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RESEARCH ARTICLE

A three-year study on the treatment of domestic-industrial mixed wastewater using a full-scale hybrid constructed wetland

Dan A[1] · Yang-yang Deng[1] · Qin-mei Guo[1] · Yu Jiang[1] · Chun-xing Chen[2,3]

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Abstract

Three full-scale constructed wetlands (CWs), namely vertical flow (VFCW), surface flow (SFCW), and horizontal flow (HFCW) systems, were combined in a series process to form a hybrid CW, which was used for the treatment performance of domestic-industrial mixed wastewater and investigated over a three-year period. The hybrid CW demonstrated that it is effective and stable during the long-term treatment of high-loading mixed wastewater under different operation years, season changes, and technology processes, with the average removal efficiencies of suspended solids, chemical oxygen demand, biological oxygen demand, total nitrogen, ammonia nitrogen, nitrate nitrogen, and total phosphorous being 84, 40, 54, 54, 70, 40, and 46%, respectively. The effluent quality of the hybrid CW reached the highest discharge standard for wastewater treatment plants. First, a variety of pollutants from the mixed wastewater were effectively removed in the subsurface processes (VFCW and HFCW) via substrate adsorption and degradation of the attached biofilm. The higher dissolved oxygen content and oxygen transfer capacity values in the VFCW were favourable for the occurrence of aerobic pathways (such as nitrification and inorganic phosphorus oxidation). In addition, with the large consumption of oxygen in the previous process, the oxygen-enriching capacity of the SFCW processes, provided aerobic potential for the next stage. In particular, the plant debris in the SFCW temporarily increased the organics and suspended solids, further increasing the C/N ratio, which was beneficial for denitrification as the main nitrogen removal pathway in the HFCW.

Keywords Hybrid constructed wetland · Domestic-industrial mixed wastewater · Long-term investigation · Removal loading · Removal dynamics · Wastewater treatment

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Dan A and Yang-yang Deng are co-first authors.

✉ Chun-xing Chen
chunxing22@163.com

Dan A
adan@zhku.edu.cn

Yang-yang Deng
yydeng@zhku.edu.cn

1 Engineering and Technology Research Center for Agricultural Land Pollution Integrated Prevention and Control of Guangdong Higher Education Institute, College of Resources and Environment, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China

2 Shenzhen Academy of Environmental Sciences, Shenzhen 518001, China

3 State Environmental Protection Key Laboratory of Drinking Water Source Management and Technology, Shenzhen 518001, China

Introduction

With rapid population growth, urbanisation, and industrialisation, 22.2 and 12.6% of the increased water consumption worldwide entering the environment was found to be mainly through industrial and domestic water, respectively (Yang et al. 2021). The concentration of pollutants in domestic wastewater is relatively low, and the main pollutants are nitrogen and phosphorus, which are more biochemically available (Saeed et al. 2014). Most industrial wastewater is recalcitrant and contains high chemical oxygen demand (COD), suspended solids (SS), and dissolved solids, which are more toxic and have poor biochemical availability (Güven et al. 2017). On the edge of cities, there is an inevitable overlap between industrial and rural areas. The anthropogenic discharge of domestic and industrial wastewater from point or non-point sources not only leads to eutrophication of watersheds and estuaries, but also induces biotoxicity and poses a risk to human health and safety (Yang et al. 2021).

For different types of wastewaters, the treatment technologies must meet the corresponding discharge requirements. Therefore, it is necessary to develop an environmentally and economically friendly treatment process to deal with mixed domestic and industrial wastewater.

Constructed wetlands (CWs) are widely regarded as an excellent tertiary treatment for wastewater because of their low operation and maintenance costs and high nitrogen and phosphorus removal efficiencies (Wu et al. 2017). This technology was initially effectively applied to domestic wastewater in municipal and rural areas (Ávila et al. 2013; He et al. 2018), and was gradually extended to natural treatment for other wastewaters, such as industrial wastewater (Wang et al. 2017; Saeed et al. 2018). Saggaï et al. (2017) conducted a 7-year continuous study on the treatment of domestic wastewater with horizontal flow (HF) CWs, and the average removal efficiencies of SS, COD, biological oxygen demand (BOD), total phosphorus (TP), and total nitrogen (TN) were 94, 80, 90, 60, and 50%, respectively. Saeed et al. (2018) employed vertical-horizontal flow (VF-HF)-integrated CWs to treat mixed industrial wastewater, and the mean solid, organics, nitrogen, and phosphorus removal in the systems were 55–95%, 74–85%, 68–80%, and 64–89%, respectively. Thus, CWs can effectively treat domestic wastewater as well as industrial wastewater and are expected to be applied to the purification of domestic-industrial mixed wastewater.

Although a few studies have evaluated the performance of CWs in treating mixed wastewater, research on the long-term operation of CWs remains limited (Vymazal 2019). Li et al. (2020) reported that the removal efficiency of TN declined by 38.2% after five years of operation of CW systems, with a relatively low average removal efficiency of COD (8%). It has been proposed that the rate of phosphorous retention is often more than 90% in young different types of CWs, possibly due to the saturation of the filtration material (Zhu et al. 2021). After long-term monitoring, the decrease in nitrogen and organic removal of CWs was attributed to a reduction in the reoxygenation capacity (Samsó & García 2013) and the lack of a carbon source (Wu et al. 2018). Surface flow (SF) CWs may gradually become a reservoir for nutrients and release them into the upper water bodies, thus limiting the application of CWs (Zhu et al. 2021). Therefore, the evaluation of the treatment performance of CWs should focus on their long-term operation and stability.

For long-term and stable purification performance, CWs with various configurations and technology combinations are considered to have the advantage of dealing with different types of wastewaters, providing more possibilities for the treatment of mixed wastewater (Melián et al. 2010; Wu et al. 2014). In single- or laboratory-scale CWs, VFCWs potentially strengthen aeration and provide an aerobic environment that promotes the decomposition of organic matter and nitrification of ammonia but are not favourable for denitrification under anaerobic conditions. Horizontal flow CWs are beneficial for the denitrification of nitrate, but have difficulty oxidising ammonia (Ávila et al. 2013). Surface flow CWs can provide more contact areas, but the removal of nitrogen and phosphorus is less effective (Vymazal 2007). Hence, a combination of various CWs is necessary to investigate the effectiveness of wastewater treatment. For example, Sakurai et al. (2021) established horizontal-vertical flow (HF-VF) CWs for domestic wastewater treatment, and the pollutant removal rates of COD, BOD, TN, and TP were 74, 93, 50, and 61%, respectively. The appearance of a combination of surface and subsurface flow CWs for over 10 years was reported by Zhu et al. (2021); they showed that the average removal efficiencies of TN and TP were 54 and 67%, respectively. Hybrid CWs have the advantage of combining aerobic and anaerobic environments. These results show the potential for the long-term operation of hybrid CWs for the treatment of domestic-industrial mixed wastewater. Furthermore, the effects of different CWs on models of pollutant removal rates may be different (Melián et al. 2010), and most current laboratory-scale CW wastewater treatments cannot be applied to full-scale CWs under similar conditions.

In this study, a full-scale hybrid CW with a combination of VF, SF, and HF CWs in series for domestic-industrial mixed wastewater treatment was continuously monitored for three years. Our objectives were (a) to assess the long-term performance of hybrid CWs for domestic-industrial mixed wastewater; (b) to compare the effects of different processes, operating periods, and seasons on the decontamination ability of hybrid CWs; and (c) to analyse the removal dynamics of hybrid CWs for domestic-industrial mixed wastewater. The knowledge obtained from this study will be helpful in providing key parameters for the long-term application of hybrid CWs for the advanced treatment of complex mixed wastewater.

Materials and methods

Hybrid-constructed wetlands

The full-scale hybrid CWs consisted of three CW processes of different configurations, namely VF, SF, and HF CWs in series with a total area of 5000 m^2, and the schematic and site picture are shown in Fig. 1. The project was designed and started in 2007 to treat local mixed wastewater, of which 60% was domestic wastewater from the surrounding schools and villages, and 40% was industrial wastewater from the drainage of electronics and auto parts factories. The wastewater treatment capacity of hybrid CWs was 2500 t/day with hydraulic loading rates (HRL) of 0.30–0.59 m/day and hydraulic retention times (HRT) of 12–28 h. The wastewater flowed through the VFCW, SFCW, and horizontal flow

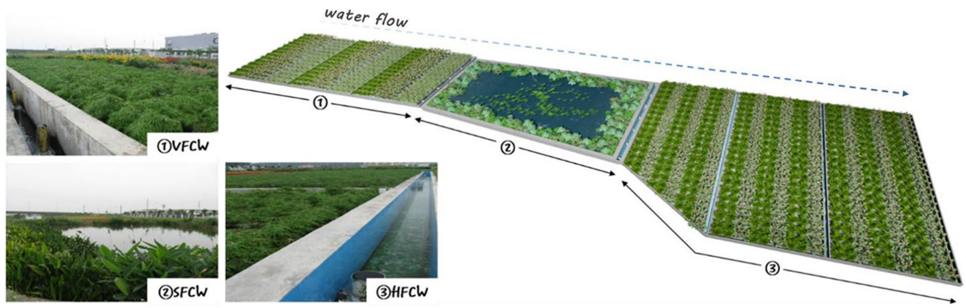


Fig. 1 Schematic diagram and site picture of the different hybrid constructed wetlands (CWs): vertical flow (VFCW), surface flow (SFCW), and horizontal flow (HFCW)

(HFCW) in turn by way of ditches or buried PVC pipes, and the structure of each CW process is fully described in the section below. The substrate used to fill the wetlands was gravel, which is inexpensive and widely available. The plants used were adapted to the local climate and habitat characteristics, and removed contaminants effectively, as evidenced by our previous study (A et al. 2020).

Vertical flow constructed wetland

The VFCW consisted of three units in parallel with a total area of 1260 m^2, and a small slope (1–2%) of the bottom was applied to promote gravitational water flow, as shown in Fig. S.1a. The substrate of the VFCW bed was mainly filled with small-size gravel (2–8 mm) with a filling depth of 1 m and a water level of 0.9 m. Among them, gravel with large diameters (20–40 mm) were only filled in the water distribution and catchment areas to prevent clogging. Each unit was planted with *Cyperus alternifolius*, *Cannaceae indica* var. *flava*, and *Thalia dealbata*, at a density of two shoots/m^2. The influent was sprayed evenly on the surface of the substrate by perforated PVC pipe, and the effluent was collected and discharged by the bottom of the perforated PVC pipe.

Surface flow constructed wetland

The SFCW consisted of an independent unit, with a total area of 1250 m^2 (Fig. S.1b). The bottom of the SFCW bed was laid with natural soil, and the water level was 0.3–1.5 m. The planting densities of the different areas in the SFCW varied. The coastal area (approximately 2 m wide) was planted with *Pontederia cordata*, *C. papyrus*, and *T. dealbata*, and the central area was planted with *Nymphaea alba*. The inlet and outlet were drained using PVC pipes diagonal to the SFCW.

Horizontal flow constructed wetland

The HFCW consisted of three units in parallel, with a total area of 2490 m^2 and bottom slope of 1–2% (Fig. S.1c). The substrate of the HFCW bed was filled with gravel in the same way as the VFCW to prevent clogging, with a filling depth of 0.8 m and a water level of 0.7 m. Each unit was planted with *C. alternifolius* and *C. indica* var. *flava* at a density of two shoots/m^2. The influent was sprayed evenly on one end of the HFCW surface by the perforated PVC pipe, and the effluent was collected and discharged by the bottom of the perforated PVC pipe.

Sampling and analytical procedure

The experiment was conducted from May 2017 to June 2020, and sampling was carried out twice a month in the first year, once every two months in the second year, and approximately once a month in the third year, for a total of 24, 6, and 10 samples, respectively. The sampling sites were the inlet of the hybrid CW and the outlets of the VFCW, SFCW, and HFCW. The samples were collected in a 1 L glass amber sampling bottle and adjusted to a pH of 3 using 4 mol/L H_2SO_4. All samples were refrigerated and transported to the laboratory, where they were stored at 4 ℃ until analysis (within 48 h). General physicochemical parameters, that is, water temperature (WT) and dissolved oxygen (DO), were simultaneously measured in situ using a YSI multiparameter water sampling metre (YSI Pro Plus, YSI Corporation, USA). General pollutant parameters, that is, SS, COD, BOD, TN, TP, ammonia nitrogen (NH_4^+–N), and nitrate nitrogen (NO_3^-–N), were determined following the national standard methods (SEPA 2002).

Mathematical procedure

Removal loading

The removal loading (RL, g/m^2/day) of pollutants reflects the quantity of pollutants that can be removed per unit area per unit time in the CWs was calculated as follows:

$$RL = Q \times \frac{C_i - C_e}{A} \quad (1)$$

where Q is the flow rate (m^3/day), A is the wetland area (m^2), C_i is the influent concentration (mg/L), and C_e is the effluent concentration (mg/L).

Area-based first-order removal rate constant

The $k_A - C^*$ first-order model is widely accepted for the design of subsurface flow CWs (Kadlec 2000; Zurita et al. 2009), in which k_A constants can be used to calculate the required surface area for the full-scale CWs under the same operating conditions. The k_A values (area-based first-order removal rate constant, m/year) of pollutants was calculated as follows:

$$k_A = \frac{365Q}{A}\ln(\frac{C_i - C^*}{C_e - C^*}) \tag{2}$$

where Q is the flow rate (m^3/day), A is the wetland area (m^2), C_i is the influent concentration (mg/L), C_e is the effluent concentration (mg/L), and C^* is the background concentration (mg/L).

Oxygen transfer capacity (OTC)

Calculation of the OTC (g/m^2/day) of CWs can reflect the system potential to remove organic matter (decomposition) and nitrogen (nitrification), and the equation is as follows (Cooper, 2005):

$$OTC = Q \times \frac{(C_{Bi} - C_{Be}) + 4.3(C_{Ni} - C_{Ne})}{A} \tag{3}$$

where Q is the flow rate (m^3/day), A is the wetland area (m^2), C_{Bi} and C_{Ni} are the BOD_5 and NH_4^+–N concentrations in the influent (mg/L), and C_{Be} and C_{Ne} are the BOD_5 and NH_4^+–N concentrations in the effluent (mg/L), respectively.

C/N ratio

The C/N ratio reflects the extent of nitrification and denitrification, and the equation is follows (Du et al. 2016):

$$C/N = \frac{C_{COD}}{C_{TN}} \tag{4}$$

where C_{COD} and C_{TN} is COD and TN concentrations (mg/L), respectively.

Statistical analysis

The results were statistically evaluated using SPSS software (version 25.0; Chicago, USA). The removal efficiencies of the different CWs were compared using analysis of variance (ANOVA). The correlation coefficients between variables were calculated using Pearson's correlation.

Results

Comparison of mixed wastewater influent with single sewage

The total influent of the hybrid CW was from domestic-industrial mixed wastewater, and the water quality compared with single wastewater is shown in Table 1. The WT was influenced by the subtropical climate in the Greater Bay Area, South China, with a three-year average of 23.9 °C. The DO value was 7.78 mg/L (aerobic) of the mixed wastewater, which was much higher than the 0.41–1.50 mg/L (anaerobic) of local domestic wastewater reported by A et al. (2020). The concentration of SS was higher in the mixed wastewater (22.7 mg/L) than that in the industrial wastewater (4.20 mg/L), whereas the concentration of COD (53.6 mg/L) was lower in the mixed wastewater than that in the single sewage (149–853 mg/L). Although the contents of TN (18.5 mg/L) and TP (1.73 mg/L) in the mixed wastewater were in the same order of magnitude as those in the single sewage (25.3–28.3 mg/L of TN and 2.15–3.35 mg/L of TP), NH_4^+–N (8.64 mg/L) and NO_3^-–N (8.28 mg/L) were quite different from those in the single sewage (24.2–33.5 mg/L of NH_4^+–N and 0.01–1.95 mg/L of NO^{--}-N). Therefore, the composition of domestic-industrial mixed wastewater is more complex than that of single industrial wastewater or domestic wastewater, and the requirement of the wastewater treatment process is even higher.

Treatment of domestic-industrial mixed wastewater by hybrid CW

Physicochemical parameters

Temporal variations in physicochemical parameters in the hybrid CW are shown in Fig. 2. Water temperature did not show any significant differences (22.2–23.9 °C) in either the total influent of the hybrid CW or the effluent from each CW ($p > 0.05$). The DO value dropped sharply from 7.78 mg/L to 0.82 mg/L after VFCW treatment, then recovered to 4.21 mg/L when passing through SFCW, and finally decreased to the lowest value (0.49 mg/L) in HFCW. The OTC was like that of DO, with the values of 27.2, 3.79, and 11.0 g/m^2/day for VFCW, SFCW, and HFCW, respectively. This was because the VFCW consumed a large amount of oxygen for aerobic reactions due to its higher DO and OTC values, resulting in a sharp decrease in DO from its effluent; the SFCW had a wide water–gas blending space due to the lack of substrate

Table 1 Water quality of influent and effluent from the hybrid constructed wetland (CW, $n=40$)

	Influent	Effluent			Wastewater		Standard[3]	
		VFCW	SFCW	HFCW	Industrial[1]	Domestic[2]	I-A level	I-B level
WT (℃)	23.9 ± 3.51[a]	23.1 ± 4.04[a]	23.1 ± 5.02[a]	22.2 ± 4.21[a]	–	–	–	–
DO (mg/L)	7.78 ± 1.34[a]	0.82 ± 0.79[b]	4.21 ± 1.63[c]	0.49 ± 0.47[b]	–	0.41–1.50	–	–
C/N	2.97 ± 0.89[a]	3.29 ± 1.61[a]	4.59 ± 2.81[b]	4.53 ± 3.43[b]	–	–	–	–
OTC (g/m²/day)	–	27.2 ± 18.5[a]	3.79 ± 15.28[b]	11.0 ± 7.05[c]				
SS (mg/L)	22.7 ± 8.21[a]	7.72 ± 3.25[b]	10.9 ± 4.67[c]	3.23 ± 0.93[d]	4.20–21.0	–	≤ 10	≤ 20
Removal (%)	–	63 ± 20	-17 ± 39	39 ± 27	–	–	–	–
COD (mg/L)	53.6 ± 16.3[a]	40.6 ± 12.9[b]	45.7 ± 15.5[b]	30.8 ± 8.33[c]	157–853	149–360	≤ 50	≤ 60
Removal (%)	–	21 ± 25	-7 ± 27	26 ± 19	–	–	–	–
BOD (mg/L)	12.5 ± 5.98[a]	7.89 ± 5.28[b]	11.8 ± 4.84[a]	4.88 ± 0.63[c]	–	–	≤ 10	≤ 20
Removal (%)	–	40 ± 14	-39 ± 27	53 ± 21	–	–	–	–
NH_4^+–N (mg/L)	8.64 ± 6.63[a]	5.71 ± 5.32[b]	4.25 ± 3.77[bc]	2.68 ± 2.53[c]	–	24.2–33.5	≤ 5	≤ 8
Removal (%)	–	37 ± 22	13 ± 19	21 ± 16	–	–	–	–
NO_3^-–N (mg/L)	8.28 ± 4.52[a]	6.87 ± 3.97[ab]	5.80 ± 3.79[b]	4.67 ± 3.46[bc]	0.01–1.08	0.35–1.95	–	–
Removal (%)	–	12 ± 75	13 ± 26	15 ± 19	–	– –	–	–
TN (mg/L)	18.5 ± 4.55[a]	13.5 ± 4.09[b]	11.1 ± 2.88[c]	8.14 ± 2.57[d]	–	25.3–38.3	≤ 15	≤ 20
Removal (%)	–	27 ± 14	12 ± 9	15 ± 9	–	–	–	–
TP (mg/L)	1.73 ± 0.62 [a]	1.34 ± 0.42[b]	1.17 ± 0.40[b]	0.89 ± 0.33[c]	–	2.15–3.35	≤ 0.5	≤ 1
Removal (%)	–	20 ± 14	10 ± 9	15 ± 11	–	–	–	–

[1]Güven et al. 2017)

[2]A et al. 2020)

[3]Discharge standard of pollutants for municipal wastewater treatment plant in China (GB18918-2002) (Ministry of Ecology and Environment of China 2003)

Different letters behind the numbers indicate significant differences at the 0.05 level according to one-way ANOVA

coverage, contributing to oxygen-enriching dissolution and the DO value rising again; the DO and OTC values of the HFCW were not as high as those of the VFCW ($p < 0.05$), but were significantly higher than those of the SFCW ($p < 0.05$), which were suitable for aerobic-anaerobic facultative reactions.

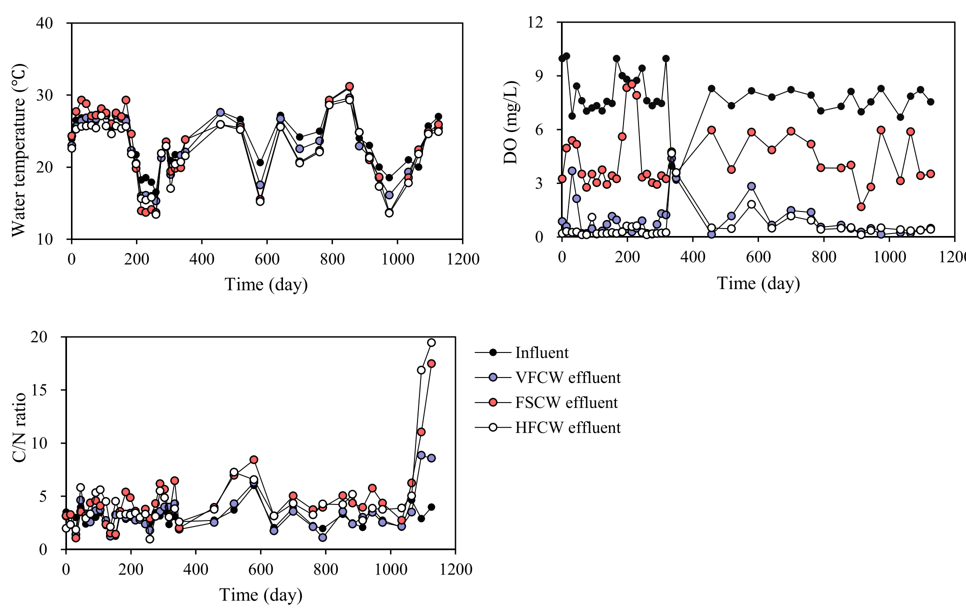


Fig. 2 Values of physico-chemical parameter in total influent and each process effluent from the hybrid CW throughout the experiment

Additionally, the C/N ratio increased from 2.97 to 3.29 in the VFCW because of the higher COD and TN removal efficiencies. Subsequently, in the SFCW, the concentration of COD increased, and the concentration of TN decreased, thus, the C/N ratio reached its highest value (4.59). Eventually, in the HFCW, both COD and TN were removed, and the C/N ratio stabilised at 4.53.

Suspended solid and organic matter

The time courses of the concentrations and removal efficiencies of SS, COD, and BOD in the hybrid CW are shown in Fig. 3 and Table 1, respectively. The hybrid CW had a significant effect on the removal of SS from mixed wastewater, with a total removal efficiency of 59–94% (average of 84%). The removal of SS was the highest in the VFCW (63%), followed by the HFCW (39%), while in the SFCW, it was negative (–17%). The organic matter in the mixed wastewater was effectively removed by the hybrid CW during long-term operation, and the total removal efficiencies of COD and BOD were 6–70 and 30–86% (average of 40 and 54%), respectively. Moreover, the removal of organic matter in the HFCW was the highest (26–53%), followed by the VFCW (21–40%), but negative in the SFCW (–39 to 7%).

Nitrogen

The time courses of the concentration and removal efficiencies of NH_4^+–N, NO_3^-–N, and TN in the hybrid CW are shown in Fig. 3 and Table 1, respectively. The influent concentration of NH_4^+–N and NO_3^-–N were 8.64 and 8.28 mg/L, accounting for 47 and 45% of TN (18.5 mg/L). After treatment, the total removal efficiencies of TN, NH_4^+–N, and NO_3^-–N were 22–90%, 2–97%, and –303–96% (averages of 54, 70, and 40%), respectively. In comparison, the removal efficiencies of TN and NH_4^+–N from different CW types were consistent, with the VFCW being the highest (27% of TN and 37% of NH_4^+–N), followed by the HFCW (15% of TN and 21% of NH_4^+–N), while the SFCW was the lowest (12% of TN and 13% of NH_4^+–N). However, there was little difference in the removal efficiencies of NO_3^-–N in the three CW types, including 12, 13, and 15% in the VFCW, FSCW, and HFCW respectively.

Phosphorous

The time course of the concentration and removal efficiencies of TP in the hybrid CW are shown in Fig. 3 and Table 1, respectively. Total phosphorous from the mixed wastewater could be effectively eliminated by the hybrid CW over an extended period, with a total removal efficiency of 13–88% (average of 46%). The removal efficiencies of TP in the sequence were VFCW (20%) > HFCW (15%) > SFCW (10%).

Comparison of hybrid CW effluent with wastewater treatment plant (WWTP) discharge

During a 3-year stable operation, the domestic-industrial mixed wastewater could be effectively purified by the hybrid CW, and the water quality compared with the discharge standards of WWTPs issued by the Ministry of Ecology and Environment of China (2003) is presented in Table 1. In the total effluent, the concentrations of SS, COD, BOD, NH_4^+–N, and TN were 1.00–5.50 (average of 3.23 mg/L), 10.3–54.8 (average of 30.8 mg/L), 3.32–6.19 (average of 4.88 mg/L), 0.30–8.87 (average of 2.68 mg/L), and 1.81–13.8 mg/L (average of 8.14 mg/L), respectively, all reaching the of I-A standard. Furthermore, TP from the total effluent reached the I-B standard with a concentration range of 0.27–1.65 mg/L (average of 0.89 mg/L). Collectively, the domestic-industrial mixed wastewater treated by the hybrid CW could meet the highest discharge standards of WWTPs.

Discussion

The effect of operation year on the hybrid CW performance

The removal loadings of pollutants from domestic-industrial mixed wastewater by the hybrid CW in different operation years are depicted in Fig. 4a. There was no significant difference in the removal loading of SS and TP among the different operation years ($p > 0.05$). Suspended solids in CWs are mainly removed by physical processes, such as filtration and precipitation (Kadlec, 2000), as well as by aerobic and/or anaerobic biodegradation (Manios et al. 2003). This depends on the presence of substrate and plant roots (Kadlec 2000), thereby achieving efficient removal of SS (Molle et al. 2008). Furthermore, TP in CWs is primarily removed by substrate adsorption, complexation, chemical precipitation, and absorption via plants and microorganisms (Xu et al. 2006). Because of the limitation of adsorption sites on the substrate surface, the adsorption and desorption of phosphorus tended to balance after a period of operation, and the continuous removal capacity of phosphorus in the CWs declined. Phosphorus-accumulating microorganisms may utilise the excess phosphorous (Wang & Mitsch 2000) and, therefore, maintain the continuous removal of phosphorus in CWs.

The removal loadings of other pollutants, that is, COD, BOD, NH_4^+–N, NO_3^-–N, and TN, were significantly lower in the first year than in the following two years ($p < 0.05$) (Fig. 4a). This was probably because the influent loading significantly increased in the following two years compared to that in the first year ($p < 0.05$) (Fig. 3). The increase in influent loading meant that more pollutants entered the CWs system per unit time, which aggravated the pollution

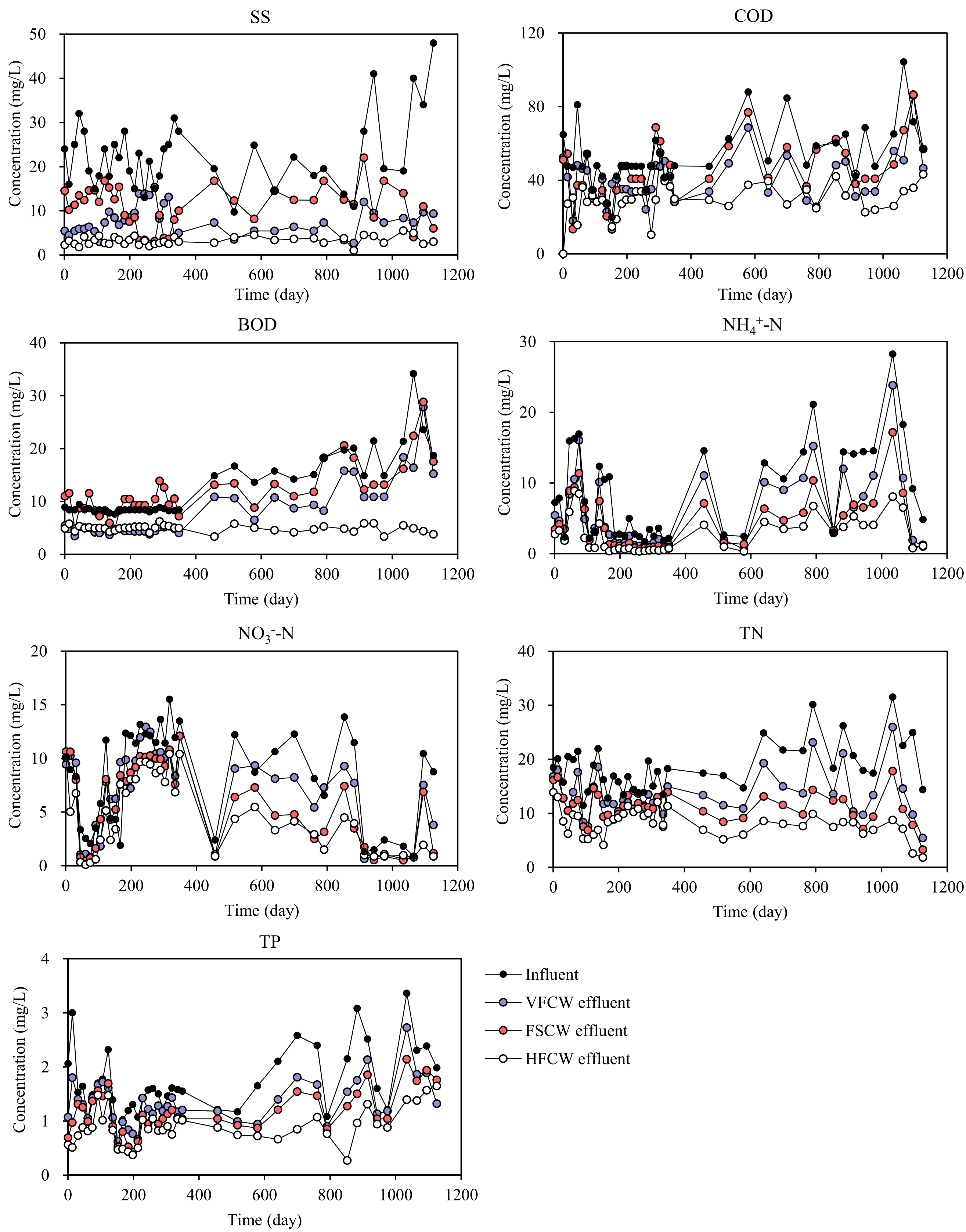
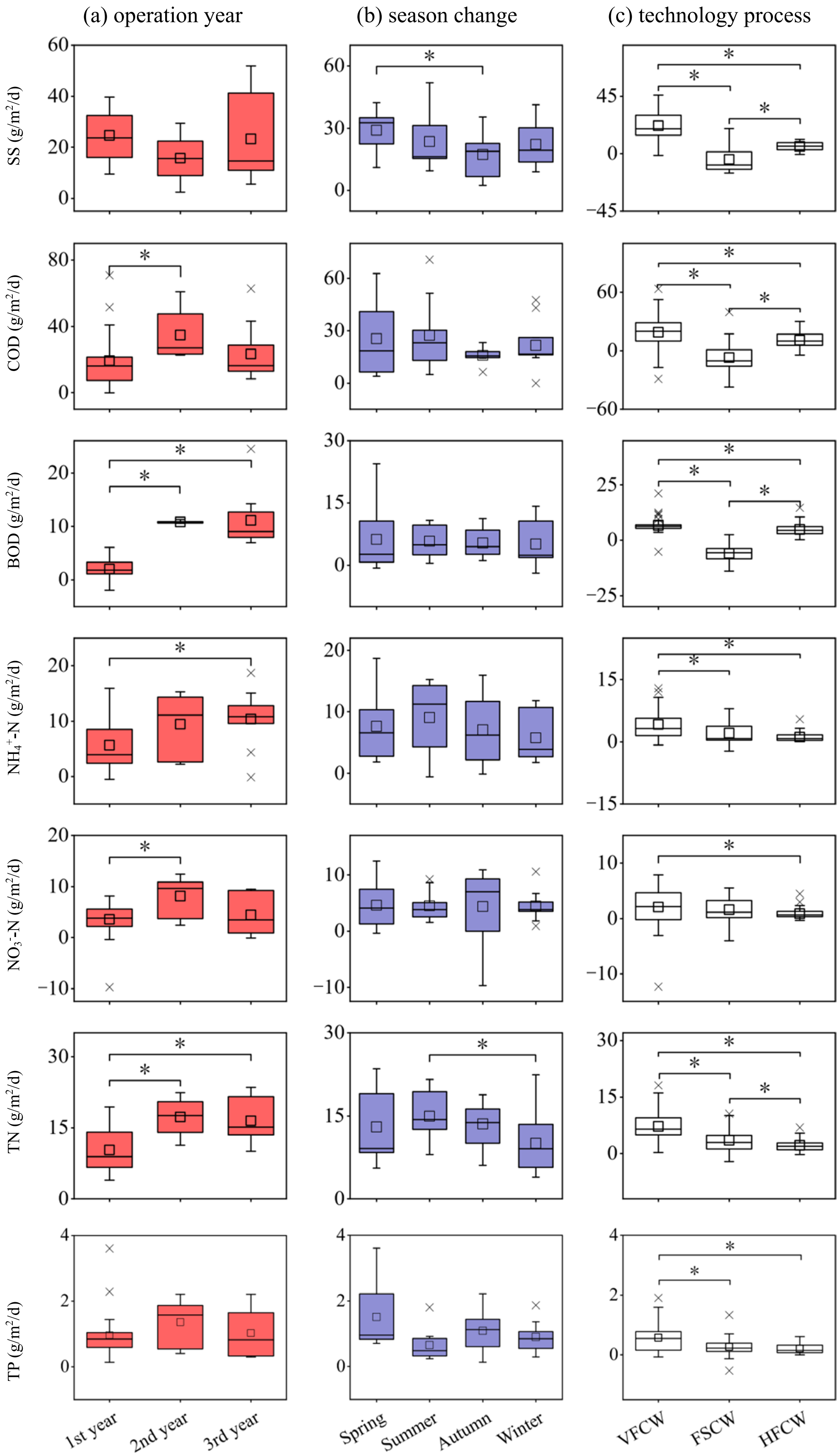


Fig. 3 Concentrations of the pollutant in the total influent and each process effluent from the hybrid CW throughout the experiment


(a) operation year
(b) season change
(c) technology process
SS (g/m²/d)
COD (g/m²/d)
BOD (g/m²/d)
NH₄⁺-N (g/m²/d)
NO₃⁻-N (g/m²/d)
TN (g/m²/d)
TP (g/m²/d)
1st year
2nd year
3rd year
Spring
Summer
Autumn
Winter
VFCW
FSCW
HFCW

◂**Fig. 4** Removal loadings of pollutant from the hybrid CW in different **a** operation years ($n = 24$ in the 1st year; $n = 6$ in the 2nd year; $n = 10$ in the 3rd year), **b** season changes ($n = 10$), and **c** technology processes ($n = 40$). The box and whisker plots on the left represent the 0th, 25th, 50th, 75th, and 100th percentiles. An asterisk indicates the significant differences at the 0.05 level according to one-way ANOVA

removal burden on the CWs. However, the removal loading of the hybrid CW had a significantly positive correlation with the influent loading of pollutants ($p < 0.05$) (Fig. 5), which meant that the removal capacity of the hybrid CW improved as the influent loading of the pollutant increased.

In the hybrid CW, the removal loadings of suspended solids and phosphorous were comparable during the three years, which was attributed to the synergistic effect of substrates, plants, and phosphorus-accumulating microorganisms, while the removal loadings of organic matter and nitrogen improved with the increase in influent loading. Moreover, the removal loading of NH_4^+–N (7.38 g/m^2/day) was much higher than that of multiple subsurface CWs worldwide (0.53 g/m^2/day) as counted by Vymazal (2007). These results confirm that the hybrid CW exhibited a stable long-term and high-efficiency response to changes in hydraulic loading.

The effect of season change on the hybrid CW performance

The removal loadings of pollutants from domestic-industrial mixed wastewater by the hybrid CW in different seasonal changes are shown in Fig. 4b. Generally, a warm climate is helpful for the growth of plants and microorganisms, which in turn promotes the uptake and degradation of pollutants, and vice versa (Zhang et al. 2015; Vega De Lille et al. 2021). Ávila et al (2017) found that the removal efficiency of pollutants (TN) from CWs reached 89% in summer, which was significantly higher than the 77% in winter. A similar phenomenon was observed in TN in this study, with the removal loading being significantly higher in summer (15.0 g/m^2/d) than that in winter (10.0 g/m^2/day) ($p < 0.05$). A significant positive correlation was observed between TN removal and WT ($p < 0.01$), as well as a negative correlation with DO ($p < 0.01$) (Fig. 5). This indicates that anaerobic denitrification was the main way to remove TN in hybrid CWs, and a higher WT was beneficial for microbial activity (He et al. 2018). The results reported by Akratos & Tsihrintzis (2007) showed that WT had a significant effect on NH_4^+–N and TKN, and that microbial denitrification was not active when WT < 15 °C, while ideal results could be achieved when WT ≥ 15 °C. Correspondingly, the removal efficiency of NH_4^+–N in the subsurface CWs was 37.9% at WT < 15 °C, and at WT > 15 °C, the removal efficiency was 69.1%, which was consistent with the previous report.

In contrast, there was no significant difference of the removal loading of COD, BOD, NH_4^+–N, NO_3^-–N, and TP among different seasons ($p > 0.05$), with values of 16.0–27.3, 5.13–6.23, 5.76–9.08, 4.38–4.60, and 0.65–1.51 g/m^2/day, respectively (Fig. 4b). Meanwhile, no significant correlation was found between the removal loading of these pollutants and WT ($p > 0.05$) (Fig. 5). Consequently, hybrid CWs are capable of resisting variations in the decontamination ability caused by seasonal changes, thereby maintaining stable and efficient performances throughout the year.

The effect of technology process on the hybrid CW performance

The removal loadings of pollutants from domestic-industrial mixed wastewater by the hybrid CW in different technology processes are shown in Fig. 4c. The SS, COD, and BOD were removed more efficiently in the subsurface processes (VFCW and HFCW) than in the surface processes (SFCW). Considering the nature of suspended solids and organic matter, subsurface processes filled with substrates can effectively intercept and/or eliminate suspended particulates via substrate adsorption. Substrates in the subsurface processes also provide attachment sites for plant and microbial growth, which is beneficial for plant uptake and microbial degradation of organic matter. Conversely, it is difficult for surface processes to remove SS because of the lack of a substrate. After years of aquatic plant growth in surface processes, the biomass in water increases with the accumulation of remains, leading to a higher content of suspended solids and organic matter. In addition, the correlation analysis showed a significant positive correlation between the removal loading of SS and the C/N ratio ($p < 0.05$) (Fig. 5), indicating that some organic particles were likely mixed in the suspended solids, which explains why the suspended solids and organic matter had similar removal results.

Nitrogen was efficiently removed in all the technological processes of the hybrid CW (Fig. 4c). According to the correlation analysis (Fig. 5), the removal loading of TN and NH_4^+–N showed a significant positive correlation ($p < 0.01$), while the removal loading of NH_4^+–N and NO_3^--N showed a significant negative correlation ($p < 0.05$), and the removal loading of TN and DO showed a significant negative correlation ($p < 0.01$). This indicated that TN removal mainly depended not only on the reduction of NH_4^+–N, but also the anaerobic reaction, such as denitrification, which was the major nitrogen removal pathway in the hybrid CW.

Additionally, the removal loading of BOD showed a significant positive correlation with TN and NH_4^+–N ($p < 0.01$), and the C/N ratio showed a significant positive and negative correlation with COD ($p < 0.01$) and NH_4^+–N ($p < 0.05$), respectively (Fig. 5). This suggests that carbon sources are an important factor in the removal of nitrogen. It has been reported that most wastewaters with a C/N

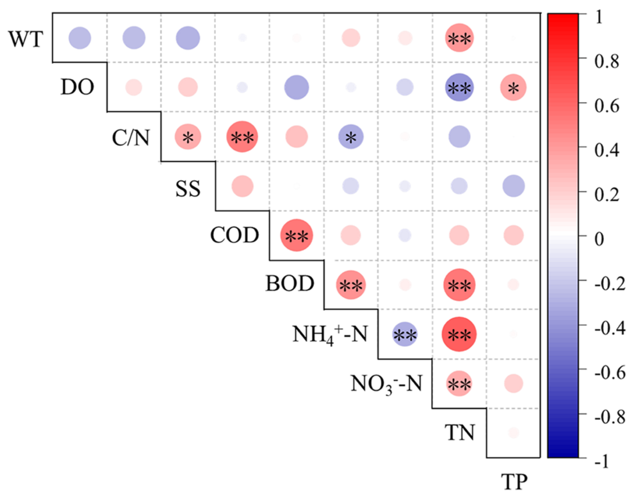


Fig. 5 Correlation between the influent parameters and pollutant removal loadings. Single and double asterisks indicate the significant correlations at the 0.05 level and 0.01 level according to Pearson's correlation, respectively

ratio of 3–5 are recognised as sufficient to support the metabolism of heterotrophic denitrifying bacteria, thereby achieving a relatively high nitrogen removal efficiency (Du et al. 2016; Tian & Yu 2020). When the C/N ratio > 4, the denitrification rate reaches its highest value (Cao et al. 2013). The removal loading of TN and NH_4^+–N was highest in the VFCW (Fig. 4c), which benefited from the ideal C/N ratio (3.29) and high OTC value (27.2 g/m^2/day) in this process (Table 1), which was favourable for nitrification. However, in the following process of SFCW and HFCW, the C/N ratio (4.53–4.59) increased, OTC values (3.79–11.0 g/m^2/day) decreased, and the denitrification reactions gradually dominated.

Since substrate adsorption is the main mechanism for phosphorus removal in CWs (Chung et al. 2008), subsurface processes with substrates were more efficient for TP removal than surface processes without substrates. Furthermore, removal loading of TP had a significant positive correlation with DO ($p < 0.05$) (Fig. 5), and the removal loading of TP was highest in the VFCW (Fig. 4c) with the highest OTC value (Table 1). Hence, the organic phosphorus from the mixed wastewater was oxidised into inorganic phosphorus in the hybrid CW, which was easily absorbed and utilised by plants and microorganisms.

In a word, the OTC was improved in the bed of the VFCW (Stefanakis & Tsihrintzis 2012), which provided good conditions for the nitrification of NH_4^+–N into NO_3^-–N (Ávila et al. 2013). The SFCW played a buffering role in the system, but simultaneously became a reservoir for nutrients (Qualls & Heyvaert 2017); and HFCW created a facultative environment suitable for aerobic and anaerobic reactions. In the presence of organic matter, denitrifying bacteria could reduce nitrate to nitrogen (He et al. 2016). Through this method of connecting different processes in series, it better corresponded to the complex characteristics of domestic-industrial mixed wastewater and realised the deep removal of organic matter and nutrients.

Comparison of removal kinetics between hybrid CW and other CWs

The k_A values of the hybrid CW compared to those of the other CWs are listed in Table 2. For research on the treatment of domestic wastewater in CWs, it was found that the k_A values of hybrid CWs (12–80 m/year) were higher than those of a single CW (2.4–51 m/year), and the k_A values of full-scale CWs (42–80 m/year) were higher than those of pilot-scale CWs (12–20 m/year). In this study, the k_A values of the hybrid CW (VF-SF-HF) for the treatment of domestic-industrial mixed wastewater ranged from 93–283 m/year, which was much higher than that of other CWs. It has been reported that k_A values are mainly dependent on influent concentrations, hydraulic loading, water level, and weather conditions (Kadlec 2000; Zurita et al. 2009). This further proved the long-term stable decontamination performance of the hybrid CW for high-loading mixed wastewater under tropical/subtropical climates. Moreover, a high k_A value implies a reduction in the area required for CWs (Zurita et al. 2009). The k_A values obtained in this study will be useful as a reference for the design and application of hybrid CW in the tropical and subtropical regions.

Table 2 Removal rate constants (K_A) calculated for the hybrid CW

	Scale	Wastewater	K_A (m/year)							Reference
			SS	COD	BOD	NH_4^+–N	NO_3^--N	TN	TP	
Hybrid CW (VF-SF-HF)	Full	Industrial-domestic	283	98	266	189	107	137	93	This study
Hybrid CW (VF-HF)	Full	Domestic	–	–	20	18	–	12	17	(Öövel et al. 2007)
Hybrid CW (VF-HF)	Pilot	Domestic	80	42	57	47	–	–	–	(Melián et al. 2010)
HFCW	Pilot	Domestic	26	27	30	8.8	11	12	–	(Zurita et al. 2009)
HFCW	Pilot	Domestic	51	28	–	2.4	18	2.7	–	(Belmont et al. 2004)

Conclusions

The hybrid CW (VF-SF-HF) had a continuously efficient treatment performance for domestic-industrial mixed wastewater during a three-year operation, and the effluent quality reached the highest discharge standard of a WWTP. The removal loading of most pollutants improved with an increase in influent loading in different operational years, which was hardly affected by seasonal changes. The k_A values of the hybrid CW for various pollutants in domestic-industrial mixed wastewater ranged from 93–283 m/year, which was much higher than that reported in other related studies. First, a variety of pollutants from the mixed wastewater were effectively removed in the subsurface processes (VFCW and HFCW) via substrate adsorption and degradation of the attached biofilm. The higher DO and OTC values in the VFCW were favourable for the occurrence of aerobic pathways (such as nitrification and inorganic phosphorus oxidation). In addition, with the large consumption of oxygen in the previous process, the oxygen-enriching capacity of the surface processes (SFCW) provided aerobic potential for the next stage. In particular, the plant debris in the SFCW temporarily increased the organics and suspended solids, further increasing the C/N ratio, which was beneficial for denitrification as the main nitrogen removal pathway in the HFCW. It has been proven that the hybrid CW has a long-term and stable decontamination performance for high-loading mixed domestic-industrial wastewater. The results obtained from this study will be helpful for the application of hybrid CW in mixed wastewater treatment in the tropical and subtropical regions.

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Data availability The datasets used and/or analysed during the current study are available from the corresponding author upon reasonable request.

Declarations

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