



## Treatment of phenol wastewater by microwave-induced $\text{ClO}_2\text{-CuO}_x/\text{Al}_2\text{O}_3$ catalytic oxidation process

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### Abstract

The catalyst of  $\text{CuO}_x/\text{Al}_2\text{O}_3$  was prepared by the dipping-sedimentation method using  $\gamma\text{-Al}_2\text{O}_3$  as a supporter.  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  were loaded on the surface of  $\text{Al}_2\text{O}_3$ , characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). In the presence of  $\text{CuO}_x/\text{Al}_2\text{O}_3$ , the microwave-induced chlorine dioxide ( $\text{ClO}_2$ ) catalytic oxidation process was conducted for the treatment of synthetic wastewater containing 100 mg/L phenol. The factors influencing phenol removal were investigated and the results showed that microwave-induced  $\text{ClO}_2\text{-CuO}_x/\text{Al}_2\text{O}_3$  process could effectively degrade contaminants in a short reaction time with a low oxidant dosage, extensive pH range. Under a given condition ( $\text{ClO}_2$  concentration 80 mg/L, microwave power 50 W, contact time 5 min, catalyst dosage 50 g/L, pH 9), phenol removal percentage approached 92.24%, corresponding to 79.13% of  $\text{COD}_{\text{Cr}}$  removal. The removal of phenol by microwave-induced  $\text{ClO}_2\text{-CuO}_x/\text{Al}_2\text{O}_3$  catalytic oxidation process was a complicated non-homogeneous solid/water reaction, which fitted pseudo-first-order by kinetics. Compared with traditional  $\text{ClO}_2$  oxidation,  $\text{ClO}_2$  catalytic oxidation and microwave-induced  $\text{ClO}_2$  oxidation, microwave-induced  $\text{ClO}_2$  catalytic oxidation system could significantly enhance the degradation efficiency. It provides an effective technology for the removal of phenol wastewater.

**Key words:** microwave-induced oxidation;  $\text{ClO}_2$ ;  $\text{CuO}_x/\text{Al}_2\text{O}_3$ ; phenol wastewater

### Introduction

Phenol and phenolic compounds are a group of organic pollutants that often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Because of their toxicity and poor biodegradability (Zahangir *et al.*, 2006), phenolic wastewaters must be specially treated before disposing off. Various treatment techniques have been applied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation (Liou *et al.*, 2005), solvent extraction (Yang *et al.*, 2006), membrane techniques (Wojciech *et al.*, 2004), adsorption (Ahmaruzzaman and Sharma, 2005), photodegradation (Will *et al.*, 2004), coagulation flocculation (Tomaszewska *et al.*, 2004), biological process (Tziotzios *et al.*, 2005) and so on. However, such technologies usually involve complicated procedures and are not economically viable.

The catalytic oxidation process is a well-established technique to decompose toxic and/or non-biodegradable organic compounds in wastewaters (Luck, 1999), which is able to oxidize organic pollutants into carbon dioxide or into products that can be eliminated by biological

treatment. Ozone, oxygen, hydrogen peroxide or a combination of them are frequently used as oxidant. But there are few reports on the use of chlorine dioxide ( $\text{ClO}_2$ ) in the catalytic oxidization processes. In fact,  $\text{ClO}_2$  is also an effective oxidant. It is a gas which, in aqueous solution, is used in water's purification and as a chemical bleaching reagent. Recently, with the development of catalytic oxidation,  $\text{ClO}_2$  has been used for the treatment of organic pollutants. Jin *et al.* (2003) have studied the catalytic oxidation of wastewaters containing phenol, *p*-chlorophenol and *p*-nitrophenol, respectively. The oxidant they used was  $\text{ClO}_2$  and the catalyst was self-made. The results showed that this method could significantly make  $\text{COD}_{\text{Cr}}$  decrease, with the removal percentage up to more than 90%.

However, the traditional  $\text{ClO}_2$  catalytic oxidation process has not been largely implemented for wastewater treatment because of the severe experimental conditions (such as the limited range of pH), longer reaction time resulting in higher economical costs, and lack of suitable catalysts, which are more active and durable under the experimental conditions. So, it is focused on by many scholars, how to shorten the reaction time, improve the adaptability of the catalytic oxidation process, and find the high durability/low cost catalysts.

Microwave induced catalytic process offers a potential

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solution to these problems. In recent years, some research progresses in microwave chemistry have presented the feasibility to apply microwave in pollution control (Wang, 2003; Zhang *et al.*, 2005). It was found that the reaction time could be shortened and the yields or the purities of the product could increase in some chemical reactions when microwave radiated simultaneously to them. The use of microwave irradiation in catalytic reactions, including decomposition of volatile organic compounds (VOC) (Hideaki *et al.*, 2004) and non-biodegradable organics in wastewater (Zhang *et al.*, 2004, 2005; Hong *et al.*, 2005), has given some remarkable results.

The microwave-induced  $\text{ClO}_2$  catalytic oxidation is a novel method for the treatment of non-biodegradable wastewater, and there are few literature reporting the process. In this study,  $\text{CuO}_x/\text{Al}_2\text{O}_3$  was used as catalyst in the microwave-induced  $\text{ClO}_2$  catalytic oxidation process to treat synthetic wastewater containing phenol under optimized reaction conditions. Comparative studies on the different  $\text{ClO}_2$  oxidation process have been carried out. Then, the reaction kinetic equation of microwave-induced  $\text{ClO}_2\text{-CuO}_x/\text{Al}_2\text{O}_3$  catalytic oxidation process has been put forward.

## 1 Experimental

### 1.1 Materials

All the reagents used were analytical-grade. The stock  $\text{ClO}_2$  solution was prepared by mixing a vitriol solution and a sodium chlorite solution. The stock  $\text{ClO}_2$  solution was stored in dark at  $4^\circ\text{C}$  and was standardized daily.

The catalyst of  $\text{CuO}_x/\text{Al}_2\text{O}_3$  was prepared according to the method by Wang *et al.* (2006), immersing certain amounts of  $\gamma\text{-Al}_2\text{O}_3$  into  $\text{CuCl}_2$  aqueous solution, followed by deposit of  $\text{Cu}^{2+}$  with the help of precipitator, then dried at  $110^\circ\text{C}$  and calcined at  $450^\circ\text{C}$  for some time. The formed  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  were loaded on the surface of  $\gamma\text{-Al}_2\text{O}_3$ . The catalytic characterization was conducted using X-ray diffraction (XRD) (D/max-rB, Rigaku, Japan) and X-ray photoelectron spectroscopy (XPS) (PHI 5700).

### 1.2 Methods

The pulse of the microwave oven was continuous and the power was adjustable, different from the reports in literature. At the beginning of each test run, 100 ml of synthetic wastewater containing 100 mg/L phenol was placed in a sealed reactor. Amounts of the catalysts and stock  $\text{ClO}_2$  solution were added. The reactor was shaken for sufficient mixture of the stock  $\text{ClO}_2$  solution into wastewater, subsequently, loaded in a reconstructive commercial microwave oven operating at 2450 MHz with the continuous power levels (50–750 W). The run time was recorded by stopwatch. Upon the arrival of the reaction time, the sealed reactor was taken out and the reagent of sodium thiosulfate ( $\text{Na}_2\text{SO}_3$ ) was added to dechlorinate  $\text{ClO}_2$  residuals.

The temperatures of the wastewater were measured using a thermocouple inserted into the wastewater. The pH

values were determined by a pH-3C pH meter. The concentrations of  $\text{ClO}_2$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$  and  $\text{Cl}^-$  in the stabilized chlorine dioxide solution were measured by the method of continuous iodimetry and precipitation titration, respectively. The suspensions were analyzed for their phenol concentrations using a 721-type ultraviolet-visible spectrophotometer by means of 4-AAP spectrophotometric method. For all the tests, blank experiments were carried out with the same experimental procedures to check the extent of phenol sorption by the glass flasks, which must be deducted. In order to check the reproducibility of the results, random tests were done for different experimental conditions.

## 2 Results and discussion

### 2.1 Factors influencing the phenol removal

#### 2.1.1 $\text{ClO}_2$ concentration

Figure 1 demonstrates the effect of  $\text{ClO}_2$  concentration on the phenol removal. The results clearly showed that, as one kind of oxidants,  $\text{ClO}_2$  could oxidize phenol with and without catalyst. But with catalyst, the removal of phenol was much higher than that without catalyst. The removal efficiency increased nonlinearly with increasing  $\text{ClO}_2$  concentration. In the presence of  $\text{ClO}_2$ , firstly, the degradation rate increased with increasing  $\text{ClO}_2$  concentration rapidly. However, with the continuous increase of  $\text{ClO}_2$  concentration, especially beyond 80 mg/L, the phenol removal efficiency increased slightly. In the microwave-induced catalytic oxidation process, when the concentration of the  $\text{ClO}_2$  solution was 100 mg/L, the removal rate of phenol was 91.66%. Compared with the microwave-induced oxidation process with catalyst, if the process without catalyst reached the same efficiency, the expense of the  $\text{ClO}_2$  solution would be more than twice.

The wastewater in microwave-induced  $\text{ClO}_2$  catalytic oxidation process will be heated under microwave irradiation, so the temperature of treated water must have a rise. In our test, the temperature of treated water would reach  $47^\circ\text{C}$  under the operation conditions, so the volatility of phenol in this process should be investigated. It can be seen in Fig.1, when the concentration of the  $\text{ClO}_2$  solution was 0 mg/L in the microwave-induced  $\text{ClO}_2$  oxidation process

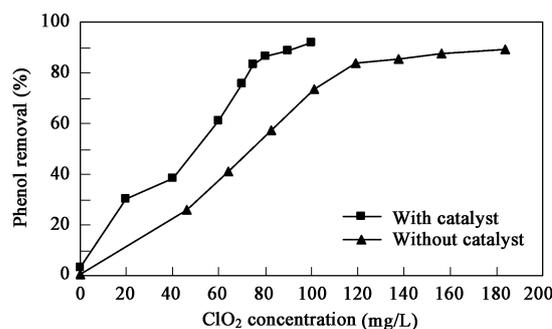


Fig. 1 Effect of  $\text{ClO}_2$  concentration on phenol removal.  $C_{\text{phenol}} = 100$  mg/L; microwave power = 50 W; time = 5 min; catalyst dosage = 50 g/L; pH = 5.6.

without catalyst, the phenol removal efficiency is only 0.78% even though the temperature of treated wastewater is 47°C, it indicates the volatilization of phenol in our test can be ignored. The corresponding point of 0 mg/L  $\text{ClO}_2$  in the microwave-induced  $\text{ClO}_2$  catalytic oxidation with  $\text{CuO}_n\text{-La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  also verified that as a supporter of catalyst,  $\gamma\text{-Al}_2\text{O}_3$  could absorb phenol, whereas the ability was very weak, the absorption of phenol was 2.57%. Therefore, the phenol removal efficiency in these tests is referential.

### 2.1.2 Dosage of catalyst

The catalyst played an important role in the microwave-induced  $\text{ClO}_2$  catalytic oxidation process. The effect of catalyst dosage on phenol removal was investigated by addition of different amount of catalyst into 100 ml of phenol wastewater, and the results are shown in Fig.2. As catalyst dosage increasing, an increase in the phenol removal was observed. When the addition of catalyst reached 50 g/L, the removal percentage of phenol could come up to over 90%. Nevertheless, the final removal percentage was not changed, showing that an excess of catalyst could not improve the efficiency of microwave-induced  $\text{ClO}_2$  catalyst oxidation.

### 2.1.3 pH effect

The pH value is one of the most important factors in the microwave-induced  $\text{ClO}_2$  catalytic oxidation process. The results are presented in Fig.3, it shows that the phenol removal depended strongly on the pH. With the catalyst, the optimum system pH value ranged from 3 to 9, it was much wider than without catalyst, which indicated

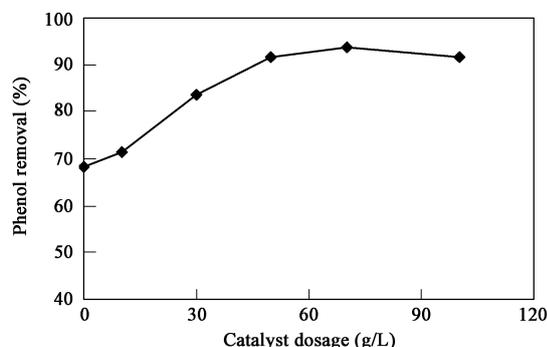


Fig. 2 Effect of the catalyst dosage on phenol removal.  $C_{\text{phenol}} = 100$  mg/L;  $C_{\text{ClO}_2} = 80$  mg/L; microwave power = 500 W; time = 5 min; pH = 5.6.

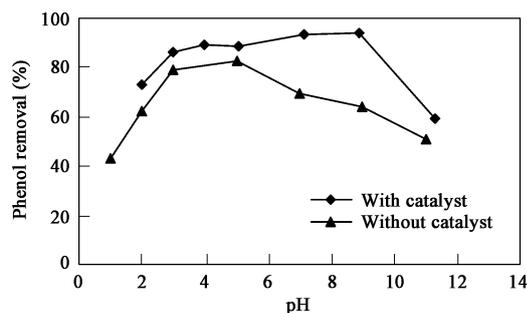


Fig. 3 Effect of the pH value on phenol removal.  $C_{\text{phenol}} = 100$  mg/L;  $C_{\text{ClO}_2} = 80$  mg/L; microwave power = 50 W; catalyst dosage = 50 g/L; time = 5 min.

that the catalyst could obviously improve not only the removal percentage of phenol but also the ability of  $\text{ClO}_2$  to adapt the change of system pH value. The appropriate pH range of traditional  $\text{ClO}_2$  catalytic oxidation process reported in the literature was lower than 7 (Xu, 2004), but in the microwave-induced catalytic oxidation process, the optimum experimental pH was 9, which indicated that catalyst associated with microwave could improve the system adaptability of pH of wastewater, suggesting this process had advantages for the engineering application.

### 2.1.4 Wastewater temperature

Figure 4 demonstrates the effect of the wastewater temperature on phenol removal. As expected, the temperature of wastewater was one of factors. The removal percentage of phenol changed with temperatures and microwave powers. At the beginning, the removal percentage increased obviously by increasing temperatures. However, the final removal percentage even decreased by increasing the system temperatures. So, changes in the phenol removal were not linearly related with temperatures in the phenol microwave-induced  $\text{ClO}_2$  catalytic oxidation process. At the same temperature, the relationships between the phenol removal and microwave powers were different, which showed that the microwave in the process acted as an induced factor.

### 2.1.5 Microwave power and irradiation time

In our study (Fig.5), it was found that the introduction of microwave irradiation could obviously shorten the reaction time, from 90 to 5 min, and the phenol could be effectively eliminated, which would greatly reduce the economical costs of the catalytic oxidation process.

Figure 5 also shows that the removal percentage of the phenol irregularly enhanced with the microwave power increasing. However, under the same power, the removal percentage increased by prolonging the run time at first, then would slowly fall off. The potential reason was that the reaction between the  $\text{ClO}_2$  and phenol was an exothermic reaction. When the power was higher or the runtime was longer, the restraining effect of high temperature was stronger than the microwave-induced effect that induced the low phenol removal percentage.

### 2.1.6 Initial phenol concentration

The effect of initial phenol concentration on its degradation is illustrated in Fig.6 with varying phenol concen-

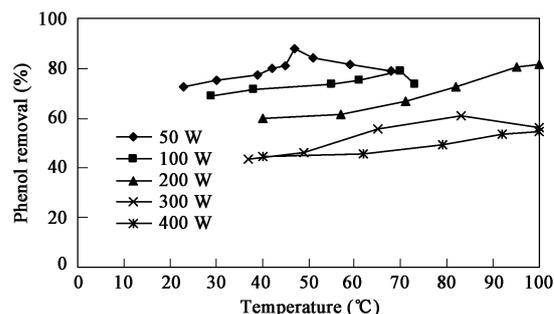


Fig. 4 Effect of wastewater temperature on phenol removal.  $C_{\text{phenol}} = 100$  mg/L;  $C_{\text{ClO}_2} = 80$  mg/L; catalyst dosage = 50 g/L; pH=5.6.

tration from 55 to 225 mg/L. The results showed that the degradation rate of phenol decreased with increasing initial phenol concentration. This could be attributed to the relative reduction of  $\text{ClO}_2$ /phenol molar ratio as phenol concentration increased. Thus, the effect of phenol initial concentration on its degradation was similar to that of  $\text{ClO}_2$  dosage, which was stated above.

## 2.2 Comparative study on the different treatment process

The mechanism of the  $\text{ClO}_2$  catalytic oxidation has not been very clarified. It was generally reported that the oxygenous group over the catalyst can initiate the  $\text{ClO}_2$  to be changed into radicals, such as  $\text{OH}\cdot$ . Microwave irradiation might expedite the removal percentage of  $\text{ClO}_2$  and could be cooperative with catalyst to initiate the more formation of free radicals in the presence of  $\text{ClO}_2$ .

To check the microwave-induced effect, the phenol removal in different treatment process was compared. The final temperature was  $48^\circ\text{C}$  and the reaction time of traditional water bath was longer than microwave-induced

process. The results are shown in Table 1 and Fig.7.

Table 1 and Fig.7 both indicate that microwave can improve the efficiency of traditional process because of its induced function and calefaction. The catalyst also can enhance the efficiency because of its function of sorption and catalysis. Fig.7 shows the phenol removal efficiency of traditional catalytic oxidation process was lower than the microwave-induced oxidation process. However, if the microwave and catalyst were used together, the removal efficiency increased obviously, and the removal percentage was more than that of summation of the respective increase, which confirmed the hypothesis mentioned above that there would be functions of microwave induced.

## 2.3 Kinetic study on the process

The reactive mechanism between  $\text{ClO}_2$  and phenol has been reported in the literature (Huang, 2002), its oxidation process could be described as two stages. Rate equation of the reaction is:

$$-dC_{\text{phenol}}/dt = k_2 C_{\text{ClO}_2}^m \times C_{\text{phenol}}^n \quad (1)$$

For the kinetic measurement, initial concentration of  $\text{ClO}_2$  was chosen to be at least ten times that of phenol  $C_{\text{phenol}}$ , thus  $C_{\text{ClO}_2}$  could be taken as invariable during the reaction. Taking  $k_1 = k_2 C_{\text{ClO}_2}^m$ , so Eq. (1) is:

$$-dC_{\text{phenol}}/dt = k_1 C_{\text{phenol}}^n \quad (2)$$

The kinetics experiments of traditional  $\text{ClO}_2$  oxidation,  $\text{ClO}_2$  catalytic oxidation, microwave-induced  $\text{ClO}_2$  oxidation and microwave-induced  $\text{ClO}_2$  catalytic oxidation system were carried out, respectively. The results are shown in Fig.8, it indicates that traditional  $\text{ClO}_2$  oxidation was available for removing phenol in aqueous solution. However, the presence of microwave irradiation or catalyst

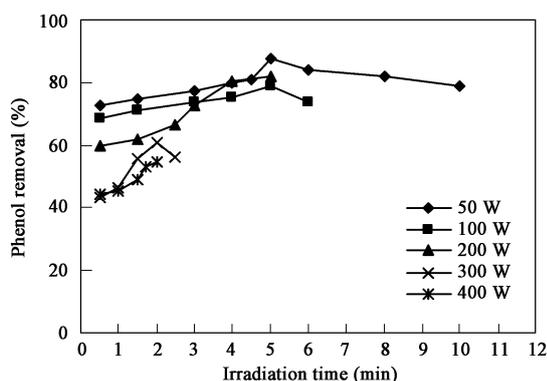


Fig. 5 Effect of microwave power and irradiation time on phenol removal.  $C_{\text{phenol}} = 100 \text{ mg/L}$ ;  $C_{\text{ClO}_2} = 80 \text{ mg/L}$ ; catalyst dosage =  $50 \text{ g/L}$ ;  $\text{pH} = 5.6$ .

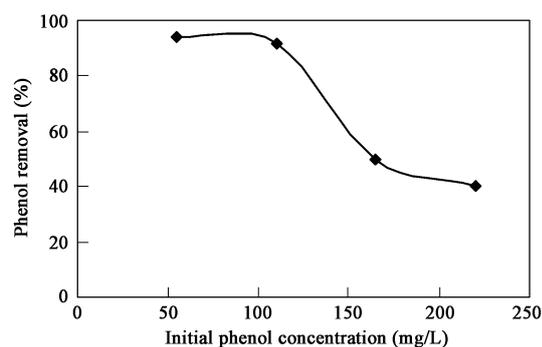


Fig. 6 Effect of initial phenol concentration on phenol removal.  $C_{\text{ClO}_2} = 80 \text{ mg/L}$ ; microwave power =  $50 \text{ W}$ ; catalyst dosage =  $50 \text{ g/L}$ ; time =  $5 \text{ min}$ ;  $\text{pH} = 5.6$ .

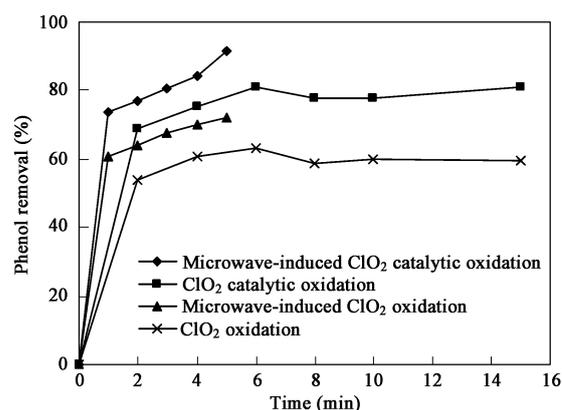


Fig. 7 Relationships between different treatment processes and phenol removal.  $C_{\text{phenol}} = 100 \text{ mg/L}$ ;  $C_{\text{ClO}_2} = 80 \text{ mg/L}$ ; microwave power =  $50 \text{ W}$ ; catalyst dosage =  $50 \text{ g/L}$ ; time =  $5 \text{ min}$ ; Temp.  $w = 320 \text{ K}$ ;  $\text{pH} = 5.6$ .

Table 1 Comparative results of the organic pollutant removal in different treatment processes

Treatment process	Residual COD (mg/L)	COD removal (%)	Phenol removal (%)
Traditional $\text{ClO}_2$ oxidation	102.8	55.11	59.39
Microwave-induced $\text{ClO}_2$ oxidation	85.3	62.75	68.34
Traditional $\text{ClO}_2$ catalytic oxidation	76.2	66.72	74.36
Microwave-induced $\text{ClO}_2$ catalytic oxidation	47.8	79.13	91.53

**Table 2 Degrading kinetic parameters of phenol with different processes**

Treatment process	Equation	$k_1$ ( $\text{min}^{-1}$ )	$R^2$
Traditional $\text{ClO}_2$ oxidation	$\ln(C/C_0) = 0.0406t$	0.0406	0.9837
Traditional $\text{ClO}_2$ catalytic oxidation	$\ln(C/C_0) = 0.0782t$	0.0782	0.9785
Microwave-induced $\text{ClO}_2$ oxidation	$\ln(C/C_0) = 0.0828t$	0.0828	0.9892
Microwave-induced $\text{ClO}_2$ catalytic oxidation	$\ln(C/C_0) = 0.1947t$	0.1947	0.9973

increased the degradation of phenol compared with traditional oxidation. Furthermore, as observed, microwave irradiation and catalyst could significantly improve the removal efficiency of phenol. It could be concluded that there existed synergetic effect between microwave irradiation and chlorine dioxide catalytic oxidation.

The experimental data were fitted with pseudo-first-order rate reactions, and the calculated kinetic parameters are presented in Table 2. Where  $k_1$  was the observed rate constant, and  $R^2$  was correlation coefficient.

Applying the pseudo-first-order rate reaction, the oxidation kinetics of phenol at different initial concentrations was also studied in the microwave-induced  $\text{ClO}_2$  catalytic oxidation process and the calculated kinetic parameters are listed in Table 3.

Obviously, the relationship between  $k_1$  and  $C_0$  is similarly linear and the degradation process fitted well to pseudo-first-order rate equation at different initial phenol concentrations. The initial phenol concentrations had influence on both of the rate constants and half-lives, the rate constants decreased and half-lives increased gradually as the  $C_0$  increased.

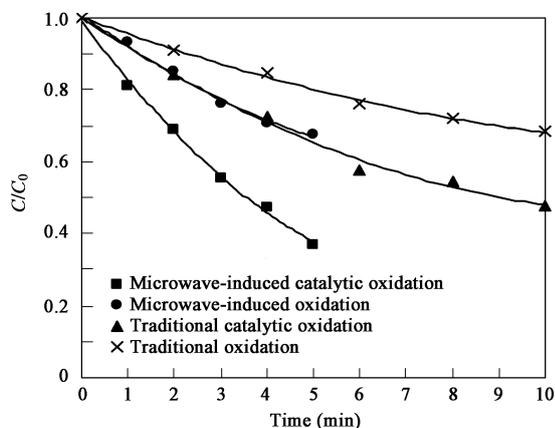


Fig. 8 Relative concentration  $C/C_0$  of phenol versus time as a function of different process.  $C_{\text{ClO}_2}^0 = 5 \text{ mmol/L}$ ;  $C_{\text{phenol}}^0 = 0.43 \text{ mmol/L}$ ; Temp. w = 320 K; pH = 4.0; microwave power = 50 W.

**Table 3 Parameters of pseudo-first-order kinetics at different initial phenol concentrations**

$C_0$ (mmol/L)	Rate equation	$k_1$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$R^2$
0.57	$\ln(C/C_0) = 0.1906t$	0.1906	3.6367	0.9894
0.43	$\ln(C/C_0) = 0.1947t$	0.1947	3.5601	0.9973
0.32	$\ln(C/C_0) = 0.2153t$	0.2153	3.2194	0.9132

### 3 Conclusions

The microwave-induced chlorine dioxide catalytic oxidation process was a novel technique for the treatment of

wastewater. When the phenol initial concentration was 100 mg/L, the phenol removal efficiency could reach 92.24%. The optimum experimental conditions were as follows: volume of phenol wastewater was 100 ml,  $\text{ClO}_2$  concentration was 80 mg/L, contact time was 5 min, microwave power was 50 W and the solution pH was in the range of 3–9.

The research on the mechanism showed that  $\text{CuO}_x/\text{Al}_2\text{O}_3$  could induce  $\text{ClO}_2$  to oxidize organic materials, and then the oxidized phenol was degraded under the irradiation of microwave. The research on kinetics suggested that the microwave induced  $\text{ClO}_2$ - $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalytic oxidation process followed that of a pseudo-first-order kinetic equation.

The improvement of traditional  $\text{ClO}_2$  oxidation process has been turned into realization by combining microwave technology and modified  $\text{Al}_2\text{O}_3$  as catalyst. On the basis of achieving the same treatment efficiency, the improved process has more advantages such as lower oxidant consuming, wider pH range and shorter reaction time. As a developing process, the microwave induced  $\text{ClO}_2$ - $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalytic oxidation process would provide a novel treatment method for the refractory wastewater and would have a broad prospect.

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