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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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ABSTRACT

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].