PPy/AQS (9, 10-anthraquinone-2-sulfonic acid) and PPy/ARS (Alizarin Red's) modified stainless steel mesh as cathode membrane in an integrated MBR/MFC system
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Yaojie Li a, Lifen Liu a,b,c,*, Jiadong Liu a, Fenglin Yang a, Nanqi Ren c

Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China
School of Food and Environmental Science and Technology, Dalian University of Technology, Panjin, China
State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001, China

Abstract

To increase effluent quality and membrane flux, membrane bioreactor was integrated with microbial fuel cell (MBR/MFC), in which functional cathode membranes could enable fouling reduction and even electro-catalytic pollutant degradation using the bio-generated electricity. Modifying stainless steel mesh (SSM) with only polypyrrole (PPy) or cheap ARS (Alizarin Red's) or expensive AQS (9,10-anthraquinone-2-sulfonic acid) doped PPy film, helped obtain high ORR (oxygen reduction reaction) activity and higher power output in the integrated MBR/MFC system. The ARS and PPy modified cathode membranes, could not only increase the degradation of (MB) methylene blue (∼90%, 1 h), but also enable higher antifouling property in filtrations. Most importantly, replacing the blank SSM, the use of PPy/AQS, PPy/ARS and PPy modified SSM, increased power density 31.37, 27.06 and 23.7 times respectively in the integrated MBR/MFC system. The new system has great application potential and economic feasibility in effective removal of COD and NH4+-N nutrients, has better effluent qualities and has higher energy recovery.

1. Introduction

Membrane bioreactor (MBR) is a device equipped with membrane in a bio-reactor [1], it has many advantages due to its high effluent quality, small space occupation and high degree of automation. However, the intensive energy consumption for aeration and membrane fouling are the main problems restricting its wide application [2,3]. So it's urgent to find a new technology to offset the energy consumption or reduce the cost of membrane.

According to previous studies [4,5], minute electric fields can be used in reducing membrane fouling in MBR and microbial fuel cell (MFC) can provide such an electric field. MBR integrated MFC is quite a promising technology in wastewater treatment and electricity production. It can directly extract electricity from diverse organic wastes through bio-electrochemical activities [6]. Many studies integrating MBR with MFC were successfully conducted [7–9]. In a bio-electrochemical MBR-MFC reactor, the maximum power density of 4.35 W/m² was obtained, using stainless steel mesh as both the cathode and the filtration material [8]. Another design used cost effective materials (carbon felt) as the cathode and a maximum power density of 6.0 W/m² was obtained by inserting MFC into MBR [9].

To improve energy output in MFC, some researchers focused on developing air-breathing MFCs equipped with stainless steel mesh as the cathode catalyst support, as it is more conductive and adjustable, in
addition to its low cost [10,11]. Others [12–14] studied cathode catalysts, such as MnOx [12,14] and Pt-Fe [13], CoNPs [15] and carbon nanotube [16]. Anthraquinone-2,6-disulfonate (AQDS) [17] can accelerate electron transfer and cathode reactions (ORR) in fuel cell. Developing effective catalyst on cathode membrane is critical for the integration of MFC with MBR.

PPy was mainly used as a substrate in catalysis for its interesting properties such as good conductivity and environmental stability, biocompatibility [18] and the catalytic activity towards ORR [19]. It can be a good alternative to Pt in MFCs due to economic advantages. MFC equipped with polyppyrol/anthraquinone-2-sulfonate (PPy/AQS) film-modified stainless steel mesh cathode could generate power at density of 575 mW/m² [20]. In a dual-chamber microbial fuel cell (MFC), polyppyrol (PPy)/anthraquinone-2,6-disulfonate (AQDS) conductive film can be used as cathode and anode [21]. However, no one is using them as membrane modules and applying them in the integrated MFC/MBR system. That’s why we put forward our research.

In this study, the modification of stainless steel mesh was realized via constant-potential anodic electro-polymerization of pyrrole. During the modification, film of PPy doped with expensive AQS (9,10-anthraquinone-2-sulfonic acid sodium salt) or cheap ARS (3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid sodium salt, Alizarin Red's), was formed on SSM and used as cathode catalysts. PPy and anthraquinone sulphonate dopants were chosen as they can be coated onto the SSM membrane quite firmly through electro-polymerization. To lower the cost, ARS (98 per kg), a typical anthraquinone dye, was used. Cyclic voltammetry (CV) tests were performed in 0.1 M Na₂SO₄ solution by using the modified electrodes as the working electrode whereas SCE and a Pt sheet (10 × 10 mm) as counter electrode.

2. Materials and methods

2.1. Cathode fabrication and characterization

A piece of stainless steel mesh (purchased from Shanghai Suta Filter Material Co., Ltd. China) was used as the substrate membrane (pore size 15 μm). Prior to use, the SSM was cleaned ultrasonically and then degreased in acetone and ethanol successively (each for 2 h), followed by rinsing with distilled water. Anthraquinone sulphonates AQS and ARS were chosen as target dopants. Their structures were shown in Fig. 1. The PPy/AQS and PPy/ARS were coated on the SSM electrode as a thin film formed by electro-polymerization in a three-electrode electrochemical cell. It was carried out on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Company, China) connected to a computer, with a saturated calomel electrode (SCE) as reference electrode and a Pt sheet (10 × 10 mm) as counter electrode, respectively.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Resistance (Ω/cm)</th>
<th>Weight increase (mg/cm²)</th>
<th>Water flux (L h⁻¹ m⁻²)</th>
<th>Average flux reduction F/F₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSM</td>
<td>1.1 ± 0.1</td>
<td></td>
<td>1433.3 ± 11.1</td>
<td>1</td>
</tr>
<tr>
<td>PPy-coated SSM</td>
<td>3.0 ± 0.2</td>
<td>3.4 ± 0.4</td>
<td>1441.1 ± 11.1</td>
<td>0.98</td>
</tr>
<tr>
<td>PPy/ARS-coated SSM</td>
<td>3.8 ± 0.3</td>
<td>3.9 ± 0.2</td>
<td>1222.2 ± 22.2</td>
<td>0.85</td>
</tr>
<tr>
<td>PPy/AQS-coated SSM</td>
<td>3.3 ± 0.3</td>
<td>5.3 ± 0.3</td>
<td>1138.9 ± 5.6</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The electro-catalysis experiments were performed at room temperature, using a three-electrode system, a beaker and CHI 600E electrochemical workstation (Shanghai Chenhua Instrument Company, China). The modified cathode electrode was used as the working electrode whereas SCE and a Pt sheet (10 × 10 mm) were used as the reference and counter electrodes respectively. The reaction system had 100 mL solution, with an initial concentration of 5 mg L⁻¹ methylene blue (MB, C₁₆H₁₈ClN₃S · 3H₂O, Shenyang reagents) and 0.05 mol L⁻¹ Na₂SO₄ as the supporting electrolyte. Air was bubbled into the solution at an aeration rate of 60 mL min⁻¹ during the degradation process.
pH was adjusted to 3 with 0.5 M H2SO4 solution and cathode voltage was at −0.4 V. The MB concentrations were analyzed by measuring the absorbance at 665 nm using a visible spectrophotometer 722E (Shanghai Spectrum Instruments Co., Ltd, China).

Additionally, in order to determine the anti-fouling properties of the modified cathode membrane, filtrations and anti-fouling experiments were carried out. The vessel for the experiments had a volume of 2 L and the aeration rate was kept at 0.2 m3/h. The effective permeate membrane area was 27 cm2. The freshly prepared PPy/AQS and PPy/ARS modified SSM were tested in filtrating yeast suspension solution, simulating mixed liquor suspended solids (MLSS) in MBR (MLSS = 0.5 g/L), while the unmodified and only PPy modified membrane were also compared. In all experiments, the MBRs were operated in a gravitational filtration mode at constant trans-membrane pressure (TMP) 4.5 kPa, so they have the same water head drop (ΔZ = 450 mm).

The permeate flux (F) was calculated though the equation \( F = q/\mu \) where \( t \) is the time interval, \( A \) is the area of the membrane, and \( q \) is the volume of the collected permeate during the time interval of every 5 min. Each experiment lasts for one hour. The \( t/V - V \) curves belong to classical filtration model and the slopes of the curves can be used for comparing the filtration capacity of different membrane modules.

2.3. The Batch MBR/MFC experiments

The setup of the experiment is shown in Fig. 2. The MFC/MBR system consisted of two chambers. One cylinder anode chamber with an effective volume of 100 mL was set in the middle and the surrounding annular space was the cathode chamber. The anode chamber was filled with granular activated carbon, with a graphite rod (d = 5 cm) inserted to collect electricity. The anode chamber wall had many holes and was wrapped with filter cloth. The cathode chamber (800 mL) had active sites for redox reactions. The morphology of PPy, PPy/AQS and PPy/ARS on SSM clearly exhibits a rough and granular surface feature, similar to Ref. [23]. The surface of PPy/AQS and PPy/ARS films is even rougher, with larger granule feature. The conductivity is higher for the doped PPy modified SSM than the PPy only modified SSM. Additionally, the PPy/ARS, PPy/AQS and PPy coated on SSM could not be removed, even under intensive wiping, indicating that the interaction between the coated films and the SSM was very strong and intensive.

To evaluate power performance of the system, the anode and cathode polarization curves and the cell power density curves were obtained by varying the external resistor over the range from 10,000 to 5 Ω when the performance of MFC approached steady state. Current Intensity (I) was calculated as \( I = U/\Omega \) (external resistance), and power (P) was calculated as \( P = U \times I \). Both I and P were normalized to the projected area of cathode surface (27 cm²) to evaluate current and power density respectively. The anode potential was measured by inserting an SCE electrode into the anode chamber; the cathode potential was calculated as the sum of the anode potential and the cell voltage. The HRT of the anode chamber was calculated from the net effective volume of the anodic chamber and influent flow rate.

The ammonium nitrogen (NH4-N), chemical oxygen demand (COD), total phosphorus (TP), turbidity (NTU), and mixed liquor suspended solids (MLSS) were measured according to the standard methods [22]. The pH value was tested in a pH meter (CT-6021A).

3. Results and discussion

3.1. SEM

The SEM images of the stainless steel mesh (SSM) and the modified SSM samples with electro-synthesized coating of PPY, PPY/ARS and PPY/AQS are shown in Fig. 3. For the composite electrodes, small particle size and high porosity are desirable because these features enable more surface active sites for redox reactions. The morphology of PPY, PPY/AQS and PPY/ARS on SSM clearly exhibits a rough and granular surface feature, similar to Ref. [23]. The surface of PPY/AQS and PPY/ARS films is even rougher, with larger granule feature. The conductivity is higher for the doped PPY modified SSM than the PPY only modified SSM. Additionally, the PPY/ARS, PPY/AQS and PPY coated on SSM could not be removed, even under intensive wiping, indicating that the interaction between the coated films and the SSM was very strong and intensive. It is favorable for bacteria attachment and biofilm formation as anodes in MFCs, it is also a good cathode and filtration material. The physical properties of the modified membrane electrodes can be found in Table 1. It is clear that the conductivity and water flux did not change much after the modification. The average flux reduction for PPY/AQS modified SSM is 0.779. It is clear that the PPY/AQS coating has much more dense structure, they polymerize on the coarse surface of the base membrane instead of around the steel wires. The larger the pore size is, the more easily membrane fouling happens. The chemical
substances may block the gaps in SSM membrane. When it was not too serious, it still has a good filtration flux as a membrane module.

3.2. Cyclic voltammograms (CVs)

To investigate the effect of incorporation of PPy, AQS and ARS in the SSM substrate, the CV curves were measured (Fig. 4). An oxygen reduction peak appeared on the CV with PPy at approximate $-0.57$ V in O$_2$ saturated solution. The value is quite similar to the reported literature of $-0.6$ V [19]. It can be seen that the incorporation of different anthraquinone sulfonate species in PPy matrix significantly improves the current generation over a broader potential range, compared with bare SSM, and increases ORR activity in the presence of oxygen. It also suggests the enhancement of specific capacitance because of the

![Fig. 3. SEM images of cathode membrane electrode with different magnification. (A) unmodified stainless steel mesh (1000×), B1–B2; C1–C2; D1–D2, the PPy, PPy/AQS, PPy/ARS, 1 and 2 corresponds to 4000× and 8000× magnification respectively.](image)

![Fig. 4. Cyclic voltammograms of (a) PPy-SO$_4^{2-}$, (b) PPy/ARS and (c) PPy/AQS modified SSM compared with bare SSM in 0.1 M Na$_2$SO$_4$ solution saturated with N$_2$ or O$_2$.](image)
increased surface area of the three kinds of electrodes. For PPy/ARS, it improved most significantly. The other reason for current improvement is the oxygen reduction on the electrodes.

To investigate further the ORR catalytic activity, both the membrane cathodes were tested under O₂ or N₂ saturated conditions. For the PPy/ARS coated SSM, the reduction peak appears at potential of −0.67 V while the PPy/AQS coated SSM is −0.73 V and −0.5 V. The additional redox peaks are observed at potentials negative to the redox potential of PPy. It was reported similarly in the literature [23,24]. These additional redox peaks are associated with oxidation–reduction processes of hydroanthraquinone/anthraquinone groups. It demonstrates the presence of the anthraquinone sulfonate species in PPy substrate.

3.3. Electro-catalysis and filtration performance

3.3.1. The electro-catalytic degradation of MB

In Fig. 5b, the removal rate of MB by electro-catalysis using different cathode membrane was shown, being faster using PPy/AQS, PPy/ARS and PPy modified SSM electrodes than the unmodified SSM. The reason is that catalyst doping increased reaction rates by reducing the activation energy. MB molecules can be oxidized by H₂O₂ species generated from the modified cathode with promoted oxygen reduction while anthraquinone sulfonate dopants work as catalysts [25], or by •OH radicals generated from anode.

A high degradation rate was maintained for the modified electrode after several cycles, indicating a good stability (Fig. 5a) and high catalytic activity. The removal rate (>94%) and stability for PPy/AQS modified electrode were a little higher than the other three, suggesting that the modified membrane is feasible for practical operation. The immobilization of AQS or ARS into PPy matrix increased the electrochemical activity and improved the stability greatly. Thanks to the stronger bonding, the electrodes can be used many times without worrying the loss of the catalyst.

3.3.2. The SSM modification improved filtration permeability

The t/V–V curves of different cathode membrane electrodes are shown in Fig. 6a. It shows that the slopes of modified membranes are smaller than that of stainless steel mesh. The slope is an indicator of membrane fouling. From the figure, the slope of the PPy, PPy/AQS and the PPy/ARS is 73, 52 and 57, while that of the unmodified stainless mesh was 81. So the PPy/AQS, PPy/ARS membrane modules have superior performance than the other two kinds of membrane modules. There are two models about membrane fouling [26]. For our modified membranes the classical filtration model fits well, the higher the slope, the higher the membrane fouling, and the more decrease in accumulated permeation volume. It happened because the membrane pore size was initially narrowed down by the particles to be filtrated, and then the deposit particles started to form a cake layer on membrane surface and decreased the flux. In Fig. 6b, the regularity in the flux changes in the three cycles yeast filtration test was shown.

The flux of modified membrane was much smaller than the blank membrane in the first filtration cycle. This is caused by the coating of PPy, PPy/AQS and PPy/ARS, blocking the open gap on stainless steel mesh, resulting in a much smaller pore size (Table 1). From the three filtration results, it is shown that the modification of the membranes can

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**Fig. 5.** The stability of the modified membrane electrodes (a) and the removal rate of MB by electro-catalysis of cathode membrane electrode (b).

**Fig. 6.** The t/V–V curves (a) of different cathode membrane electrodes and Permeate flux of stainless steel mesh, PPy, PPy/ARS and PPy/AQS membrane electrodes applying in three filtration cycles (b).
achieve much better permeation than the unmodified one, better anti-fouling properties, plus higher ORR in MFC/MBR system.

3.4. Cell voltage, power output and polarization curve

In order to verify and explore the effects of modified membrane electrodes, the MBR/MFC was operated using the same cell structure and anode system but various modified cathode membranes. It’s clear that the system cell voltage was only 0.03 V for SSM, but 0.13 V, 0.12 V and 0.11 V respectively for PPy/AQS, PPy/ARS and PPy modified SSM (Fig. 7). The low voltage generation can be attributed to the fact that there is only one graphite rod to collect electricity. Poor collection of the electricity generated may lead to lower current. Another reason was that the anode chamber was not strictly anaerobic with the polyester filter cloth as separator. But this filter separator facilitated proton transfer by permeation without using ion exchange membrane. Though the power output is small, it proved that the modification increased electricity generation (Fig. 8).

The power densities and polarization curves are indicators of the performance of MBR/MFC. As shown in Fig. 8, using the unmodified SSM membrane, the maximum power density is just 0.5 mW m\(^{-2}\) (the surface area was the projected cathode membrane area) or 13.61 mW m\(^{-3}\) (based on the volume of the anode chamber). In contrast, for the PPy/AQS modified SSM, it is 15.87 mW m\(^{-2}\) (428.49 mW m\(^{-3}\)), for PPy/ARS and PPy modified SSM, it is 13.53 mW m\(^{-2}\) (328.05 mW m\(^{-3}\)), 11.85 mW m\(^{-2}\) (320 mW m\(^{-3}\)) respectively. The increase of power densities demonstrates that modified membranes performed better catalytic ORR activity than the blank SSM membrane. The PPy/AQS coating increased power density by 31.74 times compared with the blank SSM, while the PPy/ARS and PPy coating increased 27.06 times and 23.7 times. The ARS coating is quite cost-effective in terms of enhanced power generation.

Additionally, the enhancement of cathode performance was mainly responsible for the boost of power performance. It was confirmed by the anode and cathode polarization curves (Fig. 8b). From the anode polarization curves, there were insignificant variations in the anode open circuit potentials (OCPs) and working potentials. In contrast, the variations in the cathode OCPs and cathode working potentials were pronounced depending on cathode modules with different catalysts.

3.5. The effluent qualities

For wastewater treatment systems, it is vital to evaluate the removal efficiencies of COD, nutrient and other parameters. The changes of COD and NH\(_4\)\(^+-\)N, TP, pH and NTU with different cathode membrane modules, at the hydraulic retention time (HRT) of 1.2 h in the anode chamber, are shown in Fig. 9, indicating good COD and NH\(_4\)\(^+-\)N removal efficiencies. Both the COD and NH\(_4\)\(^+-\)N removal rate can reach >95% at the end. TP removal became higher as the system operation continued reaching a very high removal rate in the end. COD removal increased when modified SSM was used. It is mainly attributed to the respiration of heterotrophic bacteria, a little part to the electro-catalytic oxidation. NH\(_4\)\(^+-\)N removal remains stable. The TP removal was higher after several cycles of treatment as the MLSS increased in the system.

One can notice quite remarkably that the COD and NH\(_4\)\(^+-\)N removal in the anaerobic effluent treatment is also very high. This is due to the fact that the anode chamber could not be made extremely anaerobic. And some electro-microorganisms are facultative aerobes. They can survive well in the anaerobic and aerobic environment well, and consume COD and nutrients. The removal rate increased when cathode activity increased, because of the increased electron transfer efficiency.

After treatment, the turbidity of the effluent is below 2 NTU without odor. It suggested that this kind of membrane module can be useful in actual practice. The effluent pH is around 7–8 which meets the discharge standard.

Compared with other MFC system, the final effluent quality is higher, as shown by comparison with following reported data. One of the first tests exploring domestic wastewater treatment using an air cathode MFC with graphite rods demonstrated a total COD removal of about 50% at the HRT = 6 h [27]. A power density of 464 mW m\(^{-2}\) (15.5 W m\(^{-3}\)) and 40%–50% COD removal was achieved by wastewater flow through the carbon cloth anode [28]. And domestic wastewater treatment was examined under two different temperatures and flow.

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**Fig. 7.** A cell voltage–time curve with an external resistance of 500 Ω.

**Fig. 8.** The power density curves (a) and anode, cathode polarization curves (b) of different cathode membrane electrodes.
modes, with the highest power densities (422 mW m\(^{-2}\), 12.8 W m\(^{-3}\)),
but COD removal was only 25.8% \cite{29}.

Overall, the advantages of this MFC/MBR system were shown in the
following aspects. (1) Cheap filter cloth worked as separator, without
using an ion exchange membrane. (2) The relatively low cost cathode
membrane had higher ORR activity. (3) Higher effluent quality was ob-
tained by filtering through the cathode membrane after sequential an-
aerobic and aerobic treatment. (4) The electro-catalytically active ORR
electrode may generate oxidizing species to degrade chemical pollutant
in wastewater, for safer or less risky effluent; exert an germicidal activity
and further enhance antifouling property of the modified SSM mem-
brane. (5) Higher power output can be obtained using the PPy/AQS,
PPy/ARS and PPy modified SSM cathode membrane. The modified
membrane material may also work as anode in the MBR/MFC system.

4. Conclusion

In this paper, PPy, PPy/AQS and PPy/ARS film were successfully
electro-polymerized and coated onto the stainless steel mesh at
constant anodic potential using 0.5 M pyrrole and 5 mM AQS or ARS.
For the first time, they are used in MBR/MFC system as cost-effective
catalysts. The novelty and benefits of the integrated MFC/MBR using
the modified cathode membrane are shown by the higher effluent qual-
ity, higher treatment efficiency and 20–30 times higher electricity

Fig. 9. The properties of the influent and the (anaerobic or aerobic) effluent in MBR/MFC system.
generation. These advantages promise the use of the membrane electrodes for constructing large-scale MFCs for wastewater treatment and bioelectricity production. Though the reactor power output was not higher enough than other researches, the energy and environmental benefits are verified.

Acknowledgments

This research was supported by China National Natural Science Foundation (Project No. 21177018) and State Key Laboratory of Urban Water Resource and Environment (Project No. QAK201204).

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