Nutrients removal mechanisms in high rate algal pond treating rural domestic sewage in East China

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Abstract This study focused on the evaluation of performance and mechanisms of a high-rate algal pond system (HRAP System) in nitrogen and phosphorus removal for rural domestic sewage treatment. A pilot scale HRAP System was located at Yangzhu Village, Jiangsu Province, east China, with treatment processes including a septic tank, two stages of HRAPs and an aquatic pond. Results showed that the HRAP System had a good performance in nutrient removal, especially in NH$_4^+$-N removal. Total removal efficiencies of COD, TN, NH$_4^+$-N and TP were 80, 51.8, 90.2 and 52.1%, respectively. About 61.6% of NH$_4^+$-N in the 1st-stage HRAP and 70.9% in the 2nd-stage HRAP were transformed into NO$_2^-$-N and NO$_3^-$-N through nitrification, and the nitrogen losses via ammonia volatilization was only 2.7% (for 1st-stage HRAP) and 8.8% (for 2nd-stage HRAP). The other 35.7% and 20.3% of NH$_4^+$-N removal were achieved by algae assimilation respectively. About 98.0% (for 1st-stage HRAP) and 84.8% (for 2nd-stage HRAP) removal of TN were attributed to algae sedimentation, while those through ammonia volatilization were only 2.0% (for 1st-stage HRAP) and 15.4% (for 2nd-stage HRAP), respectively. Therefore, the main mechanisms of NH$_4^+$-N removal in HRAP were nitrification and algae assimilation, and TN was mainly removed by algae sedimentation. About 50.7% (for 1st-stage HRAP) and 53.1% (for 2nd-stage HRAP) of phosphorus in the deposit were organic phosphates respectively, only 20.7% and 27.7% were calcium-bound and magnesium-bound phosphates. The removal mechanism of TP in HRAP could be mainly attributed to algae assimilation in forms of organic phosphate, and chemical precipitation in forms of calcium-bound and magnesium-bound.

Keywords High-rate algal pond; mechanism; nitrogen and phosphorus removal; rural domestic sewage

Introduction

With the effective management and controlling of point source pollution, non-point source (NPS) pollution became the main cause for the water quality deterioration (Liu et al., 1998; Yang et al., 2004) in the Taihu Lake drainage area. This mainly occurred in rural and suburban areas. Among all NPS pollution, untreated rural domestic sewage has been identified as a significant source of water pollution (Ren, 2002; Wang et al., 2003). Therefore, decentralized sewage treatment processes with high treatment efficiency and low energy consumption are in urgent demand for the rural domestic sewage treatment.

Attention has been paid to the high rate algal pond system (HRAP System) in wastewater treatment (Shelef and Azov, 1982; Picot et al., 1991) since Oswald et al. (1957) firstly reported its application. It is considered as one of the principal techniques for rural domestic sewage treatment due to its high nitrogen and phosphorus removal efficiency, low investment and simple management (Chen et al., 2003). HRAP System is an energy-saving process compared with an activated sludge process (Picot et al., 1992). It has a lower oxygenation requirement, and only needs a mechanically induced turbulence to enhance algal productivity. No accumulation of sludge or problems of odor and the virtual absence of pathogenic bacteria and viruses in the effluent were reported in the
HRAP process (Cromar et al., 1996). In addition, the HRAP System was found to have higher treatment efficiency compared with common stabilization ponds (Picot et al., 1992).

Although the HRAP System was widely used for wastewater treatment, few researches have been done in China, especially in rural domestic sewage treatment. Systematic studies on its nutrients removal performance and the corresponding operation parameters are needed to promote further application and development of this technology in China. In this study, a pilot scale HRAP System with two stages was investigated to treat the rural domestic sewage in the Taihu Lake drainage area. The removal mechanisms of HRAP in N and P removal were explored in this study.

Methods

Experiment set-up
A pilot scale HRAP System with two stages was installed in the Yangzhu Village, Yixing City, Jiangsu Province. The sewage from Yangzhu Village was used as system influent. A schematic diagram of this system is presented in Figure 1.

As shown, septic tank was the pretreatment unit and two stages of HRAP was the primary treatment unit, followed by aquatic pond as the post treatment unit. Each HRAP has surface area of 80 m² (16 × 5 m) with an effective depth of 0.5 m, and was equipped with an undercurrent thruster to allow an average circulation flow at 0.35 m/s. The size of aquatic pond was 8 × 2.5 × 1 m. Alternathera philoxeroides and duckweed from local area around the system were transplanted in the aquatic pond. Experiments were conducted on stable system after one month operation. Two stages of HRAP were operated at fixed hydraulic residence time (HRT) of 8 days with a stable inflow of 5 m³/d in the research period from October 2004 to August 2005, and HRT was 4 days in the aquatic pond. The system was automatically fed at daytime from 6:00 AM to 18:00 PM.

Sampling and analysis
Water samples were collected twice at 9 A.M. per week from the sampling points as shown in Figure 1. Chemical oxygen demand (COD), dissolved COD (DCOD), total nitrogen (TN), dissolved total nitrogen (DTN), ammonia nitrogen, nitrate, nitrite, total phosphorus (TP), dissolved total phosphorus (DTP), orthophosphate, suspended solids

Figure 1 Schematic diagram of the HRAP System and its process chart
(SS), and chlorophyll-a (Chl-a) were analyzed according to the *Standard Methods for Analysis of Water and Wastewater* (1997). All analyses were carried out immediately after sampling. pH was measured in situ with a portable PHB-4 pH-meter. Water temperature and DO were measured in situ with a JPB-607 oxymeter. All data were represented in mean with a standard deviation (SD).

**Ammonia volatilization rate measurement**

To evaluate the contributions of ammonia volatilization in total nitrogen removal in HRAP, ammonia volatilization rate was measured in the first-stage HRAP. In this study, the experimental apparatus was developed according to the original design by Zimmo *et al.* (2003), and recommendations of Zhuang *et al.* (1995). Detailed experimental installation is shown in Figure 2.

As shown in Figure 2, a plexiglas box (500 × 350 × 285 mm) was installed in the middle of the first-stage HRAP surface by a wood block placed on the pond walls. The open side was placed 150 mm below the water surface. Rubber tubes were fixed on one side of the plexiglas box, and an air vent hole (50 × 20 mm) was made on the opposite side of the plexiglas box. Air was pumped and trapped in two flasks in sequence, each flask containing 500 mL 2% boric acid solutions. The concentration of ammonia released in the plexiglas box was calculated according to Equation (1).

\[
\text{NH}_3 + \text{H}_3\text{BO}_3 \rightarrow \text{NH}_4^+ + \text{H}_2\text{BO}_3^- \tag{1}
\]

Ammonia volatilization can be described mathematically by the two-film mass transfer theory in which the water phase was assumed to be well mixed except the interface. It was reported that the ammonia volatilization rate was dependent on pH, water temperature and mixing conditions such as wind speed (Weiler, 1979). Annual ammonia volatilization rates in two stage HRAPs were calculated according to Equation (2), which was developed on the basis of the first-order equation presented by Stratton and Asoe (1969), and the results are shown in Table 1.

\[
N_{\text{NH}_3} = \frac{\beta_v \times 500}{d} \exp [0.13(T - 20)] \frac{[\text{NH}_4^+ - \text{N}]}{1 + 10^{[0.09018 + 2729.92(T + 273) - pH]}} \tag{2}
\]

where \(N_{\text{NH}_3}\) was the mass transfer rate of ammonia (mg N/m²/d); \(\beta_v\) was the parameter corresponding to wind speed (2.5 m/s) and herein with a value of 0.3811; \(d\) was the depth of water column in the pond (m); [\(\text{NH}_4^+ - \text{N}\)] is the concentration of ammonia nitrogen of
the grab sample from the water column below the plexiglas box (mg/L); $T$ was the water temperature ($^\circ$C).

**Phosphate fractions measurement**

Different phosphate fractions in the sediment samples were quantified by sequential extraction steps with different extractants (Röské and Schönborn, 1994; Hou, 2005). The following phosphate fractions could be quantified: (a) phosphate adsorbed to sediment surfaces; (b) iron-bound phosphate, mainly bound to Fe(OH)$_3$; (c) organic phosphate, a fraction which hitherto was designated as “organically bound phosphate”; and (d) calcium-bound and magnesium-bound phosphate, phosphate bound to CaCO$_3$, MgCO$_3$. The applied extraction steps are shown in Figure 3.

**Results and discussion**

**General performance of the HRAP System**

The water quality indexes of influent and effluent are shown in Table 2.

As shown in Table 1, the total removal efficiency of COD was 80%, in which approximately 48% of COD was removed by the septic tank, and 24% of COD was removed in the aquatic pond. COD removed by the HRAP only accounted for a small percent and was mainly occurred in the first-stage HRAP, but the DCOD in the effluent of the septic tank was largely reduced in the HRAP units and was then transformed into particulate COD which was removed subsequently through physical sedimentation in the aquatic pond. Although concentrations of TN and NH$_4^+$-N in the influent were higher compared to typical raw wastewater, the removal efficiencies of TN, NH$_4^+$-N and TP were 51.8, 90.2 and 52.1% with effluent concentrations of 40.96, 6.19 and 3.33 mg/L respectively. TN and TP removals were observed in the septic tank, the first-stage HRAP and the aquatic pond, while the removal of DTN and DTP were distinctly observed in the two ponds. Particulate TN and TP transformed from DTN and DTP in the HRAP got removed in the aquatic pond through physical sedimentation. The removal mechanisms of DTN and DTP were similar with that of DCOD and the nutrients transferring into algal biomass promoted the removal of COD, TN and TP. The increasing of the algal biomass accumulation in the HRAP could be attributed to the constant mixing, small water depth of the treatment system, and high COD, N and P concentrations in the sewage. It was noted that the average values of Chl-a in the second-stage HRAP (0.82 mg/L) were higher than in the first-stage HRAP (0.65 mg/L) although the operation conditions were almost same, which might be contributed to the restrained algae growing in

**Table 1** Ammonia volatilization rate in the HRAP

<table>
<thead>
<tr>
<th>Parameters</th>
<th>First-stage HRAP annual value</th>
<th>Second-stage HRAP annual value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.70</td>
<td>8.07</td>
</tr>
<tr>
<td>$T$ ($^\circ$C)</td>
<td>17.8</td>
<td>17.7</td>
</tr>
<tr>
<td>[NH$_4^+$-N] (mg/L)</td>
<td>16.83</td>
<td>5.96</td>
</tr>
<tr>
<td>Average ammonia volatilization rate mgN/(m$^2$·d)</td>
<td>79.06</td>
<td>62.81</td>
</tr>
</tbody>
</table>

**Figure 3** Sediment phosphorus fractionation method step
<table>
<thead>
<tr>
<th>Water quality characteristics</th>
<th>Septic tank influent Mean ± SD</th>
<th>Septic tank effluent Mean ± SD</th>
<th>First-stage HRAP effluent Mean ± SD</th>
<th>Second-stage HRAP effluent Mean ± SD</th>
<th>Aquatic pond effluent Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>554.85 ± 463.59</td>
<td>289.39 ± 92.18</td>
<td>243.18 ± 67.89</td>
<td>244.14 ± 55.49</td>
<td>110.89 ± 48.19</td>
</tr>
<tr>
<td>DCOD (mg/L)</td>
<td>–</td>
<td>186.91 ± 69.29</td>
<td>87.45 ± 49.23</td>
<td>73.87 ± 45.39</td>
<td>70.52 ± 29.87</td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>85.01 ± 38.10</td>
<td>76.75 ± 22.87</td>
<td>60.76 ± 16.22</td>
<td>54.19 ± 13.55</td>
<td>40.96 ± 17.00</td>
</tr>
<tr>
<td>DTN (mg/L)</td>
<td>–</td>
<td>69.57 ± 21.6</td>
<td>51.01 ± 15.92</td>
<td>45.17 ± 14.63</td>
<td>37.91 ± 15.29</td>
</tr>
<tr>
<td>NH₄⁺-N (mg/L)</td>
<td>62.93 ± 26.04</td>
<td>64.43 ± 20.8</td>
<td>16.83 ± 15.74</td>
<td>5.43 ± 8.34</td>
<td>6.19 ± 6.52</td>
</tr>
<tr>
<td>NO₃-N (mg/L)</td>
<td>–</td>
<td>1.22 ± 0.62</td>
<td>25.68 ± 11.69</td>
<td>35.29 ± 11.14</td>
<td>27.12 ± 15.10</td>
</tr>
<tr>
<td>NO₂-N (mg/L)</td>
<td>–</td>
<td>0.1 ± 0.32</td>
<td>4.93 ± 3.72</td>
<td>1.69 ± 1.49</td>
<td>1.92 ± 2.35</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>6.95 ± 4.11</td>
<td>5.19 ± 1.29</td>
<td>4.35 ± 0.63</td>
<td>4.05 ± 0.71</td>
<td>3.33 ± 1.11</td>
</tr>
<tr>
<td>DTP (mg/L)</td>
<td>–</td>
<td>4.15 ± 1.01</td>
<td>2.89 ± 0.54</td>
<td>2.51 ± 0.69</td>
<td>3.12 ± 1.07</td>
</tr>
<tr>
<td>PO₄³⁻P (mg/L)</td>
<td>–</td>
<td>3.97 ± 0.95</td>
<td>2.79 ± 0.49</td>
<td>2.40 ± 0.71</td>
<td>2.93 ± 1.08</td>
</tr>
<tr>
<td>Chl-a (mg/L)</td>
<td>–</td>
<td>–</td>
<td>0.65 ± 0.36</td>
<td>0.818 ± 0.40</td>
<td>0.101 ± 0.09</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>–</td>
<td>1.59 ± 0.55</td>
<td>6.82 ± 2.62</td>
<td>9.0 ± 2.8</td>
<td>1.8 ± 0.9</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>–</td>
<td>47 ± 32</td>
<td>129 ± 62</td>
<td>151 ± 65</td>
<td>20 ± 25</td>
</tr>
<tr>
<td>T (°C)</td>
<td>–</td>
<td>17.8 ± 6.8</td>
<td>17.80 ± 9.10</td>
<td>17.8 ± 9.4</td>
<td>17.2 ± 8.7</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>7.65 ± 0.4</td>
<td>7.69 ± 0.27</td>
<td>8.1 ± 0.4</td>
<td>7.1 ± 0.3</td>
</tr>
</tbody>
</table>

*Values were calculated from the data obtained over the entire research period*
the first-stage HRAP by its higher pollutants loading. A significant removal of SS (88.8%) and Chl-a (87.6%) were observed in the aquatic pond, indicating a good post treatment performance of the aquatic pond. pH in the second-stage HRAP was usually higher than in the first-stage HRAP, which could be mainly attributed to the difference of Chl-a concentration. An increasing in DO was detected in the HRAFs, illustrating that HRAP was an aerobic reactor.

**Ammonia nitrogen removal mechanisms in the HRAP**

As shown in **Table 1**, the removal efficiency of NH$_4^+$-N in the first-stage HRAP and the second-stage HRAP was 73.9% and 67.7% respectively, NOx-N in the effluent accounted for 61.6% (for the first-stage HRAP) and 70.9% (for the second-stage HRAP) of ammonia loss, indicating that nitrification was the main mechanism for ammonia nitrogen transformation. From the calculated ammonia volatilization rate (**Table 2**), only 2.7% and 8.8% of total NH$_4^+$-N removal was attributable to ammonia volatilization in the first-stage HRAP and the second-stage HRAP, respectively, illustrating that the role of ammonia volatilization in ammonia nitrogen transformation was limited. According to previous reports (**Picot et al., 1991; Garcia and Mujeriego, 2000; Nurdogan and Oswald, 1996**), nitrification, algal assimilation and ammonia stripping were considered as the main mechanisms of ammonia nitrogen removal in the HRAP. In this study, the amount of ammonia nitrogen transformation was supposed to be the results of algal assimilation with removal efficiency of 35.7% (for the first-stage HRAP) and 20.3% (for the second-stage HRAP). As shown in **Figure 4**, three processes contributing to the ammonia transformation in the HRAP followed the sequence of nitrification, algae assimilation and ammonia volatilization.

**Total nitrogen removal mechanisms in the HRAP**

**Figure 5** summarizes the annually TN transformation in the first-stage HRAP. It could be noted that 16.0 mg/L of TN in average was removed with a removal efficiency of 20.8%. Among them, 14.7 mg/L TN (92.0% of total TN removal) were removed through organic nitrogen settlement; only 1.30 mg/L TN were removed through ammonia volatilization. In the second-stage HRAP, 6.57 mg/L TN were removed with a removal efficiency of 10.8%. Among these, 84.8% TN were removed through organic nitrogen settlement and 15.2% TN were removed through ammonia volatilization. High concentration of ammonia nitrogen in influent and deep water depth may limit the algae increasing and resulted in lower algal concentration and lower pH fluctuation. In addition, significant nitrification in the HRAP reduced the pH value obviously, which may restrain ammonia stripping and particulate organic nitrogen settlement should be the principal mechanism of TN removal.

![Comparison of ammonia transform processes percent in two stage HRAPs](https://iwaponline.com/ies/article-pdf/6/6/43/418346/43.pdf)

**Figure 4** Comparison of ammonia transform processes percent in two stage HRAPs
Total phosphorus removal mechanisms in HRAP

Chemical precipitation and algal assimilation of particulate phosphorus (PP) were reported to contribute to TP removal from original studies (Picot et al., 1991; Moutin et al., 1992). Different phosphate fractions of PP samples were quantified and the results are presented in Figure 6. Organic phosphate accounted for more than 50% of PP in both two stage HRAPs, and calcium-bound and magnesium-bound phosphates accounted for 20.7% (for the first-stage HRAP) and 27.7% (for the second-stage HRAP). Adsorbed phosphate and iron-bond phosphate only accounted for a small percent. Obviously, algae assimilation in forms of organic phosphate and chemical precipitation was contributable to main part of TP removal.

Conclusions

The pilot study demonstrated that the HRAP System was good at nutrient removal, especially for $\text{NH}_4^+$-N removal, with removal efficiencies of COD, TN, $\text{NH}_4^+$-N and TP of 80, 51.8, 90.2 and 52.1% respectively. The main removal mechanisms of $\text{NH}_4^+$-N in the HRAP were attributed to nitrification and algae assimilation processes, and TN was mainly removed by algae sedimentation. However, the results showed that ammonia volatilization played a minor process for $\text{NH}_4^+$-N and TN removal. The results indicated that algae assimilation in forms of organic phosphate and chemical precipitation in forms of...
calcium- and magnesium-bound phosphate were the main mechanisms of TP removal. SS and Chl-a concentrations were mainly removed in the aquatic pond following HRAP system and improved effluent quality.

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References


