Intensified nitrogen and phosphorus removal in a novel electrolysis-integrated tidal flow constructed wetland system

Xinxin Ju, Shubiao Wu, Yansheng Zhang, Renjie Dong

College of Water Resources & Civil Engineering, China Agricultural University, Beijing 100083, PR China
Key Laboratory of Clean Utilization Technology for Renewable Energy in Ministry of Agriculture, College of Engineering, China Agricultural University, Beijing 100083, PR China

Abstract

A novel electrolysis-integrated tidal flow constructed wetland (CW) system was developed in this study. The dynamics of intensified nitrogen and phosphorus removal and that of hydrogen sulphide control were evaluated. Ammonium removal of up to 80% was achieved with an inflow concentration of 60 mg/L in wetland systems with and without electrolysis integration. Effluent nitrate concentration decreased from 2 mg/L to less than 0.5 mg/L with the decrease in current intensity from 1.5 mA/cm² to 0.57 mA/cm² in the electrolysis-integrated wetland system, thus indicating that the current intensity of electrolysis plays an important role in nitrogen transformations. Phosphorus removal was significantly enhanced, exceeding 95% in the electrolysis-integrated CW system because of the in-situ formation of a ferric iron coagulant through the electro-dissolution of a sacrificial iron anode. Moreover, the electrolyzed wetland system effectively inhibits sulphide accumulation as a result of a sulphide precipitation coupled with ferrous-iron electro-dissolution and/or an inhibition of bacterial sulphate reduction under increased aerobic conditions.

Article history:
Received 26 November 2013
Received in revised form 19 February 2014
Accepted 4 April 2014
Available online 16 April 2014

Keywords:
Tidal flow constructed wetlands
Electrolysis
Nitrogen transformation
Phosphorus removal
Sulphide

1. Introduction

Constructed wetlands (CWs) have proven to be an efficient ecological technology for the treatment of various kinds of contaminated waters (Williams, 2002; Haberl et al., 2003; Kadlec and Wallace, 2009). Compared with conventional treatment systems, CWs have lower costs and can be operated and maintained more easily (Inamori et al., 2007). The wetlands have become standard treatment technology for many countries because of the need for low-carbon, environmental friendly technologies (Brix, 1999; Vymazal, 2009).

CWs are generally categorized into surface flow wetlands and subsurface flow wetlands (SSFW). SSFW is the most common CW type in Europe; such systems have been consistently effective in the removal of biochemical oxygen demand, suspended solids, and pathogenic organisms (Vymazal et al., 1998; Garcia et al., 2003, Akratos and Tsihrintzis, 2007). However, nutrient removal is generally limited because of a lack of the oxygen content that is necessary to oxidize ammonium and of the low sorption
capacities of the common substrate materials utilized in phosphorus retention (Tanner et al., 2002). Thus, intensified CWs, such as artificially aerated and tidal-flow CWs, were developed to improve oxygen transfer in CWs (Austin and Nivala, 2009; Wallace and Liner, 2011; Saeed et al., 2012).

Artificially aerated CWs can increase oxygen transfer rate to 160 g/m² d by compressing air from the atmosphere into the wetland bed with the use of a blower (Kadlec and Wallace, 2009). Consequently, nutrient removal is intensified and the required area is reduced. However, such technology is not widespread because aeration process consumes a great deal of energy. Also, the fouling of air diffusers within CWs must be considered, as well as the provisions for replacing or chemically cleaning diffuser assemblies. Tidal-flow constructed wetlands (TFCWs) are a relatively new technology that utilizes a novel oxygen transfer method (Tanner et al., 1999; Austin, 2006; Wu et al., 2011). TFCWs are regularly filled with wastewater and then drained, and TFCWs act as passive pumps that expel and draw air from the atmosphere into pore spaces (Zhao et al., 2004; Sun et al., 2006). In this way, the oxygen transfer rate reaches 450 g/m² d (Wu et al., 2011), and the ammonium and organics treatment capacities are consequently improved significantly (Hu et al., 2012). However, denitrifier growth and activity is inhibited by either high oxygen content or inadequate electron donor sources, thus resulting in the increase in effluent nitrate content in these systems (Zhao et al., 2004).

Phosphorus removal is necessary because this element stimulates algae growth responsible for eutrophication of rivers and closed water bodies (Ikematsu et al., 2007). Phosphorus in CWs is removed through the interaction among substrates, plants, and microorganisms (Wang et al., 2013). Phosphorus removal rate decreases significantly over time. Desorption of phosphorus from substrate is thus coupled with TFCW technology to fully utilize their advantages.

In this study, a novel, tidal-operated, electrolysis-integrated CW system was developed. The dynamics of intensified nitrogen and phosphorus removal were evaluated, and the important role of current intensity in nitrogen transformations was examined. The inhibitory effect of the electrolytic process on sulphide accumulation was also analyzed.

2. Materials and methods

2.1. Laboratory-scale wetlands

The schematic diagram of two lab-scale CWs (systems A and B) is shown in Fig. 1. The electrolysis-integrated experimental wetland (system A) was composed of a perspex tube cylinder with an internal diameter of 13 cm.

\[
4\text{Fe}(s) + 10\text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow 4\text{Fe(OH)}_3(s) + 4\text{H}_2(g).
\]

In the above chemical equation, the abbreviations of (s), (l), and (g) mean the state of solids, liquids and gases respectively.

Ferric hydroxide can be used as a flocculants to remove phosphorus in wastewater. This reaction also produces hydrogen gas which is an electron donor; thus, nitrate content is attenuated under a low-carbon-source condition. Autotrophic denitrification with hydrogen as electron donor has been studied (Lee et al., 2010; Mansell and Schroeder, 2002). Results show that the technology has a good development potential. Moreover, the research of Sakakibara and Kuroda (1993) posited that an electrically driven biological denitrification process is simple and feasible, especially in the treatment of low-strength nitrate solutions.

TN removal efficiency in TFCWs is not ideal because of the high oxygen content. PO$_4^{3-}$ removal in TFCWs is generally limited because of the low sorption capacity of substrate materials, as in other CWs. Electrolysis has an advantage when used in dephosphorization and has potential for use in denitrification under low-carbon-source condition. Electrolysis is thus coupled with TFCW technology to fully utilize their advantages.

Fig. 1 – Schematic diagram of experimental laboratory-scale constructed wetlands (CWs) (system A: electrolyzed experimental CW; system B: non-electrolyzed contrast CW).
and a length of 60 cm. This cylinder was divided into two sections, the height of the upper section is 35 cm and the lower section is 25 cm. Each of the both sections had a pore volume of about 1 L. The upper section of the experimental CW was filled with zeolite (diameter ranging from 0.5 mm to 2 mm) and operated using tidal flow. The lower section was filled with bio-ceramic (diameter ranging from 3 mm to 6 mm) and integrated with electrode plates for electrolysis. An anaerobic condition was maintained at the bottom section with constant water saturation. The electrode plates (3 mm thick, 12 cm in diameter) were made of iron or graphite. These electrode plates contained pores with a diameter of 1 cm to guarantee easy passage of water, there are many holes on the plates and the distance of every adjacent holes are 2 cm (from the center to the center). Electrodes were connected using copper wires and sealed using waterproof glue. Tidal operation was initiated by a peristaltic pump and an automatic drain valve controlled by a timer. Electrolysis was initiated by a direct current power supply (RXN-305D, Zhaoxin, China) and controlled by a timer. A CW (system B) not integrated with electrolysis was designed with similar configurations. Both wetland systems operated using the same tidal flow hydraulics and with the same amount of inflow water. Juncus effusus were planted, and the column sidewall of the wetland was wrapped with black plastic cloth to prevent periphyton formation. The system was placed under a temperature of 15 °C–35 °C during the experiments in the laboratory of Bioenergy Engineering and Low Carbon Technology at China Agricultural University.

### 2.2. Experimental conditions

Synthetic wastewater containing ammonium, chemical oxygen demand (COD), and phosphate was used in this study to minimize variability in the experiment. Influent artificial wastewater was prepared by dissolving C6H12O6 H2O, NH4Cl, and KH2PO4 in tap water according to the required concentrations. The added compositions in their various phases are shown in Table 1. A trace mineral solution containing EDTA-Na (0.1 g/L), FeSO4·7H2O (0.1 g/L), MnCl2·4H2O (0.1 g/L), CoCl2·5H2O (0.17 g/L), CaCl2·6H2O (0.1 g/L), ZnCl2 (0.1 g/L), CuCl2·5H2O (0.02 g/L), NiCl2·6H2O (0.03 g/L), H2BO3 (0.01 g/L), Na2MoO4·2H2O (0.01 g/L), and H2SeO3 (0.001 g/L) was added to the artificial wastewater (1 mL/L) in all cases (Wu et al., 2012).

3 L synthetic wastewater was added into each column per day, and the hydraulic loading rate (HLR) is 226 L/m2d. In tidal operation, flooding and draining cycle occurred every 8 h with a flood/drain time ratio was 4 h:4 h. Electrolysis followed a four-hour cycle with voltage of 10 V in system A. Three iron plates and two graphite plates were arranged alternately at a distance of 2 cm. The electrolytic cycle is shown in Table 2. It was expected that nitrogen was removed in the form of nitrogen gas by using the hydrogen provided an electron donor for denitrification in the nitrogen removal mode, in which iron and graphite electrodes acted as the cathode and the anode, respectively. Phosphorus was removed in the form of iron phosphate precipitates by using dissolved iron ions in the phosphorus removal mode, in which the polarities of the electrodes were switched (i.e., iron anode). A settling time during which the system was on standby without electricity was also enforced.

The two wetlands were continuously fed with artificial wastewater for one month to allow plants and biofilms to develop in the bed. The wastewater used during the cultivation period was composed of the same materials as those used in experimental phase I. The experimental period lasted from March 2013 to October 2013 for a total period of 210 days. The total experimental period was categorized into four phases according to the varying operational conditions: Phase I is the initial condition, as described in the previous section. The influent concentration, the electrode arrangement, and the electrolytic cycle were modified separately in phases II, III, and IV, respectively. The electrolysis conditions for the different phases in the experimental CW (system A) are listed in Table 2.

### 2.3. Sampling and analysis

Wastewater samples were collected in triplicate from the inflows and outflows of both systems to evaluate system performance. The pH value, temperature, dissolved oxygen (DO) and oxidation–reduction potential (ORP) values were immediately measured using a portable Orion 5-Star meter, a pH electrode (9172BNWP, THERMO, USA), a DO electrode (086030MD, THERMO, USA), and an ORP electrode (ORION, 9172BNWP). The concentrations of ammonium-nitrogen (NH4+/N=4500–NH3 F. Phenate method), nitrite nitrogen (NO2−/N=4500–NO2− B. Colorimetric method), phosphate (PO43−/P=4500–P E. Ascorbic acid method), and sulphide concentrations (S2−/H2S–S2− B. Colorimetric method) were measured using ultra-violet and visible spectrophotometers (Gold S54T, Lengguang Tech, China) after corresponding standard pretreatment and reagent addition according to Standard Methods (AWWA and WEF, 1998). Nitrate-nitrogen

### Table 1 – Influent concentration during different experimental phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>NH4+/N (mg/L)</th>
<th>PO43−/P (mg/L)</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>30</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>II</td>
<td>60</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>III</td>
<td>60</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>IV</td>
<td>60</td>
<td>10</td>
<td>300</td>
</tr>
</tbody>
</table>

### Table 2 – Electrolytic conditions during different phases in system A with electrolysis.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Voltage (V)</th>
<th>Number of electrodes</th>
<th>Plate distance (cm)</th>
<th>Electrolytic time cycle (a:b:c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>180:30:30</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>180:30:30</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>2</td>
<td>5</td>
<td>180:30:30</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>2</td>
<td>5</td>
<td>180:45:15</td>
</tr>
</tbody>
</table>

a: The time when graphite plates were used as anodes (min).
b: The time when iron plates were used as anodes (min).
c: The settling time (min).
(NO$_3^-$–N) was analyzed using continuous flow colorimetry (SEAL Auto-Analyzer 3, British), and COD was measured using a Hach DR5000 Colorimeter according to its standard calibration and operation. Sulphate and iron ion were determined using barium acetate (880 nm) photometric method and 1,10-phenanthroline (510 nm) spectrophotometry, respectively. Fraction of O$_2$ was monitored on-line by using a portable oxygen detector (HND880-O$_2$, China) with a resolution ratio of 0.1% vol during each phase. The data computation was carried out by means of SPSS and EXCEL software.

3. Results

COD removal efficiency exceeded 90% in both electrolyzed and non-electrolyzed systems in different phases. The results, which were calculated using SPSS with a p-value of over 5%, indicated that no significant difference in COD removal rate is present between the two systems. Table 3 shows the main parameters of the outflows throughout the entire operational period. The pH values of systems A and B ranged from 6.1 to 6.5 and from 6.6 to 7.1, respectively. The ORP of the electrolyzed system A was approximately +200 mV. Meanwhile, the ORP of system B, which was not electrolyzed, was only approximately −20 mV. The effluent DO concentrations of both systems were approximately 0.8 mg/L during the experiment. The effluent temperatures of the two systems fluctuated with the room temperature, ranging from 18°C to 33°C. The average temperature in system A was approximately 1°C higher than that of system B. Fig. 2 shows the inflow and outflow concentration changes in NH$_4^+$–N and NO$_3^-$–N over time in systems A (electrolysis-integrated wetland) and B (non-electrolyzed wetlands). The average inflow NH$_4^+$–N concentration was 30 mg/L in the first phase and then increased to 60 mg/L in the next three phases. The NH$_4^+$–N outflow contents of systems A and B were not significantly different (less than 5 mg/L) in the first phase. And as the system stabilized in phases III and IV, the NH$_4^+$–N outflow concentrations were maintained at less than 15 mg/L in systems A (approximately 13 mg/L) and B (approximately 14 mg/L). The effluent NO$_3^-$–N contents of both systems were maintained at lower than 0.5 mg/L throughout the entire experiment, although nitrate accumulation (up to 2 mg/L) occurred in the electrolyzed experimental wetland (system A) during phase II. The effluent nitrite nitrogen detected in this study was always less than 0.2 mg/L.

The dynamics of influent and effluent PO$_4^{3-}$–P in both systems during the experimental phases are illustrated in Fig. 3. PO$_4^{3-}$–P inflow concentration was constant at 10 mg/L. The detected PO$_4^{3-}$–P effluent concentration in the electrolyzed system A was typically less than 0.5 mg/L, with a removal efficiency of over 95%. However, the removal rate dropped to 85% during phase III. The effluent PO$_4^{3-}$–P concentration in the non-electrolyzed system B increased gradually from 3 mg/L to approximately 7 mg/L during the experimental phases. The removal rate decreased from 43.8% to 19.8%.

The sulphate and sulphide content in the inflows and outflows were also tested in this study. The average SO$_4^{2-}$–S inflow and outflow concentrations were 45 mg/L and approximately 10 mg/L, respectively, with a removal efficiency of 77%. The S$^{2-}$ produced in the outflows of each system was relatively stable; its average concentration in the non-electrolyzed wetland system B was 0.84 mg/L, and its average concentration in the electrolyzed wetland system A was 0.005 mg/L (Fig. 4). We measured the effluent iron concentration in the electrolyzed system A because iron was adopted as an electrode material in this experiment. The result is shown in Fig. 5. The effluent Fe$^{2+}$ concentration ranged from 5 mg/L to 15 mg/L in phases I and II and then decreased to hardly detectable levels in phases III and IV as the electrolytic conditions changed. Fe$^{2+}$ content throughout the experiment was consistently less than 2 mg/L.

4. Discussion

NH$_4^+$–N removal reached approximately 80% in both electrolyzed and non-electrolyzed wetlands in this study. Outflow concentration was typically maintained at less than 15 mg/L under an inflow concentration of 60 mg/L (Fig. 2). Effective ammonium removal mainly occurred in the upper section that is under tidal operation with a high oxygenation efficiency. The positive effect of tidal operation on CW oxygenation has been reported in previous investigations (Sun et al., 2005; Sasikala et al., 2009; Sun et al., 2006; Lv et al., 2013; Wu et al., 2011). Ammonium removal at the bottom of the experimental CWs was less than 3% of total ammonium removal because the constant water saturation in this section results in an anaerobic condition. This anaerobic condition was indicated by the low ORP and DO concentrations (Table 3). Electrolysis integration at the bottom of the wetland system shows only a slight positive influence on ammonium removal even though the oxygen produced from the graphite electrode plates at the bottom of the electrolyzed wetland could travel to the tidal-flow wetland section to intensify the amount of oxygen in this wetland section and enhance ammonium removal. This effect is negligible because the produced oxygen only oxygenates the experimental system’s bottom section, which is saturated with water. The DO concentrations at the bottom sections of the two wetlands were not different, and this result was confirmed by the lack of difference in the oxygen concentrations in the air (approximately 15%) over both

---

Table 3 – Basic effluent parameters during different experimental phases.

<table>
<thead>
<tr>
<th>System</th>
<th>Phases</th>
<th>pH</th>
<th>ORP (mV)</th>
<th>DO (mg/L)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A I</td>
<td>6.5 ± 0.2</td>
<td>174.7 ± 37.2</td>
<td>1.1 ± 0.7</td>
<td>19.5 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>6.1 ± 0.4</td>
<td>231.8 ± 66.2</td>
<td>0.8 ± 0.4</td>
<td>29.5 ± 2.3</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>6.2 ± 0.4</td>
<td>173.2 ± 40.0</td>
<td>0.8 ± 0.0</td>
<td>32.3 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>6.4 ± 0.0</td>
<td>183.8 ± 7.0</td>
<td>0.7 ± 0.1</td>
<td>26.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>B I</td>
<td>7.1 ± 0.1</td>
<td>-29.0 ± 63</td>
<td>1.3 ± 0.4</td>
<td>18.8 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>7.1 ± 0.1</td>
<td>-25.8 ± 75.4</td>
<td>0.9 ± 0.4</td>
<td>28.7 ± 2.1</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>6.6 ± 0.2</td>
<td>-12.3 ± 56.7</td>
<td>0.8 ± 0.4</td>
<td>31.4 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>6.7 ± 0.0</td>
<td>-16.4 ± 3.9</td>
<td>0.7 ± 0.1</td>
<td>26.8 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

The values are expressed as average ± standard deviation.
System A: electrolyzed experimental CW.
System B: non-electrolyzed contrast CW.
experimental wetlands. However, the electrolyzed wetland had a higher ORP than the wetland without electrolysis.

Previous experiments indicate that denitrifier growth and activity is generally inhibited in wetlands under tidal operation with high oxygen content and/or inadequate carbon sources. Consequently, nitrate accumulates in the effluent (Lv et al., 2013; Wu et al., 2012). An anaerobic condition is easily induced by maintaining a saturated water level in horizontal subsurface flow CW beds as a step treatment to enhance the denitrification process and remove the nitrate accumulation in tidal-operated wetland effluent. However, this strategy depends on several factors, such as C/N ratio in the influent, and may not fully meet the denitrification process requirement (Wu et al., 2011; Vymazal, 2013; Brix, 1994). Using a carbon source as an electron donor is also critical in nitrate reduction during the denitrification process (Zhao et al., 2011; Wu et al., 2011; Kadlec and Wallace, 2009). However, the degradation rate of organic matter is quite significant as a result of the good oxygen condition in tidal-flow CWs, and residual bioavailable organic matter in the effluent is often insufficient for denitrification, thus limiting the denitrification process (Zhao et al., 2011; Sakakibara and Kuroda, 1993). The addition of external carbon sources, such as methanol, acetic acid, and glucose, reportedly enhances nitrate reduction (Abu-Ghararah, 1996; Mohseni-Bandpi and Elliott, 1998; Gomez et al., 2000; Gómez et al., 2002). However, such method is quite expensive and may not suitable for economically undeveloped regions (Kadlec, 2009; Austin and Nivala, 2009). The introduction of external carbon chemicals into wetlands may also cause additional pollution (Volokita et al., 1996; Gomez et al., 2000). Autotrophic denitrification is a process driven by hydrogen as electron donor (Zhao et al., 2011; Lee et al., 2010). Thus, a process of integrating electrolysis into hydrogen production was designed in this study to enhance autotrophic denitrification in wetland systems. Total nitrogen removal was over 75%, and no difference was observed between both wetland systems. Nitrate surprisingly accumulated in the effluent of the electrolyzed wetland during phase

---

Fig. 2 – Influent and Effluent NH$_4^+$–N/NO$_3^-$–N concentration changes during different experimental phases in systems A (electrolyzed experimental CW) and B (non-electrolyzed contrast CW).

Fig. 3 – Influent and Effluent PO$_4^{3-}$–P concentration changes during different experimental phases in systems A (electrolyzed experimental CW) and B (non-electrolyzed contrast CW).
that was produced in the tidal wetland section by ammonium oxidation. The integration of tidal-operated wetland above water-saturated wetland has a potential advantage in nitrogen removal. Moreover, the use of electrolysis may be more suitable for wastewater with low C/N ratio because denitrification in water-saturated wetlands is inhibited by the lack of organic carbon in the treatment of wastewater with low C/N ratio. Nitrogen removal in tidal-operated wetlands integrated with water-saturated wetland depends on several factors and should be investigated further.

The nitrate accumulation in electrolyzed wetlands during experimental phase II may be attributed to the following reasons. First, current intensity is well-recognized as an important factor in wastewater treatment using bio-film electrodes (Sakakibara and Kuroda, 1993; Zhao et al., 2011). The advantage of using electrolysis in wastewater treatment is not observed if current intensity is too low. However, high current intensity may also have a negative impact on the microorganisms responsible for contaminant removal (Feleke et al., 1998). The current densities reported in previous literature ranged from 0.02 mA/cm² to 2 mA/cm² (Feleke et al., 1998; Zhao et al., 2011; Sakakibara and Kuroda, 1993). The current density of 1.5 mA/cm² in experimental phases I and II of this study may not be appropriate and should be lowered. Second, the microbial nitrate reduction process requires the introduction of an anaerobic condition. Oxygen production by anodes during electrolysis destroyed the anaerobic environment in this study and increased the ORP to 200 mV, which was much higher than that in the non-electrolyzed control wetland at 0 mV (Table 3). Two iron plates and one graphite plate were removed and only one iron plate and one graphite plate were retained in the water-saturated wetland section to modify the operational condition of the electrolyzed wetland and to promote nitrate reduction. The distance between the plates was increased to 5 cm. Current intensity decreased to 0.57 mA/cm² with the extension of the distance between plates. ORP also declined from approximately 230 mV to approximately 170 mV (Table 3) as a result of the reduction in oxygen production. The accumulated nitrate was completely removed as expected, indicating that current intensity plays a vital role in nitrogen transformation dynamics. However, the knowledge regarding the nitrogen removal mechanisms in electrolyzed wetlands remains unclear and should be investigated further.

Aside from nitrogen, phosphorus is another main nutrient that causes the eutrophication of water bodies. Phosphorous removal from wastewaters in CWs is a complicated process that includes plant uptake, microbial growth, adsorption, and precipitation within substrates (Wang et al., 2013; Austin and Nivala, 2009; Paredes et al., 2007; Jenssen et al., 2005; Arias et al., 2001; Prochaska and Zouboulis, 2006). The adsorption process is still well-recognized as the main mechanism and drives numerous investigations that focus on the selection of thousands of specific soil materials (Reddy et al., 1998; Del Bubba et al., 2003; Kostura et al., 2005). Effective phosphorus performance is normally obtained at the beginning of wetland operation but is difficult to sustain for a very long time (Drizo et al., 2006; Kantawanichkul et al., 1999; Del Bubba et al., 2003). This assumption was proven in this study by the dynamics of outflow phosphorus concentrations and removal efficiencies in the non-electrolyzed wetlands. The effluent concentration...
in non-electrolyzed wetlands gradually increased from 3 mg/L to approximately 7 mg/L under an inflow PO$_4^{3-}$–P concentration of 10 mg/L throughout the progression of the experiment, as shown in Fig. 3. Removal efficiency decreased from 43.8% to 19.8% as a result of the limited adsorption capacity of the substrate used in this study. However, the effluent PO$_4^{3-}$–P concentration was always less than 0.5 mg/L in the electrolyzed wetland, and removal efficiency always exceeded 95%. The large amount of PO$_4^{3-}$–P removed is attributed to the ferric iron coagulant that formed in-situ through the electro-dissolution of a sacrificial anode (iron plate).

In addition to having a positive effect on phosphorus removal in CWs in this study, electrolysis also effectively inhibits sulphide accumulation (Fig. 4). Sulphide is an important index of water pollution as a product of bacterial sulphate reduction because it can be highly toxic to microorganisms such as nitrifiers (Wu et al., 2013). Sulphide is also a competitor for oxygen consumption (Wu et al., 2013; Armstrong et al., 1996; Pedersen et al., 2004; Koch and Erskine, 2001). The strong, rotten-egg smell of hydrogen sulphide observed during sampling events has a strong influence on the environment (Lee et al., 1999). The presence of sulphide and bacterial sulphate reduction is generally only useful in the treatment of water containing heavy metals (Wieder, 1989; Mays and Edwards, 2001; Machemer and Wildeman, 1992; Mitsch and Wise, 1998). Otherwise, sulphide should be controlled and/or avoided. Sulphide accumulation in non-electrolyzed wetlands was 0.84 mg/L, as shown in Fig. 4. Sulphide accumulation was not detected in the electrolyzed wetland. The introduction of electrolysis into the CW system effectively inhibited sulphide accumulation, thus reducing the sulphide hazard to the plants and microbes in CWs. This result may be attributed to the precipitation of produced sulphide coupled with electro-dissolved ferrous iron from sacrificial iron anodes and/or the inhibition of bacterial sulphate reduction under increased aerobic conditions.

The ferric and ferrous iron produced by electro-dissolution during electrolysis indeed enhanced PO$_4^{3-}$–P removal and sulphide control. However, high residual iron concentrations in the effluent pose another potential risk as contaminants and toxicants in the environment (van der Welle et al., 2007; Wu et al., 2013; van der Welle et al., 2008). Ferric iron was acquired by ferrous iron oxidation, and the amount of effluent ferrous iron accumulated during initial experimental phases I and II in this study ranged from 5 mg/L to 15 mg/L. Effluent iron concentration decreased to hardly detectable levels after electrode plate removal in phase III. However, PO$_4^{3-}$–P removal and sulphide control were not influenced.

Integration of electrolytical unit within the constructed wetland is efficient and could be realized in an easier way in maintenance and adjustments compared to run the electrolytical unit as a separate unit. However, the multi-interaction among nitrogen, phosphorus, sulphur, and iron in electrolysis-integrated CWs is very complex and should be investigated further.

5. Conclusion

1. In the current experiment, no significant difference was shown between the electrolysis-integrated CW and non-electrolysis-integrated CW for the removal of ammonium. However, the current intensity of electrolysis plays a vital role on nitrogen transformations. The introduction of electrolysis into CWs may be suitable for lower C/N wastewaters.

2. Electrolysis integration in CWs had a positive effect on phosphorus removal, and this effect was attributed to the ferric iron coagulant that formed in-situ through the electro-dissolution of a sacrificial iron anode.

3. The strategy of integrating tidal-operated CWs with electrolysis effectively inhibited sulphide accumulation because of the sulphide precipitation with ferrous-iron electro-dissolution and/or the inhibition of bacterial sulphate reduction under aerobic conditions.

Acknowledgments

This work was financed by grants from the project of “The National Natural Science Funds (51308536), “Specialized Research Fund for the Doctoral Program of Higher Education (20130008120018)” and “Fund for supervisor of excellent PhD dissertation of Beijing City (20131001903)”. We likewise greatly appreciate the critical and constructive comments from the anonymous reviewers, which have helped improve this manuscript.

References


