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Feasibility and advantage of biofilm-electrode reactor for phenol degradation

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Abstract

The new biofilm-electrode method was used for the phenol degradation, because of its low current requirement. The biofilm-electrode reactor consisted of immobilized degrading bacteria on Ti electrode as cathode and Ti/PbO_2 electrode as anode. With the biofilm-electrode reactor in a divided electrolytic cell, the phenol degradation rate could achieve 100% at 18 h which was higher than using traditional methods, such as biological or electrochemical methods. Chemical oxygen demand (COD) removal rate of the biofilm-electrode reactor was also greater than that using biological and electrochemical method, and could reach 80% at 16 h. The results suggested that the biofilm-electrode reactor system can be used to treat wastewater with phenol.

Key words: phenol; biofilm-electrode reactor; phenol degradation rate; chemical oxygen demand

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Introduction

Phenol compounds and their derivatives are present in the wastewater of many industries, including oil refineries, chemical plants, explosives manufacture and coke ovens. They are also used in the preparation of antiseptics, dyes, antirust products, synthetic resins, biocides, photographic chemicals, inks, varnishes, etc. In recent years, as a consequence of a great industrial growth, with special relief for the chemical industries, the presence of phenolic pollutants in the aquatic environment had a big increment (Sá and Boaventura, 2001).

Phenol is toxic to many biochemical functions and fish life (Sufit, 1978). It is water soluble and highly mobile, so that can easily reach drinking water sources downstream from discharges, and cause severe odor and taste problems and pose risks to populations even at low concentration. Various regulatory water authorities have imposed strict limits to phenol concentration in industrial discharge streams (Singleton, 1994). The Chinese legislation establishes a phenol concentration of 0.5 mg/L as the limit for wastewater discharge into natural water bodies, land or municipal sewerage systems.

Electrochemical and biological methods are commonly used in phenolic compounds removing from industrial effluents. Comparing them, electrochemical methods deal with phenol commonly with higher current, and there is no need of current for the biological method for phenol degradation, while high concentration phenol are toxic to bacterium with biological methods. Therefore, we combine electrochemical and biological methods to degrade low concentration phenol with lower current. Nowadays, biofilm-electrode reactor is mostly applied for the process of denitrification (Fan *et al*., 2001; Wang and Qu, 2003). In our previous study, 4-amino-dimethyl-aniline hydrochloride was treated with the biofilm-electrode reactor (Kang *et al*., 2007). In some research works immobilized phenol degrading bacteria electrode was used as cathode and Ti/PbO_2 electrode as anode in the biofilm-electrode reactor (Kuroda *et al*., 1997; Sakakibara and Kuroda, 1993). During the process, hydrogen gas was produced on the cathode surface by the electrolysis of water when the electric current was applied, and immediately utilized to reduce biologically phenol by the cathodic immobilized bacteria (Kuroda *et al*., 1996; Sakakibara *et al*., 1994).

The purpose of this study was to demonstrate experimentally the feasibility of using the biofilm-electrode reactor to degrade phenol, and compare its advantages with electro-chemical and biological methods.

1 Materials and methods

1.1 Enrichment, isolation, and preservation of strains

An activated sludge was collected from Tonghua Industrial Steel Works in Jilin Province, China. Ten milliliters of the sludge sample was aseptically added to shaking flasks containing 90 mL of synthetic wastewater medium supplemented with 100 mg/L phenol and incubated on a rotary shaker (120 r/min) at 35°C. During incubation, the optical density at 600 nm (OD_{600}) of the culture

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broth was monitored. After an obvious OD increase had been observed (2–3 d), 10 mL of the culture broth was transferred to a new shaking flask containing 90 mL of fresh synthetic wastewater medium. This operation was repeated three times, and spread onto agar plates containing synthetic wastewater medium. Colonies appeared on the agar plates after 3–4 d of incubation at 30°C were picked and subcultured several times to obtain pure cultures. Degrading phenol bacteria was preserved in nutrient agar slants at 4°C (Geng *et al*., 2005).

The composition of synthetic phenol wastewater used in this study contained (g/L): phenol 0.1, $(NH_4)_2SO_4$ 0.7, $CaCl_2$ 0.03, NaH_2PO_4 0.2, $MgSO_4$ 0.03 and K_2HPO_4 0.08.

1.2 Cell immobilization

The immobilized degrading bacteria electrode was prepared following procedures: mixed culture slurry of degrading phenol bacteria was obtained from steel facilities of exudates of sanitary landfill. Then it was inoculated into cathodic part of a divided electrolytic cell and aqueous synthetic wastewater including phenol was added periodically (Chang *et al*., 1999; Zhang *et al*., 2005a). The medium was replaced with a fresh one when the phenol concentration degrades zero and the same cultivation procedure was repeated. After several batch cultivations, a biofilm layer was visible on the cathode and experiments on electric current were performed (Sakakibara and Kuroda, 1993).

1.3 Experimental setup and operation

Figure 1 shows the schematic diagram of reactors. The biological reactor has immobilized degradable bacteria on the Ti cathode without current during phenol degradation process. The electrochemical reactor consists of Ti cathode and Ti/PbO_2 anode. Their electrolyte in the electrolytic cell is synthetic wastewater containing phenol. Compared to biofilm-electrode method, a passed current of 5 mA is offered for phenol degradation in the electrochemical reactor. The biofilm-electrode reactor consists of immobilized degrading bacteria on the Ti electrode as cathode and Ti/PbO_2 electrode as anode in a divided electrolytic cell. The solution of anodic part in a divided electrolytic cell has no phenol. But the solution of cathodic part in a divided electrolytic cell is synthetic wastewater with phenol.

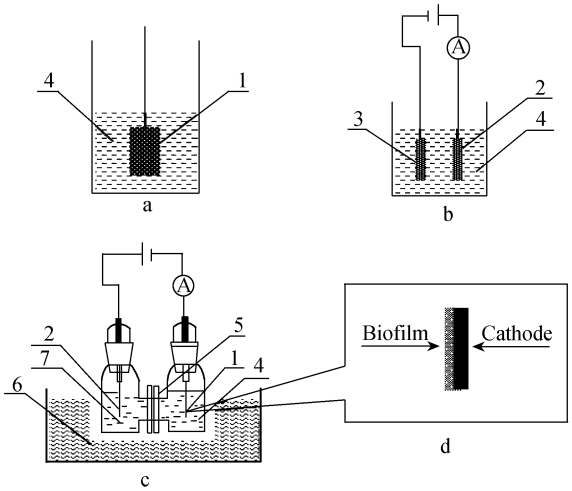

Fig. 1 Schematic diagram of the experimental apparatus. (a) biological reactor; (b) electrochemical reactor in an undivided electrolytic cell; (c) biofilm-electrode reactor in a divided electrolytic cell; (d) magnified figure of biofilm-electrode. (1) biofilm; (2) Ti/PbO_2 anode; (3) Ti cathode; (4) synthetic wastewater containing phenol; (5) membrane; (6) constant temperature cell; (7) electrolyte without phenol.

In this study, Ti is TA1 mesh which was bought from Baoji Baoye Titanium-Nickel Industry Co., in China. The mesh is rhombus and the fraction of mesh opening fraction is 45%. PbO_2 was deposited potentiostatically on Ti substrate from the aqueous solution containing (mol/L) HNO_3 1, $Pb(NO_3)$ 20.1, $Cu(NO)_2$ 0.01 with NaF 0.04 at 1.60 V. They are prepared in a single compartment cell (V = 200 mL) at room temperature for 2 h. Cu was used as cathode, and Ag|AgCl|KCl(sat.) was used as a reference electrode. Both anode and cathode have the same structure and geometric area (30 mm × 30 mm × 1.0 mm), which were set up in the middle of the cell and interelectrode gap can be changed. Volume of the solution in every reactor was 120 mL. The reactors were immersed in water batch to maintain the constant temperature 35°C.

1.4 Different reactors experiments

After a biofilm-electrode had been formed, degradation rates of the three reactors were measured at 2, 6, 8, 18 and 24 h. The electric current was kept constant at 5 mA in biofilm-electrode reactor. According to the previous report, a passed current of 5 mA is suitable for phenol degradation (Zhang *et al*., 2009). When the electric current is higher than 5 mA, a great amount of bacterium fell off from the surface of the cathode, and when the electric current is lower than 5 mA, the phenol degradation is not efficient. pH and temperature were kept the same as those in sludge cultivation. The removal of COD was tested at 16 h.

1.5 Analytical methods

Analyses were performed on daily basis. Bacterial growth was assessed by measuring OD_{600} of the samples against distilled water using a spectrophotometer (721E visible, Shanghai Spectrum Corporation, China). The concentration of phenol was measured using a high performance liquid chromatography (HPLC) (LC10AVP, Shimadazu, Japan) with a UV detector (wavelength 220 nm) and 4.6 mm × 150 mm Hypersil ODS column. The mobile phase was the methanol/water mixtures (25/75, *V/V*) with 1.2 mL/min flow rate and 40°C column temperature. COD was determined according to the standard dichromate-sulphuric acid technique by a COD determine instrument (COD-571, Shanghai Exactitude Instrument Corporation, China). The morphology of the biofilm-electrode samples was evaluated using scanning electron microscopy (SEM) (HIMADZU SSX-550, Shimadzu, Japan). All reagents were analytical grade, and water was second distilled.

2 Results and discussion

2.1 Phenol-degrading bacterium cultivation and acclimation

The variations of phenol degradation rate and the growth

of strain at different time are shown in Fig. 2. The growth rate of strains rose up slowly from 0 to 16 h, and became quickly from 16 to 22 h. It indicated that phenol degradation bacterium were in logarithmic phase. Phenol concentration began to degrade quickly from 16 to 24 h and reached 0 at 24 h. On account of complete phenol removal, the optical density of phenol degradation bacterium declined since 25 h. It implied that phenol degradation bacterium were in death phase. Therefore, phenol degradation bacterium presented during 16–22 h were selected to inoculate cathode.

The effects of phenol initial concentration on its degradation rate are shown in Fig. 3. The degradation rate was 100% when its concentration under 350 mg/L. Once the concentration exceeded 350 mg/L, the degradation rate descended dramatically. It indicated that the higher phenol concentration can restrain phenol-degrading bacterium growth. The high phenol concentration is toxic to bacterium and can result in bacterium died. It has been reported when phenol concentration exceeds 100 mg/L, phenol-degrading bacterium growth on the cathode is bad (Zhang *et al*., 2009). Thereby, the culture medium with phenol concentration 100 mg/L was selected for biofilm-electrode cultivation and the electrolyte of phenol degrading experiment.

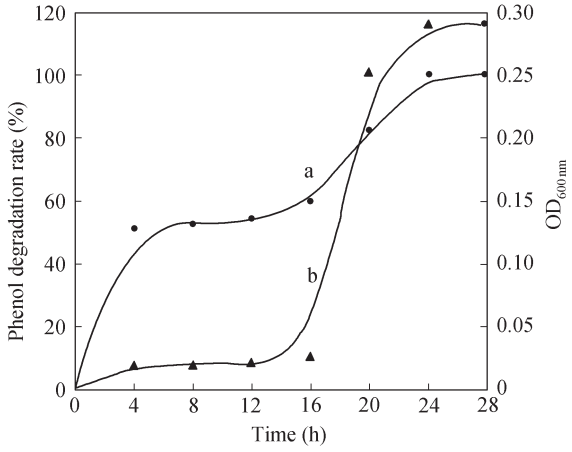

Fig. 2 Phenol degradation rate (a) and the growth curve of strain (b) as a function of time.

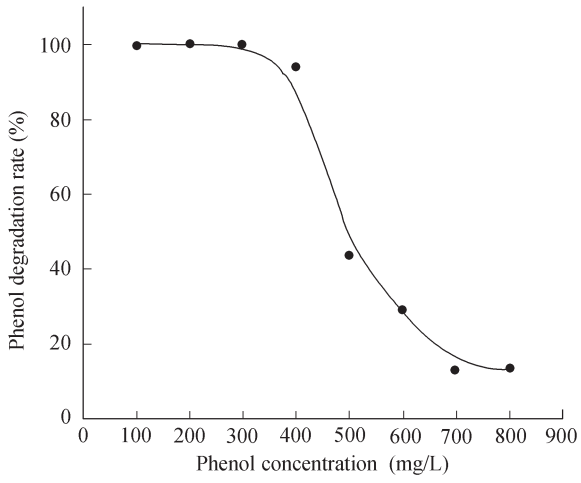

Fig. 3 Phenol degradation rate at different phenol concentrations during phenol-degrading bacterium cultivation and acclimation process.

2.2 Electron microscopy

Electrode was removed from the reactor, rinsed with a sterile medium, and cut off into small pieces (1 cm^2 × 6 mm thick) (Park *et al*., 2006). Figure 4 shows the SEM micrograph of the biofilm used in the study. The microorganisms were adsorbed on the surface of the electrode. The SEM image of biofilm-electrode surface showed that electrodes were covered with bacteria (Park *et al*., 2005).

2.3 Different reactor experiments

Figure 5 shows the time course of phenol removal from synthetic wastewater in the biological, electrochemical, and biofilm-electrode reactors in a divided electrolytic cell. Comparing with biological and electrochemical reactors, the biofilm-electrode reactor has the highest phenol degradation rate and the rate can achieved 100% at 18 h. Therefore, it can be concluded that the phenol degradation rate was affected significantly by the electrochemical process and the potential of degradation for bacteria.

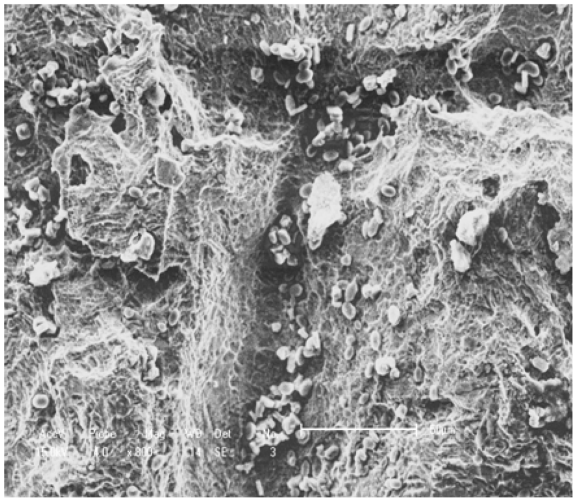

Fig. 4 Scanning electron microscopy (SEM) micrograph of phenol-degrading biofilm.

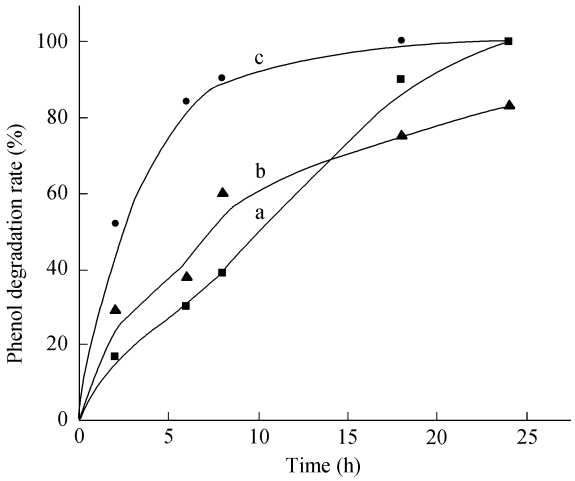

Fig. 5 Phenol degradation rate in biological reactor (a), electrochemical reactor (b), or biofilm-electrode reactor (c) in a divided electrolytic cell.

It has been reported that the phenol-degrading bacterium immobilized on cathode use the hydrogen produced through the electrolysis of water for degradation (Kurt *et al*., 1987). Moreover, on the cathode, hydrogen can be produced by the electrolysis of water or though the reduction of protons (Eqs. (1) and (2)) (Qu *et al*., 2002; Szekeres *et al*., 2001; Zhang *et al*., 2005b; Zhun and Zhun, 1994). Therefore, the degradation rate of phenol in the biofilm-electrode reactor in a divided electrolytic cell was higher than other reactors.

$$2H_3O^+ + 2e \longrightarrow H_2 + 2H_2O \quad (1)$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \quad (2)$$

Because the phenol-degrading microorganisms were enriched on the cathode and contact the cathode closely, the potential of degradation for bacteria was utilized adequately. However, the mechanism of electrolytically enhancing removal still is not clear and further studies are needed to confirm the cooperation of electrode and microbe.

The phenol degradation is more efficient in biofilm-electrode reactor of a divided electrolytic cell than electrochemical reactor. In biofilm-electrode reactor the phenol degradation rate is quicker and phenol degraded more completely than that in electrochemical reactor.

Similarly, by comparing biofilm-electrode reactor in a divided electrolytic cell and biological reactor (Fig. 5), it can be seen that phenol degradation rate in the biofilm-electrode reactor is faster than biological reactor. The condition of biofilm-electrode reactor is beneficial for the growth of phenol degradation bacterium, which may resulted in the quicker phenol degradation rate compared to biological reactor.

Figure 6 shows the removal rate of COD in the reactors using prepared synthetic wastewater containing phenol at 5 mA of electric current. The COD removal rate of the biofilm-electrode reactor in a divided electrolytic cell (80%) was higher than that of other reactors at 16 h. The results implied that phenol degradation and COD removal can almost occur simultaneously in the biofilm-electrode reactor.

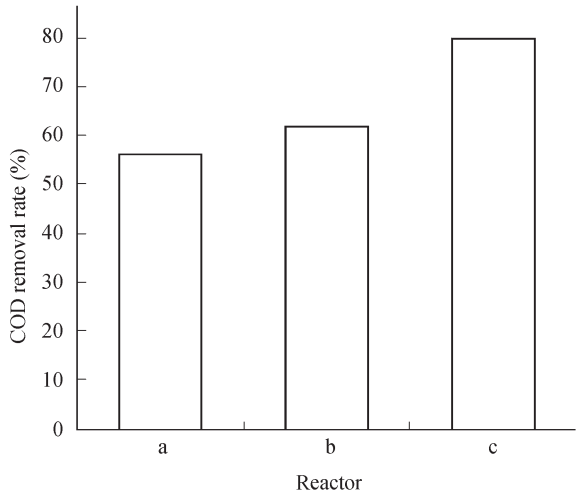

Fig. 6 COD removal rate of biological reactor (a), electrochemical reactor (b), or biofilm-electrode reactor in a divided electrolytic cell (c).

From the results of phenol degradation and COD removal rate, it can be concluded that the biofilm-electrode reactor in a divided electrolytic cell is very effective in removing COD and phenol simultaneously over approximately 18 h. The method of biofilm-electrode reactor only can degrade low concentration phenol wastewater.

3 Conclusions

A feasibility of phenol degradation treatment of wastewater containing phenol was investigated using biofilm-electrode reactor. The advantage of biofilm-electrode reactor is that the degradation of phenol can occur at low current. With the biofilm-electrode reactor in a divided electrolytic cell, the phenol degradation rate achieved 100% at 18 h, and the COD removal rate reached 80% at 16 h. From the results of the different reactors experiments, it can be seen that the phenol degraded more effectively in the biofilm-electrode reactor than by electro-chemical and biological methods. The phenol degradation and COD removal were enhanced by the cooperation of electrode and microbe. However, the further investigation is necessary for analyzing the phenomenon of COD removal in detail and to determine the treatment performance under various conditions.

Acknowledgments

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