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Preparation of highly conductive cathodic membrane with Graphene (Oxide) /PPy and the membrane antifouling property in filtrating yeast suspensions in EMBR

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The decline of flux caused by membrane fouling is a big problem in wastewater treatment and reclamation. To improve the membrane anti-fouling performance and control membrane fouling in MBR, applying an electric field has been proved efficient(the so-called EMBR)[1], in which negatively charged pollutants and extra-cellular polymeric substances (EPS) are forced to move away from the membrane surface under electric field. Using conductive membranes as cathodes combines the membrane and electrode as one, so higher efficiency in material usage and better anti-fouling performance was achieved.

To make the conductive cathode membrane, depositing conductive polymers on the surface of membrane is useful, effective and at lower economic cost, better than arranging metal cathode in the module. However, the polymer conductivity on filter cloth is not as good as metal cathode (iron, aluminium, copper). And higher resistance means high energy consumption and applying higher voltage to produce the same effect in fouling reduction. Preparing high conductivity membranes from polyester filter cloth is critical for EMBR research. Graphene (Gr) and its oxides (GO) are cheap carbon materials and their composites with polypyrrole (PPy) have excellent conductivity, suitable for use as super-capacitor, electrodes for microbial fuel cell, electrochemical oxygen reduction and pollutant removal[2-4]. In this paper, high electronic conductive membrane is prepared by modifying terylene filter cloth with Gr/GO and PPy, and tested as cathodes for anti-fouling performance, with stainless steel mesh as the anodes(distance between anode and cathode is 1 cm), in filtrating yeast suspension (simulating) sludge in EMBR.

Materials used include pyrrole (Aldrich, chemical grade purity), graphene oxide (prepared by Hummer's method), graphene (deoxidize from graphene oxide with hydrazine hydrate) and terylene filter cloth. The conductive membrane was prepared using the following methods.

Vapor phase polymerization and PPy modified membrane (VPM): First, blank filter cloth is immersed in different concentrations GO/Gr solution that had been ultra-sonically treated for some time. Dry the filter cloth and spry the APS solution on it. Then the pre-treated filter cloth is set in a sealed container filled with pyrrole (Py) vapor by heating the container at the bottom. When the polymerization is finished, filter cloth turns dark black and was successfully modified by PPy and Gr/GO. The electric resistance for the modified membrane made in this way can be as low as 710Ωcm^{-1} (modified by GO/PPY) or 680Ωcm^{-1} (modified by Gr and PPy), much lower than 2.03kΩcm^{-1} for Ppy only modified filter cloth.

Liquid phase polymerization and PPy modified membranes (LPM): First, dissolve pyrrole in ethanol and water solution, then ultrasonically mix it with graphene (or its oxide) solutions. Then dip the filter cloth (pre-treated by immersing in the APS solution and half air-dried) into this solution. Very soon a large quantity of composites PPY/GO(Gr) is polymerized on the surface of blank filter cloth and make the membrane really dark. The membrane made in this way has a resistance of 14.81kΩcm^{-1} (modified by GO/PPy) and 2.7kΩcm^{-1} (modified by Gr/PPy), compared with 8.15kΩcm^{-1} of membrane modified only by Ppy.

Since the membrane prepared by VPM is better than membrane by LPM, both in the conductivity and uniformity. Gr/PPy /filter cloth by VPM is used and tested for its anti-fouling property, with and without 1v electric field in yeast suspensions simulating the active sludge and EMBR. The test lasted for 4.5h, every 1.5h the membranewas washed, the MLSS concentration was 5g/L and air flow rate was set at 0.2m^3/h.

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Table 1. membranes modified with PPy, GO/PPy and Gr/PPy by different polymerization method

Sample	Polymerize method	Resistance($k\Omega cm^{-1}$)
Blank membrane	——	+∞
PPy	VPM	2.03±0.61
GO/PPy	VPM	0.71±0.10
Gr/PPy	VPM	0.68±0.08
PPy	LPM	8.15±0.79
GO/PPy	LPM	14.81±1.41
Gr/PPy	LPM	2.70±1.05

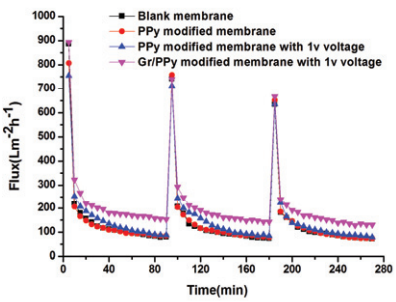

Fig 1. The flux of blank membrane, PPY and Gr/PPy modified membrane with and without applying electric field.

The filtration tests (Figure 1) results indicate that the voltage applied on the conductive membranes, increased the steady flux effectively(~1 fold higher), and the electric field suppressed membrane fouling significantly. The Gr/PPY modified membrane has relatively stable flux even after two times physical washing, better than PPY modified membrane. This Gr/PPY conductive membrane is expected to improve the efficiency of EMBR in pollutants removal, either by electrochemical oxidation or membrane separation.

The conclusions: better conductive membrane (a lowering of electric resistance by 1/3) can be obtained by modifying filter cloth with graphene (or its oxide) and PPY following the vapor phase polymerization method. The Gr/PPy modification membrane prepared by VPM has better conductivity than the LPM preparation. With 1v electric field applied, it can suppress the

fouling effectively in simulative EMBR. More application of this kind of membrane in microbial fuel cell, in electrochemical wastewater treatment process will be further studied and reported.

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