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SUSTAINABLE TREATMENT OF WASTE COCONUT WATER FROM COPRA INDUSTRY USING MICROBIAL DESALINATION CELL (MDC)

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ABSTRACT

Clean drinking water sources are polluted day by day due to improper discharge of untreated or partially treated effluents, even though more than 2% of the world's electrical energy is used for sanitation. Huge amount of coconut water is wasted from copra industries. Waste coconut water is either discharged directly into the soil or drained without any treatment from most of the small/medium-scale copra processing units. This in turn results in soil contamination, groundwater-leaching problems and emission of bad odours. Microbial Desalination cell (MDC) is a bio-electrochemical system that simultaneously generates electricity from the biodegradation of organic compounds and desalinate saline water using the electric potential created. The present study evaluates the potential of a three-chambered MDC, to reduce the organic strength of coconut water in a sustainable manner with production of bioenergy. This paper analyzed the role of various factors such as $KMnO_4$ concentration as the electron acceptor (Catholyte), concentration of saline brackish water in the central chamber, Catholyte pH, and temperature on COD removal efficiency using MDC. The electric potential generated from MDC was also measured simultaneously. Using an optimized $KMnO_4$ concentration of 2500 mg/l at pH 5 as Catholyte and brackish water concentration of 2000 mg/l in the central chamber, MDC produced a COD removal efficiency of 47.68 % using Aluminium electrode within 102 hours of detention period at ambient temperature. The cell could generate an electric potential of 1.1 V consistently for a period of more than 24 hours.

KEY WORDS : Waste coconut water, Microbial Desalination Cell, Sustainable treatment, COD removal efficiency, Copra industry, Bioenergy.

INTRODUCTION

Energy and water are the two key resources facing growing demands and constraints throughout the world, as a result of economic and population growth. Most freshwater resources face terrible contamination due to discharges from domestic, agricultural and industrial sources (Ballesteros *et al*., 2016; Li *et al*., 2020). The total primary energy supply (TPES) of India in 2017 was 882 million tons of oil equivalent (Mtoe), of which 37.4% was imported from other countries. The total emission of carbon dioxide associated with all energy sources has been recorded as 2162 Mt (IEA, 2017). A National Action Plan on Climate Change (NAPCC) was adopted in 2008 to support India's development goals, with the aim of enhancing energy efficiency, sustainable ecosystems, waste management practices, etc. Other missions were added in2015, such as waste-to-energy, which would improve energy production and minimize carbon dioxide emissions through the use of other fossil fuels (IEA, 2020).

For a developing country like India, agriculture and associated sectors are very important, employing over 70 % of the rural population and 10 percent of the urban population (Archana, 2019). Coconut cultivation and related industries generate tens of millions of jobs in Asia and around the world

(Prades *et al*., 2016). The coconut is an important agriculture crop, closely linked to India's socio-cultural requirements and plays an important role in the national economy as a viable cause of rural employment and earnings (Yamuna and Ramya, 2016). India has produced a total of 21,384.33 million nuts, the largest coconut producer in the world, according to 2018-2019 statistics reported by the Coconut Development Board (CDB). Copra and coconut oil, from several products such as desiccated coconut, coconut milk, coconut milk powder, coconut cream, and virgin coconut oil, are the most important value-added products from mature coconut fruit. Kernel and copra products are considered by almost all major coconut growing countries in Asia as their main economic product (Perera *et al*., 2015).

According to the report of *'Price Policy for Copra: 2019 Season'*, by the Ministry of Agriculture and Farmers Welfare, Government of India, 39 % nuts are used in the copra production and 14 % used for other value-added products. The enormous quantity of coconut water remained unused during copra processing, with very high COD varying from 45000 to 50000 mg/l. Coconut water is in its sweetest state at the tender coconut stage (7 to 9 months) and has wide acceptance as a natural health drink. But at maturity (10-13 months), due to the development of the kernel, the amount of water inside the shell decreases. With a higher concentration of amino acids, proteins, vitamins and minerals such as K, Na, Ca, etc., the sugar and phenolic content in matured coconut water is quite poor and this reduces the taste and acceptability of mature coconut water on the commercial sector. Upon maturity, the rise in the pH of coconut water decreases its shelf life after extraction from the nut (Tan *et al.,* 2014). Natural vinegar is a commercial product made from matured coconut water. But it is less favored due to long fermentation time (6-8 weeks), less availability of technology to extract clean coconut water and availability of cheaper synthetic vinegar on the local market (Othaman *et al.,* 2014).

The coconut industry's conventional wastewater treatment systems are based on aerobic and anaerobic bioreactor principles (Industrial Pollution Control Guidelines, Sri Lanka-No.3 1992). The aerobic bioreactor is consuming excess energy, whereas conventional anaerobic bioreactors are with very slow nutrient removal rate (Suman et al. 2018). Limited studies on the treatment of effluent from the coconut industry are available. The research available focuses on the treatment of diluted coconut water produced as effluent from the desiccated coconut industry. Effluent from desiccated coconut industries is almost five times diluted coconut water, minimizing the intensity of contamination at the source itself. A desiccated coconut industry that consumes 50,000 coconuts per day discharges about 10 m^3 of pure coconut water and 40 m^3 of wash water, creating a total of 50 m^3 of effluent per day, with an average COD of 4000 to 8000 mg/l (Industrial Pollution Control Guidelines, Sri Lanka – No.3 1992). The anaerobic degradability of wastewater from the desiccated coconut industry was studied by Chanakya *et al.* (2015). The paper stated that adaptation time for anaerobic bacteria was 15 days with low biogas generation. The author also reported that COD removal efficiency (COD above 5000 mg/l even after 30 days of detention) was decreased by the presence of inhibitors such as VFA and high lipid concentration. In order to remove suspended solids, lipids, and also to balance the pH, so as to improve the biodegradability of waste water, the author proposed primary treatments such as filtration, adsorption, and neutralization. Several physico-chemical treatments were studied by Soletti *et al.* (2005) [dissolved air flotation using Fe_3SO_4 as a flocculent agent] and Gomes *et al.* (2014) [separate and combined Fenton and electrochemical treatments] on synthetic low strength coconut industry effluent. In contrast to conventional biological treatment methods, the papers reported high efficiency with a lower strength of COD.

Numerous investigates have been performed worldwide in pursuit of wastewater recycling technologies, but most of them are energy-intensive. It is estimated that 1 to 3% of the overall energy output is used in wastewater treatment plants (Capodaglio and Olsson, 2020; McCarty *et al*., 2011). The current scenario is in the demand of sustainable, energy-efficient alternative treatment technologies. At the same time, because of global energy shortages and environmental concerns, viable renewable energy sources with low emissions of carbon dioxide are also gaining importance. One of the latest technical developments incorporating the Microbial Fuel Cell (MFC) and electro-dialysis concepts is the Microbial Desalination Cell (MDC). The system efficiently uses waste as fuel for electricity generation and simultaneously desalinates salt water (Pandey *et al*., 2016; Teli *et al*., 2016). MFCs consider biodegradable organic pollutants as a resource for generating electricity with lower carbon emissions (Sreedharan and Pawels, 2016). Wastewater treatment, electricity generation, and desalination take place simultaneously in the MDC, thus reducing overall cost.

An anode, a cathode and a central saline water chamber form a typical three chambered MDC. The cathode chamber is physically separated from the central desalination chamber by a cation exchange membrane (CEM) and the anode chamber is separated from the central desalination chamber by an anion exchange membrane (AEM). Microbes in the anode chamber oxidize the organic compounds in waste water in an anaerobic environment and produce protons and electrons within the anode chamber. Electrons are transferred to the anode and transmitted via an external circuit to the cathode. The anions and cations in the saline water must therefore move to the anode and cathode respectively, to attain a charge balance. Similar to electro-dialysis (ED) configuration, ion-exchange membranes thus generate desalination (Cao *et al.,* 2009; Saeed *et al.,* 2015). Microorganisms that generate electrical energy through the oxidation of organic matter and transfer the electrons outside their cells to an electron acceptor are called exoelectrogens. Electrical energy may be generated from organic sources, such as simple carbohydrates, glucose, domestic, agricultural or industrial waste water, or even industrial dyes using MDC. Since bacteria replicate themselves, the degradation of organic matter is achieved without the need for catalyst replenishment (Guang *et al*., 2020). The passage of electrons into an external circuit induces bio-electricity.

Typically, MDC research focused on two applications: the first focus was on MDC as an energy-efficient desalination system and the second focus was on MDC as a wastewater treatment system for residential, commercial, agricultural and related sources. The theoretical minimum energy for typical seawater desalination (35 g/l of total dissolved solids) is ~1.0 kWh/m^3, while the energy needed for desalination in the MDC is provided by wastewater biodegradation. However a large amount of non-salty Anolyte and Catholyte, with 55 to 133 times the volume of desalinated water, required very high salinity removal. Hence MDCs can be more effective for partial removals of salinity (Kim and Logan, 2013). Use of 'MDC for wastewater' is investigated addressing problems like waste management problems, increasing energy demand, and limited fossil fuel resources. According to the literature, most studies are carried out on the performance of MDCs with simple substrates of wastewater (mainly acetate) as well as low strength original wastewater (like domestic, leachate etc.) with COD ranging from 400 mg/l to 3000 mg/l (Jacobson *et al*., 2011; Luo *et al.,* 2012; Zuo *et al*., 2016; Habibi *et al*., 2020).

In India, coconut oil is produced by a large number of small scale copra industries in suburban and rural areas. In most of these industries, Copra and coconut oil are produced batch-wise (5 to 7 days of processing time), processing 5000 and 10000 nuts per batch. In most of these fields, coconut water is either dumped directly into the soil or temporarily collected and drained slowly to reduce pollution intensity. Based on the production and utilization statistics of Coconut by CDB, an average of 3200 million liters of coconut water per year is released into the environment in India without adequate treatment by the Copra industry alone. The current study focused on the treatment efficiency of high-strength coconut water with three-chambered MDC.

Practical implementation of MDC has not been realized due to significant costs, system design, scaling up and energy recovery issues (Flimban *et al*., 2019). Therefore the constraints and feasibility of this technology need to be re-examined in order to accept it as a safe treatment of waste water and to assess whether the expected benefits of this technology can potentially be achieved in the treatment of coconut water. Type of substrate, type and concentration of electron acceptor in the cathode, pH, temperature, electrode material, membrane, etc. are the key factors affecting MFC performance (Jayashree *et al.,* 2019). For the present study, the operating parameters were selected accordingly, since MDC is a modified version of MFC. In comparison to dissolved oxygen and potassium ferricyanide, potassium permanganate identified as an effective and safe Catholyte. Although $KMnO_4$ has oxidizing capacity under acidic, basic and neutral pH conditions, the $KMnO_4$ solution's oxidation potential has been reported to improve at acidic pH (Nandi 2015; Osunlaja *et al*., 2012). Brackish water concentrations ranging from 1000 to 3000 mg/l (salinity of well water in the Kochi area, Kerala, India) (Sreedharan and Pawels, 2018) were used in the central chamber as very high saline water concentrations effect biodegradability because ion migration. In this analysis, the effects of

$KMnO_4$ concentration as an electron acceptor (Catholyte), brackish water concentration in the central chamber, optimum Catholyte pH and reactor temperature, were evaluated on treatment efficiency of waste coconut water with MDC, and the corresponding electrical potential generation from cell.

Materials

In acrylic, a three-chambered MDC model was designed. The capacity of the cathode, anode, and middle chambers was 125 ml each. The chambers were physically isolated by a 30 mm diameter hole by the Cation Exchange Membrane and Anion Exchange Membrane (CEM: CMI-7000, AEM: AMI-7000, manufactured by Membranes International Inc., NJ, USA). Using nuts and bolts, the chambers were coupled. To stop leakage, rubber gaskets were used as spacers and sealed with silicone sealant. Fig.1 illustrates the layout of chambers separated by AEM and CEM respectively used for the investigation.

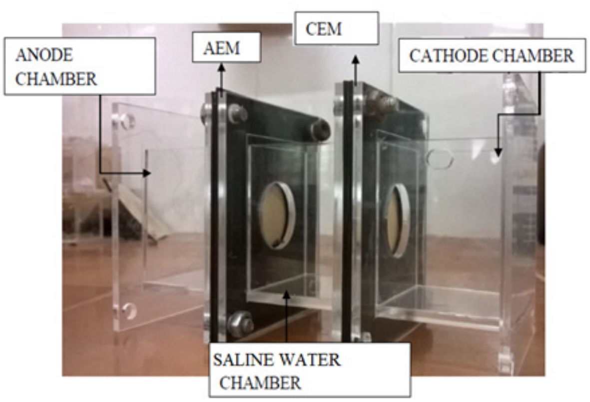

Fig. 1. Three chambered MDC cell separated by AEM and CEM

Filtered, fresh coconut water was used for each level of the investigation. The COD of raw coconut water samples ranged from 45000 to 50000 mg/l with a pH between 4.9 and 5.6. Aluminium was used as electrode material, connected externally by means of light gauge copper wire. Potassium permanganate ($KMnO_4$) was used as an electron acceptor (Catholyte), being the safest chemical (even used as a water disinfectant) compared with many other toxic chemical oxidizing agents. For the preparation of synthetic saline water laboratory grade NaCl was dissolved in distilled water. Conjugate acid-base buffers were made from various blends of citric acid and sodium hydrogen orthophosphate solutions for buffering the Catholyte.

Methodology

The entire study maintained the anoxic condition in the anode chamber with air tight sealing using silicone sealant. In order to avoid evaporation loss during the investigation period, the central saline water chamber was also kept sealed. The Anolyte, coconut water was filtered using ordinary filter paper and seeded with 1gm of yeast per liter, to accelerate the fermentation process. The measurement of open circuit voltage (V) was done on an hourly basis over a span of 7 hours daily using a digital multimeter manually. In four levels, experimental studies were carried out using batch reactors with a detention time of 102 hours. After the detention time, changes in the COD values of coconut water were measured to indicate the treatment efficiency of the MDC. The concentration of $KMnO_4$ as Catholyte was optimized during the first level of investigation. The different concentrations of $KMnO_4$ solutions: 0 mg/l, 500 mg/l, 1000 mg/l, 1500 mg/l, 2000 mg/l, 2500 mg/L, 3000 mg/l and 3500 mg/l, were compared in the MDC modules using 50 mm x 50 mm Aluminium electrodes of 0.5 mm thickness. The initial concentration of salt water in the central chamber was maintained in all cells at 1000 mg/l. MDC efficiency was demonstrated by estimating the % removal of COD (standard APHA methods, 1992) and electrical potential (V) generated from cells. The investigation limited the saline water concentration to 3000 mg/l as higher concentrations affect the microbes present in Anolyte that in turn reduce the treatment efficiency and to correlate the salinity levels of Kochi well water during different seasons. MDC's performance was analyzed at different pH conditions of $KMnO_4$ in the third level of the investigation. $KMnO_4$ solutions was loaded to MDCs at pH 3, 4, 5 and 6 using a conjugate acid-base buffer (made of 0.1 M citric acid and 0.2 M Sodium hydrogen orthophosphate). The findings were compared with the second level's non-buffered condition. One of the most influential parameters for microbial fermentation is reaction temperature. In order to enhance the yeast reaction, the fourth level of the experimental research was done at different temperature ranges. The first reactor was kept in a BOD incubator at 20 ^oC. The second MDC was placed at 40 ^0C in a hot air oven. Throughout the testing period, the third MDC was maintained at ambient room temperature, with usual day-night fluctuations between a minimum of 27 ^{0}C and a maximum of 33 ^{0}C.

RESULTS AND DISCUSSION

Effect of $KMnO_4$ concentration on performance of MDC

The effect of concentration of Catholyte, $KMnO_4$, on the efficiency of COD removal relative to the control sample is shown in Figure 2. A part of the feed seeded and held in a bottle in anoxic condition at room temperature was the control sample. The efficiency of COD removal was 34.97 % at the optimized $KMnO_4$ concentration of 2500 mg/l compared to the control sample of 10.30 % COD removal. With a 13.31 % decrease in COD even for $KMnO_4$-free MDC, indicates that natural dissolved oxygen by aeration present in water has effectively increased Anolyte's biodegradability. Hence, Catholyte plays a vital role in the treatment efficiency of MDC.

Figure 3 shows the electric potential (V) generated from different MDCs, measured as open circuit voltage, at different concentrations of $KMnO_4$ solution as Catholyte. The maximum electric

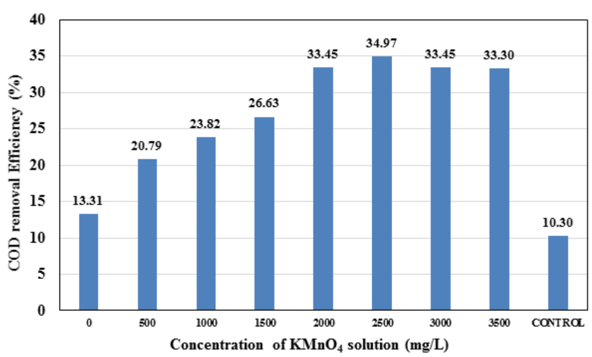

Fig. 2. Effect of $KMnO_4$ concentration as Catholyte on COD removal efficiency

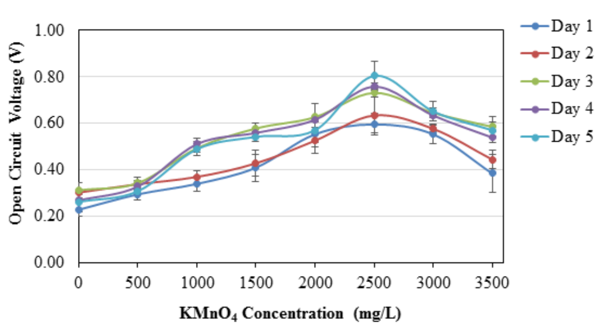

Fig. 3. Effect of concentration of $KMnO_4$ on electric potential generation from MDCs

potential of 0.8 V was created between the electrodes of MDC with Catholyte concentration of 2500 mg/l, the cell which produced maximum COD removal efficiency.

The results show that the efficient transfer of ions from the central chamber to the anode and cathode chambers, as well as the movement of electrons in the external circuit, improved the development of electrical potential in the cell and increased biodegradability in order to improve the efficiency of treatment. The current study reveals that at very high concentrations of $KMnO_4$, electron/ion transfer efficiency has been negatively affected.

Effect of concentration of salinity on performance of MDC

The overall performance efficiency of MDC is depends on the concentration of saline water in the central chamber, ionic migration is initiated from the central chamber to cell anode and cathode. Figure 4 shows a slight difference in the efficiency of COD removal from MDCs with different concentrations of saline brackish water. The maximum COD removal efficiency of 36.03 % was achieved from the cell having salinity of 2000 mg/l.

The daily average variation of electric potential generated from different MDCs with varying concentrations of saline brackish water in the central chamber is shown in figure 5. The concentration of salt water in the central chamber influences the ionic transfer and thus decreases the internal resistance in the circuit. As the salinity increases, the internal resistance of the cell lowers and hence improves the cell potential. However, due to the addition of chloride ions to the Anolyte, greater concentration affects biodegradability.

Effect of pH of $KMnO_4$ solution on performance of MDC

Catholyte concentration (2500 mg/l $KMnO_4$

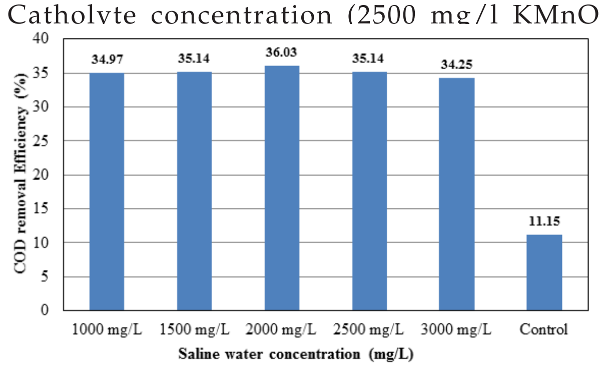

Fig. 4. Effect of Saline water concentration on COD removal efficiency of MDC

solution) and saline water concentration in the central chamber (2000 mg/l NaCl solution) in all batch reactors were kept constant at this level. In order to maximize the reactor performance, Catholyte pH values were varied to identify the optimized pH of the $KMnO_4$ solution. Figure 6 represents the effect of Catholyte pH on the COD removal efficiency. MDC exhibited a maximum COD removal of 47.94 % at pH 5. The non-buffered KMnO4 solution was found to have an alkaline pH range. While $KMnO_4$ solution has better oxidation potential at acidic pH, treatment efficiency of MDC reduces at very low pH values of Catholyte.

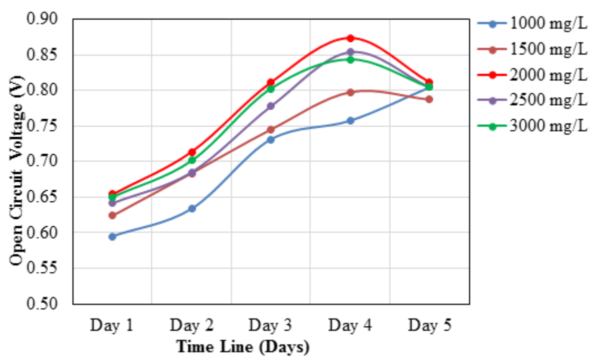

Fig. 5. Effect of salt concentration on generation of Electric Potential from MDC

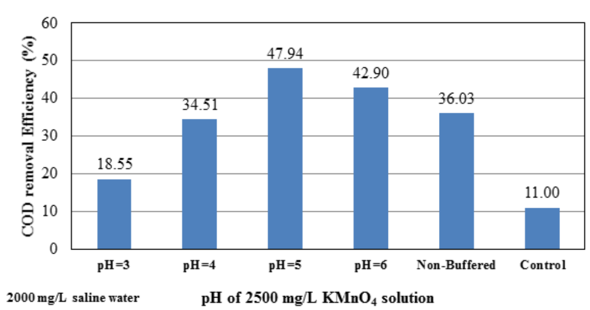

Fig. 6. Effect of pH of Catholyte on COD removal efficiency from MDC

Figure 7 shows the daily average electric potential form MDC having Catholyte buffered at different pH values compared to the non-buffered Catholyte. A maximum electrical potential of 1.11 V from the MDC was generated when the $KMnO_4$ solution was buffered at pH 5. The cell was able to consistently generate more than 1.09 V from the cell for more than 24 hours. The results were in agreement with the principle of higher oxidation potential of $KMnO_4$ solution at acidic pH compared to alkaline pH. At very low pH values of Catholyte, the driving potential for cations towards cathode chamber was reduced to reduce the overall efficiency of MDC.

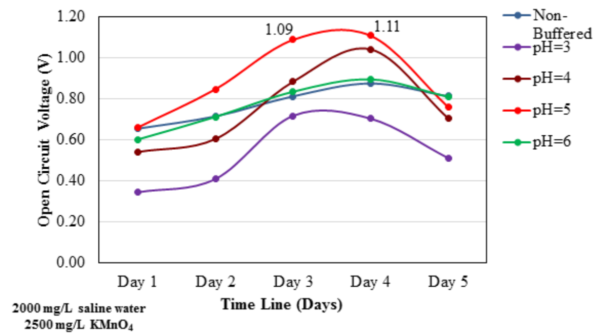

Fig. 7. Effect of pH of Catholyte on electric potential generated from MDC

Effect of Temperature on performance of MDC

The performance of MDC put under ambient temperature (under day-night variation from 27 ^{0}C to 33 ^{0}C) was better compared with controlled reactor temperatures of 20^0 C and 40 ^{0}C. The maximum daily average electric potential of 1.11V obtained with a 47.68 % COD removal efficiency. The COD removal efficiency and electric potential generated from MDCs maintained at different temperature conditions are shown in Figures 8 and 9. The findings were in agreement with the research conducted by Merritt (1966) and Walsh and Martin (1977) on the impact of temperature during wine processing by yeast in un-aerated fermentations. The coconut water fermentation by yeast in MDC also maximizes its reaction rate at an average temperature of 30 ^{0}C. Therefore, yeast can be used efficiently as a biocatalyst, economically without temperature control facilities in warmer regions.

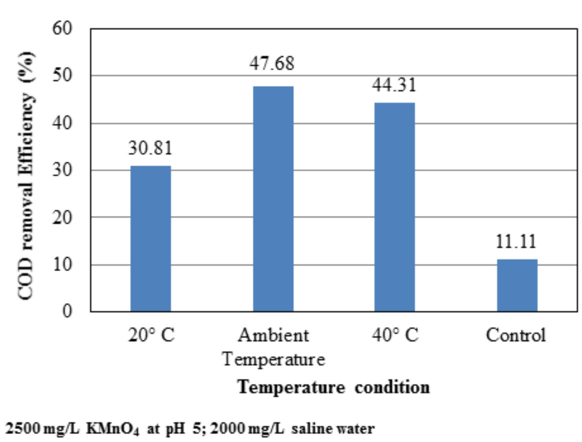

Fig. 8. Effect of reactor temperature on COD removal efficiency from MDC

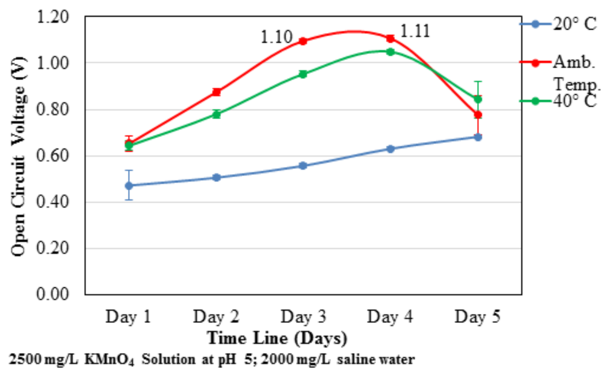

Fig. 9. Effect of reactor temperature on electric potential generated from MDC

CONCLUSION

Energy-efficient technologies, environment conservation and waste-to-energy are the major concerns of current research. Microbial Desalination Cells (MDCs) are bioreactors which extract chemical energy stored in organic compounds into electrical energy through bio-degradation. A large number of small-scale coconut-based industrial units, similar to the copra industry, manufacture value-added products with excellent nutritional quality. Owing to discontinuous and high-strength discharges, the installation of complex wastewater treatment plants to handle their effluents is not economically feasible. MDC, being a zero-energy system with electricity generation from high strength effluent, is a sustainable way to handle wastewater. Therefore, MDC is a feasible and economical solution for reducing pollution issues related to different coconut processing industries. The current study revealed that at ambient temperature, the MDC batch reactor using 2500 mg/l of $KMnO_4$ buffered at pH 5 as Catholyte and 2000 mg/l salt water in central chamber provided more than 47 % of the COD removal efficiency by using an Aluminium electrode within 102 hours of detention period.

In most of the small sale coconut processing industries operating on batch mode, it is easy to provide a detention period of 5 to 7 days for better treatment. MDC can be used as a primary treatment for small to medium scale coconut industry wastewater to reduce high organic pollution. Since bio-flocculation takes place in MDC, COD is further reduced by filtration, or chemically aided sedimentation of the treated effluent.

The optimized MDC batch reactor generates energy output and if this energy can be channelized effectively for the production processes, it can reduce fuel consumption. In order to improve the efficiency of MDC in the treatment of waste coconut water and bioenergy production, further critical parameters such as electrode materials, various types of microbial species instead of yeast as biocatalyst, the effect of mediators on more efficient capture of bio-electricity, etc. can be further studied.

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