



# Ultrasound enhanced electrochemical oxidation of phenol and phthalic acid on boron-doped diamond electrode

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## ABSTRACT

The enhancement on degradation of two typical organic pollutants, phenol (Ph) and phthalic acid (PA) on boron-doped diamond (BDD) electrode is particularly investigated in this study. Results show that ultrasound (US) has remarkable influence on electrochemical (EC) oxidation of the two pollutants including degradation efficiency, EC oxidation energy consumption, mass transport and electrochemical reaction. With US, the enhancement on degradation efficiency and decreasing of EC oxidation energy consumption of Ph are more obvious. US can also efficiently reduce the average electrochemical oxidation energy consumption (AE), decreasing by 74 and 69% for Ph and PA, respectively. Mass transport process can be greatly accelerated by US. The mass transport coefficients of Ph and PA both reach  $2.0 \times 10^{-5} \text{ m s}^{-1}$  in ultrasound-assisted electrochemical (US-EC) process, from  $5.4 \times 10^{-6}$  and  $6.7 \times 10^{-6} \text{ m s}^{-1}$  in EC, increasing by 270 and 199%, respectively. The reaction amount of Ph decreases by 79% with US, from  $6.49 \times 10^{-10}$  to  $1.39 \times 10^{-10} \text{ mol cm}^{-2}$ . For PA, the reaction amount decreases from  $1.25 \times 10^{-11}$  to  $3.11 \times 10^{-12} \text{ mol cm}^{-2}$  with US. The oxidation peak current increases by 32% for Ph. While for PA, there is no direct oxidation happened in US-EC process.

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## 1. Introduction

Advanced Oxidation Processes (AOPs), including chemical oxidation, photocatalytic oxidation, electrochemical (EC) oxidation, and sonochemical oxidation, have attracted great attention because of the increasing variety and amount of non-biodegradable pollutants and more complex structure. Each process has its unique characteristics and advantages, but it is difficult for a single oxidation process to meet the requirement for wastewater treatment in some cases. Hence, the combination of several oxidation processes has been becoming one of the promising treatment technologies and active research fields in recent years [1].

EC oxidation is considered as an environmental friendly technology with wide applications because of its excellent oxidation ability without secondary pollution. Boron-doped diamond (BDD) electrode has received wide attention in recent years for its excellent properties, such as wide electrochemical potential window, high oxygen evolution potential, low background current and high anodic stability [2,3]. It has been demonstrated that various organic pollutants can be degraded efficiently by BDD electrode in EC treatment [4]. On the other hand, it is found that ultra-

sound (US) is also effective in treating some non-biodegradable organic pollutants, such as alkylphenol ethoxylate surfactants [5], trichloroethylene [6], poly(*n*-alkyl acrylates) [7], and phthalic acid esters [8], which can be degraded and incinerated with US. The combinative methods of US and other AOPs, such as photocatalytic oxidation [9,10], ozone oxidation [11–13] and EC oxidation [14,15], have become a rapidly developing research field in recent years because US is a relatively simple technology and is easy to use.

It is widely accepted that the degradation of pollutants or the enhancement on other oxidation processes by US is due to its cavitation [16,17]. With US, the mass transport of pollutant components is promoted, so that the pollutants and oxidant or catalytic reaction surface are brought into intimate contact. At the same time, some active substances such as hydroxyl radicals are produced in bulk under the high temperature and pressure resulted from the cavitation by US, which may degrade the pollutant in some degree. However, EC oxidation of pollutants at electrode surface is complex. The mass transport and electrochemical reaction are the main factors in EC oxidation. The influences of US on these processes have not been understood clearly up to now, especially lacking of quantitative analysis on parameters of mass transport and electrochemical properties. Thus, the study on ultrasound enhanced electrochemical (US-EC) oxidation process for organic pollutants is of great significance on the applications of this combinative process in environmental engineering.

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In this work, phenol (Ph) and phthalic acid (PA) are chosen as the pollutant samples for aromatic pollutants with high toxicity and carcinogenicity due to their different electrochemical properties. US can enhance the degradation efficiency and decrease of EC oxidation energy consumption of Ph and PA on the BDD electrode. The reason of enhancement in US-EC process for degradation of organic pollutants is discussed in terms of mass transport process and electrochemical reaction.

## 2. Experimental

### 2.1. Reagents and apparatus

Ph and PA were from Sigma and all reagents were of analytical grade. EC measurements were carried out on a CHI 660 electrochemical workstation (CHI Co., USA). The ultrasonic generator was a CQJ50 ultrasonic instrument (Shanghai Ultrasonic Instrument Co., China).

### 2.2. EC and US-EC processes

EC oxidation of each organic pollutant was carried out in a cylindrical single-compartment cell with jacketed cooler to maintain constant temperature, using BDD electrode as anode with an immersed area of 24 cm<sup>2</sup>. BDD was made by chemical vapor deposition on a conductive polycrystalline silicon substrate [18]. The thickness of the obtained diamond film was about 1 μm. A titanium foil with the same area was used as cathode and the electrode gap was 1 cm. The current density was controlled constant at 20 mA cm<sup>-2</sup>. Ph and PA solutions containing 0.05 M Na<sub>2</sub>SO<sub>4</sub> were neutralized to pH 3.0 using 2 M H<sub>2</sub>SO<sub>4</sub>. The initial chemical oxygen demand (COD) should be similar for comparison, and that of Ph and PA solutions was 548 and 531 g m<sup>-3</sup>, respectively. The solution volume was 200 cm<sup>3</sup> in each run. US-EC degradation was carried out at the frequency of 33 kHz, with the power of 50 W, and other conditions were the same as those in the EC process. In order to avoid temperature increasing induced by electrode reaction or US effect, the temperature of EC and US-EC processes was kept constant at 10 °C by cooling water.

### 2.3. Analysis

Instantaneous current efficiency (ICE) can be calculated by Eq. (1) [19]:

$$ICE = \frac{[\text{COD}_t - \text{COD}_{t+\Delta t}]FV}{8I\Delta t} \quad (1)$$

where (COD)<sub>t</sub> and (COD)<sub>t+Δt</sub> are the CODs (g m<sup>-3</sup>) at time *t* and *t* + Δ*t*, respectively, *F* is the Faraday constant (96487 C mol<sup>-1</sup>), *V* is the volume of electrolyte (m<sup>3</sup>), *I* is the current intensity (A), and Δ*t* is the time interval (s), 8 is the equivalent mass of oxygen (g eq<sup>-1</sup>). For determination of COD, the standard colorimetric (titrimetric) method with closed reflux was used.

The average electrochemical oxidation energy consumption (AE) is defined as the average electrochemical oxidation energy for the removal of 1 g COD:

$$AE = \int_0^t \frac{U(t)I dt}{(\text{COD}_0 - \text{COD}_t)V} \quad (2)$$

where *U*(*t*) is the instant potential in degradation (V).

Electrochemical measurements were carried out in a conventional three-electrode cell. BDD electrode was used as the working electrode, with saturated calomel electrode (SCE) as a reference, and Pt as a counter electrode. Concentration of Ph and PA in the solution with 0.05 M Na<sub>2</sub>SO<sub>4</sub> was also 600 mg L<sup>-1</sup>. Cyclic voltammetry was used to determine the electrochemical properties of the

organic pollutants on BDD electrode with a scan rate of 500 mV s<sup>-1</sup> in the potential range between -2.0 and 2.5 V. The reaction amount on the electrode surface was determined by one-step chronocoulometry method with a pulse width of 0.25 s. According to their different oxidation current peaks, the potential range of Ph was between 0.96 and 1.91 V, and that of PA was between 1.09 and 1.73 V. All potentials in this work were against SCE.

## 3. Results and discussion

### 3.1. Enhancement in electrochemical oxidation efficiency and energy consumption by US

For the Ph and PA solutions with initial COD of 548 and 531 g m<sup>-3</sup>, respectively, experimental results with US show that COD removal of Ph is only 1.5% at 3 h, while that of PA is 1.3%. After 3 h, COD removal of both two pollutants is hardly increased. That is to say only US has no effect on the degradation of Ph and PA under the experimental condition.

In EC and US-EC processes, the evolution of ICE and COD removal of two pollutants versus time is shown in Fig. 1. In EC process, the complete incineration is defined as COD removal close to 100% [20], the time to reach the complete incineration for PA (curve a) and Ph (curve c) is 9.7 and 10.8 h, respectively. In US-EC process, it decreases to only 3.4 and 3.2 h for PA (curve b) and Ph (curve d), respectively. The time reaching complete incineration follows the order: (*t*<sub>Ph</sub>)<sub>EC</sub> > (*t*<sub>Ph</sub>)<sub>US-EC</sub> and (*t*<sub>PA</sub>)<sub>EC</sub> > (*t*<sub>PA</sub>)<sub>US-EC</sub>. It shows that US can enhance EC oxidation efficiency of both pollutants, and the complete mineralization time is greatly reduced, by 70% for Ph and by 65% for PA.

As shown in Fig. 1, curve (b) is above curve (a), and curve (d) is above curve (c). This shows that for the same COD removal ICE<sub>US-EC</sub> is obviously higher than ICE<sub>EC</sub> for both pollutants. When COD removal exceeds 30%, (ICE<sub>US-EC</sub>/ICE<sub>EC</sub>)<sub>Ph</sub> > 2.9 and (ICE<sub>US-EC</sub>/ICE<sub>EC</sub>)<sub>PA</sub> > 2.3, which shows that the current efficiency is greatly improved by US, moreover the enhancement on EC oxidation of Ph is more effective.

The variations of AE versus COD removal for PA and Ph in EC and US-EC processes are shown in Fig. 2. For PA, AE in US-EC process (curve b) is lower than that in EC process (curve a); and for Ph, AE in US-EC process (curve d) is also lower than that in EC process (curve c). It indicates that US can reduce EC energy consumption dramatically for degradation of the two pollutants. It is also observed that

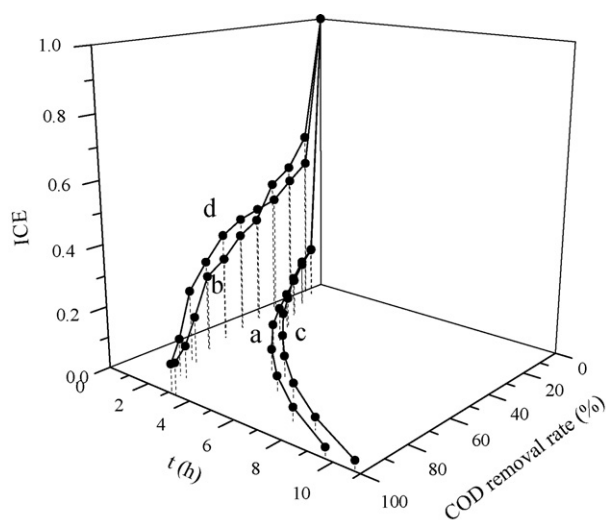


Fig. 1. The solid relationship of ICE, COD removal and time in EC and US-EC processes: (a) PA, EC; (b) PA, US-EC; (c) Ph, EC; (d) Ph, US-EC. *i* = 20 mA cm<sup>-2</sup>; pH = 3.

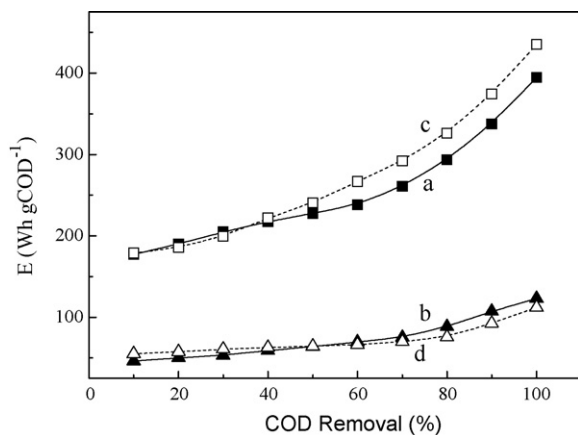


Fig. 2. The variations of AE in EC and US-EC processes: (a) PA, EC; (b) PA, US-EC; (c) Ph, EC; (d) Ph, US-EC.  $i = 20 \text{ mA cm}^{-2}$ ;  $\text{pH} = 3$ .

when COD removal is high (e.g., above 50%), AE of Ph (curve c) is higher than that of PA (curve a) in EC process, while that of Ph (curve d) is lower than that of PA (curve b) in US-EC process. This also demonstrates that the enhanced effect on Ph is stronger than that on PA. For complete incineration,  $(AE_{EC})_{PA}$  is calculated to be  $395 \text{ Wh gCOD}^{-1}$  and  $(AE_{US-EC})_{PA}$  is  $123 \text{ Wh gCOD}^{-1}$ , decreased by 69%; and for Ph,  $(AE_{EC})_{Ph}$  is  $435 \text{ Wh gCOD}^{-1}$  and  $(AE_{US-EC})_{Ph}$  is  $112 \text{ Wh gCOD}^{-1}$ , decreased by 74%, as shown in Table 1. All results show that US can enhance the degradation efficiency and decrease of EC oxidation energy consumption of pollutants on the BDD electrode. So BDD electrode may be suitable for US-EC oxidation.

### 3.2. Enhancement on mass transport process of electrochemical oxidation by US

Electrochemical oxidation efficiency of Ph and PA is increased by US, moreover energy consumption is decreased. The results show that US inevitably affects electrochemical oxidation process, and the effect of EC by US is discussed on the mass transport process and electrochemical reaction.

The limiting current density ( $i_{lim}$ ) is an important parameter in EC oxidation, which has the following relation with pollutants concentration and COD, as shown in Eq. (3) [21–24]:

$$i_{lim} = nFk_d C = \frac{Fk_d \text{COD}}{8} \quad (3)$$

where  $n$  is the number of electrons transferred for one organic pollutant molecule to be oxidized completely to  $\text{CO}_2$ ,  $k_d$  is the average mass transport coefficient of organic pollutant in EC process ( $\text{m s}^{-1}$ ), and  $C$  is the concentration of organic pollutant ( $\text{mol m}^{-3}$ ), 8 is the equivalent mass of oxygen ( $\text{g eq}^{-1}$ ).

According to the applied current density, degradation can be divided into two different operating regimes as follows.

If  $i < i_{lim}$ , the degradation is controlled by the rate of electrochemical reaction of pollutant component at electrode surface, i.e., controlled by the current density. In this case,  $\text{ICE} = 1$  and all current is utilized in pollutant oxidation [22,24]. The removal of COD versus time appears a linear relation, as shown in Eq. (4) [21]:

$$\text{COD}_t = \text{COD}_0 - \frac{8iAt}{FV} \quad (4)$$

where  $\text{COD}_0$  is the initial COD ( $\text{g m}^{-3}$ ),  $i$  is the current density ( $\text{A m}^{-2}$ ), and  $A$  is the electrode area ( $\text{m}^2$ ). Decline of COD only relies on reaction time ( $t$ ), and has nothing to do with pollutant mass transport, so that the mass transport process will not be enhanced by US.

If  $i \geq i_{lim}$ , the electrolysis on electrode surface is controlled by mass transport and  $\text{ICE} < 1$  [22,24]. The decrease in ICE is resulted from secondary reactions such as oxygen evolution, so that the removal of COD decreases exponentially, as is shown in Eq. (5) [23]:

$$\text{COD}_t = \text{COD}_0 e^{-k_d At/V} \quad (5)$$

Eq. (5) can be written as:

$$\ln\left(\frac{\text{COD}_t}{\text{COD}_0}\right) = -\frac{k_d At}{V} \quad (6)$$

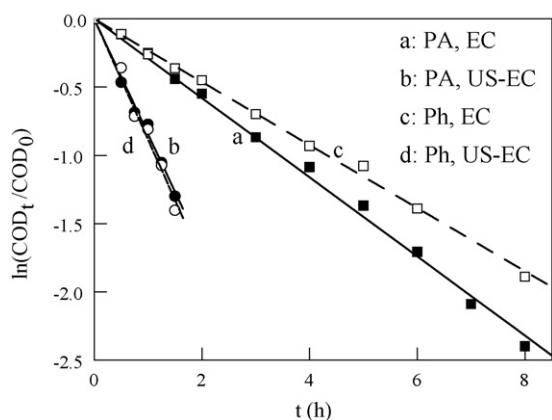
which shows a linear relationship between  $\ln(\text{COD}_t/\text{COD}_0)$  and  $t$ .

The mathematic model is suitable for degradation in EC and US-EC processes. From the analysis above, the decomposition should be controlled by mass transport ( $i \geq i_{lim}$ ). Thus for certain pollutant, the mass transport coefficients in EC and US-EC processes,  $(k_d)_{EC}$  and  $(k_d)_{US-EC}$ , can be calculated through the slope of  $\ln(\text{COD}_t/\text{COD}_0)-t$  curves by measuring  $\text{COD}_t$ , and the influence of US on mass transport in EC process can be studied.

The current density in both EC and US-EC processes is kept constant at  $20 \text{ mA cm}^{-2}$ , so that the degradation is controlled by mass transport.  $\ln(\text{COD}_t/\text{COD}_0)-t$  curves of Ph and PA in EC and US-EC processes are shown in Fig. 3. All curves (a–d) are in agreement with the linear decay function, indicating that Eq. (6) is suitable for EC and US-EC processes. The values of  $k_d$  for Ph and PA in EC and US-EC processes are obtained from the slopes of four lines, as listed in Table 1. The values of  $k_d$  increase dramatically with US, from  $6.7 \times 10^{-6}$  to  $2.0 \times 10^{-5} \text{ m s}^{-1}$  increased by 199% for PA, and from  $5.4 \times 10^{-6}$  to  $2.0 \times 10^{-5} \text{ m s}^{-1}$  increased by 270% for Ph, indicating that mass transport is enhanced by US. The enhancement on mass transport of Ph is greater. The mass transport coefficient of PA is higher than that of Ph in EC process, but they become equal in US-EC process. It means that  $k_d$  depends on US intensity instead of its property when the enhancement on mass transport by US is sufficient. There is no difference in mass transport process between Ph and PA in US-EC process, with the sound frequency of 33 kHz and power of 50 W in this work. Because US can mix deeply the solution, the diffusion coefficient of solution species is very low comparing the enhanced mass transport caused by US, that is to say that the species' own diffusion coefficient do not play a major role

Table 1  
Complete incineration AE, mass transport coefficient, reaction amount and current of phenol and phthalic acid in EC and US-EC processes.

	Phthalic acid		Phenol	
	EC	US-EC	EC	US-EC
Complete incineration AE ( $\text{Wh gCOD}^{-1}$ )	395	123	435	112
$(AE_{US-EC} - AE_{EC})/AE_{EC}$	–	–69%	–	–74%
$k_d$ ( $\text{m s}^{-1}$ )	$6.7 \times 10^{-6}$	$2.0 \times 10^{-5}$	$5.4 \times 10^{-6}$	$2.0 \times 10^{-5}$
$[(k_d)_{US-EC} - (k_d)_{EC}]/(k_d)_{EC}$	–	199%	–	270%
$\Gamma$ ( $\text{mol cm}^{-2}$ )	$1.25 \times 10^{-11}$	$3.11 \times 10^{-12}$	$6.49 \times 10^{-10}$	$1.39 \times 10^{-10}$
$(\Gamma_{US-EC} - \Gamma_{EC})/\Gamma_{EC}$	–	–75%	–	–79%
$i$ ( $\mu\text{A}$ )	418	0	532	700
$(i_{US-EC} - i_{EC})/i_{EC}$	–	–100%	–	32%



**Fig. 3.** The variations of  $\ln(\text{COD}_t/\text{COD}_0)$  during electrolysis, using a BDD anode: (a) PA, EC; (b) PA, US-EC; (c) Ph, EC; (d) Ph, US-EC. Supporting electrolyte: 0.05 M  $\text{Na}_2\text{SO}_4$ ;  $i = 20 \text{ mA cm}^{-2}$ ;  $\text{pH} = 3$ .

in the US-EC process. So the mass transport for different pollutant components in US-EC process is almost same in our experimental condition. Thus the diffusion coefficient of solution species can be neglected in our manuscript.

### 3.3. Influences on electrochemical reaction of Ph and PA at BDD anode by US

Electrochemical reaction of Ph and PA is independent of the reaction amount on the electrode surface. The more reaction amount is favorable for electrochemical reaction. However too many reaction amount may decrease the active sites on the electrode surface. So the reaction amount on the electrode surface may have positive or negative effect on the electrochemical reaction. The reaction amounts ( $\Gamma$ ) of two pollutants are measured by one-step chronocoulometry in EC and US-EC processes, which the Cottrell formula [25,26] is used:

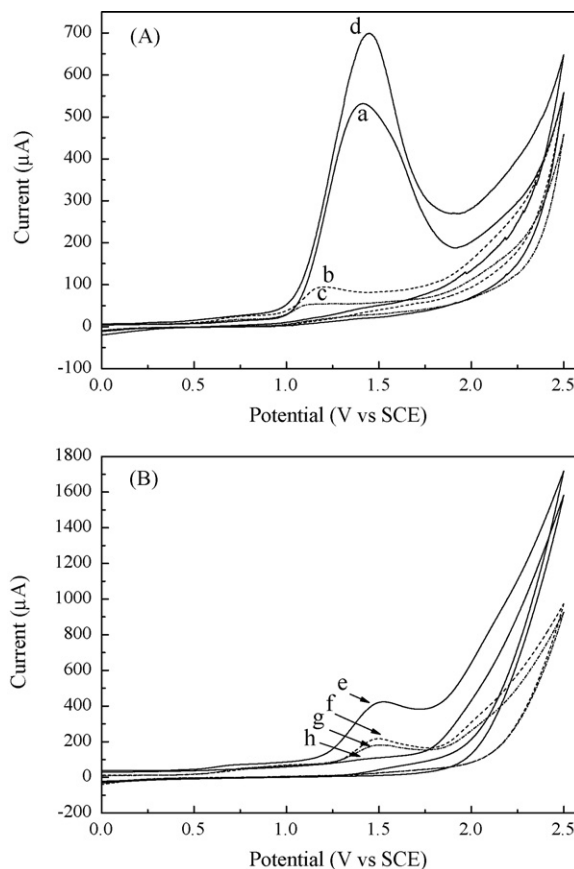
$$Q = nF\Gamma + Q_{dl} + \frac{2nFAC_{ox}^0 D^{1/2} t^{1/2}}{\pi^{1/2}} \quad (7)$$

where  $Q$  is the total amount of charge ( $\text{C cm}^{-2}$ ),  $A$  is the real area of electrode ( $\text{cm}^2$ ),  $C_{ox}^0$  is the concentration of component in a solution ( $\text{mol cm}^{-3}$ ),  $D$  is the diffusion coefficient of component in water ( $\text{cm}^2 \text{ s}^{-1}$ ),  $t$  is time (s),  $\Gamma$  is the reaction amount of component at the electrode surface ( $\text{mol cm}^{-2}$ ),  $Q_{dl}$  is the coulombs required for double-layer charging ( $\text{C cm}^{-2}$ ), and  $n$  is the number of electron of a pollutant molecule transferred in oxidation reaction at BDD electrode. The area of oxidation peak can be determined from cyclic voltammogram curves, so that the reaction amount is obtained. Both values of  $n$  for Ph and PA are calculated to be 1 [27].

The Cottrell formula shows a linear relation between  $Q$  and  $t^{1/2}$ . For Ph and PA, the intercept of the chronocoulometry line at the charge axis is the value of  $nF\Gamma + Q_{dl}$ , while for the blank medium ( $\text{Na}_2\text{SO}_4$  solution) without Ph or PA added, the intercept is  $Q_{dl}$ . The reaction amount at the electrode surface is calculated from  $nF\Gamma$ , the difference of the two values of intercept. The data are listed in Table 1. The reaction amount is much higher in EC process, a  $(\Gamma_{\text{Ph}}/\Gamma_{\text{PA}})_{\text{EC}} = 51.9$ . This is because that the hydrogen-terminated surface of BDD electrode converts to oxygen-terminated surface more readily, which is negatively charged by anodic polarization in acidic solution [28]. Since the ionization constant of Ph is smaller than that of PA, it is easier for Ph to combine with proton and brings more positive charges in the solution with  $\text{pH} = 3$ . Thus the affinity between Ph molecule and BDD electrode surface is stronger with a larger reaction amount, and more intermediates are produced to cover active sites in EC process. In contrast, the adsorption

force between BDD electrode surface and PA is weaker, so that the reaction amount is smaller with less intermediates produced in EC process. In US-EC process, the reaction amounts of both pollutants decrease remarkably with the physical effect of US, but the reaction amount of Ph is still much more than that of PA. The former is in the order of  $10^{-10}$ , and the latter is only  $10^{-12}$ . The reaction amount of Ph in US-EC process is even larger than that of PA in EC process, and  $(\Gamma_{\text{Ph}})_{\text{US-EC}}/(\Gamma_{\text{PA}})_{\text{EC}} = 11.1$ . It can be induced that the reaction amount and oxidation reaction rate of Ph at electrode surface decrease, so that it is not easy to form a dense polymer film. However, the reaction amount is still enough for EC oxidation, and the “washing” effect by US exposes more active sites at electrode surface, so that the oxidation of Ph may occur continuously and steadily. For PA, the reaction amount is too small for oxidation. So we measured electrochemical reaction current to testify the conclusion.

Electrochemical properties of the two pollutants, Ph and PA, at BDD anode in EC and US-EC processes are investigated using cyclic voltammetry, as shown in Fig. 4. Electrochemical measurements show that both Ph (curve a) and PA (curve e) have an obvious oxidation current peak at 1.41 and 1.52 V, respectively. The anodic peak current of Ph and PA is 532 and 418  $\mu\text{A}$ , respectively. With consecutive cyclic voltammetry, the peak current of Ph decreases dramatically to 95  $\mu\text{A}$ , by 82%, in the second cycle (curve b). The peak decreases and shifts negatively with the number of cycles increasing until a steady state reaches at which the peak almost disappears in the eighth cycle (curve c). The fact indicates that Ph is easy to adsorb on BDD anode and results in an obvious oxidation peak in the first cycle, but a dense polymer film is also formed from



**Fig. 4.** Cyclic voltammograms obtained at BDD electrode in 0.05 M  $\text{Na}_2\text{SO}_4 + 600 \text{ mg dm}^{-3}$  Ph (A) or PA (B): (a) first cycle; (b) second cycle; (c) eighth cycle; (d) with US; (e) first cycle; (f) second cycle; (g) fifth cycle; (h) with US. Scan rate:  $500 \text{ mV s}^{-1}$ ; scan range:  $-2$  to  $2.5 \text{ V}$ ;  $\text{pH} = 3$ .

phenoxy radicals at electrode surface during the reaction [29]. The electrode is highly passivated by deposition of the film that covers the active sites and prevents further oxidation reaction. For PA, the peak current also decreases in the second cycle to 218  $\mu\text{A}$ , by 48% (curve f). It continues decreasing until the peak current comes to 180  $\mu\text{A}$  in the fifth cycle (curve g). It demonstrates that the polymer film is also formed at BDD anode in some degree during oxidation of PA, but it is not as much as that formed by Ph. In US-EC process, the peak current of Ph (curve d) increases to 700  $\mu\text{A}$ , by 32%, which confirms that direct oxidation of Ph is improved by US. On the contrary, the oxidation peak of PA can hardly be detected in US-EC process (curve h), indicating that US makes negative effect on direct oxidation at electrode surface. PA can only be degraded through indirect oxidation by free radicals such as hydroxyl radicals formed from  $\text{H}_2\text{O}$  near the electrode surface in US-EC process. It can be further concluded that the reaction of Ph changes from mass transport control to adsorption control because the rate of mass transport is remarkably increased by US. Thus the oxidation peak current depends on adsorption of Ph and desorption of its intermediates at electrode surface, but independent of mass transport and Ph concentration in bulk. On the contrary, the reaction amount of PA at electrode surface is much less, which is too low for direct EC oxidation in US-EC process.

From the experimental results, the reasons of US-EC process for organic pollutants are further discussed on mass transport process and electrochemical reaction. US has remarkable influences on the two processes.

US can obviously accelerate the mass transport process from bulk to electrode surface. The enhancement only depends on US intensity, so that there is no difference in mass transport for different pollutant components in US-EC process. For the two pollutants studied, the rate of mass transport of PA is a little faster than that of Ph in EC process. In the US-EC process with sound frequency of 33 kHz and power of 50 W, the mass transport coefficient of Ph is increased by 270%, equal to that of PA, which is increased by 199%. Hence, the mass transport process does not affect the degradation efficiency in US-EC process.

US may have positive or negative effect on reaction amount on the electrode surface. This effect depends on electrochemical properties of pollutants and determines the pathway of oxidation of pollutants. It is easy for Ph to adsorb on electrode surface but difficult for the intermediates to desorb, which hinders EC process. Although US makes the reaction amount of Ph decreases by 79% (as shown in Table 1), it promotes the polymer intermediates desorb from electrode surface, which is of benefit to EC oxidation, so that the direct oxidation peak current is increased by 32% because of the positive effect of US. However, the reaction amount of PA is 98% smaller than that of Ph in electrochemical reaction and is further decreased by 75% under US, so that it is difficult for PA to adsorb on electrode surface in US-EC process, in which PA can only be degraded by indirect oxidation. Oxidation pathway is changed because US converts electrochemical reaction from mass transport control to adsorption control.

US can enhance electrochemical oxidation efficiency on electrode surface remarkably. This enhancement depends on the positive or negative effect of US on reaction amount on the electrode surface. In EC process, the two pollutants are degraded simultaneously by direct oxidation and indirect oxidation, and AE of Ph is higher. Though the mass transport of two pollutants is improved under US and no difference exists, the effect on reaction amount of Ph is positive while that of PA is negative in US-EC process. Therefore, AE of Ph and PA is decreased by 74 and 69%, respectively. This difference results from the fact that US can promote indirect oxidation of PA, but its direct oxidation almost disappears; while both direct and indirect oxidation processes can be promoted by US for Ph. It is the difference in oxidation pathway

that makes the enhancement on Ph more obvious, and causes more decreasing of EC oxidation energy consumption.

#### 4. Conclusions

US can largely increase EC degradation efficiency and decrease EC energy consumption for both pollutants. The enhancement of Ph is more effective because of the influences on the electrochemical oxidation process.

US can obviously accelerate the mass transport process from bulk to electrode surface, and there is no difference in mass transport process between Ph and PA in US-EC process. The reaction amount of Ph on BDD surface is quite large, which is decreased by US, with desorption of polymer intermediates promoted, so US has positive effect on EC oxidation of Ph. For PA, the reaction amount is quite little. US makes it even less, which has negative effect on EC oxidation. In EC reaction process, both direct and indirect oxidation processes are promoted by US for Ph. For PA, indirect oxidation is promoted with no direct oxidation. EC oxidation energy consumption for Ph is decreased more than that of PA for the three reasons above.

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