Assessing the Surface Water Quality of Ana Sagar Lake and its Bioremediation in Modified Constructed Wetland

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Abstract

The present study evaluates the potential of an integrated Constructed Wetland and Microbial Fuel Cell (CW-MFC) in removing Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), nitrate and phosphate along with generating electricity from the polluted water of Ana Sagar Lake, Ajmer. Two vertical downward flow CW-MFCs have been investigated (with and without plant) in batch mode for a period of 12 months. The performance of CW-MFC with the plant (system A) was better than the CW-MFC without the plant (system B), both in terms of COD, TDS, nitrate and phosphate removal and electricity generation. Dracaena trifasciata plant species were used in this study. The maximum power density of 157 mW/m², current density of 0.65 mA/m², COD removal efficiency (72%), TDS reduction (74%), nitrate removal (69%) and phosphate removal (69%) were obtained with System A. The germination rate of Vigna radiata seeds was 100% with the effluent from system A. At the end of the experiment the FTIR analysis revealed the structural changes occurring on the CW-MFC media (sand) after removal of pollutants present in the lake water.
Keywords: Constructed wetland (CW); chemical oxygen demand (COD); bio-electricity; germination rate; total dissolved solids (TDS); microbial fuel cell (MFC).

1. Introduction

Water is the world's most plentiful and most useful compound and is thus named in Sanskrit as "Jeevan." Life is not possible without water and thus our survival is directly connected to the quality of the water [1]. Worldwide, water pollution and contamination are of great concern for developing countries such as India [2]. Wetlands are essential for water bodies in natural environment. Their job is intricate and diverse. Besides being highly active as the home for fish, birds, and a number of other marine lives, including micro-organisms, wetlands provide other ecological resources, preserving natural balance and supporting human wellbeing [3]. Unfortunately, in recent times, wetlands have been largely ignored due to a lack of understanding of their position and the stress of increasing human needs (industrialization, urbanization, and agriculture) and mishandling of land resources [4]. Often there's a misunderstanding that wetlands are all wastelands. As a result, many fragile wetlands throughout India and all across the world have been lost and diverted to other uses. For the public good, this pattern needs to be monitored and reversed.

This issue assumes the added importance, particularly in a water-stressed area such as Rajasthan, where preserving every drop of rainwater is vitally important. The state of Rajasthan has rich wetland reserves, which are also depleted by the above threats. The water quality deterioration affects the floral and faunal population as well as the citizens relying on those resources. Therefore, wetland protection deserves the utmost consideration.
Ana Sagar Lake is a perennial freshwater body situated in the middle of Ajmer city (25 ° 28' and 26 ° 58' latitude north and 73 ° 52' and 75 ° 22' latitude east). The lake was constructed by then ruler Anaji Chouhan between 1135-1150 AD by building a dam across the river Luni, and was named after his name as Ana Sagar. Around 35% of Ajmer's population lives in the lake's catchment area. It is deteriorated due to anthropogenic practices, including detergent imports, agricultural operations, waste treatment, and human activity across the lake [5, 6].

The use of traditional centralized energy and cost-intensive technologies (physical-chemical-biological treatment) are found to be very minimal and not completely feasible [7-10]. Therefore, it is almost essential to find new, inexpensive and environmentally sustainable solutions for solving these hard problems.

Bioremediation is one of the key processes for the elimination of toxins from wastewater [10-14]. Numerous wastewater treatment systems, including Constructed Wetland (CW) and Microbial Fuel Cell (MFC), focus on bioremediation to eliminate wastewater pollutants. Both systems are currently being used separately for the treatment of wastewater. Four basic components are included in a typical MFC, namely anode chamber, cathode chamber, a proton exchange membrane (PEM) and an external electrical circuit for connecting both the electrodes [15, 16]. The MFC needs artificially developed redox conditions for its operation, whereas the CW has naturally occurring redox conditions [17-19]. The combined technology has recently been developed by modifying a CW by implanting a MFC into it which is termed as CW-MFC. This combined technology preserves the best aspects of both technologies and hence attracts a great deal of coverage [20].

The objective of our study was to monitor the quality of water and to evaluate the effectiveness and performance of CW-MFC systems for the Ana Sagar Lake. Two vertical downward flow pilot
scale CW-MFC systems i.e. system A (with plant) and system B (without plant) were studied for a period of 12 months under batch mode condition. The findings of the present study can be of considerable significance due to their possible applicability to treat the polluted lakes and generating electricity simultaneously.

2. Materials and methods

2.1. Materials

Two CW-MFC systems were constructed using two identical PVC pipes (Fig. 1), 350 mm in height and 105 mm in internal diameter. Aluminum plates of grade 3003 (Jindal, India) and dimensions of 95 X 45 X 10 mm were used as both the cathode and the anode for the two CW-MFC systems. A glass-wool layer of 1 cm thickness was mounted in both the systems, below the cathodic zone, which divides anode and cathode areas and thus helps to preserve MFC-like conditions. The external anode-cathode connection was made with insulated copper wire with a gauge length of 0.12 mm. The sand of particle size (1-2 mm) was collected and used as wetland media for the anode and cathode. Dracaena trifasciata plant was collected from the local nursery in Ajmer, (India) and planted in both the CW-MFC systems and was exposed to an ambient environment to provide natural conditions for the growth of the plant. The plants were grown in tap water for a week after installing the systems and then fed with Ana Sagar Lake water. The samples for analysis were collected from the outlet port.
2.2. Sample collection

All the chemicals and reagents used in the study were of high analytical grade and bought from “The scientific and General Agencies”, Jaipur (India). Purified reverse osmosis (RO) water was used for preparing all the aqueous solutions. There is a great deal of caution to be taken in selecting the process for collecting the samples. Surface water samples were taken on the 1st day of every month from the lake from January 2019 to December 2019 and were restored at 4 °C for future analysis [21]. The physiochemical characteristics were analyzed within 24 hours of sampling, as per APHA standard methods [22]. 100g of cow dung sample was collected from a
local dairy farm in Ajmer, (India) and was dried in sunlight for 2 days and was placed in the anode chamber as an inoculum in both the CW-MFC systems. Cow dung comprises of many micro-organisms that cling to the wetland media and anode stimulating the production of electricity.

2.3. Experimental details and analysis

Both the CW-MFC systems were constructed and investigated in open circuit mode for Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), nitrate and phosphate removal from the lake water. All the experiments were carried out in batch mode for evaluating the % removal of COD, TDS, nitrate and phosphate. The hydraulic retention time of 24 hours was maintained. The pH, Electrical conductivity (EC), COD, TDS, nitrate and phosphate were determined according to APHA standard methods [22]. The calculation of the experimental data was done according to [21]. The samples were collected once on the 15 days of every month for analyzing the mentioned physiochemical properties. The voltage (V) was measured using a digital handheld multimeter (Haoyue DT830D). The polarization experiment was carried out by varying the external resistance from 0.05 kΩ to 330 kΩ and the steady-state voltage output was measured after every 30 minutes. Using potassium bromide pellets, an FTIR (Perkin Elmer) spectrum of media was obtained in the range of 400-4000 cm⁻¹.

3. Result and discussion

3.1. Physiochemical parameters of Ana Sagar Lake of Ajmer city

From the analysis of various physiochemical parameters (Table 1) of lake water it can be observed that the parameters like COD, EC and TDS were surprisingly very high. However, the parameters like nitrate and phosphate were found to be within the permissible limits. The present
study reveals that during summer (April, May and June), when the temperature is at its peak, various parameters of the water quality also fluctuate accordingly. During the rainy seasons (July, August and September) due to the dilution of the lake water the pollutant concentration were slightly under control.

The temperature of Ana Sagar Lake varied between 8 °C to 32 °C during the extreme winters and summers. Changes in temperature create characteristic circulation patterns that have a profound effect on aquatic life. There was negative significant relation between electrical conductivity value and water temperature. The pH of the lake water was within the recommended range.

| Month | pH  | EC (mS/cm) | COD (mg/L) | TDS (mg/L) | Phosphate (mg/L) | Nitrate (mg/L) |
|-------|-----|------------|------------|------------|------------------|----------------|
| Jan   | 8   | 5.2        | 200        | 2430       | 2.1              | 17.9           |
| Feb   | 8.23 | 6.5        | 220        | 2400       | 2.5              | 17.4           |
| Mar   | 8.1  | 5.9        | 230        | 2400       | 2.1              | 17.5           |
| Apr   | 8.2  | 6          | 236        | 2410       | 2.3              | 18.9           |
| May   | 8.3  | 6.32       | 236        | 2420       | 2.6              | 20.0           |
| Jun   | 8.7  | 6.4        | 240        | 2300       | 2.5              | 23.0           |
| Jul   | 7.2  | 4.2        | 200        | 1500       | 2.4              | 19.4           |
| Aug   | 7.8  | 3.7        | 190        | 1450       | 2.4              | 18.5           |
| Sep   | 7.5  | 3.3        | 185        | 1400       | 2.1              | 15.2           |
3.2. Analysis of electricity generation

![Polarization Curve](image)

The maximum (Open Circuit Voltage) OCV at the ambient environment temperature was observed to be 0.9 V and 0.73 V for both systems A and B respectively. The maximum OCV was obtained on the 35th and 47th day of operation for system A and system B respectively. The polarization curve was measured after achieving the maximum OCV. The Polarization curve for both the systems is shown in Fig. 2. The maximum power density of 157 mW/m² and 78.24 mW/m², current density of 0.65 mA/m² and 0.40 mA/m² and internal resistance of 1 and 2.25 kΩ was observed with system A and system B respectively. The power generated by system A is almost 2 times higher than that of system B. It is assumed that CW-MFC with the plant raises the oxygen concentration in the root region, as a result of which the anode and cathode have a higher
redox potential gradient, which increases the rate of electron transfer through the external circuit. The higher generation of voltage could be due to higher organic matter breakage in system A. It has been observed that after 3 days of operation the power production reduced which may be due to clogging in the cathodic region or deterioration of the electrode [16]. Also, the presence of plant facilitated the reduction of internal resistance by 1.6 times, giving rise to more voltage. The maximum power density and performance of the device could be enhanced by using other novel anode electrodes, selection of different size of the media as well as by using alternative electrodes for oxygen reduction at cathode reaction.

3.3. Analysis of water quality after treatment in CW-MFC

The maximum TDS removal was 74% for system A and 61% for system B in the 3rd month of the operation (Fig. 3a). In case of TDS removal, performance of system A was better as compared to system B. Nutrient removal by the metabolic activities of the micro-organisms and the mechanical filtering effect is the major mechanism involved for TDS removal in the present systems [17-20]. It was observed that although overall efficiency of TDS removal is reasonable for both setups, during the experimental process, the efficiency of batch-wise TDS removal decreases dramatically. This is most likely due to TDS, which can clog soil pores, though it is also possible that this may be due to clogging caused by excessive use of wetland systems [16].
The maximum COD removal was 72% for system A and 47% for system B in the 3rd month of the operation (Fig. 3b). Higher removal rates were observed in system A as compared to system B. The plant root of *Dracaena trifasciata* tends to establish micro-aerobic areas in the root region that contributes in further loss of organic matter. Some of the suggested composite mechanisms for COD removal include adsorption, precipitation, oxidation, and anaerobic digestion with respect to organic matter [16-20]. The maximum nitrate removal was 69% in case of system A and 43% in case of system B in the 3rd month of the operation (Fig. 3c). Similarly, the maximum
phosphate removal was 69% for system A and 46% for system B in the 3rd month of the operation (Fig. 3d).

3.4. FTIR analysis

There was a broad, extreme band of the FTIR spectrum with a maximum of around 3400 cm\(^{-1}\). The stretching vibration of bonded and non-bonded hydroxyl groups was found to be responsible for this wide band. Spectra of the sand media sample (Fig. 4) showed several band features indicating the presence of natural organic matter. Stretching vibrations of aliphatic methyl and methylene groups, (2927 cm\(^{-1}\)) asymmetric and (2858 cm\(^{-1}\)) symmetric, were correlated with the bands between 3000 and 2800 cm\(^{-1}\). Most bands were between 1800 and 1200 cm\(^{-1}\) in the case of organic matter. The carboxylic band was responsible for the 1745 cm\(^{-1}\) peak. The band at 1556 cm\(^{-1}\) was labeled as N-H in a plane (amid-II) [20]. Two bands emerged above 1450 and 1370 cm\(^{-1}\) which can be allocated to C-H aliphatic group deformations. The wide band about 1463 cm\(^{-1}\) has been assigned to the symmetric C-O stretch of COO\(^{-}\) or OH deformation from COOH for organic component [23]. The C-O stretching of phenolic OH and/or arylmethylether was allocated to the wide band based at approximately 1260 cm\(^{-1}\), and could be representative of the lignin backbone [24]. Other bands in this range of 1800-1200 cm\(^{-1}\) could be particularly due to bending motions of CH and NH, aromatic stretch and bond vibrations of C=O. For system A, the disappearance of the 1745 cm\(^{-1}\) (free COOH group) band after pollutant adsorption confirmed the absence of free COOH groups as a result of complex formation. It was found that peaks of different functional groups were shifted to lower frequency in systems B after the adsorption of pollutant ions on the sand media surface because the bonds were stretched and weakened due to their interaction with pollutant ions during complex formation. [25]. Hence, the adsorption of pollutants on the surface of media was confirmed through FTIR spectra. There was
a decrease in the intensities of most of these bands in spectra of system A media as compared to system B media. The mineralization of wastewater and the transformation of organic matter were both carried out in this research. The wide band around (1020-1029) cm\(^{-1}\) could be designated to the Si-O vibrations. The presence of inorganic minerals like clay and quartz was indicated by several bands below 800 cm\(^{-1}\). It is worth noting that overlapping peaks below 1100 cm\(^{-1}\) have been observed due to the wide range of organic and mineral substances. Phosphate compounds' FTIR vibrations were mostly observed in the 1000-1100 cm\(^{-1}\) range, but were concealed at these wavelengths because of the of Si-O vibrations [26].
3.5. Germination Rate

In order to determine the toxic impact of the effluent obtained from both processes, the percent germination of mungbean (*Vigna radiata* L.) was examined. In a sterilized petri dish with filter paper at the bottom, 9 seeds were placed. Each petri dish was irrigated with 10 ml of untreated...
lake water, raw tap water, distilled water and the effluent from both system A & B respectively. The germination in each experimental set was recorded after 48 hrs and the germination was calculated and expressed in percentage [27]. The results of the experiment are tabulated in Table 2. The result shows that system A was more efficient than system B. The % germination in system A was 100% and system B was 90%.

Table 2. % Germination for different types of wastewater

| Sl. No. | Types of water            | % Germination |
|--------|---------------------------|---------------|
| 1      | Untreated lake water      | 50%           |
| 2      | Raw tap water             | 100%          |
| 3      | Distilled water           | 100%          |
| 4      | Effluent from system A    | 100%          |
| 5      | Effluent from system B    | 90.00%        |

**Conclusion**

This preliminary study revealed that integrated CW-MFC with the plant was more efficient as compared with the CW-MFC without plant in reducing various organic and inorganic pollutants. The highest removal rate was achieved in system A with the plant. The % germination in system A was 100% and in system B was 90%. The maximum TDS and COD removal was 72% and 74% respectively whereas the maximum nitrate and phosphate removal was found to be 69% for system A. The removal of the pollutants by CW-MFC system depends on various factors such as adsorption, precipitation, filtration, sedimentation, microbial degradation and plant uptake. This preliminary study indicates that plant-amended wetlands can be used mainly for secondary
treatment of various wastewaters. However, more investigation in terms of various plant species, anode and cathode material and length of chamber is required for future studies.

Conflict of Interest

The authors have declared no conflict of interest.

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