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Research on degradation product and reaction kinetics of membrane electro-bioreactor (MEBR) with catalytic electrodes for high concentration phenol wastewater treatment

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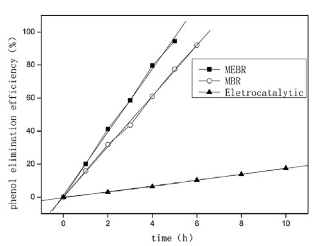
HIGHLIGHTS

- We used a novel device called membrane eletro-bioreactor (MEBR).
- Dealed with high concentration phenol wastewater.
- Efficiency of MEBR was 11.1% higher than the sum of MBR and Electrocatalytic.
- Found a new degradation product—2,6-di-*tert*-butyl-*p*-benzoquinone.

GRAPHICAL ABSTRACT



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ABSTRACT

The membrane electro-bioreactor (MEBR) is a novel technology, it treats wastewater by combining membrane filtration, electrokinetic phenomena, and biological processes in one reactor. This paper aims to deal with hard biodegradation and high concentration phenol wastewater. Investigating the influence factors such as initial concentration, voltage, pH value, temperature and mixed liquor suspended solids (MLSS) toward phenol degradation process in electrocatalytic process and membrane bioreactor (MBR), and then apply the optimum conditions in the MEBR system. Results of continuous flow experiments demonstrated that MEBR increased the quality of the treated wastewater than conventional MBR. The above technics followed the zero-order reaction kinetics. The removal efficiency of MEBR was about 11.1% higher for phenol than the sum of the two individual processes. With the help of gas chromatography/mass spectrometry (GC-MS), this qualitative analysis looks at the degradation products of phenol generated in MEBR, through which 2,6-di-*tert*-butyl-*p*-benzoquinone was confirmed as the main degradation product.

1. Introduction

Phenol and its derivatives are listed among the most serious environmental contaminants, since they are toxic, carcinogenic, teratogenic and mutagenic to humans, fish and to several biochemical functions (Zhang et al., 2011). It causes liver and kidney damage and blood pressure drop, cardiac toxicity including weak pulse, cardiac depression and reduced blood pressure (Nuhoglu and Yalcin, 2005). So the World Health Organization has therefore limited phenol concentration in drinking water to 1 μg L^{-1} (Barrios-

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Martinez et al., 2006). The increasing presence of phenols represents a significant environmental toxicity hazard. Therefore, the development of methods for removing phenols from industrial wastewater has generated huge interest. According to the literature, granular or biological activated carbon filtration, membranes processes and membrane bioreactor and so on are used to eliminate phenolic compounds from industrial wastewater. Conventional processes have been mostly physico-chemical processes, but physico-chemical methods have proven to be costly and have the inherent drawbacks due to the tendency of the formation of the secondary toxic materials such as chlorinated phenols, etc. (Arutchelvan et al., 2006; Gernjak et al., 2003). The electrochemical process is considered to be an environmentally friendly technique for water treatment, because of its advantages of ease of control and environmental compatibility (Qu and Liu, 2007).

Industrial application of the MBR technology has gained attention because of reduced HRT, low sludge production and permeate quality that can be suitable for reuse and also because of the robustness of the process that allows the operation with shock loading rates and hydraulic fluctuations (Pollice et al., 2007; Rosenberger et al., 2006). Some studies indicate that MBR membranes are very efficient in the removal of bacteria and protozoa (Ottoson et al., 2006; Wong et al., 2009; Zhang and Farahbakhsh, 2007).

In this study, we used a novel device called membrane electro-bioreactor (MEBR) to deal with high concentration organic wastewater, which has been considered a major challenge to the widespread application of membrane bioreactor (MBR) technology (Le-Clech et al., 2006; Hwang et al., 2009). The MEBR technology was based on applying a direct current (DC) field between immersed perforated catalytic electrodes, putting the catalytic electrodes at the both sides of the immersed membrane filtration module. The treatment performance with MEBR is affected by material, location and electrode design, and the applied direct current field between the unit area electrodes (Bani-Melhem and Elektorowicz, 2010; Bani-Melhem and Elektorowicz, 2011). Our experiments were expected to investigate the reaction kinetics of phenol degradation and the influence of experimental parameters such as voltage, pH, MLSS, temperature and the initial concentration of phenol, and to show the results of performance of the MEBR system for wastewater treatment in terms of COD, and phenol elimination efficiency. So can we provide some basic information to apply MEBR in treating organic wastewater.

2. Materials and methods

The activated sludge was taken from the aeration tank in the Ji Zhuangzi municipal wastewater treatment plant in the City of TianJin.

2.1. Experimental setup

A laboratory scale setup was used in this study (Fig. 1). The membrane electro-bioreactor consisted of a rectangular organic glass vessel of 60 cm × 50 cm × 70 cm, it with a working volume of 170 L, an air diffuser was located at the bottom of the reactor, the air through the gas rotameter and aeration system into the reactor, which is not only to provide good mixing of the sludge suspension and oxygen for microbial growth and metabolism, but also to create a shear stress for effective scouring of the membrane surface. The effluent was withdrawn via a peristaltic pump (model: DP-130, ShangHai magnetic pump industry). Ti/PbO_2 as anode (effective surface area = 2000 cm^2) and stainless steel as a cathode (effective surface area = 2000 cm^2) were fixed at the both sides of membrane module at a distance of 10 cm. The electrodes were connected to a digital external DC power supply (model: WYJ-3002 A Quanli Electrical Appliance Co., Shanghai). The power supply was connected to a timer to regulate the intermittent DC at an operational mode of 8 min ON–2 min OFF. All the system was controlled by PLC.

2.2. Analytical methods

Effluents and supernatants in reactor were sampled daily and analyzed by potassium dichromate method (GB11914-89) for COD, The dissolved oxygen (DO) concentration was measured using a DO meter (model OXi-330iWTW pu scientific instrument co., ShangHai), Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were performed according to Standard Methods (APHA, 1998). The concentration of phenol undegraded in the samples was determined by a modified calorimetric technique using 4-aminoantipyrine as a reagent at 510 nm by UV spectrophotometer (UV-9100, Beijing Ruili Analysis Apparatus Company, China). The degradation products of phenol in MEBR were characterized by GC-MS (gas chromatography/mass spectrometry). And the Trace GC/Polaris Q GC-MS of thermo was selected to use as experimental equipment, which was equipped with the NIST98 standard mass spectral library.

2.3. Experimental procedure

In order to improve the efficiency of the MEBR system, which could deal with the toxic and high concentration phenol wastewater in the long term, we should domesticate the microorganisms which possess the enzymatic material necessary to degrade the phenol and which is able to consume it as a substrate (Barrios-Martinez et al., 2006). We washed the activated sludge with tap water and then enriched in a container of 10 L cubage using 1000 mg L^{-1} glucose as carbon source at beginning, and other substrates including 100 mg L^{-1} NH_4NO_3, 25 mg L^{-1} $FeSO_4 \cdot 7H_2O$, 10 mg L^{-1} $MgSO_4 \cdot 7H_2O$ and 30 mg L^{-1} KH_2PO_4. Phenol was substituted for glucose gradually until it as sole carbon source (Ma and Yang, 1998), acclimation is completed when the bacterial growth constant becomes higher than to the decay constant with a complete consumption of the phenol of 1500 mg L^{-1}. An electric field is applied to domesticate the sludge, the voltage increase from 0 to 7 V gradually.

The MEBR system was with a constant flux of 1 g L^{-1} phenol and working at room temperature without control for a period of 180 days continuously. The MEBR was with an operational mode of 7 V, pH = 7.0, t = 30 °C, MLSS = 6300 mg L^{-1}, HRT = 48 h, the distance between electrodes (10 cm), and no sludge was withdrawn from the MEBR at this study (within 6 months operation). MLSS value could maintain at about 6300 mg L^{-1}, it might be assumed that the biomass in the MEBR was not changed substantially. Thus, theoretically meaning an infinite sludge retention time (SRT) (Nguyen et al., 2012). The temperature and dissolved oxygen (DO) concentration in the bioreactor were maintained at 20.0 ± 5 °C, and 4–9 mg L^{-1}, respectively (Shi et al., 2013).

A simple method for reducing membrane fouling consists in increasing the flow rate or the crossflow velocity (Barrios-Martinez et al., 2006). Aeration, turbulence and a low biomass concentration which is the case of this study made the transmembrane pressure (TMP) increase slowly, it was not reached the limitation point, which is about 45 KPa during the whole operation period, so the membrane fouling can be ignored. Therefore the ion deposition on the stainless steel and PbO_2/Ti electrodes was little and can be compensated by raising the voltage value, so it's not reduce the efficiency with time in this experiment. Literature report shows that the phenol removal efficiency may be decreased with the operating time, because bacterial growth was speculated to the