A STUDY ON ELECTROCHEMICAL OXIDATION OF CATECHOL IN CHLORIDE MEDIUM FOR WASTEWATER TREATMENT APPLICATION

D. Rajkumar, Jong-Guk Kim[†], and Kyeo Keun Kim^{*}

Research Institute of Industrial Technology, Chonbuk National University,
Chonju 561-756, Korea

*Department of Environmental Engineering, Chongju University, Naedok-dong,
Chongju 360-746, Korea

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Abstract: This paper presents the results of electrochemical oxidation of catechol for wastewater treatment applications. The studies were performed in an electrochemical undivided cell reactor using a Ti/TiO₂-RuO₂-IrO₂ anode. The preliminary investigation using various supporting electrolytes revealed that the presence of chloride removed maximum COD when compare to bromide or sulfate. Based on that, a detailed investigation was conducted to examine the effects of operating conditions such as the initial pH, chloride concentration, current density and initial catechol concentration on the removal of COD. The removal of COD using chloride as supporting electrolyte was shown to be a pseudo-first-order reaction. The results indicate that the initial rate of reaction was highly accelerated by chloride concentration and current density. The rate constant decreased as the initial resorcinol concentration increased. However, the initial pH did not show significant influence on the removal of COD. The present investigation showed the formation of high concentrations of AOX at the beginning of electrolysis, which decreased to lower levels during extended electrolysis.

Key Words: wastewater treatment, electrochemical oxidation, COD, TOC, AOX

INTRODUCTION

Most of the organic pollutants present in the industrial wastewater are either toxic or non-biodegradable. Due to their adverse impact on the environment, these wastes should properly be treated before being discharged. Among the various treatment methods available, the electrochemical technique is found to be advantageous in many ways. This technique is not only used as a pre-treatment process for the conversion of toxic compounds into biodegradable

products but also for its total breakdown into carbon dioxide and water. This method has proved effective in the treatment of dyeing wastewater, 1-4 landfill leachate, 5 lignin, 6 tannery wastewater, 7 polyaromatic hydrocarbons and tannins. Here, the pollutants are destroyed either by direct or indirect oxidation process. In the direct oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. While in an indirect oxidation process, strong oxidants such as hypochlorite / chlorine, ozone, hydrogen peroxide are electrochemically generated, which destroys the pollutants in the bulk solution by oxidation reaction. 10

[†]Corresponding author E-mail: kjongguk@moak.chonbuk.ac.kr Tel: +82-63-270-2448, Fax: +82-63-270-2449

Phenols and phenolic compounds are among the most prevalent forms of chemical pollutants in some industrial wastewater. A number of research findings are available for the electrochemical degradation of phenols by direct 11-14) and indirect 15,16) oxidation methods. However, the reports on the electrochemical degradation of dihydric phenols are not much available. Catechol (2- dihydroxy benzene) is a well-known dihydric phenol used as a raw material in the manufacture of pharmaceuticals, insecticides, photographs and dyestuffs. The black liquor of pulp and paper industry also contains significant amount of catechol. The basic structure of vegetable tannins is mostly catechol or pyrogallol based. Tannins on hydrolysis releases catechol during leather tanning process. An extremely high concentration of catechol (about 5300 mg/L) in coal carbonization wastewater has also been reported. It is reported that the wastewater released during the low temperature coal conversion¹⁷⁾ contains predominant amount of dihydric or trihydric phenols (resorcinol, catechol than phenol pyrogallol) or cresols. Anaerobic biological degradation ^{18,19)} of catechol and other dihydric phenol using upflow anaerobic fixed-film fixed-bed reactor has also been reported. However, the main draw back of this process is the inhibition potential of the substrate itself and the presence of other organic and inorganic substances on microbial activity. Chettiar and Watkinson²⁰⁾ studied the feasibility of electrochemical oxidation of phenolic compounds present in the coal conversion effluent including catechol using packed bed lead dioxide electrode. Formation of a black colored waterinsoluble condensation product on the anode was observed during the catechol degradation at high initial concentrations. The study showed 53.6% of TOC removal at 526 A/m2 in 2 hr of electrolysis for an initial catechol concentration of 100 mg/L.

Though several reports are available for phenol electrochemical degradation, oxidation of dihydric phenolic compounds for wastewater treatment by this method has been limited. Since, catechol is used as an intermediate compound for many industrial processes; an attempt was made to degrade catechol (model compound) by electrochemical method using Titanium Substrate Insoluble Anode (TSIA). The use of titanium electrode coated with noble metal oxides for wastewater treatment is very popular because of its performance, stability, cost, and lifetime.²¹⁾

MATERIALS AND METHODS

Experimental Setup

The experiments were conducted by batch process using undivided cell of 0.5 L capacity. The schematic diagram of the bench scale electrochemical reactor set up is shown in Figure 1. The anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 1 cm. The material used as titanium anode was mesh coated with TiO₂-RuO₂-IrO₂ (a mixed triple oxide). These types of dimensionally stable electrodes are widely used in chlor-alkali industries for the production of chlorine.²²⁾ Since the electrode used in the study was a mesh, it was more appropriate to report the current density values

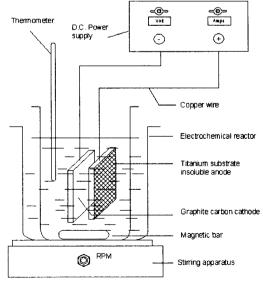


Figure 1. Schematic diagram of the bench scale electrochemical reactor set up.

as total current over the true electrode surface area, neglecting the contribution of voids in the mesh. The true metal surface of the working electrode (10x5 cm) was 27.7 cm². The cathode material used in the present study was a graphite carbon (plate type). These electrodes were dipped in the electrolyte solution. The reactor was kept in a glass bowl containing water to maintain constant temperature ($\sim 30^{\circ}$ C) of the electrolytic cell to prevent any possible loss of compounds by volatilization, Preliminary experiments showed that stirring the solution between 100 - 400 rpm does not influence the rate of reaction. Hence, the solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. A stabilized D.C power supply was used as the source of electric current for the experiments. The current and voltage were adjustable between 0-6 amperes and 0-60 voltage with digital displays.

Analysis, Instruments and Procedure

All the experimental runs were carried out twice and the analysis of each parameter was done in twice for each run. The co-efficient of variation obtained was not more than 3% for the four data points. Hence, an average value of the four data points was taken for the study. The Chemical Oxygen Demand (COD) values were determined by open reflux, dichromate titration method as described in standard methods.²³⁾ The initial pH of the electrolytic solution was set appropriately using dilute solutions of sodium hydroxide or sulfuric acid. Total Organic Carbon (TOC) of the initial and electrolyzed solution was determined using TOC analyzer micro N/C model (Analytika Jena, Germany). instrument was operated at 680°C temperature, 200 μL sample injection with oxygen flow rate of 12 mL/min and 3 min strip time. The concentration of adsorbable organic halides (AOX) at different time of electrolysis was determined according to DIN EN 1485-IDC procedure, using multi X 2000 model, AOX analyzing system (Analytika Jena, Germany).

The three steps involved in AOX measurement are, adsorption of the organochlorine compound onto the activated carbon, mineralization of organically bound halogen (chloride in this case) through combustion and determination of chloride concentration by micro coulometric titration.

RESULTS AND DISCUSSION

Effect of Supporting Electrolytes

Preliminary experiments on the electrochemical oxidation of catechol were conducted with chloride, bromide and sulfate as supporting electrolytes to investigate their effects on the removal of COD or TOC. In the indirect electrochemical oxidation process in the presence of chloride, the destruction of organic compounds is mainly by the attack of active chloro species such as chlorine and hypochlorous acid or hypochlorite ion, which are generated at the anode during the electrolysis. Similarly, bromine formed at the anode undergoes reaction in the bulk solution to form hypobromous acid or hypobromite. The active chlorine or bromine species produced during the electrolytic process are highly oxidative reagents. Figure 2 shows the electrolysis of catechol obtained with three supporting electrolytes of 2500 mg/L operated at a current density of 5.4 A/dm². It is clear that the COD removal efficiency obtained with chloride is higher than that of sulfate. Because, sulfate is an inert electrolyte that does not produce any reactive species during electrolysis except under special conditions it may produce persulfate. The COD removals were 87.7 and 26.2%, respectively for chloride and sulfate at the end of 16 Ah/L of charge passed. Since bromide present in the treated water interfered in the determination of COD, TOC removal was determined in order to compare the results with other electrolytes. When comparing chloride and bromide, the TOC removals obtained with chloride is very close to that of bromide. The TOC removals were 70.4 and 64.3% for chloride and bromide respectively. The reason may be due to

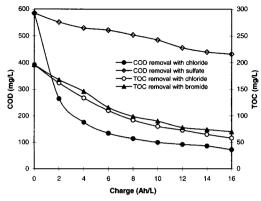


Figure 2. Effect of supporting electrolyte on the electrochemical oxidation of catechol. (conditions: initial pH = 8.0, supporting electrolyte concentration = 2500 mg/L, catechol concentration = 300 mg/L, current density = 5.4 A/dm²).

the higher oxidation potential of the active chloro species than active bromo species. For example the oxidation potential of hypochlorite and hypobromite are 0.89 and 0.74 V respectively. Pletcher and Walsh²²⁾ reported that by direct anodic oxidation, the complete conversion of organic species to carbon dioxide is not a facile reaction. However it is possible only at special conditions like using platinum electrode in a concentrated alkali or acid at 80°C. Such conditions are clearly unsuitable for wastewater treatment. Moreover, complete oxidation of larger molecules requires the transfer of many electrons and leads to high-energy consumption. In view of above, further efforts were not attempted to increase either the sulfate concentration or the time of electrolysis for catechol oxidation. However, the chloride is normally present in wastewater and also the cost of sodium chloride is very less when compared to that of bromide. Hence, it was decided further to study the electrochemical oxidation using chloride as a supporting electrolyte in detail.

Effect of Initial pH

The effect of initial pH on catechol oxidation was studied by varying the initial pH between 3.0 to 9.0. From Figure 3, it is clear that varying the initial pH did not show significant

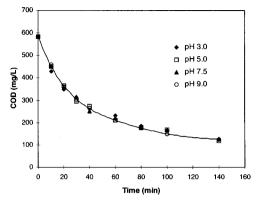


Figure 3. Effect of initial pH on the removal of COD. (conditions: chloride concentration = 2500 mg/L, catechol concentration = 300 mg/L, current density = 7.4 A/dm²).

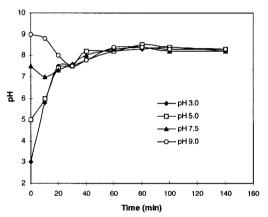


Figure 4. Variation in pH during the electrochemical oxidation of catechol. (conditions: as per Figure 3).

COD removal efficiency. The reason is that indirect electrochemical oxidation of organic compounds takes place mainly via the electrolytically generated chlorine/hypochlorite; however the production rate of chlorine/hypochlorite is not affected significantly by initial pH conditions.⁵⁾ Vijayaraghavan et al.^{4,7)} reported that during the treatment of tannery and textile effluents, under fixed current density, the chlorine production was more or less the same, irrespective of the initial pH values(3.5-8.5). Lin and Peng⁴⁾ also observed similar observation during the treatment of textile wastewater in the pH range of 5-10. The variation in pH during the electrolysis of catechol is shown in Figure 4.

It can be seen that within 40 min, the initial pH of the solution (3.0 to 9.0) changed to 7.8-8.3. Afterwards, the pH of the solution remained constant at 8.3. The reason may be due to the reaction between hydroxyl ion and carbon dioxide (formed during catechol degradation in this case) thereby forming bicarbonate buffer during the electrolytic degradation of organic compounds.⁸⁾

Effect of Current Density

An important operating variable of the electrochemical degradation process is the current density, which is the current input divided by the surface area of the electrode. Murphy et reported that the pollutant removal efficiency at a fixed charge loading was independent upon the value of current density in a direct electrochemical oxidation treatment process. On the other hand, Chiang et al. 5) reported that during the indirect electrochemical oxidation the chlorine / hypochlorite production was improved by increasing the operating current density, which led to enhanced pollutant removal. Figure 5 shows the COD reduction during the electrochemical oxidation of catechol with varying current densities under fixed charge input. During the initial periods of electrolysis, a large increase in COD removal was observed as

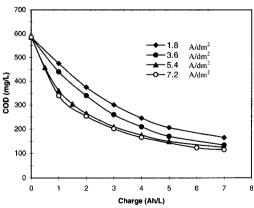


Figure 5. Effect of current density on the removal of COD. (conditions: initial pH = 8.0, chloride concentration = 2500 mg/L, catechol concentration = 300 mg/L).

the applied current density was increased from 1.8 to 5.4 A/dm². However, at the end of 7 Ah/L of charge input, there was no significant difference in COD removal for the current densities of 3.6, 5.4 and 7.2 A/dm². Considering the duration of electrolysis as well as COD removal, the optimum current density for the oxidation of catechol was 5.4 A/dm².

Effect of Chloride Concentration

The effect of chloride concentration on COD removal was studied by varying the chloride concentration from 500 to 4500 mg/L by keeping other conditions constant. Figure 6 shows that the COD removal was increased with increase in chloride concentration and charge. According to Chiang et al.5) the increase of chloride concentration in the electrolyte solution could be reducing the overpotential required for anodic oxidation of chloride and thereby generation of chlorine/hypochlorite increased. Hence, a higher COD removal was obtained at a higher chloride concentration. It is clear from the figure that though a large increase in the COD removal was obtained at the initial periods of electrolysis, the removal of COD was more or less same at the end of 7 Ah/L charge input for the chloride concentrations 2500, 3500 and 4500 mg/L. For real industrial wastewater treatments,

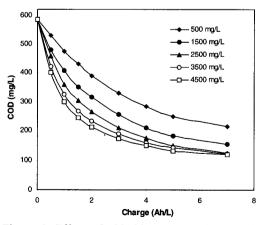


Figure 6. Effect of chloride concentration on the removal of COD. (conditions: initial pH = 8.0, catechol concentration = 300 mg/L, current density = 5.4 A/dm²).

operating at low salt concentration is always preferred in order to reduce the total dissolved solids content to meet out the discharge standards. Hence, a chloride concentration of 2500 mg/L was considered as optimum for catechol electrochemical oxidation.

Effect of Catechol Concentration

In the previous experiments, an initial catechol concentration of 300 mg/L was employed. Hence, experiments were conducted to investigate the influence of initial catechol concentration on the removal of COD by the electrochemical oxidation. Figure 7 shows the removal of COD with increasing catechol concentration. As the initial catechol concentration was increased from 100 to 500 mg/L, the percentage COD removal decreased from 94.8 to 71.3% after passing 7Ah/L charge. Such a decrease in percentage COD removal is due to an increase in the oxidation load at high catechol concentration. Though increasing initial concentration showed a decrease in the percentage COD removal, the absolute amounts of COD removal increased. The absolute amount of COD removal at 7 Ah/L were 185, 345, 460, 570 and 695 mg/L respectively for 100, 200, 300, 400 and 500 mg/L catechol concentrations. This may be explained by the fact that, under galvanostatic conditions, the production rate of

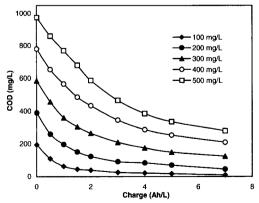


Figure 7. Effect of catechol concentration on the removal of COD. (conditions: initial pH = 8.0, chloride concentration = 2500 mg/L, current density = 5.4 A/dm²).

chlorine / hypochlorite is constant; however, the reactive species generated has non-selective nature, which results in an attack on new catechol molecules rather than on the intermediate compounds produced. Therefore, the absolute amount of COD removal (net amount) was more in higher concentrations of catechol. The result suggests that the process is effective at higher catechol concentrations and is encouraging from the viewpoint of real industrial wastewater treatment applications.

Kinetics of COD Removal

To model the experimental data of COD removal, a simple pseudo-first-order kinetic reaction was attempted. In the indirect electrochemical oxidation process, the COD removal rate is proportional to the concentration of the organic compound (pollutant) and to the chlorine/hypochlorite concentration because the indirect oxidation is mediated by chlorine/hypochlorite. Therefore, the kinetics for COD removal is

$$-d[COD] / dt = k[COD][Cl2]$$
 (1)

Electrochemical oxidation involves the application of an electrical current to the effluent to convert chloride to chlorine / hypochlorite. The chlorine / hypochlorite will oxidize the catechol and then get reduced to chloride ion. The process is then repeated in a catalytic fashion. Therefore, the concentration of chlorine/hypochlorite during the electrolysis is assumed to be a constant, and so eq 1 can be written as a pseudo-first-order kinetic equation.

$$-d[COD] / dt = k' [COD]$$
 (2)

The log plots (not shown) of the COD concentration curves show the plot of the rate expression.

$$\log \frac{[COD]_t}{[COD]_o} = -k't \quad \text{or} \quad \log \frac{C_t}{C_o} = -k't \quad (3)$$

The slope of the plot (not shown) of log

(C₁/C₀) versus time gives the value of rate constant k' (reciprocal minutes). Here, C_0 is the initial COD of catechol in milligrams per liter, and C_t is the COD value at time t. Table 1 provides the rate constant for ~ 65% COD removal together with calculated half lives. High values of correlation coefficients (above 0.9) indicate that the hypothesis of pseudo-first-order reaction of COD removal fit well. It is clear, that there is a strong linearity between the rate constant and chloride concentration. Similarly, the results show that current density also strongly influences the rate of reaction. However, as the initial catechol concentration increases the rate constant decreases significantly. Because at higher concentrations the intermediate compounds formed out of initial degradation would also be competing for further degradation at reduced rate. Since the pseudo-first-order rate constant was calculated based on COD, it showed a decrease in rate constant while increasing the concentration of catechol. Hence, the initial rate of oxidation is essentially first order in catechol concentration. The results indicate that the initial rate of reaction is highly accelerated by chloride concentration and current density. The rate constant decreases as the initial resorcinol concentration increases.

TOC Removal and AOX Concentration

To apply the electrochemical method for the treatment of industrial wastewater, it is necessary to study the mineralization of organic compound. The extend of mineralization can be studied in terms of TOC removal. Another important consideration is the formation of halogenated organic compounds. In the this study, the electrochemical oxidation of organic compounds mainly takes place by the attack of hypochlorite/ chlorine; as a result, chlorinated organic compounds (AOX) may be formed during the degradation process. AOX is defined as the sum of all halogenated organic compounds, which can be adsorbed by activated carbon. Nowadays, various environmental agencies provide very strict regulations for the discharge of AOX containing wastewater; it is necessary to check the AOX concentration after the electrochemical oxidation. Figure 8 shows the TOC removal and AOX concentration during the electrolytic oxidation of 500 mg/L catechol concentration. Though COD removal was 71.2% at the end of 7 Ah/L, the TOC removal was only 37.0%. However the removal of TOC was gradually increased to 61.4% (83.0% COD removal) after passing 22 Ah/L charge. It is clear from the figure that the formation of AOX

Table 1. Kinetic data of catechol electrochemical degradation at different operating conditions

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Conditions		COD removal (%)	Rate constant, k' (min ⁻¹)	T _{1/2} (min)	r ²
Chloride concentration (mg/L) (conditions : as per Figure 6)	500	63.2	0.0035	86.0	0.95
	1500	64.1	0.0060	50.2	0.96
	2500	64.1	0.0082	36.7	0.95
	3500	67.5	0.0094	32.0	0.90
	4500	63.8	0.0121	24.9	0.95
Initial catechol concentration (mg/L) (conditions : as per Figure 7)	100	67.3	0.0246	12.2	0.99
	200	64.1	0.0133	22.6	0.97
	300	64.1	0.0082	36.7	0.95
	400	63.3	0.0058	51.9	0.98
	500	65.5	0.0049	61.4	0.99
Current density (A/dm²) (conditions : as per figure 5)	1.8	64.8	0.0015	200.6	0.99
	3.6	64.1	0.0038	79.2	0.99
	5.4	64.1	0.0082	36.7	0.95
	7.2	65.4	0.0112	26.9	0.94

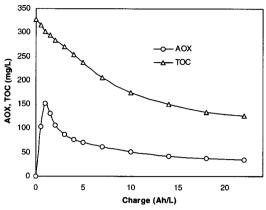


Figure 8. TOC removal and AOX concentration during the electrochemical oxidation of catechol. (conditions: initial pH = 8.0, chloride concentration = 2500 mg/L, catechol concentration = 500 mg/L, current density = 5.4 A/dm²)

at the beginning of electrolysis was very high, but increasing the electrolysis time led to a decrease of AOX content. A maximum concentration of 152 mg/L of AOX was found in the electrolysis solution at 1 Ah/L charge, and it was reduced to 34 mg/L at the end of 22 Ah/L.

CONCLUSION

The results of this study showed the feasibility of electrochemical technique for the degradation of catechol by generating chlorine / hypochlorite. The initial pH on the electrochemical oxidation of catechol is not found to be significant in the range of 3.0 to Increasing chloride concentration and current density highly influences the removal of COD. Though increasing initial concentration of catechol showed a decrease in the COD removal efficiency, the absolute amount of COD removal increased. The initial rate of COD removal is found to be a pseudo-first-order kinetics. Though the removal of COD is a grater extends for catechol oxidation by this method, the complete removal of TOC is not achieved. The formation of AOX during the oxidation process indicates further need of AOX removal before the discharge. In this study, we have selected catechol

as only a model compound, however the observations may be useful for researchers those are working in the area of wastewater treatment.

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