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1 **Enhancement of microbial fuel cell efficiency by incorporation of graphene oxide and**
2 **functionalized graphene oxide in sulfonated polyethersulfone membrane**

3

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19

20 **Abstract**

21 The present work examines, for the first time, the use of thiolated graphene oxide (TGO), in
22 polyelectrolyte composite membranes as an effective approach to enhance the MFC
23 performance. A new composite membrane based on a sulfonated polyethersulfone (SPES)
24 hybrid with GO, sulfonated GO (SGO), and TGO was fabricated and assessed in MFC. The
25 blend membranes were characterized with various techniques. The sulfhydryl (-SH) and
26 sulfonic (-SO₃H) groups enhanced the proton selectivity of the membrane and MFC

27 performance. The MFC using the SPES/SGO1.8% composite membrane generated a power
28 density of 66.4 mW/m² which was double that produced by MFC using Nafion117 membrane
29 in batch mode which lasted for 8 days. The SPES/SGO membrane was more selective
30 towards H⁺ rather than other cations (K⁺, Na⁺, and Li⁺). This was also confirmed by the
31 results of proton conductivity analysis, as the SPES/SGO1.8% membranes showed a value of
32 1.42 mS/cm which was higher than Nafion117 (1.3 mS/cm), SPES/TGO1.8% (1.25 mS/cm),
33 SPES/GO1.8% (0.56 mS/cm), and SPES (0.32 mS/cm). The higher COD removal and
34 coulombic efficiency were obtained in MFC with SPES/SGO membranes. In conclusion, it is
35 our view that the new SPES/SGO and SPES/TGO membranes can be applied favorably in
36 dual-chamber MFCs meeting their needs.

37 *Keywords:* Microbial fuel cell; Functionalized GO; Proton exchange membranes; Electricity
38 generation

39

40 **1. Introduction**

41 During the last decades, the depletion of fuel resources and a global movement toward a more
42 sustainable future, have encouraged researchers to seek technologies combined with a
43 renewable energy approach. One of the promising approaches is to try to extract energy and
44 material from waste and wastewater. Among the bio-based methods, bioelectrochemical
45 systems have attracted interest due to their potential in the generation of clean energy. A
46 microbial fuel cell is a type of bioelectrochemical system that utilizes microorganisms to treat
47 the wastewater simultaneously with electricity generation [1]. This is the field of study that
48 deals with harvesting clean energy from waste, which receives growing appeals for its eco-
49 friendly approach and promising efficiency. There are different types of MFC as dual-
50 chamber, single-chamber, wetland, soil MFC, etc. [2–4]. Generally, in a dual-chamber MFC,
51 membranes are placed between two compartments of anode and cathode, and are responsible
52 for physical separation, avoiding the substrate and oxygen crossover, as well as facilitating

53 the proton transport. There are various types of separators used in MFCs including anion
54 exchange membrane (AEM), cation exchange membrane (CEM), and bipolar membranes [5–
55 9]. For decades, Nafion[®] has been among the most popular commercially used CEM for the
56 bioelectrochemical system, which provides the transportation of protons and other cations. It
57 contains the negatively charged sulfonated group which defines its high proton conductivity
58 at the same time with an undesirable affinity for other cations as well that cause a pH
59 imbalance [10]. Additionally, Nafion[®] associates with other limitations as high price (\$1500
60 m⁻²), substrate loss as well as oxygen leakage [11]. Unfortunately, oxygen crossover may
61 decrease the coulombic efficiency and result in lower power density and inaccurate
62 measurement.

63 The MFC field is maturing, with a wealth of well-understood methods and ongoing research.
64 One of the main issues concerning the potential use of a dual-chamber MFC is the desirable
65 separation of two compartments. The membrane investigation has met with great success in
66 many aspects [11–13], but there are still many options to consider to replace the commercial
67 Nafion[®] and overcome its previously mentioned limitations [14–16]. The authors have
68 conducted a comprehensive review of the PEMs applied in a dual-chamber MFC during the
69 last 12 years [5], which provides the team with a strong background to continue the research
70 on the membranes. We have also developed a sulfonated polyether ether ketone/graphene
71 oxide (SPEEK/GO) membrane in an MFC as a PEM [17].

72 One approach to investigating the alternative material for developing novel membranes is to
73 employ the functionalized polymers either alone [18–20] or by combining with other
74 polymers [21–23] or nanoparticles [21,24] like SiO₂ [25], TiO₂ [26], GO [27,28], metal-
75 organic framework [29], etc.

76 Among these materials, Graphene oxide (GO) has attracted attention due to its significant
77 characteristics which allow researchers to utilize it in membrane structure. GO is a two-
78 dimensional nano-sheet functionalized carbon-structured material, the functionalized groups

79 allow its better interaction with a polymer matrix [30]. This material could even become
80 more of interest by grafting other nucleophilic species having nitrogen and sulfur [25,31–35].
81 The negatively charged structure of GO matches desirably with its application in the
82 formation of CEMs incorporating aromatic ionomers such as SPEEK, SPES, SPS [36–39].
83 Functionalization of GO is of great importance due to its better synergic mechanism with
84 polymers, and even higher solubility in casting solution [40] as inorganic fillers. Sulfonated
85 GO (SGO) is one of the GO derivatives which is functionalized with sulfonic groups (SO_3^-).
86 This provides GO with proton-conducting channels in the membrane matrix to enhance
87 efficiency as well as the ion exchange capacity [41]. Recently, the SGO was applied as fillers
88 in sulfonated poly(arylene ether sulfone) membranes and resulted in an efficient proton
89 conductivity of the composite membranes and high physical stability [42].
90 Another functionalized form of GO is via the thiolation (TGO), which means adding the -SH
91 groups to the structure of GO, this is also an approach to establish the negatively charged
92 channels facilitating the proton transport. A thiol functionalized reduced GO (TrGO) was
93 synthesized by refluxing GO with phosphorus pentasulfide as a novel base material for
94 graphene-nanoparticle hybrid materials [43]. Recently, TrGO developed as an efficient ion-
95 to-electron transducing layer for durable solid-contact ion-selective electrodes [44].
96 In the current paper, we have developed novel membranes based on the incorporation of GO
97 and its functionalized form (SGO and TGO) into the sulfonated polyethersulfone polymer
98 matrix. This research addresses the need for developing some cost-effective, proton-selective,
99 conductive, and efficient membranes that could alternate the use of commercial membranes
100 in an MFC. As far as we know, no previous research has compared the various functionalized
101 forms of sulfonated and thiolated GO in terms of their suitability to be used in the structure of
102 a PEM, as well as their first application in an MFC. With this aim in mind, in this paper we
103 present a full comparison of the as-synthesized membranes through the characterizations
104 including water uptake, cation exchange capacity (CEC), transference number, contact angle,

105 zeta potential, proton conductivity, and morphological studies, we also compared the result
106 with the commercially available membrane of Nafion117[®].

107

108 **2. Material and methods**

109 *2.1. Chemicals*

110 Polyethersulfone (PES Ultrason E6020P with MW = 58000 g/mol) was supplied by BASF
111 Company. Sulfuric acid (H₂SO₄), hydrochloric acid (HCl), chlorosulfonic acid (CSA),
112 dimethylformamide (DMF), and dimethylacetamide (DMAc), sodium hydroxide (NaOH),
113 sodium chloride (NaCl), potassium chloride (KCl), Lithium chloride (LiCl), sodium nitrite
114 (NaNO₂), phosphorus pentasulfide (P₄S₁₀), and Natural graphite powder (Gr) were purchased
115 from Merck KGaA (Darmstadt, Germany) and they were used as received without further
116 purification.

117

118 *2.2. Sulfonation of PES*

119 The sulfonation process of PES was carried out using chlorosulfonic acid (CSA) and sulfuric
120 acid according to the method explained by *Guan et al.*, [45]. Firstly, 5 g of PES (previously
121 dried in an oven at 70°C for 6 hours) was dissolved in 50 ml sulfuric acid (solvent) and
122 stirred for 5 hours to obtain a homogeneous solution. Then, the CSA was added dropwise and
123 carefully under vigorous mechanical stirring (250 rpm). The stirring continued for another 3
124 hours and then the solution was precipitated in an ice-water bath. The precipitate was filtered
125 and washed several times to achieve a neutral pH. Finally, the white-colored noodle-type
126 precipitate was dried overnight in a vacuum oven at 70°C to obtain the sulfonated
127 polyethersulfone (SPES).

128

129 *2.3. Synthesis of GO, SGO, and TGO and characterization*

130 The GO was prepared according to the modified Hummer's method [46] from pristine
131 graphite. The details are provided in our previous study [17]. The sulfonation process was
132 carried by the addition of a defined amount of the GO into 8 mL of 0.6 M sulfuric acid
133 solution at 70°C. Under continuous stirring, 2 mL of 0.06 M NaNO₂ solution was added
134 dropwise and kept at 70°C for 12 h. After the reaction, the solid part was collected by
135 filtration and washed with deionized water (DI) several times until the pH became neutral.
136 The SGO was then oven-dried at 70°C for 24 h [38]. The next functionalizing was conducted
137 through the thiolation. In this process, the GO was reduced through reflux by phosphorus
138 pentasulfide (P₄S₁₀) [43]. We have followed the method explained by *Pham et al.*, 2013 [43]
139 with some modifications as follows: first 100 mg of GO was sonicated (Elma, 120H) in 100
140 ml solvent of DMF for 20 min. P₄S₁₀ was then added gradually to the homogeneous solution
141 under nitrogen gas purging. The solution was then continued to be stirred for 12 hours at
142 120°C. The precipitate was filtered and washed with DI water and ethanol until neutral pH,
143 the TGO was finally left to be dried in a vacuum oven at 70°C for 20h. This is noteworthy to
144 mention that authors have previously fully characterized the GO [17], Here we just
145 display the Fourier transform infrared spectroscopy (FTIR) to estimates the major functional
146 groups of synthesized GO, SGO, and TGO.

147

148 2.4. Fabrication of membranes

149 The cation exchange membranes (CEMs) were prepared using the solution casting followed
150 by the solvent evaporation technique [47]. Generally, there are negatively charged groups,
151 such as -SO₃⁻, -COO⁻, -PO₃²⁻ or -PO₃H⁻, fixed to the membrane backbone of CEMs, enabling
152 them for a selective permeability to the cations [48]. Firstly, various contents (see Table 1) of
153 GO, SGO, and TGO were dispersed in DMAc and sonicated for 20 min, followed by 4 hours
154 of stirring. Then, the SPES (20 wt%) was added to the mixture and continued stirring for
155 another 12 hours to obtain a 20% homogenous solution. Table 1 introduces the composition

156 of the casting solution to fabricate the composite SPES membranes. After being well mixed,
 157 the casting solutions were degassed to remove the bubbles. The casting was carried out by a
 158 homemade casting knife with a thickness of 200 microns on flat glass plates. Finally, the
 159 membranes were dried at 70°C in an oven for 12 hours and annealing at 100°C for 8 h. After
 160 cooling down to ambient temperature, the membranes were peeled off from the glass by
 161 immersing it into the DI water bath.

162

163 **Table 1.** The ratio of membrane components used in the membrane structure

Membrane	Composition (wt.%)		
	SPES	GO	DMAc
SPES/GO0.6%	20	0.6	79.4
SPES/GO1.2%	20	1.2	78.8
SPES/GO1.8%	20	1.8	78.2
SPES/SGO0.6%	20	0.6	79.4
SPES/SGO1.2%	20	1.2	78.8
SPES/SGO1.8%	20	1.8	78.2
SPES/TGO0.6%	20	0.6	79.4
SPES/TGO1.2%	20	1.2	78.8
SPES/TGO1.8%	20	1.8	78.2

164

165 2.5. Characterization techniques

166 The chemical structure of GO, SGO, and TGO nanoparticles were analyzed with the Fourier
 167 transform infrared spectroscopy (Thermo Nicolet Avatar FTIR 380, USA) in the range
 168 between 400 and 4000 cm^{-1} . The elemental analyses of nanoparticles were carried out with a
 169 Thermo Finnigan CHNS Analyzer model Eager 300 for EA1112. Before elemental analysis,
 170 all samples were vigorously washed many times. The membranes were also characterized by
 171 ATR-FTIR spectroscopy, spectrum one (Perkin-Elmer, France), to study their functional
 172 groups [49] in presence of SPES. The topography 3D image of the membrane pieces was
 173 obtained using an atomic force microscopy setup (Nanoscope III from Bruker, Germany) in
 174 contact mode in the air with a scan rate of 1 Hz. The surface and cross-section morphology of
 175 samples were conducted by field emission scanning electron microscopy (FESEM-

176 TESCAN, MIRA III). To prepare the membrane samples for FESEM, they were fractured in
177 the liquid nitrogen and then coated by gold sputter.

178

179 2.6. Water uptake, Cationic exchange capacity, and oxygen diffusion coefficient

180 The presence of water in membrane structure is a key factor for ionic conductivity, however,
181 excessive water uptake (WU) would cause some drawbacks of membrane swelling, reduce
182 mechanical strength which would lead to poor performance [50]. To measure the WU of
183 membrane samples, the methods explained by *Duan et al.*, [51] were implemented. We have
184 first prepared the samples with a surface area of 5 cm², then the samples were dried one day
185 in the vacuum oven at 80°C. The dried samples were weighed (W_1) and soaked in DI water
186 for 24 h. Finally, the samples were weighed again (W_2) after careful elimination of excess
187 water. Equation (1) was applied to calculate the WU of membranes.

$$188 \quad WU (\%) = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (1)$$

189 We have also applied the acid-base titration method to measure the cation exchange capacity
190 (CEC) of the as-synthesized membrane following the AFNOR method (AFNOR NFX45-200,
191 2005 [34]). Shortly, the membranes were cut into similar sizes and soaked into 1 M HCl for
192 24 h, followed by drying in a desiccator for 48 h and weighed. Then, each piece was kept in
193 50 ml of NaCl (2 M) for 24 h and finally, the titration was conducted using NaOH (0.1 M).
194 The CEC was measured using the following equation, where M and V are the concentration
195 (mg/l) and volume (l) of used NaOH, and W (g) indicates the weight of dried membrane
196 samples.

$$197 \quad CEC = \frac{(M \times V)_{NaOH}}{W_{membrane}} \quad (2)$$

198 In the current study, we aimed to provide anaerobic biodegradation of organic load in the
199 anode compartment. To do so, we studied the presence of DO in the anode through the
200 oxygen diffusion coefficient while applying each membrane. All analyses have been

201 conducted at room temperature around 23 ± 1 . The same MFC cell was used while filled with
202 DI water on both sides. The anode side was purged with nitrogen gas till the DO level
203 dropped lower than 0.5 mg/l. The other chamber was aerated continuously. The DO
204 concentration in the anode was followed in 1-h intervals using a DO probe (WTW Multi
205 3630 IDS, UK) for a total time of 10 hours. Afterward, the oxygen mass transfer coefficient
206 (k_o) (cm/s) and oxygen diffusion coefficient (D_0) (cm^2/s) were determined using the
207 following equations:

$$208 \quad k_o = \frac{V}{At} \ln \frac{c_o - c}{c_o} \quad (3)$$

$$209 \quad D_0 = k_o L \quad (4)$$

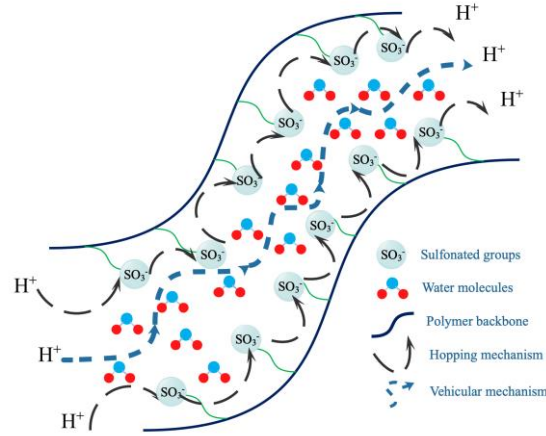
210 where c_o and c are saturated DO concentration (mg/l) and DO concentration (mg/l) in the
211 anode at the time t , respectively, V is the anode volume (cm^3), A the surface area of
212 membranes (cm^2), and L the membrane thickness (cm).

213 In the MFC, it is important to block the oxygen from migrating across the membrane and
214 entering the anodic chamber. Otherwise, the power generated by the MFC drops because the
215 oxygen is being used as electron acceptors by the bacteria rather than by the anode. After all,
216 the former is more thermodynamically favorable [52].

217

218 *2.7. Proton conductivity (σ)*

219 A high proton conductive membrane is essential for the MFC to improve its ability in
220 generating high power and current. There are two mechanisms where protons follow to pass
221 through the PEMs as a) hopping, and b) vehicular mechanisms (Fig. 1). In the hopping
222 approach, protons hop from a donor hydrolyzed site to an acceptor ionic site without the role
223 of H_2O as carrying molecules (also called Grothuss mechanisms), while in the vehicular
224 system protonated water molecules (H_3O^+) act as carriers of protons through the membrane
225 matrix [53].



226

227 **Fig. 1.** The schematic of proton transport through the membranes by hopping and vehicular
 228 mechanisms

229

230 In the present study, the resistance of the membranes was measured using a membrane
 231 conductivity test system (MCTS-A1, Iran) over the resistance ranging from 30 mΩ to 30 kΩ
 232 at a relative humidity of 100% and room temperature. The composite membranes were the
 233 first pre-treated with 1 M H₂SO₄ for 12 h followed by maintaining at DI water for 24 h before
 234 analysis. The proton conductivity of the membrane was computed from the resistance data as
 235 follows:

$$236 \quad \sigma = \frac{L}{RA} \quad (5)$$

237 where, σ is the proton conductivity of the membrane (S/cm), L the membrane thickness (cm),
 238 R the ohmic resistance of the membrane (Ω), and A is the membrane surface area (cm²).

239

240 2.8. Membrane transference number (t^+)

241 To measure the t^+ , the method applied by *Tourreuil et al.* [54] was used which principle consists
 242 of measuring the potential differences between two solutions of different concentrations,
 243 separated by a membrane, here we have chosen the Na⁺, K⁺, Li⁺, and H⁺ as the cation with n=1.
 244 To conduct the test, a two-compartment cell was applied, one of the compartments (C₁) was
 245 maintained at a concentration of 0.001 M targeted electrolyte while the second one (C₂) varies

246 in concentrations from 0.001 M to 0.01 M. The developed potential differences between the
247 two cells were measured with a digital voltmeter (high entrance impedance of 10 M Ω) using
248 two saturated calomel electrodes (SCE) from Radiometer-Analytical (France). Measurements
249 (3 replicates) were performed 5 min after membrane immersion into the solutions to ensure
250 that a steady state was established. For a charged membrane, and by using the Teorell-Meyer-
251 Sievers model [55], the theoretical membrane potential $(\Delta\phi)_{i=0}$ is expressed by [56]:

$$252 \quad \Delta\phi_{i=0} = E_1 - E_2 = (1 - 2t_m^+) \left(\frac{RT}{nF} \right) \ln \frac{c_1}{c_2} \quad (6)$$

253 where t_m^+ denotes the transport number of the cation electrolyte in the membrane phase. In the
254 present study $n = 1$ due to the choice of electrolytes. The transference numbers (t_m^+) measured
255 for the different studied membranes have to be compared with the t_m^+ in free solution which is
256 previously reported in the literature review (see Table 5) in the examined concentration range
257 [57].

258

259 *2.9. Zeta potential*

260 Membrane zeta potential was determined from tangential streaming potential measurements
261 [58,59] using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Graz) equipped with
262 Ag/AgCl electrodes and an adjustable-gap cell. Measurements were conducted at room
263 temperature with 0.001 M potassium chloride (KCl) background solutions in the pH range 3-
264 9 (the pH was adjusted with 0.05 M HCl and potassium hydroxide (KOH) solutions). The
265 distance between the membrane samples was set to 100 ± 5 mm.

266

267 *2.10. Contact angle*

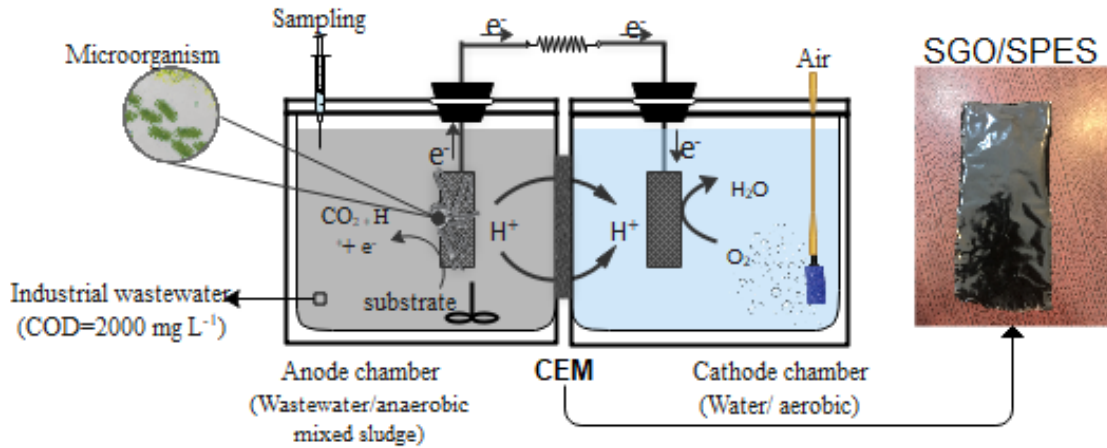
268 Water contact angles were measured by the sessile drop method using a DIGIDROP GBX-
269 DS apparatus. Contact angle has been used as an index of the wettability of the membrane
270 active layer. Before measurement, membranes were stored in a container of pure water for 24

271 h at 4 °C. The rinsed membranes were dried in a desiccator before measurement. The samples
272 were vacuum-dried for 72 h before the measurements. Membrane samples were cut into small
273 pieces and mounted in support. An approximately 2.0 µl droplet of pure water was placed on
274 the membrane specimen and the contact angle was measured with the goniometer via the
275 camera immediately after the drop placement. Contact angles were determined using a video
276 capture system and the Windrop⁺⁺ software. The reported contact angles are the average of at
277 least 10 measurements performed at different locations on the membrane surface.
278 Measurements were performed at room temperature.

279

280 *2.11. MFC design*

281 A dual-chamber MFC with a working volume of 800 mL was built from plexiglass by the
282 authors to follow the analysis [17] (Fig. 2). The anode and cathode compartments were
283 separated by a commercial CEM (Nafion117 (Sigma-Aldrich) versus as-synthesized
284 membranes) with a surface area of 16 cm². The carbon cloth (CC) material was used as anode
285 and cathode electrodes (12 cm²). The anaerobic anode chamber was filled with industrial
286 wastewater and anaerobic mixed bacteria sludge; taken from a sewage treatment plant
287 (Chamestan Industrial Park, Mazandaran, Iran), while the aerobic cathode was only
288 composed of water (The air was purged continuously). The average value from the four
289 replicate analyses with a relative standard deviation (SD) and range values of the wastewater
290 characteristics are provided in Table 2.



291

292 **Fig. 2.** The schematic of applied dual-chamber MFC

293

294 Before the start of each experiment, the nitrogen (g) was purged for 15 minutes into the
 295 anode cell to ensure the anaerobic phase and re-checked daily using a DO probe to maintain
 296 the anaerobic condition. The initial chemical oxygen demand (COD) of all systems was
 297 around 2000 mg/l. The two electrodes were connected using external resistance-induced
 298 wires and connected to an analog/digital data logger (Danesh Gostar Hamgam Ba
 299 Sanat Company (Babol, Iran)) and a personal computer (PC) to record the data. The
 300 performance of lab-scale MFC under different batch-mode conditions was conducted in terms
 301 of COD removal percentage, power production through the polarization curves, and
 302 coulombic efficiency. The power and current densities produced by the MFC were measured
 303 through the polarization curve following the ohm's law in equations 7-10. All MFCs operated
 304 for 7 days at OCV (open circuit voltage) to establish stable voltage and power; the data were
 305 recorded from the 2nd day using the analog/digital data logger. Measurements were carried
 306 out at variable resistances imposed on the MFC.

307
$$I = \frac{U}{R} \quad (7)$$

308
$$P = U \times I \quad (8)$$

309 $PD = \frac{P}{A_{anode}}$ (9)

310 $ID = \frac{I}{A_{anode}}$ (10)

311 where I, R, U, and P are current (A), Resistance (ohm), potential (V), and power (W),
 312 respectively. The power density (PD) and current density (ID) are power and current
 313 normalized by the anode surface area (A_{anode}).

314

315 **Table 2.** Characteristics of industrial wastewater applied in MFC (Chamestan Industrial Park,
 316 Mazandaran, Iran)

Parameters	Average value \pm SD	Range value
pH	6.70 \pm 0.42	6- 6.9
Total Kjeldahl Nitrogen (TKN), mg/l	21.32 \pm 0.55	18.45-22.10
Total dissolved solids (TDS), mg/l	952.43 \pm 112.70	900.5-1200
Total suspended solids (TSS), mg/l	2332.14 \pm 426.00	2100-3000
Biological oxygen demand (BOD ₅), mg/l	820.36 \pm 42.00	800-900
Chemical oxygen demand (COD), mg/l	2010 \pm 135.60	1900-2100
Nitrate-N, mg/l	74.88 \pm 2.24	70.02-77.30
Phosphate-P, mg/l	10.02 \pm 0.31	9.4-10.30

317

318 *2.12. COD removal and coulombic efficiency*

319 To study the efficiency of MFC in wastewater treatment and bioelectricity generation, the
 320 COD removal and coulombic efficiency (CE) were measured and reported in Table 6. The
 321 samples were taken from the anode compartment by a syringe at the initial time and repeated
 322 every 24 hours. The COD removal efficiency was measured for 7 days, applying the initial
 323 (COD_i) and final COD_f (mg/l) as follows:

324 $COD\ removal = \frac{COD_i - COD_f}{COD_i}$ (11)

325 We report CE based on COD changes (equation 12) defined as the fraction of electrons
 326 recovered by the current [60]. Generally, the CE could be limited by factors like electron
 327 consumption by methanogenesis, oxygen crossover, and aerobic respiration of cathode
 328 biofilm [61]. The CE value can be measured using the oxygen molecular weight (M , 32
 329 g/mol), Faraday's constant (F , 96485 C/mol), number of electrons exchanged per mole of

330 oxygen (b , 4 mol e⁻/mol O₂), the volume (l) of liquid in the anode compartment (v_{An}), and
331 Δ COD (g/l) over time t :

$$332 \quad CE = \frac{M \int_0^t I dt}{F b v_{An} \Delta COD} \quad (12)$$

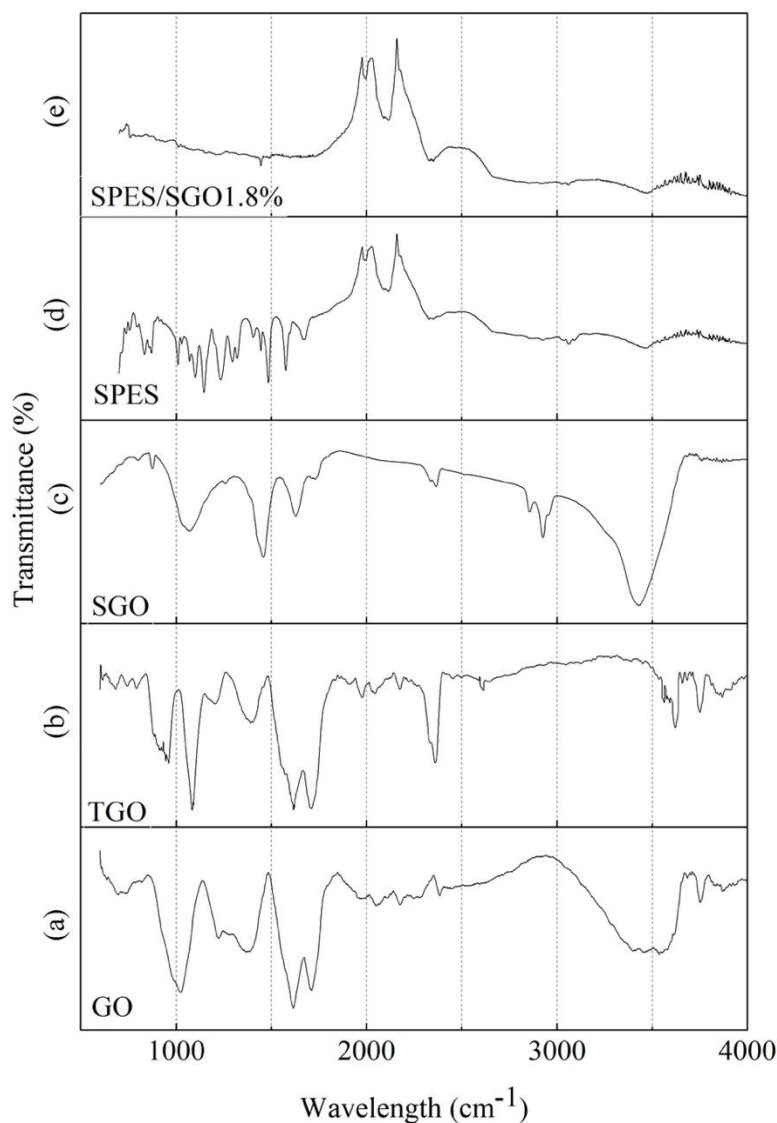
333

334 **3. Results and discussions**

335 *3.1. FTIR characterization*

336 Fig. 3 shows the FTIR spectra of GO, SGO, and TGO nanoparticles. The spectrum of GO
337 displays peaks at 3500 cm⁻¹, 1712 cm⁻¹, 1616 cm⁻¹, and 2380 cm⁻¹ which corresponds to
338 characteristic bands of stretching vibration of the hydroxyl group (-OH) [32], carboxyl
339 (COO⁻), C-C, and C-H band groups, respectively. Also, the peaks observed around 1220 cm⁻¹
340 and 1025 cm⁻¹ suggest the presence of O-C stretching and bending modes both in GO and
341 TGO samples [62]. These results support the oxidation of graphite to GO. The details of GO
342 were also reported earlier by authors [17]. The FTIR spectra of SGO present a characteristic
343 peak at 2923 cm⁻¹ assigned to the absorption of the sulfonic acid groups (-SO₃H) [63], and a
344 peak that appeared at 1060 cm⁻¹ can be attributed to the symmetric stretching vibration of -
345 SO₃H groups [64]. A broad peak presents the stretching vibration of -OH in carboxylic acid
346 and phenol groups ascribed from 3330 cm⁻¹ to 3520 cm⁻¹. a weak peak observed at 876 cm⁻¹
347 is referred to as the wagging of hydrogen out-of-plane of SGO rings [64]. During the process
348 of thiolation, we observe the depletion of -OH peak in TGO (around 3500 cm⁻¹), which arises
349 from the conversion reaction of -OH groups to the substituted -SH group. Significant
350 differences were observed in the TGO FTIR spectrum comparing to GO which provided us
351 with the successful thiolation process. Many peaks are assigned to thiol groups and amide
352 bond as: 2615 cm⁻¹ (S-H stretching) [32], 1567 cm⁻¹ (N-H stretching), 3043 cm⁻¹ and 3505
353 cm⁻¹ (N-H bending), 678 cm⁻¹ (N-H wagging) [65]. Also, it should be noted that -SH related

354 peaks are difficult to be recognized in FTIR due to the masking that happened by the
355 vibration of many peaks present in the spectrum of GO [33].
356 The ATR-FTIR spectra of SPES and SPES/SGO1.8% within the wavenumber range of 500–
357 4000 cm^{-1} are also depicted in Fig. 3. The ATR-FTIR spectroscopy measurements were
358 conducted to identify the existence of new bonds. The presence of $-\text{SO}_3\text{H}$ groups in SPES is
359 confirmed by the following peaks at 1740 cm^{-1} and 1635 cm^{-1} ascribed to the vibration of the
360 aromatic skeleton [66]. The two absorption peaks at 1020 cm^{-1} [28] and 1143 cm^{-1} [34]
361 indicate the characteristic symmetric stretching of aromatic $-\text{SO}_3\text{H}$ groups. The stretching
362 vibration in the range of 3000 cm^{-1} to 3500 cm^{-1} is assigned to O-H stretching absorption.
363 The vibration band at 2170 cm^{-1} for SPES is due to the presence of C=C stretching. Also, the
364 presence of aliphatic C-H bands is observed by the peaks at 2850 cm^{-1} to 2930 cm^{-1} . Due to
365 the overlay of the peaks with SPES, the typical peaks of GO, SGO, and TGO are not easy to
366 be observed in SPES/SGO1.8% membrane [34]. However, the SPES and SPES/SGO1.8%
367 spectra are presented as no difference was observable among the FTIR spectra of SPES/GO,
368 SPES/TGO, and SPES/SGO. Further, by comparing the spectra of both membranes in the
369 range of 500 cm^{-1} to 2500 cm^{-1} , we can observe significant differences indicating the bonds
370 between the SPES and nanoparticle s.



371
 372 **Fig. 3.** FTIR spectra of GO, SGO, and TGO, and SPES, SPES/SGO1.8% membrane sample

373

374 *3.2. Elemental analyses (CHNS)*

375 CHNS is an elemental analysis to accurately determine the concentrations of carbon, sulfur,
 376 hydrogen, and nitrogen in organic and inorganic solid samples. Table 3 presented the
 377 obtained results for GO, SGO, and TGO. This test aimed to prove the presence of sulfur more
 378 in SGO and TGO and compare it with GO samples. Here, GO showed a composition of
 379 45.34% carbon, 0.15% sulfur, while the percentage of sulfur in SGO and TGO has increased
 380 to 6.23% and 5.5%, respectively. It Confirms the successful synthesis and presence of -SO₃H
 381 and -SH functional groups in functionalized forms of GO. On the other hand, the amount of

382 oxygen has decreased in SGO and TGO which indicates the introduction of sulfonate and
383 thiol functional groups to oxygenated functional groups in GO and their replacement [35,67–
384 69]. It should be noted that the oxygen content was calculated by subtracting carbon,
385 hydrogen, nitrogen, and sulfur from 100%.

386

387 **Table 3.** CHNS analysis of GO, SGO, and TGO

Element	GO (wt%)	TGO (wt%)	SGO (wt%)
C	45.35	66.32	50.76
H	2.36	1.42	2.1
N	1.86	2.3	2.7
S	0.15	5.5	6.23
O	50.28	24.46	38.21

388

389 *3.3. Morphology and topography of the membranes*

390 The microstructure of the membranes is one of the main parameters that should be studied
391 because it will provide useful information on the distribution of the nanoparticles, ionic sites,
392 porosity, and integrity. The cross-section morphological structure of the SPES,
393 SPES/GO1.8%, SPES/SGO1.8%, and SPES/TGO1.8% have been observed through cross-
394 sectional SEM images as displayed in Fig. 4. A general look, states that the membranes are
395 greatly affected by the addition of GO, SGO, and TGO. A detailed comparison of images 4a
396 with 4b, c, and d confirms the presence of nanoparticles (NPs) and their distribution in the
397 polymer matrix and not only the surface of the membrane. A better understanding of the GO
398 structure was reported previously [17] using the XRD and SEM morphological analyses,
399 which prove that the single layer of GO, the lower crystallinity of GO, and the presence of
400 amorphous structure occurred during graphite oxidation. Further, the TEM image of GO was
401 displayed to have a characteristic 2D sheet-like structure [17]. However, the FESEM image
402 of GO sheets was layered on the SPES matrix in SPES/GO1.8%, as shown in Fig. 4b. In
403 addition, the SGO nanosheets were dispersed as revealed in Fig. 4c. The SGO nanosheets
404 demonstrate a well curvy and exfoliated overlapped structure leading from hydrophobic –

405 SO₃H groups amendment on the GO surface. Furthermore, the TGO was distributed
406 homogeneously on the SPES matrix in SPES/TGO1.8%, as revealed in Fig. 4d. There is also
407 a significant difference in thickness of the membrane before and after the incorporation of the
408 nanoparticles, where SPES has a dry thickness of 34.3 μm while this value has increased to
409 60 μm , 100 and 115 μm in SPES/GO, SPES/SGO, and SPES/TGO. This might be due to the
410 addition of NPs which has increased the viscosity of the casting solution resulting in a higher
411 thickness. A similar conclusion was stated that these changes in thickness could be related to
412 casting solution viscosity [70]. The clustering structure of GO and the ionic sites are easily
413 observed through the image 4b, 4d, and especially 4c. The SPES/SGO showed the best
414 clustering and honeycomb structures resulting from the presence of SGO nanoparticles, this
415 is due to the positive effect of sulfonated groups on providing the channels and clusters which
416 lead to facilitated proton transport. This agrees with the earlier study as claimed layered
417 structure can provide facilitate proton conductivity in parallel paths and channels to create
418 more proton transfer and adsorption of more water [34]. Besides, the membranes displayed a
419 dense structure, without visible porosity at the micrometric scale which supports their
420 application in microbial fuel cells and non-porous PEM. The non-porous structure is induced
421 from the preparation method of the solvent evaporation technique.

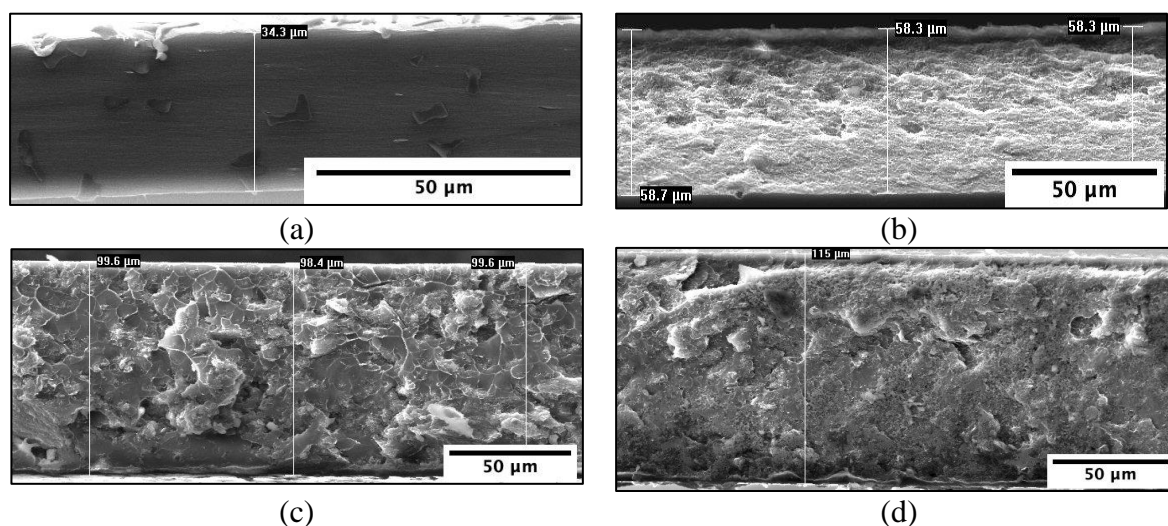


Fig. 4. Cross-sectional images of a) SPES, b) SPES/GO1.8%, c) SPES/SGO1.8%, and d) SPES/TGO1.8%

422

423 *3.4. Water uptake, contact angle, and diffusion coefficient*

424 In this section, we will illustrate experimental results on water uptake (WU), contact angle
425 (CA), and oxygen diffusion coefficient as listed in Table 4. The effect of the addition of
426 nanoparticles is observed by comparing the value of WU. As presented in Table 4, the WU of
427 the SPES membrane is around 12.33%, which is lower than Nafion117 of 17.5% as the
428 control sample. The incorporation of nanoparticles (GO, SGO, or TGO) improved the WU by
429 the membranes, significantly. within each membrane group, WU increases with increasing
430 the ratio of nanoparticles in the polymer matrix. While $-\text{SO}_3^-$ incorporated membranes
431 showed the highest value compared to other functionalized forms with a similar ratio. For
432 example, the SPES/SGO1.8% with the WU of 36.3% presented a higher value than
433 SPES/GO1.8% and SPES/TGO1.8% of 23.1 and 30%. Based on our observation, the WU
434 values higher than 40% causes instability and membrane swelling in contact with 100%
435 humidity atmosphere, this happens due to the high hydrophilicity of the membrane. The
436 results of the WU analysis are then compared with the CA test. The trend showed almost in
437 agreement with the results of CA, indicating the hydrophilicity of the membranes [71]. It is
438 worth discussing this interesting fact revealed by comparison of the PES and SPES
439 membranes. It showed that due to the presence of hydrophobic backbone polymer in PES, it
440 almost absorbed no water. This result ties well with previous studies supporting us with a
441 suitable choice of sulfonation of the bare polymer [45,72].

442 We also present the results of oxygen diffusion (D_0), which show the permeability of the
443 membrane to the oxygen. In the MFC, we favor the anaerobic degrading anode to provide a
444 suitable condition for microorganism activity and to achieve a higher produced current. This
445 theory has also been followed in earlier studies where they resulted as; the denser the
446 polymer matrix was, the lower the oxygen diffusion became [11,73]. One concern about the
447 Nafion[®] pointed out in the literature review, was its high oxygen diffusivity [5,15], which is

448 also the case here. However, the as-synthesized membranes do seem to improve this feature
 449 at least 5 times lower. Generally, by increasing the ratio of nanoparticles (from 0.6 to 1.8%)
 450 in the polymer matrix, the k_o becomes lower due to the higher density. As shown in equation
 451 (3) the membrane thickness is also a crucial factor in measuring the k_o , which was on average
 452 180, 60, 40, 60, 100, 115 mm for Nafion[®], PES, SPES, SPES/GO, SPES/SGO, and
 453 SPES/TGO, respectively (Fig. 4). In all the membranes, the wt% of 0.6 of nanoparticles was
 454 the most unfavorable, while both 1.2% and 1.8% incorporation of nanoparticles brought
 455 significant difference comparing to 0.6. This indicated the optimal percentage of
 456 incorporation is around 1.8, as the differences from 1.2 to 1.8 are much smaller than 0.6 to
 457 1.2.

458

459 **Table 4.** Water uptake, contact angle, oxygen mass transfer coefficient, and oxygen diffusion
 460 coefficient of membranes

Membrane	WU, %	Contact angle, degree	k_o , cm/s	D_o , cm ² /s
Nafion117	17.5	90 [74]	7.29E-04	1.31E-04
PES	5.41	87 [75]	nd	nd
SPES	12.33	90.1	8.50E-04	4.25E-05
SPES/GO0.6%	20.71	90.7	9.81E-04	5.89E05
SPES/GO1.2%	22	84.5	8.82E-04	5.29E-05
SPES/GO1.8%	23.13	64.3	8.50E-04	5.10E-05
SPES/SGO0.6%	28.41	78.7	5.22E-04	5.22E-05
SPES/SGO1.2%	33.54	76.0	4.36E-04	4.36E-05
SPES/SGO1.8%	36.32	78.5	4.26E-04	4.26E-05
SPES/TGO0.6%	24.55	82.2	5.00E-04	5.50E-05
SPES/TGO1.2%	26.22	71.0	4.48E-04	4.93E-05
SPES/TGO1.8%	30	70.9	4.35E-04	4.78E-05

461 nd = not determined

462

463 3.5. Transference number, cation exchange capacity, and proton conductivity

464 The motion of the ionic species ensures current transport through the electrolyte(s). the
 465 transference number (t^+) is a very important parameter giving the current value carried by
 466 each ion [76]. In an MFC working with cation exchange membranes, the transport of other
 467 cations happens with the protons, sometimes even more than protons. This transport causes

468 an accumulation in the cathode compartment that results in a large pH difference between the
469 two compartments. The pH imbalance brings some serious drawbacks [77], so in the present
470 study, it was necessary to analyze the novel membranes in terms of various cations transport.
471 Table 5 presents the transference number for four electrolytes of H^+ , Na^+ , Li^+ , and K^+ with
472 chloride as a counter ion. This has been measured from the potential differences for different
473 concentrations of each electrolyte. Considering the literature review, one of the limitations of
474 the Nafion[®] membrane was its weak selectivity to the protons [10,14], this was also observed
475 in the present study. As the data stated Nafion[®] has the highest t^+ to the potassium ion
476 followed by Na^+ , H^+ , and Li^+ . A high value of the transference number for K^+ was also
477 reported earlier [78]. Herein, the values show that the Nafion[®] membrane behaves nearly
478 equal toward the chosen cations. This is the usual order followed by some reported
479 membrane [79–81]. However, the GO functionalized membranes show various trends due to
480 the polymer matrix interaction [82]. In SPES/GO membranes it is obvious that a trend is
481 starting to form but it is still the sodium and potassium ions that showed a higher value of t^+ .
482 By increasing the ratio of GO in the membrane matrix, a slight difference from 0.72 to 0.8
483 has been achieved. The highest H^+ transference number ($t(H^+)$) belongs to SPES/SGO1.8%
484 (0.88) followed by SPES/GO1.8% (0.8), Nafion117 (0.76) and SPES/TGO1.8% (0.73).
485 Among the functionalized nanoparticles, the results proved that groups in SGO have
486 improved the membrane selectivity more efficiently than TGO and GO. We assume this is
487 more due to the synergic effects between groups of both polymer (SPES) and nanoparticles
488 (SGO). In this test, rather than the order of ions (which could be associated with different
489 parameters), the important information to extract is the differences in the value of ion
490 transference number in comparison to the Nafion117. As mentioned, the t^+ in Nafion[®] for all
491 electrolytes is somehow near to each other while in the synthesized membranes, we could
492 observe increased differences between the electrolytes, indicating the improved selectivity of
493 the proposed membranes.

494

495 **Table 5.** The transference number of H⁺, Na⁺, Li⁺, and K⁺ electrolytes for membranes

Membranes	Transference number (t ⁺)				Comparison
	H ⁺	Na ⁺	Li ⁺	K ⁺	
SPES/GO0.6%	0.72	0.71	0.62	0.78	K ⁺ >H ⁺ =Na ⁺ >Li ⁺
SPES/GO1.2%	0.73	0.87	0.63	0.86	Na ⁺ >K ⁺ >H ⁺ >Li ⁺
SPES/GO1.8%	0.8	0.82	0.76	0.79	Na ⁺ >H ⁺ >K ⁺ >Li ⁺
SPES/SGO0.6%	0.79	0.58	0.67	0.6	H ⁺ >Li ⁺ >K ⁺ >Na ⁺
SPES/SGO1.2%	0.80	0.62	0.63	0.65	H ⁺ >K ⁺ >Li ⁺ =Na ⁺
SPES/SGO1.8%	0.88	0.67	0.56	0.73	H ⁺ >K ⁺ >Na ⁺ >Li ⁺
SPES/TGO0.6%	0.72	0.68	0.58	0.48	H ⁺ >Na ⁺ >Li ⁺ >K ⁺
SPES/TGO1.2%	0.7	0.6	0.6	0.64	H ⁺ >K ⁺ >Na ⁺ =Li ⁺
SPES/TGO1.8%	0.73	0.59	0.4	0.58	H ⁺ >Na ⁺ >K ⁺ >Li ⁺
Nafion 117-0ld	0.76	0.78	0.71	0.83	K ⁺ >Na ⁺ >H ⁺ >Li ⁺
Free diffusion	0.82	0.39	0.33	0.49	H ⁺ >K ⁺ >Na ⁺ >Li ⁺

496

497 Other promising findings are proton conductivity and cationic exchange capacity as presented

498 in Fig. 5. Among all tested membranes, SPES/SGO1.8% had the highest proton conductivity

499 of 1.42 mS/cm followed by Nafion117 (1.3 mS/cm), while SPES/TGO1.8%, and

500 SPES/SGO1.2% showed slightly lower conductivity around 1.25 mS/cm. According to the

501 data provided, the lowest proton conductivity belongs to the PES membrane which also has

502 the lowest cation exchange capacity. Sulfonating the polymer cause an increase from 0.28

503 mS/cm to 0.36 mS/cm which is still not satisfying, but the addition of nanoparticles provides

504 a significant difference. This is inconsistent with the previous studies that achieved higher

505 values of proton conductivity in the case of sulfonated polyether ether ketone (SPEEK)

506 incorporated with GO [17,83]. The reason is the presence of oxygenated, sulfonated, and

507 thiolated functional groups on the GO that helps to improve the proton conductivity. It is

508 assumed that protons move through the paths and channels provided by the functionalized

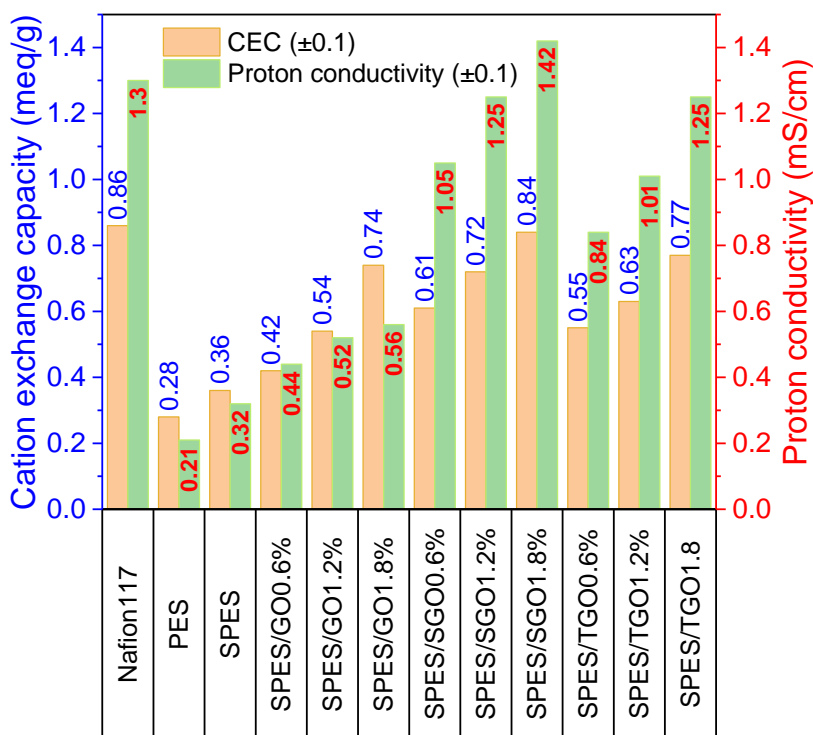
509 groups and in their presence. It could simply mean that a network has been formed between

510 these functional groups, ionic sites in SPES, and water molecules, resulting in higher proton

511 diffusion [83]. The values of proton conductivity for TGO type membranes are generally

512 lesser than SGO functionalized membranes indicating the better performance of sulfonation

513 functionalization. It is important to highlight the fact that cationic exchange capacity values
 514 are following the proton conductivity (Fig. 5). So, a membrane with higher CEC showed a
 515 higher proton conductivity as well. The order of tested membranes for cationic exchange
 516 capacity is as follows: Nafion117~ SPES/SGO1.8%> SPES/TGO1.8%> SPES/GO1.8%>
 517 SPES > PES. This was also the case in WU, so the higher the WU, the higher the proton
 518 conductivity, because the proton transfer will be much easier when there is a formation of
 519 water bonds [25]. Considering the Grotthuss mechanism [53] (Fig. 1), it is believed that
 520 proton hopping has happened between different molecular units via the hydrogen bridge by a
 521 reoriented motion. In addition to the hopping approach, we assumed that a fraction of protons
 522 has also passed through the membrane by the vehicular mechanism due to the membrane
 523 WU, fully hydrated atmosphere, and the presence of water molecules in the structure.



524
 525 **Fig. 5.** Cation exchange capacity and proton conductivity of membranes

526

527 *3.6. Contact angle (CA) and zeta potential of the membranes*

528 The relative hydrophilicity or hydrophobicity of the membrane surface was measured via
529 contact angle (CA). This is the angle formed between three phases of a solid membrane, a
530 liquid water drop, and air (or another gas) [23] and determined from the sessile drop
531 technique. It is well accepted that the lower the contact angle, the higher the hydrophilicity of
532 the surface [84]. The CA of 0° indicates a wetting surface, as $CA > 90^\circ$ a hydrophobic one.
533 While contact angle is commonly used to measure the hydrophobicity of the membrane
534 surface, the data should be used with some caution. In practice it is not an absolute value, it is
535 a relative parameter comparing different material surfaces, i.e. the membrane surface
536 roughness can influence contact angle measurement due to capillary effects, and results from
537 different measurement methods can vary considerably [85]. If roughness is higher than 100
538 nm, the measured contact angles are meaningless. On very rough surfaces, contact angles are
539 larger than on chemically identical smooth surfaces [86,87].

540 The CA for all samples was measured and displayed in Table 4. This test aimed to observe
541 the positive effect of nanoparticles on improving the hydrophilicity in the non-porous
542 structure of the SPES membrane. Generally, after the addition of functionalized nanoparticles
543 to the SPES polymer matrix, the contact angles decreased, and a more hydrophilic membrane
544 was fabricated. As shown, the highest contact angle (lowest hydrophilicity) was associated
545 with the SPES membrane at 90.1° . A similar amount was also reported by previous studies
546 [88,89]. They reported that the hydrophilicity of PES membranes was improved by blending
547 with sulfonated PES. In SPES/SGO and SPES/TGO, the CA decreases with the increase of
548 the nanoparticle wt% in the SPES matrix, defining the higher the NPs ratio was the more
549 hydrophilic the surface. SPES/GO0.6% showed the lowest contact angle as 64.3° followed by
550 SPES/TGO1.8% as 70.9° . the order of average hydrophilicity for the -GO, -SGO, and -TGO
551 functionalized membranes are as followed:
552 SPES/TGO> SPES/SGO> SPES/GO

553 As proved by the result, all the synthesized membranes have a lower CA than Nafion117
554 reported in the literature review. A study reported that incorporation of GO and TiO₂ into the
555 Nafion[®] improves the contact angle from 89.8° to 68.6° and 71.2 [90] resulting in a more
556 hydrophilic surface. It is also stated that GO is more hydrophilic than TiO₂ supporting our
557 choice of nanoparticles. For SPES/SGO1.8% due to its relative hydrophilic structure, it could
558 be less sensitive to biofouling vs more hydrophobic membranes of SPES or Nafion[®] [91].
559 Earlier it has also been stated that membranes with GO have better anti-biofouling properties
560 [92].

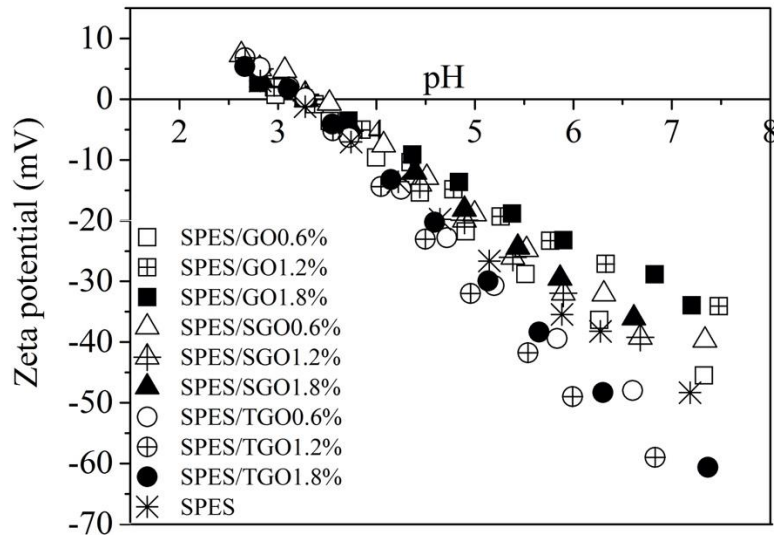
561 Another parameter we focused on was zeta potential, which is applied for measuring the
562 surface charge characteristics of the as-synthesized polymeric membranes. The results of zeta
563 potential values under different pH are displayed in Fig. 6. This value is also in relation to the
564 ion-transport selectivity by partitioning of multivalent ions into the film (Donnan exclusion)
565 [93]. Generally, it could be stated that all membranes have a negative charge at the working
566 pH of the MFC in the present study which was kept as 6.30. The negative values also stated
567 the negatively charged surface of membranes which is proof of CEM. The results revealed
568 that membranes have a negative zeta potential under pH > 3.3, which is the isoelectric point
569 (IEP) of the membranes. From Fig. 6, it is clear that if pH goes beyond a specific value, the -

570 TGO incorporated membranes show higher negativity of zeta potential than -SGO
571 membranes. We should also highlight that the zeta potential values of the SPES/SGO1.8%
572 membrane are more negative than SPES/GO1.8% and less negative than SPES/TGO1.8%.

573 The order of membranes in neutral pH is as follows:

574 SPES/TGO1.2% > SPES/TGO1.8% > SPES/TGO0.6% > SPES > SPES/GO0.6% >

575 SPES/SGO1.2% > SPES/SGO1.8% > SPES/SGO0.6% > SPES/GO1.2% > SPES/GO1.8%



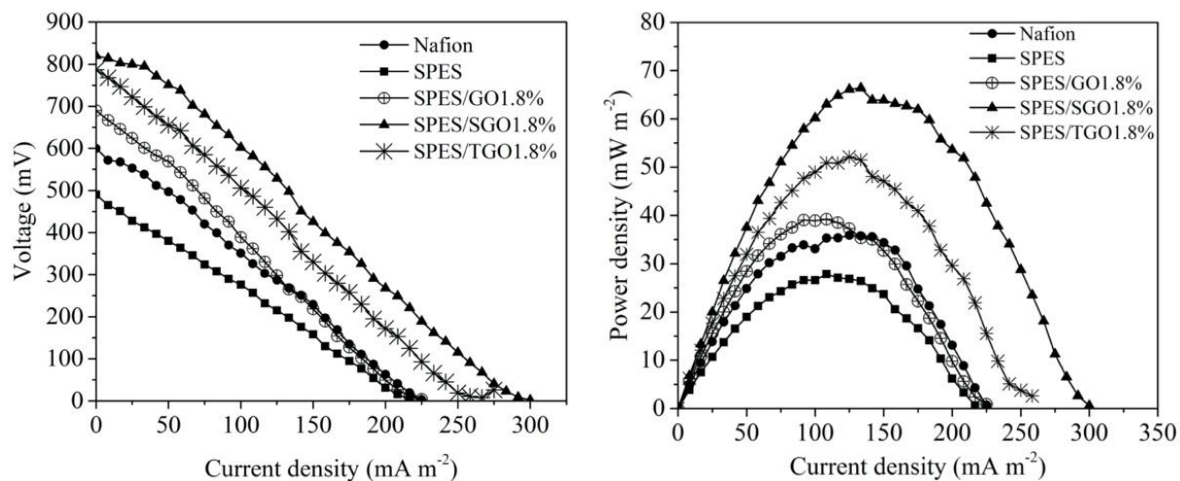
576
577 **Fig. 6.** The zeta potential of membranes in the pH range of 2.5 to 8
578

579 3.7. MFC performance

580 Fig. 7 shows the polarization curves (voltage, current density, and power density) of MFCs
581 working with Nafion117, SPES/GO1.8%, SPES/SGO1.8%, and SPES/TGO1.8% as the
582 separators. The details on P_D and I_D of other membranes are also provided in Table 6.
583 Membranes play important roles in dual-chamber MFCs [5], and their performance is
584 determined by the generated power density. The internal resistance of the MFC is the slope of
585 the I-V curve or in other words, the slope of the current versus the voltage. In this study, the
586 All the MFC reactors had the same configuration and identical substrates. Therefore, the
587 different amounts of power, current, and voltage in systems with different membranes are
588 most likely due to the membranes.
589 As expected, the highest amount of power density and current density of 66.4 mW/m^2 , and
590 300 mA/m^2 were obtained for SPES/SGO1.8%, followed by SPES/TGO1.8% (54.13 mW/m^2 ,
591 275 mA/m^2). This amount of power density is almost two times higher than MFC working
592 with Nafion117 (35.9 mW/m^2) and SPES/GO1.8% (39.2 mW/m^2), which is a significant
593 improvement in MFC performance in terms of generating electricity. The efficiency of
594 proposed SPES/SGO1.8% in MFC agrees with the previously provided data as proton
595 conductivity, CEC, WU. The lowest power density and current density are assigned to the

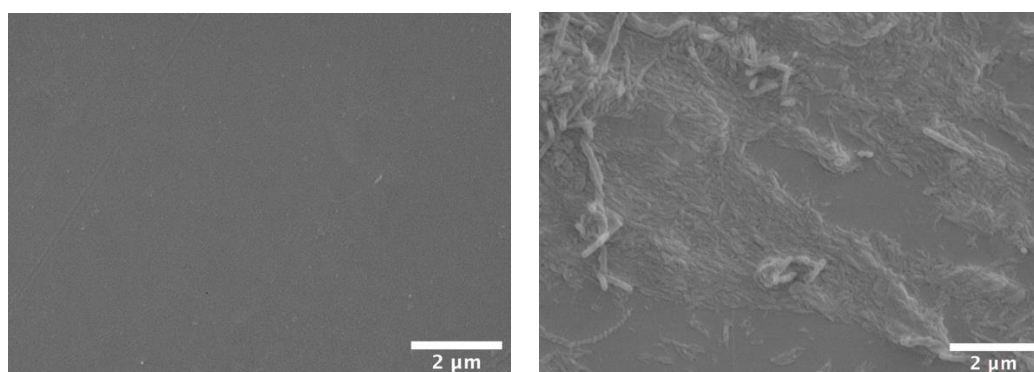
596 bare SPES membrane as 27.8 mW/m^2 and 216 mA/m^2 . These low values of PD for
597 Nafion117 and SPES are because of higher oxygen cross-over through the chamber, which
598 reduces the anaerobic condition for microorganisms [94]. The maximum voltage of about 820
599 mV was achieved with the system working with SPES/GO1.8%, followed by
600 SPES/TGO1.8%. Nafion117 reached the maximum voltage of 600 mv, which was higher
601 than SPES pure membrane and lower than SPES/GO. It could be observed the addition of
602 functionalized GO has significantly improved the MFC efficiency as generating higher
603 electricity.

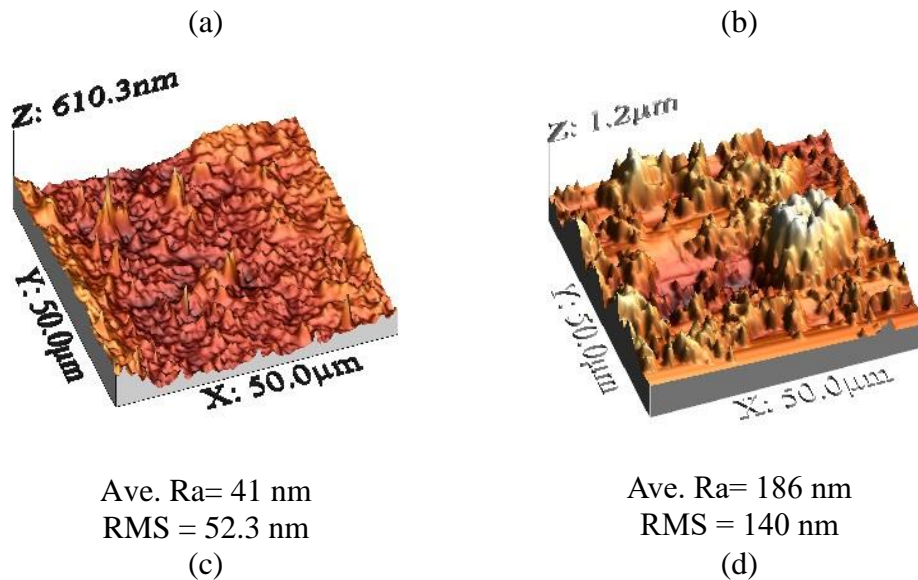
604 Earlier, we have tested SPEEK and SPEEK/GO membranes in MFC [17], where we obtained
605 an almost similar power density for Nafion117 (26 mW/m^2), but a higher amount of power
606 density for SPEEK/GO5% (53.2 mW/m^2) comparing to SPES/GO1.8% (39.2 mW/m^2). This
607 might be derived from the higher ratio of GO in the polymer matrix and the role of SPEEK
608 which is a good choice for PEM. In the current study, we have focused on a more cost-
609 effective and simpler approach by changing the polymer to PES and functionalizing GO. To
610 improve the efficiency of the membrane as CEM, we have sulfonated the polymer [71]
611 (SPES) as well as functionalizing the nanoparticles (TGO and SGO). This resulted in a higher
612 power density and voltage while applying a cheaper polymer and a decrease in usage of
613 nanoparticles to more than half (from 5% in SPEEK/GO to 1.8% in SPES/SGO and
614 SPES/TGO). All these support the idea of proposing a more cost-effective membrane in
615 parallel with better performance.



616 **Fig. 7.** Polarization curves of MFCs working with membranes: a) voltage versus current
 617 density, b) power density versus current density.
 618

619 The authors have conducted further SEM and AFM analysis of surface morphology and
 620 topography on the SPES/SGO1.8% membrane. SPES/SGO1.8% was proved to be the most
 621 suitable separator derived from earlier analyses. AFM and SEM images of the membrane
 622 surface before and after its application in an MFC are displayed in Fig. 8. The analyses have
 623 been conducted after 21 days of exposing the anode compartment. Fig. 8 a shows the surface
 624 non-porosity and homogeneity with an average roughness of 41 nm. However, we can easily
 625 observe the formation of biofilm (Fig. 8b) and a significant increase in average roughness to a
 626 value of 186 nm (Fig. 8d). The biofilm formation may cause a decrease in membrane
 627 efficiency in terms of its role on proton transport, thus result in lower MFC performance. The
 628 aim of these observations was also to follow the membrane behavior in the presence of
 629 biofilm and highlight the importance of emerging further investigation of biofouling studies
 630 on newly synthesized membranes.





631 **Fig. 8.** Surface image of SPES/SGO1.8% a) side a, b) side b, and AFM images of
 632 SPES/SGO1.8% c) side a, d) side b
 633

634 *3.8. COD removal and coulombic efficiency (CE)*

635 The COD removal and CE of MFCs with different membranes are displayed in Table 6. The
 636 COD removal percentage did not show a very significant difference in many reactors, and it
 637 was high for all the systems (COD > 70%). The amounts of COD removal ranged between
 638 72% and 89% for various membranes. The COD removal achieved by Nafion117 was about
 639 82 %, which is higher than SPES (79%), SPES/GO0.6% (75.2%), SPES/GO1.2 % (80.74%),
 640 SPES/SGO0.6% (78.21%), and SPES/TGO0.6% (72.53%). The achieved higher COD
 641 removal by the system despite the lower power density, is an indication that more substrate
 642 was used by microorganisms anaerobically digestion rather than for producing electricity
 643 [95]. The highest COD removal and CE were obtained for MFCs working with
 644 SPES/SGO1.8% (89.85%, 3.73%), SPES/TGO1.8% (88.07%, 3.2%), respectively, and
 645 durability of over 8 days at mid conditions, which indicates the best performances compared
 646 to Nafion[®] -based membrane in MFCs. As discussed above, these alternative membranes
 647 showed high power densities compared to commercial Nafion117. The CE values were low
 648 in the present study, this is possibly derived from not using any cathode catalyst [95]. The
 649 earlier study has compared a PVDF-g-PSSA and Nafion[®] membrane in an MFC, reporting a

650 low CE of 5% and 7%, respectively. They have well explained that lower CE was due to high
 651 substrate concentration and a catalyst-free cathode [61,95].

652

653 **Table 6.** COD removal, Coulombic efficiency, maximum current density, and power density
 654 of MFCs working with membranes.

Membrane	COD removal (± 5)	CE (± 0.2)	$I_D \pm 3$ (mA/m ²)	$P_D \pm 2$ (mW/m ²)
SPES	79.76	2.19	216.7	27.8
SPES/GO0.6%	75.2	2.04	218.7	28.5
SPES/GO1.2%	80.74	2.20	222.1	32.1
SPES/GO1.8%	86.47	2.28	225	39.2
SPES/SGO0.6%	78.21	2.13	233.5	46.8
SPES/SGO1.2%	85.41	2.64	276.4	61.5
SPES/SGO1.8%	89.85	3.73	300	66.4
SPES/TGO0.6%	72.53	2.18	223.6	43.4
SPES/TGO1.2%	85.22	2.51	255	51.7
SPES/TGO1.8%	88.07	3.20	275	54.13
Nafion117	82.71	2.28	233.3	35.9

655

656 4. Conclusions

657 Proton exchange membranes have been studied for decades. The role of PEMs in dual-
 658 chamber MFCs is more than just a physical separator. These are the key element in
 659 transporting the protons from the anode to the cathode compartment completing the cycle of
 660 electron transfer, besides avoiding the substrate and oxygen cross-over. There are many
 661 commercially available membranes, among which Nafion[®] is the most usually applied one. It
 662 is associated with some limitations that are subject to further studies to overcome those
 663 limitations and improve the MFC efficiency. Here, we have developed various membranes
 664 using sulfonated polyethersulfone (SPES) combined with GO as well as its sulfonated and
 665 thiolated forms (GO, SGO, and TGO). In the second step, we have conducted
 666 characterization tests of water uptake, contact angle, zeta potential, oxygen diffusion, proton
 667 conductivity, and cation exchange capacity on various prepared membranes and compared
 668 the results with Nafion117[®]. Finally, the membranes were applied in MFC reactors to test
 669 their suitability matching the features of electricity generation and bioremediation. Generally,
 670 the incorporation of functionalized GO not only improved the water uptake, cation exchange

671 capacity, oxygen diffusion, contact angle of the composite membranes but also increased
672 their proton conductivities. Broadly translated our findings indicate that SPES/SGO1.8% with
673 proton conductivity of 1.42 mS/cm, water uptake of 36.32%, cation exchange capacity of
674 0.84 meq/g, and contact angle of 78.5% showed the highest power density of 66.4, COD
675 removal of 90% and CE of 3.73%. the chemical interaction in SPES/SGO and SPES/TGO
676 and the presence of rich functionalized groups of $-\text{SO}_3^-$ and $-\text{SH}$, enhance the proton
677 movement via making the channels facilitating the transport. In summary, this paper showed
678 that the SGO nanocomposite membranes achieve the best performance followed by TGO
679 membranes and GO nanocomposite membranes, concluding that the functionalized GO
680 nanocomposite membranes are ideal candidates for utilizing microbial fuel cells. However,
681 Future research should further develop to confirm these initial findings by conducting tests on
682 biofouling of the membranes and application of those proposed membranes in continuous
683 reactors for a longer period of cycles. Besides, implementing anti-biofouling strategies might
684 prove an important area for future research.

685

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