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E-Fenton degradation of MB during filtration with Gr/PPy modified membrane cathode

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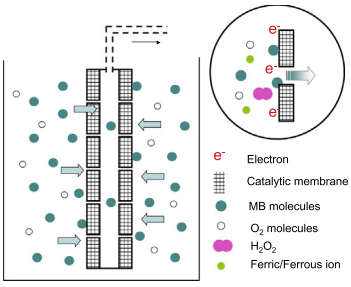
HIGHLIGHTS

- Gr/PPy modified membrane cathode catalyzed degradation of MB.
- The E-Fenton degradation of MB is more effe under filtration mode.
- Gr/PPy membrane-electrode is effective and stable.
- AQS/Gr/PPy membrane has better electrochemical performance.
- Membrane filtration coupled electro-catalysis is advantageous.

GRAPHICAL ABSTRACT

MB treated by conductive membrane in E-Fenton reactor.



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ABSTRACT

The integration of two or more conventional technologies has been proved effective in enhancing water treatment efficiency. E-Fenton degradation of pollutants by conductive functionalized polymer membrane cathode is rare. In this study, a novel conductive membrane/electrode was prepared by modifying a polyester filter cloth/fabric membrane with impregnated graphene (Gr) and coated polypyrrole (PPy) via the vapor phase polymerization method (VPM). The composite membrane has uniformly coated and firmly attached Gr/PPy, it is highly conductive, of low electric resistance. When it was used as the cathode for removing Methylene Blue (MB) by E-Fenton reactions under membrane filtration mode, with stainless iron mesh as the anode, the parameters affecting the E-Fenton reaction were investigated. It was found that appropriate aeration, pH value, membrane flux and electric field strength all affected the cathodic membrane performance in E-Fenton system. MB, the target pollutant, was significantly degraded by the in situ generated hydrogen peroxide, and the combined function of membrane and catalysis on pollutants makes the effect even better. The membrane cathode was stable and its performance was further promoted by doping with AQS (anthraquionone monosulfate), which enabled more effective integration of membrane with electro-catalysis.

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1. Introduction

1.1. Membrane combined with catalysis–catalytic membrane technology

Membrane separation technology is efficient in water and wastewater treatment [1,2]. To develop new and widely applicable membrane techniques, people are trying to integrate it with other treatment processes [3,4], such as the catalysis technology [5,6]. For the integration of membrane with catalyst, the simple and conventional way is directly adding catalysts into the membrane reactor in which catalysts catalyze the degradation of target pollutants and are recovered by the membrane [7,8]. In this system, the catalysis and membrane separation are two individual technologies just connected by the process flows. Membrane properties may be affected by the powder catalysts as they may clog the membrane pores and decrease the permeate flux. Complex operation requirement and membrane aging are the other problems [9]. Moreover, the catalyst needs to be supplied constantly into the reactor in order to maintain the adequate concentration. So it is necessary to prepare membrane that has catalytic property in itself. The catalytic membrane will generate certain reactants to react and transform the target pollutant molecules through engaged mechanisms. The multiple channel structures of the membrane guarantee high separation rate and high conversion rate of the chemical catalysis reaction.

Loading and fixing effective catalyst directly on the base membrane is a good method for preparing catalytic membrane. It combines membrane and catalyst into one entity [10,11], not only improves reaction efficiency, but also prolongs catalyst life, simplifies the process. Most importantly, it makes it possible to integrate catalysis (or electro-catalysis) with membrane or Membrane bioreactor (MBR) technology. E-Fenton reaction, as one of advanced oxidation technologies, when combined with the MBR, can greatly enhance the water treatment efficiency because of the catalytic reaction taking place on the membrane/electrode surface. Now it is with great potential and feasibility to combine cathode membrane and electro-catalysis with microbial fuel cell technology, using electric power recoverable from wastewater [12]. Preparing conductive polymer membrane with electro-catalytic activity is the key point for this research. E-Fenton oxidation had been studied widely with solid electrodes that normally did not allow liquid permeation, membrane electrode for E-Fenton had been rare, especially with polymer membranes.

1.2. Performance of Gr/PPy modified membrane cathode in electric field

Gr/PPy modified membrane had been prepared by modifying polyester filtration cloth with Gr and PPy [13]. As a conductive membrane cathode, it showed fouling suppression performance in electric field attached MBR (EMBR), but much attention and consideration about electro-catalytic pollutants removal should be given to the composite membrane, because of the excellent electrocatalysis activities of the membrane modified materials.

In EMBR, conductive membrane has been well proved efficient in suppressing membrane fouling and flux decline caused by concentration polarization [14]. When the negative potential was applied on the membrane cathode, it will have a repulsive/rejection force for the negatively charged sludge and extra-cellular polymeric substances (EPS). The membrane fouling was suppressed [15]. Also the minute electric field has a stimulating effect on the microorganism and makes them more active, so better treatment effect was obtained. The previous research about EMBR had focused on membrane fouling suppression, flux increase, property changes of active sludge and the effluent quality [16,17], not much was studied about the catalytic effect of the composite conductive membrane on water pollutants. In fact, the voltage applied on the membrane will affect water pollutants removal directly when membrane contains electro-catalytic components, so better effluent quality of EMBR will be achieved by comprehensive effect of integrating biological removal, membrane separation and catalytic degradation. In order to analyze the electro-catalysis effect of the electrode membrane, it is necessary to study pollutant degradation by the membrane alone without the microorganisms.

Both Gr and PPy are materials with excellent electric conductivity and have extraordinary performance in super-capacitor, microbial fuel cell and pollutant adsorption, with special electrocatalysis performance for pollutants degradation [18,19]. In our previous report, PPy has been successfully applied in modifying the big–pored filter membrane [16,13], and its composite with Gr has been reported in relevant field because of the excellent electrochemical properties [20,21].

1.3. Our work and the technological advantage of Gr/PPy membrane in water pollutants removal

In order to integrate the electro-chemical catalysis effect with the membrane separation effect, and further confirm the EMBR with cathode membrane having multiple effects in pollutants degradation and removal. We are trying to prepare composite polymer membrane modified by Gr/PPy with both electric conductivity and catalytic performances in this paper. The conductive polymer membrane is to be used as cathode in appropriate electric field strength for E-Fenton system, with some conditions varied (electrolyte, Fe reagents, appropriate pH and electric field) [22,23]. The stability of the modified membrane was studied, and AQS [24,25] was incorporated and studied to enhance the catalytic activity of Gr/PPy membrane. The filtration effect of the membrane will enhance the contact between catalysis membrane cathode and the target pollutant; also the catalysis effect will decrease the load of membrane and degrade those pollutants that are hard to be separated. In one word, this electro-catalysis membrane can be used for removing small molecule pollutants, as either a pretreatment for recalcitrant wastewater or a post-treatment step to upgrade the effluent quality in wastewater treatment process.

2. Experimental

2.1. Chemicals

Materials used in the experiment involved pyrrole (Shanghai Kefeng Reagent Co., Ltd.), graphene (reduced from graphene oxide prepared by Hummer's method [26,27]), aluminum spacer mesh with 3 mm in pore size and fabric membrane (polyester filter cloth, retain solids with or above 22 μm in diameter claimed by manufacturer, Shanghai Suita Filter Material Co., Ltd.). Anthraquinone-2-sulfonic acid sodium salt monohydrate (AQS) was purchased from TCI Co., Japan. Methylene blue (MB) and other reagents (H_2SO_4, $NaNO_3$, $KMnO_4$, H_2O_2, HCl, Na_2SO_4, hydrazine hydrate, aqueous ammonia, ammonium persulphate (APS)) were purchased from the Chemical Reagent Plant (Dalian, China) and used as received without further treatment. Deionized water was used during the experimental process.

2.2. Modification of the big-pored membrane with PPy or Gr/PPy composites

The VPM membrane modifying process was shown in Fig. 1 [13]. First, polyester fabric membrane (8×11 cm^2) was immersed