Treatment of Polluted Surface Water for Reclamation by Using Photocatalytic Constructed Wetland

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Abstract
This study investigates the feasibility of using combined photocatalytic process and a constructed wetland to treat polluted surface water for water reclamation. The source water was polluted by agricultural and domestic wastewater and was taken from the Wu-Lo River (WLR), Pingtung, Taiwan. The treatment efficiency of the system was evaluated by varying several operating parameters, such as hydraulic retention time (HRT), light source, and quantity of photocatalyst. Titanium dioxide coated on aluminum oxide pellet ($TiO_2/\alpha\text{-}Al_2O_3$) was used as the photocatalyst. Water parameters including TOC, BOD_5, COD, SS, NH_3-N, PO_4-P, THMs and HAA5 were monitored. The experimental results showed that the photo-constructed wetland with 2-day HRT had better treatment efficiency in terms of treated water quality than that with 0.5-d HRT. Furthermore, photocatalysis with either UVC (230~280 nm) or UVA (315~400 nm) followed by the constructed wetland further decreased these monitored water parameters, and the removal percentage increased as the quantity of photocatalyst increased. Compared with the constructed wetland treatment alone, the combination of photocatalysis and constructed wetland improves the treatment efficiency of polluted water. Evaluating the possibility of using the treated water for reclamation found that constructed wetland alone cannot remove precursors of THMs and HAA5 effectively. Nevertheless, the combination of photocatalytic process and constructed wetland were able to remove both THMs and HAA5 precursors, to decrease the formation of THMs and HAA5, and to meet the maximum contamination level (MCL) of the Disinfectants/Disinfection By-Products Rule (D/DBPR) in the US. Hence, the photocatalytic constructed wetland could be a good treatment technology for developing countries to treat agricultural and domestic wastewater for water reclamation with low operating and maintenance cost.

Keywords
Constructed wetland, disinfection by-products, photocatalysis, titanium dioxide, water reclamation

INTRODUCTION

The quantity of freshwater available worldwide is declining, and there is a pressing need for alternative more efficient use such as reuse of treated wastewater. Constructed wetlands have been used to treat municipal wastewater, acid mine drainage, industrial wastewater, agricultural and storm runoff, and effluent from livestock operation. The advantages of this technology include moderate capital costs, very low energy consumption and maintenance requirements, and benefits of increased wildlife habitat and landscape aesthetics. The mechanisms of pollutant removal in constructed wetland include biodegradation, physical removal and chemical reaction to eliminate pollutants from wastewater. Previous research has shown constructed wetland that can remove significant amounts of suspended solids, organic matter, nitrogen, phosphorus, trace elements, and pathogenic organisms in wastewater (Ou et al., 2006; Gross et al,. 2008; Kadiec and Knight, 1996)However, the constructed wetland required a longer processing time (6~30 day), a large area with treatment system and easily to the impact for climate, which were limit development of constructed wetland.

Recently, photocatalysis has received enormous attention for pollution control and indoor air purification. It has the advantages of use of inexpensive photocatalyst (TiO_2), operating under room temperature and atmospheric pressure, and nearly complete oxidation of carbon and hydrogen containing pollutants into CO_2 and H_2O(Ao et al., 2004). Thereby, the photocatalytic methods have achieved remarkable improvements, as many studies indicate that photocatalysis can be photodegradable of organic matter (Ao et al., 2004; Bekbolet et al., 2005).

However, it is little attention has been focused on used combining advanced oxidation processes (AOPs) and a constructed wetland treating wastewater, which advantage of using AOPs to make up deficiencies in constructed wetland.
This study investigates the feasibility to using combined photocatalytic process and a constructed wetland to treat polluted surface water for water reclamation.

MATERIALS AND METHODS

Experimental setup

The combined of photocatalytic process and constructed wetland studies in continuous were performed in the system illustrated in Fig. 1. Raw water was taken from Wu-Lo River (WLR), Pingtung, Taiwan was pumped continuous by a peristaltic pump (Masterflex, Cole-Parmer Co., Chicago, IL) from a reservoir to the photocatalytic process with withdrew the effluent of constructed wetland to a collection bottle. The photocatalyst preparation was used commercial material, the titanium dioxide (Degussa, P25) coated on aluminum oxide pellets (TiO_2/α-Al_2O_3). which calcined (773K) mixed oxide supports using with impregnation method (Gracia et al., 2000). Experimental simulation of UVA and UVC (10W, 28 mm o.d., manufactured by Philips) light source, which wavelength were range of 230~280 nm and 315~400 nm, respectively. Constructed wetland of structure had volume of about 15 litres tank. Reactor could be divided into two areas, first area for the simulated wetland reaction zone, the second area for the discharge current. The first area in the basal layer height of about 10 cm, including gravel and sift through 20 mesh, the little gravel, laying the upper base diameter of about 1 ~ 1.5 cm of gravel, the lower, compared with an average diameter of 0.5 cm of crushed stone. Constructed wetland was used domestic water (WLR) for four months after treatment used. The operating conditions used in this study are given in Table 1.

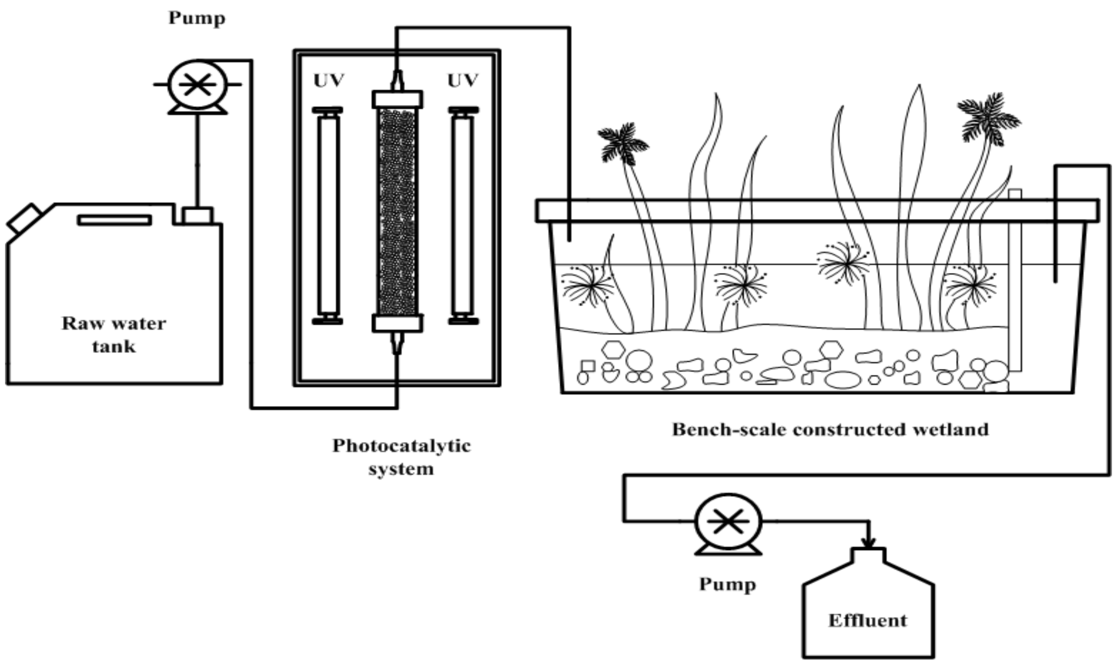

Fig. 1. Schematic representation of the photocatalytic and bench-scale constructed wetland system

Table 1. Operating conditions

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

Water source

Water samples were collected at the Wu-Lo River (WLR), Pingtung, Taiwan. The characteristics of the water from WLR are summarized in table 2. The samples were collected in 25-liter polyethylene tanks and stored at 4 °C for less than 7 days before being used in our experiments. The water temperature should be warmed back to room temperature before being used as the influent water for our treatment system.

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

Parameters	Raw water
pH	8.41 ± 0.07
UV-254 (cm^{-1})	0.105 ± 0.020
TOC (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 ± 0.53
PO_4-P (mg/L)	0.60 ± 0.07
THMs (µg/L)	118.02 ± 2.46
HAA5 (µg /L)	126.65 ± 4.13

Analytical procedures

The experiment raw and treated water of analytic items include TOC, BOD5, COD, SS, NH_3-N, PO_4-P, pH, UV254, THMs and HAA5, which these were determined according to Standard Methods (APHA, 1998), NIEA and USEPA Method (USEPA, 1995) in table 3. TOC was measured by Shimadzu TOC V-CSH 5000 analyzer (Kyoto, Japan), using combustion catalytic oxidation/NDIR method. Water samples were prefiltered through a 0.45 µm glass-fiber filter before measurement. Each sample was performed with three replicates. Ultraviolet (UV) absorption was measured at a wavelength of 254 nm wit a UV/VIS spectrophotometer (DR-5000, HACH) at room temperature. A quartz cell providing a light path of 1 cm is used. Samples are prefiltered through a 0.45-µm filter before measurement. The DBPs were extracted by organic solvents (hexane and MTBE) and analyzed by a gas chromatography (Agilent HP 6890N) that was equipped with 63Ni electron capture detector (ECD). A 30 m, 0.25 mm I.D. Supelco EquityTM-5 column (Supelco Analytical, Bellefonte, PA) was used it. The same GC-ECD and analytical column in THMs analysis was used for HAA5 analysis

Table 3. Analysis of water quality parameters

Parameter	Analytical method
pH	pH meter (NIEA W424.51A)
TOC	TOC analyzer (NIEA W532.51 C)
BOD5	5-Day BOD test (NIEA W510.54B)
COD	Closed reflux, titrimetric method (NIEA W517.51B)
SS	Dried at 103~105 ◦ C (NIEA W210.57A)
NH_3-N	Nitrogen (Ammonia) (Standard Method 4500)
PO_4-P	Spectrophotometer/ Ascorbic acid (NIEA W427.52B)
THMs	Standard Method 5710
HAA5	USEPA Method 552.2

Disinfection by-products of SDS-THMs and SDS-HAA5

The disinfection by-products (DBPs) were monitored in this study for THMs and HAA5, which were in accordance with Standard Methods 5710 method and USEPA 522.2 method. These compounds were measured in chlorinated water samples collected from raw water and treated water, which analysis of item chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), and monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), respectively. 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 incubation at room temperature according to the procedures delineated in Method 2350 (APHA, 1998).

RESULTS AND DISCUSSION

Different of HRT in photo-constructed wetland

Fig. 2 was the photocatalytic process in the different of HRT by the flux water quality parameters of changes. The experimental results shown the photo-constructed wetland with 2-day HRT had better treatment efficiency in terms of treated water quality than that with 0.5-d HRT in the catalyst amount of 225 g and UVA light operated condition. Photocatalysis of UV-irradiated titanium can able to generating OH radicals in water, which can be increasing mineralization of organic matter (Herrmann, 1998). As indicated above, photocatalytic process has promoted great organic substance transition to small organic substance, which was becoming to biological decomposition of organic matter. Additionally, Akratos and Tsihrintzis (2007) reported shown that increased operated condition of HRT could efficacious for increasing organic matter removal. Thereby, the experimental result in shown photo-construct wetland with 2-day HRT could obtain higher removal efficiency, contrast with 0.5-d HRT, TOC, BOD5 and UV254 increased percentages of 12.4, 23.4 and 11.7, respectively. Additionally, the experiment monitored concentrations of nutrients and phosphate by raw water, photocatalysis and the photo-constructed wetland, individually in table 4. The experimental results in shown that the using photocatalytic process treated wastewater could increase effluent water of nutrients concentrations as the NO_2^--N and NO_3^--N. This results in was according Antoniadis et al. (2007) reported that indicated the photocatalysis could mineralization of the organic nitrogen, increasing treat water NO_3^--N concentration, without the difference of in the outflow of the photo-constructed wetland.

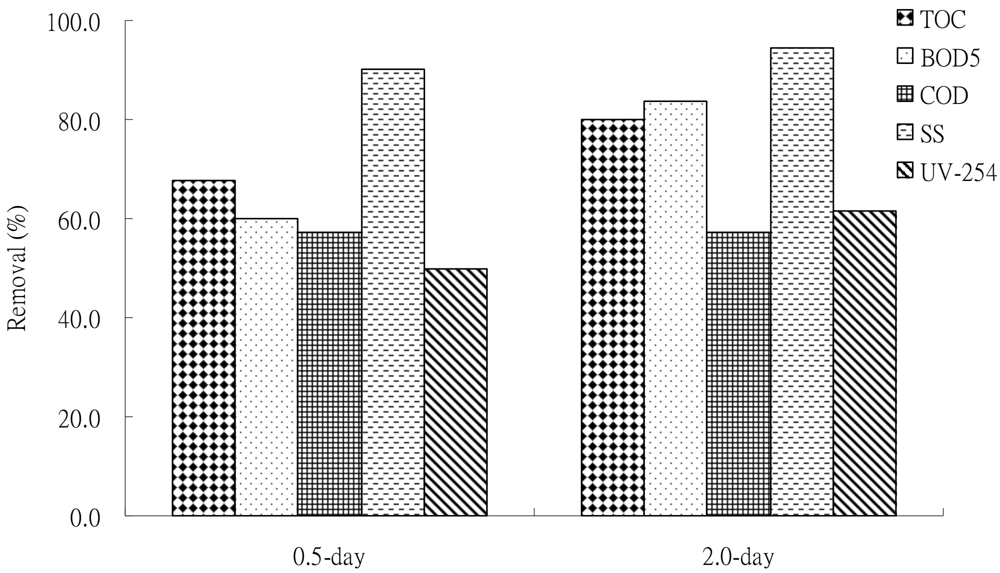

Fig. 2 The removal percentage of water parameter by photocatalytic process, the same of catalyst amounts (225 g), UVA light, and variation of HRT operated condition. (A1) 0.5-d, (A2) 2-d

Table 4. The concentrations of nutrients and phosphate by photocatalytic process with different of HRT operated condition.

	A1			A2		
	Raw	photocatalysis out	photo-constructed wetland	Raw	photocatalysis out	photo-constructed wetland
NH_3-N	5.0	3.3	0.1	5.0	0.6	0.0
NO_2^--N	0.1	0.2	0.0	0.1	0.4	0.0
NO_3^--N	1.0	2.3	0.5	1.0	3.8	0.0
PO_4-P	0.7	0.1	0.0	0.7	0.0	0.0

Unit: mg/L

A1：The combined using photocatalytic process and constructed wetland, UVA light, HRT 0.5-d, catalyst amounts (225 g).

B1：The combined using photocatalytic process and constructed wetland, UVA light, HRT 2-d, catalyst amounts (225 g).

Fig. 3 was the photocatalytic process in the different of catalyst amounts by monitored the flux water quality parameters. The experimental results in shown photocatalytic process followed by the constructed wetland further decreased organic matter, which removal percentage followed by catalysts increased with increasing. Photocatalyst used in the photocatalysis has the following basic properties, adsorption of the pollution matter, desorption of the products, and reacted with photon generated OH radicals as photon receiver, etc. (Herrmann, 1998). Thereby, the photocatalytic process of amounts of different catalyst experimental result in shown that used in maximums amount of catalyst (450 g) has significant removed efficiency at the this experimental.

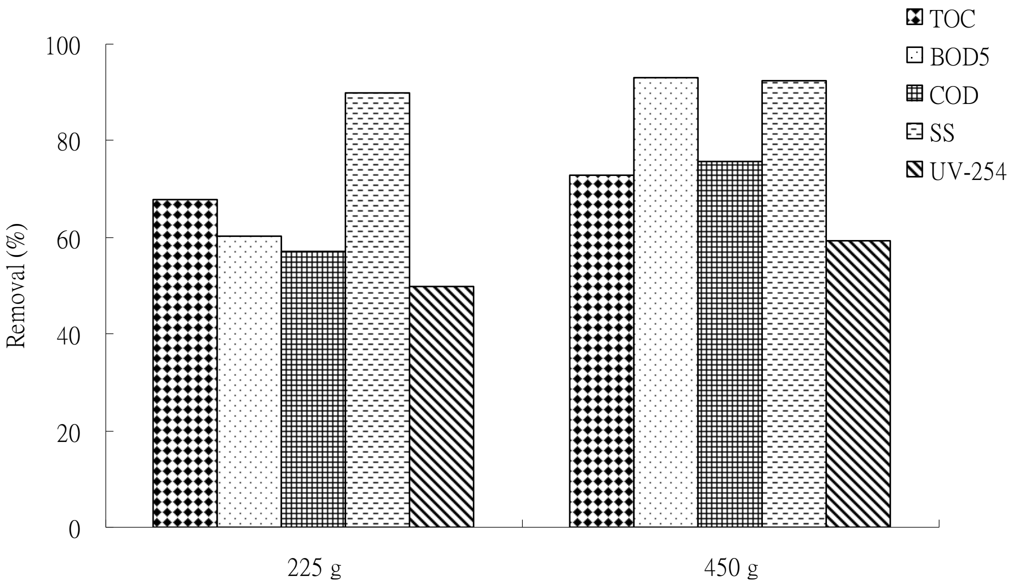

Fig 3. The removal percentage of water parameters by photocatalytic process, the same of HRT, UVA light, and variation of catalyst amount operated condition. (B1) 225 g, (B2) 450 g

Fig. 4 was used in the different operated systems treat wastewater observe for removal percentage of water parameters. The results in shown that treated water parameters TOC, BOD_5, COD, SS and UV254, alone constructed wetland removal percentage of 31.4, 62.1, 34.9, 89.4 and 43.8, the photo-constructed wetland removal percentage of 72.7, 93.0, 68.3, 92.5 and 59.4, respectively. It was clear from fig.4 that used in the combined of the photocatalytic process and constructed wetland has significantly removal efficiently than alone constructed wetland treated. The results might be attributed to photocatalysis had oxidised of organic matter, which could promote small organic matter by subsequent constructed wetland biodegrading increased removal percentage.

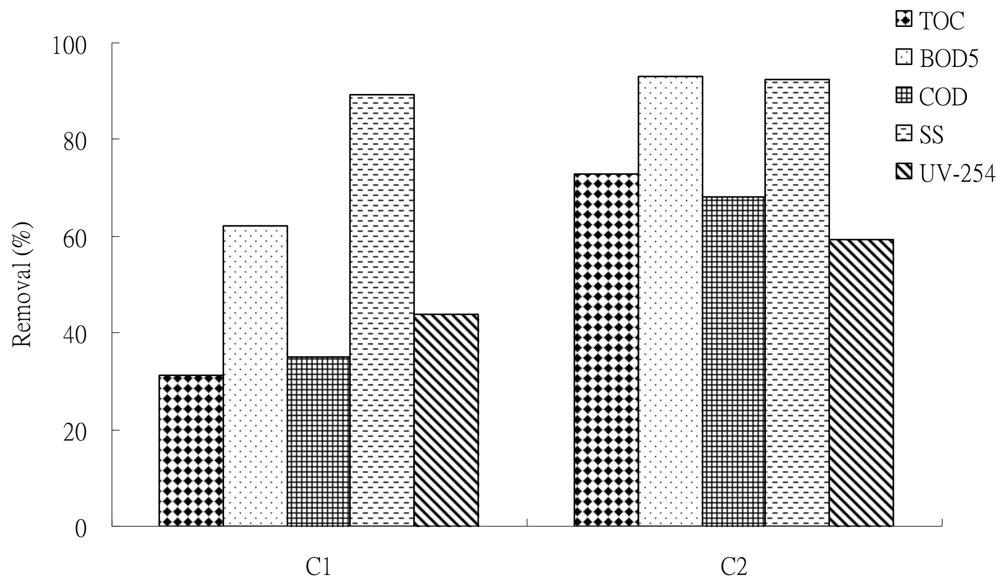

Fig. 4 The removal percentage of water parameter by the different operated system. (C1) constructed wetland alone, HRT (0.5-d), (C2) the combination of photocatalytic process and constructed wetland, photo-light (UVA), catalyst amounts (225 g), HRT (0.5-d).

Fig. 5 was used in the different operated systems treat wastewater observe for concentration of DBPs. The experimental results in shown that DBPs concentrations of treated water were significant decreased it, which the used in combined photocatalytic process and constructed wetland had meeting maximum contamination level (MCL) of the Disinfectants/Disinfection By-Products Rule (D/DBPR) in the US as THM and HAA5 concentrations, 64.8 μg/L and 46.1 μg/L, respectively. Bekbolet et al. (2005) reported shown in that photocatalytic process could be removal of aromatic moieties in humic structure with decreasing DBPs precursors. However, the photocatalytic process of DBPS removal effect had influenced by catalyst amounts and reaction priors. Nerveless, the experimental results in shown used alone constructed wetland, which had biodegraded ability to remove of UV254 and TOC, decreasing the DBPs concentration, but that did not meet stringent regulatory standards. Thereby, the photocatalytic process followed by constructed wetland was necessary.

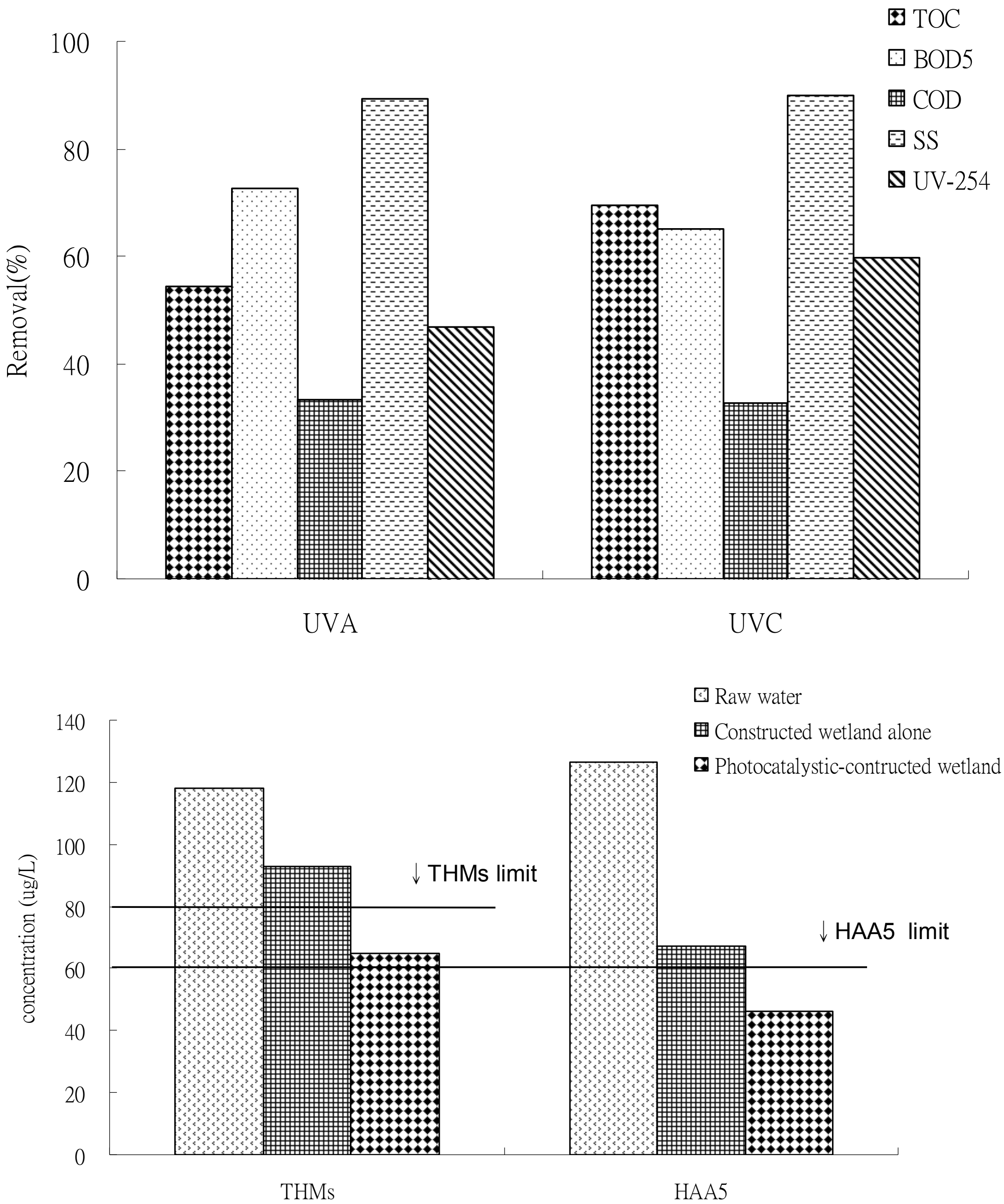

Fig. 5 The concentration of DBPs by the different operated condition systems. Operated condition of HRT (2-d), photo-light (UVC), and catalyst amounts (450 g).

CONCLUSION

Different treatment processes, including constructed wetland alone, and photocatalysis followed by constructed wetland examined. All treatment processes can effectively remove monitored water parameters. The use of a combined photocatalysis and constructed wetland results in significant reductions in TOC, BOD5, COD, SS, NH_3-N and PO_4-P levels and decreases the formation of THMs and HAA5 under the experimental conditions, which has meet the USEPA regulate standards. Hence, the photocatalytic constructed wetland could be a good treatment technology for developing countries to treat agricultural and domestic wastewater for water reclamation with low operating and maintenance cost.

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