Electrochemical degradation of 4-chlorophenol in aqueous solution using modified PbO$_2$ anode

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ABSTRACT

The electrochemical oxidation of 4-chlorophenol (4-CP) in aqueous solution was studied by electrochemical oxidation using modified PbO$_2$ electrode as anode. The influence of several operating parameters, such as initial 4-CP concentration, applied current density, and supporting electrolyte (Na$_2$SO$_4$) concentration was investigated. Ultraviolet spectroscopy and total organic carbon (TOC) measurements were conducted to study the kinetics of 4-CP electrochemical reaction and the mineralization efficiency of 4-CP. The experimental results showed that the 4-CP degradation always followed a pseudo-first-order kinetics. The higher mineralization of 4-CP and the lower current efficiency (CE) were obtained by the lower initial 4-CP concentration. The applied current density showed a positive influence on the degradation of 4-CP and the removal of TOC, but a higher applied current density led to a lower CE. Although Na$_2$SO$_4$ concentration of 0.05 M resulted in a higher 4-CP and TOC removal, the result of one-way analysis of variance (ANOVA) indicates that Na$_2$SO$_4$ concentration is not the significant parameter for 4-CP removal in electrochemical oxidation.

Key words | 4-chlorophenol, electrochemical oxidation, operation conditions, PbO$_2$ electrode

INTRODUCTION

Chlorophenols have been heavily used for the production of wood preservatives, insecticides, antifungal agents and dyes, so they can easily enter the natural environment through effluents of factories and can be found in surface water, soil and industrial water (Wang et al. 2011). Chlorophenols comprise a group of toxic organic compounds characterized as carcinogens, teratogens or environmental endocrine disruptors (Chaliha et al. 2008). The US EPA consolidated list of chemicals contains inter alia several chlorophenols under the Emergency Planning and Community Right-To-Know section (Gaya et al. 2009).

There are many methods for the treatment of chlorophenols such as adsorption, biological treatment, and chemical oxidation. However, these processes are not sufficiently efficient for the removal of these toxic organic pollutants. For example, adsorption is a process of pollutant transfer, in which the organic pollutant cannot be decomposed and thus secondary pollution is easily caused; the toxicity and the antibacterial activity of these organic compounds limit their microbial degradation in biological treatment; chemical oxidation requires costly strong oxidizers. However, the electrochemical oxidation technology has become a promising method for wastewater treatment because of its simplicity, easy control, strong oxidation performance, and environmental compatibility (Wang & Wang 2007; Zhu et al. 2008), which make this method attractive for possible practical application.

In electrochemical oxidation, a wide variety of electrode materials such as graphite, platinum, IrO$_2$, RuO$_2$, SnO$_2$, PbO$_2$ and boron-doped diamond (BDD) have been investigated in literature. Among all the materials, PbO$_2$ and BDD are the most attractive electrodes because of their high oxygen overpotential (Kapalka et al. 2009; Song et al. 2010). However, the high cost of BDD anode limits its large-scale application. Therefore, PbO$_2$ electrode has become popular due to its good electrical conductivity, favorable overpotential, high chemical inertness and low cost (Panizza & Cerisola 2003; Suryanarayanan et al. 2006). In our previous study, the electro-catalytic activity and stability of PbO$_2$ electrode was improved by the doping of carbon nanotubes (CNT) (Duan et al. 2012).

In this paper, we report the results concerning the anodic oxidation of 4-chlorophenol (4-CP) at CNT-modified PbO$_2$ electrode under galvanostatic conditions. The
influence of several parameters such as initial 4-CP concentration, applied current density and concentration of supporting electrolyte has been evaluated.

**METHODS**

**Electrode preparation**

Ti plate (30 × 50 × 0.8 mm) was used as substrate. Before deposition, the Ti substrate underwent sandblasting, 10 min of ultrasonic cleaning in acetone, 10 min of ultrasonic cleaning in deionized water, 2 h of etching in boiling aqueous 15% oxalic acid, and rinsing with deionized water. After pretreatment, the Ti substrate was first brushed at room temperature with the solution containing 20 g SnCl₄·5H₂O and 2 g SbCl₃ in 100 mL isopropanol–HCl mixture, dried at 120°C for 10 min, and then baked at 500°C for 10 min. This procedure was repeated about 10 times, and then the Ti substrate was annealed at 500°C for 1 h. Then, the pretreated substrate was electrodeposited with an intermediate layer of α-PbO₂ in alkaline solution (0.1 M PbO₂, 3.5 M NaOH) at 40°C using a conventional one-compartment cell, applying a current density of 3 mA cm⁻². Finally, CNT-modified PbO₂ film was electrodeposited on the above substrate in acid solution at 65°C, applying a current density of 15 mA cm⁻². The acid solution composition consisted of 0.5 M Pb(NO₃)₂, 0.05 M NaF plus 0.1 g L⁻¹ LAS and 5 g L⁻¹ CNT in 1 M HNO₃.

**Electrode characterization**

Cyclic voltammetry was executed in a conventional three-electrode cell using the PGSTAT302 electrochemical workstation. CNT-modified PbO₂ electrode was used as working electrode, a platinum sheet as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode.

**Batch experiment**

The electrochemical oxidation experiments were carried out by batch processes and the apparatus mainly consisted of a DC power supply, a heat-gathering style magnetic stirrer and a glass reactor. The anode (CNT-modified PbO₂ electrode) and cathode (stainless steel sheet) were positioned vertically and parallel to each other at a distance of 1 cm. During the experiments, samples were drawn from the reactor at certain intervals and then analyzed.

4-CP concentration was measured using a standard spectrophotometric method (Water & Wastewater Analytic Methods 1998).

Total organic carbon (TOC) was measured with a TOC analyzer (ELAB, China). On the basis of the TOC data, the current efficiency (CE) for the electrochemical treatment of 4-CP in aqueous solution was calculated as (Song et al. 2010a):

\[
CE = \frac{2.67FV(\text{TOC})_0 - (\text{TOC})_t}{8IM} \times 100\%
\]

where (TOC)₀ and (TOC)ₜ are the total organic carbon (g L⁻¹) at time zero and t (s), respectively; I is the current (A), F is the Faraday constant (96,287 C mol⁻¹), and V is the electrolyte volume (L).

**RESULTS AND DISCUSSION**

**Cyclic voltammetry**

The CNT-modified PbO₂ electrode was characterized electrochemically by cyclic voltammetry. Figure 1 shows typical cyclic voltammetric curves for the CNT-modified PbO₂ electrode in 0.5 M Na₂SO₄ electrolyte with and without 200 mg L⁻¹ 4-CP at a scan rate of 50 mV s⁻¹ recorded between 0.5 and 2.0 V (vs. SCE). As can be seen, addition of 4-CP to the electrolyte resulted in a well defined anodic peak at about 1.3 V (vs. SCE) corresponding to the oxidation of 4-CP. This result indicates that the 4-CP could be directly oxidized on CNT-modified PbO₂ electrode. However, the anodic peak current decreased in the subsequent scans and the peak almost disappeared in the fourth scan (not shown in Figure 1).
shown in Figure 1). This fact indicates that the electrode was highly passivated by a deposition film formed during the process of 4-CP oxidation, and this passive film covered the active sites and prevented further oxidation reaction of 4-CP (Coteiro & De Andrade 2007). Fortunately, this passive film could be destroyed and the electrode could be restored in an anodic polarization process in aqueous solution at the water decomposition potential (>2.5 V) with the same supporting electrolyte (Yang et al. 2009).

**UV spectra changes during electrolyses**

The ultraviolet (UV) spectra of 4-CP varied greatly after different periods of electrochemical oxidation, as shown in Figure 2. The UV spectra of 4-CP before the treatment presents two defined absorption bands around 225 and 280 nm and they can be attributed to $\pi \rightarrow \pi^*$ transition in aromatic rings. The peak at 280 nm is weak and the peak at 225 nm is the maximum absorption peak. During electrochemical reaction, the two absorbance bands observed around 225 and 280 nm continuously and simultaneously decreased and they disappeared after about 2 h of treatment. This inferred that the aromatic ring of 4-CP was opened during the electrochemical reaction. In addition, a new absorption band around 250 nm appeared at the beginning of the reaction, decreasing with the degradation time and disappearing after 2 h. The appearance of a new peak indicates that some intermediates were formed during the degradation of 4-CP. The total disappearance of three bands in electrochemical oxidation suggests that no further aromatic intermediates existed in the water, and the total degradation of 4-CP and its aromatic intermediates had been achieved by the oxidation with CNT-modified PbO$_2$ electrode.

**Effect of initial 4-CP concentration**

The initial concentration of pollutant is always an important parameter in wastewater treatment. In this study, the influence of the initial 4-CP concentration on the 4-CP and TOC removal efficiencies was investigated in a range from 10 to 90 mg L$^{-1}$. Figure 3(a) shows the effect of the initial concentration of 4-CP on the degradation efficiency during electrochemical reaction. In all cases, the 4-CP removal
rate was much faster during the first 30 min of electrochemical reaction. The degradation efficiency reached 75, 53, 44, 38 and 33% for the initial concentrations of 10, 30, 50, 70 and 90 mg L\(^{-1}\), respectively, after 30 min of reaction. The complete degradation was obtained after 60 and 90 min for the initial concentrations of 10 and 30 mg L\(^{-1}\), respectively. After 120 min, the removal efficiency of 4-CP for the initial concentrations of 50, 70 and 90 mg L\(^{-1}\) were 98, 96 and 72%, respectively. The inset of Figure 3(a) shows the first-order reaction kinetics fitting plots for different initial concentrations. The \(R^2\) (correlation coefficient) and values of apparent rate constant (\(k_{app}\)) determined from the straight line obtained from the first-order reaction kinetics fitting are shown in Table 1. The results indicate that the 4-CP degradation for different initial concentrations was in agreement with pseudo-first-order reaction kinetics. \(k_{app}\) reduced with the increase of initial concentration. Figure 3(b) shows that with the initial concentration of 4-CP increasing from 10 to 90 mg L\(^{-1}\), the TOC removal percentage decreased from 90% to 63% after 180 min of reaction. In contrast, the amount of TOC removed increased sharply with the increase of initial concentration, resulting in an increase of CE calculated as a function of TOC. It might be because hydroxyl radicals could react rapidly with the organic matters before the oxygen evolution in the solution at a high initial organic concentration (Samet et al. 2010; Wang et al. 2010).

**Effect of current density**

The current density of the electrochemical system has a major role in the anodic oxidation process, and it determines the oxidation reaction speed of organic materials on the anode (Song et al. 2010a). Thus, the different current

| Parameters of pseudo-first-order kinetics of 4-CP electrochemical degradation at different experimental parameters |
|------------------|------------------|------------------|------------------|------------------|------------------|
| Initial 4-CP concentration (mg L\(^{-1}\)) | Current density (mA cm\(^{-2}\)) |
| 10 | 30 | 50 | 70 | 90 | 10 | 20 | 30 | 40 | 50 |
| \(k_{app}\) (min\(^{-1}\)) | 0.0685 | 0.0467 | 0.0263 | 0.0179 | 0.0099 | 0.0026 | 0.0096 | 0.0271 | 0.0277 | 0.0405 |
| \(R^2\) | 0.9757 | 0.9657 | 0.9858 | 0.9846 | 0.9963 | 0.9984 | 0.9986 | 0.9848 | 0.9897 | 0.9766 |

The effect of current density (i.e. (■) 10 mA cm\(^{-2}\); (□) 20 mA cm\(^{-2}\); (○) 30 mA cm\(^{-2}\); (▲) 40 mA cm\(^{-2}\); (△) 50 mA cm\(^{-2}\)), on (a) 4-CP degradation with time and (b) TOC removal efficiency with time. Inset in Figure 4(b) is the CE after 180 min reaction (the initial pH: 6.5; the initial 4-CP concentration: 50 mg L\(^{-1}\); volume: 200 mL; supporting electrolyte (Na\(_2\)SO\(_4\)) concentration: 0.05 M; temperature: 30°C).
densities from 10 to 50 mA cm\(^{-2}\) were applied in this study. Figure 4 shows the influence of the current density on the 4-CP and TOC removal during the electrochemical oxidation. The results presented in Figure 4 show that the 4-CP and TOC removal percentages increased with time for all current densities. The results of first-order reaction kinetics fitting for all current densities are shown in Table 1. As can be seen in Table 1, there was a significant increase in the value of \(k_{\text{app}}\) as a function of the applied current density, which should be ascribed to the fact that higher current density led to higher production of hydroxyl radicals (Song et al. 2010a). In addition, the increased anodic current density amplified the oxygen evolution reaction, and then the formation and detachment of increased oxygen bubbles increased the diffusion of 4-CP in solution. Nevertheless, it should be noted that the CE (inset of Figure 4(b)) was lower at higher current density in our experiments. This result can be explained by the competitive electrode reaction such that evolution of \(O_2\) was obvious at a higher current density (Tahar & Savall 1998; Wang et al. 2010), which led to a higher charge consumption.

**Effect of supporting electrolyte concentration**

It is well known that the presence of electrolytes in electrochemical oxidation can increase the conductivity, diminish the resistance, and lessen the energy cost of the process (Palma-Goyes et al. 2010). The influence of the supporting electrolyte concentration on the 4-CP and TOC removal is shown in Figure 5. It was observed that the 4-CP and TOC removal efficiency increased slightly with the increase of \(Na_2SO_4\) concentration, and then decreased slightly when the \(Na_2SO_4\) concentration was higher than 0.05 M. The results of first-order reaction kinetics (Table 1) show that the \(k_{\text{app}}\) obtained at the \(Na_2SO_4\) concentration of 0.05 M was slightly higher than those of other \(Na_2SO_4\) concentrations. The highest CE (2.6%) was also obtained at the \(Na_2SO_4\) concentration of 0.05 M. Nevertheless, the electrolyte concentration does not change 4-CP and TOC removal significantly, and the \(Na_2SO_4\) concentrations of 0.01, 0.03, 0.1 and 0.2 M did not have significant differences. One-way analysis of variance (ANOVA) was used to examine the difference of all \(Na_2SO_4\) concentrations for the 4-CP removal at a significance level of 0.05. The results of ANOVA indicate that, although the electrolyte is necessary in electrochemical oxidation, \(Na_2SO_4\) concentration is not the significant parameter for 4-CP removal in electrochemical oxidation (\(F = 1.53; P = 0.24 > 0.05\)).

**Comparison between different methods**

Based on the above results, the 4-CP and TOC removal efficiency of electrochemical oxidation was compared with adsorption and Fenton processes. Table 2 presents the removal percentages of 4-CP and TOC with different methods. As can be seen, in the experimental conditions tested, the highest 4-CP removal was obtained by electrochemical oxidation, followed by Fenton and adsorption, while the TOC removal followed the sequence: adsorption > electrochemical oxidation > Fenton. These results indicate that three methods were feasible for the removal of 4-CP from wastewater. However, as proposed previously, adsorption
is a process of pollutant transfer, and the organic pollutant cannot be decomposed and thus secondary pollution is easily caused, chemical oxidation requires costly strong oxidizers, while electrochemical oxidation technology has the advantages of simplicity, easy control, strong oxidation performance, and environmental compatibility. Therefore, anodic oxidation with PbO2 electrode is an effective method to decontaminate the phenolic compounds and has promising application prospects in wastewater treatment.

CONCLUSION

Electrochemical degradation of 4-CP was studied by means of anodic oxidation on CNT-modified PbO2 anode in aqueous solution. The influence of operative conditions on 4-CP removal, total mineralization and CE was evaluated. Under the experimental conditions, the 4-CP and TOC removal efficiency was reduced with the increase of initial 4-CP concentration; however, the amount of TOC removed increased sharply with the increase of initial concentration, resulting in an increase of CE. The degradation process using higher current density showed faster degradation rate and lower CE. The results of the effect of supporting electrolyte concentration showed that Na2SO4 concentration of 0.05 M achieved the highest 4-CP and TOC removal, but the results of ANOVA indicate that Na2SO4 concentration is not the significant parameter for 4-CP removal in electrochemical oxidation. The kinetic studies showed that all the degradation of 4-CP in the study followed pseudo-first-order kinetics.

REFERENCES


First received 17 April 2012; accepted in revised form 15 June 2012