

Article

Treatment of Organic Matter and Tetracycline in Water by Using Constructed Wetlands and Photocatalysis

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Abstract: In this study, the ability of a bench-scale simulated constructed wetland (CW) to remove organic matter (OM) and tetracycline (TC) from water was examined. The performance of CW was evaluated by varying the initial concentrations of the target compounds and the hydraulic retention times (HRTs). Findings showed that OM removal efficiencies were 55.2–80.8%, 28.1–71.9% and 72.1–79.7% for ultraviolet absorbance at 254 nm (UV-254), dissolved organic carbon (DOC) and soluble chemical oxygen demand (sCOD) respectively, under 1 day-HRT, whereas higher initial DOC concentration achieved better removal efficiencies. Changing from 1 day-HRT to 2 day-HRT, the removal efficiency of OMs remained practically unchanged, while that of NH₃-N increased considerably, from 61.7% to 73.0%, implying that the removal of ammonia in CW needs a longer time for complete treatment. CW also showed an excellent performance in removing TC, especially in the first two hours of operation through the absorption process. In addition, the findings from this research revealed an improvement in effluent water quality when photocatalysis (TiO₂/α-Al₂O₃, with ultraviolet A (UVA) irradiation) was used as the post-treatment following CW, presented by the increase in removal efficiency of OMs of the combined system compared to that of CW alone. This study points to the possible and promising application of the low-cost water treatment system for dealing with OMs and TC in water.

Keywords: constructed wetlands; organic matter; tetracycline; removal efficiency; photocatalysis; water quality

1. Introduction

Declining water quality is considered a global concern due to the rapid growth of the population and the expansion of industrial and agricultural activities [1]. Therefore, the scarcity of clean, safe and adequate fresh water is predicted to become worse and worse globally in the coming decades, not only in the arid regions, but also in regions presently considered water-rich [2]. Unfortunately, the surface water in lakes, rivers, streams, and reservoirs that are used as the main source of potable water is currently polluted by a combination of both anthropogenic and natural activities. This serious problem threatens the health and well-being of humans, plants, and animals, and is a cause of climate change.

Natural organic matter (NOM) is one of the major compounds contained in surface or groundwater. NOM is considered a challenge in drinking water treatment since its presence in water results in

several negative impacts on the performance of standard water treatment processes such as granular activated carbon filtration and membrane filtration [3]. Humic acid (HA), one of the major fractions of NOM in natural water, not only causes taste and odour issues and imparts a yellowish to brown color in natural water, but also poses serious problems for treatment systems. Through various transformation processes, HA can form different kinds of disinfection by-products (DBPs) which are very toxic and harmful for human health [4]. Typically, trihalomethanes (THMs), which are the result of a reaction between the chlorine used for disinfecting tap water and natural organic matter in the water, are associated with negative health effects such as cancer and adverse reproductive outcomes. Therefore, the removal of NOM from raw water before the disinfection process is necessary and considered a great health and environmental issue [5].

Pharmaceuticals and personal care products are currently recognized as a new class of emerging pollutants and have been the subject of increasing attention and scientific consideration [6,7]. The occurrence of a huge number of pharmaceuticals in the aquatic environment has been gaining prominence because of their negative effects on human health. Although low concentrations can be currently detected in water bodies (just up to several $\mu\text{g/L}$), the continuous discharge of pharmaceutical compounds into the environment from different sources makes them “pseudo-persistent” [8]. Among a large variety of pharmaceutical compounds, antibiotics are of special concern due to their widespread use in human and veterinary medicine [9]. Especially, tetracycline (TC) is one of the most commonly used antibiotics in agricultural applications such as husbandry, cattle, swine, poultry, and fishery production, with an extensive presence in surface waters. Unfortunately, the active components in most pharmaceuticals are transformed only partially in the human body and animal body and then a mixture of metabolites and bioactive forms are excreted into the sewage systems [10].

Constructed wetlands (CWs) have been proven to be a cost-effective ecological technology for the treatment of numerous kinds of contaminated waters, including for the treatment of domestic wastewater, industrial wastewater, agricultural wastewater, landfill leachate and stormwater runoff [11,12]. A few years ago, these systems were also under study for their ability to remove emerging microcontaminants like pharmaceuticals [13]. Not only this, but the removal of NOM in water by using CWs was investigated by some researchers recently [14]. Such low-tech treatment systems are often more economical than energy-intensive engineered treatment plants, easier to operate and they provide numerous secondary benefits. The use of CWs has been successfully tested in pilot-scale and field-scale applications, contributing data on overall contaminant removal efficiency on the basis of either concentrations or loads [15,16].

Although CWs show several advantages in treating polluted water, they still have some limitations; for example, CWs require a large area of operation and long hydraulic retention time (HRT) as well. Therefore, to get the high water quality after treatment, it is necessary to investigate some methods to improve CWs' treatment efficiency, for example, incorporating with other treatment processes for complete removal of contaminants [17,18]. Recently, advanced oxidation processes (AOPs) using chemical oxidants, such as ozone and hydrogen peroxide (with or without photoassistance), have been under consideration to remove humic acid. Photocatalytic processes, or photocatalysis (PC) using TiO_2 as photocatalysts, is one of the most attractive processes because of its abundance, low cost and complete destruction of humic acid molecules by the direct oxidation process [19].

As mentioned above, the undesirable effects of NOM (represented by HA) and TC on human and animal life are serious, thus requiring efforts to limit the concentration of these compounds in water. There are various methods which can be used to deal with such a problem. To a certain extent, each technique shows good performance in removing HA and TC; however, they are recognized as either expensive or have low removal efficiency. For that reason, it is very important to seek effective methods, which not only improve the contaminants' removal efficiency but also cut down the cost of installation. Both CW and PC are being considered as promising methods that can bring benefits in terms of technical, economic and environmental aspects. In fact, these methods of purifying water can be optimized to be more viable, at a lower cost and with less energy, while at the same time minimizing

the use of chemicals and impact on the environment. However, there have been few reported studies that demonstrate the capability of CW to reduce HA and TC in polluted water as well as the potential to combine both CW and PC in removing HA from raw water.

To fill in this knowledge gap, the main objectives of this study were:

- (i) To investigate the feasibility of a CW for treating water with varying initial dissolved organic carbon (DOC) concentrations and with different HRTs.
- (ii) To evaluate the removal efficiency of TC by using only a CW system for treatment. This experiment was conducted under the condition of 1day-HRT and with different initial TC concentrations.
- (iii) To examine the feasibility of combining CW and PC in treating water with influent DOC concentrations ranging from 10 mg/L to 12 mg/L. The integrated system, biological degradation in a CW model and chemical degradation with a TiO₂-photocatalytic process, was operated in sequence. CW was considered here as a pre-treatment system, while PC played the role of a post-treatment process.

2. Materials and Methods

2.1. Preparation of the Influent Water

The raw water was collected from Jing-Si Lake in Pingtung, Taiwan. The characteristics of the raw water are shown in Table 1.

Table 1. Water characteristics of Jing-Si Lake.

Parameter	Unit	Raw Water
pH	-	7.50 ± 0.52
Alkalinity	mgCaCO ₃ /L	88.75 ± 5.00
UV-254	cm ⁻¹	0.089 ± 0.030
DOC	mg/L	3.19 ± 0.64
sCOD	mg/L	8 ± 2
NH ₃ -N	mg/L	0.127 ± 0.017
PO ₄ -P	mg/L	0.024 ± 0.011
NO ₃ -N	mg/L	0.72 ± 0.25
Tetracycline	mg/L	Not detected

With the aim of investigating the feasibility of using a CW for treating water with different initial organic concentrations, synthetic water was prepared by adding HA stock solution (1000 mg/L) with different volumes into raw water to get three initial DOC concentrations, namely 3.0–4.5 mg/L, 4.5–6.0 mg/L and 10–12 mg/L. Analytical-grade HA, purchased from Sigma-Aldrich (Steinheim, Germany), was used as a simulant. This kind of HA contains approximately 3.1 mmol/g carboxylic groups. The stock solution of HA at 1000 mg/L was prepared by mixing 1 g of HA with 62.5 mL of NaOH (2 N) solution, because HA dissolves well in alkaline conditions, and then dissolved to 1 L with deionized water (DI water) in a 1-L volumetric flask [5]. After that, this solution was put in a shaker to agitate substances in a flask and then the stock solution was filtered through a 0.45 µm membrane filter to remove the residual non-dissolved humic acid powder. Finally, the pH of HA solution was adjusted to around 8.0 and this stock solution was kept in the dark in the fridge at the temperature at 4 °C in maximum two weeks.

With the purpose to evaluate the removal efficiency of varying TC concentrations by using CW, the TC stock solution was added into raw water to get three levels of input TC concentrations (1, 5 and 10 mg/L). The stock solution of TC (1000 mg/L) was prepared by dissolving 0.1 g tetracycline hydrochloride (Sigma-Aldrich, China, purity > 95%, kept in -20 °C) in 100 mL DI water [20]. After one hour of agitation, TC stock solution was filtered through a 0.45 µm membrane filter and then stored in amber bottles at 4 °C in the fridge.

2.2. Constructed Wetland System Set-up

A bench-scale CW was set up based on a free-water flow wetland pattern, where effluent leaves from the bottom of the system [21] (Figure 1). It is a rectangular tank made of glass, with dimensions of 40 cm long, 25 cm wide and 28 cm deep. This glass tank was filled in layers with gravel in the bottom and mixture of sand and soil on the top, where *Cyperus involucreatus* were planted. *Cyperus involucreatus* is the umbrella sedge, a close cousin of the famous Egyptian papyrus plant (*Cyperus papyrus*), which has been used successfully in small-scale gravel-bed CWs in Australia and New Zealand [22]. After the system was built, it took nearly two months to run an adaptive phase in order to ensure a stable effluent quality. The system was operated by using peristaltic pumps to transfer the input water from the influent tank to CW and from CW to the effluent tank. Inside CW, treatment processes such as organic removal processes and nutrient removal processes occurred to remove both organic and inorganic substances, and then, the effluent was collected in the collecting pit in CW.

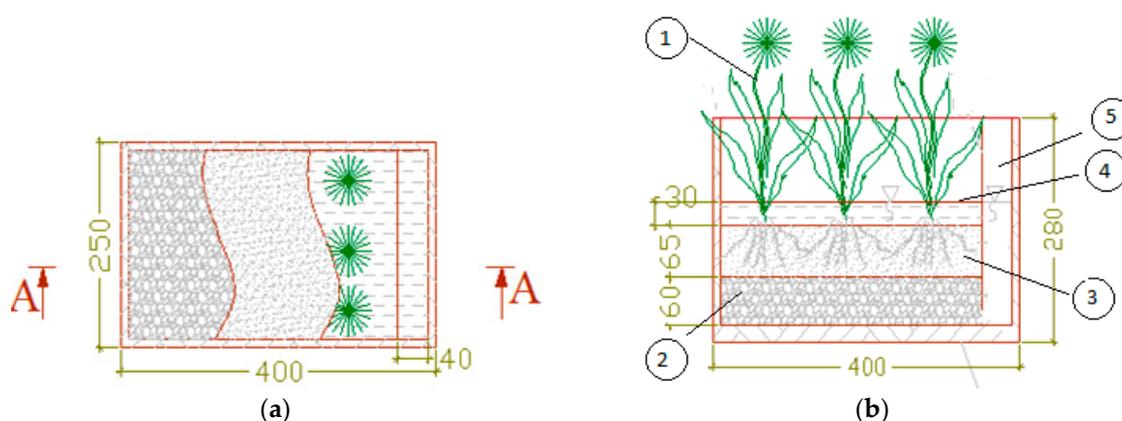


Figure 1. Structure of constructed wetland. (a) Plan view; (b) Profile A-A: (1) *Cyperus involucreatus*; (2) Gravel; (3) Mixture of sand and soil; (4) Water level; (5) Collecting pit.

2.3. Photocatalytic System Set-up

The photocatalytic experiments were performed in a 1-L cylindrical Pyrex beaker ($\varnothing 120$, $H = 150$ mm) with continuous stirring by using a magnetic stirrer. Both the reactor and the magnetic stirrer were put in a box covered with aluminium foil in all inner walls. The photocatalytic process used two UVA lamps (10 W, 28 mm O.D., manufactured by Philips (Amsterdam, The Netherlands)), which emitted light with a wavelength between 315 and 400 nm, were placed at the top of the box [19]. UVA lamps were set at 160 mm above photocatalyst and 65 mm above water level. Figure 2 illustrates the layout of a photocatalytic reactor (PCR).

Supported TiO_2 was prepared by adsorption according to the impregnation method, with $\alpha\text{-Al}_2\text{O}_3$ being used as catalytic support. Commercially available P25 type titanium dioxide (TiO_2 Degussa P25 (Tokyo, Japan), with its crystal structure comprising of approximately 80% anatase and 20% rutile and with a BET specific surface area of $50 \text{ m}^2/\text{g}$, was used as photocatalyst [19]. $\alpha\text{-Al}_2\text{O}_3$ balls (Eikme International Ltd., Hsinchu, Taiwan, size: 3–5 mm, shape in bead) were immersed in a TiO_2 solution consisting of TiO_2 Degussa P25. After that, the balls were washed by RO water until the effluent was clear; this means that all TiO_2 had been adsorbed into $\alpha\text{-Al}_2\text{O}_3$ surface [23]. Then supported catalysts were placed in an oven at 105°C for 2 h for drying and calcined in a muffle furnace at 450°C for calcination for 3 h.

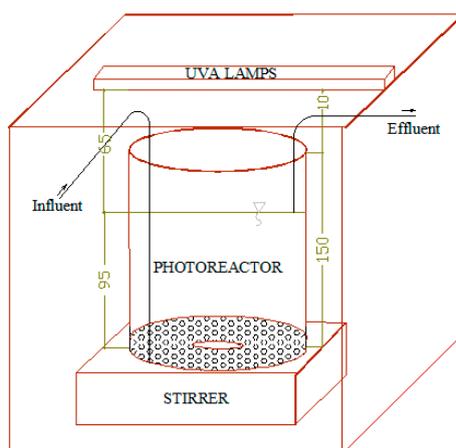


Figure 2. The layout of the photocatalytic reactor.

2.4. Experimental Operation

Three phases of the experiment were conducted to achieve three established objectives. In the first phase, the experiments were performed in a sequence to investigate the feasibility of CW for treating water containing varying initial organic concentrations. In the next step, the investigation of treatment efficiency of CW in different HRT conditions was also carried out in turn. The scheme was presented in Figure 3.

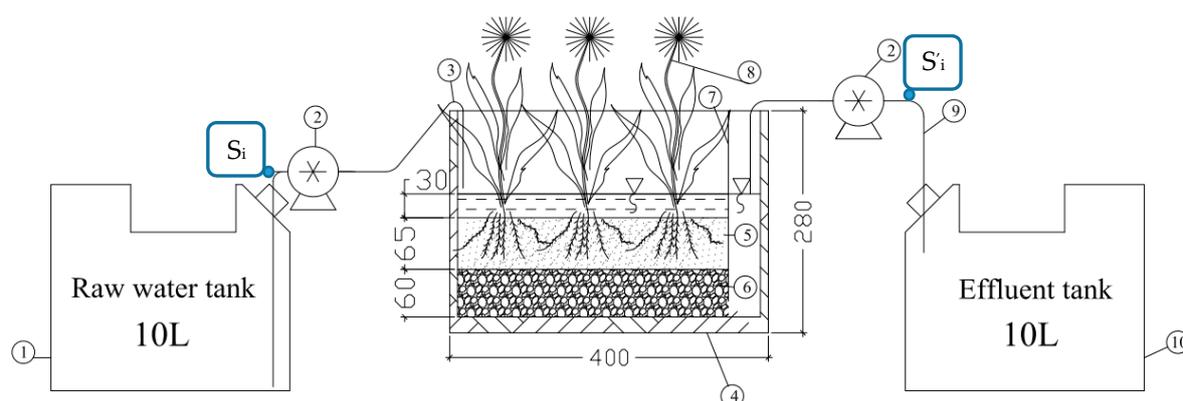


Figure 3. Layout of prototype of bench-scale constructed wetland: (1) Influent tank; (2) Peristaltic pump; (3) Influent pipe; (4) Constructed wetland; (5) Mixture sand and soil; (6) Gravel; (7) Baffle; (8) Plants; (9) Effluent pipe; (10) Effluent tank.

The volume of 6 L containing synthetic water prepared by adding HA stock solution into raw water was pumped from the influent tank into bench-scale CW. Two peristaltic pumps were used to pump water continuously from influent tank to wetland and from wetland to effluent tank. CW was operated in turn with three different input organic concentrations, including 3.0–4.5 mg/L, 4.5–6.0 mg/L and 10–12 mg/L (named run 1, 2 and 3, respectively), with the HRT was fixed at 1 day, flow rate was 3.47 mL/min. The water level in CW was maintained in the height of 30 mm above the mixture of sand and soil layer. Samples were collected daily from the influent and the effluent of CWs, where S_i , S'_i representing influent and effluent samples, respectively. Collected samples were analyzed with the following parameters: pH, alkalinity, ultraviolet absorbance at 254 nm (UV-254), DOC, sCOD, ammonia nitrogen ($\text{NH}_3\text{-N}$) and nitrate ($\text{NO}_3\text{-N}$). Only samples for analyzing DOC were stored in the fridge at 4 °C for a maximum of 1 week, the others were analyzed immediately after daily collecting.

In terms of investigating effects of the change of HRTs, CW was run under the conditions of fixed DOC concentration influent at 10–12 mg/L and 1 day-HRT and 2 day-HRT (named run 3 and

4, respectively). The flow rate of each pump was set according to different HRTs, 3.47 mL/min and 1.74 mL/min with 1 day-HRT and 2 day-HRT, respectively.

Regarding the second phase, with the aim to evaluate the removal efficiency of TC in water by using only CW system for treatment, phase 2 of this study was conducted under the condition of HRT-1day, flow rate was set up 3.47 mL/min and with different initial TC concentrations, 1 mg/L, 5 mg/L and 10 mg/L. The procedure to operate CW in this phase was mostly similar to that in phase 1. However, the influent was made different, synthetic water in this phase was prepared by adding TC stock solution with various dosages into raw water. Monitored parameters in phase 2 were pH and TC concentration. One important thing in this phase is that during the experiments, the influent tank was covered with aluminium foil to obstruct sunlight, to prevent photolysis of TC because TC can be easily degraded under the light. Samples from the influent and the effluent were collected daily in clean brown glass vials and frozen until analysis. In addition, during the first days after periods of 2, 4, 6, 12 and 24 h of operation, samples were taken to examine the change of TC concentration during the periodic time in 1 day.

In the final phase, the experiment was conducted with the combination of CW and PCR to examine the feasibility of this combined system in treating water with initial DOC concentration ranging from 10 mg/L to 12 mg/L. The combination was operated in sequence, CW was considered as a pre-treatment system, PCR played the role of a post-treatment process. The flow rate was controlled at 3.47 mL/min, corresponding to effective volumes (5 L and 0.8 L) and HRTs (1 day and 3.84 h) for CW and PCR, respectively. The amount of $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ used in PCR was 20 g. The water level in CW still remained at 30 mm above the substrate layers and the height of water in the PCR was 95 mm. Samples were collected daily from the influent and the effluent of each system (Figure 4). pH, DOC, sCOD, and UV-254 were monitored to investigate the treatment efficiency of this combined system.

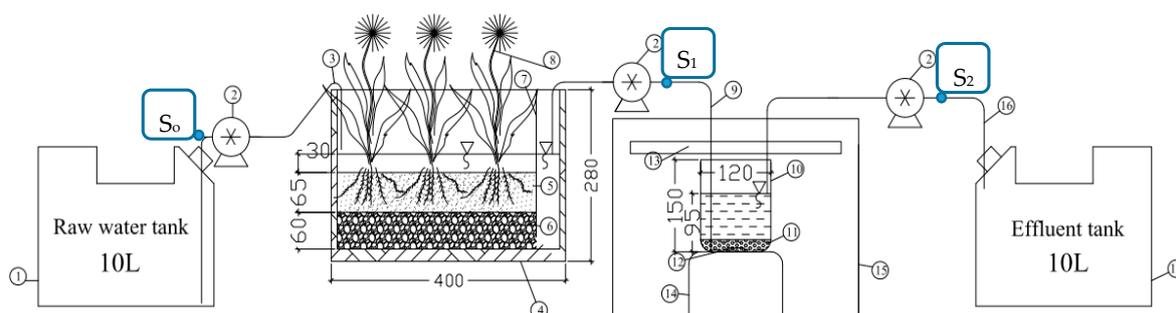


Figure 4. The layout of the prototype of a combination system (CW+PCR). (1) Influent tank; (2) Peristaltic pump; (3) Influent pipe of CW; (4) Constructed Wetland; (5) Mixture Sand and Soil; (6) Gravel; (7) Baffle; (8) Plants; (9) Influent pipe of PCR; (10) Beaker 1 L; (11) $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ balls; (12) Magnetic stir bar; (13) UVA lamp; (14) Magnetic stirrer; (15) Box covered with aluminium foil; (16) Effluent pipe; (17) Effluent tank.

2.5. Analyses

Before being analyzed, all collected samples were filtered through a $0.45\ \mu\text{m}$ membrane filter (Pall Gelman, Mexico) to eliminate the effect of suspended particles on the measurements. Water quality parameters surveyed during the experiment were pH, alkalinity, DOC, sCOD, $\text{NH}_3\text{-N}$, $\text{NO}_3^-\text{-N}$, UV-254, and TC. Sampling was conducted at the inlet and outlet of each system. Analyses were performed according to Standard Methods for the Examination of Water and Wastewater [24].

3. Findings and Discussion

3.1. Effects of the Initial Organic Concentration on the Treatment Efficiency of CW

The findings showed that in all the first three runs of the experiment, most of the selected water quality parameters, namely UV-254, DOC, sCOD, NH_3^-N experienced a significant decrease

in concentration after treatment in the CW, with removal efficiencies in the ranges of 55.2–80.8%, 28.1–71.9%, 72.1–79.7% and 60.1–61.7%, respectively (as shown in Figure 5). The removal efficiencies of UV-254 and DOC (as organic matter (OM) indicators) rose with an increase of the initial DOC concentration. At the lowest initial concentration of DOC (3–4.5 mg/L – Run 1), the efficiency in removal of OMs was relatively low (ranging $55.2 \pm 2.4\%$ and $28.1 \pm 2.4\%$ for UV-254 and DOC respectively) because most of the removed OMs were compensated by soluble microbial products released by microorganisms [25,26]. On the contrary, in Run 2 and Run 3, the CW showed better performance in the removal of OMs, with $68.2 \pm 4.0\%$ and $41.8 \pm 2.1\%$ in Run 2, followed by $80.8 \pm 0.6\%$ and $71.9 \pm 1.5\%$ in Run 3, for UV-254 and DOC, respectively.

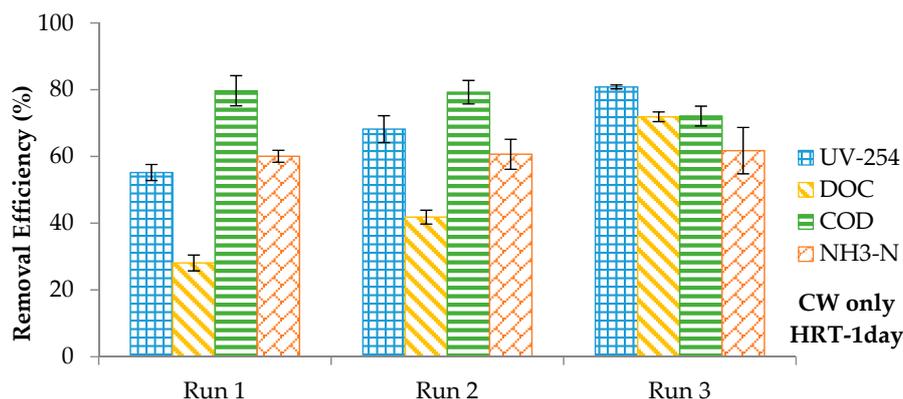


Figure 5. The effect of the initial DOC concentration on effluent water quality.

Also seen from Figure 5, sCOD removal efficiencies had a slightly decreasing tendency from 79.7% to 79.3% and to 72.1% for Run 1, Run 2, and Run 3, respectively. An explanation for this may be that through the last time of operation, plants roots may be decomposed and dissolved and therefore sCOD of effluent may increase to a higher value at the end of this experiment [27].

From the literature review, it is clear that the treatment process of CW is based on a complex number of biological and physical processes such as adsorption, precipitation, filtration, nitrification, decomposition, plant uptake, etc. Therefore, it can be explained that the reduction of OM in this study was achieved by these above mechanisms. Microorganisms attached in the substrates (soil, sand, and gravel) and in the plant root had responsibility on the degradation of labile OM through aerobic, anoxic, and anaerobic processes [28], while stable OM fractions may be accumulated on the surface of substrates and/or biofilm through an adsorption process.

In terms of the adsorption process, the reduction of non-biodegradable organic contaminants in the influent could be contributed by the adsorption of biofilm and/or substrates in CW. In fact, as observation, the color of the substrate medium (sand) changed from white to light brown, indicating that there was some adsorption of HA onto the surface of substrates and/or biofilm, and clearly, adsorption was one of the main OM removal mechanisms in the CW, which was in accordance with the findings of Saeedi et al. [25], who pointed out that the adsorption onto the biofilm was one of the NOM removal mechanisms in their experiments. Furthermore, as reported by Nguyen [29], over 90% of the OM accumulated in a gravel-bed constructed wetland over a period of 5 years consisted of recalcitrant OM fractions, indicating that CW operation in treating stable OM was probably due to the accumulation of refractory OM in the gravel bed.

Along with the substrates in the CW, plant roots might contribute to the adsorption of OM in the influent. According to the review of Trevisan et al. [30], there are different hypotheses which favor the adsorption of humic substances by plant roots. The available evidence proved that HA was absorbed in the root surface or accumulated passively in the “apparent free space” [31]. The results of the research of Nardi et al. [32] also support the interpretation that humic substances of all molecular weights can be absorbed. However, until now, the mechanisms through which humic substances interact with the

root cells and may subsequently affect plant physiology and growth have not been completely clarified yet [30].

In addition, humic substances may also be taken up by microbes. There is strong proof that HA was taken up into mycelia of *Aspergillus niger* [33]. Once taken up by plant tissues, humic materials may directly influence the growth of plants via biochemical mechanisms [34]. Prát [35] also reported microscopic evidence that HA was taken into the shoots of several plant species which were allowed to stand with their cut ends in HA solutions. It is likely that in most cases humic substances enhance microbial growth by serving as a food source [34].

Along with the biodegradation of labile OM by microorganisms, there might be some degradation of less degradable organic matter, which would be decomposed by specialized natural soil bacteria [36]. The larger molecular weight OM was firstly degraded into smaller molecule one by microorganism activity, and then absolutely eliminated gradually. During the experiment, the average removal range of UV-254 was higher than that of DOC, 55.2–80.8% compared to 28.1–71.9%, indicating that there were considerable changes in structure (simple break-up) without causing the complete mineralization of large aromatic structures [14].

In addition, an interesting result found from this study is that while the initial DOC concentrations in three runs increased, the DOC concentrations of effluents maintained nearly similar values, ranging from 2.880 ± 0.257 , 2.673 ± 0.219 , 3.119 ± 0.149 mg/L. This may imply that CW treatment could have a high tolerance of variation of DOC concentration in the influent water and maintain stable effluent water quality. This result agrees with the conclusion of Mancilla et al. [37] who indicated that there was a load fluctuation tolerance in CWs.

In terms of nitrogen removal in CWs, according to Vymazal and Kröpfelová [12], nitrogen undergoes several processes in wetlands, including ammonification, nitrification, denitrification, adsorption, bacterial degradation, and plant uptake. In this experiment, the concentration of $\text{NH}_3\text{-N}$ underwent a significant decrease and a removal efficiency higher than 60% was achieved while that of $\text{NO}_3^- \text{-N}$ increased to a slight extent from 0.956 ± 0.312 to 1.109 ± 0.255 , and from 0.707 ± 0.234 to 1.052 ± 0.155 for run 2 and run 3, respectively. In addition, it is well-known that biological nitrogen removal depends on successful nitrification (ammonia oxidation to nitrate) and the subsequent denitrification (nitrate reduction to nitrogen gas) [20]. However, in this case, plants in CW also played an important role in eliminating $\text{NH}_3\text{-N}$ concentration. As stated by Stecher et al. [38], umbrella palms should be considered when maximum NH_4^+ reduction is a treatment goal. That $\text{NO}_3^- \text{-N}$ levels showed no significant difference in the influent and effluent concentrations may be explained by the fact that the HRT in this experiment was not enough for the process of denitrification. It probably occurs in most wetland systems that the removal of nitrogen requires longer HRTs [39].

3.2. Effects of the HRT on the Treatment Efficiency of CW

In general, the levels of UV-254, DOC, sCOD, and $\text{NH}_3\text{-N}$ in the effluent in the last two runs of the first phase experiment were less than those in the influent. It can be also realized that there was a relatively stable removal during the operational period, which could be seen from the low standard deviation values. As can be seen from Figure 6, most of monitored water quality parameters in the case of a HRT of 2 days had higher removal efficiencies than those of HRT of 1 day; however, there was only a small discrepancy among all values in these two treatment processes. For example, the percentages of removal of UV-254 and DOC were 80.8 and 71.9 in the 1 day HRT test, compared to 85.0 and 73.0 in the HRT 2 day test, respectively.

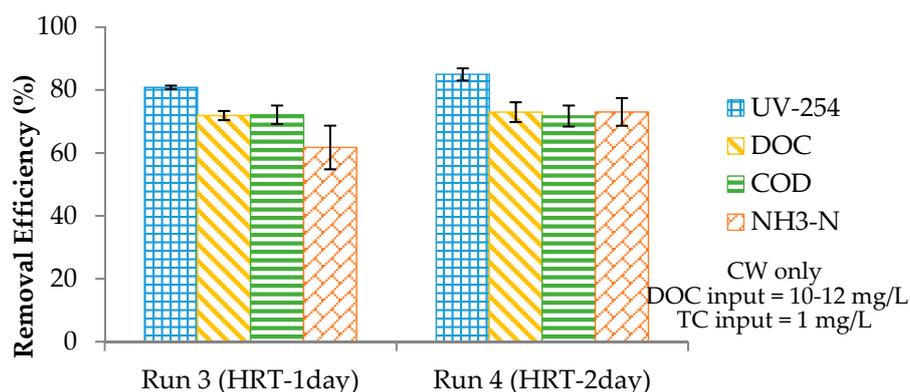


Figure 6. The effect of the HRT on effluent water quality.

In terms of OMs removal, the results showed that there was a slight decline in concentrations of UV-254, DOC and sCOD during both operation time of 1 day-HRT and 2 day-HRT. However, the difference in the removal rate of OMs between two runs was small. This can be explained by the fact that most of the labile biological organic compounds were degraded during the first day of the treatment process, although there was still a process of degradation of OM by microorganisms in CW which kept occurring on the second day, shown by a slight decrease of UV-254 from $0.178 \pm 0.012 \text{ cm}^{-1}$ for 1 day HRT to $0.135 \pm 0.017 \text{ cm}^{-1}$ for 2 day HRT. This process just helps to degrade the large molecule OM into smaller species without complete mineralization because the level of DOC in the effluent in the two cases recorded little change, at $3.119 \pm 0.149 \text{ mg/L}$ for 1 day-HRT, compared to $3.017 \pm 0.292 \text{ mg/L}$ for 2 day-HRT.

On the other hand, a considerable increase from $61.7 \pm 7.0\%$ to $73.0 \pm 4.4\%$ in the removal efficiency of NH₃-N can be seen from Figure 6 during two studied runs (Run 3 and Run 4). This leads to the conclusion that the more the contact time with the CW is, the higher ammonia removal efficiency is obtained, thanks to the more complete ammonification process. In fact, HRT plays a more significant role in the removal of ammonia [39].

3.3. The Removal of Tetracycline in the CW Treatment System

As seen from Figure 7, when the influent concentration of TC was stable during the period of operation, at $0.980 \pm 0.078 \text{ mg/L}$, $4.819 \pm 0.273 \text{ mg/L}$, and $10.481 \pm 1.070 \text{ mg/L}$, its effluent concentrations were $0.096 \pm 0.015 \text{ mg/L}$, $0.598 \pm 0.129 \text{ mg/L}$ and $0.474 \pm 0.033 \text{ mg/L}$, respectively. Corresponding TC removal rates of $90.20 \pm 1.02\%$, $87.60 \pm 2.48\%$ and $95.42 \pm 0.73\%$ were also obtained from these trials, indicating that CW system was effective in eliminating TC from the influent water.

It is well-known that the removal of TC in biologically-based treatment systems is related to a variety of physical, chemical and biological processes [40]. In this study, the removal of tetracycline as shown in Figure 7 may be achieved either through adsorption and/or biodegradation. However, it has been reported that TC was mainly removed via adsorption in biological systems while biodegradation can be completely ignored [41,42]. In addition, Thiele-Bruhn [43] declared that TC is strongly adsorbed by soil and sediments, with a high potential for adsorption ($k_D = 70\text{--}5000 \text{ L/kg}$) [44]. Therefore, partitioning onto the biofilm and solid matrix in CW was expected to play an important role. In fact, although TC is a substance with high water solubility (231 mg/L) and a low *n*-octanol/water partition coefficient ($\log_{KOW} = -1.3$), it is still considered to sorb strongly onto soil [44] and several materials such as clay, sediment, humic compounds, etc. [45]. Ionic interactions and the metal-complexing properties of TC have been proved to largely govern its adsorption characteristics [46]. Since suspended particles from the wastewater were retained in a wetland bed, sorption of dissolved organic contaminants in that organic matter and on the biofilm coating the CW bed could represent a significant mechanism for the removal of TC in CW, which was in agreement with the result which indicated that biosorption was the main mechanism of TC removal [47].

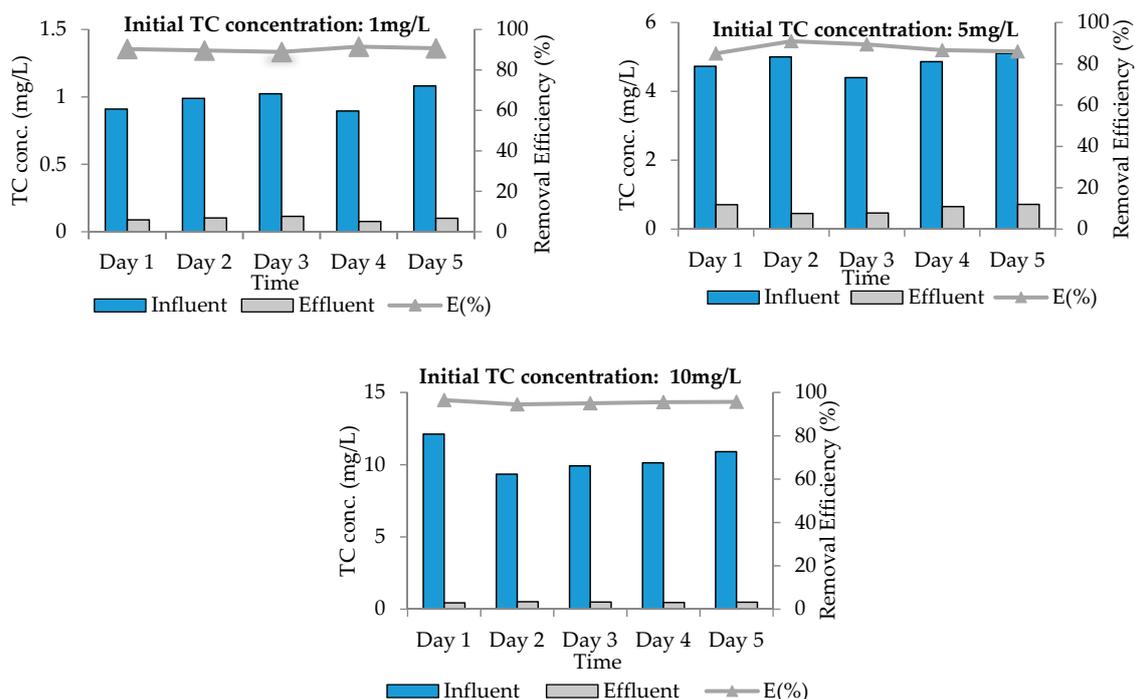


Figure 7. The effects of the initial TC concentrations on treatment efficiency of CW.

Another removal mechanism considered to be responsible for the removal of TC in this study is the photodegradation process. In fact, photodegradation is known as one of the main transformation reactions of tetracyclines in the environment [46]. Since the CW in these tests was uncovered, high photolability of TC may have occurred [8,48]. In fact, according to the study of Garcia-Rodriguez et al. [8], the difference in TC removal efficiency between experiments with a covered control and an uncovered control was really clear, $15 \pm 8\%$ and $89 \pm 3\%$, respectively.

The improvement of the removal efficiency of TC may also be attributed to the presence of plants in the CW. Plants are generally considered favorable in a CW, as they act as an anchoring surface for biofilm, pump and release O_2 to the bottom of the systems, they retain suspended particles and insulate against low temperatures. It cannot be denied that plants actively contribute to TC removal via uptake. In fact, Liu et al. [49] found that three antibiotics (ciprofloxacin HCl, oxytetracycline HCl, and sulfamethazine) could be taken up by plant roots and translocated to shoots, which was in agreement with the findings of Dettenmaier et al. [50], who observed the similar phenomenon for highly water soluble organic compounds. From these results, those authors suggested that removal of such highly water-soluble organic compounds was most likely to be driven by the transpiration water stream in the plant uptake and the translocation within plant tissues. Furthermore, they also indicated a positive correlation between the antibiotic concentration and the levels of antibiotic accumulation inside plants [51]. In addition, Di Marco et al. [52] studied the accumulation of TC in *Iberis sempervirens* L. and their results confirmed the plant's ability to take up TC. For example, a recent study reported that *Phragmites australis*, a large perennial grass from tropical and temperate regions, could successfully remediate several antibiotics, including TC, from an aqueous system [53]. Not only this, but Sengupta [54] found that *Vetiver* grass has the ability to remediate TC from a water source by taking up TC into its roots and translocating it to the shoots, and by metabolizing or transforming TC. From the literature, it can be concluded that TC can be taken up by plant roots and translocated to shoots.

Interestingly, during operation time, no visible symptoms (such as yellow spots and stripes) were observed on the *Cyperus involucreatus* leaves, which means that *Cyperus involucreatus* growth was not significantly affected by the initial TC concentration of the tests, 1–10 mg/L, and perhaps *Cyperus involucreatus* is a TC-tolerant plant. In this study, other TC removal mechanisms could occur in the

CW based on volatilization, hydrolysis [10,41] and cation exchange, with different processes often occurring simultaneously [40].

It can be seen that when the initial TC concentrations in the CW were 0.980, 4.819, and 10.481 mg/L, the TC concentrations in the effluent were 0.097, 0.598, and 0.474 mg/L, respectively. This suggests that the initial TC concentration affected the removal of TC. A lower TC concentration is probably associated with a higher removal efficiency. As mentioned above, TC was adsorbed onto biofilm, soil, and gravel with little biodegradation and there would be an adsorption coefficient that indicates the substrates adsorbed TC at a certain concentration. When the TC concentration in the influent is high enough to exceed the adsorption capacity, the media would no longer adsorb TC and this would lead to lower removal efficiency [55]. However, this phenomenon was not observed in our test at 0.980 and 4.819 mg/L of TC concentration in the influent. Even in the high TC initial concentration at 10.481 mg/L, the decrease in the TC level was significant, reaching 0.474 mg/L, which was lower than that in case where the initial TC concentration of 4.819 mg/L. This may be due to mechanisms other than adsorption which help to reduce TC concentration in water.

According to the results shown in Figure 8, TC removal in the CW system was characterized by an initial phase (0–2 h) of rapid TC removal, followed by a slower removal rate period. It was respectively found that about 81.3%, 80.6% and 95.1% of the initial TC concentrations of 0.840, 4.728, and 12.113 mg/L was removed from influent water during the first two hours for three tests. It can be assumed that the initial removal of TC was mainly due to adsorption and photodegradation, followed by other above-suggested processes. After the initial period, maybe adsorption fully reached equilibrium and thus reduces the removal rate during the later time of operation in the CW considerably [42]. In fact, according to the study of Bao et al. [56], the adsorption kinetics of TC on soils exhibits two distinct stages: a very rapid adsorption (< 1 h) during the initial stage, followed by a relatively slow adsorption. Kulshrestha et al. [57], and Fei and Li [58] also observed similar results for oxytetracycline adsorption on clay and for TC adsorption on sediments, respectively.

3.4. Performance of the Combination of Constructed Wetland and TiO₂ Photocatalysis in Treating Water

In general, using a CW in conjunction with PCR produces better effluent water quality than that obtained by using CW alone [17,59,60]. In fact, one of the drawbacks of only using CW is that the disinfection obtained in many cases is not high enough to meet the standards for the reuse of the treated water [59]. In addition, in this study, the CW effluent may consist of microbiological organisms, bacteria and OM. Effluent from the CW, therefore, has to be disinfected before being used for drinking. A post-treatment such as PC should be used to control bacteria and OM releases because of the concern regarding OM release due to the formation of potentially carcinogenic disinfection byproducts, particularly THMs, during chlorination. Indeed, PC is an emerging alternative technology for the removal of organic compounds as well as the inactivation of the bacteria [61–63]. Therefore, the application of PC is expected as an effective post-treatment process for the removal of the OMs and bacteria released by a biological process in CW.

It can be seen from the Figure 9 that the removal efficiencies of the combined system in terms of sCOD, UV-254 and DOC were 80.3, 90.0 and 76.1%, respectively, which were higher than those of CW treatment alone (71.2, 81.8, 73.8%, respectively). The results show that the combination of CW pre-treatment and the photocatalytic post-treatment helped to improve effluent water quality with less chemical consumption than if chlorination were applied after this system. In fact, Liu et al. [17] declared that the photocatalytic process might work more efficiently as a post-treatment step as it requires favorable transparency for radiation penetration. In such case, the colour of the influent which is due to the presence of HA was solved in the CW; thus, its support helps the TiO₂ photocatalysis process to be more successful and the amount of catalyst used in this step will be lower. In addition, due to the formation of OH[•] during the photocatalytic process, the reduction of UV-254 decreased more efficiently from 0.155 cm⁻¹ to 0.085 cm⁻¹.

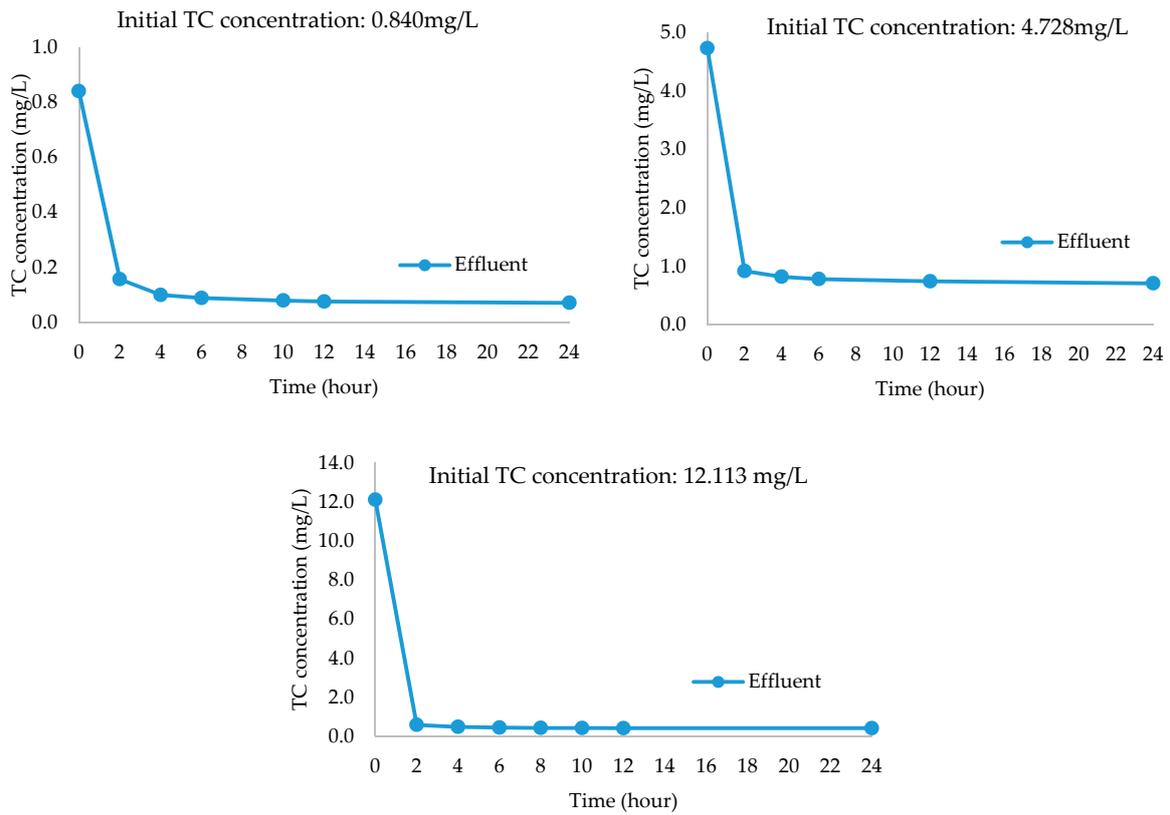


Figure 8. Time-dependent removal of TC over a period of treatment in CW with various initial TC concentrations.

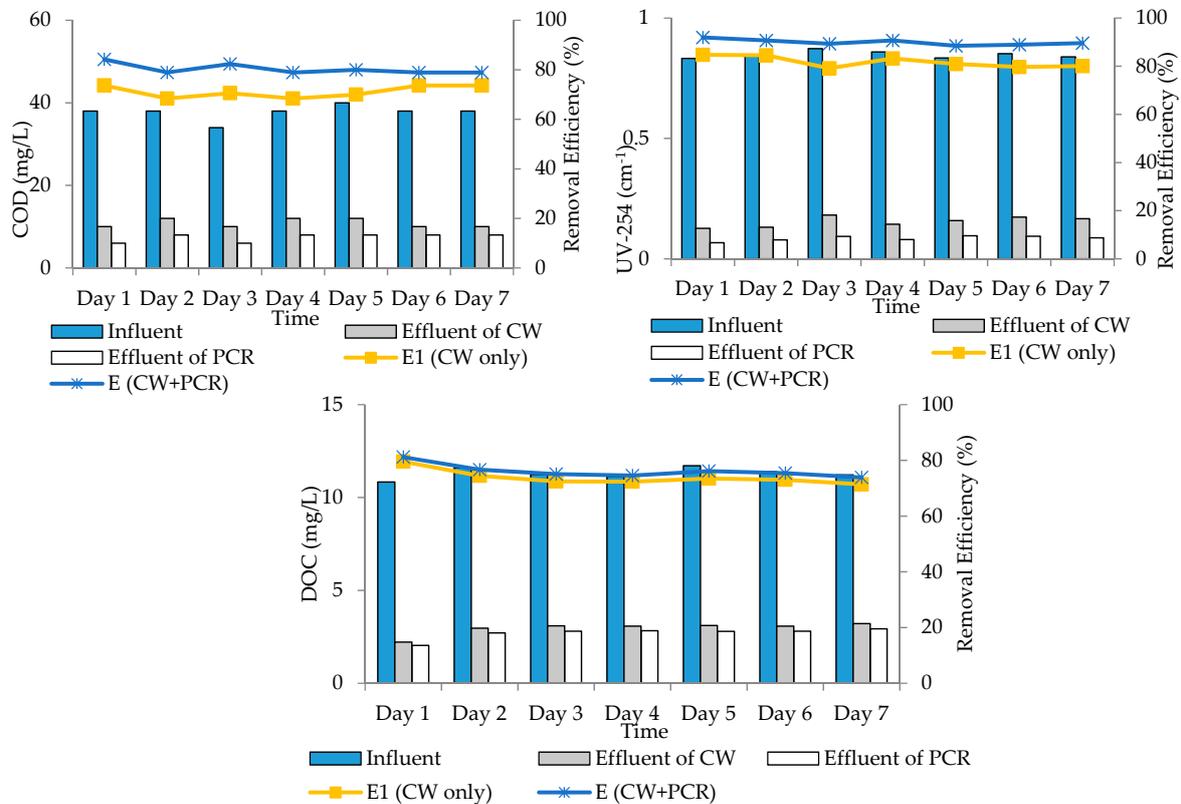


Figure 9. The influent, effluent and removal efficiency during the operation of the combined system.

However, there was a minor improvement of water quality in the effluent after the treatment of the combined system, especially in the parameter of DOC (which just increased 2.3%). This can be due to the fact that the CW followed by the photocatalytic process might not lead to a significant change in the molecular weight distribution [60]. Actually, the main purpose of using PC as post-treatment in this study was the fact that PC acts as an additional stage for further OM reduction before chlorination and reuse, with the hope that DOC concentration in effluent would be lower than the maximum contaminant level (MCL) for total THMs of drinking water quality standard. For example, Gulyas et al. reported that formed THM concentrations were above 0.01 mg/L (the guideline for German drinking water) when the concentration of TOC of the raw water exceeded 2 mg/L. In this research, the concentration of DOC in the effluent was recorded at 2.701 ± 0.300 mg/L, which may meet the MCL for total THMs regulated by the Taiwan Environmental Protection Administration (Taiwan EPA), which is 0.08 mg/L.

In terms of the sCOD parameter, sCOD in the effluent was 7.43 ± 0.98 mg/L, which was lower than the acceptable value of 25 mg/L recommended for raw water quality for drinking water by Taiwan EPA. With this sCOD value, the treated water can be considered as a potable water source.

4. Conclusions

In this research, the ability of a CW to remove OM and TC from water was investigated in a continuous scheme with various HRTs (1 day and 2 days) with varying initial DOC concentrations and TC concentrations. In different experimental runs with variable concentrations of OM operating during HRT-1 day CW treatment can have a high tolerance of variation of DOC concentrations in influent water and maintain stable effluent water quality. The discrepancy in the removal efficiency of OM between HRT-1 day and HRT-2 day was minor. This indicates that most of OM may be reduced on the first day of operation. However, HRT played an important role in the removal of ammonia in this experiment. The removal efficiency of $\text{NH}_3\text{-N}$ increased considerably with the increase of HRT.

In terms of TC removal, CW showed an excellent performance in reducing TC in water, especially in the first two hours of the operating period, when more than 80% of the TC was removed from the influent water. In addition, TC removal efficiencies of $90.20 \pm 1.02\%$, $87.60 \pm 2.48\%$ and $95.42 \pm 0.73\%$ were obtained from these trials with 1, 5, 10 mg/L of initial TC concentration respectively, indicating that the CW system was effective in eliminating TC.

In terms of applying the combination of CW and PCR ($\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$, UVA) in treating water containing OM, the findings of this research showed an improvement in the quality of the effluent. The concentration of sCOD in effluent water was estimated to be compliant with THM standards if chlorination was applied to the treated water. However, the increase in treatment efficiency of the combined system compared to that of CW alone was minor. Therefore, further research on the combination of CW and photocatalytic oxidation needs to be done to enhance the performance of this combined system.

Although the combined system decreased OM and TC successfully in this study, there are still a few limitations which must be taken into account. There is a great need to illuminate the black box CW to gain performance data for both the adsorption process and microbial activity. Also, the contribution of the plants to the overall removal process should be considered to enhance the treatment performance of CWs for specific compounds. In addition, other water quality parameters, for example, microorganisms and DBP (such as THMs) should be investigated. Further experimental investigations with longer operation time periods are required to provide more comprehensive and convincing evidence which will help gain more insights into the removal mechanism of target compounds in combined CW and PCR systems.

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References

1. Inyinbor Adejumo, A.; Adebisin Babatunde, O.; Abimbola, O.; Adelani-Akande Tabitha, A. Water pollution: Effects, prevention, and climatic impact. In *Water Challenges of an Urbanizing World*; Matjaž, G., Ed.; IntechOpen: Rijeka, Croatia, 2018; Volume 33.
2. Lou, S.; Huang, W.; Liu, S.; Zhong, G. Scarcity of Drinking Water in Taihu Lake Basin, China: A Case Study of Yixing City. *Water* **2019**, *11*, 362. [[CrossRef](#)]
3. Baghoth, S.A.; Sharma, S.K.; Amy, G.L. Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. *Water Res.* **2011**, *45*, 797–809. [[CrossRef](#)] [[PubMed](#)]
4. Wu, Y.; Zhou, S.; Ye, X.; Zhao, R.; Chen, D. Oxidation and coagulation removal of humic acid using the Fenton process. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *379*, 151–156. [[CrossRef](#)]
5. Bazrafshan, E.; Biglari, H.; Mahvi, A.H. Humic Acid Removal from Aqueous Environments by Electrocoagulation Process Using Iron Electrodes. *J. Chem.* **2012**, *9*, 2453–2461. [[CrossRef](#)]
6. Zeng, Z.-W.; Tan, X.-F.; Liu, Y.-G.; Tian, S.-R.; Zeng, G.-M.; Jiang, L.-H.; Liu, S.-B.; Li, J.; Liu, N.; Yin, Z.-H. Comprehensive Adsorption Studies of Doxycycline and Ciprofloxacin Antibiotics by Biochars Prepared at Different Temperatures. *Front. Chem.* **2018**, *6*, 80. [[CrossRef](#)] [[PubMed](#)]
7. Petrie, B.; Barden, R.; Kasprzyk-Hordern, B. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas, and recommendations for future monitoring. *Water Res.* **2015**, *72*, 3–27. [[CrossRef](#)] [[PubMed](#)]
8. Garcia-Rodriguez, A.; Matamoros, V.; Fontas, C.; Salvado, V. The influence of light exposure, water quality and vegetation on the removal of sulfonamides and tetracyclines: A laboratory-scale study. *Chemosphere* **2013**, *90*, 2297–2302. [[CrossRef](#)] [[PubMed](#)]
9. Brix, H.; Arias, C.A. The use of vertical flow constructed wetlands for on-site treatment of domestic wastewater: New Danish guidelines. *Ecol. Eng.* **2005**, *25*, 491–500. [[CrossRef](#)]
10. Kim, S.; Aga, D.S. Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants. *J. Toxicol. Environ. Health B Crit. Rev.* **2007**, *10*, 559–573. [[CrossRef](#)]
11. Kadlec, R.H.; Wallace, S. *Treatment Wetlands*; CRC Press: Boca Raton, FL, USA, 2008; p. 1046.
12. Vymazal, J.; Kröpfelová, L. *Wastewater Treatment in Constructed Wetlands with Horizontal Sub-Surface Flow*; Springer: Berlin/Heidelberg, Germany, 2008.
13. Matamoros, V.; Caselles-Osorio, A.; Garcia, J.; Bayona, J.M. Behaviour of pharmaceutical products and biodegradation intermediates in horizontal subsurface flow constructed wetland. A microcosm experiment. *Sci. Total Environ.* **2008**, *394*, 171–176. [[CrossRef](#)]
14. Lv, X.; Ruan, X. Removal of Natural Organic Matter by Integrated Vertical-Flow Constructed Wetland. In Proceedings of the Management and Service Science (MASS), Wuhan, China, 12–14 August 2011; pp. 1–4.
15. Braeckvelt, M.; Reiche, N.; Trapp, S.; Wiessner, A.; Paschke, H.; Kusch, P.; Kaestner, M. Chlorobenzene removal efficiencies and removal processes in a pilot-scale constructed wetland treating contaminated groundwater. *Ecol. Eng.* **2011**, *37*, 903–913. [[CrossRef](#)]
16. Matamoros, V.; García, J.; Bayona, J.M. Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. *Water Res.* **2008**, *42*, 653–660. [[CrossRef](#)] [[PubMed](#)]
17. Liu, R.; Zhao, Y.; Doherty, L.; Hu, Y.; Hao, X. A review of the incorporation of constructed wetland with other treatment processes. *Chem. Eng. J.* **2015**, *279*, 220–230. [[CrossRef](#)]
18. Coppini, E.; Palli, L.; Antal, A.; Del Bubba, M.; Miceli, E.; Fani, R.; Fibbi, D. Design and start-up of a constructed wetland as tertiary treatment for landfill leachates. *Water Sci. Technol.* **2019**, *79*, 145–155. [[CrossRef](#)] [[PubMed](#)]
19. Pansamut, G.; Charinpanitkul, T.; Biswas, P.; Suriyawong, A. Removal of Humic Acid by Photocatalytic Process: Effect of Light Intensity. *Eng. J.* **2013**, *17*, 25–32. [[CrossRef](#)]
20. Chen, A.; Chen, Y.; Ding, C.; Liang, H.; Yang, B. Effects of tetracycline on simultaneous biological wastewater nitrogen and phosphorus removal. *RSC Adv.* **2015**, *5*, 59326–59334. [[CrossRef](#)]

21. Hijosa-Valsero, M.; Matamoros, V.; Sidrach-Cardona, R.; Martín-Villacorta, J.; Bécares, E.; Bayona, J.M. Comprehensive assessment of the design configuration of constructed wetlands for the removal of pharmaceuticals and personal care products from urban wastewaters. *Water Res.* **2010**, *44*, 3669–3678. [[CrossRef](#)] [[PubMed](#)]
22. Chan, S.Y.; Tsang, Y.F.; Chua, H.; Sin, S.N.; Cui, L.H. Performance study of vegetated sequencing batch coal slag bed treating domestic wastewater in a suburban area. *Bioresour. Technol.* **2008**, *99*, 3774–3781. [[CrossRef](#)]
23. Gracia, R.; Cortés, S.; Sarasa, J.; Ormad, P.; Ovelleiro, J.L. Heterogeneous Catalytic Ozonation with Supported Titanium Dioxide in Model and Natural Waters. *Ozone-Sci. Eng.* **2000**, *22*, 461–471. [[CrossRef](#)]
24. Lenore, S.C.; Arnold, E.G.; Andrew, D.E. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association, American Water Works Association and World Environment Federation: Washington, DC, USA, 1998.
25. Saeedi, R.; Naddafi, K.; Nabizadeh, R.; Mesdaghinia, A.; Nasser, S.; Alimohammadi, M.; Nazmara, S. Simultaneous Removal of Nitrate and Natural Organic Matter from Drinking Water Using a Hybrid Heterotrophic/Autotrophic/Biological Activated Carbon Bioreactor. *Environ. Eng. Sci.* **2012**, *29*, 93–100. [[CrossRef](#)]
26. Chen, K.-C.; Wang, Y.-H.; Lu, Y.-C. Treatment of polluted water for reclamation using photocatalysis and constructed wetlands. *Catal. Today* **2011**, *175*, 276–282. [[CrossRef](#)]
27. Bilgin, M.; Şimşek, İ.; Tulun, Ş. Treatment of domestic wastewater using a lab-scale activated sludge/vertical flow subsurface constructed wetlands by using *Cyperus alternifolius*. *Ecol. Eng.* **2014**, *70*, 362–365. [[CrossRef](#)]
28. Faulwetter, J.L.; Gagnon, V.; Sundberg, C.; Chazarenc, F.; Burr, M.D.; Brisson, J.; Camper, A.K.; Stein, O.R. Microbial processes influencing the performance of treatment wetlands: A review. *Ecol. Eng.* **2009**, *35*, 987–1004. [[CrossRef](#)]
29. Nguyen, L. Accumulation of organic matter fractions in a gravel-bed constructed wetland. *Water Sci. Technol.* **2001**, *44*, 281–287. [[CrossRef](#)] [[PubMed](#)]
30. Trevisan, S.; Francioso, O.; Quaggiotti, S.; Nardi, S. Humic substances biological activity at the plant-soil interface: From environmental aspects to molecular factors. *Plant Signal. Behav.* **2010**, *5*, 635–643. [[CrossRef](#)]
31. Vaughan, D.; Ord, B.J. Uptake and incorporation of ¹⁴C-labelled soil organic matter by roots of *Pisum sativum* L. *J. Exp. Bot.* **1981**, *32*, 679–687. [[CrossRef](#)]
32. Nardi, S.; Pizzeghello, D.; Muscolo, A.; Vianello, A. Physiological effects of humic substances on higher plants. *Soil Biol. Biochem.* **2002**, *34*, 1527–1536. [[CrossRef](#)]
33. Ruocco, J.; Barton, L.L. Energy-driven uptake of humic acids by *Aspergillus niger*. *Can. J. Microbiol.* **1978**, *24*, 533–536. [[CrossRef](#)]
34. Vaughan, D.; Malcolm, R. Influence of humic substances on growth and physiological processes. In *Soil Organic Matter and Biological Activity*; Springer: Dordrecht, The Netherlands, 1985; pp. 37–75.
35. Prát, S. The effect of humus substances on the regeneration of plants. *Stud. Humus* **1962**, 223–235.
36. Hoffmann, H.; Platzer, C.; Winker, M.; von Muench, E. *Technology Review of Constructed Wetlands: Subsurface Flow Constructed Wetlands for Greywater and Domestic Wastewater Treatment*; Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH: Eschborn, Germany, 2011.
37. Mancilla, R.A.; Zúñiga, J.; Salgado, E.; Schiappacasse, M.C.; Chamy, R. Constructed wetlands for domestic wastewater treatment in a Mediterranean climate region in Chile. *Electron. J. Biotechnol.* **2013**, *16*, 5. [[CrossRef](#)]
38. Stecher, M.; Weaver, R. Effects of umbrella palms and wastewater depth on wastewater treatment in a subsurface flow constructed wetland. *Environ. Technol.* **2003**, *24*, 471–478. [[CrossRef](#)] [[PubMed](#)]
39. Akrotos, C.S.; Tsihrintzis, V.A. Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. *Ecol. Eng.* **2007**, *29*, 173–191. [[CrossRef](#)]
40. Matamoros, V.; Sala, L.; Salvado, V. Evaluation of a biologically-based filtration water reclamation plant for removing emerging contaminants: A pilot plant study. *Bioresour. Technol.* **2012**, *104*, 243–249. [[CrossRef](#)] [[PubMed](#)]
41. Li, B.; Zhang, T. Removal mechanisms and kinetics of trace tetracycline by two types of activated sludge treating freshwater sewage and saline sewage. *Environ. Sci. Pollut. R.* **2012**, *20*, 3024–3033. [[CrossRef](#)] [[PubMed](#)]
42. Song, C.; Sun, X.-F.; Wang, Y.-K.; Xia, P.-F.; Yuan, F.-H.; Li, J.-J.; Wang, S.-G. Fate of tetracycline at high concentrations in an enriched mixed culture system: Biodegradation and behavior. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 1562–1568. [[CrossRef](#)]

43. Thiele-Bruhn, S. Pharmaceutical antibiotic compounds in soils—A review. *J. Plant Nutr. Soil Sci.* **2003**, *166*, 145–167. [[CrossRef](#)]
44. Tolls, J. Sorption of Veterinary Pharmaceuticals in Soils: A Review. *Environ. Sci. Technol.* **2001**, *35*, 3397–3406. [[CrossRef](#)] [[PubMed](#)]
45. Guler, U.A.; Sarioglu, M. Removal of Tetracycline From Wastewater Using Pumice Stone: Equilibrium, Kinetic, and Thermodynamic Studies. *J. Environ. Health Sci. Eng.* **2014**, *12*, 79. [[CrossRef](#)]
46. Kim, S.; Eichhorn, P.; Jensen, J.N.; Weber, A.S.; Aga, D.S. Removal of Antibiotics in Wastewater: Effect of Hydraulic and Solid Retention Times on the Fate of Tetracycline in the Activated Sludge Process. *Environ. Sci. Technol.* **2005**, *39*, 5816–5823. [[CrossRef](#)]
47. de Godos, I.; Muñoz, R.; Guieysse, B. Tetracycline removal during wastewater treatment in high-rate algal ponds. *J. Hazard. Mater.* **2012**, *229*, 446–449. [[CrossRef](#)]
48. Chen, Y.; Hu, C.; Qu, J.; Yang, M. Photodegradation of tetracycline and formation of reactive oxygen species in aqueous tetracycline solution under simulated sunlight irradiation. *J. Photochem. Photobiol. A Chem.* **2008**, *197*, 81–87. [[CrossRef](#)]
49. Liu, L.; Liu, Y.-H.; Liu, C.-X.; Wang, Z.; Dong, J.; Zhu, G.-F.; Huang, X. Potential effect and accumulation of veterinary antibiotics in *Phragmites australis* under hydroponic conditions. *Ecol. Eng.* **2013**, *53*, 138–143. [[CrossRef](#)]
50. Dettenmaier, E.M.; Doucette, W.J.; Bugbee, B. Chemical Hydrophobicity and Uptake by Plant Roots. *Environ. Sci. Technol.* **2009**, *43*, 324–329. [[CrossRef](#)] [[PubMed](#)]
51. Li, Y.; Zhu, G.; Ng, W.J.; Tan, S.K. A review on removing pharmaceutical contaminants from wastewater by constructed wetlands: Design, performance, and mechanism. *Sci. Total Environ.* **2014**, *468*, 908–932. [[CrossRef](#)] [[PubMed](#)]
52. Di Marco, G.; Gismondi, A.; Canuti, L.; Scimeca, M.; Volpe, A.; Canini, A. Tetracycline accumulates in *Iberis sempervirens* L. through apoplastic transport inducing oxidative stress and growth inhibition. *Plant Biol.* **2014**, *16*, 792–800. [[CrossRef](#)] [[PubMed](#)]
53. Carvalho, P.N.; Basto, M.C.P.; Almeida, C.M.R. Potential of *Phragmites australis* for the removal of veterinary pharmaceuticals from aquatic media. *Bioresour. Technol.* **2012**, *116*, 497–501. [[CrossRef](#)]
54. Sengupta, A. Remediation of Tetracycline from Water Sources Using Vetiver Grass (*Chrysopogon zizanioides* L. Nash) and Tetracycline-Tolerant Root-Associated Bacteria. Ph.D. Thesis, Michigan Technological University, Houghton, MI, USA, 2014.
55. Qi, F.F.; Huang, M.H.; Zheng, Y.; Xu, Q. Optimization of an A(2)/O process for tetracycline removal via response surface methodology coupled with Box-Behnken design. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2015**, *50*, 735–743. [[CrossRef](#)]
56. Bao, Y.; Zhou, Q.; Wan, Y.; Yu, Q.; Xie, X. Effects of Soil/Solution Ratios and Cation Types on Adsorption and Desorption of Tetracycline in Soils. *Soil. Sci. Soc. Am. J.* **2010**, *74*, 1553–1561. [[CrossRef](#)]
57. Kulshrestha, P.; Giese, R.F.; Aga, D.S. Investigating the Molecular Interactions of Oxytetracycline in Clay and Organic Matter: Insights on Factors Affecting Its Mobility in Soil. *Environ. Sci. Technol.* **2004**, *38*, 4097–4105. [[CrossRef](#)]
58. Fei, Y.H.; Li, X.Y. Adsorption of tetracyclines on marine sediment during organic matter diagenesis. *Water Sci. Technol.* **2013**, *67*, 2616–2621. [[CrossRef](#)]
59. Araña, J.; Herrera Melián, J.A.; Doña Rodríguez, J.M.; González Díaz, O.; Viera, A.; Pérez Peña, J.; Marrero Sosa, P.M.; Espino Jiménez, V. TiO₂-photocatalysis as a tertiary treatment of naturally treated wastewater. *Catal. Today* **2002**, *76*, 279–289. [[CrossRef](#)]
60. Oller, I.; Malato, S.; Sánchez-Pérez, J.A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. *Sci. Total Environ.* **2011**, *409*, 4141–4166. [[CrossRef](#)] [[PubMed](#)]
61. Bekbölet, M. Photocatalytic bactericidal activity of TiO₂ in aqueous suspensions of *E. Coli*. *Water Sci. Technol.* **1997**, *35*, 95–100. [[CrossRef](#)]

62. Bekbolet, M.; Uyguner, C.S.; Selcuk, H.; Rizzo, L.; Nikolaou, A.D.; Meriç, S.; Belgiorno, V. Application of oxidative removal of NOM to drinking water and formation of disinfection by-products. *Desalination* **2005**, *176*, 155–166. [[CrossRef](#)]
63. Rizzo, L.; Rocca, C.D.; Belgiorno, V.; Bekbolet, M. Application of photocatalysis as a post-treatment method of a heterotrophic–autotrophic denitrification reactor effluent. *Chemosphere* **2008**, *72*, 1706–1711. [[CrossRef](#)]



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