Catalysis Today 175 (2011) 276–282

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Treatment of polluted water for reclamation using photocatalysis and constructed wetlands

Kuan-Chung Chen[a,b,*], Yu-Hsiang Wang[a], Yen-Chi Lu[a]

[a] Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Neipu, Pingtung 91201, Taiwan
[b] Emerging Compounds Research Center, National Pingtung University of Science and Technology, Neipu, Pingtung 91201, Taiwan

ARTICLE INFO

Article history:
Received 15 October 2010
Received in revised form 24 May 2011
Accepted 16 June 2011
Available online 5 July 2011

Keywords:
Photocatalysis
Constructed wetlands
Disinfection by-products
Water quality
Titanium dioxide
Reclamation

ABSTRACT

This study investigates the feasibility of using the combination of TiO_2 photocatalysis and a constructed wetland to treat polluted surface water for water reclamation. The treatment efficiency of the system was evaluated by varying the hydraulic retention time (HRT), light source wavelength, and quantity of photocatalyst. The experimental results show that the combined system with 2-day HRT had better treatment efficiency in terms of treated water quality than that obtained with 0.5-day HRT. The combined system effectively decreased the monitored water quality parameters; the removal percentages increased with increasing quantity of photocatalyst. Compared with constructed wetland treatment alone, the combined system improves the treatment efficiency of polluted water. An evaluation of the possibility of using the treated water for reclamation found that only the combined system effectively removed both trihalomethane (THM) and six haloacetic acid (HAA6) precursors, which decreased their formation to levels that meet the maximum contamination levels (MCLs) of drinking water. The proposed system is thus suitable for treating agricultural and domestic wastewater for water reclamation with low operating and maintenance costs.

1. Introduction

Freshwater has become scarce mainly due to rapid population growth, increased urbanization and industrialization, and climate change. In order to meet the increasing demand for freshwater, wastewaters are treated, purified, recycled, and reused for industry, agriculture, and domestic consumption in areas with limited water resources. For water reclamation, constructed wetlands, which serve as water treatment systems and wildlife habitat, can be used to treat wastewaters with low capital costs, ease of operation, and low maintenance requirements [1,2].

Constructed wetlands are natural systems that use physical, chemical, and biological processes to treat contaminated water and improve effluent water quality. The removal mechanisms for organic chemicals in constructed wetlands include biological degradation, sedimentation, sorption, photochemical oxidation, plant uptake, volatilization, phytovolatilization, phytoaccumulation, and phytodegradation [3]. Since organic matter, suspended solids, and nutrients are primary contaminants in domestic and agricultural wastewaters, constructed wetlands are a promising treatment option. The removal efficiency of constructed wetlands for the pollutants mentioned above depends on factors such as constructed wetland design, source water quality, temperature, vegetation, and management practices, which influence effluent quality [4,5]. Many studies have reported that constructed wetlands can effectively remove organic matter, suspended solids, fecal coliforms, pharmaceuticals and personal care products (PPCPs), and nutrients [1,6–8]. However, constructed wetlands require much more land area and longer hydraulic retention time (HRT) than do conventional wastewater treatment plants, which may make constructed wetland treatment unsuitable in high-land-cost and limited-land areas.

Although many studies have used constructed wetlands to treat urban and industrial wastewaters and investigated their treatment efficiency [1,2,5–9], few have investigated the combination of advanced oxidation processes (AOPs) and constructed wetlands [10,11]. AOPs involve the generation of hydroxyl radicals (OH•) that can decrease the levels of organic pollutants in water and increase their biodegradability. Several studies showed that AOPs, such as ozonation, followed by biological filtration can effectively remove organic matter from water [12–14]. Some researchers used titanium dioxide (TiO_2) and ultraviolet lamps as the photocatalytic material and light source, respectively, in a photocatalytic reactor as pretreatment for constructed wetland systems [10,11]. They found that the addition of photocatalysis improved organic removal

* Corresponding author at: Department of Environmental Science and Engineering, Emerging Compounds Research Center, National Pingtung University of Science and Technology, 1 Shuehfu Rd., Neipu, Pingtung 91201, Taiwan. Tel.: +886 8 7703202x7039; fax: +886 8 7740256.
E-mail address: kcchen@npust.edu.tw (K.-C. Chen).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.06.013

efficiency and increase the removal efficiencies of organic matter, nutrients, pathogenic bacteria, and pesticides of the subsequent wetland systems.

The present study investigates the feasibility of combining a TiO_2-photocatalytic process and a constructed wetland for treating polluted water for water reclamation. We hypothesized that using photocatalysis as pretreatment for constructed wetlands can convert some non-biodegradable organic matter into biodegradable matter, which improves the treatment efficiency and effluent quality of the constructed wetland system and thus shortens its HRT. Three operating parameters of the treatment system, namely HRT, catalyst amount, and light source wavelength, were the variables in the study. The effects of TiO_2-photocatalysis and wetland treatment on the removal of disinfection by-product (DBP) precursors were investigated in order to evaluate the possibility of using photocatalysis/wetland effluent as a drinking water source. The effluent water quality of the treatment system in terms of DBP formation is also discussed.

2. Materials and methods

2.1. Experimental setup and protocol

The photocatalytic constructed wetland system mainly consisted of a photocatalytic reactor, ultraviolet lamps, and a bench-scale simulated constructed wetland (Fig. 1). The raw water container had a capacity of about 25 L. Peristaltic pumps (Masterflex, Cole-Parmer Co., Chicago, IL) were used to pump raw water continuously into the photocatalytic reactor and to withdraw effluent from the simulated constructed wetland to a collection bottle at a fixed flow rate of 10 mL/min. The photocatalytic reactor consisted of four ultraviolet lamps and one photocatalytic column in an airtight glass chamber. The photocatalytic process used ultraviolet lamps (10 W, 28 mm O.D., manufactured by Philips) with two wavelengths, namely UVA and UVC with emission spectra of 315–400 nm and 230–280 nm, respectively. The photocatalytic column was a 0.34-L glass cylinder, which contained TiO_2/α-Al_2O_3 photocatalysts. The bench-scale constructed wetland was built in a horizontal subsurface flow wetland (HFSF) pattern. Its dimensions were 40 cm (L) × 25 cm (W) x 28 cm (H), for a volume of approximately 15 L. The effluent of the wetland was collected in a 4-L water tank. The bottom of the constructed wetland was a mixture of soils and gravels that formed a 5-cm-deep deposition layer. The bench-scale constructed wetland was planted with various common aquatic plants, such as reed, water grass, and potamogeton, from the riverside of the Wu-Lo River (WLR), Pingtung, Taiwan, from which the raw water was taken. Untreated WLR water was used to feed the constructed wetland system for over four months. The constructed wetland was used for the study when its treatment efficiency became stable (as determined by analyzing the effluent quality periodically). The treatment efficiency of the system was evaluated by varying the operating parameters (i.e., HRT, light source wavelength, and photocatalyst amount). The HRTs of the photocatalytic unit and bench-scale constructed wetland are the same since these two processes were connected in series. The HRT values were calculated by dividing the effective volume of the bench-scale simulated constructed wetland, which was 12 L, by the flow rate of wastewater. The operating conditions used in this study are given in Table 1.

Table 1
Operating conditions for the photocatalytic process and bench-scale constructed wetland system.

Hydraulic retention time (days)	0.5, 2.0
Catalyst (g)	225, 450
Light source	UVA, UVC
Treatment process	Photocatalysis alone, wetland alone, photocatalysis and wetland

2.2. Water source

The water samples used in this study were collected from WLR, Pingtung, Taiwan, which is polluted by domestic and agricultural wastewaters. The characteristics of the raw water are summarized in Table 2. Water samples were collected in 25-L polyethylene tanks and stored in a refrigerator at 4 °C for less than 7 days. Samples were

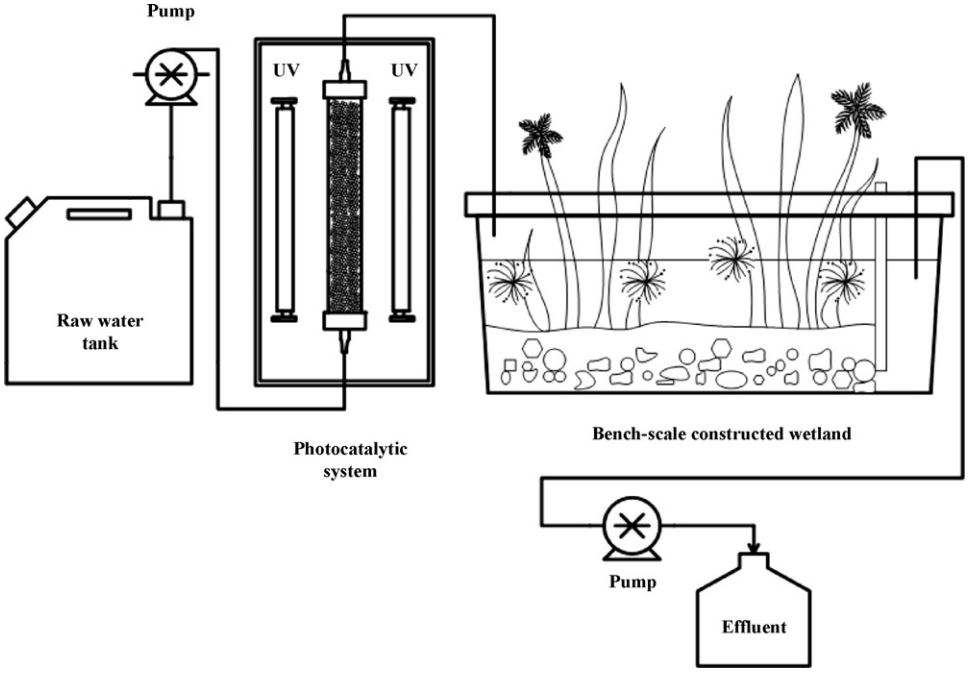

Fig. 1. Photocatalytic reactor and bench-scale constructed wetland system.

Table 2
Water characteristics of the Wu-Lo River (Pingtung, Taiwan).

Parameter	Raw water
pH	8.4 ± 0.1
UV-254 (cm^{-1})	0.105 ± 0.020
DOC (mg/L)	8.5 ± 2.9
BOD_5 (mg/L)	10.8 ± 2.4
COD (mg/L)	36.2 ± 7.4
SS (mg/L)	22.2 ± 6.3
NH_3–N (mg/L)	4.44 ± 0.5
PO_4–P (mg/L)	0.60 ± 0.1
SDS-THMs (μg/L)	118.0 ± 2.5
SDS-HAA6 (μg/L)	126.7 ± 4.1

warmed back to room temperature before being used in experiments.

2.3. Preparation of photocatalyst

TiO_2 nanoparticles were coated on commercially available α-Al_2O_3 pellets using the impregnation method [15] and used as the photocatalyst in this study. Briefly, the α-Al_2O_3 pellets (3-mm dia.) were immersed in a solution that consisted of commercially available TiO_2 specimens (Degussa P25, 80% anatase, 20% rutile, BET surface area of 50 m^2/g) with constant shaking for 5 h to impregnate TiO_2 onto the support pores. The pH of the solution was adjusted to 5.5 (H_2SO_4, 0.1N). The pellets were then washed in organic-free water until the effluent was clear, dried at 105 °C for one hour in an oven, and placed in a furnace to calcine for 24 h at 500 °C. Finally, the catalysts, which contained about 10 wt.% impregnated TiO_2, were compacted. The morphology and the semi-quantitative elemental composition of the composite oxides analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) on a Hitachi S-3000N system are shown in Fig. 2.

2.4. Analyses

All water samples were prefiltered through a 0.45-μm membrane filter (Code C cellulose acetate membrane, Toyo, Japan) before being analyzed. Water quality parameters, including dissolved organic carbon (DOC), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), suspended solids (SS), ammonia-nitrogen (NH_3–N), phosphate (PO_4–P), pH, and ultraviolet absorbance at 254 nm (UV254), were determined according to Standard Methods [16]. All experimental reagents were analytical grade. Three replicates for each sample were used. DOC was analyzed following the combustion catalytic oxidation/NDIR method using a total organic carbon analyzer (Model TOC-VCSH, Shimadzu, Tokyo, Japan). UV254 was measured with a UV/Vis spectrophotometer (DR-5000, HACH Co., Loveland, CO) at room temperature. A quartz cell providing a light path of 1 cm was used.

Simulated distribution system trihalomethanes (SDS-THMs), including chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), and six simulated distribution system haloacetic acids (SDS-HAA6), namely monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA), were measured in this study according to Standard Method 5710B [16] by using a gas chromatograph (Agilent HP 6890N) equipped with a ^{63}Ni electron capture detector (GC-ECD) and an autosampler. A 30-m, 0.25-mm I.D. Supelco Equity-5 column (Supelco Analytical, Bellefonte, PA) was used. The operating conditions of GC-ECD are described in our previous work [14]. Collected water samples were dosed with a chlorine concentration that allowed the free residual chlorine concentration to be in the range of 0.2 to 1.0 mg/L after 48 h of incubation at room temperature according to the procedures given in Standard Method 2350 [16].

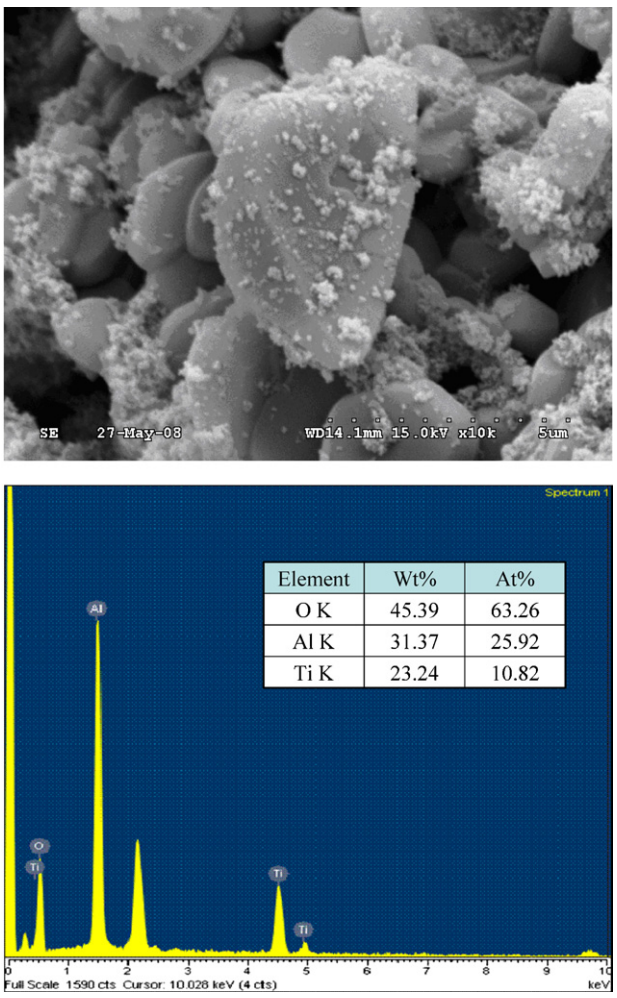

Fig. 2. (a) SEM micrograph (× 1000) and (b) EDS surface analysis of TiO_2/α-Al_2O_3 catalyst.

3. Results and discussion

3.1. Effect of hydraulic retention time (HRT)

The effect of HRT on treated water quality is shown in Fig. 3. The treatment processes studied were the constructed wetland alone, photocatalysis alone, and photocatalysis followed by the

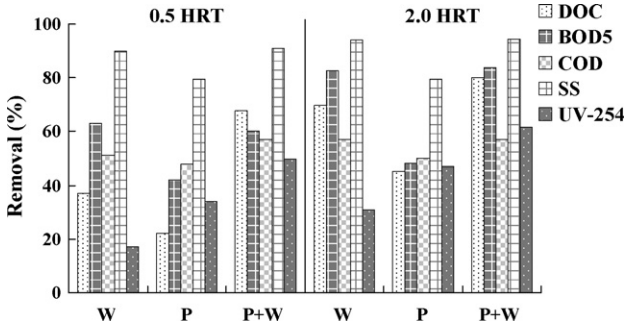

Fig. 3. Effect of HRT on effluent water quality. Operating conditions: light source: UVA, photocatalyst amount: 225 g; W: constructed wetland, P: photocatalysis, P + W: photocatalysis + constructed wetland.

constructed wetland. The treatment system was operated under two HRTs, namely 0.5 and 2.0 days, with UVA as the light source and 225 g of catalyst packed in the photocatalytic reactor. The results show that all three treatment processes tested with an HRT of 2.0 days had better removal efficiencies for all monitored water quality parameters than those obtained with an HRT of 0.5 days. The combination of the photocatalytic process and the bench-scale constructed wetland, with an HRT of either 0.5 or 2.0 days, had a significantly higher treatment efficiency compared to those of the wetland treatment alone and photocatalysis alone in terms of all monitored water quality parameters. The removal efficiencies of DOC, BOD_5, COD, and SS of wetland treatment alone are higher than those of photocatalysis alone. In the proposed treatment system, the main purpose of the photocatalytic process is not to fully mineralize/remove pollutants such as organic matter from water, but to convert non-biodegradable organic matter into biodegradable matter, which allows the subsequent biotreatment system to remove more biodegradable matter. However, due to the formation of OH• during the photocatalytic process, the reduction of UV254 was decreased more efficient by photocatalysis alone than by wetland treatment alone. The experimental results show that the photocatalytic process only removed some of the contaminants and that the constructed wetland further decreased the levels of contaminants, improving the effluent quality. Previous studies showed that a heterogeneous photocatalytic oxidation process employing a photocatalyst (TiO_2) and UV light can generate more OH•, which can rapidly oxidize and degrade persistent organic pollutants, resulting in the production of more biodegradable organics [17–19]. Therefore, the photocatalytic process as pretreatment is beneficial to the wetland system.

The formation reductions of SDS-DBPs for various HRTs and treatment processes are shown in Fig. 4. The results show that for the bench-scale constructed wetland treatment alone, the formation reductions of SDS-THMs and SDS-HAA6 increased from about 21 to 44% and from 30 to 47%, respectively, when the HRT was increased from 0.5 days to 2.0 days. The longer HRT offers more time for organic pollutants, which are recognized as DBP precursors, to be removed from water by biological activities or physical sedimentation in the wetland system. For photocatalysis alone, the formation reductions of SDS-THMs and SDS-HAA6 increased from 38 to 85% and from 62 to 93% when the HRT was increased from 0.5 days to 2.0 days. Compared with wetland treatment alone, photocatalysis has a higher reduction of DBP precursors due to the breakage of organics with conjugated or UV-absorbing bonds [20]. When the photocatalytic process was used as pretreatment for the wetland system, persistent organic pollutants were converted into small, more-biodegradable matter in the photocatalytic reactor to be consumed in the wetland system. The formation reductions of SDS-THMs and SDS-HAA6, compared with

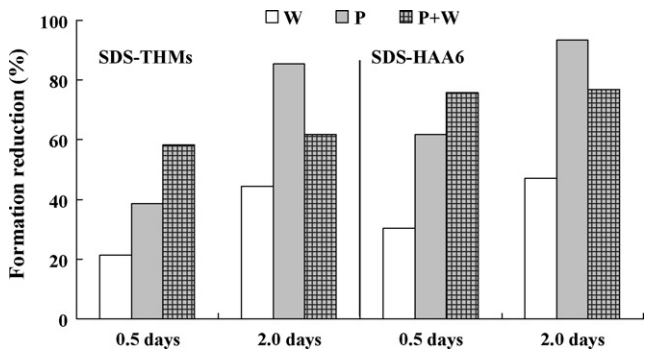

Fig. 4. Effect of HRT on the formation reduction of SDS-DBPs. Operating conditions: light source: UVA, photocatalyst amount: 225 g, HRT: 0.5 and 2.0 days; W: constructed wetland, P: photocatalysis, P + W: photocatalysis + constructed wetland.

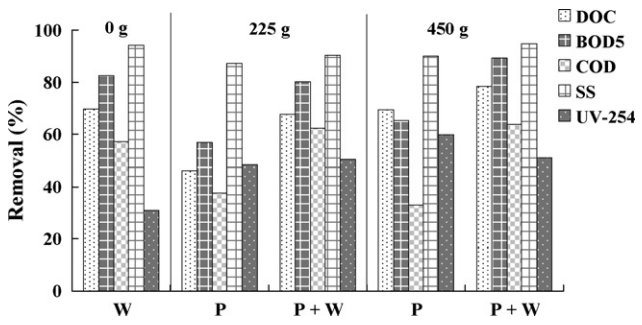

Fig. 5. Effect of photocatalyst amount on effluent water quality. Operating conditions: light source: UVC, HRT: 2.0 days; W: constructed wetland, P: photocatalysis, P + W: photocatalysis + constructed wetland.

those of wetland treatment alone, significantly increased by up to 62% and 77%, respectively. However, the combined photocatalysis and wetland system released more DBP precursors than did the photocatalysis treatment alone. It is thought that the wetland system degrades biodegradable organic matter and releases some organic matter such as biological metabolites, which can form DBPs during chlorination. For both SDS-THMs and SDS-HAA6 in the effluent of the combined system, an increase of HRT from 0.5 to 2.0 days only slightly enhanced the removal efficiencies of their precursors. This indicates that the combination of photocatalysis and the constructed wetland effectively decreases the concentration of DBP precursors in a short period of time.

The effective volume of the bench-scale simulated constructed wetland was 12 L. The flow rate of the fed wastewater was 4.2 mL/min in the experiment with a 2.0-day HRT. A 15-acre constructed wetland with a 0.5-m average effective depth, such as the Wu-Lo constructed wetland in southern Taiwan, would be able to treat 3.75×10^4 cubic meters a day (CMD) of wastewater. During our test at HRTs of 0.5 and 2.0 days, the effluent water quality of the proposed system was stable and no problems were encountered.

3.2. Effect of photocatalyst amount

The effect of the photocatalyst amount on the performance of photocatalytic treatment alone and that of photocatalysis followed by the wetland system was studied. The experimental operating conditions were: various photocatalyst amounts (225 g and 450 g) under UVC radiation with an HRT of 2.0 days. The removal efficiencies for the monitored water quality parameters are shown in Fig. 5. As shown in figure, the removal efficiency for each water quality parameter increased with increasing catalyst amount. This suggests that more hydroxyl radicals, which can react with organic pollutants, form intermediates, and cause mineralization, were produced when a higher catalyst amount was used in the photocatalytic process. The activation of $TiO_2/\alpha\text{-}Al_2O_3$ by UV radiation can be represented as a series of chain oxidation/reduction reactions that occur at the photocatalyst surface as follows [21–24]:

$$\text{Catalyst surface} + h\nu \rightarrow e^- + h^+ \quad (1)$$

where e^- is a conduction-band electron and h^+ is a valence-band hole.

The interaction of holes with water molecules or hydroxide ions produces very reactive hydroxyl radicals.

$$h^+ + H_2O \rightarrow OH\bullet + H^+ \quad (2)$$

$$h^+ + OH^- \rightarrow OH\bullet \quad (3)$$

Molecular oxygen acts as an acceptor species, which forms super-oxide ions (O_2^-) via a reduction reaction.

$$e^- + O_2 \rightarrow O_2^- \quad (4)$$

The further reduction of super-oxide anions produces hydrogen peroxide or peroxide anions, which can subsequently be involved in the following reactions.

$$O_2^- + H^+ \rightarrow HO_2\bullet \quad (5)$$

$$H^+ + O_2^- + HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

The photoconversion of hydrogen peroxide produces OH• free radical groups.

$$H_2O_2 + UV \rightarrow 2\,OH\bullet \quad (7)$$

The OH• radicals are very reactive and attack the organic pollutants, degrading them into intermediates, which are eventually converted to carbon dioxide and water.

$$OH\bullet + \text{organic pollutants} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad (8)$$

Using photocatalysis in conjunction with a constructed wetland to treat raw water produces better effluent water quality than that obtained using the photocatalytic process alone (Fig. 5). The treatment by a constructed wetland alone has higher removal percentages for DOC, BOD_5, and SS than those obtained using photocatalysis alone and the combined system with a catalyst amount of 225 g. Of noted, the effluent of a natural biosystem such as a wetland, unlike that of artificial physical–chemical treatment processes, in general contains a certain amount of organic matter that results from either residual pollutants or biological metabolites when it is used to treat polluted water. This implies that a wetland system may maintain a steady water quality level of its effluent. In this study, we observed that the concentrations of DOC, BOD_5, COD, and SS in the effluents of the wetland and combined photocatalysis and wetland system are very similar (data not shown). Moreover, increasing the photocatalyst amount from 225 to 450 g increased the removal efficiencies for the water quality parameters in the combined photocatalysis and constructed wetland treatment system. Several studies indicated that the degradation efficiency of organic material by photocatalysis first increases with the increasing of photocatalyst dosage and then decreases [25,26]. Sin et al. [27] explained that a higher amount of photocatalysts produces more active sites in a solution; however, an excess amount of photocatalyst can influence the light absorption on photocatalyst surface area. Gad-Allah et al. [21] reported that increasing the TiO_2 photocatalyst amount effectively accelerated the reaction rate of hydroxyl radicals with organic matter, but that the reaction rate decreased when the amount of photocatalyst was over the optimal dose. The higher amount of photocatalyst (450 g) used in the photocatalysis and wetland system seems to have been over the optimal dose; therefore, it did not significantly improve the treatment efficiency.

For the formation reductions of SDS-DBPs, experimental results show that SDS-THMs and SDS-HAA6 formation decreased by 21 and 47%, respectively, when using constructed wetland treatment alone (Fig. 6). The formation of SDS-THMs and SDS-HAA6 was further decreased to 47 and 50%, respectively, when using the combined photocatalysis and constructed wetland system with a photocatalyst amount of 225 g. When the photocatalyst amount was increased to 450 g, it was found that only the formation of SDS-HAA6 was further decreased to 64%. It is believed that the wetland system may release some organic substances into the treated water that can react with chlorine and form DBPs. This may result in an increase of some DBP concentrations and a decrease of the removal of some DBP precursors.

3.3. Effect of light source wavelength

Two wavelengths of UV light source, namely UVA and UVC, were used to evaluate the influence of light source wavelength on effluent water quality. The removal percentages for monitored water parameters with a photocatalyst amount of 450 g after 0.5-day HRT treatment by photocatalysis and the combined photocatalysis and wetland system are shown in Fig. 7. For treatment with photocatalysis alone, using UVA as the light source yielded slightly better removal percentages for water quality parameters than those obtained using UVC as the light source. Generally, the rate constant of photocatalysis by UVC irradiation on the TiO_2 surface is higher than that by UVA irradiation. Puma et al. [28] used photocatalysis to degrade endocrine disrupting chemicals and reported that the rate constant for UVC was twice that for UVA irradiation. This implies that using UVC irradiation on the photocatalyst (TiO_2) produces more OH• to attack organic pollutants than the amount obtained using UVA irradiation. However, the oxidation rate is also subject to the concentrations of radical scavengers such as carbonates [29], which widely reside in the raw water. Therefore, some oxidation intermediates needed more time to be mineralized. As shown in Fig. 7, the difference of removal efficiencies between UVA and UVC was mainly due to the characteristics of the raw water. For example, the DOC concentration for the UVA experiment was 9.7 mg/L, and that for the UVC experiment was 13.6 mg/L. The higher DOC concentration in the influent water may result in more contaminants being adsorbed onto the surface of the photocatalyst, which prevents the entire light irradiation of UVC from being used for the excitation of the photocatalyst to produce hydroxyl radicals [30]. In addition, Venkatachalam et al. [30] reported that the mineralization rate of 4-chlorophenol (4-CP) at 365 nm was slightly higher than that at 254 nm during photocatalysis. They indicated that the band gap excitation of electrons on TiO_2 with a light source at 254 nm promotes electrons across the band gap to the conduction band with high kinetic energy. This enables electrons to reach the solid–liquid interface easily, suppressing the electron–hole recombination in comparison to that obtained at 365 nm. Therefore, this mechanism may play an important role in

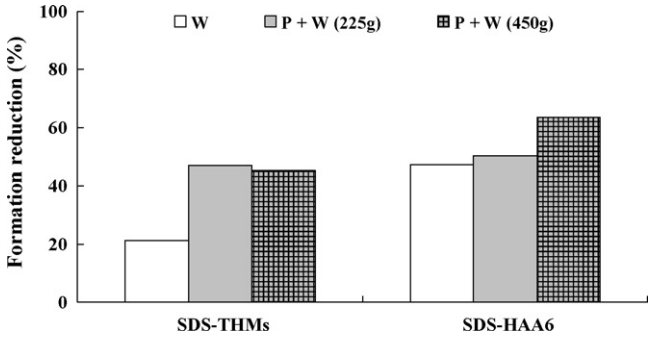

Fig. 6. Effect of photocatalyst amount on the formation reduction of DBPs. Operating conditions: light source: UVC, HRT: 2.0 days; W: constructed wetland, P + W: photocatalysis + constructed wetland.

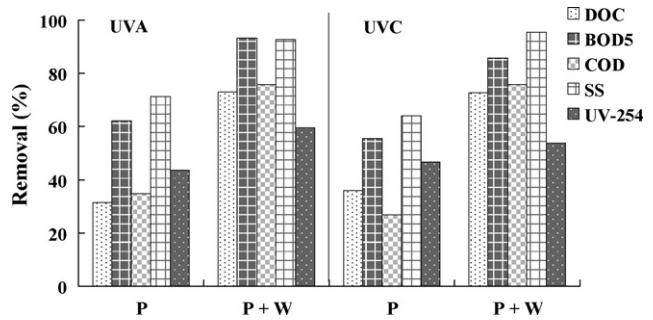

Fig. 7. Effect of UV wavelength on effluent water quality. Operating conditions: photocatalyst amount: 450 g, HRT: 0.5 days; P: photocatalysis, P + W: photocatalysis + constructed wetland.

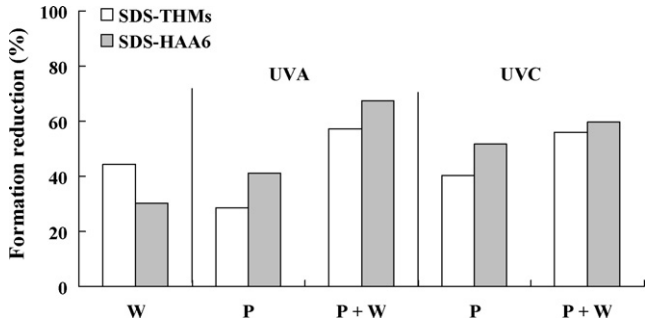

Fig. 8. Effect of UV wavelength on the formation reduction of DBPs. Operating conditions: photocatalyst amount: 450 g, HRT: 2.0 days; W: constructed wetland, P: photocatalysis, P + W: photocatalysis + constructed wetland.

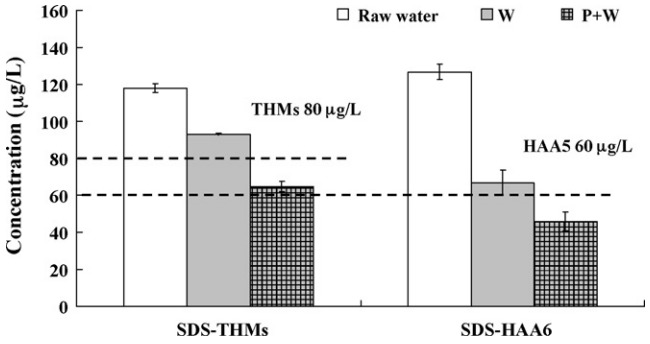

Fig. 9. Effect of various treatment processes on the concentrations of DBPs. Operating conditions: light source: UVC, photocatalyst amount: 450 g, HRT: 2.0 days; W: constructed wetland, P + W: photocatalysis + constructed wetland.

limiting the formation of OH• on the surface of the catalyst under UVC irradiation, lowering the mineralization rate of 4-CP.

For the combination of the photocatalytic process and the bench-scale constructed wetland under various UV irradiation conditions, the results show that the irradiation wavelength did not significantly affect the removal percentages for the monitored water quality parameters. The photocatalytic process can convert high-molecular-weight compounds into low-molecular-weight compounds [31], which are expected to be effectively removed by the subsequent constructed wetland system through biodegradation and homogenisation.

The percentage decreases of SDS-DBPs in the effluent water when using the wetland alone, photocatalysis alone, and combined photocatalysis and wetland system treatment are shown in Fig. 8. For treatment by the constructed wetland alone, the formation of SDS-THMs and SDS-HAA6 decreased by 44 and 30%, respectively. This demonstrates that the bench-scale constructed wetland removed some DBP precursors, such as aliphatic and aromatic organics fractions [32]. Wei et al. [33] reported that 37 and 20% of DOC and THMs, respectively, were removed with treatment by a laboratory-scale horizontal subsurface flow constructed wetland. In our study, the formation reductions of SDS-THMs and SDS-HAA6 by the photocatalytic process were 29 and 41% with UVA irradiation and 40 and 52% with UVC irradiation, respectively. The photocatalytic process in combination with the bench-scale constructed wetland system effectively decreased the formation of SDS-THMs and SDS-HAA6 by 57 and 67% with UVA irradiation, and by 56 and 60% with UVC irradiation, respectively. These results are consistent with the removal efficiencies of DOC and UV254 (Fig. 7).

3.4. Control of disinfection by-product formation

The SDS-DBP concentrations in the raw water and effluent water of the wetland treatment alone and those of the combined photocatalysis and wetland system were compared with drinking water standards in order to evaluate treatment performance and the feasibility of using the effluent water as a drinking water source. The experiment was conducted using UVC as the light source with a photocatalyst amount of 450 g and an HRT of 2.0 days. The formation levels of SDS-THMs and SDS-HAA6 in raw water and effluent water of the constructed wetland and the combined photocatalysis and wetland system are shown in Fig. 9. It should be noted that the Taiwan Drinking Water Standards (TDWS) only regulates the maximum contaminant level (MCL) for total THMs (TTHMs), which is 80 μg/L [34]. Since the WLR water was contaminated by agricultural and domestic wastewater, the formation of SDS-THMs in raw water was 118.0 μg/L, which does not meet the MCL of TTHMs for TDWS. The formation of SDS-HAA6 in raw water was measured as 126.7 μg/L. This value does not meet the MCL of 60 μg/L regulated by the United States Environmental Protection Agency. After treatment by the bench-scale constructed wetland alone, the formation of SDS-THMs and SDS-HAA6 was reduced to 92.9 and 67.0 μg/L, respectively. This indicates that 21 and 47% of the precursors of SDS-THMs and SDS-HAA6 were removed, respectively, during the wetland treatment. As can be expected, the combination of photocatalysis and the constructed wetland removed more precursors of SDS-THMs and SDS-HAA6, which resulted in the formation of these SDS-DBPs decreasing to 64.8 and 46.1 μg/L, respectively. $CHCl_3$ was the predominant compound of SDS-THM species, followed by $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ in all water samples. For SDS-HAA6, the major species was DCAA, which accounted for approximately 80–90%.

The results show that using photocatalysis as pretreatment for the bench-scale constructed wetland increases the removal efficiencies of precursors of DBPs and decreases the formation of SDS-DBPs in the effluent water to meet the requirements of drinking water standards. The combined photocatalysis process and constructed wetland system has the potential to treat water polluted by agricultural and domestic wastewaters. The combined system effectively reduces the formation of DBPs in treated water, allowing the effluent water to be used as a drinking water source.

4. Conclusion

The findings of this research show that using a combined photocatalysis and bench-scale constructed wetland system significantly reduced the levels of the monitored water parameters and decreased DBP formation under experimental conditions. Compared with the bench-scale constructed wetland treatment alone, the addition of a photocatalytic process as pretreatment increased the treatment efficiency of the subsequent bench-scale constructed wetland and improved treated water quality. The relatively short HRT of the combined photocatalysis and bench-scale constructed wetland system compared with that of conventional constructed wetlands indicates that it could be used for water reclamation in confined areas where land cost is high or the land area is limited. The light source wavelength influenced the treated water quality of photocatalysis but had no impact on treatment efficiency of the subsequent bench-scale constructed wetland. Moreover, the formation levels of DBPs in the effluent water meet the MCLs for drinking water standards under optimal experimental operating conditions, which makes the combined system capable of treating water polluted by organic contaminants and of producing water that can be used for drinking. A study on the durability of the photocatalyst is recommended in order to determine the performance of the combined system over time. The treatment efficiency of the combination of constructed wetland followed by photocatalysis should also be determined since the constructed wetlands are very efficient at reducing organic materials and sus-

pended solids. Other water quality parameters, such as pesticides and PPCPs, should be investigated if the effluent water is to be used for households.

Acknowledgement

The authors would like to thank the National Science Council (NSC) of Taiwan, R.O.C., for financial support under grant NSC 97-2815-C-020-002-E.

References

[1] N. Ran, M. Agami, G. Oron, Water Res. 38 (2004) 2241–2248.
[2] A. Gross, O. Shmueli, Z. Ronen, E. Raveh, Chemosphere 66 (2007) 916–923.
[3] G. Imfeld, M. Braeckevelt, P. Kuschk, H.H. Richnow, Chemosphere 74 (2009) 349–362.
[4] C.S. Akratos, V.A. Tsihrintzis, Ecol. Eng. 29 (2007) 173–191.
[5] F.J. Diaz, A.T. Chow, A.T. O'Geen, R.A. Dahlgren, P.K. Wong, Water Res. 43 (2009) 2750–2760.
[6] H.R. Hadad, M.A. Maine, C.A. Bonetto, Chemosphere 63 (2006) 1744–1753.
[7] M.A. Maine, N. Sune, H. Hadad, G. Sanchez, C. Bonetto, Chemosphere 68 (2007) 1105–1113.
[8] E. Llorens, V. Matamoros, V. Domingo, J.M. Bayona, J. Garcia, Sci. Total Environ. 407 (2009) 2517–2524.
[9] V. Matamoros, J. Garcia, J.M. Bayona, Water Res. 42 (2008) 653–660.
[10] A. Antoniadis, V. Takavakoglou, G. Zalidis, I. Poulios, Catal. Today 124 (2007) 260–265.
[11] J. Arana, C.G.I. Cabo, C.F. Rodriguez, J.A.H. Melian, J.A.O. Mendez, J.M.D. Rodriguez, J.P. Pena, Chemosphere 71 (2008) 788–794.
[12] A.A. Yavich, K.H. Lee, K.C. Chen, L. Pape, S.J. Masten, Water Res. 38 (2004) 2839–2846.
[13] L.S. Li, W.P. Zhu, P.Y. Zhang, Z.L. Zhang, H.H. Wu, W.Y. Han, Chemosphere 62 (2006) 1514–1522.
[14] K.C. Chen, Y.H. Wang, Y.H. Chang, Desalination 249 (2009) 929–935.
[15] R. Gracia, S. Cortes, J. Sarasa, P. Ormad, J.L. Ovelleiro, Ozone-Sci. Eng. 22 (2000) 461–471.
[16] APHA, Standard Methods for the Examination of Water and Wastewater, 20th, 1998, Washington, DC, USA.
[17] A. Garcia-Ripoll, A.M. Amat, A. Arques, R. Vicente, M.F. Lopez, I. Oller, M.I. Maldonado, W. Gernjak, Chemosphere 68 (2007) 293–300.
[18] I. Oller, W. Gernjak, M.I. Maldonado, L.A. Perez-Estrada, J.A. Sanchez-Perez, S. Malato, J. Hazard. Mater. 138 (2006) 507–517.
[19] H. Yang, G.Y. Li, T.C. An, Y.P. Gao, J.M. Fu, Catal. Today 153 (2010) 200–207.
[20] K.K. Philippe, C. Hans, J. MacAdam, B. Jefferson, J. Hart, S.A. Parsons, Environ. Technol. 31 (2010) 1423–1434.
[21] T.A. Gad-Allah, S. Kato, S. Satokawa, T. Kojima, Desalination 244 (2009) 1–11.
[22] L. Gu, Z.X. Chen, C. Sun, B. Wei, X. Yu, Desalination 263 (2010) 107–112.
[23] O.K. Dalrymple, E. Stefanakos, M.A. Trotz, D.Y. Goswami, Appl. Catal. B-Environ. 98 (2010) 27–38.
[24] A.K. Benabbou, Z. Derriche, C. Felix, P. Lejeune, C. Guillard, Appl. Catal. B-Environ. 76 (2007) 257–263.
[25] C.H. Chiou, R.S. Juang, J. Hazard. Mater. 149 (2007) 1–7.
[26] S.K. Pardeshi, A.B. Patil, Sol. Energy 82 (2008) 700–705.
[27] J.C. Sin, S.M. Lam, A.R. Mohamed, Kor. J. Chem. Eng. 28 (2011) 84–92.
[28] G.L. Puma, V. Puddu, H.K. Tsang, A. Gora, B. Toepfer, Appl. Catal. B-Environ. 99 (2010) 388–397.
[29] L. Rizzo, S. Meric, M. Guida, D. Kassinos, V. Belgiorno, Water Res. 43 (2009) 4070–4078.
[30] N. Venkatachalam, M. Palanichamy, V. Murugesan, J. Mol. Catal. a-Chem. 273 (2007) 177–185.
[31] S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas, R. Amal, Environ. Sci. Technol. 42 (2008) 6218–6223.
[32] D.M. Quanrud, M.M. Karpiscak, K.E. Lansey, R.G. Arnold, Chemosphere 54 (2004) 777–788.
[33] L.L. Wei, Q.L. Zhao, S. Xue, T. Jia, F. Tang, P.Y. You, Ecol. Eng. 35 (2009) 1405–1414.
[34] TWEPA, Drinking Water Quality Standards, Taiwan Environmental Protection Administration, 2005, http://law.epa.gov.tw/en/laws/359367440.html.