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Evaluation of the potential of various aquatic eco-systems in harnessing bioelectricity through benthic fuel cell: Effect of electrode assembly and water characteristics

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ABSTRACT

Six different types of ecological water bodies were evaluated to assess their potential to generate bioelectricity using benthic type fuel cell assemblies. Experiments were designed with various combinations of electrode assemblies, surface area of anode and anodic materials. Among the 32 experiments conducted, nine combinations evidenced stable electron-discharge/current. Nature, flow conditions and characteristics of water bodies showed significant influence on the power generation apart from electrode assemblies, surface area of anode and anodic material. Stagnant water bodies showed comparatively higher power output than the running water bodies. Placement of cathode on algal mat (as bio-cathode) documented several folds increment in power output. Electron-discharge started at 1000 Ω resistance in polluted water bodies (Nacaharam cheruvu, Hussain Sagar lake Musi river), whereas, in relatively less polluted water bodies (Uppal pond/stream, Godavari river) electron-discharge was observed at low resistances (500/750 Ω).

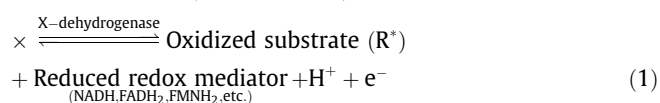
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1. Introduction

Ecological water bodies are systems embedded with large group of living beings functioning together symbiotically and balance the ecological status of the water bodies and surroundings. Homeostatic structure and function of living system is supported by chemical, physical and organic activity in biotic systems (Aoki, 2006). Along with living component, water eco-systems also consist of nutrients and organic matter as an integral part stored in the sub-surface and aquatic sediments representing a large and potential source of energy (Reimers et al., 2001; Bond et al., 2002; Holmes et al., 2004; Lowy et al., 2006; He et al., 2007; Rezaei et al., 2007). Ecological water bodies can be used for harvesting energy using natural habitants by placing electrode in the sediment (anode) and connecting it in an electrical circuit to another electrode (cathode) in the overlying water layer (Reimers et al., 2001; Bond et al., 2002; Holmes et al., 2004). The microbial communities naturally present in water bodies metabolize the available organic matter and liberate electrons (e^-) and protons (H^+) as part of biochemical reactions through electron donor/electron acceptor mechanism. If electrodes are present, the e^- flow from anode to cathode through an external circuit, while H^+ diffuse through the water between the electrodes (Rezaei et al., 2007) and develops potential difference (voltage) necessary for current

generation. The e^- and H^+ then react at the cathode with oxygen, forming water (Venkata Mohan et al., 2008a). The release of e^- and H^+ takes place in a sequence during which redox mediators get reduced by accepting H^+ from the substrate (R–H) in the presence of X-dehydrogenase. The H^+ ions are released into the surrounding medium oxidizing the redox mediators to accept another H^+ (Eq. (1)).

Substrate (R–H) + Redox mediator
(NAD^+ , FAD^+ , FMN , etc.)



Microorganisms inhabit anoxic sub-surface environments (sediment) which are rich in organic matter and mediate electron transfer by either direct bacterial transfer, i.e., without addition of exogenous e^- carriers (Tender et al., 2002; Bond et al., 2002; Bond and Lovley, 2003; Lowy et al., 2006) or by excretion of redox components (Mahadevan et al., 2006). Apart from bacterial metabolism, current was also found to generate by the oxidation of sediment reductants (Lowy et al., 2006). Microbes in the sediment surface layer preferentially reduce O_2 during oxidation of organic matter, leaving MnO_2 , Fe_2O_3 and SO_4^{2-} unutilized, which are reduced microbially in sediment layers (Lowy et al., 2006). As a consequence, each layer accumulates more potent reductants (Mn^{2+} , Fe^{2+} and S^{2-}) with increasing sediment depth and the resulting reductant gradient

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generates the voltage (Reimers et al., 2005; Ryckelynck et al., 2005). An attempt was made in this study to enumerate the potential of various types of water bodies viz., streams, river, pond and lakes in harnessing bioelectricity using benthic type fuel cells. The experiments were designed and performed by varying electrode assemblies, circuit configuration, anode surface area and placement of electrodes as factors and results are discussed in concurrence with the characteristics of respective water bodies.

2. Experimental methodology

2.1. Water bodies

Six water bodies with diverse functional properties, flow pattern and nature were selected for the experiments. Details of selected water bodies, location, sampling period and physico-chemical characteristics are depicted in Table 1. Among them, three are stagnant water bodies composed of two ponds (Uppal, Hyderabad and Nacharam cheruvu, Nacharam) and one lake (Hussain Sagar lake, Hyderabad). In the case of three running water bodies, two are rivers (Godavari river, Rajahmundry and Musi river, Hyderabad) and one is a stream (Uppal, Hyderabad). Algal mat cover was observed on the surface of stagnant water bodies.

2.2. Experimental design

Initially thirty two experimental combinations of anode–cathode assemblies/circuit configurations were designed and their performance was evaluated in Nacharam cheravu. Among them, nine combinations showed detectable and stable e^- discharge. Further, these nine combinations were studied with all other five water bodies (Fig. 1). In all the experiments anode was placed under the sediment of the water bodies. One to three anodes were used by connecting in series. Three placements of cathode viz., on the surface of water body or 2.5 cm below the surface of water body or on the surface of algal mat (stagnant water bodies only) were evaluated. Nine experimental combinations were studied in stagnant water bodies where there is a possibility of algal growth. Only six experimental combinations were operated in running water bodies due to lack of algal growth. Plain graphite plates (5×5 cm; 10 mm thickness) without any surface treatment and catalytic impregnation were used as electrodes for both cathode (surface areas: 75 cm^2) and anode (perforated by providing nine uniform size holes of 10 mm diameter to increase the overall surface area to 83.56 cm^2). Stainless steel rod was used as anode in some experiments (surface area of 15 cm^2 ; cylindrical shape). Copper wires were used for contact from electrodes and contact area

was sealed with epoxy material. The electrode assembly resembled sediment/benthic type fuel cell configuration. All the experiments were performed between 9.30 and 11.30 am in winter season (October, 2006 to February, 2007). During the study period maximum ambient temperature varied between 27 and 32°C (average humidity, 61–42%). Water samples were collected from the water body for analyzing the characteristics during the study.

2.3. Bio-electrochemical analysis

Current (I) and potential difference/voltage (V) were recorded using auto range digital multimeter (MetraVi 901) by connecting to circuit in series across various external resistances (50 – 1000Ω). Power (mW) was calculated using $P = IV$, where, I denotes current (mA) and V represents voltage (mV). Power density (mW/m^2) and current density (mA/m^2) were calculated by relating power and current with the surface area (m^2) of the anode, respectively. A variable resistance box was used to select an applied external resistance for current measurement. Samples from water bodies were analyzed for chemical oxygen demand (COD; closed refluxing method), biochemical oxygen demand (BOD), total volatile fatty acids (VFA), total dissolved solids (TDS), pH/oxidation–reduction potential (ORP) and dissolved oxygen (DO) according to the standard methods (APHA, 1998).

3. Results and discussion

3.1. Bioelectricity generation potential of water bodies

Experiments evidenced the feasibility of harnessing energy in the form of electricity in water bodies by means of electrode assembly (Fig. 2). The extent of power output was found to depend on the nature and composition of water body in concurrence with electrode assemblies. Stagnant water bodies showed comparatively higher power and current outputs (35.08 mW/m^2 ; 100.53 mA/m^2 at 50Ω) compared to running water bodies (15.56 mW/m^2 ; 62.23 mA/m^2 at 50Ω). Algal growth in the form of mat was observed on the surface of the stagnant water bodies. Power generation was observed to be almost doubled by placing cathode over the algal mat (as bio-cathode). Among the three stagnant water bodies, Nacharam cheruvu showed higher power outputs (35.08 mW/m^2 ; 100.53 mA/m^2 at 50Ω) followed by Hussain Sagar lake (33.46 mW/m^2 ; 98.13 mA/m^2 at 50Ω) and Uppal pond (17.86 mW/m^2 ; 62.23 mA/m^2 at 50Ω). In the case of running water bodies, Musi river evidenced higher power and current densities (15.56 mW/m^2 ; 62.23 mA/m^2 at 50Ω) followed by Uppal stream (12.77 mW/m^2 ; 55.05 mA/m^2 at 50Ω) and Godavari river

Table 1
Nature and characteristics of aquatic eco-systems used for evaluating bioelectricity generating potential.

Water body location	Nature of water body/ flow pattern	Nature of composition/visibility	Location	Characteristics					
				pH	TDS ^a	COD ^a	VFA ^a	DO ^a	WQI ^b
Uppal pond, Hyderabad, India	Pond/stagnant water	Domestic and industrial waters/low algal mat cover	$17^\circ24'07.04''\text{N}$, $78^\circ34'40.37''\text{E}$, elevation, 1550 ft	6.1	1260	360	72	0.76	47.27
Nacharam cheruvu, Hyderabad, India	Pond/stagnant water	Domestic outlets/algal mat cover	$17^\circ25'55.74''\text{N}$, $78^\circ32'59.04''\text{E}$, elevation, 1673 ft	6.2	560	420	120	1.21	72.79
Hussain sagar, Hyderabad, India	Lake/stagnant water	Domestic and Industrial/turbid with little algal mat cover	$17^\circ25'43.53''\text{N}$, $78^\circ28'21.80''\text{E}$, elevation, 1670 ft	6.4	630	420	48	1.15	67.56
Uppal, Hyderabad, India	Stream/running water	Domestic and industrial wastewater/polluted	$17^\circ22'59.82''\text{N}$, $78^\circ33'32.32''\text{E}$, elevation, 1542 ft	6.0	1220	480	86	0.78	73.65
Musi river, Hyderabad, India	River/running water	Domestic and industrial wastewater/polluted	$17^\circ23'07.05''\text{N}$, $78^\circ30'26.32''\text{E}$, elevation, 1588 ft	5.8	1080	510	102	0.42	75.63
Godavari river, Near Kovvur, India	River/running water	Domestic wastewater/turbid	$17^\circ00'58.43''\text{N}$, $81^\circ44'18.05''\text{E}$, elevation, 63 ft	6.7	240	40	ND	3.91	7.88

^a In mg/l; ND, not detected.

^b Water quality index.

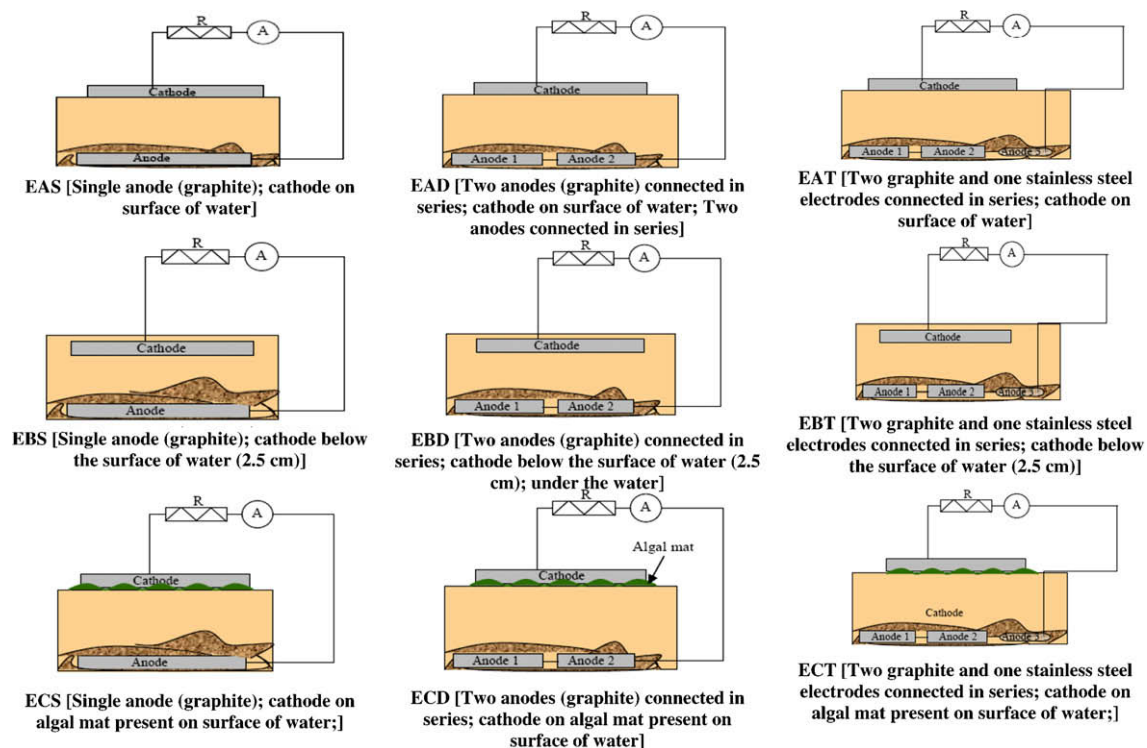


Fig. 1. Schematic details of the various experimental variations with respect to benthic fuel cell configurations studied.

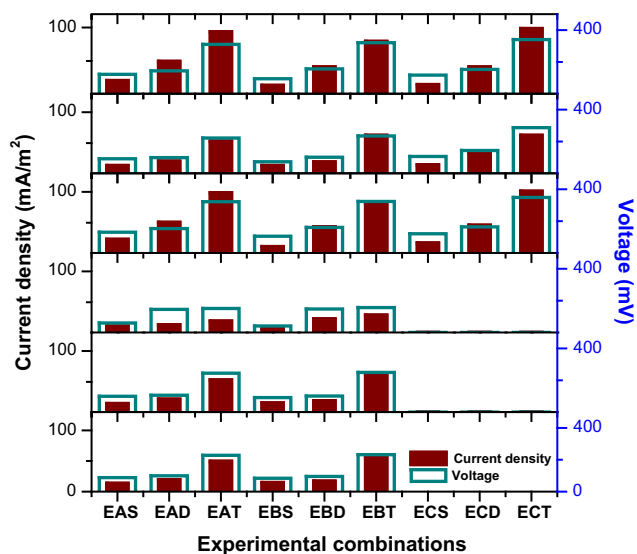


Fig. 2. Change in current density and voltage with the function of experimental variations.

(4.51 mW/m^2 ; 28.72 mA/m^2 at 50Ω). Nacharam cheruvu illustrated higher power output among the studied water bodies and Godavari river documented lower power output.

3.1.1. Influence of external resistance

Effect of applied external resistance ($1000\text{--}50 \Omega$; series) on benthic fuel cell performance was studied for all the experimental combinations (Fig. 3). Increase in e^- discharge (current generation) was observed with decreasing external resistance. Rapid increase in e^- discharge with the function of applied external resistance was observed in Nacharam cheruvu (1000Ω :

1.67 mW/m^2 ; 750Ω : 6.66 mW/m^2 ; 500Ω : 11.66 mW/m^2 ; 250Ω : 21.42 mW/m^2 ; 50Ω : 35.08 mW/m^2) and Hussain Sagar lake (1000Ω : 1.64 mW/m^2 ; 750Ω : 4.91 mW/m^2 ; 500Ω : 9.01 mW/m^2 ; 250Ω : 18.83 mW/m^2 ; 50Ω : 33.46 mW/m^2) among the three stagnant water bodies studied. Uppal pond evidenced gradual increase in e^- discharge with respect to applied external resistance (1000Ω : 1.37 mW/m^2 ; 750Ω : 4.12 mW/m^2 ; 500Ω : 7.58 mW/m^2 ; 250Ω : 11.72 mW/m^2 ; 50Ω : 17.86 mW/m^2). Among the running water bodies Godavari river (1000Ω : 0.57 mW/m^2 ; 750Ω : 1.32 mW/m^2 ; 500Ω : 2.27 mW/m^2 ; 250Ω : 3.21 mW/m^2 ; 50Ω : 4.51 mW/m^2) and Uppal stream (1000Ω : 0.84 mW/m^2 ; 750Ω : 3.08 mW/m^2 ; 500Ω : 5.3 mW/m^2 ; 250Ω : 7.22 mW/m^2 ; 50Ω : 12.77 mW/m^2) evidenced gradual increase in e^- discharge whereas Musi river (1000Ω : 0.9 mW/m^2 ; 750Ω : 2.71 mW/m^2 ; 500Ω : 6.61 mW/m^2 ; 250Ω : 11.41 mW/m^2 ; 50Ω : 15.56 mW/m^2) showed rapid discharge of e^- with the function of applied external resistance. Operation of fuel cell at higher power density represents operation at lower voltages (lower cell efficiency), while operation at peak power density can cause instability because the system has a tendency to oscillate between lower and higher current densities (Venkata Mohan et al., 2007a, 2008b,c,d,e). In the case of Nacharam cheruvu, Hussain Sagar lake and Musi river discharge of e^- started at 1000Ω resistance irrespective of the experimental variations studied. Whereas, in the case of Uppal (pond and stream) and Godavari river, e^- discharge was evidenced comparatively at lower resistance (500Ω and 750Ω) with all the experimental combinations studied which can be attributed to the lower power generation potential of the system. However, effective e^- discharge observed at lower resistances might be the probable reason for the drop in potential difference.

3.1.2. Electrode assembly

Electrode assembly in fuel cell design is one of the crucial aspects. Cathode placement showed significant influence on the

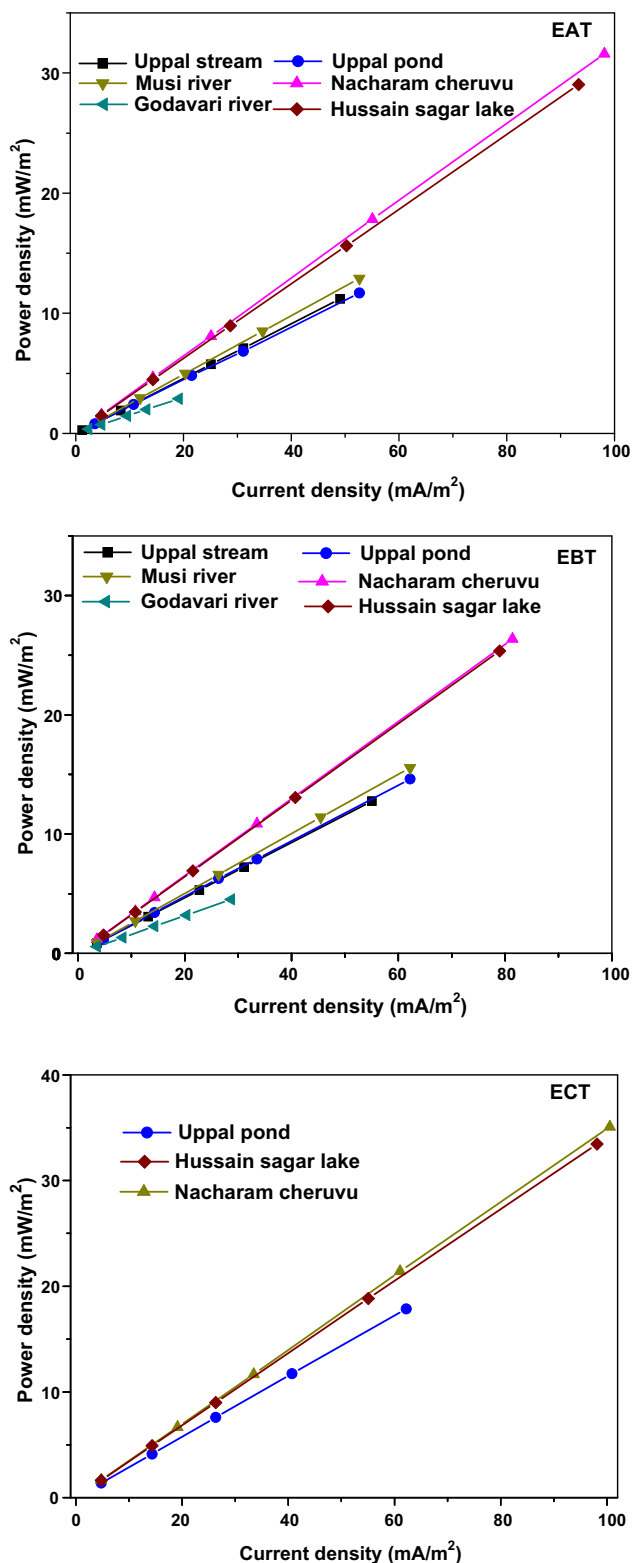


Fig. 3. Change in power and current densities in concurrence with external resistance (50–1000 Ω) during the operation of benthic fuel cell.

power generation potential. In stagnant water bodies, three cathode placements (on the surface of water body, 2.5 cm under the surface and on algal mat present on surface of water body) were studied. Among the three placements, cathode positioning on the algal mat evidenced higher power output compared to the other placements. The power generation potential was almost doubled

by placing cathode on the algal mat. This may be attributed to the possibility of excessive oxygen release by the algal activity wherein the strong electro-negativity of oxygen reduces H^+ leading to higher potential difference. In the case of running water bodies algal growth was not observed on the surface and hence only six experimental combinations were studied. On the contrary, negligible change in power generation potential (by 0.3 times) was observed by changing cathode placement from surface of water body to 2.5 cm inside of the water surface irrespective of the nature of the water body. This phenomenon might be attributed to the presence of low oxygen availability to reduce H^+ .

3.1.3. Anodic material and surface area

Enhancement in power output was observed by increasing the surface area of the anode. Adding second graphite to anode resulted in almost doubling of the power output. Enhancement in power output with increase in anodic surface area was observed irrespective of variation in the cathode placement and flow pattern of the water bodies. Using stainless steel anode in the electrode assembly (as third anode along with two graphite anodes) evidenced about 8 to 9 times improvement in the power output irrespective of the experimental variations studied. In stagnant bodies (Nacharam cheruvu) marked improvement in power generation was observed with increase in the surface area of the anode [cathode on surface, 2.98 mW/m^2 (single anode); 7.74 mW/m^2 (two anodes); 31.6 mW/m^2 (three anodes; hybrid with stainless steel)]. Similarly cathode placed on algal mat showed higher power output than the other two placements [cathode on algal mat, 2.03 mW/m^2 (single anode); 7.46 mW/m^2 (two anodes); 35.08 mW/m^2 (three anodes; hybrid with stainless steel)]. In the case of running water bodies also power increased with increase in the anodic surface area (Musi river; cathode on surface, 1.44 mW/m^2 (single anode); 2.3 mW/m^2 (two anodes); 12.9 mW/m^2 (three anodes; hybrid with stainless steel)]. Cathode placed below the surface of water body did not show much variation in the power generation [cathode below the surface, 1.43 mW/m^2 (single anode); 1.95 mW/m^2 (two anodes); 15.56 mW/m^2 (three anodes; hybrid with stainless steel)].

3.2. Water quality characteristics of aquatic eco-systems

Although, origin, flow conditions, nature and functional activities of the water body are important, the characteristics of water also play a crucial role in the power generation. Organic matter and other components present in wastewater are essential for microbial metabolic reactions which are required for current generation. Physico-chemical parameters viz., pH, VFA, TDS, COD, BOD and DO were analyzed in all the water bodies (Table 1). Except Uppal pond (360 mg/l), the other two stagnant water bodies showed the same COD concentration (420 mg/l). Running water bodies showed wide variation in COD concentrations unlike stagnant water bodies. Musi river showed higher COD concentration (510 mg/l) compared to Uppal stream (480 mg/l). Godavari river showed the presence of lowest COD levels (40 mg/l) among all the water bodies. pH levels varied between 5.8 and 6.7 in all the water bodies. Godavari river recorded near neutral pH (6.7) while Musi river documented lower pH (5.8) among all the water bodies. Uppal pond showed higher TDS concentration in both stagnant and running flow conditions (stagnant, 1260 mg/l; running, 1220 mg/l) followed by Musi river (1080 mg/l), Hussain Sagar lake (630 mg/l) and Nacharam cheruvu (560 mg/l). Godavari river showed lowest TDS concentration (240 mg/l) among all the water bodies. Stagnant water bodies evidenced low DO concentration (varied between 0.76 and 1.2 mg/l) compared to running water bodies (varied between 0.42 and 3.9 mg/l). Godavari river showed the presence of higher concentration of DO among all the water bodies studied

while Musi river showed lower DO concentration. VFA (metabolic intermediate generated from fermentation) concentration generally serves as biomarker in enumerating the metabolic function persisting in the water body. VFA concentration varied between 0 and 120 mg/l. Nacharam cheruvu and Musi river evidenced higher concentrations of VFA, while Godavari river did not show its presence.

The pollution parameter monitored for the assessment of the quality of any system gives an idea of the pollution status with reference to that particular parameter; whereas quality indices make use of a series of judgments into a reproducible form and compile all the pollution parameters into some convenient approach to get a composite influence of all the parameters of overall pollution. Indexing concept represents the overall quality of water with respect to the selected factors. Previously developed method of indexing based on weighted arithmetic quality mean method (Venkata Mohan et al., 1996) is adopted in the present study for water quality index (WQI).

$$WQI = \frac{\sum_{i=1}^n W_i \times Q_i}{\sum_{i=1}^n W_i} \quad (2)$$

where Q_i = sub-index of the i th factor, W_i = the unit weight of the i th factor and 'n' is the number of factors considered. The sub-index (Q_i) of the factor is calculated by

$$Q_i = \sum_{i=1}^n \frac{(M_i \pm I_i)}{(P_i - I_i)} \quad (3)$$

where, M_i is the measured value of the pollutant of the i th factor. I_i is the ideal value of the i th factor, which is considered as zero for all the factors under the present study. P_i is the permissible limit of the i th factor. WQI was calculated taking TDS, DO, pH and BOD as four pollution parameters using standard permissible limits (IS 2296, 1982; A-drinking water source without conventional treatment). All the water bodies except Godavari river, showed WQI between 47.27 and 75.63 falling into 'poor' category of water quality (Table 1). Godavari river showed relatively good quality of water (WQI, 7.88) than the other water bodies.

3.3. Power generation potential with the function of water body characteristics

Apart from electrode assembly, power generation was also found to depend on the nature and characteristics of the water body. In this direction an attempt was made to correlate the power generation potential with the characteristics of each water body.

3.3.1. Substrate concentration

The extent of pollution present in water bodies also had direct influence on the power output. Substrate concentration of the water body showed significant influence on the power generation as they act as carbon source (electron donor) for the benthic metabolic activity. Water bodies containing higher organic matter were able to generate higher power output. Among the three stagnant water bodies, Nacharam cheruvu (420 mg COD/l) and Hussain Sagar (420 mg COD/l) evidenced higher power generation compared to the Uppal pond (360 mg COD/l). Moreover, water bodies containing simple substrate were able to generate higher power output due to easy degradability of the substrate. The biodegradable nature of water guides the rate and extent of substrate metabolism. Higher biodegradability enumerates substrate amenability for easy biodegradation. Apart from higher COD concentration, Nacharam cheruvu (BOD/COD, 0.69) and Hussain Sagar (BOD/COD, 0.64) evidenced relatively higher degradability. In the case of Uppal pond although the COD concentration was good, the biodegradability (BOD/COD, 0.52) was relatively less. The low biode-

gradability showed negative effect on the power generation. Similar substrate concentration and power generation was observed with Musi river (510 mg COD/l; BOD/COD, 0.59) and Uppal stream (480 mg COD/l; BOD/COD, 0.61). On the contrary, Godavari river had lower substrate concentration (40 mg COD/l) among all the water bodies and corroborated well with lower power output observed.

3.3.2. Dissolved oxygen (DO)

The DO concentration is one of the important parameters when bioelectricity generation is concerned in fuel cell operation. The decreasing oxygen gradient over the depth of water creates the necessary potential difference naturally without the need of using membrane for generating potential difference between anode and cathode (He et al., 2007). Due to the presence of higher oxygen concentration, H^+ released during the substrate metabolism gets neutralized before reaching the cathode (Venkata Mohan et al., 2008f). However, lower DO concentration helps in good H^+ and e^- transfer in fuel cell operations. Stagnant water bodies showed higher power generation than the running water bodies which can be attributed to the presence of low DO concentration. Stagnant water bodies showed presence of DO concentration between 0.76 and 1.2 mg/l as compared to the running water bodies which varied between 0.42 and 3.9 mg/l. Lower DO concentrations generally lead to anoxic conditions which facilitate fermentable reactions leading to e^- and H^+ generation. Moreover, the presence of low oxygen concentration in anoxic microenvironment did not scavenge the released e^- and H^+ . On the contrary, in running water bodies, continuous flow conditions facilitates higher levels of DO which will have negative influence on proton release and electron transfer mechanism. In stagnant water bodies, input of oxygen was less due to non-flow condition, even though algal symbiotic mechanism yielded some oxygen which might be consumed by physiological needs of the eco-system. In spite of the flow conditions, DO levels also depend on other factors such as, pollution load, climatic condition, nature of pond activity, etc. DO concentration also correlated well with the concentration of the organic substrate resulting in substrate metabolism. Higher substrate concentration and the resulting metabolic activities consume the oxygen present in the water body resulting in low DO levels manifesting anoxic conditions. The presence of pollution load may be the reason for the observed low DO concentrations in Musi river and Uppal stream. On the contrary, presence of low carbon concentration and prevailing turbulent mixing conditions in Godavari river supported higher DO concentration apart from lower power outputs.

3.3.3. Total dissolved solids (TDS)

TDS concentration of the water bodies showed marked influence on power generation. Inorganic salts increase the ionic strength and in turn the conductivity of water which is important in the case of proton transfer in fuel cell operations. The performance of microbial fuel cells was observed to be effective when used with wastewater containing high ionic strength (Liu et al., 2005). About 85% increase in power generation was observed by adding NaCl at a concentration of 300 mM (Liu et al., 2005). Among the six water bodies studied, Uppal pond and Musi river showed higher TDS concentration compared to the other water bodies. But the power generation potential of these water bodies was not higher compared to Nacharam cheruvu and Hussain Sagar. Even though presence of salts stimulates electron/proton transfer mechanism, optimum TDS concentration is required in concurrence with the substrate concentration. Solution conductivities can only be increased within the limits suitable for bacterial growth. Non-halophilic bacteria enriched in freshwater and wastewater environments have optimal growth at low ionic strength (<1.2% or 220 mM NaCl (Maier et al., 2000) and low growth at high

ionic strength (3%) (Atlas, 1984). Godavari river showed lower TDS concentration among all the water bodies studied.

3.3.4. pH

pH of the water body plays a crucial role especially with respect to substrate metabolism and resulting e^- and H^+ release. pH plays a critical role in governing the metabolic pathway and depending on the organism and growth condition, changes in external pH can bring about alterations in several primary physiological parameters, including internal pH, concentration of other ions, membrane potential and proton-motive force (Futai and Tsuchiya, 1987; Kaback, 1986). Neutral pH limits the H^+ concentration in the solution but acidophilic pH is favorable for the H^+ transfer in between anode and cathode (Liu et al., 2005). Moreover, acidophilic pH favors growth of acidogenic bacteria (Venkata Mohan et al., 2007b, 2008h) that leads to acidogenic pathway during degradation of substrate generating H^+ and e^- to make power. Bacteria under neutral pH is susceptible to methanogenic activity where the e^- and H^+ gets reduced along with CO_2 to form methane. Methanogenic activity is suppressed under acidophilic pH and the protons shuttle between the metabolic intermediates during substrate degradation (Venkata Mohan et al., 2007b, 2008h,i). Except Godavari river all other water bodies showed pH near 6, which support acidogenic substrate metabolism. VFA enumerates extent of the acidogenic activity in anaerobic degradation process. VFA and pH are integral expressions of the acid-base conditions of any anaerobic process as well as intrinsic index of the balance between two of the most important microbial groups viz., acidogenic and methanogenic. The presence of VFA in Nacharam cheruvu correlated well with the observed higher power outputs. Operation of MFC under acidophilic conditions (pH 5.5 and 6) helps to limit the methanogenic bacteria activity (Venkata Mohan et al., 2007a, 2008b,c,d,e). Acidophilic pH around 6 compared to a near neutral pH can increase conversion efficiency of the substrate to H^+ and e^- . pH range of 5.5–6 was considered to be ideal to avoid both methanogenesis and solventogenesis (Hawkes et al., 2002; Venkata Mohan et al., 2007b, 2008h).

In running water bodies the bacterial population along with substrate may get washed away due to the continuous runoff, which might be the reason for the observed lower power output. Moreover, protons and electrons generated may get scavenged/neutralized due to presence of oxygen in dissolved form. The low power output in running water bodies can also be attributed to the dynamic condition where the organic matter present in water gets washed off continuously resulting in less contact between bacteria and substrate. Low potential difference recorded may also be attributed to the absence of algal mat in running water bodies which in turn resulted in reduced power output. Due to the existence of non-flow conditions in stagnant water bodies, long time contact between organic matter and bacteria present in the sediment (benthic) is always possible. Moreover, prospects exist for continuous growth of bacterial population especially in sediments/benthic without possibility of runoff that can degrade the substrate present in water and generate power. The observed higher power generation capability in stagnant water bodies might be attributed to the observed low DO concentration. Godavari river has low substrate concentration and high DO and the characteristics corroborated the observed low power generation.

4. Conclusions

Feasibility of harnessing bioelectricity from aquatic eco-systems was observed through employing benthic type fuel cell assemblies. The extent of power output was found to depend on the characteristics of eco-systems (nature, flow conditions and

characteristics) apart from the electrode assembly. Stagnant water bodies showed higher power output than the running water bodies. Cathode placements on algal mat evidenced higher power output. Polluted eco-systems showed higher power yield. Ecological water bodies could be considered as good platform to harness energy in the form of bioelectricity due to the persisting microbial activity. However, considerable optimization of both physical and chemical factors regarding the design is required.

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References

- Aoki, I., 2006. Ecological pyramid of dissipation function and entropy production in aquatic ecosystems. *Ecol. Complex* 3, 104–108.
- APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Atlas, R.M., 1984. *Microbiology: Fundamentals and Applications*. Macmillan Publishing Company, New York.
- Bond, D.R., Holmes, D.E., Tender, L.M., Lovley, D.R., 2002. Electrode-reducing microorganisms that harvest energy from marine sediments. *Science* 295, 483–485.
- Bond, D.R., Lovley, D.R., 2003. Electricity generation by *Geobacter sulfurreducens* attached to electrodes. *Appl. Environ. Microbiol.* 69, 1548–1555.
- Futai, M., Tsuchiya, T., 1987. In: Rosen, B., Silver, S. (Eds.), *Ion Transport in Prokaryotes*. Academic Press, Inc., San Diego.
- Hawkes, F.R., Dinsdale, R., Hawkes, D.L., Hussy, I., 2002. Sustainable fermentative hydrogen production: challenges for process optimization. *Int. J. Hydrogen Energy* 27, 1339–1347.
- He, Z., Shao, H., Angenent, L.T., 2007. Increased power production from a sediment microbial fuel cell with a rotating cathode. *Biosens. Bioelectron.* 22, 3252–3255.
- Holmes, D.E., Bond, D.R., O'Neil, R.A., Reimers, C.E., Tender, L.R., Lovley, D.R., 2004. Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments. *Microbiol. Ecol.* 48, 178–190.
- Kaback, H.R., 1986. Active transport in *Escherichia coli*: passage to permease. *Ann. Rev. Biophys. Chem.* 15, 279–319.
- Liu, H., Cheng, S., Logan, B.E., 2005. Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. *Environ. Sci. Technol.* 39, 5488–5493.
- Lowy, D.A., Tender, L.M., Zeikus, J.G., Park, D.H., Lovley, D.R., 2006. Harvesting energy from the marine sediment–water interface II Kinetic activity of anode materials. *Biosens. Bioelectron.* 21, 2058–2063.
- Mahadevan, R., Bond, D.R., Butler, J.E., Esteve-Nunez, A., Coppi, M.V., Palsson, B.O., Schilling, C.H., Lovley, D.R., 2006. Characterization of metabolism in the Fe(III)-reducing organism *Geobacter sulfurreducens* by constraint-based modeling. *Appl. Environ. Microbiol.* 72 (2), 1558–1568.
- Maier, R.M., Pepper, I.L., Gerba, C.P., 2000. *Environmental Microbiology*. Academic Press, New York.
- Reimers, C.E., Tender, L.M., Fertig, S., Wang, W., 2001. Harvesting energy from the marine sediment–water interface. *Environ. Sci. Technol.* 35, 192–195.
- Reimers, C., Girguis, P., Westall, J., Newman, D., Stecher, H., Howell, K., Alleau, Y., 2005. Using electrochemical methods to study redox processes and harvest energy from marine sediments. In: *Goldschmidt Conference Abstracts. Oxidation–reduction reactions in marine sediments*.
- Rezaei, F., Richard, T., Brennan, R., Logan, B.E., 2007. Substrate-enhanced microbial fuel cells for improved remote power generation from sediment-based systems. *Environ. Sci. Technol.* 41, 4053–4058.
- Ryckelynck, N., Stecher III, H.A., Reimers, C.E., 2005. Understanding the anodic mechanism of a seafloor fuel cell: interactions between geochemistry and microbial activity. *Biogeochemistry* 76, 113–139.
- Tender, L.M., Reimers, C.E., Stecher, H.A., Holmes, D.E., Bond, D.R., Lowy, D.A., Pilobello, K., Fertig, S.J., Lovley, D.R., 2002. Harnessing microbially generated power on the seafloor. *Nat. Biotechnol.* 20, 821–825.
- Venkata Mohan, S., Nithila, P., Jayarama Reddy, S., 1996. Estimation of heavy metals in drinking water and development of heavy metal pollution index. *Environ. Sci. Health A* 31 (2), 283–289.
- Venkata Mohan, S., Veer Raghuvulu, S., Srikanth, S., Sarma, P.N., 2007a. Bioelectricity production by mediatorless microbial fuel cell (MFC) under acidophilic condition using wastewater as substrate: influence of substrate loading rate. *Curr. Sci.* 92 (12), 1720–1726.
- Venkata Mohan, S., Bhaskar, Y.V., Muralikrishna, T., Chandrasekhara Rao, N., Lalit Babu, V., Sarma, P.N., 2007b. Biohydrogen production from chemical wastewater as substrate by selectively enriched anaerobic mixed consortia:

- Influence of fermentation pH and substrate composition. *Int. J. Hydrogen Energy* 32, 2286–2295.
- Venkata Mohan, S., Veer Raghuvulu, S., Sarma, P.N., 2008a. Biochemical evaluation of bioelectricity production process from anaerobic wastewater treatment in a single chambered microbial fuel cell (MFC) employing glass wool membrane. *Biosens. Bioelectron.* 23, 1326–1332.
- Venkata Mohan, S., Mohanakrishna, G., Purushotam Reddy, B., Sarvanan, R., Sarma, P.N., 2008b. Bioelectricity generation from chemical wastewater treatment in mediatorless (anode) microbial fuel cell (MFC) using selectively enriched hydrogen producing mixed culture under acidophilic microenvironment. *Biochem. Eng. J.* 39, 121–130.
- Venkata Mohan, S., Mohanakrishna, G., Srikanth, S., Sarma, P.N., 2008c. Harnessing of bioelectricity in microbial fuel cell (MFC) employing aerated cathode through anaerobic treatment of chemical wastewater using selectively enriched hydrogen producing mixed consortia. *Fuel* 87, 2667–2676.
- Venkata Mohan, S., Saravanan, R., Veer Raghavulu, S., Mohanakrishna, G., Sarma, P.N., 2008d. Bioelectricity production from wastewater treatment in dual chambered microbial fuel cell (MFC) using selectively enriched mixed microflora: effect of catholyte. *Bioresour. Technol.* 99 (3), 596–603.
- Venkata Mohan, S., Veer Raghuvulu, S., Sarma, P.N., 2008e. Influence of anodic biofilm growth on bioelectricity production in single chambered mediatorless microbial fuel cell using mixed anaerobic consortia. *Biosens. Bioelectron.* 24 (1), 41–47.
- Venkata Mohan, S., Mohanakrishna, G., Sarma, P.N., 2008f. Effect of anodic metabolic function on bioelectricity generation and substrate degradation in single chambered microbial fuel cell. *Environ. Sci. Technol.* 42, 8088–8094.
- Venkata Mohan, S., Lalit Babu, V., Srikanth, S., Sarma, P.N., 2008h. Bioelectrochemical behavior of fermentative biohydrogen production process with the function of pH microenvironment. *Int. J. Hydrogen Energy* 33 (17), 4533–4546.
- Venkata Mohan, S., Lalit Babu, V., Sarma, P.N., 2008i. Effect of various pretreatment methods on anaerobic mixed microflora to enhance biohydrogen production utilizing dairy wastewater as substrate. *Bioresour. Technol.* 99, 59–67.