Eutrophic-water treatment using a hybrid system of stabilization ponds and constructed wetlands

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Abstract
A hybrid system of stabilization ponds and constructed wetlands located in XingYun Lake, China, was used on a eutrophic water system to determine the pollutant removal efficiency. Results indicated that the technology was an effective way of removing nitrate nitrogen, chlorophyll a and algae, with removal efficiencies reaching 95.20%, 98.45%, and 99.87%, respectively. The removal efficiency was evaluated using a first-order model. The model was adequate in predicting pollutant concentration except from May to July 2002, suggesting that the effects of hydrology and vegetation density should be considered for a more accurate prediction.

Keywords: hybrid system, eutrophic water, stabilization ponds, constructed wetlands, removal efficiency, correlation.

Introduction

Rapid urbanization and industrialization in China have resulted in excessive water consumption and water quality degradation, also resulting in contaminated water such as eutrophic water, which needs to be disposed before it could flow into riverine landscapes. The growth of industry and agriculture to meet human demands due to increasing population causes an annihilation of water ecosystems and an augmentation of water pollutions [1, 2]. Soluble nitrogen and phosphorous compounds stimulate eutrophication of surface water [3], resulting in algae bloom, poor transparency, and nasty odours which worsen water quality.

Stabilization ponds (SPs) are one of the simplest and cost-effective types of biological treatment processes, making them a preferred technology for the handling, treatment, and disposal of industrial wastewater as well as municipal wastewater for small communities [4]. The long hydraulic retention time (HRT) and good dilution enable SP to withstand organic and hydraulic shock loading [5]. This approach relies on natural processes to remove pollutants with the aid of various floating or submerged aquatic plants [6].

Constructed wetlands (CWs) are simple, effective treatment systems with low operational costs, which can be very useful in developing countries [7–9]. They are particularly suited for treating diffuse sources of pollution, such as urban and agricultural runoff [2]. Most of the time, CWs can be constructed using local materials, significantly lowering construction costs [9, 10]. Wetland vegetation, whether emergent or submerged, provides valuable biological functions to ecosystems, including phytoremediation of nutrients, pesticides, and heavy metals [11–14]. Nonetheless, an often overlooked function of wetland vegetation is its physical capacity to increase the roughness or surface area of the respective channel, which reduces water velocities, improves the sedimentation and pollutant mitigation processes [15], and further affects the hydrodynamic process of water flow.
At present, studies on the hybrid of SP and CW for eutrophic water treatment, as well as investigations on the removal efficiencies of chlorophyll a (Chl-a) and algae, are limited. This work is one of the biggest applications of converting eutrophic water into landscape water in China. The aim of this paper is to extend the monitoring results to evaluate the removal efficiencies of the hybrid system, followed by further evaluation using a first-order removal model.

Materials and methods

Description of the treatment wetland

The present study was conducted in XingYun Lake (XYL), Yunnan Province, in the southwest of China (E: 102°46', N: 24°19'), where the climate is warm and wet, with rainfall in the summer. The annual average temperature is 15.6 to 23.8°C; generally, the average temperature difference between the coolest and hottest months is less than 10°C. The annual average precipitation is about 800 to 950 mm, with 130–150 rainy days throughout the year, and the period of abundant precipitation is from June to September. The treatment system consisted of the primary stabilization pond (SP1), primary gravel-based wetland (CW1), secondary stabilization pond (SP2), and secondary gravel-based wetland (CW2) (in series), whose areas were 145.5 m² (19.4 m long, 7.5 m wide), 314.6 m² (16.3 m long, 19.3 m wide), 125.1 m² (13.6 m long, 9.2 m wide), and 349.5 m² (14.5 m long, 24.1 m wide), respectively, corresponding to the designed HRT of 7.0, 2.5, 7.6, and 2.5 hours. The system adopted gravitational flow for convenient and economical operations, in which the influent flow was 1000 m³·d⁻¹ and the hydraulic loading rate was 1 m³·m⁻²·d⁻¹.

SP1 was planted with Eichhornia crassipes (Mart.) Solms; CW1 was planted with Phragmites communis Trin. and Typha angustifolia L.; SP2, with Pistia stratiotes L. and Eichhornia crassipes (Mart.) Solms.; and CW2, with Arundo donax var. versicolor and Canna chinensis W. The vegetation density was approximately 5–10 plants·m⁻² in the CWs. These indigenous plants were selected because they can easily adapt to the surrounding environment and for their flower colour, which was considered for aesthetic reasons.

A schematic overview of the hybrid system is depicted in Figure 1.

Measurement of water quality parameters

The treatment system was operated from September 2001 to March 2003. All samples were measured at the Yuxi environmental monitoring station. They were taken monthly at six sampling sites in the system: at the inlet of the system and at the outlet of each cell (Figure 1). All samples were immediately brought back to the laboratory and stored at 4°C before analysis. They were collected and determined in accordance with the Chinese Standard Methods (State Environmental Protection Administration of China, 2002). Physicochemical water parameters, such as pH, DO, and water temperature (T), were determined in situ using a pH meter, a DO meter, and a thermometer, respectively.

Data analysis
Statistical and variance analyses were performed using Excel 2003 and SPSS 17.0, respectively. Data were transformed into natural logarithms to approximate a normal distribution when necessary, and the normality and homogeneity of the variance was checked via a Kolmogorov-Smirnov test. Pearson’s correlation was performed to determine the cross-correlations between variables, and significant differences were determined via an analysis of variance (ANOVA).

We calculated HRT on a monthly basis using the average inflows, outflows, and treatment volume (Equation 1). The \( k-C^* \) model of Kadlec and Knight [16] was used to calculate the constant based on the measured concentrations (Equation 2).

\[
HRT = \frac{V}{Q} \\
C_{out} - C^* = (C_{in} - C^*)\exp(-k \times HRT)
\]

where \( V \) is the cell volume (m\(^3\)); \( Q \) is the average net inflow, \( Q = \) influent quantity-outflow quantity (m\(^3\)·d\(^{-1}\)); \( C^* \) is the background concentration (algae \( 10^4 \)·L\(^{-1}\), Chl-\(a\) mg·m\(^{-3}\)); \( C_{in} \) is the influent concentration; \( C_{out} \) is the effluent concentration; and HRT is the hydraulic retention time (d).

The influent quality background concentrations were: biochemical oxygen demand (BOD\(_5\)), \( 3.11 \) mg·L\(^{-1}\); chemical oxygen demand (COD\(_{Mn}\)), \( 5.08 \) mg·L\(^{-1}\); total phosphorus (TP), \( 0.08 \) mg·L\(^{-1}\); total nitrogen (TN), \( 1.03 \) mg·L\(^{-1}\); algae, \( 261.74 \times 10^4 \)·L\(^{-1}\); and Chl-\(a\), \( 32.95 \) mg·m\(^{-3}\).

**Results**

**BOD\(_5\) removal**

The final removal efficiency of the 6# site was 60.84%. Among these sampling sites, the removal efficiencies in 2# and 4# were only 22.28% and 41.83%, respectively. Tsalkatidou et al. [17] agreed that the BOD\(_5\) removal did not improve with plant presence in the wetlands and they reported similar BOD\(_5\) removal for the planted wetlands and the filtered effluent of the stabilization pond. Furthermore, Hench et al. [18] indicated that the removal efficiencies for BOD\(_5\) in domestic wastewater treatment are lower for the unplanted wetland compared with the vegetated one. Cameron et al. [19] also reported a BOD\(_5\) concentration reduction of 34.00% from the surface free wetland system treating municipal lagoon effluents.

**COD\(_{Mn}\) removal**

Similar to the BOD\(_5\) results, the COD\(_{Mn}\) concentrations in 2# to 6# were lower than that in 1#, and the final removal efficiency was only 34.80% after the water were passed through a connective treatment cell. The pollution of XYL mainly came from urban and agricultural areas, and the final removal efficiency for COD\(_{Mn}\) was lower than that for BOD\(_5\). Among the sampling sites, the removal efficiencies in 2# and 4# were only 4.78% and 6.95%, respectively, indicating that the COD\(_{Mn}\) removal efficiency in the SPs was limited.

**TN removal**

In general, TN removal mechanisms in the SP and CW systems are very complex and include nitrification, denitrification, plant and microbial uptake, among others. Several experimental studies on N removal in CW treatment confirmed that unplanted treatment had a lower N removal compared with planted treatment [1]. With plant growth, dissolved inorganic nitrogen is absorbed and incorporated into the biomass. However, the biomass is recycled to nonliving organic and inorganic matter during plant respiration and death. In this study, most of the TN concentrations in subsequent treatment cells were lower than in the inlet. The removal efficiencies of 2# and 4# were 0 and 13.97%, respectively, and the final removal...
efficiency was 50.00%. Cameron et al. [19] reported a TN concentration reduction of 37.30% from the surface free wetland system treating municipal lagoon effluents.

**Ammoniacal Nitrogen (NH$_4$-N) removal**

NH$_4$-N is considered as one of the important sources of eutrophication. During the sampling period, the NH$_4$-N concentration in 1# increased sharply from May to July 2002, and rose correspondingly in subsequent sites. The final removal efficiency was 54.13%. Cameron et al. [19] also reported a 51.72% reduction in NH$_4$-N from the surface free wetland system treating municipal lagoon effluents. Reed and Brown [20] agreed that the increase of NH$_4$-N concentration in the effluent frequently occurs when the preliminary treatment prior to CW is a pond with a high algae biomass. Subsequent decomposition of these algae produces additional ammonia, which is not easily nitrified because of insufficient DO in the wetlands and results in low removal [21].

**Nitrate Nitrogen (NO$_3$-N) removal**

NO$_3$-N is also considered as an important source of eutrophication. The NO$_3$-N concentration in each sampling site were less than 0.50 mg·l$^{-1}$ from July 2002 to March 2003, with a final removal efficiency of 95.20% during the whole sampling period. In the present studies, a low DO concentration resulted in low NO$_3$-N, which supports the hypothesis that denitrification is the major mechanism of NO$_3$-N removal [21].

**TP removal**

TP removal mechanisms include substrate sorption, biomass storage, and formation of new sediments. Most TP removal are affected by the media bed [22] and associated with the physicochemical and hydrological properties of the filter media [23]. At the same time, biological P removal may also be taking place [1], given that plants, algae, and microorganisms all utilize P as an essential nutrient [24, 25]. With plant growth, dissolved inorganic or organic phosphorus is absorbed, stored, and incorporated into the biomass. This nutrition is returned to the system after the plant decays. Therefore, to maintain a sustainable TP removal, plants utilizing phosphorus from the biomass should be harvested timely. In this present study, most of the TP concentrations in the subsequent sampling sites fluctuated with the inlet value during the running period, with a final removal efficiency of 68.83%.

**Chl-a removal**

Chl-a has been used as an index of eutrophication for a long time. Cullen [26], for instance, addressed the use of Chl-a as an index for the biomass of a primary producer. Boyer et al. [27] noted that Chl-a is the principal variable used as a trophic state indicator, and the agreement between plankton primary production and algal biomass is perfect, with the latter being an excellent trophic state indicator. During the present experimental period, most of the Chl-a concentrations were kept low, especially in 6#. Chl-a concentration increased correspondingly during algae bloom; however, the final removal efficiency reached 98.45%, indicating that the hybrid system was effective for Chl-a removal.

**Algae removal**

Phytoplankton blooms are commonly called algae blooms. An algal biomass is associated with the visible symptoms of eutrophication, and is usually the cause of the practical problems resulting from this phenomenon [27]. During the present experimental period, most algae concentrations in the subsequent treatment cells were kept low, especially in 6#, where the concentrations dropped to zero. The final removal efficiency reached 99.87%, indicating that the treatment exhibited a high algae removal efficiency.
Discussion

Removal efficiency analysis

From the aforementioned results, the removal efficiencies for NO$_3$-N, Chl-a, and algae were high, reaching up to 95.20%, 98.45%, and 99.87%, respectively. The removal efficiency for COD$_{Mn}$ and BOD$_5$ were limited during the whole period, in which the loading was reduced by 30% to 50%. The removal efficiencies for TN and TP were around 50% during the present experimental period. Generally, dissolved inorganic nitrogen and phosphorus are absorbed, stored, and incorporated into the biomass. To maintain the high removal efficiency, plants which uptake nitrogen and phosphorus should be harvested before the occurrence of decay. Thullen et al. [28] found that proper vegetation management improves water treatment as well as wildlife.

Cross-correlation coefficient analysis

Table 1 shows the cross-correlation coefficients between each variable, which were calculated using the following formula (Equation 3):

$$r = \frac{\sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{N} (x_i - \bar{x})^2 \sum_{i=1}^{N} (y_i - \bar{y})^2}}$$

(3)

where $x_i$ and $y_i$ are the parameter values, and $\bar{x}$ and $\bar{y}$ are the mean values of the two parameters. Cross-correlation coefficients range from -1 to +1, where -1 perfectly implies the inversely correlated variables and +1 implies perfectly correlated variables.

Table 1. Correlation matrix from September 2001 to March 2003

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD$_{Mn}$</th>
<th>BOD$_5$</th>
<th>TN</th>
<th>NH$_4$-N</th>
<th>NO$_3$-N</th>
<th>TP</th>
<th>Chl-a</th>
<th>Algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD$_{Mn}$</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>0.880*</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>0.984**</td>
<td>0.856*</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>0.867*</td>
<td>0.611</td>
<td>0.921**</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>0.831*</td>
<td>0.646</td>
<td>0.807</td>
<td>0.793</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td>0.984**</td>
<td>0.835*</td>
<td>0.956**</td>
<td>0.868*</td>
<td>0.900*</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chl-a</td>
<td>0.847*</td>
<td>0.778</td>
<td>0.751</td>
<td>0.582</td>
<td>0.868*</td>
<td>0.900*</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td>0.793</td>
<td>0.750</td>
<td>0.682</td>
<td>0.492</td>
<td>0.818*</td>
<td>0.850*</td>
<td>0.994**</td>
<td>1.000</td>
</tr>
</tbody>
</table>

*Significant at the 0.05 level (2-tailed)  ** Significant at the 0.01 level (2-tailed)

In Table 1, COD$_{Mn}$ strongly correlated with TN (with an absolute value of $r=0.984$) and TP (with an absolute value of $r=0.984$); TN strongly correlated with NH$_4$-N (with an absolute value of $r=0.921$) and TP (with an absolute value of $r=0.956$); and Chl-a showed a strong correlation with algae (with an absolute value of $r=0.994$), probably because of good algae removal, which in turn enhanced the Chl-a removal efficiency.

Kinetic equation analysis

Removing nitrogen and phosphorus from eutrophic water is necessary; however, focusing on other indices, such as NO$_3$-N, Chl-a, and algae is also important, because their high content may accelerate eutrophication in an open body of water. Generally, organic matter removal can be described as a first-order reaction in a continuous flow configuration [6]. Based on the experimental data, the first-order removal model was adequate in predicting the pollutant concentration for all periods except from May to July 2002, which may be attributed to the non-realistic presuppositions of the model. Therefore, some other biological
variables, such as nutrient loading in an aquatic system that restrains vegetation growth, and vegetation density that affects water flow velocity distribution, should be considered in the calculation and analysis.

Kadlec [29] reported that the failure of the first-order removal model is mainly because the plug-flow presumption is rarely satisfied in reality. Many CW treatments have spatial distributions of the vegetation density, which affects the spatial distributions of the flow velocity and treatment efficiency. A calculation system coupled with vegetation density, as well as other factors such as biological variables and microorganism growth effects, may increase the accuracy of the first-order removal model. Goulet et al. [30] mentioned that these biological variables are all associated with the productivity of an aquatic system and are of particular relevance to wetlands receiving higher nutrient loading.

Conclusions

We discussed the results of the experiments to evaluate the removal efficiencies of the coupled SP and CW hybrid system. During the running period, the final high removal efficiencies for NO$_3$-N, Chl-$a$, and algae can be attributed to the construction of SP, which interconnected the primary and secondary CW. Chl-$a$ showed a strong correlation with algae, indicating a consistent relationship of good agreement between plankton primary production and algal biomass. The removal efficiency for BOD$_5$ was higher in SPs than in CWs, indicating that plants in the CW did not improve the removal of BOD$_5$. The effluent concentration of TP exceeded that of the influent during the sampling period, which suggests that the SPs and CWs were acting as a nutrient source, and that these plants should be harvested timely before they start to decay. Precipitation may have influenced nutrient effluent concentrations because of HRT reduction during rainfall, which may have also caused the reduction in plant nutrient uptake. The first-order removal model can predict the pollutant removal accurately, except during the storm season. This failure can be attributed to either the sudden changes in nutrient concentration or the conflict between the flow velocity variable and the ideal plug-flow pattern hypothesis, which resulted from the vegetation density.

The present paper is an initial report on a hybrid system using SP and CW. Additional studies on process optimization using full-scale experiments are necessary. Further research should investigate the relationship between the hydrodynamic principle, HRT, and plant density, and whether pollutants are leaching from the hybrid system. For the latter, regular monitoring of the groundwater surrounding the hybrid system should be performed.

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References

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