Constructed wetland using corncob charcoal substrate: pollutants removal and intensification
Mao Liu, Boyuan Li, Yingwen Xue, Hongyu Wang and Kai Yang

ABSTRACT
To investigate the feasibility of using corncob charcoal substrate in constructed wetlands, four laboratory-scale vertical flow constructed wetlands (VFCWs) were built. Effluent pollutant (chemical oxygen demand (COD), NH\textsubscript{4}+-N, total phosphorus (TP)) concentrations during the experiment were determined to reveal pollutant removal mechanisms and efficiencies at different stages. In the stable stage, a VFCW using clay ceramisite substrate under aeration attained higher COD (95.1%), and NH\textsubscript{4}+-N (95.1%) removal efficiencies than a VFCW using corncob charcoal substrate (91.5% COD, 91.3% NH\textsubscript{4}+-N) under aeration, but lower TP removal efficiency (clay ceramisite 32.0% and corncob charcoal 40.0%). The VFCW with raw corncob substrate showed stronger COD emissions (maximum concentration 3,108 mg/L) than the corncob charcoal substrate (COD was lower than in effluent). The VFCW using corncob charcoal substrate performed much better than the VFCW using clay ceramisite substrate under aeration when the C/N ratio was low (C/N = 1.5, TN removal efficiency 36.89%, 4.1% respectively). These results suggest that corncob charcoal is a potential substrate in VFCWs under aeration with a unique self-supplying carbon source property in the denitrification process.

Key words | aeration, C/N ratio, carbon source, charcoal, constructed wetlands, denitrification

INTRODUCTION
Constructed wetlands (CWs) have been widely used in the latest three decades for their unique advantages of low energy consumption and operating cost. However, there are also some drawbacks that limit their application in some areas. For example, CWs require more space than normal wastewater treatment plants; substrates are easily clogged if inlet water is not pretreated well (Aiello et al. 2016). While, with the rapid development of the modern city, less and less space is available, which has become a key factor in deciding a city’s future. The removal of pollutants in a CW is confusing, mainly because of the complicated process, which includes sedimentation, filtration, precipitation, volatilization, adsorption, plant uptake, and various microbial processes (Wu et al. 2014). There are various ways to improve pollutant removal efficiency, such as artificial aeration (Liu et al. 2016), plant optimization (Fan et al. 2016), substrates optimization (Guan et al. 2015), and effluent recirculation.

Substrates are the main constituent of CWs, playing a major role in pollutant elimination. Inorganic materials like sand, zeolite, gravel, and steel slag are ideal substrates in the removal of organic pollutants and have already been used in typical full scale CWs. However, nitrogen removal efficiency is limited due to insufficient dissolved oxygen (DO) in the nitrification process and insufficient organic supply in the denitrification process (Kadlec et al. 2005). Organic substrates such as mulch, oak leaf, and sheep manure have showed good performance in the removal of nitrogen (Zhang et al. 2016), but chemical oxygen demand (COD) leaking from these materials may lead to serious water pollution. To overcome this problem, new materials (Guo et al. 2016a, 2016b), combined type of CWs (Li et al. 2016) have been introduced to improve COD and nutrient removal efficiencies simultaneously.

Charcoal is a porous, low density, and carbon-rich material made by combusting biological materials such as corncob, or wheat straw, under non-oxygen conditions. It is widely used as soil amendment (Lehmann et al. 2016). While, to date, few studies have shown its performance in pollutant removal as a substrate in CWs. The founding of microbial biomass (Lehmann et al. 2011) increase and pollutant adsorption ability would improve pollutant removal efficiencies in CWs. Charcoal is reported to stimulate root growth
sometimes (Breazeale 1906), which may help the transportation of oxygen in CWs. Besides, the composition of charcoal changes with different combustion times and temperatures (Keiluweit et al. 2010), which means controlling charcoal properties is easy and environmentally friendly. Thus, the remaining organic composition of corncob charcoal may serve as an organic carbon source in the denitrification process, leading to a high removal rate of nitrogen.

In this study, in order to figure out the feasibility of using corncob charcoal substrate in CWs, corncob charcoal that was combusted at a relatively low temperature and clay ceramisite were used as substrates. Artificial aeration was introduced to help the growth of biofilms and improve the pollutant removal in a vertical flow constructed wetland (VFCW). Different C/N ratios were set to reveal the self-supplying carbon source property of corncob charcoal in the denitrification process.

**METHODS**

**Laboratory-scale wetland systems**

Four laboratory-scale VFCWs (system A: aerated CW with corncob charcoal substrate; system B: aerated CW with raw corncob substrate; system C: aerated CW with clay ceramisite substrate; system D: non-aerated CW with corncob charcoal substrate) were built from PVC (Figure 1). VFCWs each of 10 cm diameter × 100 cm depth were constructed with outlets at the bottom, middle and top. Coarse gravels (1–2 cm in diameter) were used as a supporting layer at the bottom (10 cm in height) to help the distribution of air, and the top was filled with 10 cm of gravels and sands to support the growth of plants. The remaining space was filled with substrate. All substrates including corncob charcoal and clay ceramisite were firstly washed with tap water to remove ashes and then filled into columns to a height of 80 cm. A small amount of artificial aeration (2 L·min⁻¹ m⁻²) was deployed to systems A, B, and C by air diffusers (4 cm in height and 3 cm in diameter) which were installed at the bottom with rotor flowmeters and air valves to show and control the aeration rate (16 mL/min). *Iris wisionii* C.H. Wright was selected and planted at a density of 1 plant per system (127 plant per square meter). Each system had an average porosity of 33.3% with an average working volume of 2.6 L (7.8 L in total).

Corncob charcoal substrate (average diameter 1.2 cm) was prepared by combusting raw corncob in a muffle furnace at 250 °C for 80 minutes under nitrogen protection before crushing into pieces. This process was easy to realize.

![Figure 1](https://iwaponline.com/wst/article-pdf/76/6/1300/449683/wst076061300.pdf)
and environmentally friendly, and its product, corn cob charcoal, had good physical properties with low bulk and grain density (116 kg/m³ and 290 kg/m³).

Clay ceramisite was bought in Shuqian, Jiangsu province, China. Its physical properties were similar to corn cob charcoal at 1.1 cm in diameter on average, 292 kg/m³ and 584 kg/m³ (bulk and grain density).

Operation of the wetland columns

In the first 80 days, all systems were operated by a sequencing fill and empty batch mode with hydraulic retention time (HRT) of 24 h (hydraulic loading 0.33 m³ m⁻² d⁻¹). Influent water was prepared by 250–460 mg/L NaAc, 100 mg/L NH₄Cl, 20 mg/L KH₂PO₄, and 1 mL trace solution per 15 L influent. The trace solution contained, as follows (per liter): 0.9 mg FeCl₃, 0.15 mg H₂BO₃, 0.18 mg KI, 0.03 mg CuSO₄·5H₂O, 0.06 mg MnCl₂·4H₂O, 0.12 mg ZnSO₄·7H₂O, 0.15 mg CoCl·7H₂O, 0.06 mg Na₂MoO₄·2H₂O, and 10 mg EDTA. Synthetic wastewater was pumped into all systems at 8 o’clock, and water samples were taken on the next day in the middle of each column, after which effluent was discharged from the outlet at the bottom.

After 80 days, systems A and C were selected to continue the experiment on the influence of C/N ratio on nitrogen removal efficiency to reveal whether organic carbon in charcoal can be used as a carbon source in the denitrification process. Influent synthetic wastewater was synthesized by NaAc (60, 120, 250, 500 mg/L), 100 mg/L NH₄Cl, 20 mg/L KH₂PO₄, 60 mg/L NaNO₃, and 1 mL trace solution per 15 L influent. Systems A and C were operated under 16 mL/min aeration with an HRT of 24 h. Every C/N ratio experiment was conducted for 7 days, and water samples were taken on the last 3 days in the middle of each column.

The whole experiment operated and lasted for 5 months.

Sampling and analysis

Water samples were taken from influent and effluent (in the middle outlet of each column) to analyze the removal efficiencies of organics, nitrogen and phosphorus. NH₄-N, NO₃-N, NO₂-N, COD, and TP were determined immediately following the methods described in the standard method (APHA/AWWA/WEF 2005). DO was measured by a DO meter (YSI 550A, USA). Statistical analysis of the data was performed using the SPSS software package (SPSS 16.0). All data were presented as mean ± SD, and the level of significance was set at P ≤ 0.05 for all analyses.

RESULTS AND DISCUSSION

Overall performance of VFCWs during starting stage

COD removal

Figure 2 shows COD concentrations across the experiment, in which microorganism grew and COD concentrations in the effluent water became stable gradually. Overall, systems A and C showed good performance for COD removal, with effluent concentrations of 50, and 28 mg/L respectively after 40 days, which can comply with Class I (A) of the wastewater discharge standard (GB18918-2002) in China. The COD removal rates of A and C (75%, and 86% respectively) were a little lower than in other studies, such as 95% (Chen & Vymazal 2015), which can be explained by the low amount of aeration (16 mL/min), short hydraulic retention time (HRT = 24 h, compared with the other study’s 36 h) and running period. At the end of the study (day 80), the COD of systems A and C dropped to 16.9, and 9.8 mg/L (removal rates of 91.5%, and 95.1% respectively), which is consistent with other findings (Li et al. 2014). In CWs, COD is eliminated mainly by microorganism digestion in suitable conditions and adsorption by certain substrates. That is to say, both corn cob charcoal and clay ceramisite are ideal substrates for microorganism growth in VFCWs. However, in system D (corn cob charcoal without aeration), the effluent COD was a little higher (10.35 mg/L on average) than that of the influent and varied with it, which infers the leaking of organic substances in corn cob charcoal. The difference in effluent COD concentrations between systems A and D suggests that oxygen (average DO was 2.4 mg/L, 1.1 mg/L, respectively) plays an

![Figure 2](https://iwaponline.com/wst/article-pdf/76/6/1300/449683/wst076061300.pdf)
important role in microorganism growth and in organic pollutant removal, which is in accordance with other studies (Nivala et al. 2013). In system B, effluent COD concentrations were much higher than that of the influent, increasing gradually in the first 31 days to a maximum concentration of 3,108 mg/L and then decreasing to about 620 mg/L. This was in agreement with another study (Warneke et al. 2011), which reports that maize cob releases an elevated amount of total organic carbon. Compared with system B, the release of organic matter is much less in system A, indicating that carbonization of corn cob (an organic substrate) can reduce the release of organic matter to a large extent.

On days 1, 4, and 7, systems A and D effluent COD grew gradually but was lower than the influent. In this period, substrate adsorption played the chief role in COD removal and came to saturation within days. In system A, microorganisms grew in the presence of oxygen, along with which the adsorbed COD on the surface of the substrates was consumed. Thus on day 10, the COD in system A decreased while in system D it increased. After this, the COD in system A varied with the influent wastewater and gradually came to a relatively stable concentration. On day 1, the COD in systems A and D was much lower than that of system C, showing that charcoal substrates have a larger COD adsorption capacity.

NH₄⁺-N removal

Figure 3 shows the NH₄⁺-N concentrations of each system during the experiment. After 31 days, a significant difference in NH₄⁺-N removal appeared; system A showed the best performance, followed by systems C, B and D. NH₄⁺-N removal efficiency largely depends on microbial biomass through nitrification and microorganism assimilation (Hu et al. 2016), which means corn cob charcoal substrates have favorable conditions for the growth of nitrifiers. At the end (day 80), NH₄⁺-N concentration dropped to 2.4, and 1.35 mg/L with removal rates of 91.3% and 95.1%, in A and C respectively. The NH₄⁺-N removal rates are much higher than in a conventional CW, indicating that aeration enhanced the removal of NH₄⁺-N. As for system B, effluent NH₄⁺-N was very low in the initial period (from day 1 to day 21, average NH₄⁺-N 9.24 mg/L), and then increased dramatically to 26.5 mg/L. This may have something to do with COD concentrations. When the organic loading is high, biomass assimilation proceeds through incorporation of NH₄⁺-N to fulfill nutrient requirements (Sun et al. 2005), and this may play a vital role in NH₄⁺-N removal in system B. In the initial period, organic matter that can be easily used by microorganisms firstly was released from the substrates, which enhanced microorganism assimilation. After that, COD decreased, so microorganism assimilation was limited, leading to a smaller need for NH₄⁺-N. Low pH (5.5 on average) and DO (1.91 mg/L on average) also inhibit the assimilation ability of certain microorganisms.

Adsorption by substrate is also a way of NH₄⁺-N removal. The different NH₄⁺-N concentrations on day 1 and day 4 reveal that the adsorption capacity of corn cob charcoal is greater than that of clay ceramisite.

TP removal

Phosphorus in CWs is removed by plant uptake, accretions of wetland soils, microbial immobilization, and substrate adsorption (Seo et al. 2005). Figure 4 shows TP concentrations during the experiment. Like COD and NH₄⁺-N concentrations, TP was relatively low in the first 7 days (the adsorption period), and then varied with influent (except in system B), reaching a stable stage (after 31 days). In the stable stage TP concentration is about 2.6, 3.7, 3.3, 4.5 mg/L (systems A, B, C, D respectively), indicating that corn cob charcoal substrate under aeration is the most suitable condition for the removal of TP. For the adsorption capacity of TP, clay ceramisite and corn cob charcoal are similar, since a similar effluent TP concentration on day 1 (1.64, and 1.69 mg/L for corn cob charcoal and clay ceramisite respectively). The reason for the TP increasing dramatically was the same as the NH₄⁺-N increase (system B on day 25). TP in systems A and D was 2.6, 4.5 mg/L respectively in the stable stage, indicating that aeration can
enhance the removal of TP. This is consistent with other studies which report that aeration increased the removal rate of TP and COD (Pan et al. 2015).

Nitrate removal efficiency under different C/N ratios

The other object of this study was to investigate whether organic substances released from corn cob charcoal can be used by denitrifiers to solve the problem of an insufficient carbon source in the denitrification process (Guo et al. 2016a, 2016b). In CWs, nitrification and denitrification are considered to be the major roles of nitrogen removal (Saeed & Sun 2012; Chyan et al. 2016). In this study, artificial aeration was introduced to reduce the limitation of insufficient oxygen that would hinder the nitrification process. The denitrification process is often impaired by the lack of organic material. Table 1 shows the concentration of NO$_3$-N, NO$_2$-N, and NH$_4^+$-N, of systems A and C under different C/N (N = NO$_3$-N + NO$_2$-N + NH$_4^+$-N) ratios in the presence of 16 mL/min aeration. Almost all NH$_4^+$-N in both systems was converted under different C/N ratios, and NO$_3$-N can be ignored compared with NO$_2$-N. This can be attributed to the 16 mL/min aeration, which enhanced nitrification activity.

Figure 5 shows the tendency of effluent NO$_3$-N of systems A and C. Although the decline in the C/N ratio led to NO$_3$-N increase in both systems, system A showed much better NO$_3$-N removal performance than system C. When the C/N ratio was below 7, the NO$_3$-N in system C become higher than in the influent; this phenomenon was observed in system A when the C/N ratio was under 3. This C/N ratio was lower than in other studies, which reported that the optimal C/N ratio was 25 (Kumar et al. 2010), 10 (Zhao et al. 2010), and 6 (Zhi & Ji 2014; Zhu et al. 2014). When C/N was set to 1.5, effluent NO$_3$-N was 24.61 (system A), 37.18 mg/L (system C), and TN (TN = NO$_3$-N + NO$_2$-N + NH$_4^+$-N = 11.56 + 0 + 27.44 = 39.00 mg/L) removal rates were 56.89% (system A) and 46.7% (system C), indicating that the denitrification process was inhibited in both systems.

When VFCWs with corn cob charcoal substrate are used in treating ammonia-rich wastewater, to ensure enough organic carbon source in the denitrification process, the C/N ratio should be higher than 3 (horizontal coordinates of the intersection point of effluent A’s NO$_3$-N curve and influent NO$_3$-N curve), while VFCWs with clay ceramisite substrates should be higher than 7 (horizontal coordinates of the intersection point of effluent C’s NO$_3$-N curve and influent NO$_3$-N curve). Considering the Class I (A) wastewater discharge standard (GB18918-2002) in China, TN should be lower than 15 mg/L. That is to say, C/N should be higher than 2.7 and 6.2 (horizontal coordinates of the intersection points of effluents A and C’s NO$_3$-N curves with standard discharge concentration), for A and C respectively (influent NO$_3$-N, NO$_2$-N, are ignored due to low concentration). All these statistics confirmed the idea that the remaining organic carbon source in corn cob charcoal can be utilized as an electron donor in the denitrification process.

Table 1 | Characteristics of influent and effluent under different C/N ratios (mean ± SD)

<table>
<thead>
<tr>
<th>C/N ratio</th>
<th>NH$_4^+$ (mg/L)</th>
<th>NO$_3$ (mg/L)</th>
<th>NO$_2$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent</td>
<td>Effluent A</td>
<td>Effluent C</td>
</tr>
<tr>
<td>1.5</td>
<td>27.44 ± 0.31</td>
<td>0.93 ± 0.21</td>
<td>0.24 ± 0.08</td>
</tr>
<tr>
<td>3.0</td>
<td>27.22 ± 0.40</td>
<td>0.76 ± 0.09</td>
<td>0.44 ± 0.15</td>
</tr>
<tr>
<td>5.0</td>
<td>26.65 ± 0.23</td>
<td>0.30 ± 0.00</td>
<td>0.58 ± 0.32</td>
</tr>
<tr>
<td>8.0</td>
<td>27.01 ± 1.10</td>
<td>2.97 ± 0.39</td>
<td>2.54 ± 0.16</td>
</tr>
</tbody>
</table>

—, Concentration under detection limit; ND, Not determined.
Variation of organics and nitrogen in a cycle in systems A and C (C/N = 8)

The time-profile of the NH₄⁺-N, NO₃⁻-N, NO₂⁻-N, and COD concentrations during the 24 h treatment phase in systems A and C are shown in Figure 6. The concentrations of NO₃⁻-N were below 0.5 mg/L after 2 h in both systems during the cycle. COD and NH₄⁺-N concentration curves in system A are similar to those of system C. However, the NO₃⁻-N concentration curve in these two systems showed a large difference.

The most part (95% in system A, 88% in system C) of the influent COD was removed within 8 hours after feeding in both systems. After that, the COD in system A increased a little, while in system C it decreased, and then became mainly stable in the rest of the cycle (after 12 h, the COD of systems A and C was around 25 and 8 mg/L, respectively). If artificial aeration is introduced to VFCWs, HRT can be shortened from days (Toet et al. 2009) to 12 hours. This lower HRT means a smaller requirement for building area and lower costs.

In system A, the NO₃⁻-N concentration decreased rapidly from 15.7 mg/L to less than 0.5 mg/L (0–3 h) and then became stable (3–8 h); after that, it gradually increased to 2 mg/L (8–24 h). In system C, the first 8 h (0–8 h) are similar to system A, after 8 h, NO₃⁻-N grew much faster than in system A to 9.7 mg/L. In this operating condition, NO₃⁻-N came from the influent and NH₄⁺-N from the nitrification process by nitrifiers, and was consumed in the denitrification process by heterotrophic microbials. The decline of NO₃⁻-N, and NH₄⁺-N in the first 4 hours, indicates simultaneous nitrification and denitrification occurred in both systems. After 12 hours, NH₄⁺-N became relatively stable, while NO₃⁻-N increased to a different extent. The adsorbed and stored NH₄⁺-N in the nitrifiers may be the feed of the nitrification process. The difference between systems A and C can be explained by the different substrate. In this period, the remaining organic substances in corncob charcoal may act as a carbon source, which limited the denitrification process.

CONCLUSIONS

Corncob charcoal can be used in CW to achieve fine pollutant removal efficiencies (91.5% COD, 91.3% NH₄⁺-N, 40.0% TP). The pollutant (COD, NH₄⁺-N, TP) adsorption capacity of corncob charcoal is larger than inorganic clay ceramisite. Artificial aeration plays a vital role in pollutant removal in VFCWs.
Organic substances remaining in the corn cob charcoal can be utilized as an electron donor in the denitrification process, thus resulting in better removal efficiency of NO$_3^-$-N, which may solve the existing problem that NO$_3^-$-N accumulates in CWs. NO$_3^-$-N concentration decreased with the increase in C/N ratio in both systems, but there was less NO$_3^-$-N in corn cob charcoal VFCWs. To meet the Class I (A) wastewater discharge standard (GB18918-2002) in China, the minimum C/N ratio was 2.7 (VFCW using corncob charcoal) and 6.2 (VFCW using clay ceramisite) under 2 L min$^{-1}$ m$^{-2}$ atmospheric aeration.

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