Table 1: Open circuit potential (OCP), maximum current density, maximum power density, internal resistances recorded against measured external resistances for pH 4 to 9.

pH	Maximum OCP (V)	External resistance (Ω)	Internal resistance (Ω)	Maximum current density (mA/m^2)	Maximum power density (mW/m^2)
4	0.319	1000	2288	19.4	1.9
5	0.361	1000	686	42.8	9.2
6	0.598	820	675	84.6	29.4
7	0.674	1000	1332	57.8	16.7
8	0.394	1000	1447	32.2	5.2
9	0.326	1000	1650	24.6	3.03

by plotting current density against potential and power density was measured at the various external resistances (6.8, 4.7, 2.7, 1, 0.82, 0.68, 0.47, 0.33 kΩ). To measure ohmic resistance, the MFC was operated with a 6.8 kΩ external resistance first. After system stabilization, the current was interrupted by a relay. Rapid stabilization of OCP was observed at higher external resistance and a relatively high potential drop and slow stabilization of the voltage was observed at lower external resistance, which might be due to effective electron discharge at lower external resistance. During the start-up of polarization curve, activation losses can be clearly observed in order to initialize the electron transfer from bacteria towards the electrode which results in a fast voltage decay or activation over potential at higher external resistance for all the pH studied. During a period of resistance change, the voltage recorded at a particular resistance is inflated. At very low and very high pH of 4 and 9, the overshoot shape is produced when the voltage inflation started to slow down. For pH 5, 6 and 7, the ohmic losses seems to be less corresponding to pH 4, 8 and 9, that can be seen from low internal resistance. In addition, a limited mass transfer of substrate towards the anode was observed at pH 5, 6 and 7, whereas, a steep decrease of the cell voltage near the maximum current densities during the polarization curve was observed for pH 7 and 8, respectively. Fig. 4 also shows the variation in power performance with respect to pH. The point at which maximum power density was obtained on the polarization curve is generally described as the cell design point of that particular MFC. High performance of fuel cell with respect to maximum power density output can be obtained on the right side of the cell design point [27]. Cell design point of comparatively all pH's were obtained at 820 -1000 Ω corresponding to maximum power density at acidophilic pH of 6 (maximum current density: 84.6 mA/m^2 and maximum power density: 29.4 mW/m^2 at 820Ω). The polarization curves were linear in the ohmic polarization region, where the power density reached its maximum value. When this pH was 4, 8 and 9, the power output was detrimentally affected as shown by power curves produced with very high internal resistance, which restricted the power output by causing a significant decrease in the operating potential due to ohmic limitations [30]. The emergence of overshoot can also be observed at pH 4 and pH 9 which concomitantly decreases the power output [31]. The MFC operated at pH 4, 8 and 9 was devoid of biofilm formation which results in an increased internal resistance, which deteriorated the performance and reproduced the overshoot (pH-4 and 9). In accordance with Winfield *et al*. [31], healthy anodophilic microbial community reduced the internal resistance and eliminate any power overshoot. The fuel cell exhibited a relatively effective electron discharge at pH 5, 6 and 7 where internal resistance was almost equal or less than external resistance. For all studied pHs, the current generation was decreasing with increasing external resistance which is consistent with literature and indicated typical fuel cell behaviour. Evidently, the change in microenvironment pH 4, 8 and 9 were incompatible for mixed culture to operate in and the electron demand could not be maintained for better fuel cell operation [31].

Electrochemical Activity Analysis: Electrochemical activity as a function of pH change during MFC operation was evaluated by cyclic voltammetry, an electrochemical-analytical technique used for the characterization of electrochemical systems that also helps to elucidate the electrochemical reactions taking place on/at the electrode surface. CV also measures the potential difference across the interface and the redox activities of the compounds involved in the biochemical system, both in solution as well as compounds attached to the bacteria. During the maximum current output under various pH conditions, voltammograms were recorded *in situ* in the MFC, which showed noticeable variation in the electron transfer processes and current generation. Fig. 5 shows the analysis of the CV profiles (vs. Ag/AgCl), which indicates noteworthy variations in the electron discharge and energy generation patterns as a function of the operated pH. The voltammogram shows a three-step change in the

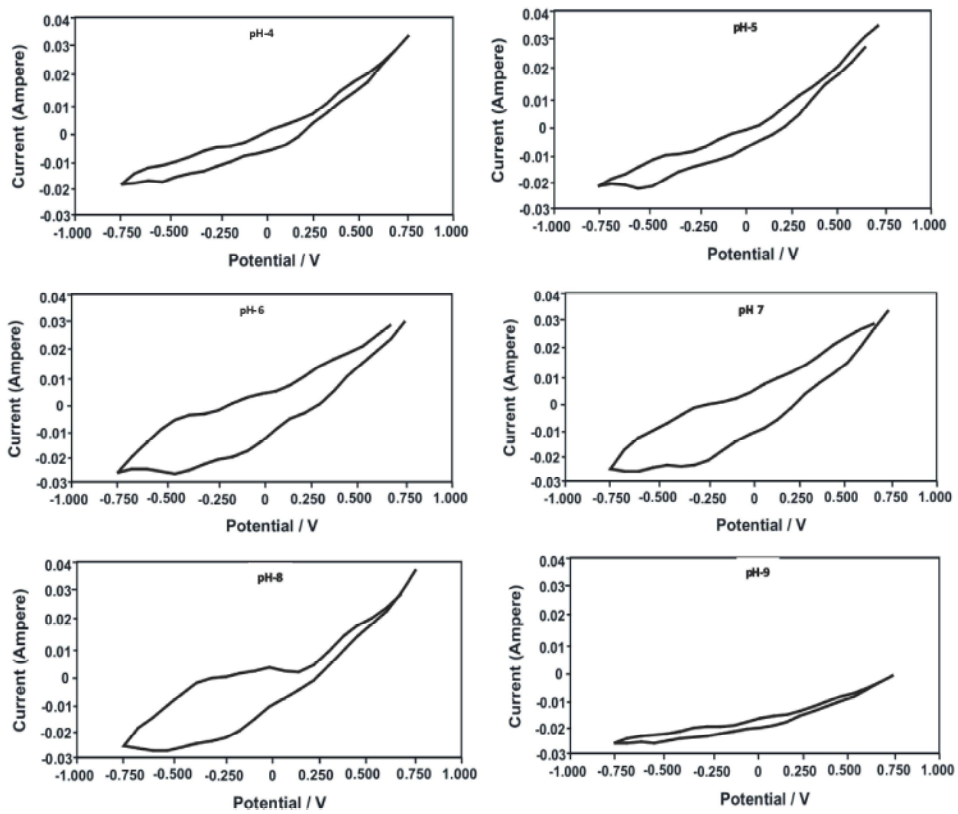

Fig. 5: Cyclic voltammetry behaviour for oxidation phenomenon from pH 4-9.

oxidation peaks, however, indicating the occurrence of a three-electron transfer process at three different peak potentials. Oxidation peaks at the potential of -0.45 V, -0.15 V and +0.35 V (vs. Ag/ AgCl) were observed at all pH values. At pH 5, 6 and 7, these peak potentials are clearly observed in the forward scan with the maximum current of 0.02 mA recorded for pH 7 followed by 0.016 mA for pH 6 and 0.01 mA for pH 5. Contrary to this, voltammograms obtained at pH 4, 8 and 9 were devoid of some of these peaks or the peak intensity was very low with irregular peak patterns in the forward scan. Additionally, it can also be inferred that DET through biofilm-driven catalysis [32] or the functionality of active ionic groups on the bacterial enzymes were probably responsible for the higher oxidation peaks that occurred at pH 5, 6 and 7, respectively. Additionally, electrogenic bacteria could also lead to more electrochemical activity leading to electricity generation towards anode [33]. Substrate to energy conversion via metabolic activity can be governed by an oxidation peak which is accompanied by electron discharge and thus provides a good evidence for the presence of an electrochemical activity and provides information regarding the metabolic activity occurring in the system [34]. Moreover, the CV results are also in good agreement with current profiles generated in Fig. 2 and suggest that stabilization of the MFC performance for DSW could be achieved under acidic (pH 5-6) to neutral conditions.

CONCLUSION

A single chamber MFC with readily available materials was fabricated in this study. The performance was tested at various operating conditions of pH for electricity generation using DSW as the substrate, cow dung as inoculum. The feasibility of current generation and wastewater treatment was evaluated and the factors that affected the power output were also discussed. The pH effect of wastewater was correlated with microbial electrochemical activity, maximum current and power production. The pH of 6-7 and resistance of 820-1000 Ω was found to be suitable for the maximum current and power density generation. Cyclic voltammetry was employed to investigate electrochemical responses which demonstrate a three-electron transfer mechanism in the MFC. The low coulombic output of MFC was proposed to the loss of electrons for various biological activities other than electricity generation. The study of electricity production combined with distillery wastewater as substrate would approach the application and the performance of MFC in the future.

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Persian Abstract

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چکیده

یک پیل سوختی میکروبی تک محفظه (SCMFC) با استفاده از پساب حاصل از صنایع تقطیر الکل (DSW) و میکروارگانیزمهای موجود در فضولات گاو بعنوان مایه تلقیح در pH ۴-۹ راه اندازی شد. حداکثر جریان در MFC به (۰/۱۶-۰/۱۹ mA) pH ۸-۹ به دست آمد، در حالیکه مواد آلی پساب (COD) به ترتیب (۶۸٪) pH ۶ > (٪ترتیب (۰/۴۶ mA) pH ۶ > (۰/۴ mA) pH ۷ > (۷۹) pH ۷ > (٪۸۰-۸۱) pH ۸-۹ کاهش یافت. افت بازده کولومبیک ناشی از نوسانات سیستم دریافت کننده الکترون و نفوذ هوا به راکتور می باشد. از منحنی پلاریزاسیون حداکثر دانسیته جریان ۸۴ mA/m^2 و دانسیته توان ۲۹ mW/m^2 با مقاومت درونی ۸۲۰ Ω (pH ۶) حاصل شد. ولتامتری چرخه‌ای (CV) فرآیند انتقال ۳ الکترونی، بهترین پاسخ شیمیایی در ۷ و ۶ pH را نشان می-دهد. در شرایط عملیاتی مطلوب MFC پاسخ مثبتی را برای تولید بیوالکتریسیته نشان داده است.