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Synthesis of proton exchange membranes for dual-chambered microbial fuel cells

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Abstract: Proton exchange membranes (PEMs) were synthesized using three different compositions of poly(oxyethylene) (POE), poly(vinyl alcohol) (PVA), chitosan (CS) and phosphoric acid (PA) in weight ratios of 1:1:1:1, 1:2:1:1 and 1:3:1:1 by physical blending and the casting method. Water uptake of the membrane increases with increasing concentration of PVA. A higher percentage of water uptake signifies a higher ion exchange capacity (*IEC*) of the synthesized membrane. The synthesized membranes were evaluated in microbial fuel cells (MFCs) and the performance observed. The synthesized membranes were characterized for identification of precursor material and inter polymer interactions using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy analysis, respectively. The removal of chemical oxygen demand (*COD*) depends on the microbial activity in the anodic chamber. In the present study, the composition of the membrane was optimized and compared with other membranes that had been synthesized by different compositions of all materials. COD removal in the MFC-3 setup connected with an M-3 membrane was found to be 88 %.

Keywords: ion exchange capacity; chemical oxygen demand; water uptake; power density; current density; open circuit voltage.

INTRODUCTION

Microbial fuel cells (MFCs) are used for power generation from wastewater through microbial oxidation of organic contaminants.[1] Proton exchange membranes (PEM) physically separate the anode from cathode.[2] Commercial membranes, such as nafion®, are highly conductive due to their structural properties. The material nafion® consists of three parts *viz*., a poly(tetrafluoroethylene) backbone, side chains connected with the molecular backbone and ion clusters consisting of sulfonic ions. Nafion has high ion exchange capacity and proton con-

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ductivity due to the above-mentioned functional groups.[3] There are many advantages of Nafion 117 membrane in fuel cell applications. However, several problems associated with Nafion still exist, including oxygen leakage from the cathode to the anode, substrate losses and biofouling,[4] conductivity at low water content and poor mechanical strength at high temperatures.[3–5] The proton exchange membranes are associated with some other major problems, such as surface layer losses from the membranes and the migration of protons. An efficient proton exchange membrane possesses a high ion exchange capacity in aqueous condition.[6,7] Due to these drawbacks, alternate approaches have been developed, such as opting by MO_2 (where M = Zr, Si, Ti),[8] by non-fluorinated polymer electrolytes,[9] and by inorganic and organic composite membranes.[10]

Jiang and Tang[11] discussed the effects of layer-by-layer (LbL) self-assembly of polyelectrolyte bilayers on methanol permeability and proton conductivity of Nafion membranes and studied the crossover properties of modified Nafion membranes for the application in direct methanol fuel cells (DMFCs). Magnetic ion-conducting nanoparticles were prepared by Hasanabadi *et al.*[12] for PEM applications. The surface of the γ-Fe_2O_3 nanoparticles was modified *via* silanation followed by the oxidation of the terminal mercapto groups to form functional sulfonate groups and studied the effect of sulfonation on proton conductivity, activation energy, methanol permeability and selectivity. Sadrabadi *et al.*[13] described the preparation and characterization of novel ion exchange polymer nanocomposites for fuel cells applications. Montmorillonite (MMT) nanoclay was modified using amino benzotriazole (BTA) *via* ion exchange. They found that Nafion/BTA–MMT-3.0 wt. % membranes were able to provide over three times more power output than Nafion-117. Erkatal *et al.*[14] demonstrated a novel proton conducting membrane consisting of poly(vinyl alcohol) (PVA), poly(2--acrylamido-2-methylpropane sulfonic acid) (PAMPS) and 1,2,4-triazole, which was fabricated by physical blending, casting and solvent evaporation techniques. The *in situ* chemical cross-linking was performed using glutaraldehyde (GA). Momlouk and Scott[15] synthesized a composite membrane with BPO_4 (boron phosphate) with an excess quantity of PO_4 (BPO_x) and investigated the enhancement of ion exchange capacity in high temperature ranges. In this study, sulfonic and sulfuric acid were replaced by phosphoric acid due to its good chemical and electrochemical properties.

Poly(vinyl alcohol) (PVA) and phosphoric acid (PA) mixtures were used in previous literature, whereby good mechanical strength but a low open circuit voltage (*OCV*) of 436 mV and a very low current density of 1 mA cm^{-2} were evidenced.[16,17] Daries *et al.*[18] reported the synthesis of a proton exchange membrane consisting of PVA, sulfamic acid (SA) and poly(oxyethylene) (POE). The MFC connected with this membrane had a maximum *OCV* value of 516 mV. The maximum power and current density of PVA–SA–POE separator was found to be 7.16 W m^{-3} and 1.72 A m^{-3}, respectively, but it was low when compared with Nafion 117 under identical conditions.[18] Ghasemi *et al*. reported the synthesis of a PEM using sulfonated poly(ether ether ketone) (SPEEK) and evaluated the performance of the MFC. The power production of the MFC with SPEEK was 77.3 mW m^{-2}, which is still lower than the Nafion 117 value of 106.7 mW m^{-2}.[19] Hence, there is a need to focus on the synthesis of a membrane with a suitable composition for MFC applications.

The present study was focused on the synthesis of proton exchange membranes using water-soluble polymers with different weight ratios. Polymers such as poly(oxyethylene) (POE), used as plasticizer,[18] and poly(vinyl alcohol) (PVA) were used to increase the water transport due to their hydrophilic properties.[20] Phosphoric acid (PA), an alternative to sulfamic acid[18] and sulfonic acid,[15] has specific properties, such as excellent thermal, chemical and electrochemical stability in fuel cell applications. Chitosan (CS) is a low-cost biopolymer that can provide chemical stability and electronic properties to membranes.[20] The synthesized PEMs were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy for the identification of precursor material and inter polymer interactions, respectively. The water uptake and ion exchange capacity of the synthesized membranes were quantified to optimize the composition of the membrane. The synthesized membranes were used in a MFC and the performance of the same was monitored with respect to open circuit voltage (*OCV*), power and current density, and compared with the conventional Nafion 117 membrane. Chemical oxygen demand (*COD*) removal of wastewater was measured using the synthesized membranes in the MFCs.

EXPERIMENTAL

Materials

Poly(oxyethylene) (POE-600) was purchased from Sigma–Aldrich, India, poly(vinyl alcohol) (PVA), potassium hydrogen phosphate and sodium hydroxide were purchased from Merck, India; sulfuric acid, propan-2-one and phosphoric acid (PA) were purchased from Fisher Scientific, India; chitosan (CS) was purchased from SRL Pvt. Ltd., India, glutaraldehyde (GA) was purchased from Loba Chemie, India; D-glucose anhydrous purified, potassium manganite (VII), calcium chloride, magnesium sulfate heptahydrate, ammonium chloride, *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylmethanamide (DMF) were purchased from Rankem, India. All the reagents and chemicals were used as received. Unless otherwise mentioned, distilled water was used for all the experiments.

Synthesis of membranes

The quantity of POE, PVA, CS and PA used for the synthesis of membranes in the weight ratio of 1:1:1:1 (M-1), 1:2:1:1 (M-2) and 1:3:1:1 (M-3). *N*-Methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylmethanamide (DMF), used as organic solvents, were mixed in the volume ratio of 1:1. The mixture was used for dissolving POE, PVA, CS and PA according to the various compositions. The mixture was maintained at a temperature of 80 °C using a hot plate with continuous stirring for 4 h, in order to dissolve everything completely in the solution. Finally, the prepared solution was cast into three different glass Petri dishes up to the mark in order to maintain the thickness of all synthesized membranes and dried in an oven at 50 °C for 24 h. The thickness of the synthesized PEMs were measured using a digital screw gauge (Mituotoyo, Japan) and were found to be 0.2±0.001 mm. The dried membranes were immersed into a cross-linking solution consisting of 1.5 wt. % glutaraldehyde (GA), 0.5 wt. % of sulfuric acid, 48 wt. % of acetone and the remaining distilled water for 3 h. Subsequently, the cross-linked membranes were washed several times with distilled water to remove traces of glutaraldehyde.[21]

Construction of MFCs

Laboratory scale dual chambered batch microbial fuel cells were fabricated for this study. The two chambers, with a capacity of 1000 mL each, were made up of polyacrylic material with dimensions of each compartment 12.5 cm (height)×9 cm (length)×9 (width). Both the chambers were connected using a flange, in which the proton exchange membrane was placed. Rubber gaskets were used to prevent leakages and silicone gel was used for binding the gaskets. Carbon electrodes in the form of rod were used as anode and cathode. The dimensions of the electrode were 1.5 cm diameter and 12.5 cm effective height. Power and current density were calculated based on an anode area of 60.6 cm^2. One chamber was closed with an airtight lid, which served as the anode, while the other chamber was left open to the atmosphere, acted as the cathode. The effective diameter of the membrane connecting the two chambers was 2.5 cm.

The setups of microbial fuel cell MFC-1, MFC-2, MFC-3 and MFC-4 were with M-1, M-2, M-3 and Nafion-117 PEM, respectively. The microbial fuel cell MFC-4 setup with Nafion 117 was taken as a reference. The anodic compartment was filled with 300 mL of sludge. The initial chemical oxygen demand (*COD*) value of sludge was 11400 mg L^{-1}. Synthetic wastewater was prepared as per the composition reported in the literature.[22] The amount of wastewater filled in anodic chamber was 700 ml. Initial *COD* and pH of synthetic wastewater was 560 mg L^{-1} and 7.3, respectively. *COD* of the mixture was found to be 5760 mg L^{-1}, which was taken as reference for the calculation purpose. Potassium permanganate ($KMnO_4$) of 0.2 g L^{-1} concentration was filled in the cathodic chamber, as reported in the literature.[23] Potassium permanganate was used as a catholyte for enhancing the reduction of H^+ in the cathode compartment.[23] Experiments were performed at a room temperature of 28 °C. The closed chamber acted as an anode for anaerobic treatment. The initial pH of potassium permanganate solution was measured as 7.2. During the study, pH of the solution was maintained at 7, by adding few drops of 1 M NaOH or 0.5 M H_2SO_4, as required.[24]

Characterization

Scanning electron microscopy (SEM). Morphological analysis of the synthesized membrane surface was realized using SEM (JEOL 6380A). The synthesized membranes were cut into small portion and kept in sample bags prior to SEM.

X-Ray diffraction (XRD). In order to identify the materials used in the synthesis of the PEM membranes, X-ray diffraction (XRD, PANalytical 3kW X'pert Powder) analysis was performed using CuK_α with a scanning rate of 5° min^{-1} and 2θ ranging from 5 to 80°.

Fourier transform infrared spectroscopy (FTIR). The synthesized membranes were examined using FTIR (Bruker, Alpha Model) for identification of polymer interactions. A small piece of synthesized membrane was used for the analysis in the ATR mode. The spectra were obtained between 4000 and 500 cm^{-1}.

Water uptake. The membranes were dried using a closed hot air oven at 50 °C for 15 min to remove the moisture content. The membranes were weighed using an analytical balance (Sartorius, BSA 2245-CW) with a readability of 0.1 mg. The dried membranes were then soaked in deionized water for 24 h. Membrane surfaces were wiped with tissue paper and then the wet membrane weighed. Water uptake of the synthesized membranes was calculated using Eq. (1):

$$\text{Water uptake} = 100\frac{W_\text{w} - W_\text{d}}{W_\text{d}} \tag{1}$$

where W_d is the weight of the dried membrane and W_w is the weight of the wet membrane.[25-27] Swelling ratio was found to be lesser than 5 %, which is reasonable as reported in the literature.[35]

Ion exchange capacity (IEC). The *IEC* of the synthesized membrane was measured using the standard procedure reported in the literature.[28,29] The synthesized membranes were immersed in 1 M HCl for 24 h and washed with distilled water to remove excess acid. Subsequently, the membrane was soaked in 1 M NaCl solution for 24 h. The NaCl solution was titrated with 0.01 M NaOH to determine the concentration of the exchanged protons with phenolphthalein as the indicator.

The *IEC* of the synthesized membrane was calculated using Eq. (2):

$$IEC = \frac{ab}{m} \tag{2}$$

where *IEC* is the ion exchange capacity in meq g^{-1}, *a* is the volume of NaOH consumed in mL, *b* is the concentration of NaOH in molarity and *m* is the weight of the dried membrane in g.[30]

Calculations of the power and current density

The potential difference across the MFCs was measured using a digital multimeter without any load. The current was measured by connecting various resistances (10, 20, 47, 100, 427 and 1000 Ω) to the MFCs, in accordance to the Ohm law. The current density was calculated by dividing the current by the anode area. The power density was calculated using the following Eq. (3):

$$P = \frac{RI^2}{A} \tag{3}$$

where *R* is the applied external resistance, *I* is the current and *A* is the surface area of anode.[12] Polarization curves were plotted for the membranes as per the standard procedure mentioned in the literature.[31-33]

Measurement of COD. The *COD* in wastewater samples were measured by the closed reflux method using the standard procedure mentioned elsewhere.[34] The samples were heated at 150 °C for 2 h in a thermo-reactor (DRB200). After cooling, the sample was titrated against ferrous ammonium sulfate (FAS) with ferroin as the indicator.

COD in the sample was calculated as follows:

$$COD\ (\text{mg L}^{-1}) = \frac{8000(A - B)M}{V_\text{sample}} \tag{4}$$

where *A* is the volume of FAS required for the titration of the blank (mL), *B* is the volume of FAS required for the titration of the sample (mL), *M* is the concentration of FAS in mol dm^{-3}, and V_sample is the volume of sample (mL).[34]

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The SEM surface images of three membranes M-1, M-2 and M-3, synthesized using various recipes, are shown in Fig. 1a–c. The surface morphology shows that all constituents of the membranes were homogeneously distributed throughout the membranes without any major migration or phase segregation.[35] The SEM images confirmed that pores were not significant in the synthesized membranes.

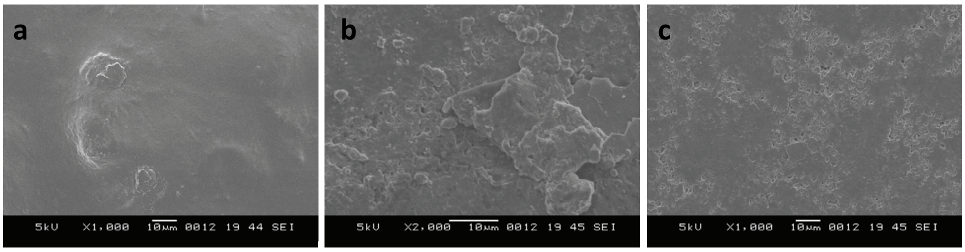

Fig. 1. SEM images of PEMs synthesized using various recipes: a) M-1, b) M-2 and c) M-3.

X-Ray diffraction (XRD) analysis

The XRD pattern of membranes synthesized using various recipes are shown in Fig. 2. The strong crystalline peak at 19.2° and the weak peak at 40.2° confirm the presence of poly(vinyl alcohol).[36] The peak at 10° corresponds to the presence of chitosan in the synthesized membranes.[37] The peak at 23.34° corresponds to POE-600.[38] The H_3PO_4 present in all the membranes was of non crystalline form and hence the peak was not observed in the XRD patterns.[39]

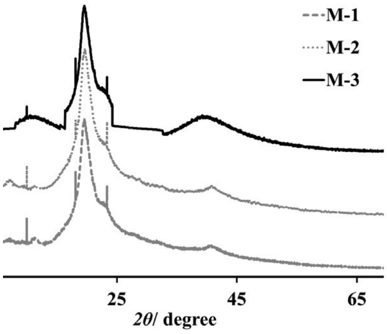

Fig. 2. XRD patterns of membranes synthesized using various recipes.

Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR transmittance spectra of the synthesized membranes using different compositions are presented in Fig. 3. The broad peak seen between 3500 and 3000 cm^{-1} represents –OH stretching and C–H stretching, which confirmed the presence of PVA.[14] Peak at 1670 cm^{-1} corresponds to carboxylic group (C=O), while the peak at 1590 cm^{-1} (–NH_2) represents carbonyl groups; both the peaks confirmed the presence of chitosan at the edges.[40] The C–H stretching observed at 2887 cm^{-1} was due to the presence of POE–600.[38] The phosphate group peaks were observed between 650–550 cm^{-1} and 1300–910 cm^{-1}.[41]

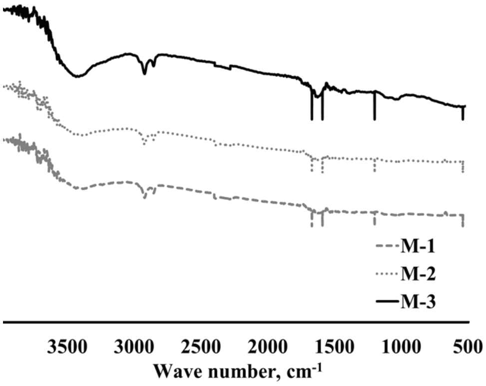

Fig. 3. FTIR spectra of all synthesized membranes using various recipes.

Water uptake

The water uptake by all the synthesized membranes are shown in Fig. 4 and the values for M-1, M-2 and M-3 were 30.20, 33.15 and 36 %, respectively. The water uptake value increased with increasing PVA concentration. Water uptake of the Nafion-117 membrane was 30 %, which matches well with the reported literature.[42] Compared with the water uptake by pristine Nafion-117, the values of water uptake for synthesized membranes were slightly higher. This could be due to the hydrophilic nature of PEG and PVA.[24] PVA is more hydrophilic in nature due to the –OH groups.[43] The content of PVA in the M-3 membrane was higher and hence, the water uptake of M-3 membrane was higher than for the M-1 and M-2 membranes. The higher value of water uptake signifies a higher ion exchange capacity (*IEC*).[42]

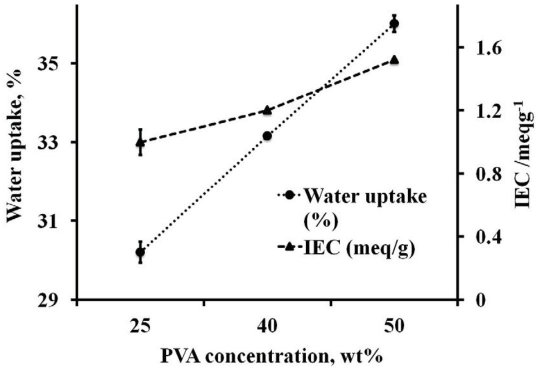

Fig 4. Water uptake and *IEC vs.* PVA concentration of the synthesized membranes.

*Ion exchange capacity (*IEC*)*

The *IEC* is a measure of relative concentration of acid groups within PEMs.[44] The ion content is characterized by the mass of dry membrane per molar equivalents of ion conductor. Fig. 4 shows the ion exchange capacities of the three synthesized membranes, *i.e.*, 1, 1.2 and 1.52 meq g^{-1}, respectively, according to increasing the concentration of PVA. A membrane that had a higher concentration of PVA yielded a higher *IEC* value. PEG provided the backbone for a PEM; CS has a good electronic property and hence enhanced the *IEC*.[20] The *IEC* for the Nafion-117 membrane was 0.91 meq g^{-1}, which is comparable with the literature value.[42] The *IEC* values of the synthesized membrane were higher than the *IEC* of the Nafion 117 membrane.

Performance of the MFCs

Power density and polarization curves. The power density curves of the microbial fuel cells with various synthesized membranes, while the other factors were constant are presented in Fig 5, from which it could be seen that the power density trend for MFC-1, MFC-2 and MFC-3 passes through a maxima and then drops because of microbial oxidation of organic and inorganic contaminant present in wastewater. This trend matches well with the reported literature.[19]

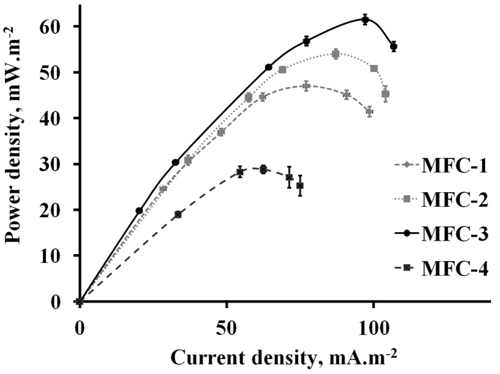

Fig. 5. Power density curves of the synthesized membranes and Nafion-117 membrane in MFCs setups.

The performance of MFC-3 with an M-3 membrane showed a better performance when compared with the other MFCs with an M-1 or M-2 membrane. Fouling prevents the exchange of protons in dual chambered MFCs.[45–47] The maximum values of power density are given in Table I. The maximum values correspond to the membrane without fouling. However, the power densities of M-1, M-2, M-3 and Nafion 117 were reduced to 42.5, 46.3, 56.9 and 25.9 mW m^{-2}, respectively. The reduction in the power density might be due to fouling of the membrane.

The polarization curves, voltage *vs*. current density,[48] of various synthesized membranes in MFCs are shown Fig. 6. The reduction in the over potentials, particularly the ohmic overpotential, was caused by the higher ion exchange capacity of the M-3 membrane. The over potential of M-2 and M-1 membranes were less than the over potentials of M-3, which resulted in a better performance of the membrane and a lower potential loss.

TABLE I. Summary of the performance factors of various synthesized membranes and a Nafion-117 membrane in MFCs.

MFC	Membrane^a	$P_{max}{}^b$ / mW m^{-2}	$I_{max}{}^c$ / mA m^{-2}	Open circuit voltage^d, V	*COD* removal^e, %
MFC-1	M-1	48.1	99.0	0.89	82
MFC-2	M-2	55.1	104.0	0.94	86
MFC-3	M-3	63.3	107.3	1.07	88
MFC-4	Nafion 117	29.7	74.4	0.615	78

^{a}Data are expressed as type of membranes; ^{b}maximum power density; ^{c}maximum current density; ^{d}maximum open circuit density; ^{e}maximum *COD* removal

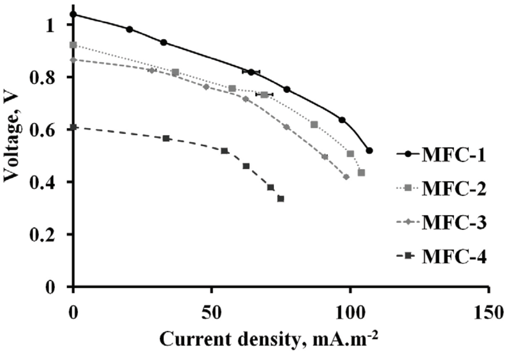

Fig. 6. Polarization curves of the synthesized membranes and the Nafion-117 membrane in MFCs setups.

The open circuit voltage (*OCV*) of the MFCs with different membranes was measured at steady state (SS) condition and the results are shown in Fig. 7. In a typical plot of *OCV vs*. time, there are three stages, *viz.,* microbial growth, energy production and microbial death.[49] There was a rapid increase in *OCV* in the first stage, which was due to microbial growth and colonization, a stable period of

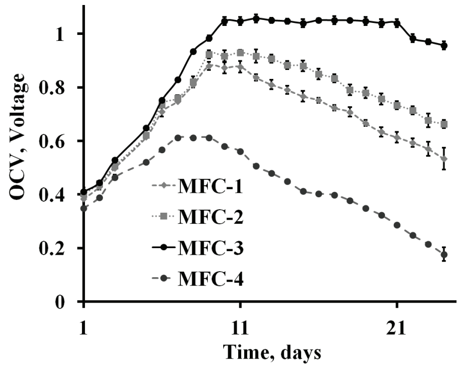

Fig. 7. *OCV* of various synthesized membrane in MFCs *vs*. time.

energy production in the MFC and the death of the microbial cells that led to a decrease in the *OCV*.[49] In the case of MFC-3 with M-3, the energy production stage was significant when compared to those of MFC-1, MFC-2 and MFC-4 with M-1, M-2 and Nafion-117, respectively. MFC-3 generated a more stable *OCV* among all the MFCs. The *OCV*s of MFC-1, MFC-2, MFC-3 and MFC-4 were 0.89, 0.94, 1.07 and 0.615 V, respectively. The reason for this order might be the ion exchange capacity of the membranes.

COD removal. The *COD* removal (%) over time is shown in Fig. 8. The MFCs connected with M-1, M-2 and M-3 and Nafion-117 membrane yielded 82, 86, 88 and 78 % *COD* removal, respectively. Oxygen diffuses relatively rapidly through the M-1 membrane (synthesized with low amount of PVA) from the cathode to the anode when compared with M-3 (high PVA). This transfer of oxygen might be due to the crossover problem of the membrane. As the oxygen transfer was greater in the membrane synthesized with low amount of PVA, the availability of an anaerobic bacterial community in the anodic chamber decreases. Hence, the *COD* reduction was lower with the M-1 membrane. However, in the case of membrane synthesized with a high PVA content (M-3), the diffusion of oxygen was lower and hence, the *COD* reduction was high. The *COD* removal results were in agreement with the microbial activity in anodic chamber and proved the efficiency of the membrane efficiency, which was in agreement with the *IEC* results. The *COD* removal (%) of the MFC-3 setup was higher than were those of the other setups. MFC-3 was efficient when compared to MFC-1, MFC-2 and MFC-4.

The values of maximum power density, current density, open circuit voltage (*OCV*) and *COD* removal (%) of MFC-1, MFC-2 and MFC-3. connected with the M-1, M-2 and M-3 membranes, are summarized in Table I. Among the three MFC setups, MFC-3 performed better by yielding higher power density, current density, open circuit voltage (*OCV*) and *COD* removal. M-3 membrane has higher water uptake and ion exchange capacity when compared with M-2 and M-1 membranes.

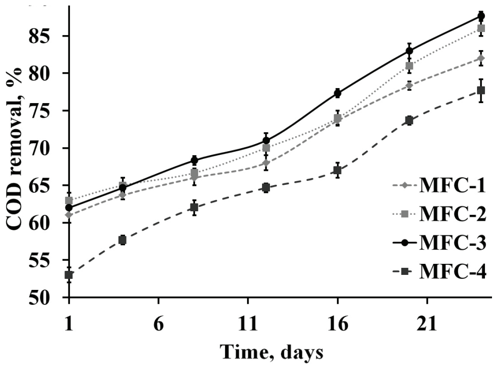

Fig. 8. *COD* removal of wastewater in anodic compartment of MFCs *vs*. time.

CONCLUSIONS

The membranes synthesized in this study significantly improved the power density of the MFCs. The improvement in the MFC power density is a direct consequence of the improved ion exchange capacity of the membranes. These membranes acted as an effective barrier to bacterial migration from the anode to the cathode, which would otherwise have reduced the performance of the MFCs. The MFC-3 setup using the M-3 membrane exhibited the highest value of power density, current density and *OCV*. The *COD* removal of MFC-3 with the M-3 membrane yielded a higher value when compared with the other MFCs. The M-3 membrane was more effective and efficient when compared with the other three membranes (M-1, M-2 and Nafion-117). The improved performance of M-3 membrane was due to its higher quantity of PVA.

ИЗВОД

СИНТЕЗА ПРОТОН-ИЗМЕЊИВАЧКИХ МЕМБРАНА ЗА ДВОКОМОРНЕ МИКРОБНЕ ГОРИВНЕ ЋЕЛИЈЕ

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Протон-измењивачке мембране (PEM) су синтетисане полазећи од три различита састава поли(етилен-оксида) (PEO), поли(винил-алкохола) (PVA), хитозана (CS) и фосфорне киселине (PA) у масеном односу 1: 1:1:1; 1:2:1:1 и 1:3:1:1, користећи поступак физичког мешања и изливања из раствора. Апсорпција воде полимерних мембрана је расла са повећањем садржаја PVA. Већи проценат апсопције воде значио је уједно и већи капацитет измене јона (*CEC*) синтетисаних мембрана. Синтетисане мембране су окарактерисане у погледу састава и интеракција између полимених компоненти помоћу дифракције X-зрака и инфрацрвене спектроскопије са Фоуријеовим трансформацијама, редом. Затим су перформансе полимерних мембрана проверене у микробним горивним ћелијама (MFC). Показано је да проценат смањења хемијске потрошње кисеоника (*COD* / %) зависи од микробне активности у анодној комори. Основни циљ ових истраживања је био да се одреди оптимални састав мембране на основу поређења својстава са осталим синтетисаним мембранама различитог састава и једном комерцијалном мембраном. Установљено је да је смањење *COD* у MFC-3 микробној горивној ћелији са M-3 полимерном мембраном износило 88 %.

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