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Original Research

Effective Purification in Constructed Wetlands Using Strontium-Doped TiO_2 Coated on Porous Ceramic Filter Media

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Abstract

This research is the first report on the purification of domestic wastewater in respect to the application of strontium-doped TiO_2 coated on porous ceramic filter media (Sr-TiO_2/PCFM) in eight laboratory-scale vertical flow constructed wetlands under irradiation of UV light. All the major pollutant parameters of wastewater were investigated. The online parameters showed that the decrease of dissolved oxygen (DO) reached 68.89% and in the constructed wetlands group which had the Sr-TiO_2/PCFM material and had a certain anti-clogging ability. By the presence of photocatalyst Sr-TiO_2/PCFM material, the removal efficiency of COD reached over 80% and eventually stabilized at a higher level (over 71%). Besides that, the Sr-TiO_2/PCFM material in constructed wetlands improved the average removal efficiency of total phosphorus (TP), total nitrogen (TN), NH_4^+-N, total suspended solids (TSS), and turbidity by 60.89%, 34.89%, 41.87%, 21.10%, and 36.85%, respectively. With Sr-TiO_2/PCFM material, under the irradiation of UV light, the overall removal efficiency of organic matter removal in terms of dissolved organic carbon (DOC) was 52% in 4 h, which was the best compared with other constructed wetland groups. The results of this study may in turn support improved testing and better optimization of constructed wetland systems for wastewater treatment.

Keywords: constructed wetlands; filter media beds; photocatalytic; humic acid (HA); strontium-doped TiO_2 coated on porous ceramic filter media (Sr-TiO_2/PCFM)

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Introduction

Currently, constructed wetlands and their improved and combined forms are widely used to treat domestic sewage and some other industrial wastewater [1-6]. Constructed wetlands, as typical natural and environmentally friendly systems, use rooted water-tolerant plants and gravel or soil media to provide treatment of wastewater [7-9]. As a green treatment technology, constructed wetlands have the unique advantage of producing higher effluent quality without the input of fossil energy, thereby reducing operational costs [10-12]. In terms of pollutant removal from wastewater, the sublayer occupies the largest volume in the structure of constructed wetlands and often plays a critical role, since the sublayer provides attachment surfaces for microbial communities and ingredients for bioreactions. The nature of constructed wetland sublayer is also an important factor that determines the environmental condition (such as redox potential) inside the porous spaces [7]. Tanner et al. [13] found that gravel occupies a considerable proportion of the bed volume in constructed wetlands, generally leaving an interstitial void space of between 30% and 45%. Sublayer types and grading methods have a significant impact on the purifying effect of constructed wetlands on pollutants in sewage. The type of support sublayer also has been the topic of recent research studies on constructed wetlands [14]. For example, gravel bed hydroponics, which consists of sloping channels lined with a waterproof membrane and hydrophytes planted in a matrix filled with gravel or an equivalent aggregate, has been demonstrated to be effective for sewage treatment in Egypt [15]. The grain size, composition and effective depth of the filter media are also important, and can simultaneously satisfy the treatment process while maintaining oxygen renewal in the sublayer and avoiding clogging of the bed [16]. Typically, coarse, well-sorted sand with minimal fines is recommended [17]. Bohórquez et al. [18] showed that the efficiency in the removal of total suspended solids, ammonia nitrogen and organic matter of the sand beds was significantly better than gravel beds. If the particle size of filter media is too small or contains a high percentage of dust, the risk of clogging in the wetland would increase and become hydraulically overloaded. Moreover, for promoting the removal of organics and nitrogen in constructed wetlands, the sublayer should meet the following characteristics: (a) to enhance nitrification, denitrification and organics removal, the co-existence of aerobic and anoxic/anaerobic pores inside the matrix should be provided; and (b) to minimize the dependency of denitrification metabolism on the presence of available carbon in wastewater, an internal carbon source is also needed. However, the commonly implemented gravel substrates in treatment wetlands do not provide carbon, thus there are some limits on purification.

Based on the successful synthesis of the highly absorbent and environmentally friendly photocatalytic material in our previous experiment [19], the strontium-doped TiO_2 coated on porous ceramic filter media (Sr-TiO_2/PCFM) was chosen as one kind of substrate in the matrix of constructed wetland sublayer. The aim of this study was to investigate the effect of Sr-TiO_2/PCFM on the effective purification wastewater in the constructed wetland. The results of this study may be helpful in providing guidelines for the design and management of constructed wetland systems for wastewater treatment.

Materials and Methods

Constructed Wetland

Three groups of laboratory-scale constructed wetland columns made of glass 45 cm in height, 25 cm in length, and 25 cm in width (Fig. 1) were used in the study. Each group had from two to four models as shown in Fig. 2.

All the tanks were filled with identical coarse sand to a depth of 40 cm. At the bottom of each column, there was a 10 cm gravel layer composed of large pebbles. In addition, about 1 cm layer of porous ceramic filter media (PCFM) and Sr-TiO_2/PCFM materials were laid on top of the bed media depending on each type of laboratory-scale constructed wetland set.

A water inlet was set on the surface, which is close to the upper center of the reactor. An outlet pipe was connected to the down circle of diameter 2.5 cm. Synthetic wastewater was fed into each tank unit from a wastewater tank through the distribution channel system with control valves and wastewater influent being prepared daily. Treated wastewater was discharged from the bottoms through puncture tubes. Pitot tubes were

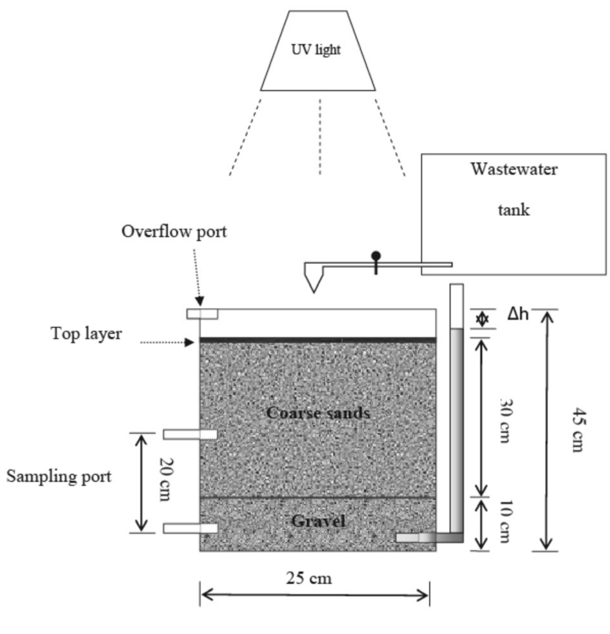

Fig. 1. Detailed diagram of the laboratory model.

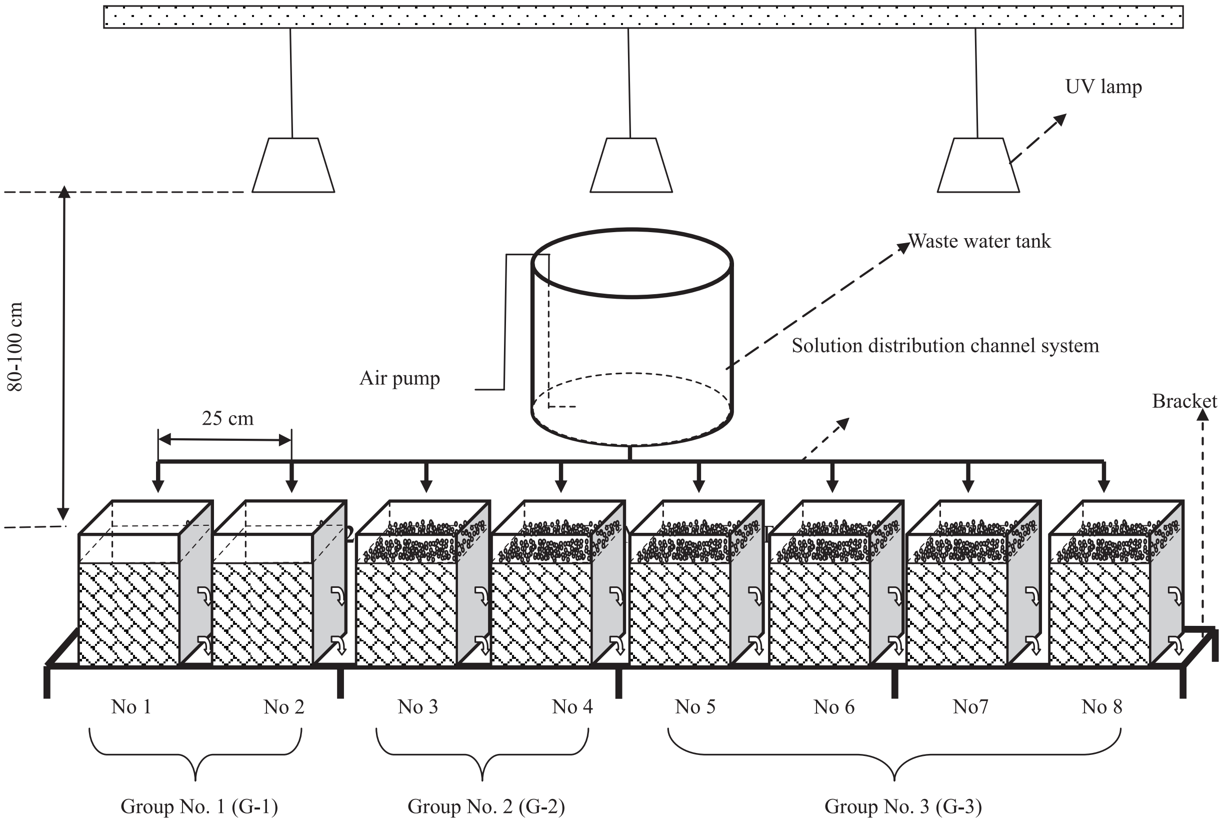

Fig. 2. Schematic description of the experimental model used for research.

set at 20 cm intervals along the depth to measure the hydraulic conductivity of each layer.

The systems were named group No. 1 (G-1), group No. 2 (G-2) and group No. 3 (G-3), respectively, where:

– Group No. 1 includes tanks No. 1 and No. 2, which had only bed media matrix layer (coarse sands and gravel), which means without the photocatalysis layer.
– Group No. 2 includes tanks No. 3 and No. 4, which had PCFM layer and bed media matrix layer (coarse sands, gravel), which also means without photocatalysis layer but with filter media layer .
– From tank No. 5 to tank No. 8 is group No. 3, which had Sr-TiO_2/PCFM material placed at the upper layer.

Constant values for hydraulic loading rate, solution temperature, and influent pollutant concentrations were used to facilitate interpretation of the model output. The system was illuminated by ultraviolet (UV) light with frequency 8-10 h per day and 56-66 h per week, corresponding to the period of solar illumination and the variation light/dark conditions to mimic seasonal changes. The experiment was carried out from October 2017 to February 2018, which was not growing season at the Institute of Hydrobiology in Wuhan, China. Therefore, the experimental setups were unplanted. The experiment lasted for about 160 days, until the surface of the wetland was seriously flooded, simulating the complete cycle of wet-accelerated clogging of the wetland. All the experiments are operated under laboratory conditions and the effluent samples in each model were performed in duplicate.

Wastewater

Domestic wastewater was used as influent for the constructed wetland reactors in this study. The hydraulic load was 0.5 $m^3/(m^2.d)$ before the system was steady. In order to speed up the clogging of wetlands, freshly filtered sediments of lakes were added as a source of suspended solids because the properties of sediment were similar to those of wet solids [20]. The quality values measured of influent wastewater were described in Table 1.

The suspended solids of influents were removed as much as possible by using the inlet screen of wetland and the sieve in the pump as well as the pipeline networks.

Table 1. Quality parameters of the influent wastewater.

Parameters	pH	TSS (mg/L)	COD (mg/L)	TP (mg/L)	TN (mg/L)	NH_4^+–N (mg/L)	DO (mg/L)
Influent wastewater quality	7.20±0.36	27.75±7.01	105.99±5.42	7.80±1.37	12.38±3.81	6.28±1.09	6.59±1.05

The wastewater was let flowing into the wetland system twice daily from 8:30 to 11 a.m. and from 2:30 to 5 p.m.

Measurements

Water Quality Monitoring

In order to assess the performance of the wetland systems, samples from influent and effluent were collected at two-week intervals into pre-cleaned 500 mL plastic bottles. Immediately after collecting pH, conductivity and dissolved oxygen (DO) were measured using portable pH and DO probes (Thermo ORION 7-STAR). Water samples were analyzed for total suspended solids (TSS) within 24 h in the laboratory according to standard methods (State Environmental Protection Administration of China, 2002). For measuring chemical oxygen demand (COD) we used a fast digestion–spectrophotometric method; for total nitrogen (TN) and NH_4^+–N, we used Nessler's reagent spectrophotometry method; and for total phosphorus (TP) we used an ammonium molybdate spectrophotometric method. Turbidity was measured with a turbidity meter (BZ-1Z), and UV_{254} was measured as absorbance at the wavelength of 254 nm. The dissolved organic carbon (DOC) was measured using a TOC-analyzer (TOC-V CSN 5050 Shimadzu, Japan). The UV/Vis absorbances of the HA at λ = 254 nm were measured using a UV-vis spectrophotometer (Shimadzu UV-1800 model). Removal efficiencies for wastewater parameters were calculated as the percentage change in concentration from influent to the effluent using Eq. (1):

$$\eta = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

…where η is removal efficiencies, C_o is the concentration of the wastewater parameter in the influent, and C_e is the concentration of the same wastewater parameter in the effluent.

Statistical Analysis

The significant treatment differences between each group system were evaluated using one-way ANOVA test for normally distributed data and Mann-Whitney test for non-normal data at 0.05 significance level. The correlation was identified using the linear regression test. The statistical analysis was performed with MS EXCEL 2010, Origin 8.5 and SPSS 13.0 software package for Windows, and the statistically significant level was set at p<0.05.

Results and Discussion

Changes in Online Parameters between Various Wetland Groups

Fig. 3 shows the changes in DO and pH with extended runtime for various wetland system groups. It can be seen that the variation patterns of these indicators in each wetland group are uniform and the differences are not significant. With the extension of the operation time until the wetland gradually clogged, the DO of each group gradually decreased slightly. The largest decrease was in group No. 3, in which it reached 68.89%. After the wastewater passes through

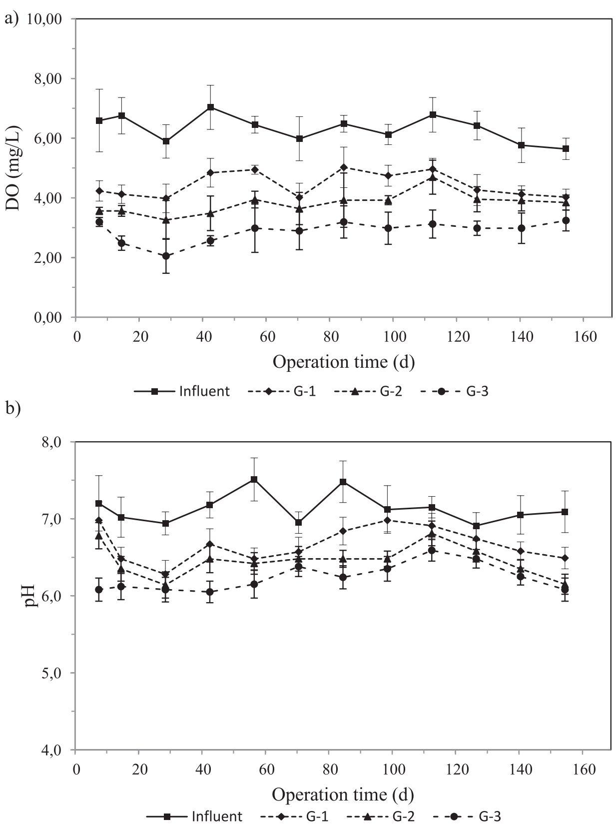

Fig. 3. Changes of a) DO and b) pH during tests of the examination systems.

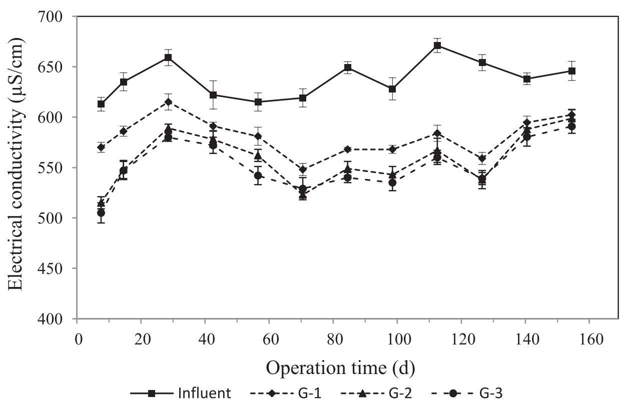

Fig. 4. Changes in electrical conductivity during tests of the examination systems.

the wetland systems, it showed a certain degree of anoxic state. The DO of the effluent in the later state in each group of the phenomenon is relatively high. This is consistent with the observation that the wastewater surface of group No. 3 is late and the phenomenon of blockage is less obvious. This indirectly shows that the long-term hydraulic state of the group No. 3 wetland, which had Sr-TiO_2/PCFM material, is better and had a certain anti-blocking ability. The pH of the effluent of all systems has decreased, which showed a result of nitrification and the gradual decomposition of pollutants in the influent to produce organic acids and other acidic substances. Group No. 3 has a relatively large reaction, and the pH of the effluent is the smallest overall.

Due to the high adsorption characteristics of PCFM and Sr-TiO_2/PCFM materials [19], along with the retention of the matrix and the occurrence of chemical reactions, the charged salt ions in the influent wastewater were partially removed and the conductivity of the effluent decreased (Fig. 4). This function of the system group No. 1 is relatively weak, and strongest was in group No. 3, which may be due to the content of the matrix gravel-bed. On the other hand, with an amount of PCFM and Sr-TiO_2/PCFM materials, which has high adsorption characteristics in the matrix gravel-bed, there is a small difference in the effluent conductivity of groups No. 2 and No. 3.

Pollutant Removal Efficiencies

Measuring the amount of natural organic matter in sources of surface waters has been of particular interest for municipal drinking water purification and wastewater facilities. When raw water containing natural organic matter is chlorinated in the disinfection process, potential carcinogens known as disinfection by-products (DBPs), such as trihalomethanes and haloacetic acids, are formed. To understand the role of natural organic matter in water treatment, the characterization of natural organic matter in the wastewater should be done. Dissolved organic carbon (DOC), chemical oxygen demand (COD), UV_{254}, pH, and turbidity are common water quality parameters assessed by water treatment facilities in their quality control.

Table 2 summarized the average removal rate and the effluent concentration value of the effluent of each wetland system on the major pollution indicators. Overall, the removal and trend of change of major pollutants in the influent wastewater in all systems are the same, including COD and turbidity reduction. However, the removal efficiency of NH_4^+-N and TN was relatively low.

The Purification of COD and TSS

Generally, COD is one of the key parameters that need to be explored to see the effectiveness of each

Table 2. Average removal rate of pollutants of the systems (mean value ± standard deviation).

Item	Influent	Group No. 1		Group No. 2			Group No. 3		
		Effluent	Removal rate (%)	Effluent	Removal rate (%)	Net removal rate* (%)	Effluent	Removal rate (%)	Net removal rate* (%)
COD (mg/L)	105.99±5.42a	75.02±6.59b	29.21	51.12±7.60b	51.64	22.43	25.87±9.54b	75.59	46.38
TP (mg/L)	7.80±1.37a	4.46±1.89b	40.00	3.68±0.58b	52.82	12.82	3.05±0.91b	60.89	20.89
TN (mg/L)	12.38±3.81a	9.54±3.01b	22.94	8.47±2.05b	31.58	8.64	8.06±1.98b	34.89	11.95
NH_4^+-N (mg/L)	6.28±1.09a	5.01±1.38b	20.22	3.96±1.04b	36.94	16.72	3.65±0.64b	41.87	21.65
Turbidity (NTU)	26.05±1.24a	22.64±2.04b	13.09	21.06±2.13b	19.15	6.06	16.45±1.25b	36.85	23.73
TSS (mg/L)	27.75±7.01a	25.87±6.59b	6.77	22.64±4.08b	18.41	11.64	21.06±6.12b	21.10	14.33
DO (mg/L)	6.59±1.05	4.02±0.27	/	3.84±0.25	/	/	3.24±0.35	/	/
Conductivity (μS/cm)	612.8±6.8	602.3±5.7	/	598.7±8.6	/	/	590.8±6.9	/	/
pH	7.20±0.36	6.49±0.14	/	6.15±0.13	/	/	6.08±0.15	/	/

a, b indicated there were significant differences between two groups ($p<0.05$)

* Net removal rate = (the average removal rate of group No. X) – (the average removal rate of group No. 1) (X = 2, 3)

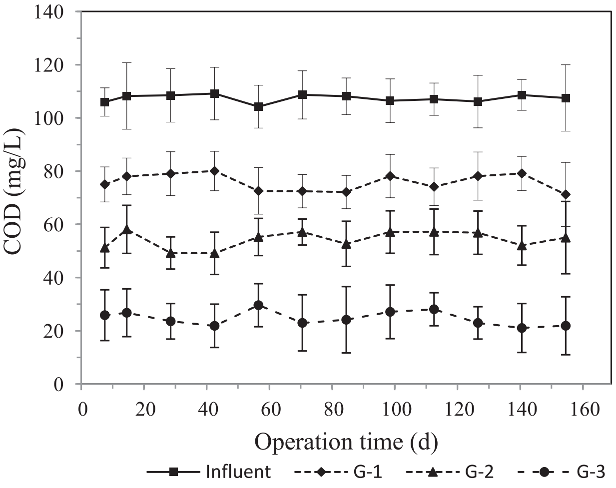

Fig. 5. COD in influent and effluent of the examined wetland systems during tests.

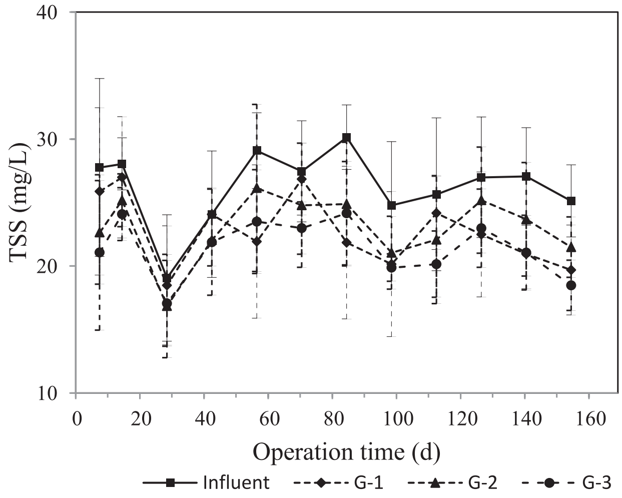

Fig. 6. Changes in TSS concentrations in influent and effluent during tests.

group of wetlands. The COD of the influent wastewater was determined to vary between 105.99±5.5.32 mg/L and 109.15±9.87 mg/L, respectively. Fig. 5 showed that during the treatment process, the decrease of the concentration of the organic pollutants, determined as COD was observed in most cases. Due to the presence of the high adsorption PCFM and Sr-TiO_2/PCFM materials, the effluent COD removal rate of group No. 2 and group No. 3 were better than group No. 1. Especially, by mixing the influent wastewater with the photocatalyst material (Sr-TiO_2/PCFM) in its sublayer under UV light, the removal efficiency of COD was highest (over 80%) and eventually stabilizes at a high level (over 71%) in group No. 3. As shown in Table 2, after operating time treatment, the average COD removal efficiency of group No. 3 was 23.95% and 46.38% more than in group No. 2 and group No. 1, respectively. Additionally, when analyzing and comparing COD concentrations between influent and effluent in each collection time point, the removal efficiency of COD increased with an extended retention time and higher influent COD concentrations. This result was consistent with the finding of Zhu et al. [21]. This rule may stem from the fact that with the extended operation time, sublayer voids were gradually filled with contaminants that had been trapped and a large number of growing microorganisms, which further strengthens the filtration and increases the removal rate. At the same time, the wetland system had undergone domestication and maturation. Microbial utilization and biochemical reactions had been continuously enhanced, and a relatively stable biofilm had been gradually formed on the surface of the filler. These results show the superior efficiency in the removal of organic compounds of the Sr-TiO_2/PCFM material and its potentials for water treatment.

TSS reduction in wetlands is supported by physical processes such as filtration, sedimentation and microbial assimilation within the wetland substrate media [22]. Although effluent water quality improved after the operation time, removal rates for TSS were low throughout most of the research period. It is difficult to interpret a clear trend from the data for TSS concentrations over time (Fig. 6). When the data for influent and effluent concentrations of TSS for each group was analyzed, several periods can be seen in which removal was low. It was suggested that TSS removal rates would be quite low if incoming pollutant concentrations are low [23]. Another factor could be the permanent eutrophic conditions of the system, which may result in the effluent and TSS concentrations being even higher than the influent concentrations at some point in time. The average TSS removal percentage was 6.77%, 18.41%, and 24.11%, for group No. 1, group No. 2 and group No. 3, respectively. At the later stage, group No. 3 showed marginally around 5-10% better TSS removal compared to the other group systems. This slightly higher TSS removal at system group No. 3 may be a result of improved filtration through high absorption characteristics of the Sr-TiO_2/PCFM material. These results were consistent with Manios et al. [24], who illustrated that TSS removal depends on the type and size of the substrate media.

The Purification Effect of TP

Fig. 7 shows that the removal rate of TP in each group gradually decreased, and finally tended to be stable. This was due to in the unplanted wetland systems, the removal of TP mainly depends on the matrix adsorption and retention, followed by the absorption and utilization of microorganisms. When the wetland first starts to operate, the matrix has large adsorption capacity, and the TP deficiency is large and the removal rate is high. With the prolonged running time, the increase of matrix adsorption saturation leads to a decrease in the efficiency of phosphorus removal, and the accumulation of biofilm may affect the process of

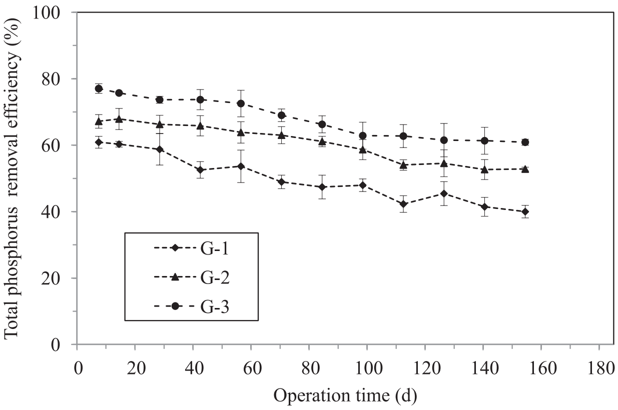

Fig. 7. Total phosphorus removal efficiency during tests of the examination systems.

wastewater mass transfer of phosphorus to the substrate, resulting in a gradual decrease in the removal rate. The use of biological consumption reaches a balance between supply and demand, and the removal rate tended to be stable. Combining with Table 2, the average removal rate of TP in the system group No. 3 (60.89%) was significantly better than that of groups No. 1 (40.00%) and No. 2 (52.82%). In addition, the experiments were carried out under UV lamp irradiation and proved that the photocatalytic reaction had been promoted by the Sr-TiO_2 nucleus on the surface of PCFM. That was because the Sr-TiO_2 nucleus serves as an ultramicro closed circuit photo-electrochemical cell that then decreased the concentration of surface electrons. Thus, the recombination rate of photogenerated electron-hole pairs was reduced and the photocatalytic activity was advanced.

The Removal Rate of TN and NH_4^+-N

Fig. 8 shows that the overall change rule of the removal effect of effluent from each group system on TN was the same. After the wastewater matured, the removal rate gradually increased and then fluctuated and stabilized. The ammonia nitrogen removal rate of each system decreased slightly after the acclimation process increased, and the removal efficiency of nitrogen after the long-term operation of the system group No. 3 was relatively stable. Due to the experiment being carried out without planting plants, the main mechanism of nitrogen removal in wetlands is physical and chemical adsorption, and the role of microorganisms on the surface of fillers. The system continues to run, biofilm gradually forms and stabilizes, and the removal efficiency of NH_4^+-N and TN increased. In the later stage, due to the accumulation of biofilms and clogging substances, the entry and conduction of oxygen were affected, which in turn affect the progress of nitrification, resulting in a decrease in the removal rate of ammonia nitrogen, and no further removal of TN was promoted.

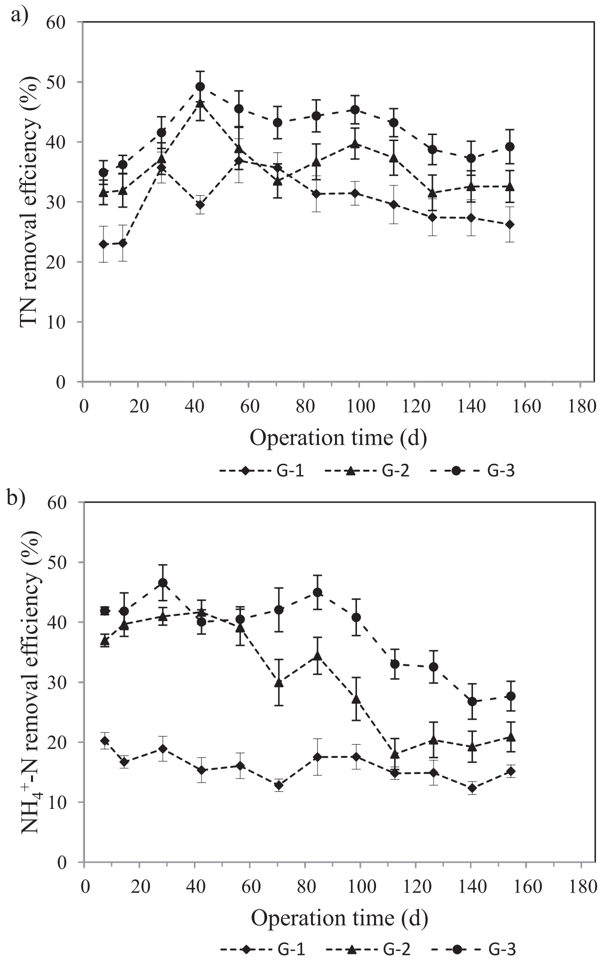

Fig. 8. TN a) and NH_4^+-N b) removal efficiency during tests of the examination systems.

Water Turbidity

Turbidity, caused by the presence in water of particulate matter such as clay, silt, colloidal particles, plankton, and other microscopic organisms, is a measure of the wastewater's ability to scatter and absorb light. This depends on a number of factors, such as the size, number, shape, and refractive index of the particles and the wavelength of the incident light [25]. The presence of suspended particles in the water will vary from acting as scatter of the light to the complete limiting of the solar treatment, by hindering the penetration of the light in the water; this will depend on the number of particles and the turbidity of the treated water. Therefore, water turbidity is not desirable for photocatalytic process treatments, even at low concentrations because suspended particles such as fecal material, solid materials, etc., protect the microorganisms against radiation. Contaminated turbid water may be pre-treated using the simple and low-cost filtration system to remove as much as possible of the suspended particles in the wastewater before treatment with the solar process. Therefore, it is important before intending to address water disinfection by the photocatalytic process

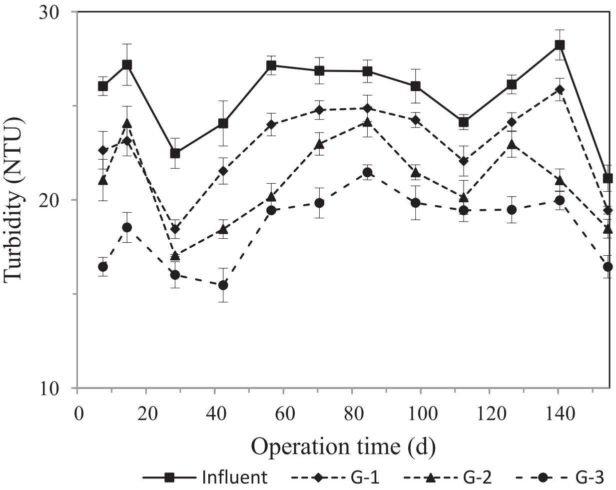

Fig. 9. Changes over time in average turbidity during tests of the examination systems.

to evaluate its efficiency on disinfecting large volumes of natural clear water of turbidity less than 30 NTU, as recommended in SODIS references [26, 27].

As shown in Fig. 9, the overall turbidity removal rate of each group system gradually reached 13.09%, 19.15%, and 36.86% for groups No. 1, No. 2 and No. 3, respectively, at the begin state of the systems. Throughout the operation process, the removal efficiency eventually stabilized at a relatively low level. This rule may originate from the fact that with the prolonged operation time, sublayer voids are gradually filled with contaminants that have been trapped and a large number of growing microorganisms, which strengthens the filtration function and decreases the removal rate. However, the system group No. 3 still achieved the highest efficiency (more than 22.22% at the end of experiment time) in the photocatalytic process with UV irradiation. The decrease of removal rate in group No. 3 can be explained as follows: when the turbidity increases, the suspended particles absorb heat from light and warm the water. Warmer water holds less oxygen and organisms begin to suffer. Molecular oxygen is an electron acceptor that generates oxidative $OH^{\bullet}$ radicals. Additionally, the organic particles compete with bacteria for both oxidative $OH^{\bullet}$ radicals and the photoactive sites of TiO_2; and the particles induce a reduction of light penetration through turbid wastewater by the scatter effect. Therefore, the activity of the Sr-TiO_2/PCFM catalyst was negatively affected.

Organic Matter Removal in Terms of Dissolved Organic Carbon

Organic matter accumulation is a typical feature in the function of constructed wetlands for treating wastewater. Organic matter accumulation provides long-term storage of carbon and nutrients and a sustainable supply of carbon for microbial denitrification [28]. However, the accumulated organic matter which was described as the major contributing factor for clogging constructed wetlands (particularly at the wastewater inlet zone) and may lead to a decline in wastewater retention time [28, 29]. Tanner et al. [13] found that 80% of the organic matter is unstable and readily degradable in a horizontal-flow wetland used to treat dairy wastewater. However, it has been reported that over 90% porous media of the wetland clogged by organic matter are refractory organic compounds, and 63-96% is in the form of humic acids, fulvic acids and humins [28]. Therefore, the removal of refractory organic compounds, more specifically humic acid (HA), is one of the necessary things and has created new challenges for reducing clogging problems in constructed wetlands.

Since the presence of dissolved natural organic matter is known to significantly change the rate and mechanism of $OH^{\bullet}$ radical reaction with aromatic compounds, the self-inhibition of HA + $OH^{\bullet}$ reactions by humic substances may have become important. It should be also noted that the TiO_2 photocatalytic oxidation of humic acid increased their biodegradability with irradiation [30].

The effects of UV light irradiation on the dissolved organic carbon of humic acid in the wastewater of each group have been investigated. Fig. 10 showed the change of dissolved organic carbon as a function of irradiation time. In the system group No. 3, dissolved organic carbon could be removed but not completely. The dissolved organic carbon decrease of 52% was observed in 4 h but further irradiation was not effective at all in removing the remaining dissolved organic carbon. This indicates that part of humic acid in the wastewater has transformed into very refractory products. Our previous studies [19] of this research have not achieved the complete mineralization of humic acid in the UV/TiO_2 system, either. The chemical nature of the non-degradable dissolved organic carbon portion remains unknown. We may speculate that the reaction of $OH^{\bullet}$ radicals increased the portion of humic acid with less hydrophobic, less absorbing, and less aromatic characters, in general. However, the other material reactions with HA in groups No. 1 and No. 2 suspension induced little change in dissolved organic carbon

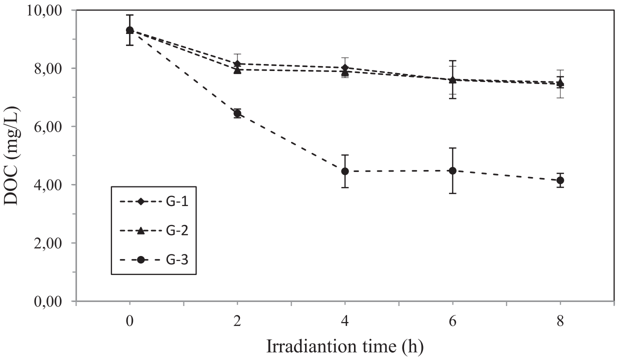

Fig. 10. Dissolved organic carbon change of humic acid solutions irradiated with UV light.

content. The minor reduction in dissolved organic carbon was attributed to the complete degradation of some degradable low molecular weight organic substances initially present in group No. 1 and system group No. 2. Although the observed spectral change was evidence of the electron transfer reactions of humic acid on TiO_2, they did not induce mineralization at all. Even under UV illumination, the complete mineralization of humic acid could not be achieved. Having complex macromolecular structures with many redox centers, humic acid seems to have both electron-donating and electron-accepting centers that shuttle electrons to and from the conduction band of TiO_2, which makes them withstand many electron transfers without undergoing mineralization.

Conclusions

In conclusion, each group system has the best effect on COD, TP and turbidity reduction in influent wastewater, but is relatively not too high in removal effect on TSS, NH_4^+-N, and TN. The reason may be that the removal of turbidity mainly depends on the retention and adsorption of wetland substrates. The role of microbes is very small due to all the group being unplanted. In system group No. 3, which has Sr-TiO_2/PCFM material in sublayer, significantly improved the removal efficiency of TP reached 60.89% as the high absorption characteristics of Sr-TiO_2/PCFM. Besides, the average removal efficiency of TN, NH_4^+-N, TSS, and turbidity in the presence of Sr-TiO_2/PCFM material at the top layer of constructed wetlands achieved 34.89%, 41.87%, 21.10%, and 36.85%, respectively. Under UV light irradiation time, the natural organic matter removal in terms of dissolved organic carbon was achieved in high efficiency (52%) in group No. 3, while there was little change in dissolved organic carbon content in other groups. The initially complete degradation of some degradable low molecular weight organic substances made the minor reduction in dissolved organic carbon attributed, while complete decomposition of the ubiquitous high molecular weight organic material in waters, commonly referred to as natural organic matter, is generally not observed.

This work demonstrates that the Sr-TiO_2/PCFM material can act as a photocatalyst for the degradation of refractory pollutants as humic acid and treatment of wastewater. Our findings might extend the applications of Sr-TiO_2/PCFM as an efficient photocatalyst for wastewater purification and provide a promising photocatalyst material because of its high activity and great stability.

It should be noted that this experiment did not plant plants in the wetland system. Thus our results were presented without considering along with the effect of planted wetlands. In fact, the planted wetlands also play an important and complicated role. Despite great accumulation of organic matter, the study of Tanner and Sukias [13] stated that the gravel porosity in the planted wetlands was better retained than in the unplanted ones. Besides, the role of vegetation in constructed wetlands should not be ignored in the study of Chan et al. [31], when the effect of nitrogen removal and the "dischargeable oxygen release rate" on the organic matter were investigated by using an "*in-situ* test" method. On the other hand, it should call for further investigation of the effects of plants on the purification process of wastewater in constructed wetlands using Sr-TiO_2/PCFM material.

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Conflict of Interest

The authors declare no conflict of interest.

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