Short Communication

Assessment and Optimization of Formaldehyde Removal Using Tidal Flow Constructed Wetlands

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Abstract

Assessment of formaldehyde (HCHO) removal using constructed wetlands (CWs) was scarcely ever reported. Here, the feasibility of HCHO removal was studied in tidal flow CWs (TFCWs) with/without wetland vegetation (*Canna indica* L.). The HCHO removal efficiencies of TFCWs with various initial loads (25, 50, 75, and 100 mg L^{-1}) were investigated, then the impact of influent pH and DO values on HCHO removal was evaluated. Results showed that microbiological degradation was the main HCHO removal pathway. The aerobic condition (DO concentration >4 mg L^{-1}) and neutral/weak alkaline pH (approximately 7-8) was favorable for the HCHO removal. In order to upgrade the HCHO removal potential, a two-stage cyclic CW (t-TFCW) was designed. For an influent HCHO concentration around 100 mg L^{-1}, t-TFCW showed a stable and efficient HCHO removal performance, where the average HCHO removal rate was found to be 98.1% after a 6- hour treatment.

Introduction

Formaldehyde (HCHO) was known as a carcinogenic volatile organic compound (VOC), which exists in organisms or external environments in the forms of gaseous, dissolved, or combination state [1]. The HCHO water pollution is generally present in the discharge water of chemical and pharmaceutical industries. The condensation water of phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins, as well as the wash water of urotropin synthesis were the typical high HCHO-containing wastewater [2]. In addition, the formalin solution used in biological and medical fields for preservative treatment is also the emission source of HCHO water pollution [3].

Up to the present, many scholars have been devoted to the HCHO pollution abatement. Various adsorbents such as bio-char and Alumina nanoparticles were developed to capture the HCHO from the air and contaminated water [4, 5]. However, the approach of physical adsorption is not suitable for practical engineering applications because of the reversibility

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of the adsorption process. Also, the removal of HCHO via advanced oxidation processes, including Fenton reagent oxidation, photocatalytic oxidation, wet oxidation process, and other catalytic oxidation with efficient catalysts, have been widely studied [6]. Even though these methods exhibit a high-performance for HCHO removal, they are costly and pose a risk of secondary pollution. Compared with the methods mentioned above, biological treatment can achieve considerable and sustainable HCHO removal at a low cost. Previous studies have demonstrated that sustainable removal of low concentration HCHO can be achieved by phytoremediation [7]. To date, a few microbiological treatment cases for the HCHO removal have been reported. For example, with the adding of methanol, an efficient HCHO degradation was achieved in a membrane-aerated biofilm reactor [8]. Maria et al. [9] proved that the presence of a static magnetic field increased the HCHO removal efficiency of activated sludge. Moreover, an anaerobic sequencing batch biofilm reactor was reported to be an efficient device for HCHO removal, while the disadvantage is that the anaerobic HCHO degradation process resulted in the accumulation of byproducts [10]. Since both plants and microorganisms have the potential to eliminate HCHO pollution, the combined remediation of plant and microbe may be a practical approach for treating HCHO wastewater.

CWs are a reliable wastewater treatment technology with low investment and low energy consumption, in which the wetland vegetation and the domesticated microbial communities have the potential to remove a wide variety of pollutants from wastewater. Many studies indicated that CWs could remove dissolved organic matter (DOM) efficiently [11], and also showed a high-performance for the removal of toxic organic pollutants [12]. However, research on HCHO removal using CWs was still scarcely reported. Only one previous study proposed that CWs were probably a convenient device for HCHO removal [13]. Therefore, there is a lack of investigation on HCHO removal using CWs, and there is no report on the optimization of wetland structure to obtain an efficient HCHO removal.

This study aims to evaluate the potential of HCHO removal using TFCWs. The removal efficiencies of HCHO at various influent concentrations (25, 50, 75, and 100 mg L^{-1}) were determined, as well as for TFCWs of non-vegetated and vegetated. Moreover, the impact of influent pH and DO on HCHO removal was assessed in a TFCW with vegetation. Based on the exploration in the TFCWs, a two-stage cyclic TFCW was developed, which showed high efficiency of HCHO removal.

Material and Methods

Laboratory-Scale Wetlands and Synthetic Wastewater

Polyvinyl chloride (PVC) cylinders with a height of 52 cm and an internal diameter of 16 cm were used to simulate lab-scale vertical flow wetland devices
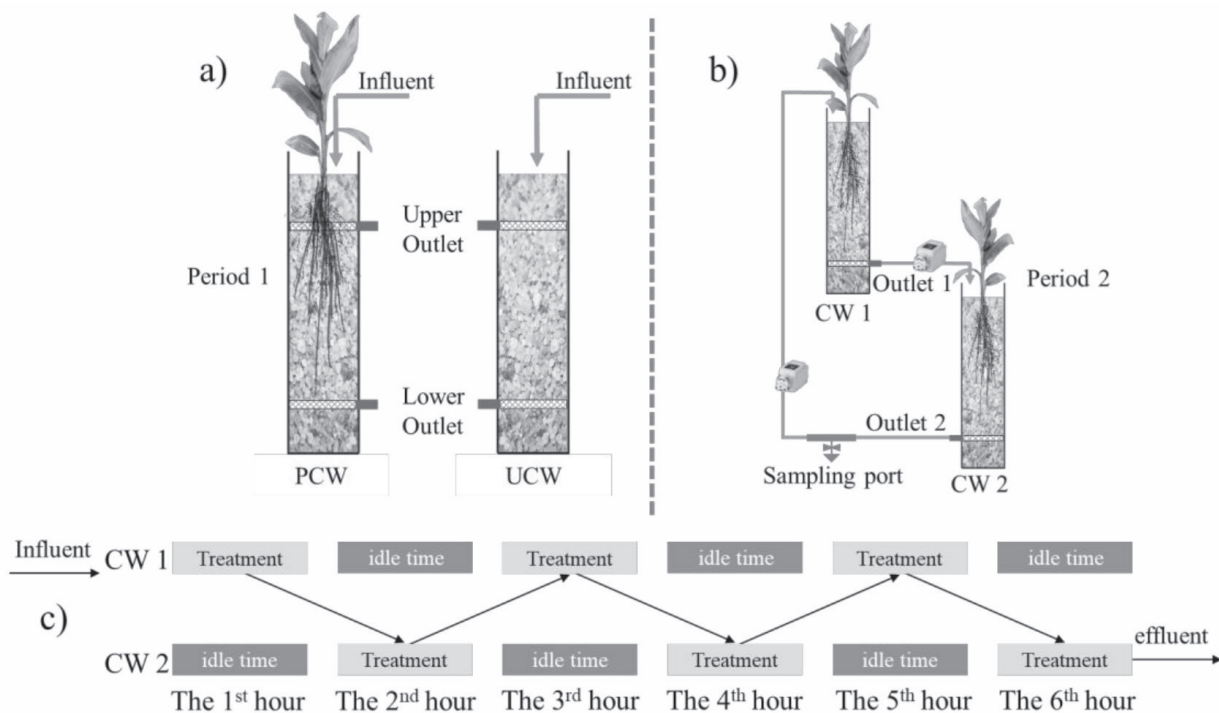

Fig. 1. Schematic diagram of the experimental device. a) The TFCW used during period 1 and 2; b) The two-stage cyclic TFCW used during period 3; c) The operation strategy of a two-stage cyclic TFCW in period 3 (the effluents were continuously recycled between CW 1 and CW 2, and each single TFCW can atmospheric reoxygenation during the 1-hour idle time).

(Fig. 1a). The four cylinders were filled with quartz sand (diameter: 3 to 5 mm) up to 50 cm (effective volume: 2.5±0.2 L). Two outlets were set on each TFCW. Namely, 8 cm and 40 cm above the bottom of the device was named as Upper outlet and Lower outlet, respectively. Disease-free *Canna indices* L. with similar size (110±10 g fresh weight for each) was planted in two reactors named PCW, while the other two reactors were left unplanted (UCW). The CWs were inoculated with activated sludge from Songjiang sewage-treatment plant (Songjiang District, Shanghai). During the domestication stage (lasts for 21 days), synthetic wastewater was prepared with tap water, and the composition was as follows (mg L^{-1}): formaldehyde, 50; Glucose, 105; NH_4Cl, 34; KNO_3, 108; KH_2PO_4, 7; $MgCl_2 \cdot 6H_2O$, 60; $ZnCl_2$, 11; $CaCl_2$, 18; $CuSO_4 \cdot 5H_2O$, 0.03; $FeSO_4 \cdot 7H_2O$, 0.25; $MnSO_4 \cdot H_2O$, 1; $Na_2MoO_4 \cdot 2H_2O$, 0.3; $CoCl_2 \cdot 6H_2O$, 0.03; and H_3BO_4, 6.

Experimental Conditions and Operation

CW reactors were placed on the balcony from April to July, and the average air temperature was around 25ºC. Synthetic wastewater was fed into the CW reactors under a tidal flow mode, with a hydraulic residence time (HRT) of 24 h. For each inflow event, the initial HCHO concentration in CWs was stabilized by three complete flushes with the corresponding synthetic wastewater, before the final inflow. The influent pH values were adjusted using 2 M NaOH or HCl solution. The influent DO was controlled by purging with N_2 or aeration, before adding the HCHO solution. The experiments were divided into 3 periods. In period 1, the HCHO removal efficiency at different initial HCHO concentrations (25, 50, 75, and 100 mg L^{-1}) was investigated. The effluents were collected from the Upper and Lower outlets hourly. During period 2, the impact of influent pH (around 5, 6, 7, 8 and 9) and DO (approximately 2, 3, 4, 5, 6, 7, 8, 9, and 10) on HCHO removal was assessed in PCWs with a 6 h-HRT. For period 3, a two-stage cyclic TFCW which consists of two single TFCWs was constructed to optimize the HCHO removal (Fig. 1b). The operation strategy (Fig. 1b and c) was conducted to: firstly, simulated wastewater was fed into CW 1. After that, the effluents were continuously recycled between CW 1 and CW 2 by pumps hourly. Thus, each CW has an idle time of 1 hour for the atmospheric reoxygenation before the wastewater inflow.

Sampling and Analyses

Before the determination of water quality parameters, all the water samples were filtered through the 0.45-μm filter membrane (Navigator, China). The pH, DO in influents and effluents were measured with a dual-probe multi-parameter meter (HQ40d, Hach, USA). HCHO concentration in wastewater was measured with Nash reagent [13]. A portable HCHO meter (RCH-188, Ruichao, China) was installed above the wetland devices (0.5 m higher than the surface of the wetland substrate) to monitor the level of HCHO volatilized into the air.

Calculation and Statistical Analysis

Removal rates of HCHO were calculated with the following equation:

$$HCHO \ removal \ (\%) = \frac{C_0 - C}{C_0} \times 100\%$$

...where C_0 is the initial HCHO concentration in synthetic wastewater, and C is the HCHO concentration in effluents.

Five replicates were conducted for each different experimental condition (parameter changes, including initial HCHO concentration, pH, and DO). Statistical analysis of HCHO removal was conducted by the analytical software SPSS 20.0. The significant differences were assessed by Duncan's multiple range test at $P<0.05$.

Results and Discussion

Formaldehyde Removal by Single TFCW

Within 1 m^3 around the TFCWs, the average HCHO concentration in the air was 0.008 mg m^{-3} throughout the experiments, which was far below the air quality standard for HCHO stipulated with the World Health Organization (0.1 mg m^{-3}) [14]. Therefore, the volatilization of HCHO in this study can be ignored. Fig. 2 shows the time courses of HCHO removal in PCW and UCW, with the initial HCHO concentration of 25 to 100 mg L^{-1} in period 1. In consideration that the atmospheric reoxygenation mainly occurred in the upper part of the CW [15], and different DO distribution was generally presented vertically from top to bottom for a vertical flow CW. The removal efficiencies of HCHO between the upper and lower part were also compared.

It is generally accepted that vegetation has the potential to remove the water-soluble HCHO by absorbing, transporting, and metabolizing [16]. Besides, the roots can maintain favorable ecological circumstances for rhizospheric microorganisms [17], which contributed to the degradation of organic contaminants. However, data from Fig. 2a) and b) show that the HCHO removal efficiencies were similar between the upper part of PCW (U-PCW) and UCW (U-UCW). An initial HCHO concentration of 25 mg L^{-1} could be removed after 5-h treatment. More than 98% of the HCHO was removed from U-PCW and U-UCW within 8 hours when the initial HCHO concentration was 50 mg L^{-1}. By contrast, Fig. 2c) and d) show an apparent
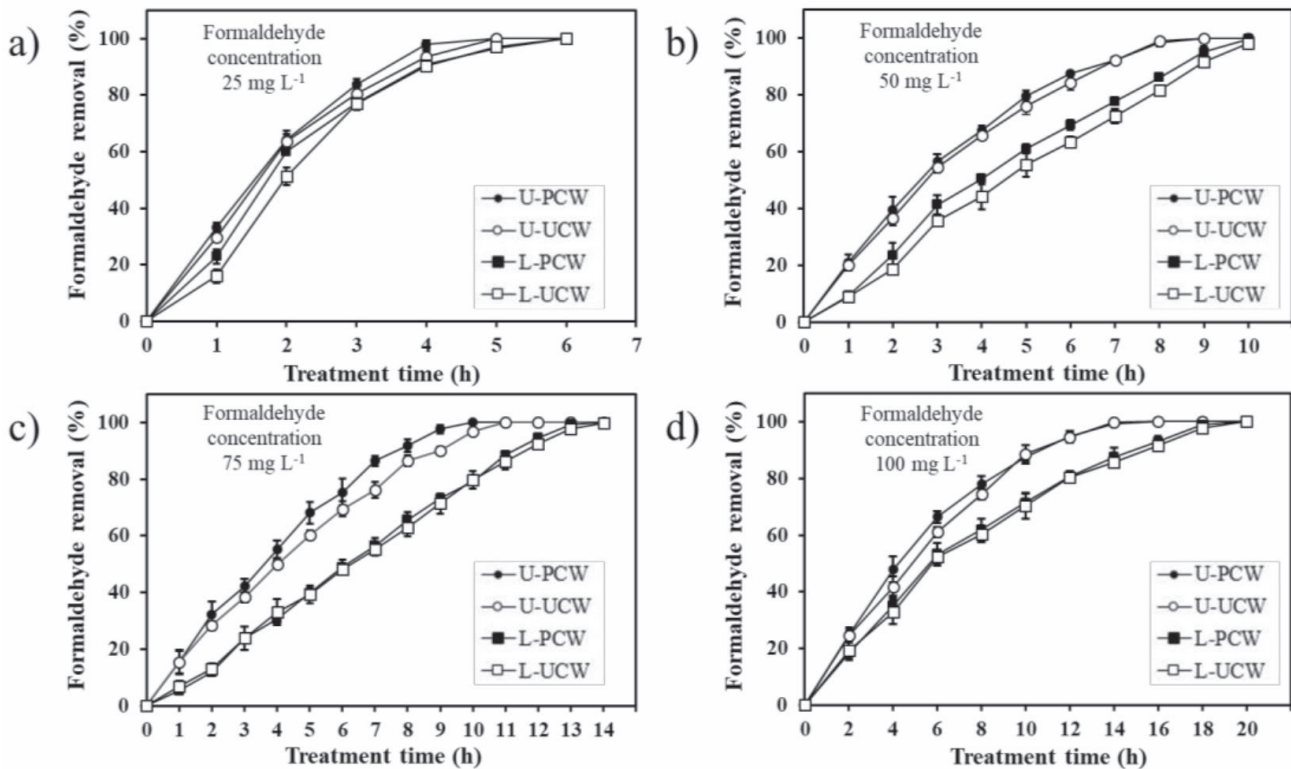
Fig. 2. HCHO removal performance in TFCW with the initial FA concentration of a) 25, b) 50, c) 75, and d) 100 mg L^{-1}, respectively.

difference in HCHO removal between the U-PCW and U-UCW. As the influent HCHO concentration was 75 and 100 mg L^{-1}, U-PCW had a significantly higher HCHO removal than those in U-UCW during the 4th to 9th hours and the 2nd to 8th hours of the treatment, respectively ($P<0.05$). These results indicate that wetland vegetation (*Canna indices* L.) promoted HCHO removal, while the primary pathway to remove HCHO from CWs was microbiological degradation.

For the TFCWs of both non-vegetated and vegetated, the effluents from the upper outlets exhibited remarkably lower HCHO contents, compared with those from the corresponding lower outlets. For example, with an influent HCHO concentration of 100 mg L^{-1}, the HCHO could be removed within 14 hours in U-PCW, while for the lower part of PCW (L-PCW), it took 20 hours. This observation was corroborating to the previous research that the HCHO was mainly removed by the upper portion of a biofilter bed [18]. Previous studies have demonstrated that the methylotrophic bacteria, which using HCHO as the carbon source and molecular oxygen as the electron acceptor, can eventually metabolize HCHO into CO$_2$ [19]. Also, it has been reported that the atmospheric reoxygenation generally occurred in the upper portion of the TFCW from 0 to 10 cm depth [20]. Given the above, it is speculated that the DO level in interstitial water of the wetland substrates might be a key factor, which affects the HCHO biodegradation.

Impacts of Influent pH and DO on Formaldehyde Removal

The impacts of influent pH and DO values on HCHO removal (influent HCHO concentration: 100 mg L^{-1}) were performed in PCW (Fig.3). U-PCW showed generally higher HCHO removal rates than the lower portion at various initial pH and DO conditions. The HCHO removal increased sharply when the pH increased from 5.1 to 7.2. The corresponding increases for U-PCW and L-PCW were 38.6 and 33.9%, respectively. However, a decreased HCHO removal performance was obtained in PCW when the influent pH over 8.09. These results indicate that the HCHO removal was greatly affected by the influent pH, and a neutral or weakly alkaline condition was conducive to HCHO removal (Fig. 3a). According to Fig. 3b), PCW had a low performance of HCHO removal with the initial DO values of 2.0 and 3.1 mg L^{-1}, while the DO concentration of 4.1 mg L^{-1} allowed a removal efficiency of 55.36% in U-PCW and 49.33% in L-PCW, respectively. A further increase in influent DO concentration showed a limited contribution to HCHO removal.

Formaldehyde Removal by Two-Stage Cyclic TFCW

The tidal operation was generally considered a reliable strategy for the reoxygenation of CWs [21]. Based on the exploration of HCHO removal in single TFCWs, a two-stage cyclic TFCW (t-TFCW) was
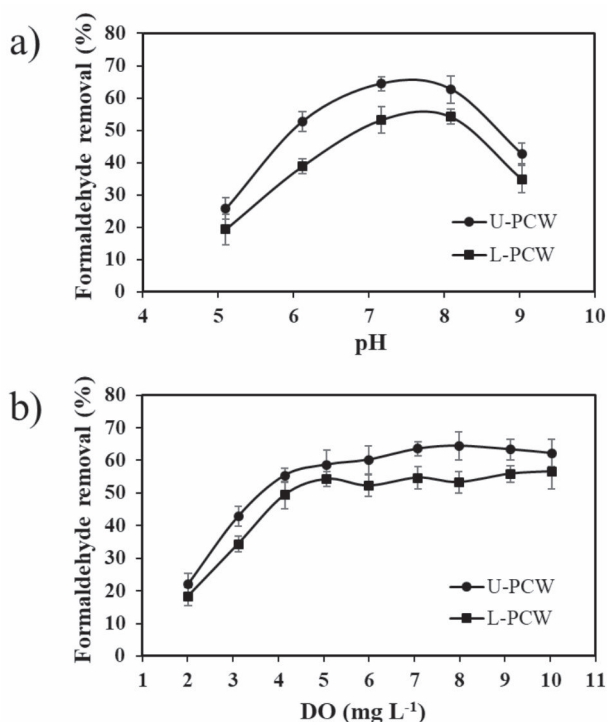
Fig. 3. Impact of influent pH (a) and DO (b) on HCHO removal of the TFCW (the initial HCHO concentration was around 100 mg L^{-1}, and the HRT was 6 h).

constructed to upgrade the HCHO removal. As shown in Fig. 1c), the synthetic wastewater was circulated between CW1 and CW2, and each individual TFCW can be atmospheric reoxygenation during the idle time (1 hour) after 1-hour operation. Fig. 4a) shows that stable and efficient HCHO removal was achieved in the t-TFCW throughout the operation process (50 treatment cycles). With an influent HCHO of 98.4±1.8 mg L^{-1}, t-TFCW obtained a HCHO removal of 52.5% within 2 hours, and 98.1% of the HCHO could be removed after a 6-hour treatment (Fig. 4b).

Conclusions

The HCHO removal in TFCW mainly depended on microbiological degradation, and wetland vegetation was conducive to HCHO removal. Aerobic condition (DO concentration > 4 mg L^{-1}) and neutral/weak alkaline pH (approximately 7-8) was favorable for the HCHO removal. This study also demonstrated that HCHO could be efficiently removed by a two-stage cyclic TFCW, which was proposed as an environment-friendly and effective strategy for HCHO containing wastewater treatment. Further studies should focus on the microbial mechanisms to support the preliminary findings of this study.
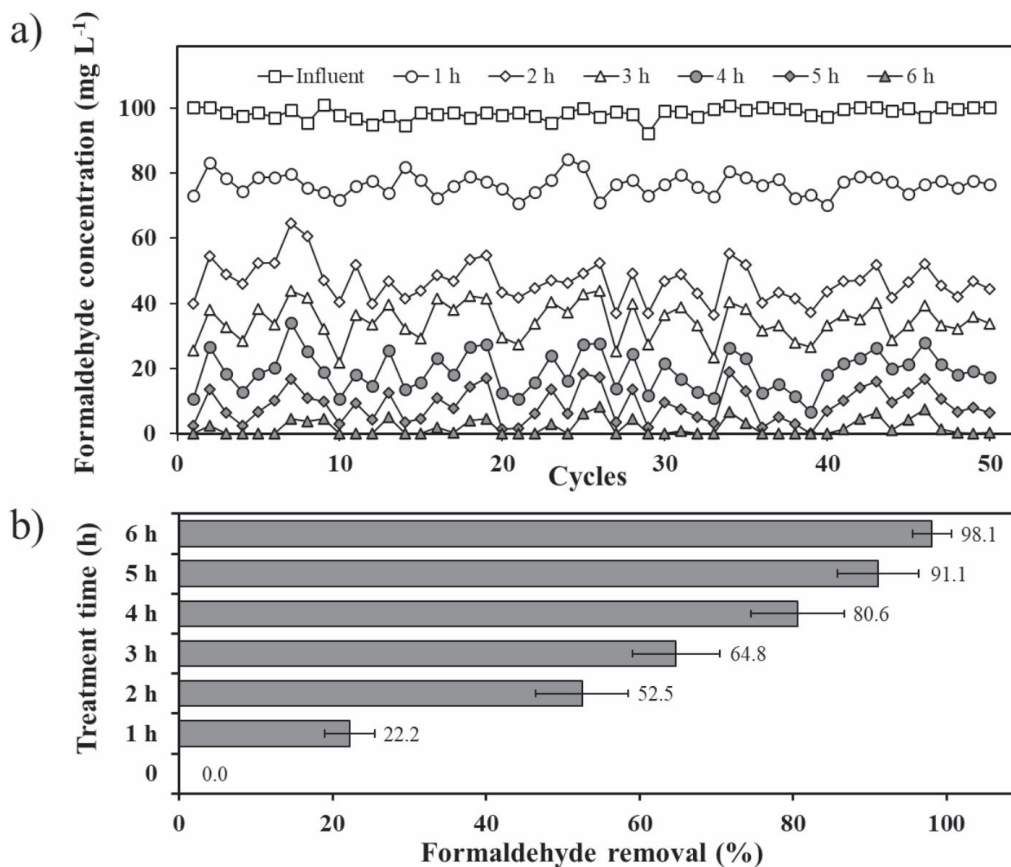

Fig. 4. Residual HCHO concentration a) and average HCHO removal b) in the effluents of the two-stage cyclic TFCW. The treatment times were 1, 2, 3, 4, 5, and 6 h, respectively. The values in figure b) are means±SD (n = 50).

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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