Efficacy of A Novel Electrolysis Integrated Tidal Flow Constructed Wetland System in Nutrient Removal

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Abstract – Constructed wetlands have proven to be an efficient ecological technology for the treatment of various kinds of wastewater. Nutrient removal in ordinary constructed wetlands are generally limited because of lack of oxygen content that is necessary to oxidize ammonium and of the low sorption capacity of the common substrate materials utilized in phosphorus retention. Tidal-flow constructed wetlands are a relatively new technology that utilizes a novel oxygen transfer method. Also electrocoagulation is an efficient method for the removal of phosphorus. Therefore a novel electrolysis-integrated tidal flow constructed wetland was setup to evaluate the nutrient removal. The average removal efficiencies of COD and NH₄⁺-N were about 73% and 87% in the two experimental wetlands at influent COD concentration of 1200 mg/L and ammonium nitrogen concentration of 120 mg/L regardless of electrolysis integration. In the non-electrolyzed wetland system, effluent phosphate concentration initially decreased and gradually increased from 6.17 mg/L to 8.86 mg/L. The effluent PO₄³⁻-P concentration was always less than 0.7 mg/L in the electrolyzed wetland system and removal efficiency exceeded 98%. Owing to the ferrie iron coagulant formed through the electro-dissolution of the iron anode, electrolysis integration not only exerted a positive effect on phosphorus removal but also inhibited nitrate accumulation by the autotrophic denitrification with hydrogen as the electron donor.

Keywords – Constructed wetlands, Tidal flow constructed wetlands, Electrolysis, Electron donor, Organic matter

I. INTRODUCTION

The failure of traditional centralized sewage treatment systems for their wide spread application in rural areas lead to the increased popularity of efficient alternative technologies such as Constructed Wetlands (CWs) [1] & [2]. CWs have gained popularity worldwide due to its lower cost, less operation and maintenance requirements [3].

Constructed wetlands (CWs) are “engineered systems, designed and constructed to utilise the natural functions of wetland vegetation, soil and their microbial populations to treat contaminants in surface water, groundwater or waste streams” [4] and they are proven to be an efficient ecological technology for the treatment of various types of contaminated water [5]. But the removal of nutrients and organic matter in conventional CWs are generally found to be limited because of less oxygen content in the system to oxidise ammonium and less sorption capacity of common substrate materials for phosphorus retention [6] & [7].

As a result of this, nitrification process is identified as a limiting step of total nitrogen (TN) removal [8].

Tidal-flow constructed wetlands (TFCWs) adopt relatively new method of oxygen transfer in which the wetland bed is alternatively filled and drained of the wastewater to be treated. During the flooding phase, as the wastewater level rises in the wetland bed, air in the wetland matrix is repelled into the atmosphere. During the draining phase, when the wetland bed is drained, the retreating wastewater will act as a passive pump that draws atmospheric oxygen into the wetland bed. When several flood and dry cycles takes place, it is known as a tidal cycle [10]. Adopting the tidal strategy has found to increase the oxygenation capacity of a wetland system and thereby better removal efficiency of nutrients and organic matter can also be obtained [10].

The high oxygen transfer rate of TFCW systems is having an adverse impact on the TN removal. This is because high oxygen content in the system inhibits the activity of denitrifiers resulting in high concentration of nitrate in the effluent [11]. Electrolysis is a well-known method for the phosphorus removal. During electrolysis hydrogen gas is liberated at the cathode and autotrophic denitrification using hydrogen as the electron donor is identified under low carbon source condition [12] & [13]. So in this study a TFCW system is integrated with electrolysis to get the combined advantages of a tidal flow and electrolysis.

II. MATERIALS

Materials used for the setting up of laboratory scale tidal flow constructed wetland systems are been discussed here.

A. Wetland Vegetation

The selection of the wetland vegetation is an important factor which affects the performance of the wetland system. The plant species used in the experimental TFCW systems was Napier Bajara grass (Pennisetum purpureum) (Fig.1) It is a monocot perennial grass in the Poaceae family. It is tall and forms in robust bamboo-like clumps. Napier Bajara grass has great potential as a biofuel feedstock. A total number of 2 stem cuttings were planted in each constructed wetland system for the experimental study.
B. Laboratory-Scale Wetlands

The laboratory-scale wetlands utilized in this study are shown in Fig. 2. Two wetland systems were used in this study: one was electrolysis-integrated experimental wetland system and other one was non-electrolysed experimental wetland system. Both the wetland systems were made up of PVC tube cylinders with an internal diameter of 13 cm and length of 60 cm. Both the wetland systems were divided into two sections; the lower section of the experimental CW was filled with glass beads (diameter of 4–7 mm) to a depth of 25 cm and the upper section was filled with soil in which the wetland plant was grown and operated with a tidal strategy. The bottom sections of both the systems were maintained anaerobic through constant water saturation throughout the study.

In the electrolyzed wetland iron electrodes were integrated with the bottom section of the wetland. Iron electrodes were used as both anode and cathode. In total, four iron electrode plates (11 × 3 × 0.5 cm) were used, which was kept at a spacing of 2 cm. These electrode plates were porous (diameter of 1 cm) to ensure easy water passage in the vertical direction. The electrodes were connected by using copper wires.

Tidal operation was generated by alternate flooding and draining of the wetland bed. This was provided by a flow control valve provided at the same level of the wetland bed at both the systems. Electrolysis was generated by DC-regulated power. These two wetland systems were operated with the same tidal strategy and inflow water.

III. Methodology

Wetland plant Napier Bajara was planted in both the systems. Then the synthetic wastewater was prepared and wetland bed was fed with it for a period of 20 days for the development of biofilm. Operating conditions of hydraulic loading rate - 0.5 m³/m²/day, flooding period - 8 hr, draining period – 16 hr were adopted. In electrolyzed constructed wetland system, electrolysis was carried out for 3 hours daily.

Samples were collected in triplicate form from the outlet of both the systems and were analysed for pH, DO, COD, NH₄⁺-N, NO₃⁻-N, NO₂⁻-N and PO₄³⁻-P.

A. Experimental Conditions

Synthetic wastewater containing ammonium (NH₄⁺-N), Chemical Oxygen Demand (COD) and phosphate (PO₄³⁻-P) was employed to minimize variability in the experiment. Influent high strength synthetic wastewater was prepared with C₆H₁₂O₆, NH₄Cl, and KH₂PO₄ dissolved in tap water according to the required concentrations. The added compositions were COD 1200 mg/L, NH₄⁺-N 60 mg/L, and PO₄³⁻-P 10 mg/L. A trace mineral solution was added to the synthetic wastewater (1 ml/L) in all cases. A stock solution of the synthetic waste water as well as the mineral solution were prepared and stored at 4°C.
From this stock solution, synthetic waste water was prepared by diluting it 10 times. The flood and drain cycle was set to occur every 24 h for the tidal operation; the flood/drain time ratio was 8h: 16 h. The electrolysis was carried out with a voltage of 5 V. After electrolysis, a settling time of 45 minutes was provided for the settling of the in-situ coagulants that were formed during the process of electrocoagulation.

**B. Sampling and Analysis**

Wastewater samples were collected from the outlet of both the systems to evaluate the performance of the systems. Three samples were collected daily– first sample during the flooding phase, second sample at the end of settling period after electrolysis and third sample during the draining phase. The pH value and Dissolved Oxygen (DO) were immediately measured with a pH meter and DO meter respectively. COD was measured by using the standard method as mentioned in APHA manual. The concentrations of ammonium nitrogen (NH$_4^+$-N), nitrate nitrogen (NO$_3^-$-N), nitrite nitrogen (NO$_2^-$-N) and phosphate (PO$_4^{3-}$-P) were measured by using Ion Chromatography.

### IV. RESULTS AND DISCUSSIONS

The results obtained from the sample analysis are discussed in detail below.

**A. Effect on Chemical Oxygen Demand (COD) removal**

The effluent COD concentration changes during the different experimental phases in the electrolyzed CW and non-electrolyzed experimental CW is shown if Fig.3.

![Fig. 3 Effect on Chemical Oxygen Demand (COD) removal](image)

The average COD removal efficiency for wetland systems with and without electrolysis integration is 72% and 73% respectively. It is found that there is no significant effect on between COD removal in both the systems. The COD removal mechanism can be explained as settleable organics are rapidly removed in wetland systems under quiescent conditions by deposition and filtration. Attached and suspended microbial growth is responsible for removal of soluble organics. Organic compounds are degraded both aerobically and anaerobically. The oxygen required for aerobic degradation is supplied directly by diffusion or oxygen leakage from the macrophyte roots into the rizosphere. Uptake of organic matter by the macrophytes is negligible compared to biological degradation [14]. In a tidal flow constructed wetland system, due to the higher efficiency of oxygen transfer to the wetland bed, aerobic degradation will pre-dominate the anaerobic degradation. Aerobic degradation of soluble organic matter is governed by the aerobic heterotrophic bacteria according to the following reaction,

\[(\text{CH}_2\text{O}) + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}\]

**B. Effect on NH$_4^+$-N removal**

The effluent NH$_4^+$-N concentration changes during the experimental period in the electrolyzed experimental CW and non-electrolyzed CW is shown in Fig.4.

The NH$_4^+$-N removal efficiency for wetland systems with and without electrolysis integration is 88.3% and 86.85% respectively. The removal rate of NH$_4^+$-N in the both wetland systems with and without the integration of electrolysis was not significantly different. The removal of ammonium occurred mainly in the section of experimental CWs under tidal operation with high oxygenation efficiency. The removal mechanism of ammonium is explained as wastewater is rhythmically filled and drained in TFCWs and functions as a passive pump to repel and draw air from the atmosphere into the matrices [15]. The treatment capacity of ammonium and organics is then significantly improved [9]. Wetland with electrolysis integration is having a slight positive influence on NH$_4^+$-N removal [16].
The electrolysis integration is having a slight positive influence on the removal of ammonium which is mainly due to the release of oxygen at the bottom portion of electrolysed CW system during the electrolysis process. This oxygenates the system better than the non-electrolysed CW system, thereby resulting in better performance in terms of ammonia removal.

C. Effect on NO$_3^-$ -N removal

The effluent NO$_3^-$-N concentration changes during the experimental period in the electrolyzed experimental CW and non-electrolyzed CW is shown in Fig.5. Average NO$_3^-$-N value for wetland systems with and without electrolysis integration are 0.35 mg/L and 0.81 mg/L respectively. Based on the results obtained from the previous experiments, it is found that the activity of denitrifiers is generally restricted in TFCW system owing to the high oxygen content and thus resulting in increased concentration of nitrate in the effluent [17] [18]. Therefore for the better removal of nitrate nitrogen, anaerobic conditions must be maintained in the TFCW system. Organic carbon as an electron donor is always critical for the reduction of nitrate during denitrification [19]. But the high oxygenation efficiency in a TFCW system results in better degradation of the organic matter. This leads to insufficient carbon source in the effluent thereby limiting the denitrification process [11] [13]. This problem can be overcome by the external addition of carbon source. But this method is found to be expensive [19] and the addition of carbon chemicals may cause secondary pollution [20]. Autotrophic denitrification is a process where hydrogen is the electron donor [11] [21].

The integration of electrolysis for the production of hydrogen to enhance autotrophic denitrification in the wetland system in this study was designed based on the above mentioned consideration. But the lower value of nitrate in the effluent of the both the systems may be due to the presence of sufficient amount of organic carbon source in the effluent leading to denitrification using carbon source as the electron donor [21]. Therefore the integration of electrolysis in a TFCW system is advantageous for nitrogen removal especially for wastewater with low C/N ratio.

D. Effect on PO$_4^{3-}$ -P removal

The effluent PO$_4^{3-}$-P concentration changes during the experimental period in the electrolyzed experimental CW and non-electrolyzed CW is shown in Fig.6. The PO$_4^{3-}$-P removal efficiency for wetland systems with and without electrolysis integration are 98.4% and 51.27% respectively.

Nitrogen and phosphorus are two main nutrients that cause eutrophication in the water bodies. The important phosphate removal mechanisms in a CW include adsorption, plant uptake, precipitation within substrates and plant uptake [22] & [23]. Among these, adsorption is identified as the major removal mechanism [24] & [25]. But it is found that better phosphorus removal is obtained at the beginning of the operation but it is difficult to maintain for a long time [25] & [26]. The effluent concentration in non-electrolyzed wetlands initially decreased and then gradually increased throughout the progression of the experiment, as shown in Fig. 6.
However, the effluent $\text{PO}_4^{3-}$ concentration was always less than 0.7 mg/L in the electrolyzed wetland, and removal efficiency always exceeded 98%. The large amount of $\text{PO}_4^{3-}$ removed is attributed to the ferric iron coagulant that formed in-situ through the electro dissolution of a sacrificial anode (iron plate).

**E. Effect on $\text{pH}$**

The effluent pH changes for both wetland systems are shown in Fig. 7.

Average value of pH for wetland systems with the integration of electrolysis is 5.91 and without the integration of electrolysis are 6.25. The integration of electrolysis in the tidal wetland decreased the pH value from approximately 7.2 in the influent to approximately 6.0 in the effluent. This decrease in pH was due to the consumption of $\text{OH}^-$ under the precipitation of $\text{Fe}^{2+}$ and $\text{OH}^-$ produced during the electrolysis and further oxidization to $\text{Fe(OH)}_3$ by the oxygen produced at the anode.

**F. Effect on Dissolved Oxygen (DO)**

The effluent DO concentration changes during the experimental period in the electrolyzed experimental CW and non-electrolyzed CW is shown in Fig. 4.8

Average values of DO for wetland systems with and without electrolysis integration are 1.39 mg/L and 1.33 mg/L respectively. The constant water saturation at the bottom portion of both the wetland systems resulted in an anaerobic condition, which is responsible for the lower DO concentrations in both the systems. Wetland system with electrolysis integration is having a slight higher value of DO as compared to the wetland system without electrolysis integration. This slight increase in value can be attributed to the release of oxygen from anode during the electrolysis process which increases oxygen at the bottom portion of the electrolysis integrated system.
Fig. 8 Effect on Dissolved Oxygen (DO)

V. CONCLUSIONS

From the results obtained during the first phase of the experimental study, the major conclusions are as follows:

1. The integration of electrolysis in the tidal wetland decreased the pH value from approximately 7.2 in the influent to 6.0 in the effluent. This decrease in pH was due to the consumption of OH under the precipitation of Fe\(^{2+}\) and OH produced during the electrolysis.

2. The average value of dissolved oxygen of both the systems was 1.3 mg/L due to the anaerobic condition at the bottom portion of the systems due to constant water saturation.

3. The average COD removal efficiency of electrolyzed and non-electrolyzed wetland systems was obtained as 72.5% under the influent COD concentration of 1200 mg/L.

4. The average ammonium removal efficiency of electrolyzed and non-electrolyzed wetland systems was obtained as 87% under the influent ammonium concentration of 120 mg/L.

5. No significant difference was observed between the wetland systems with and without electrolysis integration for the removal of ammonium and organic matter.

6. Electrolysis integration in CWs had a positive effect on phosphorus removal with removal efficiency of 98% and this effect was attributed to the ferric iron coagulant that formed in-situ through the electro-dissolution of sacrificial iron anode.

7. In non-electrolyzed system, the effluent phosphate concentration initially decreased and later on increased from 6.17 mg/L to 8.86 mg/L as the experiment proceeded.

REFERENCES


