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# Polysulfone Composed of Polyaniline Nanoparticles as Nanocomposite Proton Exchange Membrane in Microbial Fuel Cell

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## ABSTRACT

Proton exchange membranes play a critical role in the performance of Microbial Fuel Cells (MFCs) but their high price was always a big deal for commercialization of MFCs. In the present study, doped and undoped polyaniline nanoparticles/polysulfone nanocomposites membranes as a new type of PEM, were fabricated and applied in the MFC and their performance was compared with Nafion 117 as a traditional and expensive PEM. The obtained results show that MFC working by undoped Pani/Ps generated 78.1 mW/m$^2$ which is higher than doped Pani/Ps system with 62.5 mW/m$^2$. However, Naion 117 generated the highest power than other types of membrane by 93 mW/m$^2$. It means that undoped Pani/Ps can compete in power generation with Nafion 117 and this is an outlook toward commercialization of MFC.

**Keywords:** Microbial Fuel Cell, Proton Exchange Membrane, Nanocomposite, Pani

## 1. INTRODUCTION

Microbial Fuel Cell (MFC) is a type of fuel cell using microorganisms as biocatalyst on anode to oxidize the substrates to the electron and protons under anaerobic condition as well as metabolic products while the potential at cathode surface reduces due to getting electron and protons (Liu *et al*., 2012). It means, MFC is a fuel cell that treats wastewater and generates electricity simultaneously. In addition, MFCs can be applied for production of hydrogen, biosensors for organic content of wastewater, sulphide and nitrogen removal as well (Ghangrekar and Shinde, 2007; Virdis *et al*., 2008). In the previous study, we used this type of membranes for desalination purpose. However, in this study, we intend to apply them as proton exchange membrane in microbial fuel cell (Alam *et al*., 2011). Generally MFCs consisted of two chambers that were separated by a Proton Exchange Membrane (PEM). Many factors play a part in the performance of the MFCs, such as the kind of electrode, type of microorganisms, media composition, PEM and distance between cathode and anode (Ghasemi *et al*., 2011; 2012; Sedighi *et al*., 2012). The role of PEM is

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to prevent the transfer of bacteria from anode to cathode as well as reduce the diffusion of oxygen from cathode to anode (Sun *et al*., 2009; Tang *et al*., 2010). In most studies of MFCs, Nafion 117 has been used as PEM, a few also used anion exchange membrane. However, one of the main reasons that still MFCs has not become commercialized are these membrane are expensive and approximately account for 38% capital cost of the MFCs (Ghasemi *et al*., 2012; Rozendal *et al*., 2006). So this problem, led to more research on synthesis and application of novel types of economically applicable membranes (Dewan *et al*., 2008). For instance, Rahimnejad *et al*. (2011) developed $Fe_3O_4$/PES nanocomposites membrane with various concentration of ferric oxide nanoparticles from 0 to 20 percent in PES polymeric matrix. They compared the power output of the nanocomposites membranes with Nafion 117 as the common PEM in MFC. They finally concluded that $Fe_3O_4$/PES nanocomposites membrane produces more power than other types of fabricated membranes and even Nafion 117. The reason was higher conductivity of the nanocomposites membrane, lower pore size that prevents from movement of media from anode to cathode and oxygen from cathode to anode and also lower roughness. Recently, interests for development and application of conducting polymer as material for membranes due to some unique properties like high thermal and chemical stability have been interestingly increased (Alam *et al*., 2011; Choi *et al*., 2008). Among the family of conducting polymer polyaniline (PANI) has mostly been used due to simple and low cost synthesis, high environmental stability moreover it has unique electroactive properties that can be controlled reversibly in the presence of acids such as hydrochloric acid (Qaiser *et al*., 2011; Ren and Zeng, 2008). Due to these properties and also high capital cost of Nafion117, in this study we fabricated polysulfone (PS)/doped PANI nanocomposites membranes and applied this to the MFC system as PEM. The performance of this membrane was compared with Nafion117 as the common PEM in MFC and also PS/undoped PANI nanocomposites membrane to get the effect of doping in the membrane performance.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals and Polyaniline Preparation Method

The chemicals and method of preparation of PS/PANI nanocompodite PEM is same as our previous study exactly (Alam *et al*., 2011).

### 2.2. Traditional PEM

The efficiency of new synthesized nanocomposites membranes was compared with Nafion 117 as the traditional PEM in MFC. Before applying to the system, Nafion 117 went under three stages of pretreatment as follow: 3% $H_2O_2$, washed with deionized water, 0.5 M H2SO4 and finally washed with deionized water. In order to maintain the membrane for good conductivity, the cell anode and cathode compartments were filled with deionized water when the MFC was not in use (Rahimnejad *et al*., 2011).

### 2.3. Enrichment of the Electrochemically Active Bacteria (EAB) on Anode

Palm Oil Mill Effluent (POME) anaerobic (Selangor, Malaysia) sludge was employed to inoculate the reactor in the anode chamber. The media contained 3 g of glucose, 0.05 g of yeast extract, 0.1 g of KCl, 0.7 g of $NaH_2PO_4.4H_2O$, 1.5 g of $NH_4Cl$, 2.5 g of $NaHCO_3$ (all from the Merck company), 10 ml solution of Wolfe's mineral and 10 mL of Wolfe's vitamin solution added per litre. All the electrochemical tests were conducted in batch modes in a 30°C incubator. The cathode chamber contained a phosphate buffer solution consisting of 2.76 g $L^{-1}$ of $NaH_2PO_4$, 4.26 g $L^{-1}$ of $Na_2HPO_4$, 0.31 g $L^{-1}$ of $NH_4Cl$, 0.13 g $L^{-1}$ of KCl (Ghasemi *et al*., 2011).

### 2.4. MFC Configuration

Two cylindrical and H-shaped chambers were set up from Plexiglas, with aninner diameter of 6.2cm and a length of 14cm, separated with Nafion 117, which acted as the Proton Exchange Membrane (PEM). Oxygen was continuously fed to the cathode by an air pump (80 mL $min^{-1}$). Both the cathode and the anode surface areas were $12cm^2$ and the MFC operated in an ambient temperature and a neutral pH (6.5-7) in the anode and cathode compartments. The pH was adjusted using a phosphate buffer solution. Plain carbon paper (Gas Hub, Singapore) was employed as the 'untreated' anode. The cathode consisted of carbon paper coated with 0.5 mg $cm^{-2}$ Pt.

### 2.5. Calculation and Analysis

The current and the produced power of the system were measured by use of this Equation 1 and 2 respectively:

$$I = \frac{V}{R} \quad (1)$$

$$P = V \times I \quad (2)$$

where, I is the current (amp), V is the voltage (volt), R is the resistance (ohm) and P is the power in watt.

The Coulombic Efficiency (CE) was calculated as the current over the time until the maximum theoretical current was achieved. The evaluated CE over time was calculated through the following formula Equation 3:

$$CE = \frac{M\int_0^t Idt}{FbV_{an}\Delta COD} \quad (3)$$

where, M is the molecular weight of oxygen (32), F is Faraday's constant, b = 4 indicates the number of electrons exchanged per mole of oxygen, $V_{an}$ is the volume of the liquid in the anode compartment and Δ COD is the change in the Chemical Oxygen Demand (COD) over time, 't' .

A Potentiostat-Galvanostat (HAK-MILIK FRIM 04699A-2007) was used to test the oxidation and reduction of organic compounds by microorganisms as a biocatalyst. The potential range was between -0.3 to 0.75 The working electrode, for the attachment of microorganisms, was made of Carbon Paper (CP) and the reference electrode was Ag/AgCl. Pt was applied as a counter electrode. The scan rate was adjusted to 50 mV/s.

### 2.6. Electrochemical Impedance Spectroscopy

For obtaining the resistance of the membranes, they were subjected to the Electrochemical Impedance Spectroscopy (EIS) before applying in the MFCs. The frequency of 1-10 KHz were conducted by a Frequency Response Analyser (FRA) (Model 1255 solartron analytical, Hamshire, UK) equipped with an electrochemical interface connected to a PC for getting a Nyquist plot using Z plot software. The resistance was calculated by fitting of the half circle curve by fit circle function in the Nyquist graph.

### 2.7. Membrane and Microorganisms Characterization

The dispersion of Pani nanoparticles in PES matrix was observed by Transmission Electron Microscopy (TEM) (Philips, class CM12; Netherlands). The atomic force microscopic (AFM, Niegra Prima, Russia) was employed to measure the roughness and pore size of the membranes because these properties are important in biofouling matter. The functional groups of Pani attached to the Pani were verified by using FTIR spectroscopy (Nicolet 6700 FTIR, Thermo Scientific). Scanning Electron Microscope (SEM) (Supra 55vp-Zeiss, Germany) was used to characterize the attached microorganisms on the anode electrode.

## 3. RESULTS

### 3.1. FTIR of Pani

**Figure 1** depicts the FTIR spectrum of produced Pani. Actually functional groups, molecular geometry and inter/intra molecular interactions can be gotten from FTIR. The characteristic peaks of Pani would appear in the range of 600-1800 $cm^{-1}$ (Lu *et al*., 2011). The peak around 800 $cm^{-1}$ revealed the existence of para-distributed aromatic rings. The peaks between1250-1335 $cm^{-1}$ is the characteristic of the conducting aromatic amine group (C-N). Moreover, the peaks around 1501 and 1615 attributed to the quinoid and benzenoid rings of Pani. The mentioned characteristic of peaks confirms the formation of Pani (Trchova *et al*., 2004; Lu *et al*., 2011).

### 3.2. Bacteria Attachment on the Anode Electrode

**Figure 2** shows the attachment of microorganisms on the electrode surface. It shows that different kinds of bacteria can be attached on the electrode surface acting as biocatalyst in oxidation of organic substrates in media. Cluster of microorganisms are grown fully on anode surface. These microorganisms work as active biocatalyst at anode surface for production of bioelectricity in anode compartment.

The CV of the electrode before and after inoculation was shown in **Fig. 3**. A single redox peak can be observed around 0.075 for the electrode after inoculation which proves that the microorganisms are active for oxidation and reduction processes. **Figure 3** also shows that the oxidation peak (the upper peak) is larger than the reduction peak (at the bottom of the graph) which proves that the attached bacteria mostly oxidize the organic substrates in the anode chamber for generation of electricity.

### 3.3. AFM

**Figure 4** depicts two and three dimensional AFM pictures of the undoped Pani/Ps. The results of NOVA software analysis for pore size and roughness of all membranes are shown in **Table 1**.

As can be seen in the **Table 1**, all the membrane pore size are less than 100 nm which are less than the size of microorganisms (0.5 to 2 μm) so it can prevent from migration of microorganisms from anode to cathode. Roughness also reveals the tendency of membranes for fouling (or biofouling). Rough surface fouls more easily than smooth surface because surface area will be increased with roughness (Rahimnejad *et al*., 2011). As **Table 1** shows, Pani nanocomposite membranes have lower roughness even lower than than Nafion 117. So it means that the fouling possibility in these membranes is less than Nafion 117.

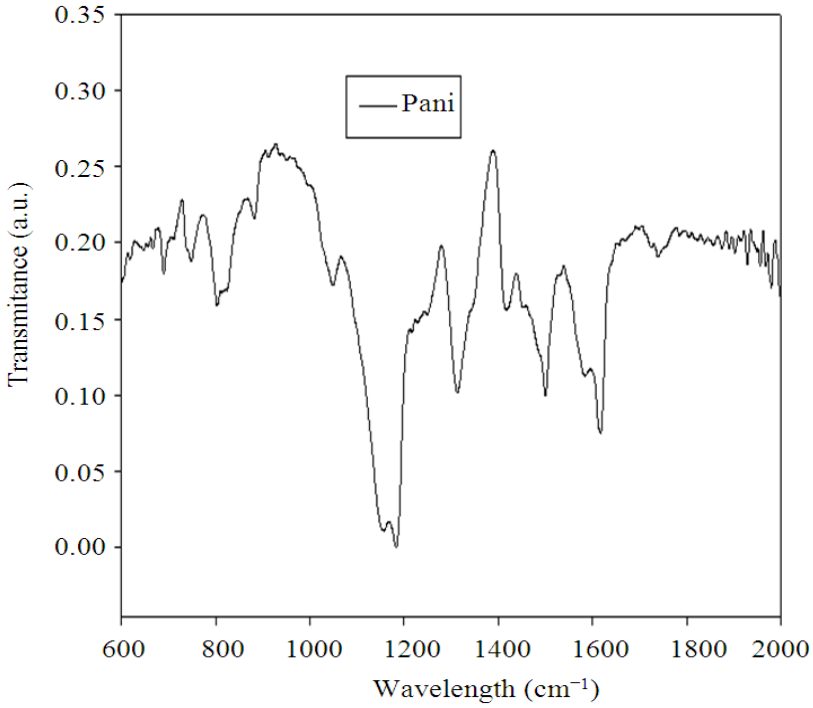



**Fig. 1.** FTIR analysis of the Pani

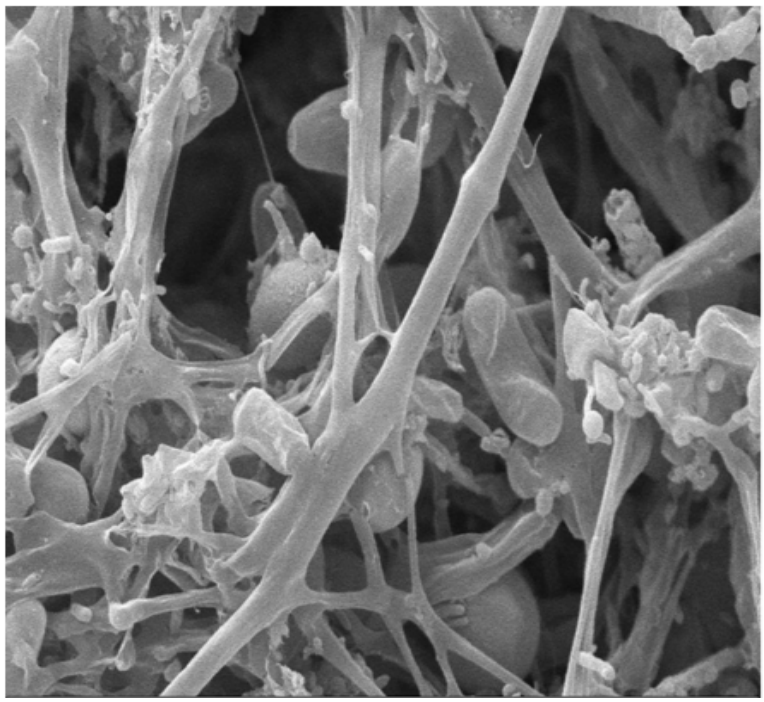


**Fig. 2.** Microorganisms attachment on the anode electrode

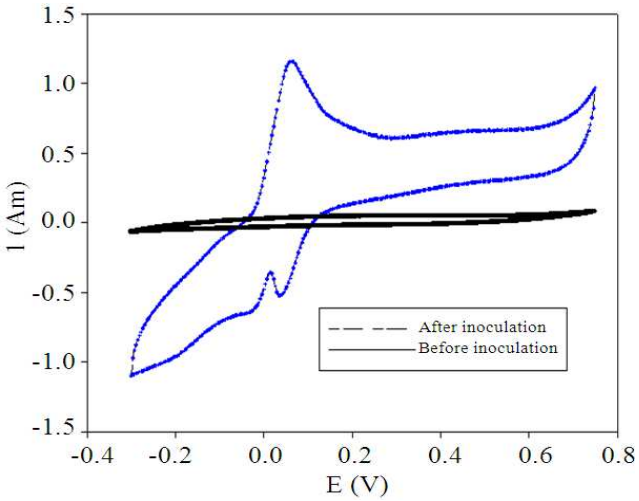
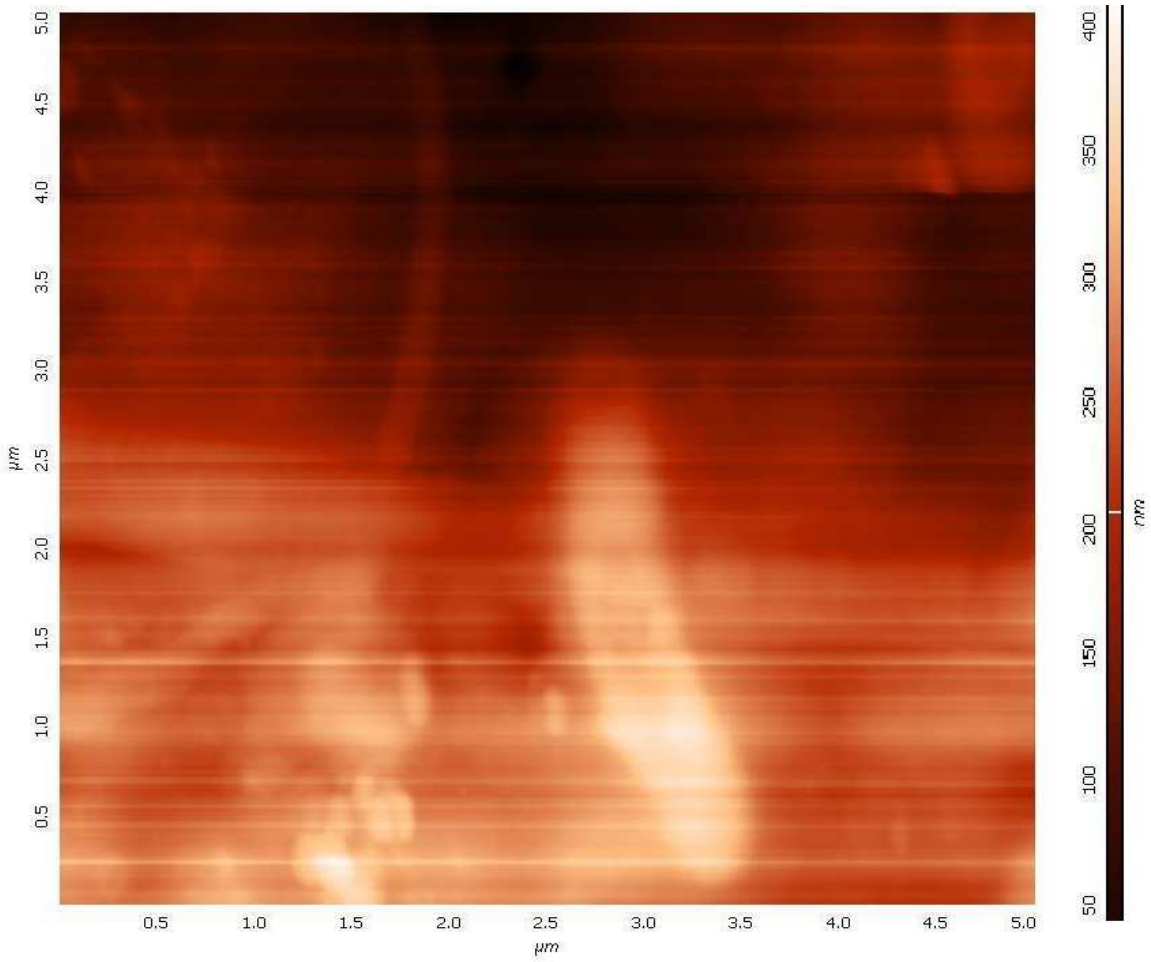
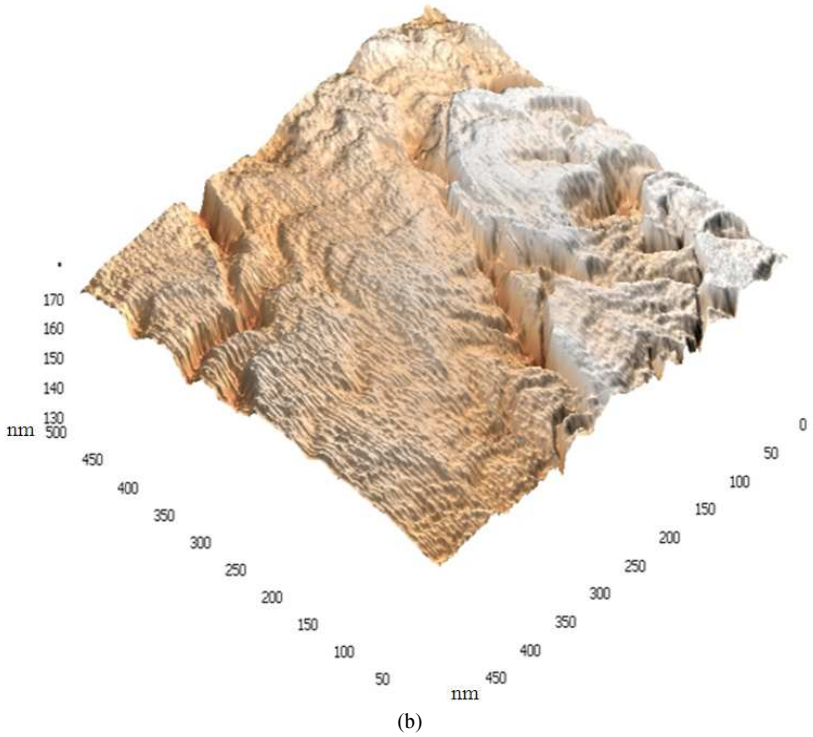



**Fig. 3.** CV of the media before and after inoculation

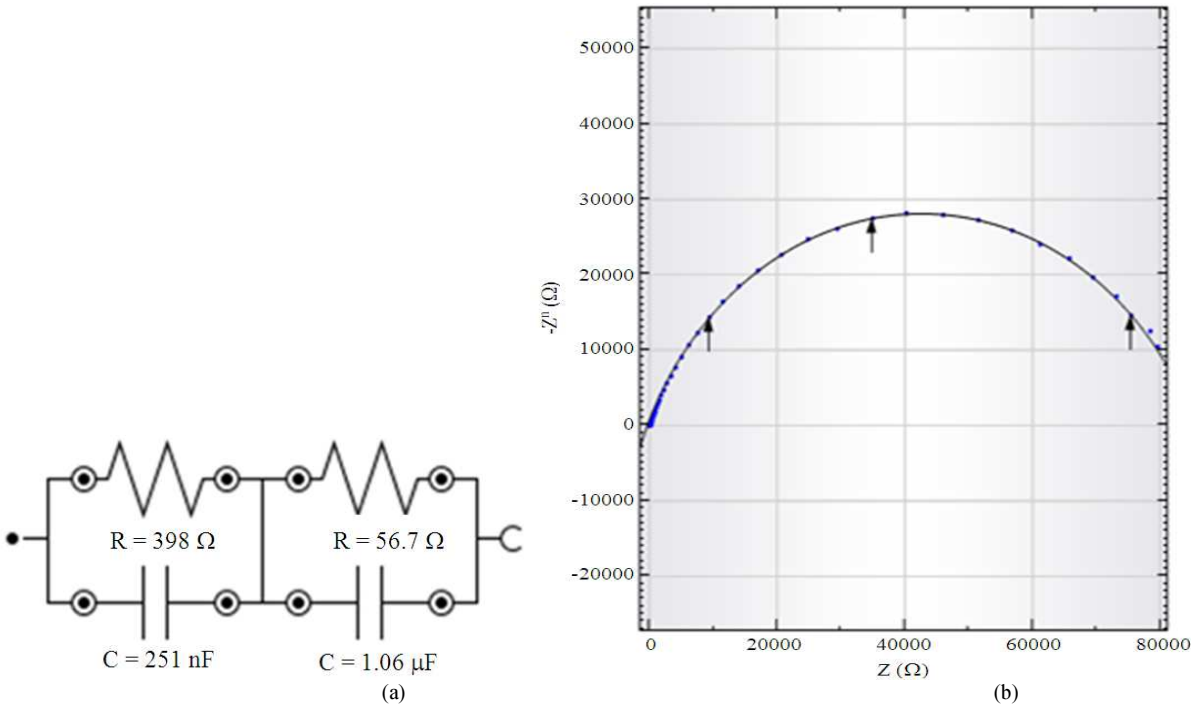



(a)




(b)

**Fig. 4.** (a) Two and (b) three dimensional AFM pictures of the undoped Pani/Ps




(a) (b)

**Fig. 5.** (a) Equivalent circuit for MFCs' electrochemical system with different membranes and (b) EIS result the MFC system

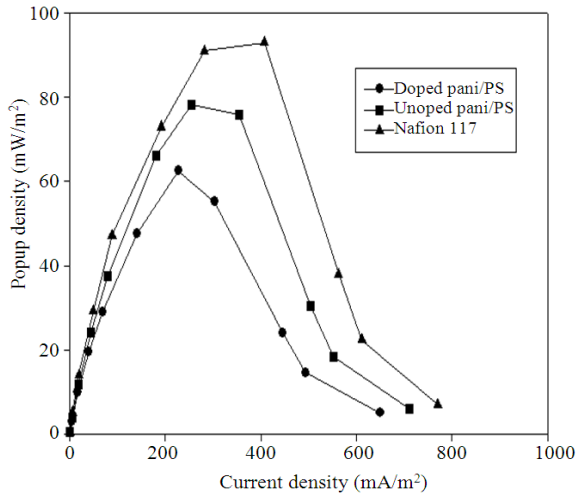



**Fig. 6.** Power density graph of the MFCs

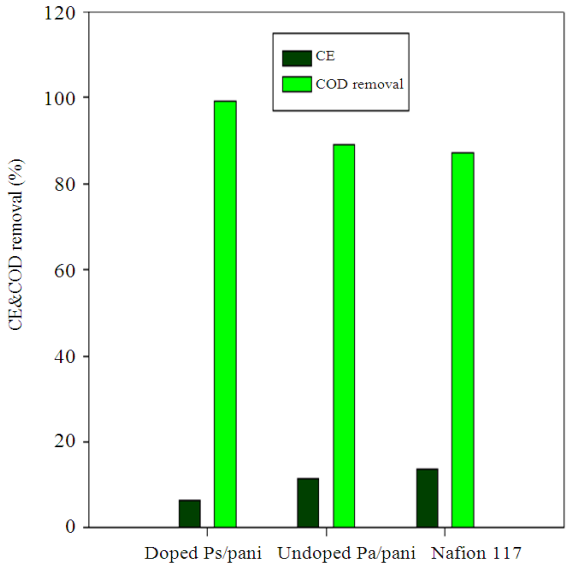



**Fig. 7.** CE and COD removal of the MFC systems

**Table 1.** Pore size and roughness of the membranes

| Membrane | Pore size (nm) | Roughness (nm) |
|---|---|---|
| Doped Pani/Ps | 518 | 11.6 |
| Undoped Pani/Ps | 187 | 28.9 |
| Nafion 117 | 314 | 62.5 |

**Table 2.** Resistance and capacity of the membranes in the MFC system

| Membrane | $R_1$ (Ω) | Capacity ($\mu F_1$) | $R_1$ (Ω) | Capacity ($\mu F_1$) |
|---|---|---|---|---|
| Doped Pani/Ps | 571.0 | 1.05 | 247.0 | 1.05 |
| Undoped Pani/Ps | 398.0 | $251\times10^{-3}$ | 56.7 | 1.06 |
| Nafion 117 | 40.6 | 1.00 | 93.0 | 1.00 |

### 3.4. Resistance of the Membranes

The resistance of the membranes was measured by fitting software of EIS. A sample fitted semi-circle for undoped Pani/Ps was shown in **Fig. 5** and the obtained results were presented in **Table 2**. The protons can pass through the membrane or stay in the membrane to be saved. Clearly, when the membrane resistance and capacity is higher, passing of charges through that is more difficult and causes the decline of membrane performance (Wagner, 2002; Wagner and Gulzow, 2004). As can be seen in **Table 2**, undoped Pani/Ps has the lowest resistance whereas the doped Pani/Ps has the highest resistance. The reason refers to the high conductivity of Pani which has good effect on the proton exchange capability of the Pani/Ps composite membrane. However, since the presence of $H^+$ functional group increases the capacity of doped Pani/Ps membrane, the trapped proton cannot be passed easily.

## 4. DISCUSSION

### 4.1. Power density

The power density graph of the MFC systems was shown in **Fig. 6**. As this figure shows, the MFC with the doped Pani/PS PEM produced 62.5 $mW/m^2$ in 228 $mA/m^2$ which is the lowest power generation compared to Nafion 117 and undoped Pani/Ps. It can be due to the presence of protonic groups ($H^+$) in the structure of the doped Pani/PS membrane (Devanathan, 2008; Takahashi *et al*., 2008). Once the membrane was deprotonated by $NH_4OH$ and formed undoped Pani/PS, the power generation was increased and reached to the 78.1 $mW/m^2$ at 255.2 $mA/m^2$. It means that the power generation increases by 20% with deprotonation of Pani/Ps membrane. The highest power generation was with the Nafion 117 as the common PEM in MFC which was 93 $mW/m^2$ in 407.8 $mA/m^2$.

### 4.2. CE and COD

**Figure 7** shows the coulombic efficiency and COD removal of the MFC systems. As can be seen in all cases, the COD removal is above 80% which shows that the capability of MFCs for wastewater treatment as well as electricity production (Min *et al*., 2005) that was shown in section 4.1. The graph shows that the highest COD removal was for the system working with the doped Pani/Ps. The reason might refer to the passing of some media from the membrane, because higher pore size as well as higher hydrophilicy (Alam *et al*., 2011) of the membrane

compared to the Nafion 117 and undoped Pani/Ps enable the substrate to pass through the membrane and migrate to the cathode. It also makes the oxygen to come to the anode and degrade the organic substrate aerobically and decrease the oxygen demand (Feng and Li, 2003; Min and Logan, 2004). The graph obviously shows that the CE of the undoped Pani/Pa (11.3%) and Nafion 117 (13.6%) PEM are very close together and higher than doped Pani/Ps (5.6%) that is due to better anaerobic condition for degradation of substrates to the electricity. However, due to larger pore size, doped Pani/Ps cannot make the system anaerobic as well as the two other PEMs.

## 5. CONCLUSION

Doped and undoped Pani/Ps nanocomposite PEMs were fabricated and applied in MFC. The study showed that doping of Pani does not have good effect on the performance of nanocomposites PEM, whereas undoped Pani/Polysulfone PEM could generate the power of about 84% of Nafion 117. The improvement of power generation may result from elimination of $H^+$ functional group. That causes easier passing of $H^+$ from the anode to the cathode from the surface of doped Pani/Ps as well as decreasing the pore size of membrane that block the migration of oxygen to the anode that disturbs the MFC operation.

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