Purification efficiency of zeolite and two planted grasses on sewage and relationship with carbon-nitrogen-phosphorus ratios in simulated constructed wetland system

Xia Liu, Guohui Ning, Jianzhi Xie, Chunjing Liu and Ming Li

ABSTRACT

For achieving the economical and efficient configuration of constructed wetlands (CWs), a simulated device of vertical flow CWs was used to investigate the effects of different volume ratios of substrates to two cold-resistant plants on pollutant concentrations as well as their ratios in effluent under different inflow domestic sewage concentrations. The average removal rates (ARRs) of ammonia nitrogen, total nitrogen (TN) and total phosphorus were 82.7%, 84.9% and 80.6% respectively in the treatments with zeolite but no plants, which increased by 22.6%, 20.8% and 14.9% compared with those without zeolite and plants. However, in the treatments with zeolite and planted grasses, the ARRs of the three pollutants were over 90%, and those of chemical oxygen demand were lower. The removal rates of ammonia nitrogen, TN and total phosphorus had negative correlations with C:N and N:P ratios and positive correlations with the C:P ratios. Increasing the ratio of zeolite to soil from 1:1 to 2:1 had no significant effects in the removal efficiency. It was suggested that planting Lolium perenne or Poa annua on the substrate with a zeolite to soil volume ratio of 1:1 could be considered as the optimum combination to purify the domestic sewage in north rural areas of China.

Key words | carbon-nitrogen-phosphorus ratio, domestic sewage, Lolium perenne, Poa annua, removal rate, zeolite

INTRODUCTION

The deficiency of clean water sources has been increasing and has become one of the most widespread problems plaguing people of all developing countries (Zhang et al. 2014). In recent years, many efforts have been made to protect water resources, especially sources of drinking water, particularly in rural areas in China (Ye & Li 2009). In various wastewater treatment technologies, constructed wetlands (CWs) have been considered as a green, reliable and promising wastewater treatment technology (Vymazal 2011; Wu et al. 2015) due to the superiority of simple operation and low implementation cost (Wu et al. 2014), and are used to treat domestic wastewater (Babatunde et al. 2008; Fountoulakis 2009; Mburu et al. 2013), especially in small communities and remote locations (Wu et al. 2015).

Zeolite is an environmentally friendly material with a relatively large surface area. It has a strong exchange and adsorption ability, and can adsorb pollutants efficiently with the characteristics of low cost and high performance (Delkash et al. 2015). There are many studies on the applications of zeolite in municipal wastewater and industrial wastewater treatments (Bruch et al. 2011; Wen et al. 2012; Mojiri et al. 2016). As reported, zeolite has good removal effects on ammonia nitrogen, total phosphorus and organic matter in constructed wetlands (Gikas & Tsihrintzis 2012; Vera et al. 2014; Nakamura et al. 2017) and in landfill leachate treatment (He et al. 2017). However, to the best of our knowledge, there are few applications of zeolite in the dispersal of domestic sewage.

Plants are another vital part of CWs, but they must be harvested every year to remove contaminants adsorbed from sewage, which requires a lot of manpower and material resources. In developing countries, the choice of economically viable plants in CWs may add economic benefits besides treating wastewater and saving cost (Zurita et al. 2009).
Many studies on the removal of pollutants have demonstrated that selection of plant species is of importance (Ranieri et al. 2013). Perennial ryegrass (Lolium perenne L., abbreviated as PR) belongs to the mesophytic species and is a highly nitrophyllous plant. It has been selected for high production potential (Zaman et al. 2008), and is increasingly used for the treatment of wastewater (Cao et al. 2010; Chen et al. 2013). By contrast, there are few reports about the applications of Kentucky bluegrass (Poa pratensis L., abbreviated as KB) in CWs. Notably, these two plants, i.e., Lolium perenne L. and Poa pratensis L., both have strong cold resistance (the lowest temperature of growth is −18 °C).

In this study, chestnut-brown soil, zeolite and gravel were taken as wetland substrates, and PR and KB as wetland plants. The inflow and outflow concentrations of ammonia nitrogen (NH₃-N), total nitrogen (TN), total phosphorus (TP) and chemical oxygen demand (COD) were determined under the conditions of high (TN 42.64 mg L⁻¹, TP 8.08 mg L⁻¹, COD 430.59 mg L⁻¹), medium (TN 31.32 mg L⁻¹, TP 5.06 mg L⁻¹, COD 297.33 mg L⁻¹) and low (TN 22.75 mg L⁻¹, TP 3.01 mg L⁻¹, COD 16 0.27 mg L⁻¹) contents of domestic sewage respectively by simulating the vertical flow constructed wetland for three days of hydraulic retention. The combined effects of different volume ratios of substrates to wetland plants on the concentration of each pollution indicator and the relationship between the removal rates and the carbon-nitrogen-phosphorus ratio were explored. The economical and efficient combination of substrates and plant species was screened for rural areas in north China. Our work can provide a theoretical basis for the design of a constructed wetland demonstration project, and has great significance for the stable operation of CWs in the cold region of north China. Meanwhile, the results in this work are helpful for the comprehensive understanding of the sewage purification mechanism and improved purification effect of internal CWs.

MATERIALS AND METHODS

Site description

The simulated CW system was built in 2015 at the West Campus of Hebei Agricultural University (115°21′E, 38°37′N), Baoding City, Hebei Province, in Northeast China. This work was the preparation for the pilot-scale project in Chongli District, Zhangjiakou City in North China, where the snow can be preserved for more than 150 days. The average winter temperature is −12 °C, and the average annual temperature is 4 °C. Hence, the wetland plants must be cold-resistant, and a depth of the collecting pipeline system of 1.2 m underground and an insulated house to keep the wetlands running in winter were designed in our pilot-scale constructed wetland. Additionally, we conducted this research in the warm season to obtain the optimum effective configuration under the largest pollution load because of the big difference from 2.5 L d⁻¹ in winter to 17.4 L d⁻¹ in summer according to the results of our investigations. The aim of this work was to explore the economical and efficient combination of substrates and plants in CWs in order to remove the excessive nutrients in domestic wastewater from scattered rural households and thus improve the river water quality.

Tested plants and substrates

The main criteria for choosing plants include a hygrophilous attribute, strong cold resistance and a certain economic value. PR and KB are both cold-resistant herbaceous plants and can survive the low temperature (PR −18 °C; KB −20 °C). Their basic characteristics are shown in Table 1. These two well-grown species with similar figures were taken from the lawn belonging to the Greening Department in Hebei Agricultural University. During the collection process, it is very important to keep the integrity of the roots in order to ensure that they are not damaged. The collected plants were placed into a container containing a certain amount of water, and their upper halves were wrapped with newspaper to protect the plants. These plants were transferred carefully to the laboratory. Then the soil adhered to their roots was gently removed and cleaned off, and any rotten and dead leaves were picked off. Afterwards, these plants were cultured in the water for the follow-up test.

Zeolite and gravel were both taken from Jiangsu Province. Zeolite had a diameter of 2–4 mm, a porosity of 50% and a bulk density of 1.28 t/m³, and the gravel had a diameter of 4–8 mm and a bulk density of 1.65 t/m³. Soil samples were collected from Chongli District in Zhangjiakou City, and the soil layer was 0–15 cm beneath the earth surface. The soil type was chestnut soil and the soil texture was sandy loam (Table 2). The plant roots in the soil were removed and then the soil samples were dried in air for the subsequent experiment.

Tested domestic sewage

The tested domestic sewage was artificially prepared with high, medium and low concentration gradients, according
Table 1 | The basic characteristics of Lolium perenne L. and Poa annua L.

<table>
<thead>
<tr>
<th>Species</th>
<th>Morphological characteristics</th>
<th>Living habits</th>
<th>Value and utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR (Lolium</td>
<td>PR is a perennial herbaceous plant with developed fibrous roots, thin rhizomes, strong tillering</td>
<td>PR has low requirement for the soil; likes moisture; can produce tillers and</td>
<td>PR has a high concentration of nutrients including vitamins, protein and minerals. It</td>
</tr>
<tr>
<td>perenne L.)</td>
<td>stem and a clustering stem. Leaf ligule length is about 2 mm, sometimes with auricle. Blades</td>
<td>keep dynamic roots, and live through the winter under low temperatures (~18 °C);</td>
<td>can be used as forage and is the best winter feed for livestock, such as cattle, sheep,</td>
</tr>
<tr>
<td></td>
<td>have tiny hairs. Spike length is about 20–30 cm, with spikelets having 5–11 flowers. Caryopsis is</td>
<td>can be planted during February to November; suitable for winter cultivation.</td>
<td>etc.</td>
</tr>
<tr>
<td></td>
<td>fusiform.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KB (Poa</td>
<td>KB is an annual or winter grass with erect, smooth and glabrous stem. The length of the ligule</td>
<td>KB likes wet soils; can survive the winter under a ~20 °C low temperature with</td>
<td>KB is a kind of good feed for pigs, poultry and so on due to rich nutrients.</td>
</tr>
<tr>
<td>pratensis L.)</td>
<td>is about 1–5 mm. Panicles are broadly ovate and of 3–7 cm in length; spikelet is ovate, with</td>
<td>no covers; keeps green at ~9 °C.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3–5 flowers. Caryopsis is spindly and about 2 mm long.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 | Physical and chemical properties of soil

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Organic matter (g kg⁻¹)</th>
<th>Available nitrogen (mg kg⁻¹)</th>
<th>Available phosphorus (mg kg⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chestnut soil</td>
<td>14.85</td>
<td>54.56</td>
<td>3.02</td>
<td>8.60</td>
</tr>
</tbody>
</table>

to our investigating pollutant contents (NH₃-N 10.8–38.1 mg L⁻¹, TN 18.7–47.8 mg L⁻¹, TP 3.1–7.0 mg L⁻¹, COD 455.3–587.4 mg L⁻¹) in the study area of the pilot-scale project, as shown in Table 3. The preparation method is provided in Table 4.

Experimental device and design

The experimental device was a cubic plastic device of 9.5 cm in length, 8.5 cm in width and 40 cm in height, as shown in Figure 1. The substrate was loaded into the device in the order of gravel, zeolite and soil from bottom to top. At the bottom of the device, the gravel layer of 5 cm was loaded. In the middle part, there were natural zeolite and soil in different volume ratios. At the top, there was a 5 cm water storage zone. The outlet was set at the bottom of the device.

The volume ratios of zeolite to soil were set as 0:1, 1:1 and 2:1 (marked as Z:S = 0:1, Z:S = 1:1 and Z:S = 2:1) respectively. For each volume ratio, there were three groups. The first group was the control test with no plants; in the second group, PR was planted; in the third group, KB was planted. In order to investigate the removal ability of different treatments, high, medium and low inflow concentrations of sewage were designed in the experiment. The details of the processing system arrangement are in Table 5. Hence, there were 27 treatments and each of them was repeated three times. Two species of grasses with similar individual traits were selected and transplanted into the experimental device. The average temperature of inflow sewage was 26.1 °C and its pH was 7.29. After 15 days of culture, the experiment was started formally.

Table 3 | Inflow concentration of the domestic sewage (mg L⁻¹)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>NH₃-N</th>
<th>TN</th>
<th>TP</th>
<th>COD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>15</td>
<td>14.91</td>
<td>22.75</td>
<td>150</td>
</tr>
<tr>
<td>Medium</td>
<td>30</td>
<td>33.91</td>
<td>31.32</td>
<td>5</td>
</tr>
<tr>
<td>High</td>
<td>45</td>
<td>44.00</td>
<td>42.64</td>
<td>8</td>
</tr>
</tbody>
</table>

Note: The NH₃-N concentration is higher than TN mainly because ammonia is volatilized from the mixed solution before reacting with alkaline potassium persulphate solution, and the higher the concentration of ammonia nitrogen the more the obvious volatilization.
The vertical flow of artificial wetlands was simulated, and the inflow method was intermittent water supply. According to Prochaska et al. (2007), CWs with low batch frequencies (two times per week) can result in high COD removal and sufficient nitrification. Hence, the hydraulic retention time was set to 3 d. The water volume filled into the device in each period was designed as 1,370 mL, and the hydraulic load was 0.056 m$^3$ m$^{-2}$ d$^{-1}$ in mountainous areas with few people and more land. The outflow concentrations of NH$_3$-N, TN, TP and COD were measured in 30 days. The impact of evaporation/evapotranspiration on the flux balance will be monitored and the concentrations of BOD$_5$ and PO$_4^{3-}$ must be surveyed in the pilot-scale CWs.

### Measurement items and analysis method

All indicators of the sewage water samples were determined by the technique in ‘Water and Wastewater Monitoring and Analysis Methods’ (4th edn) edited by the Editorial Board of National Environmental Protection Agency (2002). The concentrations of NH$_3$-N (mg L$^{-1}$) were determined by Nessler’s reagent colorimetric method (GB7479-87). TN concentrations (mg L$^{-1}$) were determined by alkaline potassium persulfate ($K_2S_2O_8$) digestion followed by spectrophotometry (GB11894-89). TP concentrations (mg L$^{-1}$) were determined based on Mo-Sb spectrophotometry (GB1183-89) after potassium sulfate ($K_2SO_4$) digestion. The potassium dichromate ($K_2Cr_2O_7$) method was used to determine COD concentration (mg L$^{-1}$). Acidity of the water was measured with a pH meter and the water temperature was also recorded.

### Data analysis

The experimental data were statistically analyzed by SPSS 19.0 software package for Windows and Excel 2016. The t-Student confidence interval for 95% probability was calculated to statistically compare the differences among the mean removal efficiency values. A one-way between-groups analysis of variance (ANOVA) was used to evaluate the significance of the effects of volume ratios of zeolite to plants on removal efficiency values of the four pollutants. Duncan’s multiple range test method was carried out to provide the individual differences, and the significance degree was defined as $p < 0.05$ for all cases. Furthermore, a two-way ANOVA was conducted to explore the combined effects of plants and substrate ratios on removal efficiency values of different pollutants. Linear regression was used to figure out

### Table 4

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Industrial glucose</th>
<th>Potassium dihydrogen phosphate</th>
<th>Urea</th>
<th>Magnesium chloride</th>
<th>Calcium chloride</th>
<th>Iron sulfate</th>
<th>Potassium sulfate</th>
<th>Magnesium sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>1,125</td>
<td>168.4</td>
<td>17.1</td>
<td>5.9</td>
<td>3.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Medium</td>
<td>750</td>
<td>112.3</td>
<td>10.7</td>
<td>4.0</td>
<td>2.2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Low</td>
<td>375</td>
<td>56.1</td>
<td>6.4</td>
<td>2.0</td>
<td>1.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Zeolite : Soil</th>
<th>Plant</th>
<th>Inflow concentration and serial Codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z:S = 0:1</td>
<td>Control</td>
<td>Low (CL)</td>
</tr>
<tr>
<td>PR</td>
<td>PL</td>
<td>PM</td>
</tr>
<tr>
<td>KB</td>
<td>KL</td>
<td>KM</td>
</tr>
<tr>
<td>Z:S = 1:1</td>
<td>Control</td>
<td>Low (CL1)</td>
</tr>
<tr>
<td>PR</td>
<td>PL1</td>
<td>PM1</td>
</tr>
<tr>
<td>KB</td>
<td>KL1</td>
<td>KM1</td>
</tr>
<tr>
<td>Z:S = 2:1</td>
<td>Control</td>
<td>Low (CL2)</td>
</tr>
<tr>
<td>PR</td>
<td>PL2</td>
<td>PM2</td>
</tr>
<tr>
<td>KB</td>
<td>KL2</td>
<td>KM2</td>
</tr>
</tbody>
</table>

The vertical flow of artificial wetlands was simulated, and the inflow method was intermittent water supply. According to Prochaska et al. (2007), CWs with low batch frequencies (two times per week) can result in high COD removal and sufficient nitrification. Hence, the hydraulic retention time was set to 3 d. The water volume filled into the device in each period was designed as 1,370 mL, and the hydraulic load was 0.056 m$^3$ m$^{-2}$ d$^{-1}$ in mountainous areas with few people and more land. The outflow concentrations of NH$_3$-N, TN, TP and COD were measured in 30 days. The impact of evaporation/evapotranspiration on the flux balance will be monitored and the concentrations of BOD$_5$ and PO$_4^{3-}$ must be surveyed in the pilot-scale CWs.

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the relationship between the removal rates and the ratios of carbon, phosphorus and nitrogen (C:N, C:P and N:P).

RESULTS AND DISCUSSION

The growth status of the two plants was very good in the treatments under the low domestic sewage concentration, and better than that under the medium or high concentration of domestic sewage having low toxicants level (e.g. heavy metals) and in the warm season. In the late post-trial under a high inflow concentration of domestic sewage, the leaves of the two grasses exhibited mild and severe withering; meanwhile, the growth status was not very high. Therefore, the low domestic sewage concentration favored the growth of the two plants and PR’s tolerance to domestic sewage was greater than KB’s.

Nitrogen

The results in Table 6 indicated that the outflow NH₃-N and TN concentrations were in the ranges of 0.95–5.59 mg L⁻¹ and 0.88–5.39 mg L⁻¹ respectively under the low inflow concentration, which met the primary discharge standard (NH₃-N ≤ 8 mg L⁻¹, TN ≤ 20 mg L⁻¹) according to the national discharge standard for sewage (GB 18918-2002). Under the medium inflow concentration, the NH₃-N and TN outflow concentrations were 1.81–11.85 mg L⁻¹ and 1.96–12.57 mg L⁻¹ respectively. The NH₃-N outflow concentration met the primary discharge standard only in the treatments without zeolite addition, while all TN outflow concentrations met the primary discharge standard. However, the NH₃-N outflow concentration in the treatments without zeolite met the secondary discharge standard (NH₃-N ≤ 20 mg L⁻¹).

Under the high inflow concentration, the TN outflow concentration (1.96–12.57 mg L⁻¹) met the primary discharge standard, and most of the NH₃-N (2.95–20.87 mg L⁻¹) outflow concentrations met the secondary discharge standard.

The removal efficiency values of NH₃-N and TN in the treatments with zeolite were higher than those in the non-zeolite treatments, and those in the treatments with planted grasses were higher than those without plants (Figure 2). There were no significant differences among removal rates under all the three inflow concentration levels (p > 0.05).

Regardless of inflow concentration levels, the average removal rates (ARRs) of NH₃-N and TN showed significant differences when Z:S = 0:1 and Z:S = 1:1 or when Z:S = 0:1 and Z:S = 2:1, while there were no significant differences when Z:S = 1:1 and Z:S = 2:1 at the p = 0.05 level (Figure 3). Furthermore, the removal rates of the treatments with planted grasses and the control unvegetated treatments had no significant differences at the p = 0.05 level, although the two grasses were beneficial to the removal of pollutants.

In the treatments with no plants, when the ratio of zeolite to soil was Z:S = 0:1 (without zeolite addition), the ARRs were 60.1% (52.6%–62.5%) and 64.2% (56.3%–76%) for NH₃-N and TN respectively. When the ratio of zeolite to soil was 1:1 and 2:1, the ARRs of NH₃-N amounted to 80.9% and 84.9% respectively and that of TN increased to 84.5% and 85.1% respectively. In the case of planting two grasses, the removal efficiency under the low concentration was higher than that under the high or medium concentration. The ARRs of NH₃-N and TN in PR were slightly higher than those in KB. When Z:S = 0:1, the ARRs of NH₃-N and TN were 73.9% (69.3%–77.0%) and 78.4% (75.2%–86.9%) respectively in PR, and 70.9% (66.6%–79.0%) and 74.9% (69.2%–84.7%) respectively in KB. However, the ARRs of NH₃-N and TN in the treatments

![Table 6](https://iwaponline.com/wst/article-pdf/78/3/545/482078/wst078030545.pdf)
Previous research shows that zeolite can increase the adsorption capacity and the capacity for shrinking and swelling, which in turn alters the hydraulic regime and thus the retention time (Bruch et al., 2011, 2014). In this study, it was observed that the removal efficiencies for pollutants in the treatments with zeolite were higher than those in the treatments without zeolite, particularly those for nitrogen and phosphorus. Nitrification – denitrification is generally considered as the main mechanism for nitrogen removal in wetlands (Ye & Li, 2009; Ding et al., 2016), the other reason is that natural zeolite has the capacity for the sorption of ammonia from wastewater (Markou et al., 2014). According to the recommendation of Grady & Lim (1980), the general requirement for nitrification is COD/TN > 8. In this study, the values of COD/TN in the effluent were all more than 14.9. Hence, the main removal mechanism for nitrogen could be the nitrification effect. This study showed that the planting of two grasses favored nitrogen removal, and PR increased the removal efficiency by 13.8% for NH₃-N and 14.2% for TN compared with those in the treatments without zeolite and plants, and by 12.6% for NH₃-N and 8.6% for TN compared with those in the treatments with zeolite but without plants. This is close to the result that the direct uptake of N by the PR accounted for 18.17% of the total N removal (Chen et al., 2013).

Total phosphorus

The outflow concentrations of TP in all treatments under the low inflow concentration dropped from 3.01 mg L⁻¹ to the range of 0.19–0.69 mg L⁻¹, which met the primary discharge standard (TP ≤ 1 mg L⁻¹) according to the national discharge standard for sewage (GB 18918-2002). Under the medium inflow concentration (5.06 mg L⁻¹), the outflow concentrations of TP in the treatments with zeolite were in the range of 0.43–1.05 mg L⁻¹, which met the primary discharge standard; by contrast, those in the treatments without zeolite were in the range of 1.36–1.55 mg L⁻¹, which meet the secondary discharge standard (TP ≤ 5 mg L⁻¹). Under the condition of high inflow concentration, all outflow concentrations of TP (0.81–2.69 mg L⁻¹) met the secondary discharge standard (Table 7).

As Figure 4 shows, the removal efficiency of TP in the treatments with zeolite was higher than that in the non-zeolite treatments. When the ratios of zeolite to soil were 1:1 and 2:1, the removal efficiencies of TP were very close to each other. The TP removal rates under the three inflow concentrations had no significant differences (p > 0.05). Under the unvegetated condition, the TP removal rates with zeolite were all more than 90%. With no consideration for the inflow concentration and the proportion of zeolite, the ARRs of NH₃-N and TN in PR were 92.8% (90.3%–94.7%) and 93.7% (90.6%–96.7%) respectively, while those in KB were 91.6% (89.7%–93.2%) and 92.0% (88.8%–96.1%) respectively.
under the medium inflow concentration were slightly higher than those under the low and high inflow concentrations. In the case of planting the two grasses, the TP removal rates in PR were better than those in KB and have the highest values under the low inflow concentration.

With no consideration of domestic sewage concentration levels, the results in Figure 5 indicated that the ARR was 66.7% (66.7%–68.8%) for TP in the control treatments without zeolite or plants, and exhibited significant differences relative to that in the treatments with zeolite (p < 0.05). When the ratios of zeolite to soil were 1:1 and 2:1, the ARR of TP in the treatments with the zeolite to soil ratio of 2:1 were higher than those in the treatments with the zeolite to soil ratio of 1:1, and the differences were not significant (p > 0.05). Nevertheless, the differences in the ARRs of TP between the treatments without zeolite and those with zeolite were significant except for the treatments with the zeolite to soil ratio of 1:1 in KB.

For phosphorus removal, the main mechanism is zeolite adsorption. Currently, some studies have found that substrates such as gravel and lava rock (Almeida et al. 2017), fishpond bund material and completely decomposed granite

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**Table 7** The average concentration of each pollution index of outflow water (mg L⁻¹) (SD in parentheses)

<table>
<thead>
<tr>
<th>Level</th>
<th>Plant</th>
<th>Z:S = 0:1</th>
<th>Z:S = 1:1</th>
<th>Z:S = 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>No</td>
<td>0.69 a (0.05)</td>
<td>0.66 a (0.13)</td>
<td>0.60 a (0.14)</td>
</tr>
<tr>
<td></td>
<td>PR</td>
<td>0.59 a (0.26)</td>
<td>0.23 b (0.05)</td>
<td>0.19 b (0.02)</td>
</tr>
<tr>
<td></td>
<td>KB</td>
<td>0.65 a (0.11)</td>
<td>0.50 a (0.09)</td>
<td>0.44 a (0.08)</td>
</tr>
<tr>
<td>Medium</td>
<td>No</td>
<td>1.55 a (0.42)</td>
<td>1.05 b (0.11)</td>
<td>0.98 b (0.16)</td>
</tr>
<tr>
<td></td>
<td>PR</td>
<td>1.36 a (0.27)</td>
<td>0.63 b (0.15)</td>
<td>0.43 b (0.04)</td>
</tr>
<tr>
<td></td>
<td>KB</td>
<td>1.50 a (0.08)</td>
<td>0.95 b (0.31)</td>
<td>0.80 b (0.10)</td>
</tr>
<tr>
<td>High</td>
<td>No</td>
<td>2.69 a (0.74)</td>
<td>1.62 a (0.50)</td>
<td>1.52 a (0.45)</td>
</tr>
<tr>
<td></td>
<td>PR</td>
<td>2.27 a (0.15)</td>
<td>1.06 a (0.22)</td>
<td>0.67 b (0.11)</td>
</tr>
<tr>
<td></td>
<td>KB</td>
<td>2.70 a (0.80)</td>
<td>1.41 b (0.28)</td>
<td>0.81 b (0.09)</td>
</tr>
</tbody>
</table>

Superscripts a, b represent significant differences (p < 0.05); SD in parentheses.
(Lai & Lam 2009), organic coco-peat and cupola slag (Saeed et al. 2012) had desirable phosphorus removal effects. However, zeolite has been proved to be a better material for adsorbing and releasing phosphorus (Markou et al. 2015). Ciosek et al. (2016) had demonstrated that an optimized clay-zeolite medium enhanced TP removal efficiency by chemical adsorption and reached 72 ± 2.9% TP removal after 3 hours. Additionally, phosphorus is taken up significantly through plant roots (Almeida et al. 2017). In this study, the plantation of PR increased the removal efficiency by 8.5% for TP compared with those in the treatments without zeolite, and by 6.9% for TP compared with those in the treatments with zeolite.

Organics

According to the national discharge standard for sewage, only under the condition of low inflow concentration, the outflow COD concentrations were within the range of 63.52–90.54 mg L⁻¹, which met the secondary discharge standard (COD ≤ 100 mg L⁻¹); under medium and high inflow concentrations, the outflow COD concentrations cannot meet the discharge standard (Table 7).

The removal of COD in the treatments with zeolite was not as good as that of nitrogen or phosphorus, and very close to that of COD in the treatments without zeolite. The introduction of the two grasses had a better removal effect on COD than no planting, and the removal rate of COD in PR was the best. In all treatments, the removal efficiency of COD was highest under the low inflow concentration, followed by the medium inflow concentration, but the differences among the three inflow concentrations were not significant (p > 0.05) (Figure 4). The results in Figure 5 indicate that the removal efficiency of COD showed no significant differences for the three proportions of zeolite addition at the p = 0.05 level. Under the condition of no plants, the ARR of COD was only 35.0% (27.6%–46.7%) in the treatments without zeolite. When the ratios of zeolite to soil were 1:1 and 2:1, the ARRs of COD were 31.3% and 32.5% respectively. When the grasses were planted, zeolite addition has little effect on the degradation of COD, or even resulted in lower removal efficiency of COD than that in the treatments without zeolite. In the treatments without zeolite, the ARRs of COD in PR and KB were 60.4% and 54.3% respectively, which increased by 13.7% and 7.6% respectively relative to those under the condition of no plants. After zeolite addition (Z:S = 1:1 and 2:1), the ARRs of COD were 50.3% (39.0%–56.9%) and 46.4% (37.4%–57.2%) in the treatments with PR and KB respectively, which increased by 18.4% and 14.5% respectively relative to those in the control treatments without plants.

Wetland plants play an important role in CWs for the growth, reproduction and decomposition of microorganisms by taking up nutrients and transferring oxygen to the rhizosphere (Fang et al. 2013). Most studies confirm the positive effects of macrophytes in CWs, such as the most widely used reed (Phragmites australis) (Çakir et al. 2015), Typha species (Bonanno & Cirelli 2017). In our work, the results showed that PR and KB had a better degradation effect on COD, and the ARR increased by 25.4% for COD in the treatments without zeolite but with plants, and by 19.0% in those treatments with zeolite and plants. Moreover, the treatments planted with PR had better removal efficiency than those planted with KB and unvegetated treatments. Nevertheless, some researchers considered that the influences of vegetation on organics removal in CWs were not unanimously agreed (Vymazala & Kröpfelová 2009), and that the soil-plant component caused no changes in outflow quality (Sklarz et al. 2008). This coincided with our results that the zeolite-plant combination had lower removal effects on COD compared with the ARR of N and P. The reason might be that the rhizodeposition products of plants provided the carbon source to the ecosystem (Zhai et al. 2013) and stronger retention than soil. In fact, there was no statistically significant correlation between plant and zeolite addition at the p = 0.444 level in our work.

Relationship between purification effects and ratios of carbon, nitrogen and phosphorus

The mass ratios of C:N (COD/TN), C:P (COD/TP) and N:P (TN/TP) under different inflow sewage concentrations ranged from 7.0 to 10.1, from 53.1 to 53.3, and from 5.3 to 7.6 respectively. From the results in Figure 6, it could be seen that the ratios of C:N (54.8–92.1) and C:P (225.6–376.8) in the treatments with zeolite and planted PR were higher than those in the treatments with zeolite and planted KB (C:N ranged from 41.5 to 90.1, and C:P ranged from 155.9 to 320.2). However, in the treatments with two plants and without zeolite, the ratios fluctuated in narrower ranges (C:N ranged from 14.9 to 22.5, and C:P ranged from 95 to 111). The order of N:P ratios, in treatments with Z:S = 1:1, was: control treatments without plants (4–5.6) > treatments with PR (5.3–3.7) > treatments with KB (1.8–4.1). In treatments with Z:S = 2:1, at low or medium inflow concentration levels, the N:P ratios from PR treatments (4.6–6.6) were higher than those from KB treatments (2.9–3.6); at

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the high concentration level, the N:P ratio from PR treatment (5.7) was lower than that from KB treatment (6.2).

On the whole, the ratios of C:N, C:P and N:P under the three inflow sewage concentrations showed no significant differences. However, in the effluent of all treatments with zeolite, the ratios of C:N and C:P increased and those of N:P decreased. In the treatments with planted grasses, C:N ratios always increased no matter what the ratio of zeolite to soil was, whereas C:P ratios decreased in the treatments with Z:S = 0:1 and 1:1 under medium or high inflow concentration and increased in the treatments with Z:S = 2:1. N:P ratios in the treatments with planted grasses showed a declining trend compared with those in the treatments with no plants. These results showed that removal effects for N and P were more efficient in the combined treatments with substrates and plants due to the adsorption, whereas the removal efficiency for COD was poor.

The regression equations in Table 8 demonstrated the removal rates of TN, NH₃-N and TP had negative correlations with C:N and N:P ratios and positive correlations with C:P ratios, except that the TP removal rate under the high inflow concentration had a positive correlation with the C:N ratio. Nevertheless, the regression equations of the COD removal rate and C:N, C:P and N:P ratios were not significant.

There are few reports about the relationships between ratios of C, N, P in wastewater and their removal efficiency. Fontenot et al. (2007) found that a C:N ratio of 10 produced the best results in terms of maximum N and C removal from the shrimp aquaculture wastewater. Xin et al. (2010) demonstrated that 83%–99% N and 99% P could be removed by microalgae when the ratios of N:P in wastewater were 5–12. In our work, though, the ratios of C:N in high inflow sewage concentrations was 10.1, the higher removal rates appeared in the lower C:N ratios of inflow sewage. Furthermore, when N:P ratios were 2–7 in the outflow sewage, the higher removal efficiency and plants with good growth had been obtained.

**CONCLUSION**

The inflow concentration levels of artificial domestic sewage (TN 22.75–42.64 mg L⁻¹, TP 3.01–8.08 mg L⁻¹) had no significant influences on the removal efficiency of pollutants...
at the same ratios of zeolite to soil. Nevertheless, there were higher removal rates under the low sewage concentration, and the outflow concentration could meet the first class discharge standard in the warm season. The addition of zeolite significantly increased the removal efficiencies of NH$_3$-N, TN and TP, but the increase of the zeolite to soil ratio from Z:S = 1:1 to Z:S = 2:1 did not significantly increase the removal efficiencies. Zeolite addition led to the increase of C:N and C:P ratios but the decrease of N:P ratios in effluent. The removal rates of TN, NH$_3$-N and TP had negative correlations with C:N and N:P ratios and positive correlations with C:P ratios. Nevertheless, the removal rate of COD had no significant correlation with carbon, nitrogen and phosphorus ratios. It was suggested that planting Lolium perenne or Poa annua on the substrate with a volume ratio of zeolite to soil of 1:1 could be the optimum combination to purify domestic sewage in rural areas of north China.

**ACKNOWLEDGEMENTS**

The research was financially supported by the sub-projects of National Major Science and Technology Project of China, ‘Integration and demonstration of water environmental protection and control technology for the key tributaries of the Qingshui river (2015ZX07203-005-02)’. Thanks to Xue Jiang for her monitoring of data during the experiment.

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First received 18 October 2017; accepted in revised form 10 July 2018. Available online 23 July 2018

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