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Electrochemical Oxidation of Phenol Using Graphite Anodes

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ABSTRACT

The effects of current and pH on the electrochemical oxidation of phenol on graphite electrodes is investigated in this study. There was no sign of deterioration of the graphite bed after 5 months of operation. Phenol removal efficiency was a function of the current applied and was around 70% at a current of 2.2 A. The increase of phenol removal efficiency with current is attributed to the increase of ionic transport which increases the rate of electrode reactions responsible for the removal process. The percentage of complete oxidation of phenol increases with current, with a maximum value of about 50%. However, at pH 0.2 it is slightly higher than that at pH 0.5 at all currents. The phenol removal rate increases with increases of current and pH. While the current (CO_2) efficiency reaches a maximum value in the current range of 1.0–1.2 A, it increases with an increase of acid concentration. The findings of this study have important implications: While anodic oxidation of phenol on graphite can achieve acceptable removal of phenol, the extent of oxidation should not be overlooked.

INTRODUCTION

Phenol, which is listed as a priority pollutant by the US Environmental Protection Agency, is considered to be one of the major water pollutants that need

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recovery, removal, or destruction. It reacts with chlorine during water treatment and produces chlorophenols which are carcinogenic (1). Even at low concentrations, phenol causes the taste and odor of fish, and it has deleterious effects on bacteria, alga, mammals, and human beings (2).

Phenolic wastes arise in many segments of such process industries as coke ovens, oil refineries, plastic industries, rubber reclamation, and explosives (3). The conventional processes used for the detoxification of phenolic wastewater include solvent extraction (4), biodegradation (5), and activated carbon adsorption (6). Electrochemical oxidation of many chemical constituents has been studied by a number of researchers for possible application in industrial waste treatment (7–10).

Anodic oxidation of phenol for wastewater treatment applications was investigated by De Scure and Watkinson (11) on lead dioxide packed-bed anodes. They reported that phenol is readily oxidized in aqueous solution. They also found that the amount of phenol oxidized increased with an increase in current density and decreased with increases in initial phenol concentration, electrolyte flow rate, and average particle size of the lead dioxide pellets. In a more recent study, Comninellis and Pulgarin (12) used SnO_2 anodes for the oxidation of phenol. Their analysis of the reaction intermediates and carbon balance showed that the main path was oxidation of phenol to CO_2.

Anodic oxidation systems are usually operated at low pH to minimize electrode inhibition (13). The effect of pH on the anodic oxidation of phenol was studied by De Scure and Watkinson (11). They suggested that at low pH (less than 3), where phenol is essentially nonionized, the initial step of oxidation is the two electrons phenoxonium ion reaction:

$$C_6H_6O \rightarrow C_6H_5O^+ + H^+ + 2e^- \qquad (1)$$

whereas at high pH values where phenol is ionized, the one electron free radical reaction takes place.

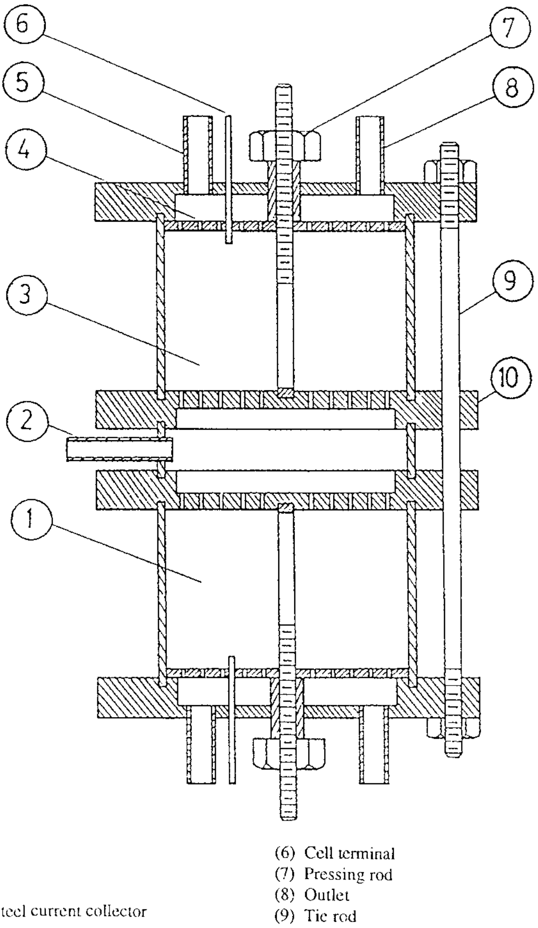
$$C_6H_5O^- \rightarrow C_6H_5\dot{O} + e^- \qquad (2)$$

De Scure and Watkinson (11) and Kirk et al. (14) found that while phenol was readily oxidized on lead dioxide anodes, decreasing the total organic carbon (TOC) of the wastewater was much more difficult. This is of great concern from a toxicity point of view because the intermediate products, mostly quinones, are more hazardous than phenol, the original toxicant in the wastewater (15). Accordingly, complete oxidation of phenol to CO_2 should be achieved to guarantee environmentally safe discharges.

Previous work (11) on the effect of pH on phenol anodic oxidation was motivated by pH-induced phenol ionization. However, this study will investigate the effect of pH variation on the anodic oxidation of phenol in the nonionized phenol range. Additionally, research on quinones production (11, 14) did not investigate the effect of pH variation in the nonionized phenol range, which is attempted in this study. Furthermore, the study investigated the removal of phenol under the above-mentioned variables in a flowthrough graphite electrochemical cell. A similar graphite reactor configuration has not been investigated previously for phenol destruction in relation to pH variation and quinones production.

MATERIALS AND METHODS

The experimental cell used in this study is shown in Fig. 1. The principal features of the cell are the two porous electrodes. Each porous electrode was contained in a Plexiglas cylinder with two end plates of Teflon with grooved



(1) Cathode
(2) Feed inlet
(3) Anode
(4) Stainless steel current collector
(5) Vent
(6) Cell terminal
(7) Pressing rod
(8) Outlet
(9) Tie rod
(10) Teflon flange

FIG. 1 Schematic diagram of the experimental cell.

rings. The feed entered through an opening in the central ring. On the feed side of each electrode, 100 holes (1.5 mm diameter each) were drilled in the Teflon. The current collectors consisted of 3-mm thick stainless steel plates, each containing 100 holes of 1.5 mm diameter each. Perforation in the Teflon plates was spaced in a geometrical pattern to give a uniform flow while still maintaining structural strength. Electrical connections were made of stainless steel rods drilled into the plate. The perforated stainless steel plate was held in place by a stainless steel rod through which the bed was compressed as shown in Fig. 1. Sealing was affected by compression of four externally threaded aluminum rods located peripherally on the end plates. The graphite bed was formed of compacted particles passing sieve no. 20 and retained on sieve no. 200. The basic properties of the electrodes are shown in Table 1.

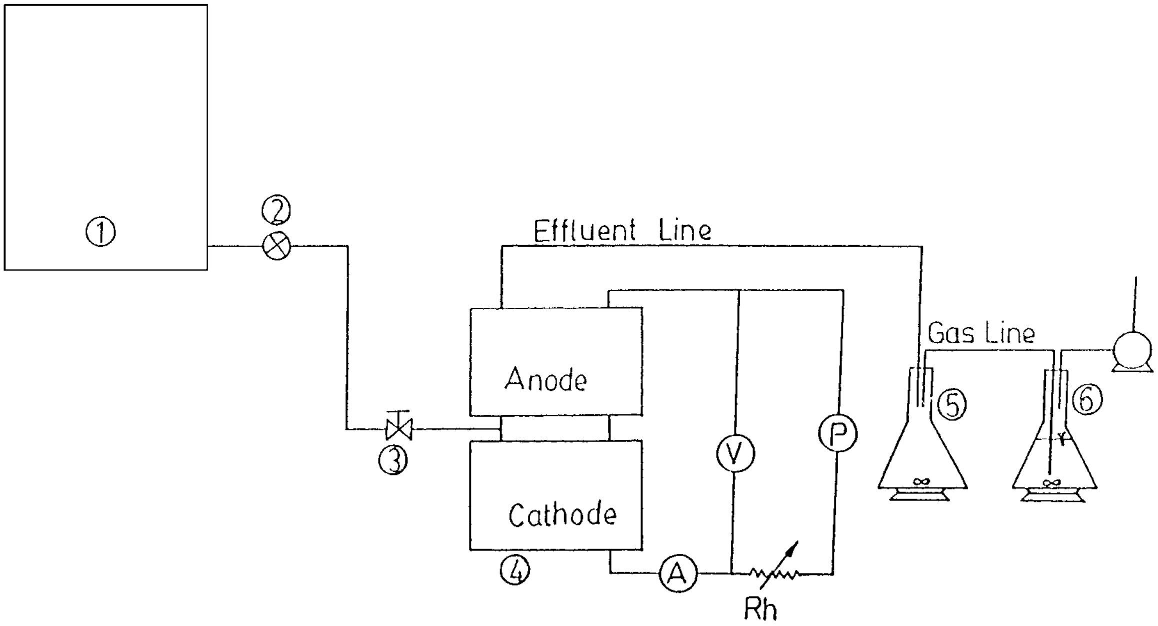
The electrical circuit used in the work is shown in Fig. 2. The potential (V) and the current (A) were measured between the anode and the cathode. The cell was connected to a Physikalische Lemmebrmittle (DC) power supply (model SV-5910).

The feed flowed from a 20-L constant head tank placed 1.25 m above the central ring of the cell. Upward flow through the anode was adapted to enable the gas bubbles produced in the oxidation process to escape easily. The flow was controlled by a needle valve. The flow rate was determined by filling a measuring cylinder over half an hour. Ninety-nine percent of the flow passed through the anode and 1% through the cathode. Samples were taken after a time interval three times larger than the detention time as suggested by Bennion and Newman (16) to make sure that steady-state conditions were reached.

A 500 mg/L phenol stock solution with 0.1 M H_2SO_4 was prepared as a synthetic feed wastewater for the study of phenol removal efficiency. On the other hand, for the investigation of the pH effects, a phenol stock solution (1000 mg/L) was used as a synthetic feed wastewater. The latter solution was divided into two portions. The pH of one portion was reduced to 0.5 while for

TABLE 1
Basic Characteristics of Each Porous Electrode

Parameter	Value
Diameter, mm	88.00
Height, mm	58.00
Mass of graphite, g	440.00
Specific gravity	1.69
Shape factor	0.85
Specific area of graphite, cm^{-1}	179.50



(1) Tank
(5) CO_2 absorber
(2) Needle valve
(6) Vacuum pump
(3) Liquid trap
(4) Experimental cell

V : Voltmeter
A : Digital Multimeter
P : DC Power supply
Rh : Rheostat

FIG. 2 Schematic of the experimental apparatus.

the other portion it was reduced to 0.2. pH adjustment was achieved by the addition of concentrated H_2SO_4.

Phenol concentration in the effluent was determined by a Varian Gas Chromotograph (GC) (model 3400) attached to a Varian Integrator (model 4290). The concentration was determined by applying the external standard method with an accuracy limit of 5%. The column used in the analysis was a 2-m long stainless steel column packed with 80/100 mesh Cromosorbed (acid-washed) coated with a 15% free fatty acid phase. A flame ionization detector (FID) was used. The operating conditions of the GC were adapted from the *Standard Methods* (17). Phenol concentrations of five samples of anolyte for each run were measured. The average of the closest concentrations of four samples was considered as the phenol effluent concentration.

The carbon dioxide (CO_2) produced from the anodic oxidation of phenol resulted from the evolving gas and the anolyte. The gas bubbles were separated from the anolyte by using a liquid trap and absorbed in 0.05 M barium hydroxide. The dissolved CO_2 was stripped from the anolyte by sparging with nitrogen and absorbed in 0.05 M barium hydroxide. The barium hydroxide was backtitrated with 0.05 M hydrochloric acid.

RESULTS AND DISCUSSION

The color of the effluent was green in the first 10 hours of operation, after which the green color disappeared. The green color is attributed to the oxidation of some chemicals which are attached to the fresh graphite surface. Those chemicals might be electrochemically active and expected to be oxidized more easily than phenol. This is supported by the fact that oxidation of phenol increased with time until a steady state was reached (when those chemicals were oxidized). The steady state, asserted by the achievement of three identical consecutive effluent phenol concentrations, was reached after 50 hours of operation. There was no deterioration in the graphite bed in about 5 months of operation.

Figure 3 depicts the relationship between phenol removal efficiency and current. The figure shows that phenol removal efficiency increases with an increase in current. This is attributed to an increase of ionic transport which increases the rate of electrode reactions responsible for the removal process. The aforementioned result agrees with previous findings (11, 14). However, the rate of increase in removal efficiency decreased with an increase in current. This can be attributed to the fact that the graphite area, not the applied current, was limiting the oxidation reactions.

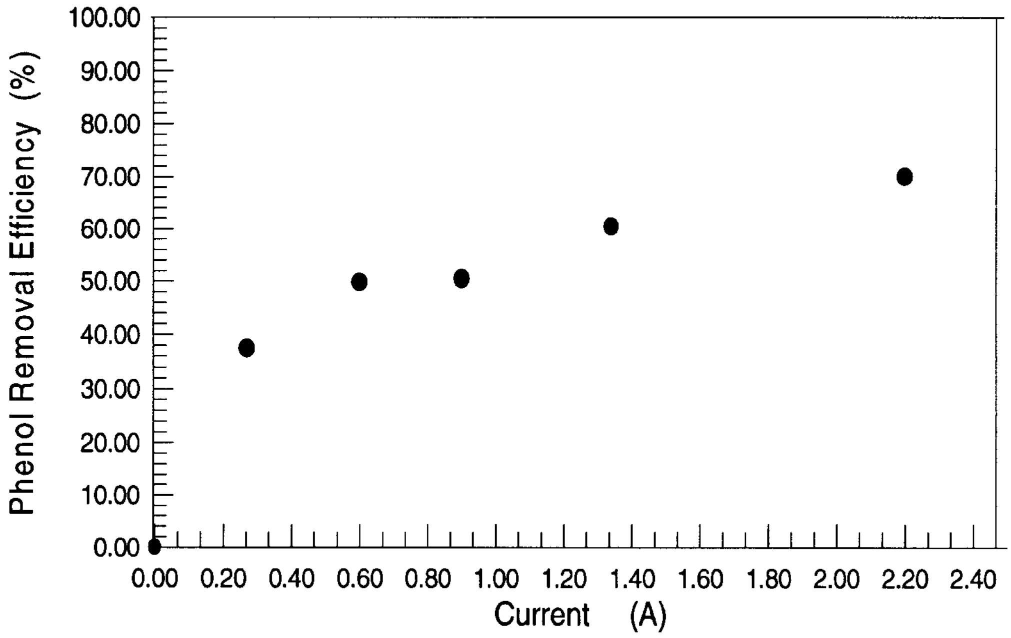


FIG. 3 Relationship between phenol removal efficiency and current (initial concentration of phenol is 500 mg/L and the flow rate is 8.9 mL/min).

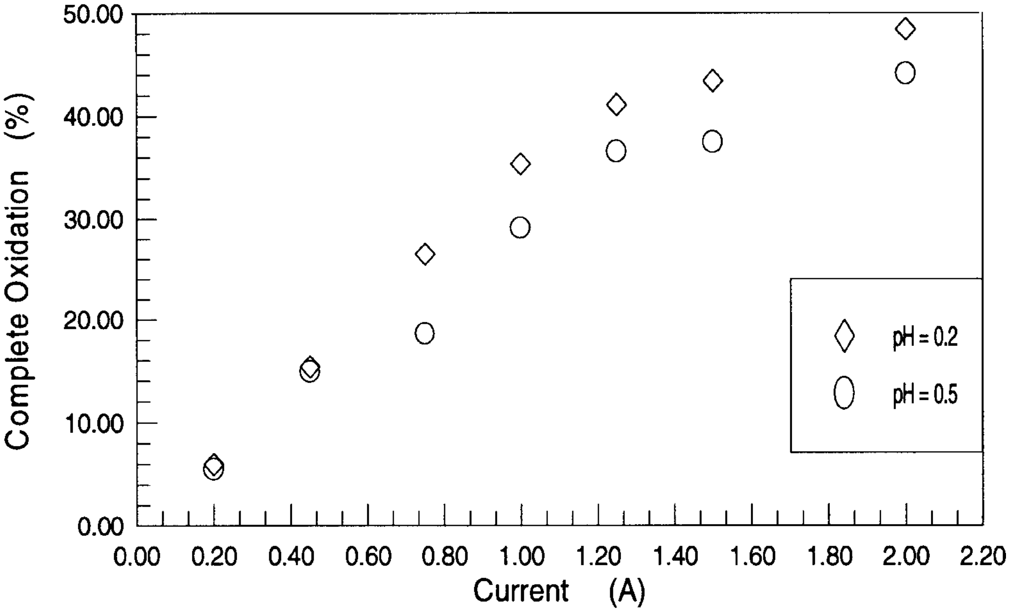


FIG. 4 Relationship between percentage complete oxidation of phenol and current under different pH values (initial concentration of phenol is 1000 mg/L and the flow rate is 15.5 mL/min).

The percentage of complete oxidation is defined as the amount of phenol converted to CO_2 as a percentage of the total amount of phenol oxidized. Figure 4 shows that the percentage of complete oxidation increases with current, with a maximum value of about 50%. This trend agrees with the results of De Scure and Watkinson (11) who used a lead dioxide packed-bed anode. It also agrees with the results of Kirk et al. (14) who used the same type of anode with a recirculating anolyte. Their results were interpreted according to the following reaction sequence:

$$C_6H_6O + H_2O \rightarrow C_6H_4O_2 + 4H^+ + 2e^- \tag{3}$$

$$C_6H_4O_2 + 6H_2O \rightarrow C_4H_4O_4 + 12H^+ + 2CO_2 + 12e^- \tag{4}$$

$$C_4H_4O_4 + 4H_2O \rightarrow 4CO_2 + 12H^+ + 12e^- \tag{5}$$

where C_6H_6O is phenol, $C_6H_4O_2$ is benzoquinone, and $C_4H_4O_4$ is maleic acid.

The formation of benzoquinone is of importance from a toxicity point of view. While the measured phenol in the effluent could be very low, a very high percentage of the influent phenol would have been oxidized and discharged as benzoquinone. Quinones were reported to be more hazardous than phenol (15).

It is obvious from Fig. 4 that the percentage of complete oxidation at pH 0.2 is slightly higher than that at pH 0.5 at all currents. This is in agreement with the findings of Kirk et al. (14) who reported that higher acid concentration promotes the breakdown of benzoquinone, resulting in greater conversion of phenol to CO_2.

Figure 5 depicts the relationship between phenol removal rate and current at different pH values. As expected, the figure shows that the removal rate of phenol increases with current. Furthermore, it is shown that the phenol removal rate at pH 0.2 is generally higher than that at pH 0.5. It is observed from the figure that the rate of change in the removal rate decreases with an increase of current. This trend is consistent and best explained by the fact that the percentage of complete oxidation increases with current.

Current (CO_2) efficiency is defined as the actual quantity of CO_2 produced divided by the theoretical quantity of CO_2 formed by the same current according to Faraday's law. Figure 6 shows that the current (CO_2) efficiency reaches a maximum value in the current range of 1.0 to 1.2 A. At higher currents, side reactions (mainly oxygen evolution) become excessive, which reduces the current (CO_2) efficiency. Figure 6 also shows that the current (CO_2) efficiency increases with an increase of acid concentration. This is because conversion to CO_2 is promoted, as described previously.

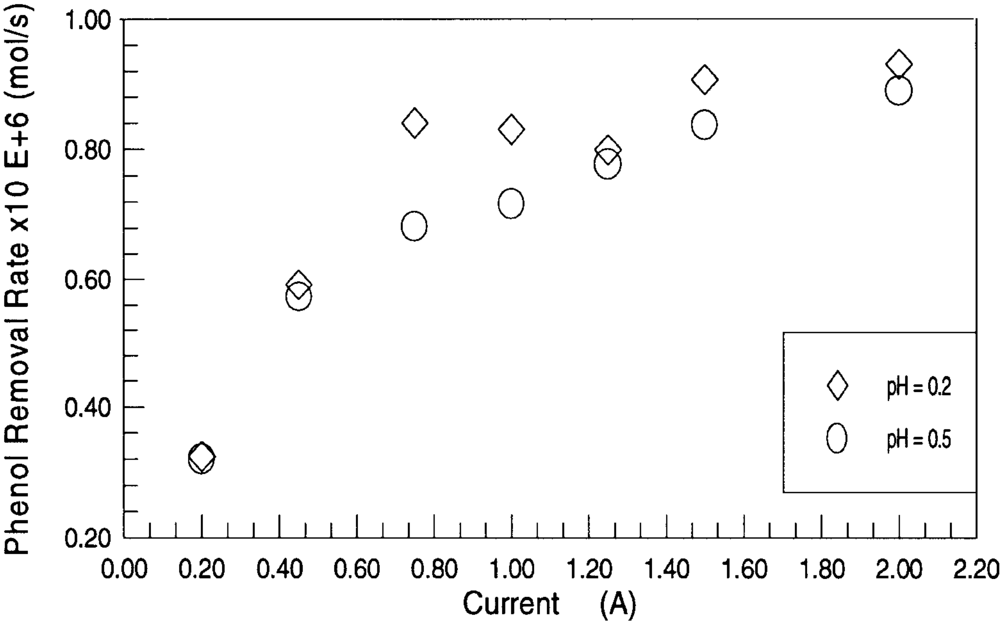


FIG. 5 Relationship between phenol removal rate and current under different pH values (initial concentration of phenol is 1000 mg/L and the flow rate is 15.5 mL/min).

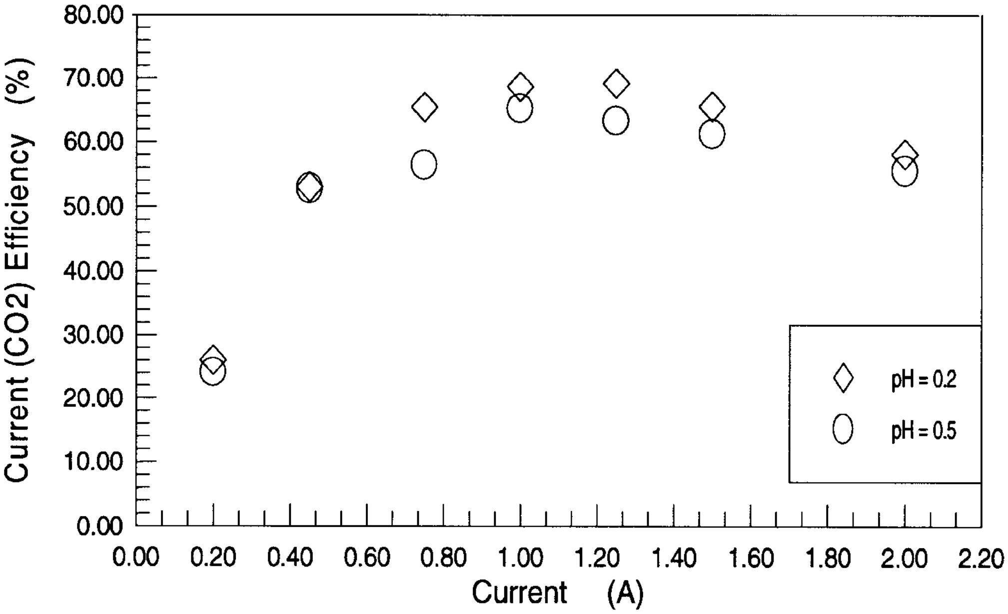


FIG. 6 Variation of current (CO_2) efficiency with current under different pH values (initial concentration of phenol is 1000 mg/L and the flow rate is 15.5 mL/min).

SUMMARY AND CONCLUSIONS

Electrochemical oxidation of phenol on graphite electrodes was achieved with an acceptable removal efficiency. There was no sign of deterioration of the graphite bed after 5 months of operation. Phenol removal efficiency was a function of the current applied and was around 70% at a current of 2.2 A. The increase of phenol removal efficiency with current was attributed to the increase of ionic transport which increases the rate of electrode reactions responsible for the removal process.

The percentage of complete oxidation of phenol increases with current, with a maximum value of about 50%. However, at pH 0.2 it was slightly higher than at pH 0.5. On the other hand, the phenol removal rate increased with current and was higher at pH 0.2 than at pH 0.5. Current (CO_2) efficiency reached a maximum value in the current range of 1.0 to 1.2 A and increased with an increase of acid concentration.

The findings of this study have important implications. While anodic oxidation of phenol on graphite can achieve acceptable removal of phenol, the extent of oxidation should not be overlooked. Partial oxidation to CO_2 results in an effluent rich in quinones that are more toxic than phenol. While anodic oxidation systems are usually operated at low pH in order to minimize electrode inhibition, the percentage of complete oxidation of phenol increases with a decrease of pH.

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