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Improvement of COD removal and electricity generation in a MFC through embedding sulfonated reduced graphene oxide in a SPEEK proton exchange membrane

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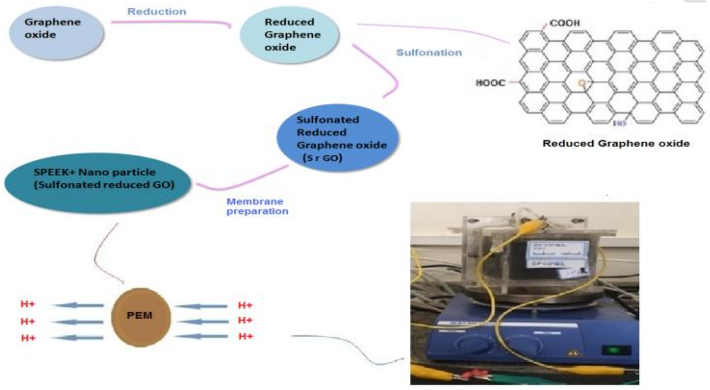
GRAPHICAL ABSTRACT



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ABSTRACT

Graphene oxide has attracted many interests in the recent decade due to its unique mechanical and chemical properties. This study focuses on the modification of graphene oxide and preparation proton exchange membrane (PEM) by sulfonated poly ether ether ketone (SPEEK) as base polymer for using in MFC as a modified membrane to remove COD and electricity generation. The scanning electron microscope (SEM) images, Fourier transform infrared (FTIR) and contact angle measurements were used to verify hydrophilic properties of the synthesized membranes. First, preparation procedures and properties of sulfonated reduced graphene oxide are briefly described. Subsequently, modification of proton exchange membrane from SPEEK polymer with prepared nano particle of sulfonated reduced graphene oxide 0.5 wt. % and its operation in MFC was considered. COD removal, power density, current density and coulombic efficiency were monitored during the process operation to evaluate the MFC performance. During the process operation, COD removal, power density, current density, and coulombic efficiency were tracked to assess the MFC performance. The power density and current density, 39.43 mW/m^2 and 161 mA/m^2 and the columbic efficiency 48.9 % was obtained, respectively. The COD removal of 89.5 % was obtained.

1. Introduction

Wastewater treatment and water reuse using cutting-edge technology are essential for future generations due to the severe decline in available water resources and the sharp rise in water use. Many different treatment technologies have been used to treat different wastewaters with various characteristics, including biological processes (Asadi, 2011; Pirsaheb et al., 2015), photocatalytic degradation (Ghasemi et al., 2016a, 2016b), coagulation and flocculation processes (Abbasi et al., 2022), adsorption (Sharafi et al., 2015), and membrane filtration (Samari et al., 2020; Vatanpour et al., 2022; Zangeneh et al., 2020). Natural treatment techniques have also been employed to treat municipal and industrial wastewaters as affordable alternatives to the aforementioned strategies. They have a lower reactor volume output as compared to mechanical treatment systems because of their prolonged retention times (Bonakdari and Zinatizadeh, 2011; Mansouri et al., 2012).

Fuel cells are an efficient, pollution-free source of clean energy, but their high cost is a drawback. Recent technological advancements have made it possible to generate electricity from natural resources.

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Microbial fuel cells (MFC) are one form of fuel cell on which current attention has been placed (Saniei et al., 2022).

Graphene oxide (GO) in comparison with graphene (G), has the benefits of low price, production in large-scale, and available processing. Graphene often used as a precursor for the reduced graphene oxide production (RGO). In recent studies on GO, scientists have noticed that GO also has main properties which are related to rich active oxygen-with functional groups (Stankovich et al., 2007). Some studies reported the capability of sulfonated aromatic polymers as the Proton exchange membranes for MFC. The low price and high mechanical and chemical stability of these polymers improve their potential as a PEM (Dai et al., 2014; Han et al., 2011; Lim et al., 2014). In many cases of polymers, the sulfonated PEEK is a suggested material which has similar structure to Nafion with sulfonic acid groups and hydrophobic backbone (Li et al., 2013). As mentioned the sulfonated PEEK obtained from sulfonation of PEEK with high concentrated sulfuric acid. The SPEEK can be considered as a promising proton exchange membrane (PEM) which is a substitution for Nafion. Due to increasing of stability and providing better proton exchange ability, some modification is required due to improve its potential as a proton exchange membrane (PEM). This modification of SPEEK can be obtained by blending of polymer with many additives such as inorganic or organic fillers (Gaowen and Zhentao, 2005; Nunes et al., 2002). Graphene oxide is a derivative material of graphene with special properties in its structure .GO has a layered structure and oxygen containing groups which are attached to the basic plane (Marcano et al., 2010; Si and Samulski, 2008). Application of graphene oxide to the base polymer in the preparation of membranes can affect the properties like the flexibility and stability of the synthesized membranes (Lian et al., 2010; Zhao et al., 2015). Existing of sulfonated groups in the structure of membrane is the factor can improve the operation of proton exchange membranes. The sulfonation of graphene oxide as a filler incorporated with membranes increase the ability of the synthesized membrane in the protons transition, so the absence of sulfonated groups with GO reduce the proton conductivity (Xu et al., 2011). The other strategy used to increase proton conductivity of nano composite membranes is the application of sulfonated reduced graphene oxide with sulfonated polymer to improve proton exchange ability. Considering that the sulfonation groups can affect the improvement of reduced GO nanoparticle property in the synthesized nano composite membranes, the sulfonation of rGO was performed. Two methods of preparation of the aryl diazonium salt as the sulfonation agent was employed. The sulfonated agent of aryl diazonium salt was prepared by two procedures: coupling method and radical method. Two synthesized sulfonated nanoparticles were used in the proton exchange membranes structure of SPEEK. The synthesized PEM membranes were used in MFC cells and the operation considered as modified nanocomposite membranes in the improvement of MFC performance. As mentioned (GO) is the derivative of graphene, containing a layered structure with oxygen in different groups, such as –COOH, –OH and –O– groups, on its basic structure and edges (Jiang et al., 2014, 2013). Graphene oxide (GO) is exfoliated form of graphite oxide and is the intermediate product which is between graphite and graphene and obtained by thermal treatment and mechanical (vigorous stirring or ultra-sonication) and chemical (ionic liquids) methods on graphite oxide. Graphene oxide was synthesized by Hummer method. In the following, the reduced –GO was prepared in the presence of Na_2CO_3.The fabricated nano composite proton exchange membrane (PEM) modified with sulfonated reduced –GO 0.5 % wt. nano particle was used in MFC for consideration of COD removal and electricity generation.

2. Materials and methods

2.1. Synthesis of GO nanoparticles

Generally, two steps are applied for graphene – based sulfonation: (1) GO reduction to obtain reduced graphene oxide (rGO) and (2) rGO sulfonation. Hydrazine (N_2H_4), Sodium borohydride ($NaBH_4$) and Na_2CO_3 can be used as reduction agents (Chauhan et al. 2009, Garg et al. 2010). In this study the reduced GO nanoparticles were prepared using sodium carbonate. Diazonium salts are classified as organic compounds having a general formula of $RN2^+X^-$ where R and X may be an alkyl or aryl residue and an (in)organic anion, respectively (Garg et al., 2014). The presence of aryl group in diazonium salts often show stability in aqueous solutions at temperatures lower than 5 °C and in the following the method for the synthesis of diazonium salts is presented. The diazonium salt achieved from aryl amin (sulfanilic acid) in the presence of HCL and $NaNO_2$, then the solution was blended to the rGo nanoparticle and Fe powder by temperature controlling below 5 °C. Finally, the obtained mixture was stirred for 3-4 h to produce sulfonated reduced graphene oxide.

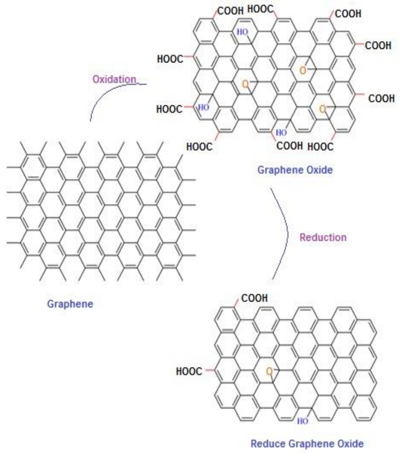


Fig. 1. Schematic image of the procedure of the rGO preparation.

According to the procedure, the diazonium salt was prepared in the presence of Fe powder through a radical reaction with rGO (c-c coupling reaction). In the next step, the nitrogen gas was released and sulfonated r GO was achieved as a result of the reaction of the radical agent and rGO. Based on literatures, the synthesized sulfonated rGO (s rGO) nanoparticles were used in proton exchange membrane fabrication with SPEEK. The fabricated proton exchange membranes with sulfonated reduced graphene oxide were used in MFC cell successfully.

2.2. Preparation of sulfonated PEEK

In the procedure of synthesis of sulfonated PEEK (SPEEK), the PEEK polymer and 90ml of sulfuric acid 95-98 % were mixed together. By stirring the mixture continuously, dissolving the polymer was completed. By adding obtained mixture to deionized water with using ice bath the precipitation was occurred. For the next step, washing of the sulfonated PEEK was done with distilled water to reach a pH of 6-7. In the final step, the sulfonated PEEK was dried (Kim et al. 2016). In this work, the synthesized SPEEK was used as a base polymer which then was modified with synthesized nanoparticle sulfonated –rGO 0.5 wt. % to be used as a proton exchange membrane (PEM) in MFC. The sulfonated PEEK was dried as the last stage (Kim et al. 2016). In this study, generated nanoparticle sulfonated -rGO was utilized to modify the base polymer SPEEK such that it could be employed as a proton exchange membrane (PEM) in MFCs.

2.3. Fabrication of PEM membranes

To produce bare membrane from SPEEK (M_0), a certain amount of sulfonated SPEEK (20 wt. %) was dissolved in the solvent Di methyl Acetamide (DMAC), after that it was sonicated for 20 minutes to form homogeneous solution. Then, membrane sheets were prepared on flat glass using the casting solution. The manufactured membrane sheets were placed in an oven set at a temperature below 70 °C for the drying process.

Then, the casting solution was employed to prepare membrane sheets on flat glass. For drying step, the fabricated membrane sheets were kept in the oven at temperature of below 70 °C. Next, the SPEEK nano filtration membranes blended with sulfonated reduced graphene oxide were fabricated. The accurate amount of Sulfonated reduced graphene oxide (0.5 %wt.) were dissolved in DMAC and sonicated for 20 minutes. After that precise amounts of SPEEK (20 wt. %) was dissolved in the prior solution and sonicated for 20 minutes again. Then, the homogeneous achieved solutions were stirred for 24 hours. In the following, casting solutions were sonicated again and casted on the flat glasses. The synthesized membranes kept in the oven in 70 °C to evaporate solvent and finally were dried. The composition of synthesized membranes is presented in Table 1. in detail. As mentioned earlier, the high amounts of nanoparticle may cause membrane fouling which leads to membrane agglomeration, so the average content of nanoparticle (0.5 wt. %) was considered as optimal percentage to improve membrane antifouling properties.

Table 1. The composition of prepared membranes for SPEEK membrane and nano composite SPEEK membrane with reduced graphene oxide nanoparticle made by radical method as M_0, M_1, are presented in detail.

Membrane	SPEEK, wt. %	Solvent	Type of nanoparticles, wt. %
M_0	20%	DMAC	
M_1	20%	DMAC	Sulfonated r-graphene oxide 0.5% (radical)

2.4. Membranes characterization
2.4.1. FT-IR test

The FT-IR test was utilized with respect for the functionalized groups of the nanocomposite structure. Analysis and discussion were conducted on the FT-IR spectra of produced nanoparticles.

2.4.2. Morphology of the membranes

Scanning electron microscopic (SEM) testing was used to examine the morphology of the produced membranes. The structural and cross-sectional characteristics of the produced membranes were evaluated using the SEM images.

2.5. Hydrophilicity of the membranes

The contact angles of the manufactured membranes were examined in order to look into how the nanoparticles affected the hydrophilicity of the membranes. The measurements allow us to see the variation in the calculated contact angle values.

2.6. MFC structure and performance

Plexi glass was used to fabricate the MFC system, which was designed in two chambers. Thermal glue was used to seal the MFC system. Both cathode and anode electrodes were made of carbon fiber. In anodic chamber, the COD removal efficiency factor was assessed. The microbial fuel cell's performance was evaluated. To assess the system's ability to generate power, the variables of voltage (v) and current (I) were tracked. Using an external resistance, the MFC functioning was investigated. To achieve better operation, MFC performance was monitored using PEMs containing host polymer of SPEEK with resistances (0.09KΩ, 0.21KΩ, 2.15KΩ, 21.73KΩ, 85KΩ, 224KΩ) to achieve more power density value. The formulae listed below were used to calculate the power and current factors:

$$P = V \times I \quad (1)$$
$$I = \frac{V}{R} \quad (2)$$

The four variables in these equations were power (P), cell voltage (V), current (I), and external resistance (R). By measuring the initial COD concentration value at the beginning of the cycle and the final COD value at the end of the retention period, the COD removal efficiency was calculated. The solution from feed (milk powder) with a COD of 2500 mg/l was prepared for MFC system. The Eqs. 3 and 4 were used for calculating the COD removal efficiency and coulombic efficiency (CE), to assess the MFC operation. The properties of the feed were showed in detail in Table 2.

$$\text{COD removal \%} = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{final}}}{\text{COD}_{\text{in}}} \times 100 \quad (3)$$
$$CE = \frac{M_s \int_0^t I\, dt}{F * b_{es} * V_{An} * \Delta C} \quad (4)$$

Table 2. The detailed composition of the feed utilized in the anode.

Parameters	Unit	Amounts
COD	mg/l	2400-2500
TN	mg/l	30-40
TP	mg/l	0.9-1.2
pH	-	6.0

3. Results and discussion
3.1. Characterization of the fabricated membranes
3.1.1. FT-IR analysis

Fig. 2 represents the results of FT-IR analysis. The presence of peak 1574 cm^{-1} in the radical spectrum can also be related to N = N diazo vibrations, although the broadening of this peak represents the overlap of other functional groups and it can be said that there is little possibility of coupling reaction alongside the radical reaction and a percentage Diazo bonds are formed. The peak flattening in different regions indicates the growth of sulfonated benzene groups as a branch on the graphene surface.

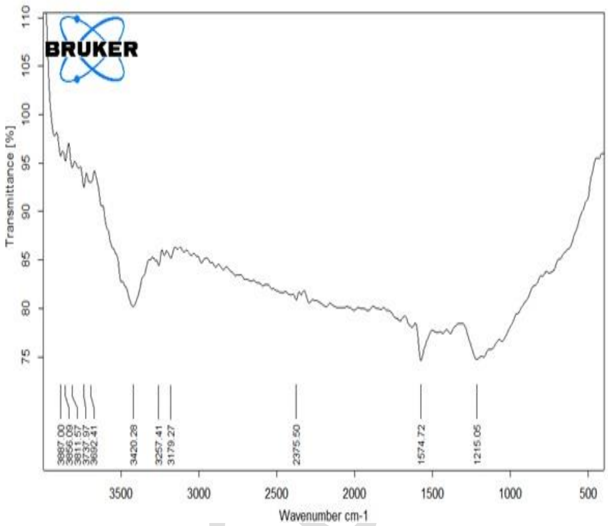
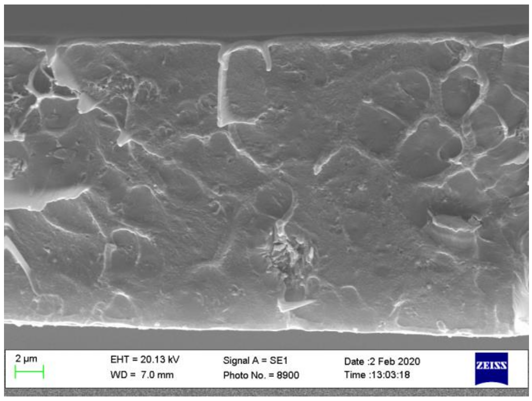


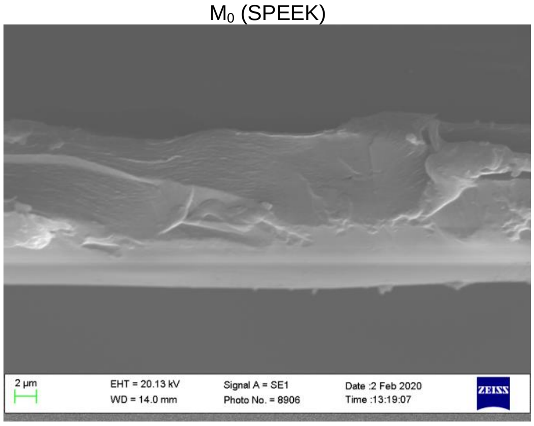
Fig. 2. The FT-IR spectrum of prepared nanoparticles from sulfonated rGO by radical methods.

3.1.2. Membrane structure and morphology

Fig. 3 displays cross-sectional (SEM) images of the SPEEK nanocomposite membrane that is naked and one that contains 0.5% weight of srGO nanoparticles. Based on the resulting SEM images, the homogenous dispersion of nanoparticles was seen across the membrane structure (Narayanaswamy Venkatesan and Dharmalingam, 2015).



M_0 (SPEEK)



M_1 (SPEEK-sulfonated-rGO 0.5%wt. radical)

Fig. 3. SEM images of the synthesized membranes of SPEEK (M_0) and M_1 (SPEEK-sulfonated-rGO 0.5%wt. radical).

The SEM images of SPEEK based nanocomposite membranes with sulfonated reduced graphene oxide nanoparticles 0.5 wt. % prepared in procedure of radical reaction of diazonium salt. As mentioned, the homogenous structure can be observed from the obtained SEM images of the synthesized membranes. The non-porous shape of the modified membranes prevents oxygen from crossing from the cathode chamber to the anode chamber, improving the performance of the MFC system.

3.2. Contact angles

The modification of membrane's hydrophilicity can affect the increasing of the antifouling properties of the proton exchange membrane. Thus, the contact angle measuring of the fabricated membranes were performed from M_0 and M_1. This is a convenient method to evaluate the hydrophilicity of these modified membranes. The measured contact angles are shown in Fig. 4. According to the results, smaller values improve the hydrophilicity properties of the membranes which affect their operation.

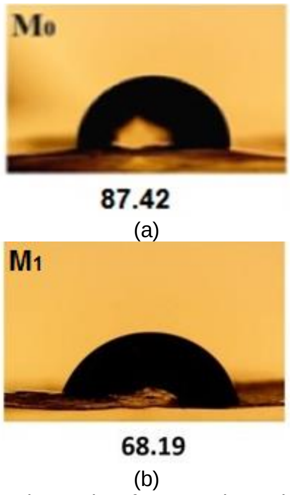


Fig. 4. Contact angle results of prepared membranes:a) SPEEK (M_0) and b)sulfonated reduced graphene oxide 0.5% wt.(radical)-SPEEK (M_1).

3.3. MFC performance
3.3.1. Power density and columbic efficiency

The created SPEEK nanocomposite membrane with sulfonated rGO 0.5 wt. %, whose nanoparticle was synthesized by radical technique, demonstrated power density value of 39.43 mW/m^2 as a created proton exchange membrane with starting COD (2500 mg/L). Then, MFC performance in cell containing proton exchange membrane (PEM) with host polymer of SPEEK in the presented resistances: 0.09 KΩ, 0.21KΩ, 2.5KΩ, 21.73KΩ, 85KΩ, 224KΩ was considered to reach higher power density. The results were achieved from SPEEK PEM with sulfonated rGO radical 0.5 wt. % (M_1) as a hydrophilic nanoparticle with power density and current density, 39.43 mW/m^2 and 161mA/m^2 respectively. The coulombic efficiency 48.9 % was achieved. The results show improving performance of the MFC. The results of COD and CE measurements are presented in Fig. 5 and the operation factors of MFC are listed in Table 3. The curve of the measured power and current of SPEEK nano composite membrane with sulfonated reduced graphene oxide 0.5 wt. % nanoparticle made by radical method as M_1 in different resistances is presented in Fig. 6. It shows the obtained values of power and current of the MFC system with fabricated proton exchange membrane.

Table 3. The obtained value of power density and current density and Columbic efficiency of prepared membranes of SPEEK as M_0 and SPEEK with sulfonated reduced graphene oxide 0.5% nanoparticle made by radical method as M_1 is presented in detail.

Membrane	Maximum power density, mW/m^2	Current density, mA/m^2	Columbic efficiency, %	COD removal, %
M_0	41.93	166	40.7	96.2
M_1	39.43	161	48.9	89.5

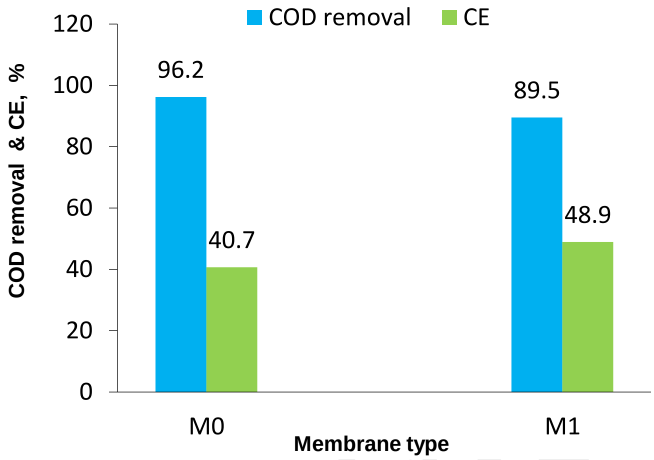
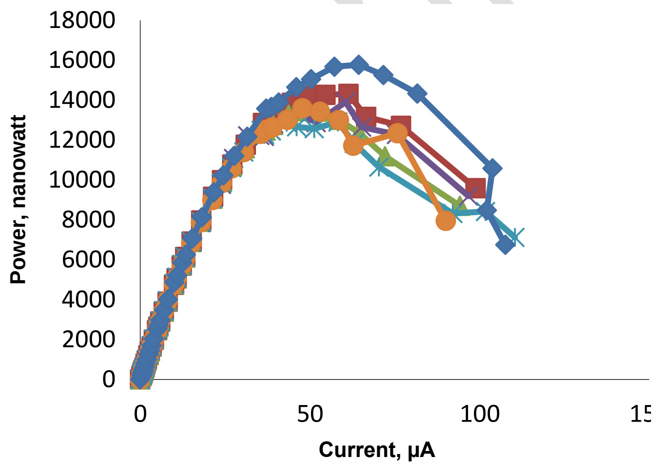


Fig. 5. The obtained results from COD and CE of the fabricated membranes: SPEEK (M_0) (Saniei et al. 2022) and sulfonated r GO-SPEEK radical (M_1).



M_1 (SPEEK-sulfonated rGO 0.5 %wt.-radical)

Fig. 6. Polarization curves of SPEEK nano composite membrane with sulfonated reduced graphene oxide 0.5% wt. nanoparticle made by radical method as M_1 in different resistant values.

4. Conclusions

In this work, the performance of the MFC system was examined using proton exchange membranes made of SPEEK and sulfonated reduced graphene oxide (0.5%wt.) by radical technique. The obtained results demonstrated the ability and compatibility of the prepared membranes as a proper proton exchange membrane for COD removal and electricity generation. The coulombic efficiency 48.9% and the COD removal 89.5% were obtained. The power density and current density of 39.43 mW/m^2 and 161mA/m^2, respectively, were achieved. According to these results, not only the proposed MFC system can be effective in electricity generation, it may also provide an attractive solution for organic pollutants removal from wastewater.

Author Contributions

Nasim Saniei: Conceptualization, methodology, analysis and interpretation of results, writing
Nahid Ghasemi: Supervision, designing, reviewing and editing
Ali Akbar Zinatizadeh: Supervision, designing, reviewing and editing
Sirus Zinadini: Reviewing and editing
Majid Ramezani: Reviewing and editing

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Conflict of Interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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