

# Determination of reaction rate constants for phenol oxidation using SnO<sub>2</sub>/Ti anodes coupled with activated carbon adsorption in the presence of TiO<sub>2</sub> as catalyst

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## ABSTRACT

Series of experiments for phenol degradation with assistance of TiO<sub>2</sub> catalyst at pH of 6.5 and temperature of 25°C were conducted using a lab-scale electrochemical reactor constructed in our laboratory. According to the results, at the presence of the TiO<sub>2</sub> catalyst the removal of phenol was increased and first-order kinetics could describe the evolution of phenol concentration. For inspecting the relationship between rate constants and dosage of TiO<sub>2</sub>, two possible kinetics were proposed in this study. Contrasted to the abundant experimental data, a reasonable kinetics was obtained for the estimation of phenol concentration effluent during continuous flow of raw wastewater, especially when the TiO<sub>2</sub> dosage was less than 0.5 g L<sup>-1</sup>. The model obtained from these experiments could be employed for the calculation of rate constants at different TiO<sub>2</sub> dosage and the necessary dosage of catalyst when a discharge standard was designed.

**Key words** | activated carbon adsorption, electrochemical oxidation, phenol, rate constant, titanium dioxide (TiO<sub>2</sub>)

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## INTRODUCTION

It is widely considered that electrochemical oxidation coupled with adsorption by activated carbon (AC) is a relatively straightforward way for reduction of aromatic compounds in aqueous solution, especially for both phenol and its derivatives due to the generation of hydroxyl radicals (Torres *et al.* 2003; Siné & Comminellis 2005). This kind of process is characterized by both higher space-time yields and lower operating cost because of the huge specific areas of electrodes composed by planar anodes and packed fillings (Lipp & Pletcher 1997). Hence, the designed oxidation of organic matters would occur both at the surface of anodes and bipolar/monopolar AC particles. However, lacking of the effective kinetics related to the accurate design and operation of this kind of reactor for the degradation of organics restricts the widely transfer of the technology. Among various technical problems, the estimation of energy consumption and reaction time, which determines the volume of the electrochemical reactor, are far superior to any other studies during the industrial applications. In a previous publication, we proposed a mathematical model that permits to predict the power

consumption via current efficiency and equilibrium constant for phenol oxidation on SnO<sub>2</sub>/Ti anodes and there is a good agreement between theoretical data and experimental results when operated under different residence time and applied current density (Wang *et al.* 2007). On the other hand, the greater capital investments of equipment and electrodes depend on the effective volume of the reactor, which is strongly controlled by the reaction time. Therefore, determination and increase of the overall kinetic rate by some special ways, such as employment of proper catalyst are very important. In practice, additional generation of hydroxyl radicals has been recognised as very effective in oxidizing hazardous organic compounds. Of kinds of the catalysts, a semiconducting material, titanium dioxide (TiO<sub>2</sub>), is widely employed in photocatalytic and photoelectrochemical oxidation of organic substances because its bandgap corresponds to the generation of electron/hole pairs resulting in production of hydroxyl radicals (Giménez *et al.* 1997; Chen *et al.* 2002; Angela-Guiovan & Cesar 2004). In addition, the organics also could be absorbed by TiO<sub>2</sub> (Zhang *et al.* 2008, 2009) for further

oxidation so as to decrease the residence time of wastewater. Now that oxidation could take place at the surface of AC, the enhancement of degradation rate might be achieved when using  $\text{TiO}_2$  as catalyst or adsorbent, resulting in the reduction of reaction time. To our knowledge, the employment of  $\text{TiO}_2$  particles as catalyst in electrochemical oxidation coupled with AC adsorption hasn't been reported in the past literatures. This study attempts to investigate the relationship between electrochemical oxidation, AC adsorption and  $\text{TiO}_2$  catalysis. At the same time, empirical models were proposed to describe the intrinsic mechanisms of the combined process.

The main goals of this paper imply the following steps: confirmation of the reaction order during electrochemical oxidation of phenol; derivation of relations between the rate constants and the dosage of  $\text{TiO}_2$ ; evaluation of the kinetics by abundant experimental data with the presence and absence of the catalyst from the designed lab-scale experiments.

## EXPERIMENTAL

Synthetic solutions composed of analytically pure phenol (Merck, 99.5% pure) and deionized water were used for the performance of these experiments.  $\text{SnO}_2/\text{Ti}$  material and stainless steel having an area of  $0.04 \text{ m}^2$  ( $20 \text{ cm} \times 20 \text{ cm}$ ) employed as anodes and cathodes, respectively, were manufactured by Flag Corporation, China. The electrodes were fixed in the rectangular electrode chamber with an inter-electrode distance of 50 mm and the electrode gaps were filled with AC.  $\text{TiO}_2$  (Degussa P25) suspension and wastewater were injected into the reactor by peristaltic pumps, according to the flow rate calculated from working volume and residence time. More details about the equipment and characteristics of AC used in the electrolysis are given in our previous work (Wang *et al.* 2008).

In practice, it may be necessary to reclaim and reuse the  $\text{TiO}_2$  catalyst so as to decrease the operation cost of the process. In these experiments, the  $\text{TiO}_2$  suspension wasn't separated from the treated wastewater.

These experiments were carried out with initial phenol concentration of  $1,603.5 \text{ mg L}^{-1}$  under pH value of 6.5 at constant temperature of  $25^\circ\text{C}$ . Phenol concentration measured by the method based on spectrophotometric analysis at 510 nm of the developed color resulting from the reaction of phenol 4-aminoantipyrine according to *Standard Methods* (APHA/AWWA 1998) was used to determine the rate constants by the plots of  $\ln(C_t/C_0)$  vs reaction time.

## RESULTS AND DISCUSSION

### Determination of phenol reaction order at the presence of $\text{TiO}_2$

As shown in Figure 1, the concentrations of phenol all decrease with the increasing of reaction time at applied current of 40 A, but to different degrees. For example, phenol removal efficiency was obtained only by the value of 69.9% without the application of  $\text{TiO}_2$  at reaction time of 90 min, compared to the removal rate of 94.1% when employing  $\text{TiO}_2$  as catalyst with dosage of  $0.6 \text{ g L}^{-1}$ , which indicated that  $\text{TiO}_2$ , usually used as photocatalyst, also could effectively enhance the electrochemical oxidation of phenol.

Previous literature proposed that the degradation of phenol during electrolysis could be described by first-order kinetics (Alnaizy & Akgerman 2000; Ince & Apikyan 2000; Polcaro *et al.* 2000). In our experiments, the decrease of phenol concentration during the electrochemical oxidation was well fit by first-order reaction. In addition, the first-order kinetics was also applicable at the presence of  $\text{TiO}_2$  employed as catalyst for the electrocatalytic process. The rate constant of electrocatalysis was 2.3 times than that of electrochemical process with the value of  $0.0136$  and  $0.0314 \text{ min}^{-1}$ , respectively. The experimental result testified the existence of the synergetic effect of  $\text{TiO}_2$  as catalyst to the electrochemical oxidation of phenol. The enhancement of phenol removal with  $\text{TiO}_2$  may be due to the two factors. Firstly, the catalyst could be absorbed by AC, leading to the retardation of oxygen evolution effectively because of its high overpotential. Therefore, the phenol oxidation could be operated with higher current efficiency. Secondly, the application of  $\text{TiO}_2$  could generate much more electrons and holes in

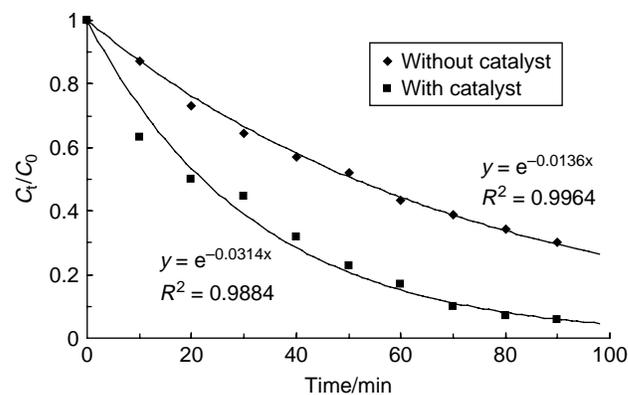


Figure 1 | Comparison of phenol oxidation at the presence and absence of  $\text{TiO}_2$  at current of 40 A,  $\text{TiO}_2$  dosage of  $0.6 \text{ g L}^{-1}$ , initial phenol concentration of  $1603.5 \text{ mg L}^{-1}$ , pH 6.5 and temperature of  $25^\circ\text{C}$ .

electric field, which are favorable for the phenol degradation (An *et al.* 2004). In addition, these electrons are easily captured by surface of electrodes and bipolar/monopolar particles, decreasing the possibility of their recombination. These mechanisms based on previous reports could explain the phenomena observed in these experiments, but a further investigation still should be conducted to have a clear understanding of the role played by TiO<sub>2</sub> in electrochemical process.

### Reaction kinetics

In a packed bed electrode reactor, without a turbulence promoter, the reaction is always in mass transfer controlled process. When the solutions with higher concentration are injected in the system, perhaps the adsorption is much more rapid than electrochemical oxidation; at the same time, desorption of phenol from internal of AC to solutions will soon commence when the concentration of solutions decreases to a considerably low level (Polcaro *et al.* 2000; Fockedeey & Van Lierde 2002). Once the velocities of adsorption, desorption and electrochemical oxidation are equal, the dynamic equilibrium would be achieved, however, this equality would be broken if TiO<sub>2</sub> catalyst was employed, causing the decrease of phenol concentration in solutions. From the experiments above, the synergetic influence of TiO<sub>2</sub> on phenol degradation was indeed confirmed. Therefore, based on the first-order kinetics for phenol oxidation, the description of the evolution of phenol concentration could be expressed by:

$$[\text{Ph}]_t = [\text{Ph}]_0 \exp(-kt) \quad (1)$$

where  $[\text{Ph}]_0$  and  $[\text{Ph}]_t$  are the phenol concentration of influent and effluent ( $\text{mg L}^{-1}$ ),  $k$  is the rate constant ( $\text{min}^{-1}$ ) and  $t$  is reaction time (min).

The rate constant is determined by applied voltage, operating current, temperature, materials of anodes and kinds of pollutants, etc. Furthermore, the application of catalyst and compressed air also could increase the values of the rate constants (Kesselman *et al.* 1997; An *et al.* 2004). The mechanism for the electrochemical oxidation of phenol assisted with TiO<sub>2</sub> and air was proposed in our previous paper (Wang *et al.* 2008), but an accurate fit between experimental data and kinetics was difficult to achieve. In this study, the effect of catalyst on the rate constant was supposed as following:

$$k = k_0 + k_1 X^\alpha \quad (2)$$

or

$$k = k_0 \exp(k_2 X^\beta) \quad (3)$$

where  $k$  and  $k_0$  are the rate constants at the presence and absence of TiO<sub>2</sub> catalyst,  $X$  is the dosage of TiO<sub>2</sub> ( $\text{g L}^{-1}$ ),  $k_1$ ,  $k_2$ ,  $\alpha$  and  $\beta$  are constants in the electrocatalytic process.

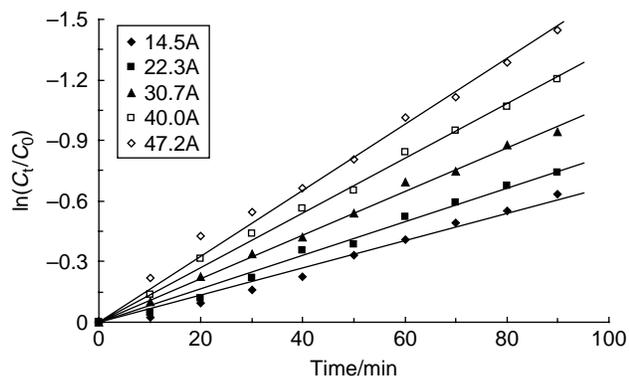
From Equations (2) and (3), without the synergetic influence of catalyst, i.e.  $X = 0$ , the global reaction constant could be described by:

$$k = k_0 \quad (4)$$

The plots of  $[\text{Ph}]_t/[\text{Ph}]_0$  vs  $t$  by experimental data without the assistant of catalyst could be used to obtain  $k_0$ , which was only determined by electrochemical conditions and configurations of reactor or anodes. The constants of  $k_1$ ,  $k_2$ ,  $\alpha$  and  $\beta$  were easily obtained from other experiments under different dosage of TiO<sub>2</sub>, by description of the proposed first-order kinetics. Meanwhile, the constants of  $k_1$  and  $\alpha$  could be acquired by the plots of  $(k - k_0)$  vs  $X$ ; at the same time, the values of  $k_2$  and  $\beta$  could be obtained by the relations of  $\ln(k/k_0)$  vs  $X$ , under a constant operating electrochemical condition.

### The effect of current on phenol oxidation at the absence of TiO<sub>2</sub>

For inquisition of  $k_0$  related to applied current ranging from 14.5 to 47.2 A, these experiments were performed in the absence of TiO<sub>2</sub>. From Figure 2, we could observe that the greater current corresponds to much more removal of phenol under constant reaction time, that is to say, the higher the current, the larger the rate constant. For example, when a current of 14.5 A was applied, the rate constant was only  $0.0068 \text{ min}^{-1}$ , while it was increased up to  $0.0164 \text{ min}^{-1}$  under the applied current of 47.2 A. The rate constant of the latter was about 2.4 times higher than that of the former. From this point of view, a higher applied current was beneficial for increasing phenol oxidation rate, which could result in reducing the working volume of reactor under a constant discharge standard. However, the larger current would increase the oxygen evolution on anodes, despite of the employment of DSAs, leading to the decrease of current yields. During reactions, current was determined by applied voltage as described by Ohm's law; increasing current necessarily caused more energy consumption when cell voltage was much higher than the overpotential of electrode materials, accelerating the main side reaction in aqueous media, water oxidation. The results obtained from these

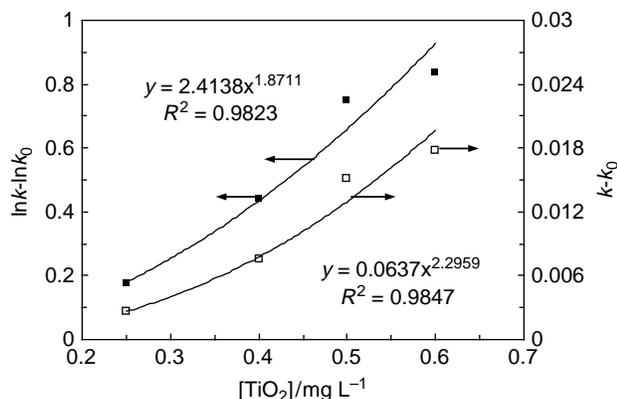


**Figure 2** | Dependence of phenol oxidation rate constants on applied current at initial phenol concentration of  $1,603.5 \text{ mg L}^{-1}$ , pH 6.5 and temperature of  $25^\circ\text{C}$ .

experiments were consistent with the previous works with regard to factors influencing the kinetics of the packed bed electrode reactor (Fockedeý & Van Lierde 2002; Xiong & Karlsson 2002).

### Examination of suggested models

Constant parameters were achieved by using different operating current and  $\text{TiO}_2$  dosage. Furthermore,  $k_1$ ,  $\alpha$ ,  $k_2$  and  $\beta$  could be obtained by the experimental data under a constant current with designed  $\text{TiO}_2$  dosage. For example, Figure 3 depicts results described by Equations (2) and (3) at constant current of 40 A. Seen from this figure,  $k_1$  and  $\alpha$ ,  $k_2$  and  $\beta$  were 0.0637 and 2.2959, 2.4138 and 1.8711 with perfect regression coefficient of 0.9847 and 0.9823, respectively, which indicated that perhaps Equations (2) and (3) proposed in this study all could provide an accurate estimation of rate constants. By substituting these values to Equations (2) and (3), a comprehensive form of  $k$  was rewritten as follows:



**Figure 3** | Obtainment of the values of  $k_1$ ,  $k_2$ ,  $\alpha$  and  $\beta$  with various  $\text{TiO}_2$  dosage at operating current of 40 A, initial phenol concentration of  $1,603.5 \text{ mg L}^{-1}$ , pH 6.5 and temperature of  $25^\circ\text{C}$ .

$$k = k_0 + 0.0637X^{2.2959} \quad (5)$$

$$k = k_0 \exp(2.4138X^{1.8711}) \quad (6)$$

The rate constants obtained from series of experiments conducted under a constant applied current with various  $\text{TiO}_2$  dosage were listed in Table 1. The experimental reaction constants ( $k_{\text{exp}}$ ) were achieved through the regression of real values during electrocatalytic process by first-order kinetics. Calculated rate constants using Equations (5) and (6) were also presented in this table ( $k^{\text{b}}$  and  $k^{\text{c}}$ ). Comparison between the predicted values and experimental data showed that the two equations all could describe the synergetic effect of  $\text{TiO}_2$  on rate constants during electrochemical oxidation of phenol, but the data calculated by equation (6) were more precise (with higher regression coefficient) than those of Equation (5), especially when the applied current was less than 40 A. The results revealed that Equation (6) was more efficient to obtain an estimation of rate constants using this designed reactor, although calculated rate constants were slightly smaller than the experimental data when the  $\text{TiO}_2$  dosage was less than

**Table 1** | Comparison of experimental data and calculated results by the two proposed kinetics

<i>I</i> (A)	<i>U</i> (V)	[TiO <sub>2</sub> ] (g L <sup>-1</sup> )	<i>k</i> <sub>exp</sub>	<i>k</i> <sup>b</sup>	<i>k</i> (min <sup>-1</sup> )		
					<i>R</i> <sub>1</sub> <sup>2</sup>	<i>k</i> <sup>c</sup>	<i>R</i> <sub>2</sub> <sup>2</sup>
14.5	8	0.25	0.0085	0.0094	0.9952	0.0081	0.9954
		0.40	0.0116	0.0146	0.9900	0.0105	0.9941
		0.50	0.0137	0.0198	0.9844	0.0132	0.9955
		0.60	0.0170	0.0265	0.9851	0.0172	0.9974
22.3	12	0.25	0.0102	0.0109	0.9958	0.0099	0.9962
		0.40	0.0129	0.0161	0.9881	0.0128	0.9944
		0.50	0.0171	0.0213	0.9799	0.0161	0.9929
		0.60	0.0222	0.0280	0.9717	0.0210	0.9914
30.7	16	0.25	0.0130	0.0134	0.9981	0.0129	0.9982
		0.40	0.0178	0.0186	0.9983	0.0167	0.9992
		0.50	0.0216	0.0238	0.9946	0.0209	0.9976
		0.60	0.0278	0.0305	0.9931	0.0273	0.9974
40	20	0.25	0.0162	0.0162	0.9939	0.0163	0.9939
		0.40	0.0211	0.0214	0.9936	0.0210	0.9933
		0.50	0.0287	0.0266	0.9909	0.0263	0.9909
		0.60	0.0314	0.0333	0.9822	0.0344	0.9814
47.2	25	0.25	0.0199	0.0190	0.9977	0.0196	0.9981
		0.40	0.0254	0.0242	0.9993	0.0253	0.9993
		0.50	0.0315	0.0294	0.9982	0.0317	0.9973
		0.60	0.0381	0.0361	0.9993	0.0415	0.9957

$k_{\text{exp}}$ : regressed from experimental data;  $k^{\text{b}}$  and  $k^{\text{c}}$  calculated by Equations (5) and (6), respectively.

0.5 g L<sup>-1</sup> under each operation current, while those were higher than real values under the dosage of 0.6 g L<sup>-1</sup> with the current of 40 and 47.2 A. From this table, another phenomenon was observed that the values predicted by Equation (6) were lower than the experimental results at higher TiO<sub>2</sub> dosage. Perhaps, this was due to the blockage of micropores of AC by TiO<sub>2</sub> particles, which decreased the expected bipolar/monopolar area, leading to the reduction of  $k_0$ .

Substituting Equation (6) into Equation (1), an overall kinetic model for phenol electrocatalytic oxidation was obtained:

$$[\text{Ph}]_t = [\text{Ph}]_0 \exp[-k_0 \exp(2.4138X^{1.8711})t] \quad (7)$$

Using Equation (7), when the rate constant  $k_0$  was achieved through designed experiments under an applied current, phenol concentration effluent could be calculated by the dosage of TiO<sub>2</sub> at a given reaction time. On the other hand, the dosage of TiO<sub>2</sub> also could be obtained when discharge standard was presetted.

## CONCLUSIONS

Electrocatalytic oxidation of phenol on SnO<sub>2</sub>/Ti anodes using packed bed reactor assisted with TiO<sub>2</sub> was examined in detail. First-order kinetics could be used to describe the evolution of phenol oxidation in the presence of catalyst, TiO<sub>2</sub>. Contrasted to the phenol degradation in the absence of catalyst under the same reaction time, the reduction of phenol concentration was increased during electrocatalysis. By designed experiments, a model was proposed to estimate the phenol concentration effluent:  $[\text{Ph}]_t = [\text{Ph}]_0 \exp[-k_0 \exp(2.4138X^{1.8711})t]$ . The results calculated from the equation are in good agreement with experimental data. Furthermore, the rate constants and the required dosage of TiO<sub>2</sub> for phenol oxidation could be easily predicted at a given electrochemical condition.

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