A bio-electrochemical membrane system for more sustainable wastewater treatment with MnO2/PANI modified stainless steel cathode and photosynthetic provision of dissolved oxygen by algae

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ABSTRACT

A competitive sewage treatment technology should meet the standard of water quality requirement and accomplish recovery of potential energy. This study presents such a new system, with coupled membrane bioreactor-microbial fuel cell features, which can not only treat wastewater, but also recovers energy from wastewater by electricity generation, and form a new resource by photosynthesis while providing the dissolved oxygen by algae. Specifically, in the system, the MnO2/polyaniline is used to modify the stainless steel mesh and to function well as system membrane and cathode, with satisfactory filtration and catalysis performance. The system enables continuous wastewater treatment with stable pollutant removal and electricity generation. Under the membrane flux of 119.4 L m⁻² h⁻¹, a maximum power density of 1.2 W m⁻³ can be achieved, the algae multiply 6.1 times, and satisfactory wastewater treatment effect is achieved.

INTRODUCTION

Membrane bioreactor (MBR) processes are gaining increasing popularity for wastewater treatment in recent years, but membrane fouling is still a key technical problem. Several recent studies found that electrochemical membrane fouling control can be realized (Liu et al. 2012a, 2012b; Wang et al. 2013b). And studies used conductive membrane as cathode of microbial fuel cell (MFC) to generate the minute electric field to alleviate membrane fouling (Liu et al. 2012a; Wang et al. 2013a). This avoids the additional supply and arrangement of an electric field. In those studies, mechanical aeration was adopted to maintain the dissolved oxygen (DO) in the water and provision of electron acceptor in MFC, which is a real disadvantage in term of energy consumption (Logan et al. 2006). Therefore, to make up, photosynthetic bio-electrochemical research which uses photosynthetic micro algae to generate and maintain the DO in water is becoming very popular. The enriched green alga presents itself as an available resource (Raman & Lan 2012).

In configuration, photosynthetic bio-electrochemical MFC generally adopts double chamber model which is not only complex in operation, but also not making full use of the algae. Therefore, a tertiary treatment system, including anaerobic, aerobic treatment and algae processing was introduced, which meets discharge water quality requirements and continuously produces energy (Zhou et al. 2012).

Stainless steel (SS) net was often used as cathode in MFC, but its cathode catalytic activity is not high enough to guarantee high efficiency electricity generation. To enhance its cathode performance, researchers from Belgium used oxidative heating treatment of the SS to form an oxide surface layer for better catalytic activity (Guo et al. 2013). However, unmodified SS net, even a 500 mesh one, cannot guarantee as good micro-filtration effect as membrane in water treatment.

In this study, SS (304, 500 mesh) would be modified using MnO₂ and polyaniline (PANI) to achieve efficient membrane filtration and electricity generation. A bio-electrochemical membrane system with a MnO₂/PANI modified SS membrane cathode would be constructed and tested. Immobilization algae would be used to provide DO

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enriched water for the membrane cathode instead of aeration.

**MATERIALS AND METHODS**

**Reactor setup and operation**

The MBR-MFC reactor consists of two cylinder tubes, the centered inner tube is the anode chamber (13.5 cm long and 4 cm in diameter; empty bed volume 170 mL) filled with activated carbon particles, acclimated with electricity-generating microbes. The cylinder has punched holes all over and its outside was covered with polyethylene (PE) non-woven fabrics as separator. The concentric annular space between the two cylinders was the cathode chamber (volume 565 cm³). The framed cathode membrane module is made of modified 500 mesh SS (100 cm², 5 cm × 10 cm × 2 pc), and functions as filter membrane. The external resistor was 1,000 Ω.

The constituent of artificial wastewater was CH₃COONa (1.25 g L⁻¹), NaCO₃ (20 mg L⁻¹), NH₄Cl (44.6 mg L⁻¹), K₂HPO₄ (40 mg L⁻¹), CaCl₂ (23 mg L⁻¹) and MgSO₄ (37 mg L⁻¹). Wastewater was continuously pumped into the anodic chamber using a peristaltic pump with the feed rate 0.11 L h⁻¹, resulting in a filtration flux of 22.7 L m⁻² h⁻¹. The effluent from the anodic chamber continuously permeated/flowed into the cathode chamber through the separator. There was a separate set of algae pond (600 mL), which allow liquid cycle between the pond and the cathode chamber, linked by a hose and a pump. A schematic of the system can be found in Figure 1.

Oxygen enriched liquid solution in algae pool was pumped into the cathode chamber (1 L h⁻¹), and the cathode chamber liquid solution (with CO₂) continuously flowed into the algae pond by gravity, resulting in a balance of water level between the cathode chamber and the algae pool. The hydraulic retention time for anodic chamber and cathode chamber were 1.5 h and 4.7 h. The effluent was finally discharged by pump at the rate of the membrane flux.

**Preparation of immobilized algae beads of the algae pond**

*Chlorella pyrenoidosa* was purchased from Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China) and cultivated in a blue-green medium (BG11) (He et al. 2014). The algae cells in logarithmic growth phase were harvested by centrifugation at 3,500 rpm for 10 min and mixed with 5% sodium alginate solution, then the mixture was dropped into the pre-cooled 2% CaCl₂ solution with a 10 mL syringe over the liquid surface at 15 cm distance and fallen mixture formed *Chlorella* beads in the solution. The solution was continuously stirred using a glass rod then stored in a 4 °C refrigerator for 4 h to complete *Chlorella* immobilization (He et al. 2014). With the effect of chemicals and low temperature, the mixture of
Chlorella and chemicals presented as gel beads and sink at the bottom of algae pond, which was expressed in this research as immobilized Chlorella beads. Chlorella was trapped and grow inside the gel-like beads until the leakage occurred. Chlorella may be one of the factor of membrane fouling as its micron size if it flows into cathode chamber, Chlorella immobilization beads could keep Chlorella growing stably in pond.

Preparation of catalytic and conductive membrane cathode

The membrane mentioned in this study (unmodified SS and modified SS) was not typical traditional membrane, but conductive membrane, which could be used as membrane and generated minute electric field to alleviate membrane fouling at the same time. Solution of 0.5 mol L\(^{-1}\) CuSO\(_4\) was prepared and then the polished clean SS mesh was put in. Under 4 V voltage (current is 0.93 A), after 180 s galvanization, the SS was lifted out, then dried at 60 °C. Then, in 10.5 g L\(^{-1}\) acidic potassium permanganate solution of 60 °C water bath, the plated SS was soaked for 12 h to complete MnO\(_2\) in situ chemical vapor deposition.

Two kinds of solutions, A and B, were prepared. For solution A, dissolving 1.25 mmol ammonium persulfate in 1 mL deionized water. For solution B, mixing 0.921 mL phytic acid and 5 mmol aniline in 2 mL deionized water. By spraying solution A and then solution B equally at the surface of MnO\(_2\) modified SS, the final modification of SS by MnO\(_2\)/PANI was completed (Pan et al. 2012).

Analysis and calculations

Total algae biomass was calculated by measuring the optical density of the anolyte at 650 nm (Li et al. 2008). Voltage outputs were recorded by a data acquisition system. After stable voltage outputs were obtained, polarization curves were obtained by varying the external resistances from 9,999 to 10 Ω (Chandra et al. 2012). Power was calculated as \(P = V^2 R^{-1}\), where \(P\) = power, \(V\) = voltage, and \(R\) = resistance. Power density was normalized by reactor volume (W m\(^{-3}\)). The power density were calculated based on the anode volume according to the reference (Liu & Logan 2004). DO was monitored by a DO meter (JPB-607A, INESA Co., China). Chemical oxygen demand (COD\(_C\)), ammonium-nitrogen and turbidity were measured by standard methods (APHA/AWWA/WEF 2005).

RESULTS AND DISCUSSION

Effect of SS modification on electricity generation

Manganese dioxide has excellent capacitive and catalytic performance, which is low cost and widely applied (Chatzidaki et al. 2007; Devaraj & Munichandraiah 2008; Qu et al. 2009). Manganese dioxide was considered an effective catalyst for oxygen reduction reaction and could be used in MFCs. A maximum power density of 696.3 mW m\(^{-2}\) with the current density of 0.25 mA cm\(^{-2}\) was achieved in a manganese dioxide cathode in two chamber MFC (Sun et al. 2008). A maximum power density of 210 mW m\(^{-2}\) was produced from the MFC with in situ formed MnO\(_2\)/CNTs cathode, which was 2.3 times of that produced from the MFC using mechanically mixed MnO\(_2\)/CNTs (Zhang et al. 2011).

The cathode modified by MnO\(_2\) could increase power density; however, previous results indicated that MnO\(_2\) in situ deposition would detach after cathode was soaked in the water over hundreds of hours (Yang et al. 2016). When an electrical-conductive PANI layer was formed on the outside of manganese, it can increase the stability and conductivity of the SS mesh based cathode membrane. Thus, in-situ deposition MnO\(_2\)/PANI was used in this study. The scanning electron microscope of MnO\(_2\) and MnO\(_2\)/PANI modified SS membranes can be found in Figure 2. PANI polymerized on the surface of MnO\(_2\), strengthened the stability of MnO\(_2\)/PANI on cathode.

After the operation became stable in algae pond and biorephotoelectrochemical membrane system, the cell voltage and polarization curve were measured. As shown in Figure 3(a), when unmodified SS was used as cathode, power density was just 0.08 W m\(^{-3}\) based on the anode volume. Using MnO\(_2\)/PANI modified SS cathode, the power density was increased to 1.2 W m\(^{-3}\), which was 15 times that using unmodified SS cathode. Internal resistance of the system was decreased from 1,300 Ω to 230 Ω after MnO\(_2\)/PANI modification. In previous literature, 328.05 mW m\(^{-3}\) power density was obtained in an integrated MBR/MFC system of PPy/ARS modified SS mesh cathode membrane (Li et al. 2014). The maximum power density of MFC/MBR system with C–Mn–Fe–O catalyst in cathode membrane was 1.358 W m\(^{-3}\) in a setup with an aerator (Li et al. 2015). In this research, aerator was removed but the power density was comparable with the result obtained with aerator because of the good performance of algae.

The cell voltage changes before and after using MnO\(_2\)/PANI modified SS as cathode in the system is shown in
Due to the light intensity changes, the cell voltage fluctuated regularly during the day and the night time. Sunlight was the power source of photosynthesis for algae, which was used to provide cathode oxygen. Output voltage fluctuated day and night followed by light intensity, and similar phenomena was observed in several previous photosynthetic MFC publications (He et al. 2009; Malik et al. 2009; Zhang et al. 2012b). Power or voltage generation increased when the light was on and decreased in the dark. In Zhang’s research, maximum stable power density of 61 ± 1 mW m⁻² was obtained at the end of the light period, while only less than 5 mW m⁻² was observed at the end of the dark period. In this study, maximum voltage output was around 0.13 V when unmodified SS was used in the system, it was increased to 0.35 V after the cathode was changed to the MnO₂/PANI modified one (Figure 3(b)). Periodic variation happened for the voltage due to illumination during day and night when using SS and MnO₂/PANI cathodes. Output voltage was much higher after the cathode was modified, it was kept around 0.25 V even in the night time. If output power density was calculated based on one piece of membrane cathode area 50 cm², it was about 24.5 mW m⁻² during the day and 12.5 mW m⁻² at night when modified SS used as cathode. It has been proved that the membrane cathode successfully prevented the pore clogging by applying 0.2 V cm⁻¹ electric field (Liu et al. 2013b). A bio-electrochemical membrane reactor (BEMR) generated 0.2 V cell potential and fouling reduction was realized using internally supplied electric field in the BEMR, maximum power density achieved by reactor was 2.6 mW m⁻² (Liu et al. 2013a). Modification cathode improved voltage output and supplied a minute electric field to mitigate fouling.

The growth of algae and change of DO and pH profiles in cathode chamber during one day

Chlorella was used in this research to provide oxygen for cathode chamber. 150 g immobilized Chlorella was added
into the pond, which was about 10% in volume of algae pond plus cathode chamber. Total biomass content increased from $2 \times 10^9$ to $1.22 \times 10^{10}$ cell mL$^{-1}$ in 10 days, which was 6.1 times increase of the initial biomass. A leakage of immobilized Chlorella occurred since the seventh day, therefore immobilized Chlorella in the system was refreshed every 7 days. DO was an important factor in aerobic microbial growth and it is an electron acceptor for MFC cathode. Fluctuations of DO during one typical day were recorded when SS was used as cathode, as shown in Figure 4. When DO was increased to 8 mg L$^{-1}$ in the morning, the maximum voltage was increased to about 0.13 V (Figure 4). After 20:00, DO decreased and oxygen supply for cathode was reduced, and voltage output decreased remarkably.

The pH value of algae solution gradually rose with the photosynthesis process. Algae solution and cathode solution was cycled so pH in cathode chamber fluctuated during the day. It rises gradually in daylight time and reduces when in the dark (Figure 4). DO was kept above 9 mg L$^{-1}$ at 17:00, but the cell voltage began to slightly decrease, probably caused by pH fluctuation or oxygen permeation to the anode. It should be noticed that the integration of algae with such a wastewater treatment system, can not only save aeration energy consumption, and provide DO to the bio-electrochemical system, but also it can be recovered as a biomass resource. Integrated with bio-electrochemical wastewater treatment, oil-rich algae may be tested to recover more energy, and present itself as a valuable feedstock for biodiesel fuel production. With this research developing well in the future, electricity cost for aeration operation may be saved, more power could be obtained in bio-electrochemical membrane system.

Roles of algae and membrane cathode in the system in wastewater treatment

Algae were designed in the system to provide oxygen for the cathode of MFC to replace aeration, which would reduce energy supply for aeration, also it uptakes nitrogen and promotes nitrogen removal. When MFC was used for wastewater treatment, a comparison between the MFC with conventional treatment systems (activated sludge...
and anaerobic digestion) has been accomplished, including energy consumption, sludge production, loading rate and so on. Based on the reference, energy input for aeration was very high and energy consumption for activated sludge was 0.7–2 kWh/kg COD (Pant et al. 2011). Low sludge production, none energy input for aeration and direct conversion of substrate energy to electricity were considered as the advantage of those MFC wastewater treatment process. In an MFC without aerator, there was no aeration energy consumption. To compare the effect of algae and membrane cathode on the final effluent water quality, three operational experiments were carried out and the results are compared in Table 1. Operation duration was 5 days for each experiment and external circuit was disconnected during the test. In Test A, only cathodic and anodic components were involved, influent flow from anode to cathode under an anaerobic environment, no aeration was provided. In Test B, algae pond was connected into the system, so cathodic component was aerobic with DO enriched water supply. In Test C, membrane cathode was added to filtrate the effluent in cathode chamber, the effluent quality comparison is shown in Table 1.

The COD\(_{Cr}\) concentration from final cathodic effluent in Test A and Test B were around 31 to 33 mg L\(^{-1}\), which was comparable with the conventional activated sludge effluent and confirms to first grade A discharge standard of pollutants for urban wastewater treatment plants (COD\(_{Cr}\) ≤ 50 mg L\(^{-1}\)) by the Ministry of Environmental Protection of the People’s Republic of China. Without algae pond connected in test A, DO was similar with DO value in test B at night. There was an additional algae pond in Test B, so the cathode was rich in oxygen, and there was no formation of nitrite nitrogen. After the introduction of algae pond, COD removal of effluent in cathode chamber was almost the same (from 92.9 to 93.3%), while ammonium-nitrogen removal was increased from 70.3 to 94.9%. Ammonium-nitrogen was the nitrogen source of synthetic sewage in this research and we did not focus on the mass balance of nitrogen species when this research was designed. However, in such an MFC-MBR-algae combined system, conversion of ammonium to nitrate takes place, and algae could consume the nitrate species, in the following research a more comprehensive analysis about ammonium-nitrogen and nitrate-nitrogen should be studied to finish the mass balance of nitrogen species.

After membrane component (Test C) was added in the system, turbidity removal by the membrane was 85.7%, the COD in effluent after membrane filtration was decreased to 25 mg L\(^{-1}\) (from 32 mg L\(^{-1}\) before membrane filtration). There was no significant change in ammonia nitrogen removal compared with Test B. After SS modification, pore size of membrane has been reduced from 15 μm to 2.4 μm. The pure water membrane flux decreased from 75,600 to 119.4 Lm\(^{-2}\) h\(^{-1}\), which mean an increase in filtration performance and increased foulants retention capacity. The membrane cathode makes the system more efficient in removing COD and turbidity and obtaining satisfactory effluent quality.

**CONCLUSIONS**

In a bio-electrochemical membrane system featured and operated by coupling MBR-MFC with an SS-based membrane cathode and carbon granule anode, the modification of the SS mesh with MnO\(_2\)/PANI significantly increased electricity generation and filtration effect in wastewater treatment. Effluent quality was enhanced after filtration by modification membrane comparing with direct discharge of effluent from the cathode chamber. Introducing algae

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**Table 1** | Operation and water quality comparison in test A, B and C (water quality was analyzed once a day for 5 days, results showed the average value)

<table>
<thead>
<tr>
<th>Operation unit involved</th>
<th>Test A</th>
<th>Test B</th>
<th>Test C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent → anode → cathode effluent</td>
<td>Influent → anode → cathode effluent</td>
<td>Influent → anode → cathode effluent</td>
<td>Influent → anode → cathode effluent</td>
</tr>
<tr>
<td><strong>Water quality</strong></td>
<td><strong>Influent</strong></td>
<td><strong>Anode</strong></td>
<td><strong>Cathode</strong></td>
</tr>
<tr>
<td>COD (mg L(^{-1}))</td>
<td>464 ± 13</td>
<td>99 ± 4</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>Ammonia-N (mg L(^{-1}))</td>
<td>11.46 ± 0.36</td>
<td>6.55 ± 0.38</td>
<td>3.4 ± 0.21</td>
</tr>
<tr>
<td>Nitrite-N (mg L(^{-1}))</td>
<td>0</td>
<td>0.34 ± 0.04</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>Turbidity (mg L(^{-1}))</td>
<td></td>
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pond (with immobilized algae) to the system, provided the DO to the cathode chamber, by allowing flow of oxygen-rich water from the algae pond back to cathode chamber. This increased ammonia nitrogen removal and saved aeration energy consumption. Anti fouling MBR-MFC system with a modified membrane cathode but without aeration was successfully tested in our research. Immobilized algae could multiply and increase its quantity by photosynthesis, uptake nitrogen and provide DO in water for the membrane cathode.

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