Effect of oxygen states in horizontal subsurface flow constructed wetlands on the removal of organic matter, nutrients, some metals and octylphenol

An Truong Nguyen, Tam Minh Thi Le*, Viet Quoc Tran, Viet Ngoc Truong, Luan Thanh Nguyen, Phi Hoang Tan Nguyen, Trang Huyen Thi Nguyen

Abstract—**Constructed wetland is a low cost, effective technology and it is still in the state of improvement to enhance the treatment efficiency, especially in nutrient and trace elements treatment. This study investigated the effect of aerobic and anoxic conditions in Horizontal Subsurface Flow Constructed Wetland (HSFCW) on nutrient, organic, metal and Octylphenol - OP (Endocrine disrupting chemical) treatment. Two HSFCWs were constructed: HSFCW1 with three aerobic compartments; HSFCW2 with two aerobic compartments, one anoxic compartment. The two HSFCWs had the same design parameters (fiters, plants), except oxygen conditions. The results showed that aerobic and anoxic HSFCW may increase the efficiency of Nitrogen removal by 10%, but decreased by 11% in the efficiency of OP treatment (one of the EDCs). The efficiency of treatment of pollutants, including NH_4^+-N, COD, TP, Mn, Fe, Al and Cu between two HSFCWs were not significantly different; the average efficiency was 99%, 84%, 97%, 96%, 96%, 72% and 73%, respectively. Therefore, the anoxic compartment of HSFCW still provided the effective removal of organic matter, metals and octylphenol, but it also improved nitrogen removal efficiency by up to 92%.**

Index Terms—**Horizontal Subsurface Flow Constructed Wetland, Oxygen, Phragmites australis, Nitrogen, Metals, Octylphenol.**

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1 INTRODUCTION

Inefficient wastewater treatment or directed discharge pollutants containing nutrient contaminants (nitrogen, phosphorus), organic (e.g. BOD, COD), hazardous (e.g. metals, PCB) and trace elements (Antibiotics, pesticides, endocrine disrupting chemicals – EDCs) can pollute the water environment. Over-discharge of nutrient contaminants leads to eutrophication, which is one of the global problems that negatively impact on water quality for domestic, industrial and agricultural usage [1]. In addition to eutrophication, the presence of trace metals, EDCs in water threatens to human health, especially endocrine system disorders [2]. Biological process or biofilm (MBR) is a widely used technology nowadays, but demanding high costs of operating and consuming large amounts of energy; This leads to a limited access of the remote rural areas to these technologies [3]. Therefore, there is a need for an alternative technology that ensures the ability to remove nutrient contamination, trace elements, as well as minimal energy demand and operating costs. One of friendly environment technology, Constructed Wetlands (CWs) is a technology that satisfies the costs of operating and removal efficiency [4]. CWs are built to simulate the processes of treating pollutants in the nature, with the appropriate human modification for efficient wastewater treatment through the physical and chemical, biological processes thanks to the composition of plant, filter materials (sand, gravel, rock) and microorganisms [5], they can remove 51% TN, 54% TP, 63% COD and also hazardous substances such as metals, EDCs [6]. The heavy metals are removed or retained through several mechanisms including: uptake of vegetations, adsorption on sediment or deposition in by both aerobic and anoxic/anaerobic processes [7]. These mechanisms work also on EDCs removal by constructed wetlands, because the main removal pathways of the target EDCs is their biodegradation [8].

Although plants and microorganisms are capable of treating nutrient contaminants like nitrogen, in order to remove completely nitrogen (i.e. Nitrogen is absorbed by microorganisms, plants or turn back gas N2), it is necessary to ensure both nitrification and denitrification occurring in CWs [9]. The low dissolved oxygen concentration (DO) in CWs leads to an incomplete nitrification and the nitrogen is not effectively treated [9]. There is some method to raise DO in CWs, such as applying Horizontal Subsurface Flow Constructed Wetland (HSFCW) and using an aeration pump to ensure aerobic conditions in HSFCW, it can increase the TN removal by 25% to 51% compared to no-aeration CWs [9].

There have been many studies to improve the efficiency of nutrient contamination in CWs by maintaining aerobic condition for nitrification. However there are very few studies about the denifitrication in HSFCW, even the denitrification is extremely necessary for TN entirely removal [10]. This study evaluated the effect of the combined aerobic and anoxic HSFCW on nutrient, organic, metals and octylphenol - OP (Endocrine disrupting chemical) treatment efficiency.

2 MATERIALS AND METHODS

2.1. System configuration

Two HSFCW models were located at Bach Khoa University, exposed to natural air with a size of 2.4m x 0.9m x 0.8m (L x W x H), each HSFCW was divided into 3 compartments, each compartment 2.4m x 0.3m x 0.8m. The three-compartment HSFCW1 was aeration; HSFCW2 only having the first and third aeration compartments and the second compartment was prevented to the oxygen (Fig 1). Both HSFCW systems used *Phragmites australis* (except for second compartment of HSFCW 2), filter materials were 50 cm thick, including 5 cm gravel (D = 30 - 50 mm), 20 cm small gravel (D=5 – 8mm), 15cm quartz sand (D = 1 - 2mm) and 10cm rock (D = 12-15mm) in the order from the bottom to the HSFCW surface.

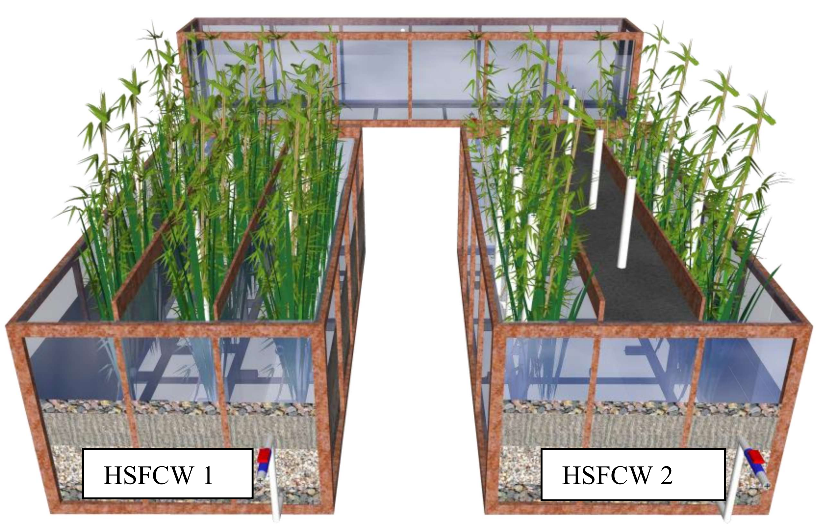

Fig 1. Schematic of the pilot-scale HSFCW, HSFCW1: aerobic HSFCW, HSFCW2: combined aerobic and anoxic HSFCW

2.2. Operation conditions and sampling

The influent wastewater used in this study was diluted landfill leachate which was obtained from a closed landfill in Ho Chi Minh City (Vietnam). The characteristics of the influent are shown in Table 1. In the first 60 days, the systems were fed with tap water and diluted wastewater for bed layer stabilization and plant adaptation. Then they were operated officially in 30 days with 6 days of hydraulic retention time (HRT) and 60L/day of hydraulic loading rate (HRT), it means the wastewater was kept two days in each compartment of HSFCW.

Samples were taken every 2 days, at four sampling points: influent, end of the first compartment, end of the second compartment and end of the third compartment (output sample) of each HSFCW. Environmental parameters are checked at the sampling site. Samples were analyzed in the sampling day, or freezed at -18°C for later analysis. During the 30 days operation, there were four operation times equal to four HRTs, each HRT lasted 6 days and. The values in Table 1 were the average values of 4 operation times (N=4).

TABLE 1.
INFLUENT CHARACTERISTICS (MEAN ± STANDARD DEVIATION, N=4) IN HSFCW

Nutrient (mg/L)		Metals (µg/L)		EDCs (ng/L)		DO (mg/L)
COD	381.11 ± 40.20	Al	66.18 ± 6.26	OP	412.59 ± 70.98	0.43 ± 0.15
TP	32.96 ± 3.47	Fe	1337.93 ± 172.88	-	-	-
NH_4^+-N	127.87 ± 6.49	Mn	91.15 ± 9.82	-	-	-
NO_3^--N	1.96 ± 0.21	Cu	50.78 ± 5.20	-	-	-
NO_2^--N	3.94 ± 3.51	-	-	-	-	-

2.3. Analytical methods and statistical analyses

Chemical Oxygen Demand (COD), Ammonium (NH_4^+-N), Nitrate (NO_3^--N), Nitrite (NO_2^--N), Total Phosphorus (TP) and Metals (Al, Fe, Mn, Cu) were analyzed according to Standard Methods [11]. Octylphenol (OP) in wastewater were determined after filtration and processed as previously described by Minh et al. (2016) [12]. Dissolved Oxygen (DO) were measured by Multi WTW 3210.

All the data and figures were described in this study, which were the average of four HRT experiment with standard deviation. Paired t-test (95% confidence level) was performed to examine the effect of DO concentration on the pollutant removal between the aerobic CWs (HSFCW1) and the combined aerobic/anoxic CWs (HSFCW2). Excel 2016 (Microsoft Corporation) was applied to achieve these purposes.

3 RESULTS AND DISCUSSION

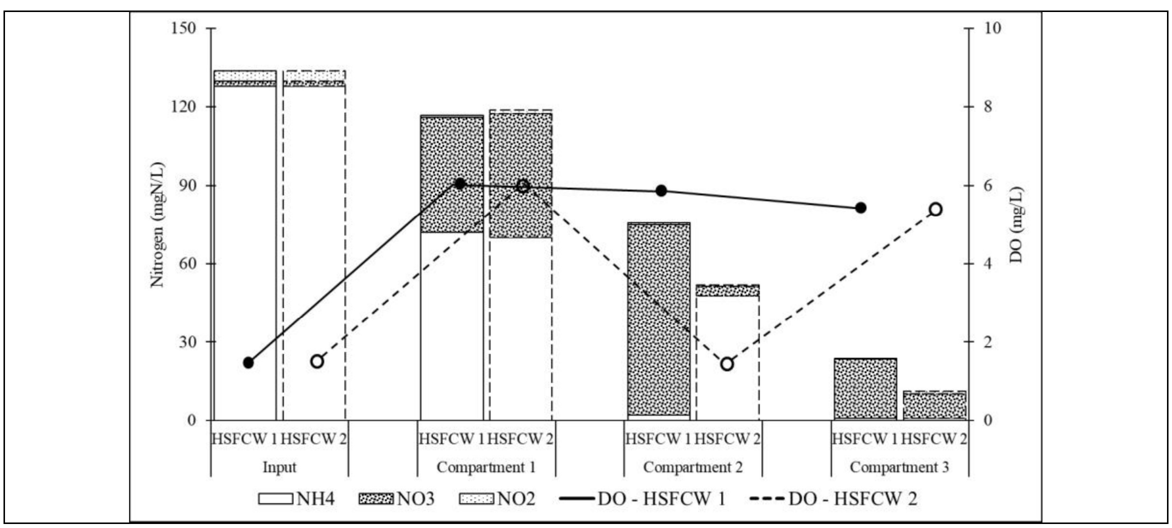

Fig 2. Comparison the changes of NH_4^+-N, NO_3^--N, NO_2^--N concentrations between HSFCW1 and HSFCW2

3.1. Effect effect of aerobic and anoxic conditions HSFCW on on nitrogen removal efficiency

The total nitrogen concentration (TN) including NH_4^+-N, NO_3^--N and NO_2^--N of both HSFCWs gradually decreased following each compartment. There was a significant difference in the concentrations of NH_4^+-N or NO_3^--N in the second compartment between two HSFCWs ($P < 0.01$) which helped HSFCW2 (combined aerobic and anoxic CWs) get the TN removal ability better than HSFCW1 (aerobic CWs), as results 92% and 82% of TN treatment efficiency, respectively. However the t-test results showed that there was no difference in NH_4^+-N treatment efficiency between the aerobic and combined HSFCW ($P > 0.05$), their efficiency reached up to 99% of NH_4^+-N removal. The main reason leading to TN removal differences in two HSFCWs was the ineffective treatment of NO_3^--N in the second compartment of HSFCW1.

The NH_4^+-N concentration of the two HSFCWs decreased by 44%, equivalent to 55 mg/L/2d after going through the first compartment. The reduction of NH_4^+-N concentration was due to the absorption of reeds and microorganisms, and thanks to the nitrification process (DO> 5 mg/L) that converted ammonium into nitrate. Thus, NO_3^--N levels increased to 45 ± 2 mg/L/2d after the first compartment of HSFCWs.

The difference in design between the two HSFCWs was the second compartment of the HSFCW2, this compartment was designed to prevent the oxygen contact, while the second compartment of the HSFCW1 was aerated as the first and third compartment. For the denitrification in CWs, the DO requirement should lower than 0.5 mg/L [1], DO concentration in the second compartment of HSFCW2 was 0.5 ± 0.1 mg/L still ensured the denitrification performance, this was illustrated in Fig 2, with the reduction of NO_3^--N in HSFCW2 was 45 ± 8 mg/L/2d. Meanwhile, the levels of NO_3^--N in the second compartment of HSFCW1 continued to increase by 29 ± 5 mg/L/2d. It can be explained by the nitrification in HSFCW1, because the DO in this compartment was still higher than 5 mg/L, which was able to convert NH_4^+-N into NO_3^--N. Therefore, NH_4^+-N concentration was removed 99% even just at the second compartment of HSFCW1. On the other hand, based on Fig 2, it was found that TN in the second compartment of HSFCW1 decreased by about 40 mg/L, this TN reduction was mainly the reduction of NO_3^--N. The reduction of NO_3^--N, in this case, was not due to the denitrification, but the NO_3^--N absorption of the reed and microorganisms, which ranged from 20 – 40 mg/L/2d. This means that plants and microorganisms in the HSFCW play an important role in the NO_3^--N treatment, which was easily seen in the third compartment (aerobic compartment) of both HSFCWs.

The third compartment of the two systems was aerobically designed, DO > 5 mg/L, thus the nitrification happened in both HSFCW. Finally, NH_4^+-N in wastewater was eliminated 99% at this compartment, about 47 ± 5 mg/L/2d in HSFCW2. However this nitrification was not significant for HSFCW1, since NH_4^+-N was already removed 99% in the second compartment, but NO_3^--N was not significantly reduced at that compartment. It was also said that there still was a large amount of NO_3^--N in HSFCW1 while its concentration in HSFCW2 was low. Therefore HSFCW2 gave a better NO_3^--N treatment efficiency than HSFCW1 as well as TN removal after all.

3.2. COD and TP treatment

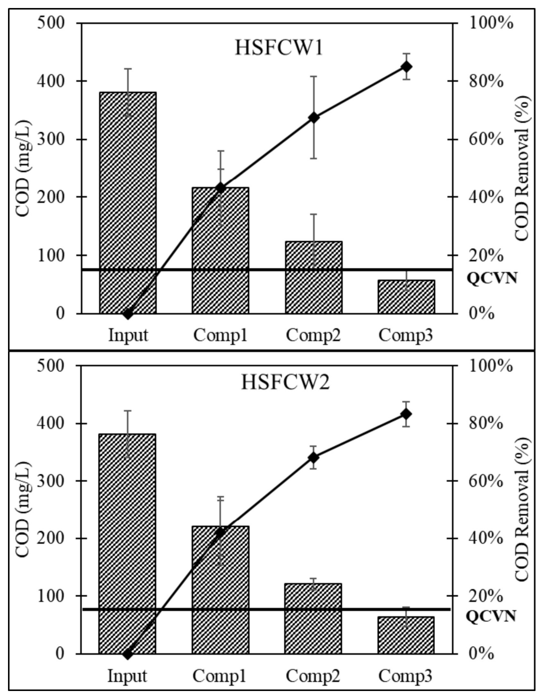

Fig 3. Changes of COD concentration and removal efficiency following each compartment (a) HSFCW1 and (b) HSFCW2

During the study period, the COD concentration decreased gradually through each compartment (Comp), the efficiency achieved over 80% (Fig 3) and there was no significant difference in removal efficiency between the two HSFCWs. Wastewater was transferred through the three compartments of the HSFCW with 6 days of HRT, equivalent to 2 days per compartment. In 6 days of HRT, the treatment effect was significantly correlated with HRT ($R^2 > 0.9$, Fig 4), the effective treatment increased by 30 - 40% compared to the previous compartment, however the prolongation of HRT may result in a lack of correlation between HRT and the removal efficiency because of the treatment limitation of plants and microorganisms. Although the removal efficiency of COD could be improved under aerobic condition, in this study COD concentration in the anoxic condition (compartment 2 of HSFCW2) still provided a good treatment efficiency and there was no difference to the aerobic compartment of HSFCW1 ($P > 0.05$). This result is quite similar to the research of Li et al. (2014) [9] which was stated that if the first and the last compartment of HSFCW were the aerobic conditions, the COD treatment efficiency would be ensured. In this study, all the first and third compartment of both HSFCWs were kept for DO > 5 mg/L, so the COD efficiency of the two systems was quite similar. The efficiency of COD removal of HSFCW1 and HSFCW2 was 85% and 83%, respectively, and the outlet concentrations were 57 ± 17 mg/L and 64 ± 17 mg/L, they all met the National Technical Regulation on Industrial Wastewater (QCVN 40:2011/BTNMT) (Fig 4).

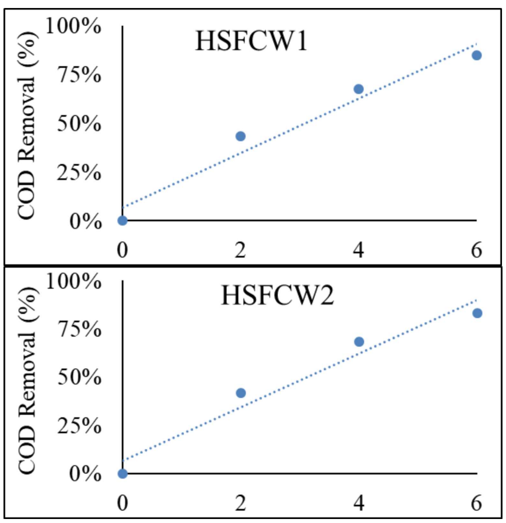

Fig 4. The correlation between COD removal and HRT (day)

The TP removal ability of the HSFCWs also has the same trend with COD for both HSFCW1 and HSFCW2. The efficiency of TP removal of HSFCW1 and HSFCW2 was 98% removal and 96% respectively (Fig 5). In addition, in 6 days of HRT, TP removal efficiency has a high correlation with HRT ($R^2 > 0.8$, Fig 6), it is also consistent with COD removal efficiency. At the end of the six days of HRT, the outlet concentration of the HSFCW1 and HSFCW2 the were 0.8 ± 0.1 mg/L and 1.4 ± 0.4 mg/L, they all met QCVN 40:2011/BTNMT. Moreover, based on Fig 5 found in the second compartment of two HSFCWs, the TP removal efficiency reached to 90%. It was also said that the usage of the anoxic or aerobic condition in the second compartment of HSFCW did not cause a significant effect to the TP removal efficiency ($P > 0.05$).

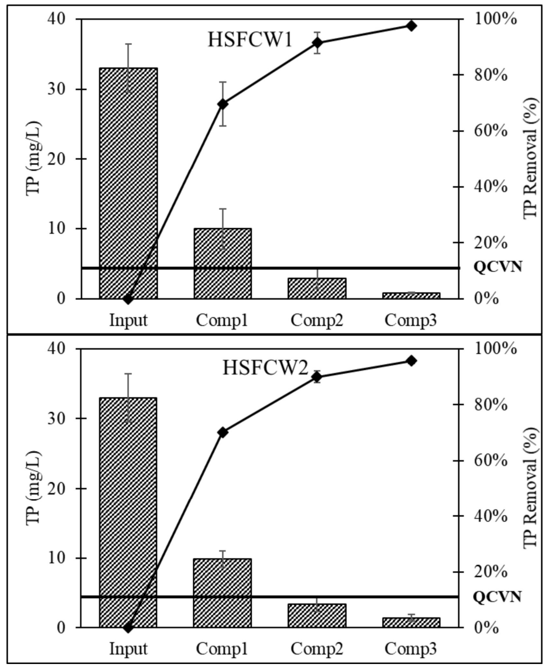

Fig 5. Changes of TP concentration and removal efficiency following each compartment (a) HSFCW1 and (b) HSFCW2

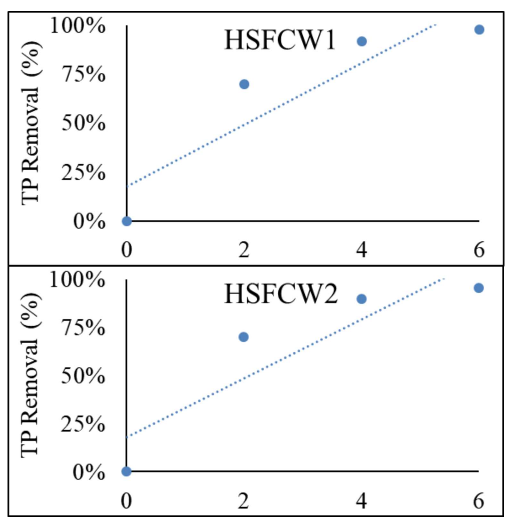

Fig 6. The correlation between TP removal and HRT (day)

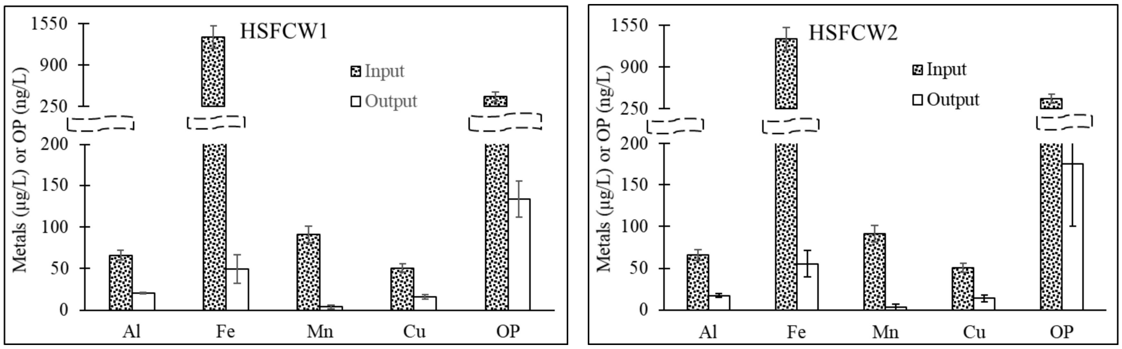

Fig 7. Input and output concentrations of Metals and EDCs in HSFCW1 and HSFCW2

3.3. Metals and EDCs treatment

The removal efficiency of metals ranged from 68% to 97% in both HSFCWs, especially Fe and Mn could be treated up to 90% (Fig 7), there was no difference in the efficiency of metal treatment between the aerobic HSFCW and the combined aerobic/anoxic HSFCW ($P > 0.05$) in the metal removal. These results are also consistent with the review of Vymazal et al. (2016) on the heavy metals removal by HSFCW [7].

However, for the OP parameter (one of the EDCs) showed a slight difference, the HSFCW1 performed better than the HSFCW2, the efficiencies were 68% and 57% respectively. This difference can be attributed to the second compartment of the HSFCW2 which was lacked oxygen and vegetation. Although in the anoxic conditions, some of the EDCs could be removed better than aerobic HSFCW such as NPEO [8], OP in this study was not, the HSFCW1 with all three aerobic compartments and planted for better efficiency than the HSFCW2 that contained only two aerobic compartments.

4 CONCLUSIONS

The combination of aerobic and anoxic HSFCW has enabled both nitrification and denitrification processes, which helped the HSFCW2 removed nitrogen up to 92%. In addition, the anoxic position in mid-HSFCW did not reduce the removal efficiency of other pollutants. Therefore, there were no significant differences in effective treatment of ammonium, COD, Metals, except OP. The removal efficiency for NH_4^+-N, COD, TP, Mn, Fe, Al and Cu respective were 99%, 84%, 97%, 96%, 96%, 72% and 73%. The removal efficiency of OP was 68% and 57% for HSFCW1 and HSFCW2, respectively.

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Tác động của điều kiện oxi đến hiệu quả xử lý chất ô nhiễm dinh dưỡng và một số kim loại nặng và Octylphenol

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***Tóm tắt*—Đất ngập nước kiến tạo là một công nghệ thân thiện với môi trường, có chi phí vận hành thấp nhưng vẫn đảm bảo hiệu quả xử lý, tuy nhiên cần có một số cải thiện về hiệu quả xử lý, đặc biệt chất dinh dưỡng và các chất vi lượng. Nghiên cứu này đánh giá tác động của điều kiện hiếu khí và thiếu khí trong hệ thống đất ngập nước kiến tạo dòng chảy ngang (HSFCW) tác động lên hiệu quả xử lý chất dinh dưỡng, hữu cơ, kim loại và octylphenol - OP (chất gây rối loạn nội tiết). Hai mô hình HSFCW được xây dựng với thông số thiết kế giống nhau, mỗi hệ thống có ba ngăn, HSFCW1 có ba ngăn hiếu khí, HSFCW2 có hai ngăn hiếu khí và một ngăn thiếu khí, cả ha hệ thống đều sử dụng vật liệu lọc là cát, sỏi và thực vật (Phragmites australis) giống nhau. Kết quả cho thấy hệ thống kết hợp hiếu khí và thiếu khí giúp nâng hiệu quả xử lý Ni-tơ thêm 10%, tuy nhiên lại giảm 11% hiệu quả xử lý OP (một trong các EDCs). Hiệu quả xử lý các chất ô nhiễm gồm NH_4^+-N, COD, TP, Mn, Fe, Al và Cu giữa hai hệ thống không có sự khác biệt lớn, hiệu suất trung bình lần lượt là 99%, 84%, 97%, 96%, 96%, 72% và 73%. Việc kết hợp với điều kiện thiếu khí giúp HSFCW nâng cao hiệu quả loại bỏ Ni-tơ, giúp loại bỏ đến 92%, ngoài ra ngăn thiếu khí của HSFCW vẫn đem lại hiệu quả loại bỏ tốt các chất hữu cơ, kim loại và octylphenol.**

***Từ khóa*—Đất ngập nước kiến tạo dòng chảy ngang, Nồng độ oxi, Phragmites australis, Nitrogen, Kim loại, Octylphenol.**