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Treatment of two different water resources in desalination and microbial fuel cell processes by poly sulfone/Sulfonated poly ether ether ketone hybrid membrane

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The PS (Polysulfone)/SPEEK (sulfonated poly ether ether ketone) hybrid membranes were fabricated and modified with low and high DS (degrees of sulfonation) for the desalination of brackish water and proton exchange membrane in microbial fuel cell. The results illustrated that SPEEK has changed the morphology of membranes and increase their hydrophilicity. PS/SPEEK with lower DS (29%) had the rejection percentage of 62% for NaCl and 68% for $MgSO_4$; while it was 67% and 81% for PS/SPEEK (76%) at 4 bars. Furthermore, the water flux for PS at 10 bar was 12.41 L m^{-2} h^{-1}. It was four times higher for PS/SPEEK (29%) which means 49.5 L m^{-2} h^{-1} and 13 times higher for PS/SPEEK (76%) with means 157.76 L m^{-2} h^{-1}. However, in MFC (microbial fuel cell), the highest power production was 97.47 mW/m^2 by PS/SPEEK (29%) followed by 41.42 mW/m^2 for PS/SPEEK (76%), and 9.4 mW/m^2 for PS. This revealed that the sulfonation of PEEK (poly ether ether ketone) made it a better additive for PS for desalination, because it created a membrane with higher hydrophilicity, better pore size and better for salt rejection. Although for the separator, the degree of sulfonation was limited; otherwise it made a membrane to transfer some of the unwanted ions.

1. Introduction

Nowadays, it is widely recognised that worldwide water supplies fail, and therefore wastewater (industrial wastewater, brackish water, etc.) becomes valuable as a potential source of water. Since the earliest times, these two major potential resources of water (industrial wastewater and brackish water) have been truly considered as waste and were mostly thrown away and not used as a water source [1,2]. Most water is used for irrigation (above 70%) and direct human use (drinking and washing). For this reason, a need arose for the treatment of wastewaters for human or irrigation use; but sources of water were limited [3].

The nanofiltration technique is becoming an increasingly important technology for its high capability of removing and cleaning all pathogens, multivalent ions, salts, and tiny organic molecules, in contrast to traditional methods such as physical cleaning, etc. also another technique that attracts a great deal of attention in these days is MFC (microbial fuel cell) technique which simultaneously treat the wastewater and produce electricity. MFC is known also as “ waste to wat” means by using wastewater and treatment to produce electricity [4]. Therefore, membranes (especially nanofiltration membranes) are widely used in the treatment

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Abbreviation

PS	polysulfone
SPEEK	sulfonated poly ether ether ketone
FTIR	Fourier transform infrared spectroscopy
NMR	nuclear magnetic resonance
AFM	atomic force microscopy
RSM	root mean square
COD	chemical oxygen demand
CE	Coulombic efficiency
DS	degree of sulfonation

and purification of brackish wastewater, agriculture, and pharmaceuticals to produce drinking water from brackish and salty water. As a result, there is an extensive interest in the development and application of polymeric membranes in industrial works [5–9]. PS (Polysulfone) is the most common polymer employed as a membrane material due to its high glass transition temperature, good mechanical properties and excellent thermal and chemical stability, as well as a very good ability for forming membranes; however, the hydrophilicity of this material limits its application in membrane technology systems and fuel cell also since hydrophobic membranes foul rapidly in the separation, desalination or purification processes. Among all the factors that affect membrane characteristics, membrane surface chemistry and composition play an important role for enhancing the performance of the membrane. Membranes that display high permeation, high rejection, combined with high fouling resistance are now under increased attention for marketing purposes [10,11]. The physico-chemical properties of a polymer, as well as hydrophilicity/hydrophobicity of a membrane, can be changed if the membrane was prepared from the multi-component polymeric mixtures or blends [12]. Among the various polymers that possess diverse mechanical, thermal and electrical properties that also have high crystallinity would be PEEK (poly ether ether ketone). This is due to very strong intermolecular interactions with polymeric chains. As a result, PEEKs are practically insoluble in most of the solvents. Hence, PEEKs are not simply modified in the easy reaction known in organic chemistry and are definitely unable to form porous membranes by traditional phase inversion methods [13–15]. Therefore, it should first be sulfonated by sulphuric acid and then added in small amounts to the membrane for improving the membrane properties. The mechanical and thermal properties of PEEK progressively deteriorated with sulfonation and that formed high term stability; especially for highly sulfonated SPEEK (sulfonated poly ether ether ketone) polymers [16]. As reported in the literature, the enhanced effect of SPEEK was mostly due to its increasingly hydrophilic characteristics and very high conductivity. Since SPEEK displayed the ability to provide sulfonic acid groups ($-SO_3H$) for membranes that had the capability of separating charged molecules (such as salts and proteins), it became a key component of NF membrane development and applicability as well as proton exchange membranes (with a conductivity of about 2×10^{-2} S/cm at room temperature) that want to conduct protons or other cations [17–19]. Moreover, numerous studies illustrated its ability for removing humic substances and impurities from water (surface water) with very low or no fouling properties; this was attributed to the high porosity and high charges of the blend that were associated with SPEEK. Also by changing the degree of sulfonation the capability for exchange the protons will be changed [20]. At 2013, Wentao Yang et al. [21] studied on the control of pore size of membrane and application of the membranes in separation process. They fabricated PAN (polyacrylonitrile) membranes by different acids (glacial acetic acid, fumaric acid and citric acid) with combination of phase inversion and chemical reaction method. The average pore sizes of membranes with different acid contents were 0.1 μm for GA (glacial acetic acid), 0.14 μm for FA (fumaric acid) and 0.17 μm for CA (citric acid). Also the membranes which fabricated with GA, FA and CA had the porosities of 61%, 52% and 52% respectively. The highest water flux related to membrane prepared by GA with about 3700 L $m^{-2}.h^{-1}$ while it was about 2900 and 2300 L $m^{-2}.h^{-1}$ for membranes prepared by FA and CA in the pressure of 0.25 MPa respectively. A porous membrane has been applied in MFC by Rahimnejad et al. [22] in 2012. They have fabricated ferric oxide nanoparticle (Fe_3O_4) with four different compositions (5, 10, 15 and 20% Fe_3O_4) and PES (poly ether sulfone) nanocomposite membranes. The fabricated membranes had pore sizes of 3.9, 5.8, 20 and 39.1 nm respectively while measured membrane roughnesses were reported 31, 47.6,71.9 and 129.23 nm respectively for different compositions of Fe_3O_4 in PES. Finally it was observed that the MFC working with Fe_3O_4 (15%)/PES produced highest power (20 mW/m^2) than other membranes.

In this study, PS and PS/SPEEK composites with two different DS (degree of sulfonation), were used for the separation of salts from water; the flux of pure water and salt water were measured in these membranes; and the rejection percentage of membranes for monovalent and divalent salts was calculated. They were also applied as a separator in MFC to observe the effect of the degree of sulfonation on performance of a porous membrane on the performance of MFC.

2. Experimental

2.1. SPEEK preparation

In order to synthesize of SPEEK, 20 g of PEEK (Poly Ether Ether Ketone) powder (Goodfellow Cambridge Limited, UK) was slowly dissolved in 500 mL of 95–98% concentrated sulphuric acid (R & M Chemicals, Essex, UK). This solution was stirred vigorously until the entire PEEK was dissolved completely. Next, the homogenous solution was continuously and thoroughly stirred at a controlled temperature of 80 °C for 2 and 4 h (in this study) in order to obtain various DS. The SPEEK solution was then poured into a large excess of ice water so as to precipitate the SPEEK. The solid was then collected by filtering the solution through a Whatman filter paper. Finally, the SPEEK was dried at 70 °C to remove any remaining water before use [23].

2.2. Determination of DS

The degree of sulfonation was measured by 1H Nuclear Magnetic Resonance (FT-NMR ADVANCE 111 600 MHz with Cryoprobe) spectroscopic analysis (Bruker, Karlsruhe, Germany). Before measurement, the SPEEK was dissolved in dimethyl sulfoxide (DMSO-d6). The DS was calculated by the following equation:

$$\frac{DS}{S-12 \quad DS} = \frac{A_1}{A_2} \tag{1}$$

Where "S" was the total number of hydrogen atoms in the repeat unit of the polymer before sulfonation, which was 12 for PEEK; A_1(H13) was the peak area of the distinct signal; and A_2 was the integrated peak area of the signals corresponding to all other aromatic hydrogen. To calculate the percentage of the DS (DS %), the answer for DS had to be multiplied by 100 [24,25].

2.3. Membrane preparation

The required amount of SPEEK and PS (3 wt%/97 wt%) were mixed together in N Methyl 2 Pyrrolidone (NMP, >98% Purity) or Dimethyl formamide (DMF, 99.9% Purity) as solutions. Then they were stirred in 60 °C for 2 h until a homogenous solution was achieved [26,27]. The solution was then cast on a glass plate with a casting knife (Filmographe: Doctor Blade 360099003) and was subsequently immersed in a non-solvent bath containing distilled water at 25 °C. The prepared membranes were then automatically separated from the glass. Afterwards, the prepared membranes were kept in the water before use [22].

2.4. Water uptake

Water uptake of the membranes was calculated using the following formula:

$$Water \quad uptake = \frac{M_{wet} - M_{dry}}{M_{dry}} \tag{2}$$

Where M_{wet} and M_{dry} are the weight of the membranes in both wet and dry states, which should be divided by the weight of the dry membrane [28].

2.5. Flux and rejection percentage

The thoroughly washed membranes were first cut into the dead end circular experiment disk that had a 0.049 cm radius. The distilled water was then fed to the disc from a pressure cylinder, and the water flux was calculated after 30 s from the appearance of the first bubble. The water flux was calculated using the following formula:

$$J = \frac{Q}{\Delta t\, A} \tag{3}$$

Where J ($L\, m^{-2}\, h^{-1}$) was the permeation flux of membrane for pure water, Q was the volume of permeate solution (L), Δt was the permeation time in h and A was the membrane area in (m^2).

The rejection percentage of membranes was calculated (based on pure solution of each salt) versus 1 g/l of NaCl and $MgSO_4$ solution by the following:

$$\%R = 1 - \frac{C_P}{C_f} \times 100 \tag{4}$$

Where C_p was the permeating concentration and C_f was the feed concentration [29].

2.6. MFC configuration

Two cubic shaped chambers were constructed from Plexiglas, with a height of 10 cm, width of 6 cm, and length of 10 cm (giving a working volume of 420 ml). They were separated by a PEM (proton exchange membrane). Air was continuously fed into the cathode by an air pump at a rate of 80 ml/min. Both the cathode and the anode projected surface areas of 12 cm^2. The cathode was carbon paper coated with 0.5 mg/cm^2 Pt, and the anode (as described above) was plain carbon paper [30]. Fig. 1 shows a schematic of an MFC. The cathode and the anode were separated by a PEM (ex: PS/SPEEK). The system was connected to a multimeter and data are collected in a computer.

2.7. Enrichment

Palm Oil Mill Effluent (POME, Indah Water Konsortium) anaerobic sludge was used for the inoculation of MFCs. The media contained 5 g of glucose, 0.07 g of yeast extract, 0.2 g of KCl, 1 g of $NaH_2PO_4.4H_2O$, 2 g of NH_4Cl, 3.5 g of $NaHCO_3$ (all from Merck company), 10 ml of Wolfe's mineral solution and 10 ml of Wolfe's vitamin solution (added per litre). All the experiments were conducted in an incubator at 30 °C. Furthermore, the cathode chamber contained a phosphate buffer solution, which consisted of 2.76 g/l of NaH_2PO_4, 4.26 g/l of Na_2HPO_4, 0.31 g/l of NH_4Cl, and 0.13 g/l of KCl (all from Merck company) [31].

2.8. Calculation

Nicolet 5700 FTIR (Thermo Electron, USA) was performed to identify the functional group of the PEEK and SPEEK membrane. Scanning Electron Microscopy (SEM, Supra 55vp-Zeiss, Germany) employed to observe the attachment of microorganisms onto the surface of the anode electrode. Moisture had to be removed from the biological samples (POME mix culture sludge) by critical drying. They were then coated with a conductive material (such as gold or carbon), with a thickness of approximately 20–50 nm, in order to make them conductive for the SEM analysis and also for observing the surface and cross-section of the membranes under magnification of 10,000x. Due to observing the cross-sections, the membranes were cut using nitrogen gas (N_2) and coated with a 30–50 nm thickness of gold [32].

To measure the COD (chemical oxygen demand), the samples were first diluted 10 times and mixed with 2 ml of diluted samples with a digestion solution of a high-range COD reagent, then heated at 150 °C for 2 h in a thermo reactor (DRB200), which was read with a spectrophotometer (DR 2800). The voltage was measured using a multimeter (Fluke 8846A), and the power density curve was obtained by applying different loads to the system and calculating the power at different loads [33].

The current was measured using the equation:

$$I = \frac{V}{R} \tag{5}$$

Where I is the current (amps), V is the voltage (volt), and R is the applied external resistance (ohm).

The power density was calculated using the following equation:

$$P = R \times I^2 \tag{6}$$

Where R is the applied external resistance (ohm) and I is the current (amps) (calculated using Eq. (1))

The CE (Coulombic efficiency) is the percentage degradation of organic materials that is converted to electricity and is calculated as current over time until the maximum theoretical current is achieved. The evaluated CE over time was calculated using the following equation [34]:

$$CE = \frac{M \int_0^t I\, dt}{F\, b \quad V_{an}\, \Delta COD} \tag{7}$$

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 liquid in the anode compartment, and ΔCOD is the change in the COD (chemical oxygen demand) over time, *'t'*. All experiments were conducted at least three times (average values or typical results are presented

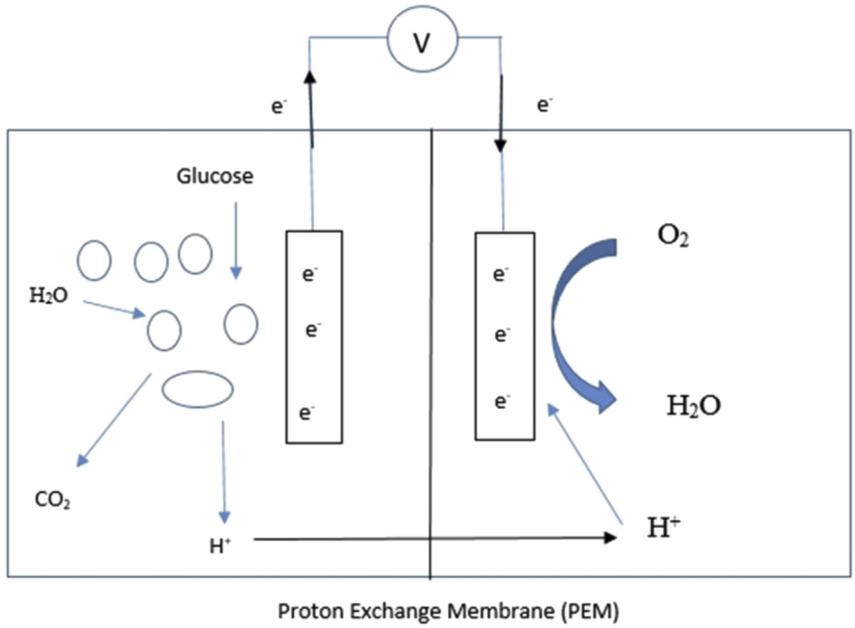

Fig. 1. Schematic of an MFC.

below). NOVA software (version 1.0.26.1443) was used to measure and calculate porosity after obtaining AFM (atomic force microscopy) from our membranes. The data are then processed using Eq. (8) [35].

$$\%Porosity = \int \frac{A_n}{S} \times 100 \tag{8}$$

Where, S is the total surface of a typical sample, A is the surface area of each pore, and n is the number of pores (the device detect them). All information is produced using NOVA software. Porosity is in the range of 0–100%.

2.9. Analysis

Nicolet 5700 FTIR (Thermo Electron, USA) was performed to identify the functional group of PS and PEEK membranes. Scanning electron microscopy (SEM, Supra 55vp-Zeiss, Germany) was implemented to observe the surface and cross section of membranes. The Veeco Multi-Mode SPM with a Nanoscope V controller was utilised to characterise the surface roughness of the membrane and pore size and porosity. The small squares of the prepared membranes were cut and glued on metal substrates. The membrane surfaces were examined in a scan size of 5 μm × 5 μm. All measurements were performed on dried membrane samples under ambient atmospheric conditions and the membrane surface was imaged in the tapping mode.

In order to determine the hydrophilicity of each membrane, their contact angles were measured. The contact angle is the angle at which a liquid/vapour interface meets a solid surface. Generally, it is the result of surface free energies composed of liquid, solid, and surrounding vapour. To measure the contact angle, first, a water droplet was placed on the membrane's surface using a syringe; next, the contact angle was measured with a contact angle metre (Kruss, DSA30B) [14]. All desalination and MFC experiments were repeated three times and their average values were reported.

3. Results and discussion

3.1. Characterization of membrane

3.1.1. FTIR Analysis

Fig. 2 shows the FTIR analysis of PEEK and SPEEK. The figure shows that the absorbance graph was quite similar, and the biggest difference was at 3200–3500 cm^{-1} wavelength. However, there were some small peaks at 1235, 1083, and 710.55 cm^{-1}. The difference between them was proved by these peaks to be the introduction of SO_3^- group by sulfonation to the PEEK. These SO_3^- groups were introduced after the PEEK was blended with the sulfonated groups. The other peaks belonged to the polymer and OH group, which was therefore a good choice for membrane fabrication. The peaks at 3443.24 cm^{-1}, 1253.55 cm^{-1}, 1083.37 cm^{-1}, 1026.35 cm^{-1}, and 710.55 cm^{-1} were assigned to the stretching of the O–H group,

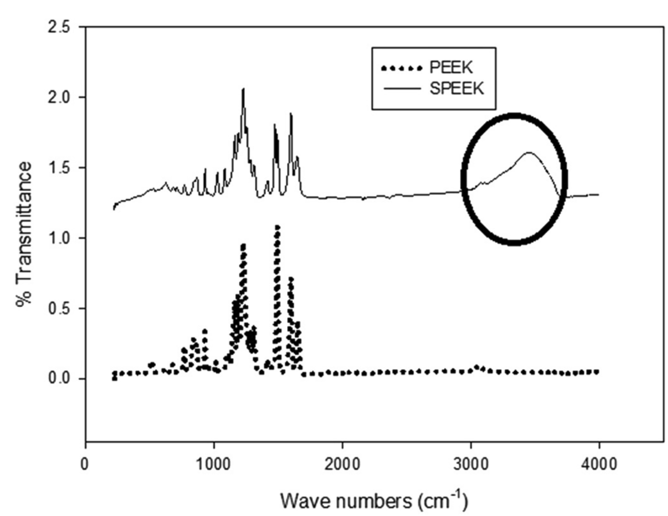

Fig. 2. FTIR spectra of PEEK and SPEEK.

asymmetric stretching of O═S═O, symmetric stretching vibration of O═S═O, stretching of S═O, and stretching of S–O of the sulfonic acid group in SPEEK, respectively [36].

Moreover, the peak at 1491.93 for PEEK was C–C group, which was converted to two new peaks of 1473.06 and 1492.31 at SPEEK due to the substitution of sulfonic acid groups.

3.1.2. DS (degree of sulfonation) of SPEEK

Fig. 3 presented the DS of the SPEEK where A_1 equalled to 1 and A_2 equalled to 13.88. The degree of sulfonation of the SPEEK after 4 h in sulphuric acid was equal to 76%. After 2 h, the SPEEK had the DS of about 29%. After 4 h, the polymer cannot be formed. The highest amount of DS was 76%. This meant that mixing PEEK and sulphuric acid for more than 4 h will spoil the structure of the polymer that was in the main matrix of the membrane.

3.1.3. Membrane morphology

As studied, membrane morphology is one of the most important characteristics of membranes that affect membrane performance and the separation process. Membranes are generally formed under the influence of several factors; which mostly contain interactions of polymers, solvents and non-solvents, and casting rate. The morphology of membranes is also an important feature of water sorption, mobility, rejection, and selectivity. The surface of the studied membranes are shown in Fig. 4(a–c). As can be seen in the figures, the surface of PS does not show high porosity (Fig. 4a). Meanwhile, the porosity was increased in PS/SPEEK to 29% and reached very high at 76%. The PS/SPEEK (76%) shows that the degree of porosity is very high and more homogeneous than other studied membranes [37]. PS/SPEEK showed a lower porosity with an approximately larger diameter, which was also the same for PS. The structures of the membranes are illustrated by their cross-sections in Fig. 4(d to f). Fig. 4d represents the cross-section of PS shown as a sponge-like structure. Meanwhile, it's converted finger-like structure, with many macro voids in PS/SPEEK hybrid membranes, is shown in Fig. 4e and f. The macro void and finger type structures are the result of fast coagulation. The PS/SPEEK, with high DS has more macro voids and finger type structures [27]. This means that the size of the pores and the number of finger like structures decreased; while the number of them increases. This

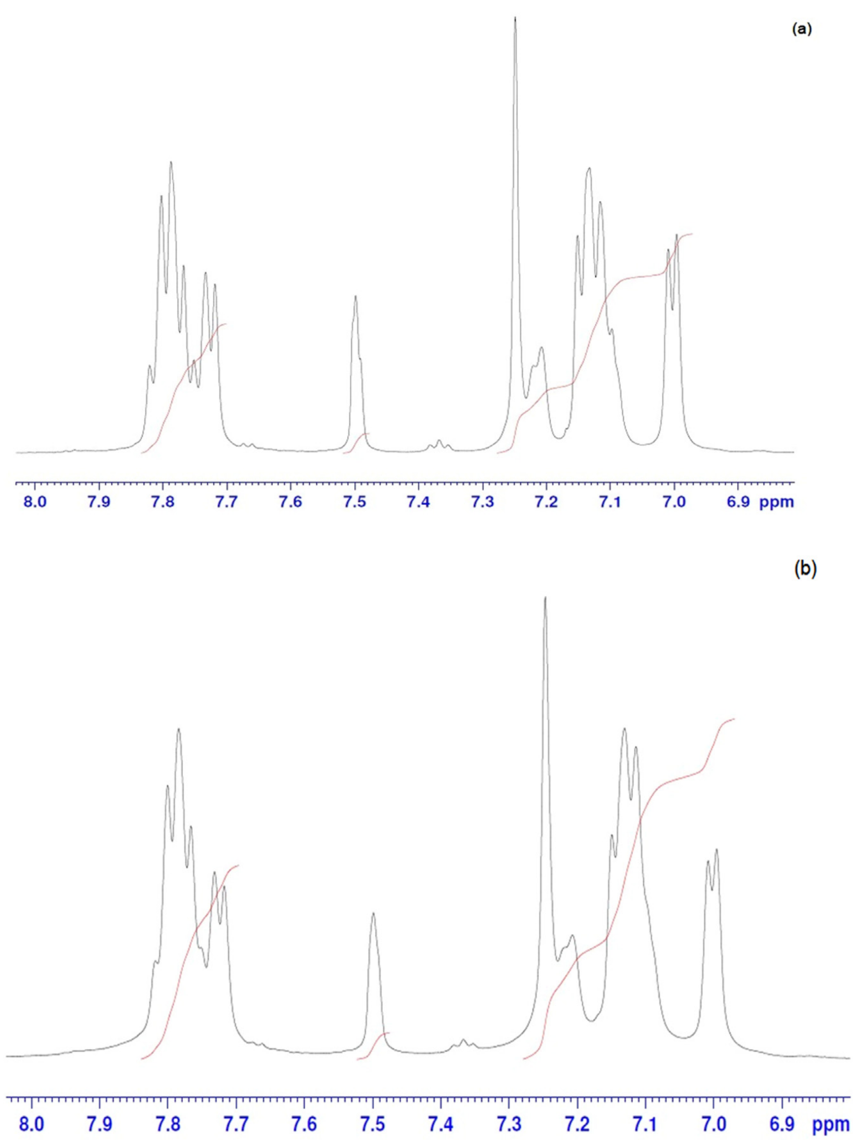

Fig. 3. NMR results of a) SPEEK (29%) and b) SPEEK (76%).

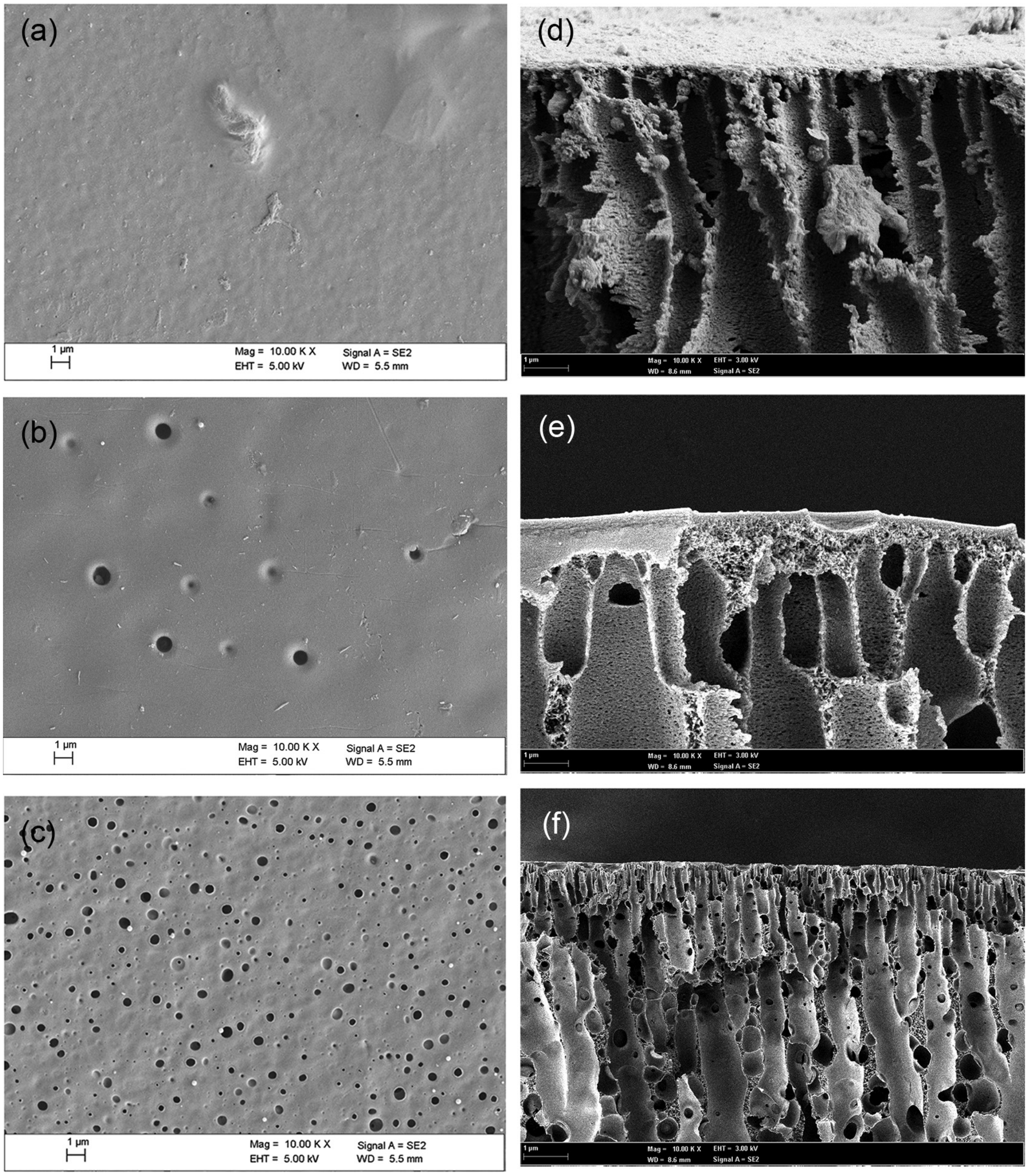

Fig. 4. SEM image of the cross section of a) surface of PS, b) surface of PS/SPEEK (29%) c) surface of PS/SPEEK (76%) d) cross section of PS e) cross section of PS/SPEEK (29%) f) cross section of PS/SPEEK (76%).

may be the result of high numbers of higher DS, which causes higher hydrophilicity and faster coagulation. The macro voids and finger like structures are an important factor in water flux, permeability, the rejection of salts and the selectivity of membranes [38].

3.1.4. Contact angle

The contact angle was defined as the angle that was conventionally measured through the liquid once its interface met a solid surface and created an angle. In reality, it presented the wettability of the solid surface. As can be seen from the table below (Table 1), the PS/SPEEK with 76% DS had the lowest contact angle, which meant that it had the highest tension for wettability and resulted in the highest hydrophilicity. Next, by decreasing the DS, the contact angle increased to 54.2°, and the highest contact angle belonged to pure PS with 62°. This signified that the elevation of DS directly affected the hydrophilicity of membranes and caused an increase.

3.1.5. Water uptake

The Water uptake of membranes, is one of the most important characteristics defined as the number of water molecules per

Table 1
Contact angle of different membranes.

Membrane	Contact angle (θ°)
PS	62
PS/SPEEK (29%)	54.2
PS/SPEEK (76%)	48.8

hydrophilic groups of membranes. In fact, water uptake measures the swelling behaviour of the membranes. Water uptake was influenced by several factors: pre-treatment of membranes with different agents, hydration rate, hydrophilic and hydrophobic groups attached to the membranes and temperature of the water. Higher water uptake revealed a higher ability for proton conductivity of membranes. Furthermore, it exhibited the ability of membranes to absorb water. Barragan et al. [39] and also Ilbeygi et al. [20] reported that water uptake, or the ability of a membrane to absorb water, enhanced the membrane proton conductivity.

Fig. 5 presents the water uptake of different membranes. The figure demonstrates the PS/SPEEK (76%) with the highest DS had the highest water uptake of 37%, followed by PS/SPEEK (29%) with water uptake of 22%. The lowest water uptake belonged to PS (5%). This illustrates that when the hydrophilicity of membranes increased, their water uptake also increased. This was due to the tendency of membranes to keep and adsorb water.

3.1.6. Membrane roughness and porosity

AFM was used as the topography of membranes that determined the amount of their characteristics. For the measurement of membrane roughness, pore size and porosity, AFM was employed. The AFM revealed that PS had the pore size of about 268 nm. However, with the addition of the SPEEK, the morphology and roughness of membranes were altered. The PS/SPEEK (24%) had smaller pore size of about 89 nm. It was interpreted that the addition of SPEEK was mostly absorbed on the top layer of the membranes since SEM and hydrophilicity had also reported the same results, confirming this effect. By the addition of the SPEEK with the highest DS (76%), the pore size was again decreased to around 26 nm. It meant that the top layer of PS/SPEEK (76%) was denser than all the membranes, and also, its selectivity was higher (Fig. 6).

The amount of porosity was also reported in Table 2. As shown, the porosity was similar to the pore size, following a rule. The highest porosity, as expected, belonged to PS/SPEEK (76%) which was around 71%, followed by PS/SPEEK (26%) which was 48% and PS which had the lowest porosity of 33%. It represented the SPEEK's effect on membrane morphology.

The table reports that, the number of mountains and valleys increased with the addition of SPEEK which also increased the DS; therefore, the surface of membranes displayed a smoother shape. The SEM displayed this by showing a decrease in the dense layer,

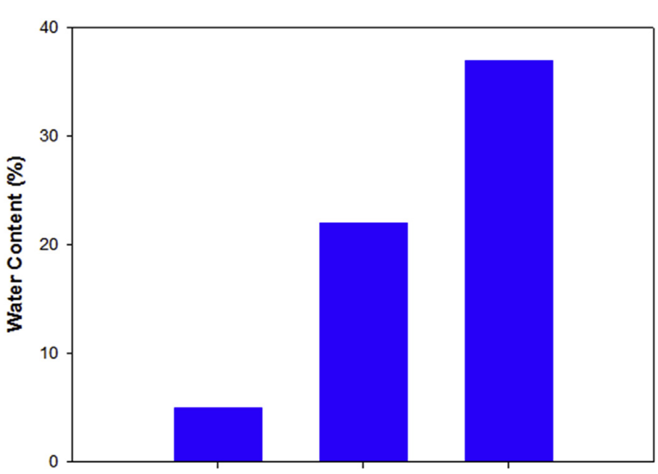

Fig. 5. Water content of different membranes.

which was at the top of the membrane. The random height of the macroextracture was mostly measured by the RMS, and as expected, it followed the same order since the highest and roughest was for PS and the lowest was for PS/SPEEK (76%).

4. Results and discussion

4.1. Application of membrane for desalination

4.1.1. Pure water flux

The pure water flux of different membranes in the range 1–10 bars was shown in the Fig. 7. The figure presents the increase of pure water flux by applying the PS/SPEEK hybrid membrane to PS pure membrane. This may be due to the higher hydrophilicity of hybrid membranes than pure PS. By increasing the pressure to 10 bars, the flux for the PS was approximately 12.4 L m^{-2} h^{-1}. By applying PS/SPEEK (29%), the amount of water flux increased four times and reached to 49.7 L m^{-2} h^{-1}. Interestingly, it increased to 154.7 L m^{-2} h^{-1} for PS/SPEEK (76%) which was more than three times of PS/SPEEK (29%). The large effect of DS was displayed by this result. The higher hydrophilicity, higher porosity, as well as, lower RMS may result to the increment in water flux. This may also be due to the introduction of new –OH groups to the surface of membranes with higher DS. It means that by PS/SPEEK (76%) hybrid membrane, the higher flux can be achieved in the lower pressure than PS/SPEEK (29%) and after that neat PS and so the desalination system needs lower pressure and energy for treatment of brackish water by PS/SPEEK (76%).

4.1.2. Salt rejection

Fig. 8 shows the rejection percentage of NaCl and $MgSO_4$ salts with different membranes at 4 bars. Two salts were tested in this experiment: the first was monovalent salt and the second was divalent salt. As expected, from the mass transfer phenomenon, the rejection percentage of divalent salt ($MgSO_4$) was higher than the monovalent salt (NaCl) in all 3 membranes [13,40]. This may be due to the fact that divalent ions (Mg^{2+}, SO_4^{2-}) had more ionic charge than Na^+Cl^- which caused more rejection; especially with the PS/SPEEK hybrid membranes since they contain SO^{3-} and OH^- groups. The rejection percentage of NaCl for the PS, PS/SPEEK (26%) and PS/SPEEK (76%) was 34%, 62% and 67%, respectively, while for $MgSO_4$ it was 34.8%, 68% and 81%; similar to previous membranes. It should be noted that the rejection percentage of NaCl and MgSO4 was almost the same for PS membrane means 34% and 34.8%, respectively. Their difference increased when PE/SPEEK (29%) was applied –62% and 68%-, and reached the maximum when PS/SPEEK (76%) was the membrane for desalination which was (67–81%). The results displayed the difference of membranes in brackish water desalination and prove that by increasing the DS of SPEEK in hybrid membranes, the rejection properties revealed the capability of membranes to increase in the water purification [41].

4.2. Application of membrane in MFC

During the next steps, the self-fabricated membranes were applied in MFC to observe their efficiency in wastewater treatment and energy production.

4.2.1. Power generation and polarization curves

Fig. 9 shows power generation and polarization curve membrane graphs. The goal of applying these membranes in MFC is to find how much energy they will produce and the capability of systems for wastewater treatment. As the figure shows, PS/SPEEK (29%) produced 97.47 mW/m^2, which was the highest amount of produced electricity of all applied membranes. The next MFC was

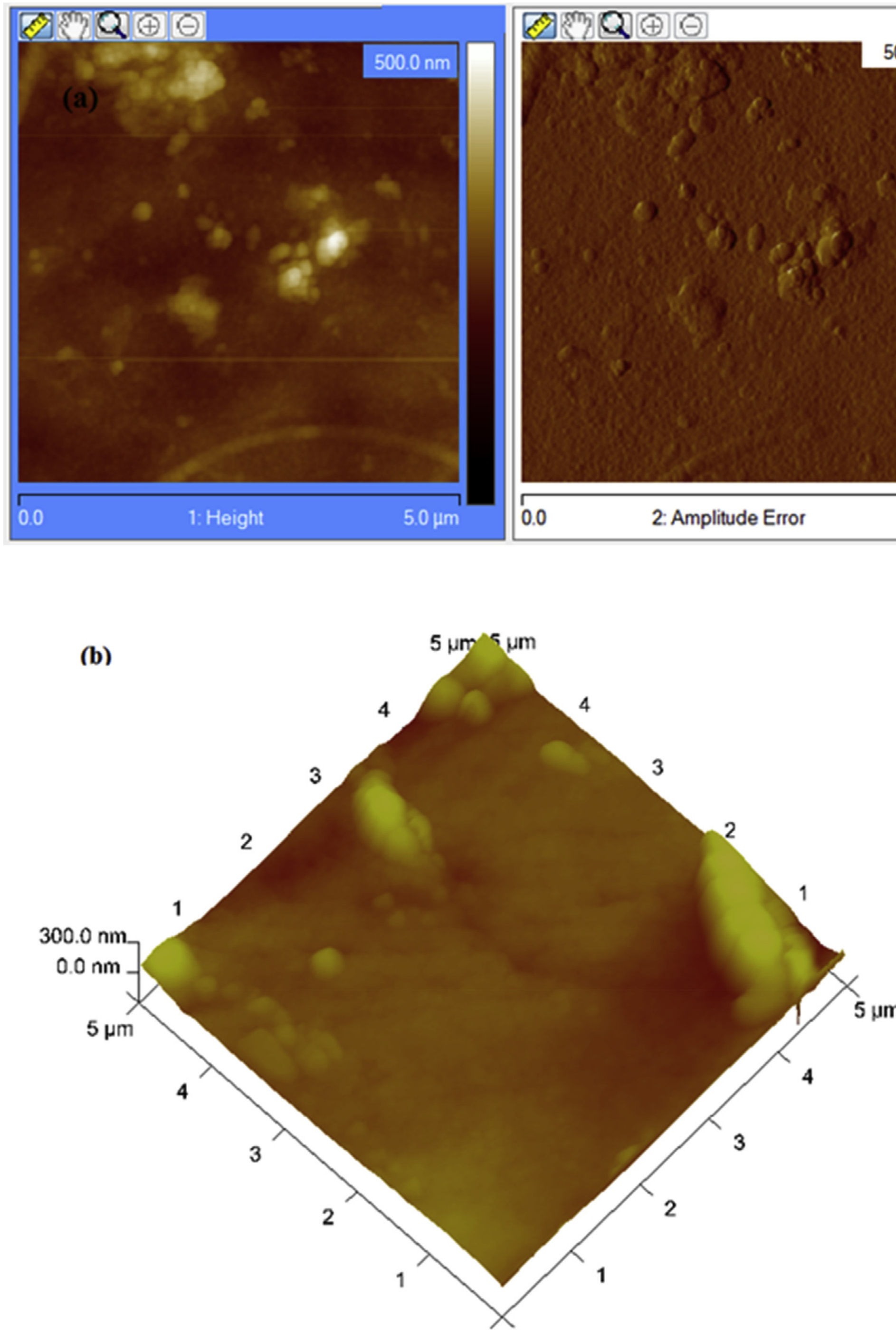

Fig. 6. AFM pictures of PS/SPEEK (29%) a) 2D-image, b) 3D-image.

PS/SPEEK (76%), which produced 41.42 mW/m^2 and the lowest produced energy (15.4 mW/m^2) was with MFC which was working by PS as membrane. However, as previously mentioned, the PS/SPEEK (76%) should have a higher proton exchange capacity; but the PS/SPEEK (29%) had a higher power output. This may have been because the PS/SPEEK (76%) eased the passing of protons and other cations, as well as media such as Na^+; K^+ etc., which disturbed the power production system [42]. The final power production belonged to the system working with PS and had lowest proton conductivity and ion exchange capacity. The polarization curves for the systems are shown in Fig. 9b. The polarization curve was used to identify the system's resistance. In fact, the first part of the system is activation positional and the second is internal resistance. As the figure shows, the different systems had almost the same activation potential. However, the amount of internal resistance of

Table 2
Average pore size, roughness, porosity and RMS characteristics of membranes.

Membrane	Average pore size (nm)	Porosity (%)	Roughness (nm)	RMS (nm)
PS	268	33	548	303
PS/SPEEK (29%)	89	48	172	94
PS/SPEEK (76%)	26	71	88	35

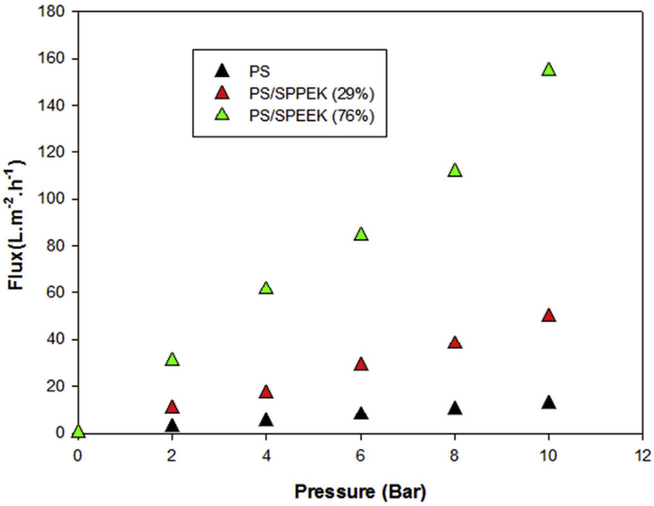

Fig. 7. Water flux of different membranes at different pressures.

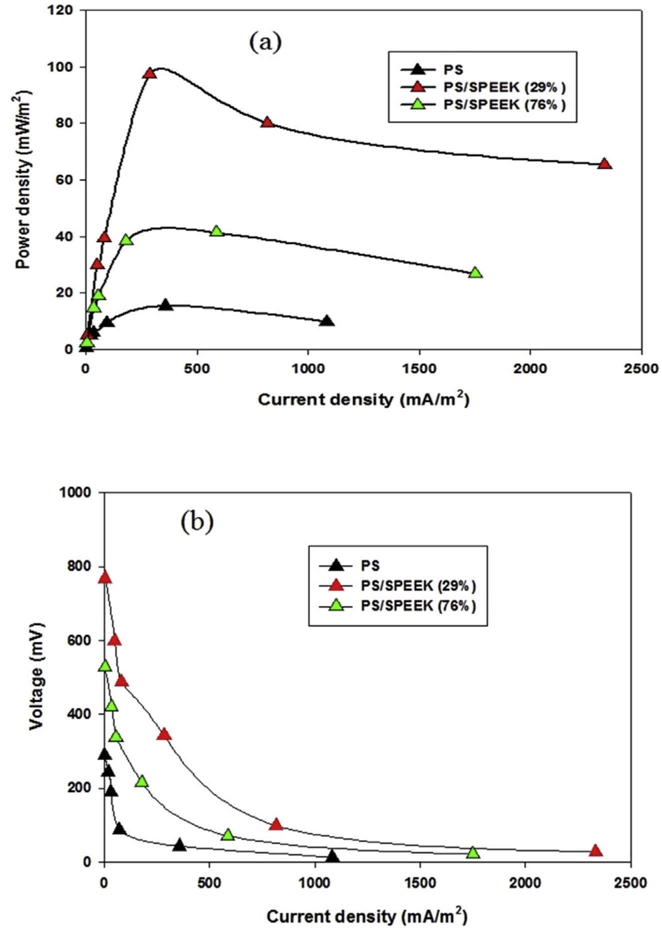

Fig. 9. a) Power density and b) Polarization curve of the different MFC systems.

the systems was 1342.4, 1535.7, and 1512.7Ω for PS, PS/SPEEK (29%), and PS/SPEEK (76%), respectively. The calculations show that the internal resistance of the systems were also almost the same. The slightly higher internal resistance of the PS/SPEEK (29%) can be attributed to higher activity, fouling problems (i.e., biofouling and mineral fouling), and ruining of the membrane's structure due to facing more cathode and anode media and solutions. The polarization curve was drawn for the MFC in a stable condition whilst working [43].

4.2.2. COD removal and CE

The COD removal and CE of the systems, working with different membranes, is shown in Fig. 10. As can be seen, the highest COD removal was 99% for PS/SPEEK (76%); and 86% and 57% for PS/SPEEK (29%) and PS, respectively. This may be due to the passing of some ions from PS/SPEEK (76%), which aided degradation by the oxygen that purged into the cathode. Furthermore, the CE, which is the fraction of coulomb produced to the total theoretical coulombs of the substrate of the system, was 22.4, 12, and 5% for PS/SPEEK (29%), PS/SPEEK (76%) and PS, respectively. This was because the consumption of organic substrate in the PS/SPEEK (29%) was for electricity production — unlike PS/SPEEK (76%), which was for oxygen crossover from the cathode to anode, for degradation. Because of a weak transfer of ions and conductivity, PS had the lowest CE.

Table 3 the reported data were taken from the systems used in the desalination and MFC processes. Simple comparison identifies which system works better; and is therefore, proper for use. These proper systems are highlighted in red in the table [44,45].

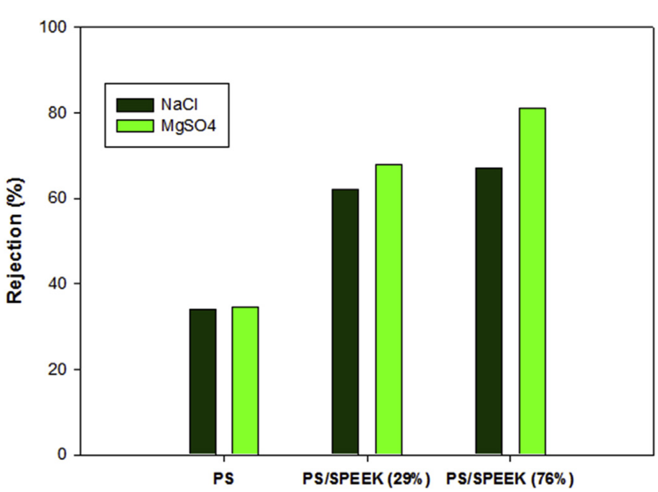

Fig. 8. Rejection percentage of NaCl and $MgSO_4$ of different membranes at 4 bars.

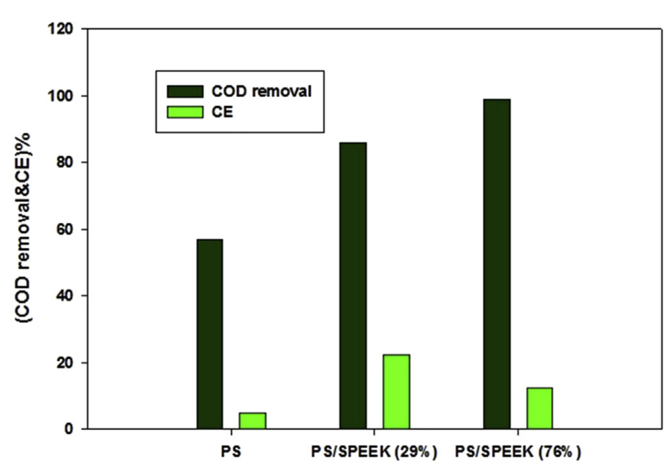

Fig. 10. COD removal and CE of the systems.

Table 3
Summary of data taken from the systems in desalination and MFC.

Membrane	P_{max} (mW/m^2)	I_{max} at P_{max} (mA/m^2)	COD removal (%)	CE (%)	Flux (L m^{-2} h^{-1})	Permeability (L.m^{-2} h^{-1} bar^{-1})	Rejection (%)	
							NaCl	$MgSo_4$
PS	15.4	358.3	57	4.8	5.1	1.244	34	34.5
PS/SPEEK (29%)	97.47	285	86	22.4	16.8	4.88	62	68
PS/SPEEK (76%)	41.42	587.5	99	12.5	61.3	14.85	67	81

5. Conclusion

The fabrication of PS/SPEEK blended membranes, for the desalination of brackish water and for application in MFC using self-fabricated membranes, was successfully demonstrated here.

From this study, it can be concluded that:

a) The best degree of sulfonation of SPEEK, for the desalination of brackish water, was 76%. For desalination purposes (as expected), the divalent salts had a higher rejection percentage than the monovalent salts. Further studies are essential to optimise the DS and maximise the desalination performance.
b) However, for MFC, increasing DS will increase the proton exchange capability, but different cations, such as Na^+, K^+ etc., in the media, other than proton, the increment of DS for reaching the best performance is limited at 29%.
c) It has been found that, the degree of sulfonation will increase the hydrophilicity, conductivity and ion exchange capacity of membranes. This makes it a useful method for making better membranes for desalination purposes (in lower pressure, cause higher flux of water and higher rejection percentage of salt ions). Meanwhile, the DS has limitations for use in biological fuel systems; because there are several useless cations (Na^{2+}, K^{2+},Ca^{2+}, Mg^{2+}, NH^{4+}) within the media that are transferred to the cathode.
d) In this research, application of a membrane in different processes of desalination and MFC were compared. It can be generally concluded that, one type of porous membrane can be used for both desalination and MFC. So in desalination it needs lower energy for purification of water and in MFC produce higher energy (Electricity). However, it should be prepared for each of these applications by different functionalizing methods. Even though this means that the type of membrane for these actions can be same, the membranes must undergo different processes to reach their optimized performance for each application.

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