TP loads in the studied hybrid system were estimated to be 35 $\pm$ 19, 7 $\pm$ 2, 6 $\pm$ 2, and 1 g/m^2 per day, respectively.

The current carbon and nutrient removal efficiencies were much higher than the previous results obtained from a similar type of full-scale hybrid CW consisting of a storage tank, a AA VF, a HF, and a landscaped ecological pond, used to treat domestic wastewater [7]. Pan et al. [7] reported that the annual average COD, NH_4^+-N, TN, and TP removal efficiencies were 34.1%, 58.4%, 31.1%, and 41.6%, respectively. The performance of our AA hybrid system was also comparable with the same type of full-scale hybrid CW without AA with similar COD inflow concentrations but lower hydraulic loading rates of 27–36 cm/day [17]. The removed COD loads in the studied AA hybrid CW were in agreement with the high removed COD loads of approximately 35 g/m^2 per day (in aerated VF) and 29 $\pm$ 2 g/m^2 per day (in aerated HSSF) as referred by Tang et al. [6] and Fan et al. [24], respectively, which were higher than 20 gCOD/m^2 day measured in other studies by Liu et al. [25]. Higher removed COD loads of 54 g/m^2 per day were measured in an intermittently aerated VF system by Foladori et al. [26].

Vymazal [18] in his review paper reported average TN and NH_4^+-N removal of 62% (24 systems) and 75% (23 systems), respectively, from different combinations of full-scale hybrid systems treating municipal sewage around the world, which were consistent with the current results. The nitrogen removed loads in our study were consistent or higher than the rates reported in previous studies on full-scale and pilot-scale CWs with different aeration strategies [6,21,24,25]. In a full-scale continuously aerated HSFW, Butterworth et al. [21] reported NH_4^+-N removed loads up to 6 g/m^2 per day. Vymazal [18] studied different combinations of hybrid systems and estimated that the NH_4^+-N removal varied between 2 $\pm$ 2 to 3 $\pm$ 3 g/m^2 per day, whereas the single stage VF and HF CWs resulted in average removals of 2 $\pm$ 2 and 1 $\pm$ 7 g NH_4^+-N/m^2 per day, respectively, which is more than three times lower than the current NH_4^+-N removed loads. The removed TN loads in the studied AA hybrid system were higher than the 6 gTN/m^2 per day measured by Foladori et al. [26] in an intermittently aerated VF CW. Vymazal [18] estimated TN removed loads up to 4 $\pm$ 5 g/m^2 per day for full scale hybrid CWs without AA, whereas the single stage VF and HF without AA showed a removal load of approximately 2 $\pm$ 4 and 1 $\pm$ 2 gTN/m^2 per day, respectively. These removal rates were markedly lower than the current TN removed load. Generally, TP removal efficiency in CWs varied from 40% to 90% [5,8] with removed load varied between 0.1 and 0.2 g/m^2 per day [8]; considering this efficacy, TP removal rates were relatively good in our studied AA hybrid CW.

Table 1. The overall distribution of pollutants concentrations along with the treatment stages [1].

Sampling Sites [2] (#)	**1-Inflow**	**2-ST-In**	**3-OT-In**	**4-CST-In**	**5-VF-In**	**9-HF-In**	**12-CWP-In**	**13-Outflow**
pH	7.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	7.1 ± 0.1	7.1 ± 0.1	7.1 ± 0.1
Temp. (°C)	17.9 ± 6.3	17.8 ± 6.2	17.9 ± 6.3	18.1 ± 6.6	18.1 ± 6.6	17.9 ± 6.2	18.1 ± 6.4	18.2 ± 6.4
EC (µS/cm)	797 ± 59	726 ± 57	711 ± 58.	711 ± 56	698 ± 61	629 ± 50	655 ± 53	637 ± 32
Turbidity (NTU)	48 ± 18	26 ± 13	21 ± 10	12 ± 9	11 ± 9	7 ± 7	5 ± 3	6 ± 3
COD (mg/L)	193 ± 84	165 ± 89	120 ± 59	78 ± 22	69 ± 20	41 ± 15	28 ± 12	28 ± 11
TN (mg/L)	53 ± 8	51 ± 8	50 ± 9	42 ± 8	38 ± 10	28 ± 8	20 ± 6	19 ± 6
NH_4^+-N (mg/L)	43 ± 8	40 ± 7	39 ± 9	21 ± 10	19 ± 10	14 ± 8	11 ± 6	10 ± 6
NO_3^--N (mg/L)	0.6 ± 0.4	0.6 ± 0.4	0.7 ± 0.3	8.8 ± 2.4	7.9 ± 2.5	8.7 ± 2.5	5.1 ± 1.7	5.1 ± 1.5
NO_2^--N (mg/L)	0.1 ± 0.05	0.1 ± 0.03	0.1 ± 0.10	0.5 ± 0.09	0.4 ± 0.10	0.5 ± 0.08	0.3 ± 0.07	0.3 ± 0.07
TP (mg/L)	4.8 ± 1.0	4.1 ± 0.8	4.2 ± 0.9	3.3 ± 1.0	3.2 ± 0.9	2.7 ± 0.8	1.8 ± 0.8	1.7 ± 0.8

Notes: [1] All data are presented as the means ± standard deviation (SD). n = 24 for all samples; [2] Inflow (In) water quality at different treatment stages of the studied CW. 2-ST-In, 3-OT-In, 4-CST-In, 5-VF-In, 9-HF-In, and 12-CWP-In means inflow concentration at the septic tank, oxidation tank, cross-flow sedimentation tank, vertical baffled flow wetland, horizontal subsurface flow wetland, and clean water pond. The number before each stage indicates sampling point out of total 13 water sampling points.

3.2. Water Temperature and DO Profile

The monthly average wastewater temperatures of the hybrid system (at the inflow, subsequent treatment stages and outflow wastewater temperature) are presented in Figure 2a. The annual average water temperature during the experimental period was around 18 °C with a maximum and minimum water temperatures reading of 26 °C and 6 °C, respectively. The nutrient removal efficiency was evaluated and classified into two seasons: high temperature (May to October) and low temperature (November to April). The average water temperatures were ranged between 17.5 ± 0.0–26.0 ± 0.4 °C and 5.5 ± 0.1–16.6 ± 0.3 °C during warm and cold seasons, respectively, with a seasonal difference of approximately 10 °C.

DO values increased significantly throughout the experimental periods at the OT (from 0.4 ± 0.5 to 2.3 ± 2.8 mg/L) and MA-VBFW (from 1.7 ± 1.8 to 4.9 ± 4.4 mg/L) stages due to the presence of continuous AA (Figure 2b). In addition, NADs in HSFW also significantly increased DO concentrations (from 0.9 ± 1.2 to 2.8 ± 3.1 mg/L). In case of seasonal variations, the influent DO values were slightly higher in summer (0.5 ± 0.1 mg/L) than those in winter (0.4 ± 0.2 mg/L), but these differences were found to be insignificant. Interestingly, the outflow DO values were significantly higher during winter (4.2 ± 1.0 mg/L) than the summer seasons (3.3 ± 0.5 mg/L). This might be due to the low temperatures in winter that supports high solubility of DO [13,27]. However, in aerated treatment units (OT and MA-VBFW), variations of DO concentrations in summer and winter seasons were almost similar, suggesting a stable aeration throughout the year and maintenance of a suitable condition for nitrification in these aeration steps. This performance was slightly different from the results reported by Pan et al. [7] in a similar type of hybrid system, where authors reported that outflow DO values of the AA VF and HF were below 1 mg/L during winter and concluded that AA was less effective in the cold season. Although authors found that overall annual average DO values significantly increased from 0. 5 ± 0.5 to 3 ± 2 mg/L at the AA VF outlet and 2 ± 1 mg/L at the HF outlet [7]. Previous studies on full-scale or lab-scale CWs with different aeration strategies reported that effluent DO values varied between 3 and 11 mg/L [28], which is consistent with the annual average DO outflows (3.7 ± 0.8 mg/L) of our studied full-scale hybrid system.

The DO results indicated that the OT and MA-VBFW treatment stages maintained mostly an aerobic condition whereas HSFW had mostly anoxic and anaerobic conditions. The DO values increased by 1.9 mg/L at NAD in between every two sections of a HSFW bed, and decreased immediately to 0.4 ± 0.5 mg/L, which represented anoxic condition before the next NAD. This phenomenon was consistent with the similar type of HSFW reported by Zhai et al. [16], where authors found NADs increased DO values from 0.3 ± 0.1 mg/L to 3.8 ± 0.1 mg/L, but after a 5.5 m subsurface plug flow in the HSFW bed, the DO concentrations decreased back to 0.3 ± 0.2 mg/L. Ye and Li [29] studied on a towery hybrid CW to treat domestic wastewater where authors reported that the second stage (out of three stages) consisted of three circular cells (water over flow from upper cell to the subsequent cells referred as towery system) increased the DO value of approximately 1.7 mg/L, which is almost the same or slightly lower than the DO concentrations increased by NADs in our study. The current DO values indicated a suitable condition for nitrification at the OT and MA-VBFW stages and denitrification in the HSFW stage. A limited amount of macro/micro-scale nitrification is still possible in HSFW due to the NAD between the two HSFW sections and plants oxygen root release [16,17].

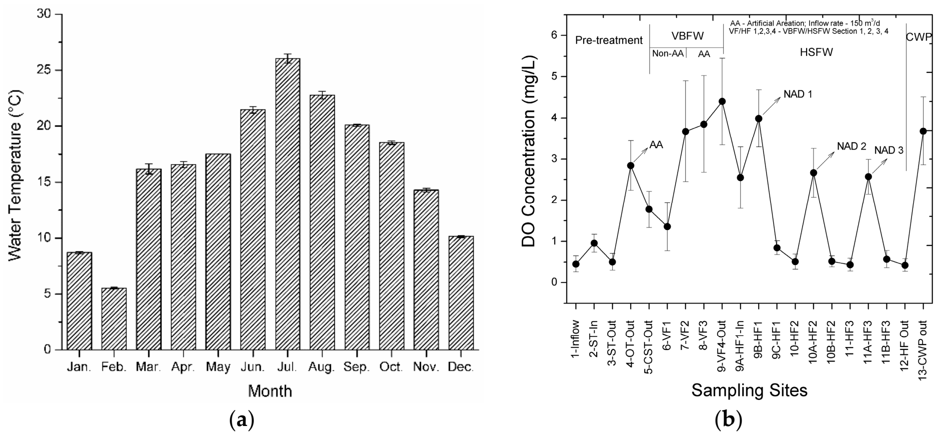

Figure 2. The water temperatures and dissolved oxygen (DO) levels in the studied hybrid system. (**a**) Average monthly water temperatures; (**b**) Annual average DO concentrations along with the flow routes of the investigated hybrid constructed wetland (CW).

3.3. Seasonal Variations of Organic and Nitrogen Removal

Seasonal variations of COD, TN, and NH_4^+-N removal efficiency and distributions of NOx (NO_3^--N and NO_2^--N) at different treatment stages of the studied hybrid system during summer and winter seasons is presented in Figure 3. The average concentration of inflow COD was almost similar during both seasons but total removal efficiency was significantly higher ($p < 0.05$) during summer (88% ± 6%) that in winter (77% ± 11%). The present COD removal efficiency during both seasons was much higher than the full-scale AA hybrid system reported by Pan et al. [7]. Compared with the other treatment stages, the first treatment stage (ST unit) contributed to the highest COD reduction during both seasons. The same phenomenon was also reported by the other researchers studied on hybrid systems that consisted of multiple treatment stages [30]. However, due to the high COD removal in ST unit during summer (43% ± 19%) in contrast with winter (27% ± 17%), total COD removal efficiency was significantly better during summer. Otherwise, COD removal rates in all treatment units showed similar performance during both seasons. In fact, in wetland beds (VBFW and HSFW), COD removal efficiencies were slightly higher during winter because of the low removal rate in pre-treatment stages.

AA influenced the OT unit to perform better COD reduction after the ST stage. Moreover, the MA-VBFW contributed more to the COD reduction than the HSFW because of AA [7].

Previous studies also reported that various aeration strategies significantly increased COD removal in various types of full-scale and lab-scale CWs [2,7,10,27]. Organic removal in CWs generally occurs through the sedimentation, filtration, interception, and microbial degradation in both aerobic and anaerobic conditions [5], but aerobic degradation is predominant for dissolved COD removal [6]. AA assists in improving mixing and increases aerobic condition in CWs, thus enhancing COD removal especially in winter [10,13,27].

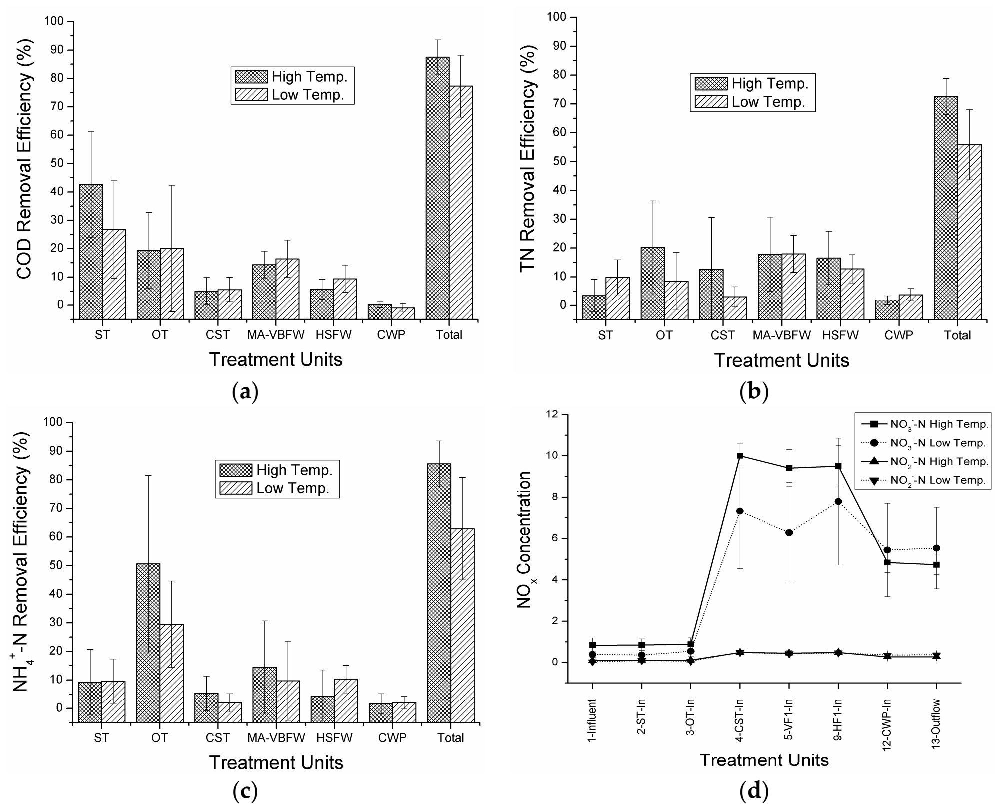

Figure 3. Stepwise removal efficiency of organics and nitrogen. (**a**) Chemical oxygen demand (COD) removal efficiency in all treatment units during summer and winter; (**b**) Total nitrogen (TN) removal efficiency at different treatment stages during summer and winter; (**c**) Ammonium nitrogen (NH_4^+-N) removal efficiency at different treatment stages during summer and winter; (**d**) Distribution of NOx (NO_3^--N and NO_2^--N) concentrations along with the treatment flow routes during summer and winter.

Nitrogen was found mainly in the form of NH_4^+-N. Inflow NH_4^+-N on average accounted for 80% ± 4% and 78% ± 6% of TN in warm and cold periods, respectively. On the contrary, outflow NH_4^+-N concentrations were found to be 39% ± 19% and 63% ± 14% of TN during warm and cold seasons, respectively. The inflow TN and NH_4^+-N were almost similar during both seasons but the outflow concentrations were significantly higher during winter ($p < 0.05$), suggesting that the low temperatures had a negative effect on both TN and NH_4^+-N removals. Figure 3b,c represented stepwise mean removal efficiencies of TN and NH_4^+-N in the investigated hybrid system during high and low temperatures. NH_4^+-N removal efficiency was found to be higher than TN removal in both seasons. TN and NH_4^+-N removal efficiencies during the warm period were 73% ± 6% and 86% ± 8%, respectively, whereas during cold period 56% ± 12% and 63% ± 18%, respectively. Compared with the cold period, the average removal efficiencies of TN and NH_4^+-N were significantly increased ($p < 0.05$) during summer of approximately 17% and 23%, respectively. Maximum TN and NH_4^+-N removals were observed in the OT and MA-VBFW units during both seasons where AA was applied, which suggests that the aeration had a positive influence on nitrogen removal [2,5,9,10]. In addition, the HSFW performed significantly in removing TN during both seasons (17% ± 9% summer and 13% ± 5% winter). However, NH_4^+-N removal efficiency at the HSFW stage was higher in winter (10% ± 5%) than that in summer (4% ± 9%). This was due to the comparatively low NH_4^+-N inflow concentrations (9 mg/L) in the HSFW stage and high NH_4^+-N oxidations in previous OT and VBFW stages during summer. However, the HSFW significantly decreased NO_3^--N (summer from 10 ± 1 to 5 ± 1 mg/L and winter 8 ± 3 to 5 ± 2 mg/L) concentrations during both seasons (Figure 3d). Since then, the inflow NOx concentrations were less than 1 mg/L throughout the experimental period, but the OT and MA-VBFW units significantly increased NO_3^--N concentrations and limited increase of NO_2^--N. These phenomena indicated that the proper nitrification occurred in these steps due to AA [6,9,10]. In contrast, the HSFW subsequently decreased NO_x (mostly NO_3^--N) concentrations, which suggested that denitrification occurred in the HSFW stage [10]. However, the outflow NO_3^--N concentrations of the wetland during both seasons indicated an incomplete denitrification in the HSFW stage [10] which can be attributed to the lack of available organic carbon sources [9,31].

In addition to the microbial nitrification and denitrification, ammonia volatilization especially in the OT unit, plant nitrogen uptake and ammonia adsorption in the VBFW and HSFW units also contributed to the TN removal in the studied system [2,6,8,9]. The average pH measured at all treatment stages of the wetland was 7.2 ± 0.1 during both seasons, which should therefore limit the contribution from ammonia volatilization [8,29]. Plants uptake can significantly remove nitrogen in CWs (around 20% of total nitrogen removal) [6,9]. Vymazal and Kröpfelová [30] reported that plants uptake in experimental multistage hybrid CW treated municipal sewage (saturated vertical flow, free-drain vertical, and horizontal flow units in series) can remove up to 26% of the nitrogen inflow load. The current study showed that AA improved nitrification in the OT and MA-VBFW stages and the subsequent denitrification in the HSFW stage during both summer and winter seasons. Generally, TN removal efficiency in CWs varied between 40% and 70% [8,27]; considering this range, the nitrogen removal in the studied system during both seasons was good.

3.4. TP Removal

The seasonal variations of TP removal efficiencies at different treatment stages are shown in Figure 4. Although the inflow TP concentrations were almost the same during both seasons, its removal efficiencies were significantly higher ($p < 0.05$) in summer periods (78% ± 6%) than those in winter periods (46% ± 18%). Compared with the other treatment units, the highest TP removal rates (28% ± 34%) were observed in the OT unit during summer; during winter, the HSFW unit showed the best removal rates (15% ± 6%) (Figure 4). The HSFW contributed more to TP removal than the VBFW throughout the experimental period. In summer, TP removal efficiencies at the OT and MA-VBFW stages were fluctuating because of the inflow variations in TP concentrations. However, final TP outflow concentrations were more stable in summer compared with those in winter. TP removal in CWs mainly refers to the physical processes such as substrate adsorption and chemical precipitation [2,4,5,10,27].

Previous studies reported that different AA strategies significantly improved TP removal in CWs [2,6], whereas some studies did not find any significant differences between aerated and non-aerated CWs [5,10,27]. However, the reported studies on TP removal with or without AA suggested that AA provided more stable TP removal rates through the better mixing of phosphorus with the substrate media [6,10,27], improving aerobic conditions and DO, thus increasing the chemical precipitations and microbial degradations of phosphorus [1,6,27]. The present TP removal rates in the OT stage during summer were more than three times the TP removal rates of a non-aerated oxidation pond reported by Wang et al. [5], indicating the positive influences of AA in the studied system for TP removal. However, during winter, despite the same aeration and aerobic conditions, TP removals were significantly lower than those in the summer seasons, indicating that AA was less effective at low seasonal temperatures. This might be due to the decrease in microbial activities and plant uptake of TP during winter. In a lab-scale AA VBFW, Tao et al. [10] also reported a significant decrease in

TP removal rates during winter (65%) compared to that in summer (74%). In addition, plant uptake can significantly contribute to the TP removal efficiencies (approximately 10%–75%) [4,6,12,27,30] which is generally decreased during the winter season because of plant dormancy or dieback [10]. However, current TP removal efficiencies during both seasons were much higher than the full-scale AA hybrid system reported by Pan et al. [7].

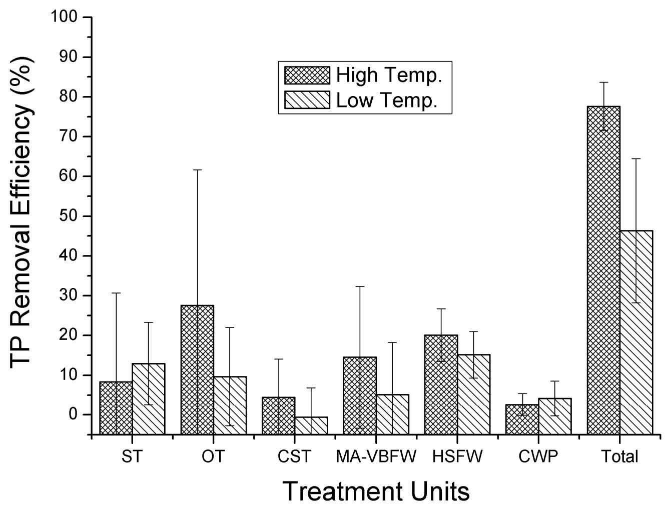

Figure 4. Total phosphorus (TP) removal efficiency in different treatment stages during summer and winter.

3.5. Water Temperature vs. Pollutants Removal

Significant positive relationships ($p < 0.01$) between water temperatures and removal efficiencies of TN, NH_4^+-N, NO_2^--N, and TP were observed with Pearson correlation coefficients of 0.9, 0.8, 0.9, and 0.9, considering both summer and winter seasons. The correlation results revealed that, except for the NO_3^--N, all other nitrogen species and TP removal efficiencies significantly increased with temperature. Previous studies also reported that the air or water temperatures directly correlated to the pollutants removal rates [7,14]; in spite of the same AA, both TP and TN removal rates were found to be significantly lower in winter compared with that in summer [10,13,27]. This was due to the decrease in microbial activities and plant uptake (dormancy or dieback) during low temperatures [10]. The optimum temperatures for nitrification and denitrification are ranges within 28–36 °C and 60–70 °C, respectively, whereas temperatures lower than 5 °C can inhibit the activities of both nitrifying and denitrifying bacteria and consequently decrease nitrogen removal rates [31]. However, pH, mass loading, available carbon and nitrogen, redox condition, and microbial diversity in CWs can also influence nitrogen removal rates in addition to the temperature [31,32].

4. Conclusions

AA was applied in a full-scale hybrid CW to evaluate the pollutant removal performances, particularly the nutrient removal. The continuous aeration was used in a pre-treatment unit (OT) and the main treatment unit (VBFW) over a period of a year. Results from the full-scale system suggested that this new hybrid CW can achieve relatively good pollutant removal rates including nutrient removal (TN and TP approximately 65%). AA significantly improved the aerobic conditions and thus enhanced nutrient and organics removal efficiencies in the studied system. However, despite the same aeration strategy and almost similar aerobic conditions throughout the year, nutrient removal rates were significantly lower in winter than those in summer. Our study indicated that AA was less effective at low temperatures which might be due to the decreased microbial activities and plant uptake during winter seasons. However, additional enhancement of nutrient removal in the studied hybrid system is still possible using different aeration strategies and carbon inputs, which needs further investigation.

Acknowledgments: This research is financially supported by the National Natural Science Foundation of China (grant No. 51208533 and 51478062), the National Science and Technology Major Project: Water Pollution Control and Management (2013ZX07312-001-03), and the Fundamental Research Fund for the Central Universities in China (106112016CDJZR218805). Special thanks to Taylor Lee Sivils, Sarik Salim, and Md. Milon Hossain for their kind help in improving the language of the manuscript.

Author Contributions: Jun Zhai conceived and designed the full-scale system and experiments; Jun Xiao and Jingsong Xiao performed the experiments; Md. Hasibur Rahaman analyzed the data; Md. Hasibur Rahaman and Yasinta John wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, H.; Hu, Z.; Zhang, J.; Ngo, H.H.; Guo, W.; Liang, S.; Fan, J.; Lu, S.; Wu, H. Optimizations on supply and distribution of dissolved oxygen in constructed wetlands: A review. *Bioresour. Technol.* **2016**, *214*, 797–805. [CrossRef] [PubMed]
2. Zhong, F.; Wu, J.; Dai, Y.; Xiang, D.; Cheng, S.; Ji, H. Performance evaluation of wastewater treatment using horizontal subsurface flow constructed wetlands optimized by micro-aeration and substrate selection. *Water Sci. Technol.* **2015**, *71*, 1317–1324. [CrossRef] [PubMed]
3. Wu, S.; Kuschk, P.; Brix, H.; Vymazal, J.; Dong, R. Development of constructed wetlands inperformance intensifications for wastewater treatment: A nitrogen and organic matter targeted review. *Water Res.* **2014**, *57*, 40–45. [CrossRef] [PubMed]
4. Martín, M.; Gargallo, S.; Hernández-Crespo, C.; Oliver, N. Phosphorus and nitrogen removal from tertiary treated urban wastewaters by a vertical flow constructed wetland. *Ecol. Eng.* **2013**, *61*, 34–42. [CrossRef]
5. Wang, X.; Tian, Y.; Zhao, X.; Peng, S.; Wu, Q.; Yan, L. Effects of aeration position on organics, nitrogen and phosphorus removal in combined oxidation pond-constructed wetland systems. *Bioresour. Technol.* **2015**, *198*, 7–15. [CrossRef] [PubMed]
6. Tang, X.; Huang, S.; Scholz, M.; Li, J. Nutrient Removal in pilot-scale constructed wetlands treating eutrophic river water: Assessment of plants, intermittent artificial aeration and polyhedron hollow polypropylene balls. *Water. Air. Soil Pollut.* **2009**, *197*, 61–73. [CrossRef]
7. Pan, J.; Zhang, H.; Li, W.; Ke, F. Full-scale experiment on domestic wastewater treatment by combining artificial aeration vertical- and horizontal-flow constructed wetlands system. *Water Air Soil Pollut.* **2012**, *223*, 5673–5683. [CrossRef]
8. Vymazal, J. Removal of nutrients in various types of constructed wetlands. *Sci. Total Environ.* **2007**, *380*, 48–65. [CrossRef] [PubMed]
9. Maltais-Landry, G.; Maranger, R.; Brisson, J.; Chazarenc, F. Nitrogen transformations and retention in planted and artificially aerated constructed wetlands. *Water Res.* **2009**, *43*, 535–545. [CrossRef] [PubMed]
10. Tao, M.; He, F.; Xu, D.; Li, M.; Wu, Z. How artificial aeration improved sewage treatment of an integrated vertical-flow constructed wetland. *Pol. J. Environ. Stud.* **2010**, *19*, 183–191.
11. Wang, X.; Chen, J.; Kong, Y.; Shi, X. Sequestration of phosphorus from wastewater by cement-based or alternative cementitious materials. *Water Res.* **2014**, *62*, 86–96. [CrossRef] [PubMed]
12. Vera, I.; Araya, F.; Andrés, E.; Sáez, K.; Vidal, G. Enhanced phosphorus removal from sewage in mesocosm-scale constructed wetland using zeolite as medium and artificial aeration. *Environ. Technol.* **2014**, *35*, 1639–1649. [CrossRef] [PubMed]
13. Ouellet-Plamondon, C.; Chazarenc, F.; Comeau, Y.; Brisson, J. Artificial aeration to increase pollutant removal efficiency of constructed wetlands in cold climate. *Ecol. Eng.* **2006**, *27*, 258–264. [CrossRef]
14. Faulwetter, J.L.; Gagnon, V.; Sundberg, C.; Chazarenc, F.; Burr, M.D.; Brisson, J.; Camper, A.K.; Stein, O.R. Microbial processes influencing performance of treatment wetlands: A review. *Ecol. Eng.* **2009**, *35*, 987–1004. [CrossRef]
15. Brix, H. Do macrophytes play a role in constructed treatment wetlands? *Water Sci. Technol.* **1997**, *35*, 11–17. [CrossRef]

16. Zhai, J.; Zou, J.; He, Q.; Ning, K.; Xiao, H. Variation of dissolved oxygen and redox potential and their correlation with microbial population along a novel horizontal subsurface flow wetland. *Environ. Technol.* **2012**, *33*, 1999–2006. [CrossRef] [PubMed]
17. Zhai, J.; Xiao, H.W.; Kujawa-Roeleveld, K.; He, Q.; Kerstens, S.M. Experimental study of a novel hybrid constructed wetland for water reuse and its application in Southern China. *Water Sci. Technol.* **2011**, *64*, 2177–2184. [CrossRef] [PubMed]
18. Vymazal, J. The use of hybrid constructed wetlands for wastewater treatment with special attention to nitrogen removal: A review of a recent development. *Water Res.* **2013**, *47*, 4795–4811. [CrossRef] [PubMed]
19. Wang, L.; Li, T. Effects of seasonal temperature variation on nitrification, anammox process, and bacteria involved in a pilot-scale constructed wetland. *Environ. Sci. Pollut. Res.* **2015**, *22*, 3774–3783. [CrossRef] [PubMed]
20. Arias, C.A.; Oirschot, D.V.; Kilian, R.; Pascual, A.; Carvalho, P.N.; Lv, T.; Zhang, Y.; Brix, H.; Alvarez, J.A. Design and performance evaluation of a highly loaded aerated treatment managing effluents from a food processing industry in Denmark. *Water Pract. Technol.* **2015**, *10*, 644–650. [CrossRef]
21. Butterworth, E.; Dotro, G.; Jones, M.; Richards, A.; Onunkwo, P.; Narroway, Y.; Jefferson, B. Effect of artificial aeration on tertiary nitrification in a full-scale subsurface horizontal flow constructed wetland. *Ecol. Eng.* **2013**, *54*, 236–244. [CrossRef]
22. Butterworth, E.; Richards, A.; Jones, M.; Mansi, G.; Ranieri, E.; Dotro, G.; Jefferson, B. Performance of four full-scale artificially aerated horizontal flow constructed wetlands for domestic wastewater treatment. *Water* **2016**, *8*, 365. [CrossRef]
23. Bureau, N.E.P. *Analytical Methods for the Examination of Water and Wastewater*, 4th ed.; Environmental Science Press: Beijing, China, 2002.
24. Fan, J.; Zhang, B.; Zhang, J.; Ngo, H.H.; Guo, W.; Liu, F.; Guo, Y.; Wu, H. Intermittent aeration strategy to enhance organics and nitrogen removal in subsurface flow constructed wetlands. *Bioresour. Technol.* **2013**, *141*, 117–122. [CrossRef] [PubMed]
25. Liu, L.; Zhao, X.; Zhao, N.; Shen, Z.; Wang, M.; Guo, Y.; Xu, Y. Effect of aeration modes and influent COD/N ratios on the nitrogen removal performance of vertical flow constructed wetland. *Ecol. Eng.* **2013**, *57*, 10–16. [CrossRef]
26. Foladori, P.; Ruaben, J.; Ortigara, A.R.C. Recirculation or artificial aeration in vertical flow constructed wetlands: A comparative study for treating high load wastewater. *Bioresour. Technol.* **2013**, *149*, 398–405. [CrossRef] [PubMed]
27. Zhang, L.Y.; Zhang, L.; Liu, Y.D.; Shen, Y.W.; Liu, H.; Xiong, Y. Effect of limited artificial aeration on constructed wetland treatment of domestic wastewater. *Desalination* **2010**, *250*, 915–920. [CrossRef]
28. Zapater-Pereyra, M.; Kyomukama, E.; Namakula, V.; van Bruggen, J.J.A.; Lens, P.N.L. The effect of aeration and recirculation on a sand-based hybrid constructed wetland treating low-strength domestic wastewater. *Environ. Technol.* **2016**, *37*, 1923–1932. [CrossRef] [PubMed]
29. Ye, F.; Li, Y. Enhancement of nitrogen removal in towery hybrid constructed wetland to treat domestic wastewater for small rural communities. *Ecol. Eng.* **2009**, *35*, 1043–1050. [CrossRef]
30. Vymazal, J.; Kröpfelová, L. Multistage hybrid constructed wetland for enhanced removal of nitrogen. *Ecol. Eng.* **2015**, *84*, 202–208. [CrossRef]
31. Hsueh, M.L.; Yang, L.; Hsieh, L.Y.; Lin, H.J. Nitrogen removal along the treatment cells of a free-water surface constructed wetland in subtropical Taiwan. *Ecol. Eng.* **2014**, *73*, 579–587. [CrossRef]
32. Chang, J.J.; Wu, S.Q.; Liang, K.; Wu, Z.; Liang, W. Comparative study of microbial community structure in integrated vertical-flow constructed wetlands for treatment of domestic and nitrified wastewaters. *Environ. Sci. Pollut. Res.* **2015**, *22*, 3518–3527. [CrossRef] [PubMed]

© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (http://creativecommons.org/licenses/by/4.0/).