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Anodic oxidation of salicylic acid at Ta/BDD electrode

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Abstract: Boron-doped diamond (BDD) film electrodes using Ta as substrates were employed for anodic oxidation of salicylic acid (SA). The effects of operational variables including initial concentration, current density, temperature and pH were examined. The results showed that BDD films deposited on the Ta substrates had high electrocatalytic activity for SA degradation. There was little effect of pH on SA degradation. The current efficiency (CE) was found to be dependent mainly on the initial SA concentration, current density and temperature. Chemical oxygen demand (COD) was reduced from 830 mg/L to 42 mg/L under a current density of 200 A/m^2 at 30 °C.

Key words: Salicylic acid (SA), Anodic oxidation, Ta/BDD, Current efficiency (CE), Electrocatalytic activity
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INTRODUCTION

Salicylic acid (SA) is widely present in industrial effluents. This aromatic organic compound is very toxic. It can stimulate skin and mucous membrane, and react with protein. In addition, it can bring about tinnitus, qualm, naupathia and electrolytical turbulence. Therefore, effective removal of SA is very important.

Currently, the major processes for treatment of wastewater containing SA include extraction (Fong and Chow, 1992), adsorption (Ayranci and Duman, 2006; Deosarkar and Pangarkar, 2004), ozonation (Liu *et al*., 2006; Ernst *et al*., 2004), and photocatalytic oxidation (Vamathevan *et al*., 2002; Adán *et al*., 2006). The extraction can recover SA. However, the loss of extraction reagent may cause secondary pollution. Adsorption is effective in removing SA, but it is difficult to regenerate the sorbents exhausted. Ozonation is known to be effective in opening the aromatic ring of SA, but its efficiency in further mineralizing the intermediate products formed is poor. On the other hand, although photocatalytic oxidation has demonstrated its high efficiency in degrading SA, the high cost and short lifespan of lamps are still critical problems.

In recent years, there is growing interest in anodic oxidation for toxic and refractory organic pollutants degradation (Panizza *et al*., 2001; Polcaro *et al*., 2005; Cañizares *et al*., 2005; Dhiman and Becker, 2007; Brillas *et al*., 2007; Murugananthan *et al*., 2007). It has many advantages including high oxidation efficiency, compactness in equipment, and simplicity in operation (Chen *et al*., 2003a). This process has been effectively used to degrade phenol, cyanide, carboxylic acids, benzoic acid, polyacrylates, and dyes (Chen *et al*., 2003b). However, little information about anodic oxidation of SA is available in literature. In this study, anodic oxidation of SA at Ta/BDD electrodes was investigated. The major objective is to investigate the efficiency of anodic oxidation of SA under different conditions.

MATERIALS AND METHODS

Electrode preparation and characterization

Hot filament chemical vapor deposition

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(HFCVD) was used to prepare diamond film electrodes. H_2 and CH_4 were used as the reactive gases. $B(OCH_3)_3$ was selected as a boron dopant and its concentration in the reactive gases was 16×10^{-6} in term of boron. Ta disks, 2 mm thick and 12.7 mm in diameter, were used as the substrates. Boron-doped diamond (BDD) films were deposited under typical conditions: substrate temperature 850 °C, filament temperature 2120~2150 °C, CH_4 1%, filment-substrate distance 8 mm, and deposition time 15 h. More details about the HFCVD apparatus and preparation procedures can be found elsewhere (Chen *et al.*, 2003a; 2003b).

The quality of BDD films was characterized using Raman spectroscopy (3000, Renishaw, UK). The morphology of the films was examined using scanning electron microscopy (SEM, JSM-6300F, JEOL, Japan).

Anodic oxidation

Ta/BDD was used as the anode, and a stainless steel plate was used as the cathode. The electrochemical reactor was 130 mm high and 30 mm in diameter, and was operated in batch. More details about the electrochemical reactor can be found elsewhere (Chen *et al.*, 2003a). Wastewater was synthesized by dissolving a proper amount of SA ($C_7H_7O_3$, analytical grade, 99+%) in deionized water. The volume of the solution was 35 ml. Na_2SO_4 (1500 mg/L) was used as the supporting electrolyte. The temperature was controlled using a water bath.

Chemical oxygen demand (COD) was measured using COD reactor and direct reading spectrophotometer (DR/2500, Hach Company, USA). Current efficiency (CE) is defined as the ratio of current used in oxidizing pollutants to the total current in the circuit, and can be calculated by the following equation (Chen and Chen, 2006):

$$CE=\frac{COD_t-COD_{t+\Delta t}}{8000\times I\times\Delta t}FV\times100\%, \qquad (1)$$

where COD_t and $COD_{t+\Delta t}$ are the COD values at times t and $t+\Delta t$ (mg/L); I is the electrolysis current (A); Δt is the electrolysis time (s); F is Faraday's constant, 96500 (C/mol) electrons and V is the volume of solution (L).

RESULTS AND DISCUSSION

Characterization

1. Raman analysis

Fig.1 shows the Raman spectra of the BDD film deposited. There is a sharp peak around 1336 cm^{-1}, slightly away from the characteristic signature of the diamond structure, 1332 cm^{-1}, revealing the presence of diamond. Weak and broad bands were detected, which were from amorphous or graphitic sp^2 carbon impurities. By normalizing the band intensities with the cross-sectional scattering coefficients, the sp^2 carbon content in the film is estimated to be less than 0.5%, indicating good diamond quality.

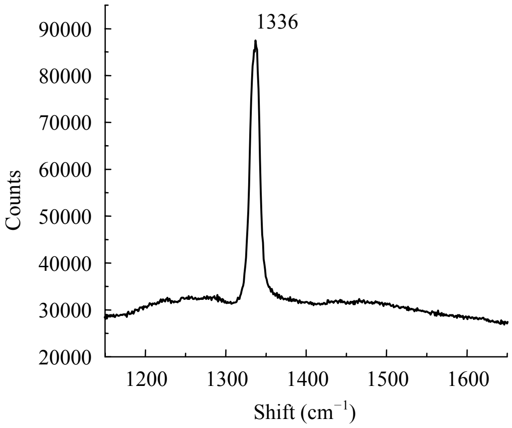

Fig.1 Raman spectra of the films deposited

2. Surface morphology examination by SEM

Fig.2 shows the typical SEM image of the BDD film. Well-defined diamond crystals can be observed clearly. The diamond crystals are highly faceted and the crystallite size is 1~4 μm. The film is perfect without any noticeable cracks.

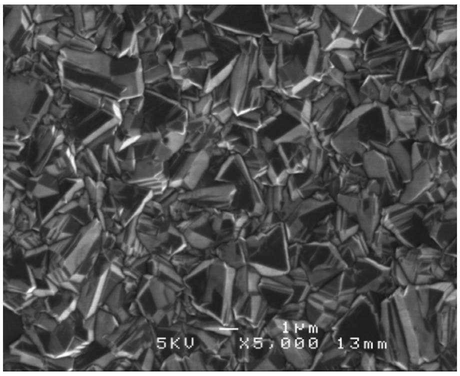

Fig.2 Typical SEM images of the films deposited

Anodic oxidation of SA at Ta/BDD

Anodic oxidation of SA at Ta/BDD was investigated under different conditions. The major variables investigated included the initial SA concentration, current density, reaction temperature and pH value.

1. Effect of initial concentration

Since the concentration of SA in industrial wastewaters may vary from time to time, it is necessary to investigate anodic oxidation of SA under different initial concentrations. Fig.3 shows the experimental result. It was found that low residual COD level could be achieved for all solutions after oxidation. COD was reduced from 166~830 mg/L to 1~42 mg/L, with removal efficiency of over 95% being obtained, indicating that the Ta/BDD electrode can mineralize SA effectively. In contrast, only 3% and 38% of SA were mineralized after 300 min of irradiation by photochemical oxidation and photocatalytic oxidation, respectively (Adán *et al.*, 2006). It was observed that small amounts of polymeric products were formed during anodic oxidation. This is essentially a common phenomenon for the anodic oxidation process.

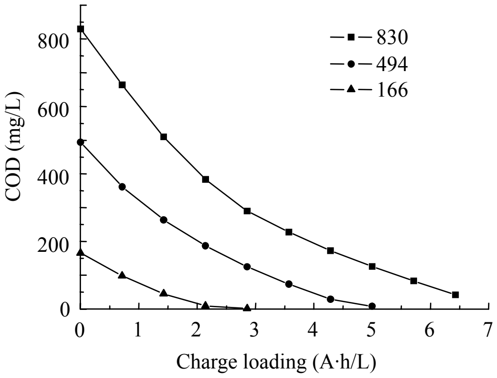

Fig.3 Effect of initial SA concentration on the temporal evolution of COD. Current density 200 A/m^2; temperature 30 °C; Na$_2$SO$_4$ 1500 mg/L

Fig.4 shows the variation of the instantaneous CE with COD for oxidation of different concentrations of SA. Obviously, instantaneous CE decreased with COD. This behavior can be ascribed to mass transfer limitation due to the gradual decay in pollutant concentration. Moreover, instantaneous CE was affected by the initial concentration. At a given COD value, instantaneous CE decreased significantly as the initial SA concentration increased. This is associated with the formation of more polymeric products at a high initial SA concentration than at a low initial SA concentration, since polymeric products are difficult to degrade once produced (Chen and Chen, 2006).

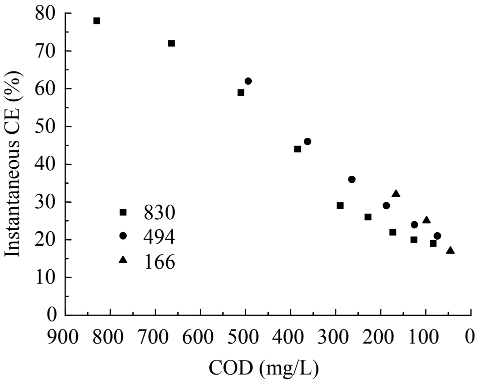

Fig.4 Variation of instantaneous CE with COD. Current density 200 A/m^2; temperature 30 °C; Na$_2$SO$_4$ 1500 mg/L

2. Effect of current density

Current density is a very important variable in electrochemical engineering. In order to achieve a balance of reaction time minimization and CE maximization, different current densities are used at different oxidation stages in industrial applications. Fig.5 shows the residual COD variation with the current density for oxidation of SA at a given charging loading. It was observed that the residual COD increased as the current density increased at a given charge loading. The residual COD was 10 mg/L at 50 A/m^2, but increased to 190 mg/L when the current density increased to 300 A/m^2. This is consistent with

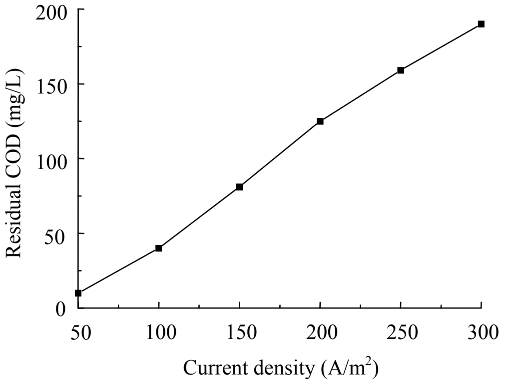

Fig.5 Effect of current density on the residual COD. Initial COD 494 mg/L; pH 3.0; temperature 30 °C; Na$_2$SO$_4$ 1500 mg/L; charge loading 3.57 A·h/L

that reported by Panizza *et al.*(2001). As current density reaches a certain value, referred to as limiting current density, the degradation rate does not increase any more and is determined by the mass transfer rate. The increased current beyond the limiting current density is not for oxidizing pollutants but for producing O_2, resulting in a decrease in CE. In addition, it was found that the amount of polymeric products increased with an increase in current density. This further explains why the residual COD increases with the current density.

3. Effect of temperature

Fig.6 shows the residual COD variation with the reaction temperature at a given charge loading. The residual COD was 125 mg/L at 30 °C, but reduced to 29 mg/L only when the temperature increased to 60 °C. This indicates that high reaction temperature favors SA degradation. It was found that the amount of polymeric products formed decreased as the reaction temperature increased. This partially explains why the residual COD decreased as the reaction temperature increased. Peroxodisulfate, generated from the oxidation of SO_4^{2-} ions, which is employed as supporting electrolyte in the medium, can also play an important role in the degradation of pollutants with high reaction rate (Muruganantha *et al.*, 2007). This mediated oxidant can be greatly enhanced with increasing temperature. This also partially explains the above conclusion. In addition, since the diffusion rate increased with the temperature, an increase in the reaction temperature could bring about an increase in the degradation rate, especially in the later stage, leading to a further reduction in the residual COD.

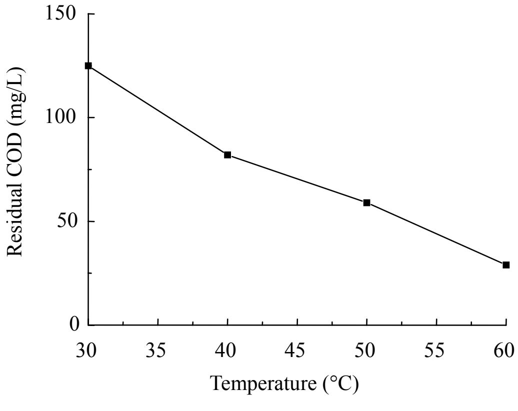

Fig.6 Effect of temperature on the residual COD. Initial COD 494 mg/L; current density 200 A/m^2; pH 3.0; Na_2SO_4 1500 mg/L; charge loading 3.57 A·h/L

4. Effect of initial pH

Many contradictory results were obtained from investigating pH effect on the anodic oxidation process. This may be associated with the differences in properties of chemical compounds tested and the electrodes used (Chen and Chen, 2006). In order to know if SA could be oxidized effectively at Ta/BDD electrodes in a wide pH range, the pH effect was investigated, and the result is shown in Fig.7. It was found that the effect of pH on anodic oxidation of SA at Ta/BDD is not significant. The residual COD changed only within a narrow range of 125~137 mg/L when pH increased from 3 to 10, which is in a good agreement with the result for anodic oxidation of Orange II at Ti/BDD (Chen and Chen, 2006). This indicates that pH adjustment before treatment is not necessary in most cases.

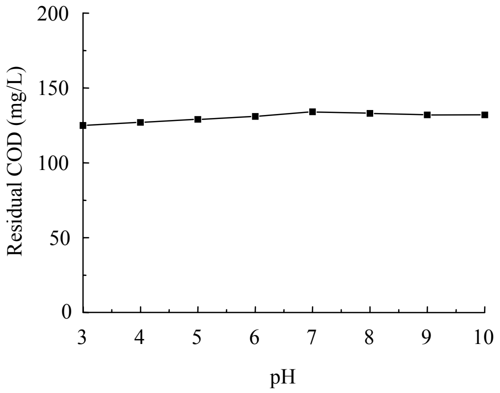

Fig.7 Effect of pH on the residual COD. Initial COD 494 mg/L; temperature 30 °C; current density 200 A/m^2; Na_2SO_4 1500 mg/L; charge loading, 3.57 A·h/L

CONCLUSION

BDD films have been successfully deposited on Ta substrates. The films obtained exhibit well-defined diamond features. It was found that SA could be oxidized effectively at Ta/BDD electrodes. COD was reduced from 830 mg/L to 42 mg/L under a current density of 200 A/m^2 at 30 °C. High reaction temperature and low current density are favorable for SA degradation at Ta/BDD. The pH effect was found to be independent of pH in the investigated range of 3.0~10.0.

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