Influence of Some Operating Parameters on Electro-Oxidation of Phenol using Boron Doped Diamond Anode and Graphite Cathode

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ABSTRACT
The influences of current density, initial pH, initial phenol concentration and Na2SO4 electrolyte dosage on electro-oxidation of 100-1000 mg L−1 phenol using Boron-doped Diamond (BDD) anode and graphite cathode were investigated. The evolutions of phenol and its oxidation byproducts were monitored with HPLC and GC-MS instruments. Removal efficiencies of phenol, Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) were found to be mainly influenced by initial pH and initial phenol concentration with current density and Na2SO4 dosage having less significant effects. Complete oxidation of phenol was achievable under acidic and neutral pH regardless of initial phenol concentration; while under basic pH, accumulation of intermediary byproducts severely hindered the oxidation of 100 mg L−1 phenol. Effective electro-oxidation of phenol was kinetically controlled process by direct oxidation process mediated by the electro-generated hydroxyl radicals (OH) produced at the BDD anode surface. The evolutions of TOC, COD and phenol oxidation byproducts suggests initial pH and initial phenol concentration dependant pathways from which effective phenol oxidation been initiated by speciation molecules and subsequent generation of aromatic intermediates which were further converted to aliphatic acids. The final step in the pathway involved the destruction of the aliphatic acids to CO₂.

Key words: Electro-oxidation, phenol, oxidation pathways, operating parameters, boron doped diamond, graphite electrode

INTRODUCTION
Phenol is a common contaminant found in wastewater streams from a number of industries such as refinery, petrochemical, plastic, paper and pulp, textiles, detergent, pesticides and pharmaceutical industries (Berne and Cordonnier, 1995; Li et al., 2005). Improper discharges of phenolic wastewater from such industries are likely to lead to detrimental environmental consequences as phenol is toxic substance that poses great risk to aquatic life, micro-organisms and mammal (Busca et al., 2008). As such, stricter discharge limits for phenols was recently brought down to as low as 0.1 mg L⁻¹ (PME, 2001; USEPA, 2006). Numerous treatment technologies have been suggested for effective destruction of phenol in aqueous matrixes (Busca et al., 2008). Cheap biological treatment technologies are ineffective due to the bio-recalcitrant nature of phenolic compounds. Chemical oxidation techniques have been proposed for effectiveness with
electrochemical oxidation methods receiving greater attention in recent years (Awad and Abuzaid, 1999; Comninellis and Nerini, 1996; Comninellis and Pulgarin, 1991, 1993; Koparal and Ogtuveren, 2002; Koparal et al., 2002; Studki et al., 1991). This can be attributed to characteristics such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness that electrochemical methods offer which give them an edge over other conventional technologies (Juttner et al., 2000; Rajeshwar and Ibanez, 1997). However, the practical applications of most of these anodes materials are mired by a number of problems such as loss of activity due to surface fouling of glassy carbon (Gattrell and Kirk, 1990), limited service life of TiSnO₃ (Correa-Lozano et al., 1997) and SnO₂ (Correa-Lozano et al., 1997), release of toxic ions by PbO₂ (Panizza and Cerisola, 2005), selective oxidation of IrO₂ (Comninellis, 1994) and low current efficiency.

Boron Doped Diamond (BDD) electrodes, newer anodic materials, have recently attracted the attention of many researchers because of their very distinctive characteristics (Beck et al., 1998; Fisher et al., 1998; Kraft, 2007; Panizza and Cerisola, 2005; Panizza et al., 2001; Troster et al., 2002). The characteristics of these materials, such as hardness, resistance to fouling, longer operating life span, polarity reversibility, stability, wide potential window for water discharge and electro-generation of powerful oxidants (hydroxyl radicals, OH·) render them excellent candidate anodes for effective oxidation of organic compounds (Cui et al., 2009; Gueven et al., 2009; Kraft, 2007; Liu et al., 2009; Nasr et al., 2009; Panizza and Cerisola, 2005; Panizza et al., 2001; Troster et al., 2002). This present study investigates the effect of current density, pH, initial phenol and electrolyte concentrations on the mechanism and efficiency of phenol oxidation using a batch reactor equipped with BDD anode and graphite cathode.

MATERIALS AND METHODS

Chemical reagents: High purity phenol (AnalaR), benzoquinone (AnalaR), hydroquinone (AnalaR) and catechol (AnalaR), were freshly used without any further purification. Analytical grade H₂SO₄ (Sigma-Adrich) and NaOH (Sigma-Adrich) were used for pH adjustment. Similarly, all other chemicals used were of high purity obtained from either AnalaR or Sigma-Adrich. Phenol (100, 500 and 1000 mg L⁻¹) in sodium sulfate solutions used in all the electrolytic experiments were prepared with purified water obtained from a Millipore Ultrapure system (conductivity <5x10⁻⁸ S cm⁻¹ at 25°C).

Experimental procedure: Electrolyses were undertaken in batch mode using an undivided 2000 cm³ capacity reactor made up of internal glass compartment and external Flexiglas® material (Fig. 1). Constant room temperature of solution during any experiment was controlled with (HAAKE GE). Synthetic thin-film Boron-Doped Diamond with niobium substrate (CONDIAS, Germany) and graphite material (CONDIAS, Germany) both 10 cm in diameter, served as the working and counter electrode, respectively. Sodium sulphate was used as the aqueous phase supporting electrolyte. All electrolyses were carried out at galvanostatic state with constant current supply from FD110-5AD model Kenwood DC power source. Voltage fluctuations during electrolyses were automatically recorded using an integrated series Keithley 2700 digital millimeter data acquisition system. During electrolyses, homogenous mixing of supplied current and species in solution were provided by mechanical stirrer (Eurostar digital IKA Werke) equipped with polymer shaft and blade operating at constant speed of 1200 rpm. Samples drawn at specified time intervals are capped in pre-cleaned 20 or 40 mL glass and analyses followed immediately.
Fig. 1: Experimental set-up

**Analyses of phenol and its oxidation byproducts:** Concentrations of phenol and its aromatic oxidation intermediate compounds (i.e., benzoquinone, hydroquinone and catechol) were quantified using high performance liquid chromatography (WATERS 1525) equipped with photodiode array detector (WATERS 2996) and Spergel C18 reversed-phase column. The most suitable mobile phase was analytical grade methanol and deionized water (1/4, vol/vol) at a flow rate of 1 mL min⁻¹ and injection volume of 10 μL. The column temperature and pressure were 25°C and 195-2000 atmospheres, respectively, while the analytical wavelength of the Photodiode Array Detector (PDA) was set at 270 nm. Broader qualitative analyses were conducted using gas chromatograph (890N, Agilent) and mass selective detector (5973, Agilent). The column used was Fused silica capillary column 30 m by 2.55 μm while extraction solvent was HPLC grade dichloromethane.

The percent phenol converted to CO₂ and aromatic intermediates, relative to oxidized phenol were calculated from the TOC data based on stoichiometric mass balance, respectively, using the relationships in Eq. 1 and 2 (Iniesta et al., 2001; Tahar and Savall, 1998):

\[
CO_2(\%) = \left(\frac{[TOC]_0 - [TOC]_t}{[Phenol]_0 - [Phenol]_t}\right) \times 100
\]

\[
\text{Aromatics}(\%) = \left(\frac{\text{Aromatics}}{[\text{Phenol}]_0 - [\text{Phenol}]_t}\right) \times 100
\]

where, (TOC)_0, (TOC)_t, (Phenol)_0 and (Phenol)_t are the total organic carbon and concentration of phenol at times 0 and t, respectively. The term \([TOC]_t - [TOC]_0/6\) represents the mole number of phenol converted to CO₂. (Aromatics) is the concentration of aromatic intermediates. All concentrations are in mmol dm⁻³.

**Chemical oxygen demand (COD) and total organic carbon (TOC) analyses:** COD was determined with the aid of ECO25 Thermoreactor and 10 μL precision digital burette (BRAND, Germany) using closed-refluxed titrmetric method according to standard procedure as described by other authors (APHA, 1995; Jirka and Carter, 1975). TOC was analyzed using TOC-V CSH analyzer model (Shidmazu, Japan).
Average current efficiency (ACE) and specific energy consumption (SEC): ACE was estimated according to the rate of COD decay using Eq. 2 (Boye et al., 2002; Cominellis and Plattner, 1988; Cominellis and Pulgarin, 1991; Gandini et al., 2000; Morao et al., 2004; Panizza et al., 2001). SEC with respect to phenol removal was estimated from Eq. 4.

\[
ACE = \frac{(\text{COD}_0 - \text{COD}_{\text{eq}})}{8i_{\text{app}} \Delta t F V_c}
\]

\[
E_{\text{phenol}} = \frac{-\int_{t_1}^{t_2} \frac{V_c}{W} \, dt}{(3600)(1000)}
\]

where, COD$_0$ and COD$_t$ represent chemical oxygen demand at time zero and $t$ in mol O$_2$ m$^{-3}$, respectively, $F$ is the Faraday’s constant in C mol$^{-1}$, $V_c$ is reservoir volume in m$^3$, $i_{\text{app}}$ is applied current, $E_{\text{phenol}}$ is the specific energy consumption in kWh/g-phenol, $W$ is the weight of phenol removed at time $t$ and $V_c$ is the cell potential in Volts.

RESULTS AND DISCUSSION

Typical variations of cell voltage-time during electrolysis as illustrated in Fig. 2 show stability of the cell voltage throughout the experimental runs. This indicated that the anode had neither passivated nor its performances deteriorated, a common phenomenon associated with many electrode materials during electrolysis of phenols (Belaid et al., 2006; Canizares et al., 2009).

Effect of operating parameters on removal of phenol, TOC and COD: Typically, for 100 mg L$^{-1}$ initial phenol concentration, good removal of phenol, TOC and COD were obtained at pH 2 and 7 with an increase in current density having a slight effect on the removal efficiencies. Figure 3 shows under pH 2 and 1000 mg L$^{-1}$ Na$_2$SO$_4$ electrolysis condition, the removal efficiencies for phenol, TOC and COD were found to improve from 97.57, 89.88 and 83.31-99.18, 98.01 and

![Graph showing cell voltage variations](image)

Fig. 2: Typical variations of cell voltage with electrolysis time.
89.21% for an increase in current density from 30-60 mA cm\(^{-2}\), respectively. In complete contradiction to that, Fig. 4 shows very poor removals of TOC and COD at pH 12 in spite of the good corresponding removal of phenol. While, the effect of electrolyte concentration Fig. 5 shows reveals that slightly better removals of TOC and COD were achievable at Na\(_2\)SO\(_4\) dosage of 1000 mg L\(^{-1}\) compared to higher dosage of 3000 and 5000 mg L\(^{-1}\).

**Effect of initial phenol concentration on phenol, TOC and COD removals:** Figure 6, shows irrespective of the pH level, tremendous increase in removals of both TOC and COD were achieved when phenol initial concentration was increased from 100 to 500 and 1000 mg L\(^{-1}\). The total removal efficiencies for phenol, TOC and COD at the three levels of the initial phenol concentrations were (100, 95.40 and 99.26%), (5.44, 52.75 and 71.92%) and (15.97, 62.2 and 79.56%), respectively. With the exceptions of operating at initial pH 12, the phenol, TOC and COD decay profiles suggest a kinetically controlled process. Under such scenarios, steady state of

![Image of Figure 3](image-url)

**Fig. 3:** Influence of current density on removal of phenol, TOC and COD (100 mg L\(^{-1}\) phenol, pH 2 and 1000 mg L\(^{-1}\) Na\(_2\)SO\(_4\)).

![Image of Figure 4](image-url)

**Fig. 4:** Influence of pH on removal of phenol, TOC and COD (100 mg L\(^{-1}\) phenol, 30 mA cm\(^{-2}\) current density and 1000 mg L\(^{-1}\) Na\(_2\)SO\(_4\)).
Fig. 5: Influence of electrolyte concentration on removal of phenol, TOC and COD (100 mg L\(^{-1}\) phenol, pH 2 and 30 mA cm\(^{-2}\) current density)

Fig. 6(a-b): Effect of initial phenol concentration on phenol, TOC and COD removal efficiencies for 4.5 h electrolysis at (a) Initial pH 12, current density; 60 mA cm\(^{-2}\) and (b) Initial pH 2, current density; 30 mA cm\(^{-2}\).

Complete phenol oxidation were attainable regardless of experimental conditions. Conversely, at pH 12, the decay profiles clearly indicated that phenol conversion to other organic compounds dominated the process.

**Effect of initial phenol concentration on ACE and SEC:** ACE was found to increase with increase in initial phenol concentration at both applied current density of 30 and 60 mA cm\(^{-2}\) (Fig. 7a). At 100 mg L\(^{-1}\) initial phenol concentration, the maximum achievable ACE of about 10.5 and 1.55% increased to 85 and 76% when the initial phenol concentrations was increased by 10 folds under the two current densities, respectively. Moreover, the corresponding effect of initial phenol concentration on SEC depicted in Fig. 7b reveals that SEC drastically decreases with increase in initial phenol concentration. The SEC approximated at 387.7 and 1349 kW h kg\(^{-1}\) phenol under the two experimental conditions, was drastically reduced to as low as 18.98 and 74 kW h kg\(^{-1}\) phenol due to the 10-folds increments in the initial phenol concentration, respectively.
Fig. 7(a-b): Effect of initial phenol concentration on, (a) Average current efficiency (ACE) and (b) Specific energy consumption (SEC)

These discrepancies in ACE trends could be attributed to mass transport effects and unwanted side reactions (Gherardini et al., 2001; Panizza et al., 2001). At the higher initial phenol concentrations, more phenol molecules could reach the electrode surface and more supplied current was used for direct phenol oxidation via attack by the generated OH\(^{-}\) radicals. In this way, the amount of OH\(^{-}\) that was likely to be wasted and/or consumed in side reactions was reduced and hence the increased in current and removal efficiencies obtained at higher phenol concentrations (Zhi et al., 2003; Marselli et al., 2005).

Mechanism of electrochemical oxidation of phenol: The foregone observations suggest that the dominant mechanism for the electro-oxidation of phenol was the direct mechanism mediated by OH\(^{-}\) radicals. This mechanism for BDD electrode (inactive electrode) is a heterogeneous process that takes place within the vicinity of the surface of the BDD anode. As such the electro-generated OH\(^{-}\) radicals produced were speculated to be mainly responsible for the oxidation of phenol (Alfaro et al., 2006). However, other investigators reported that additional in-situ produced oxidants that can promote indirect electrolysis may also scavenge OH\(^{-}\) radicals thereby reducing the process efficiency (Fujishima et al., 2005; Zhi et al., 2003; Marselli et al., 2003; Murugananthan et al., 2008). Furthermore, Murugananthan et al. (2008) lamented that part of the electro-generated OH\(^{-}\) at BDD can be wasted under certain conditions by parallel parasite reactions such as \(\text{O}_2\) evolution and production of peroxodisulfate (\(\text{S}_2\text{O}_8^{2-}\)) and/or hydrogen peroxide as \(\text{S}_2\text{O}_8^{2-}\) and \(\text{H}_2\text{O}_2\) are weaker oxidants compared to OH\(^{-}\). In fact, these authors found such intermediary oxidants (\(\text{S}_2\text{O}_8^{2-}\) and \(\text{H}_2\text{O}_2\)) to have insignificant impacted on mineralization of some organic compounds under their experimental conditions. Marselli et al. (2003) also showed that the OH\(^{-}\) radicals were mainly responsible for oxidation on BDD anode and they indicated that the OH\(^{-}\) radicals is raw material for the generation of \(\text{H}_2\text{O}_2\) which could be further oxidize to \(\text{O}_2\). Similarly, \(\text{S}_2\text{O}_8^{2-}\) can decompose to \(\text{O}_2\), monopersulfate and \(\text{H}_2\text{O}_2\) (Fujishima et al., 2005). Thus, the formation of some in-situ generated oxidants can mediate secondary reactions that are capable of impairing the electro-oxidation process as they are prone to promoting unwanted side reactions that diminish both the mineralization and current efficiencies. Using sulfuric acid electrolyte and at applied current density of 23 mA cm\(^{-2}\), Serrano et al. (2002) showed that the main anodic reaction was oxidation of sulfate to \(\text{S}_2\text{O}_8^{2-}\) at higher concentration of sulfuric acid (>2 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\)) and
optimum operating temperature was 9°C, while lower concentration of the \( \text{H}_2\text{SO}_4 \) mainly led to the decomposition of the generated \( \text{S}_2\text{O}_8^{2-} \). Other investigators (Michaud et al., 2000) have shown that high current efficiency for peroxodisulfuric acid formation can be achieved with concentrated \( \text{H}_2\text{SO}_4 \) (7.5 mol dm\(^{-3}\)) at high current densities (200 mA cm\(^{-2}\)) and near room temperature of 25°C. Moreover, data reported by Vatistas et al. (2005) indicated that a high organic compound oxidation rate using \textit{in-situ} generated peroxodisulfate can be reached by increasing the reaction temperature from 25-70°C due to activation of the \( \text{S}_2\text{O}_8^{2-} \) at higher temperature. They showed that at sufficiently high temperature, the oxidation of sulfate ions (from \( \text{H}_2\text{SO}_4 \)) to peroxodisulfate is capable of suppressing the side reaction of oxygen evolution and the induced indirect oxidation in the bulk of the wastewater supplemented the direct process that take place on the BDD anode. Even though, effect of other sources of the \( \text{SO}_4^{2-} \) ions on activation of the \( \text{S}_2\text{O}_8^{2-} \) were not taken into account in any of these previous studies, however, it was speculated based on the forgone analyses that activation of electro-generated \( \text{S}_2\text{O}_8^{2-} \) from \( \text{Na}_2\text{SO}_4 \) didn’t occur within the experimental parameters covered in the present study.

**Analysis of mechanism of phenol oxidation:** The average regression coefficients (R\(^2\)) for respective calibration curves for phenol and its aromatic oxidation intermediates quantified using a set of HPLC instruments were all above 99.88%. A typical superimposed HPLC chromatograms for samples analyzed provided in Fig. 8 show benzoquinone, hydroquinone, catechol and phenol separated were well detected at eluding times of 1.581, 1.86, 2.296 and 3.055 min, respectively.

Figure 9 further explains the reason for the inability to mineralize the generated aromatic intermediates at the lowest phenol concentration (100 mg L\(^{-1}\)). The percent compositions of the byproducts depicted in Fig. 9b and 9c indicate that, the oxidation of phenol was initiated by generation of the aromatic intermediates which were further converted to other unaccounted byproducts phenol with very negligible conversion to CO\(_2\). This observation was physical noticed during electrolysis at pH 12 and 100 mg L\(^{-1}\) phenol concentration by the brownish color of the solutions which increased in darkness with treatment time and persisted till the end of the 210 min reaction time. In contrast, considering the plots in Figure 10 for 1000 mg L\(^{-1}\) phenol, the generated intermediates were continuously further oxidizable to CO\(_2\); with clear indication that complete oxidation of phenol was quite possible at longer treatment times.

Corroborating these observations, other authors (Gattrell and Kirk, 1990) suggested that polymers formation due to phenol oxidation could be avoided by operating at low pH, high potential and appropriete selection of electrode material. Similarly, Canizares et al. (2002) reported complete mineralization at pH 12 regardless of other experimental conditions using BDD anode. At initial COD of 1084-1170 mg L\(^{-1}\) (=500 mg L\(^{-1}\) phenol), Tian et al. (2006) also degraded phenol on Ti/BDD anode irrespective of initial pH. However, Comninellis and Pulgarin (1991) reported that operating at alkaline media (pH>9), low current density (<30 mA cm\(^{-2}\)), high temperatures (> 50°C) and high phenol concentration (>4700 mg L\(^{-1}\)) could favor passivating film formation rather than phenol oxidation.

**Proposed pathways for phenol oxidation:** Sample extraction for the GC-MSD qualitative analyses was performed based on standard method procedure (EPA Method 3510C). In spite of very small peaks for other unconfirmed, phenol (m/e = 94), benzoquinone (m/e = 108) and catechol or resorcinol (m/e = 110) and several organic acids that included propanoic acid butanoic acid, hydrazinecarboxylic acid, acetic acid, maleic, fumaric, oxalic, acetic and formic confirmed are the compounds have the highest presence in samples analyzed.
Fig. 8: Typical superimposed HPLC chromatograms showing retention times for phenol and its aromatic oxidation byproducts at different electrolysis times during electro-oxidation of phenol.

As stated earlier, initial phenol concentration and pH were found to be the main controllers of the pathways for oxidation of phenol. For that, the primary stage in the oxidation of phenol was speculated to be mainly pH-dependent as it is well known that the speciation of the phenol molecules takes place with respect to its inherent pKₐ in pure water solution. Phenol is slightly acidic in nature possessing pKₐ of 9.89. Thus, at pH > 9.89 phenol deprotonates yielding phenolate ions (i.e., phenoxy radicals) and hydroxyl ion. The relative proportion of phenol to the phenolate ions in aqueous phase is pH dependant, with basic pH (pH > 9.89) yielding more stable phenolate ions due to resonant stability of the phenolate ions in the range of that pH. At pH around 12, phenol in molecular form is expected to be totally converted to the phenolate ions. Other authors (Vermillion and Pearl, 1964) opined that even at pH < 9.89, the bi-electronic discharge of phenol molecules leads to the formation of phenonium cations. According to these authors, phenonium cations can react to form polymeric products in acidic medium while phenolate ions initiate polymerization in alkaline medium.

**Acid and neutral initial pH:** Figure 11 is the pathway for oxidation of phenol under these scenarios was initiated by phenol molecule losing an electron to produce phenonium cations.
Fig. 9(a-c): Profiles for oxidation of 100 mg L⁻¹ phenol at pH 12; 60 mA cm⁻²; 5000 mg L⁻¹ Na₂SO₄

Fig. 10(a-c): Profiles for oxidation of 1000 mg L⁻¹ phenol at pH 12; 60 mA cm⁻²; 5000 mg L⁻¹ Na₂SO₄
which favored the oxidation pathway A1→A2→A3→A4→A5 with complete oxidation of phenol quite possible regardless of initial phenol concentration. It was speculated that hydroxylation of ring of the phenonium cation (-A2) was responsible for the formation of the catechol, resorcinol and hydroquinone compounds which were further converted to benzoquinone (-A3) (Cui et al., 2009; Muruganathan et al., 2008), all these compounds were well detected in HPLC and GS-MS analyses. Subsequently, the hydroxylated compounds were further oxidized to form quinone compound by dehydrogenation reaction with OH· radicals (Canizares et al., 2005; Muruganathan et al., 2008). Consequently, the entire generated phenolic ring molecules were further oxidized and converted to ring cleavage small fragmented products via aromatic ring openings which produced the short chain aliphatic acids (-A4) (Canizares et al., 2005) as supported by the GC-MS qualitative analyses as well as the consistent pH decay observed during electrolyses. In addition, it was experimentally shown by other authors (Canizares et al., 2005; Muruganathan et al., 2008), that aliphatic acids are formed in the final step prior to CO₂ conversion when phenolic compounds undergo electrochemical oxidation process. The opening of the aromatic rings and subsequent oxidation of the succeeding aliphatic compounds generated was considered to be the final limiting step towards successful completion of oxidation of phenol to CO₂ (-A5).

**Initial basic pH:** For basic pH as depicted in Fig. 11, the possible initial phenol concentration dependent pathways postulated with all the routes mediated by phenoxy radicals formation (-B1)
from phenol speciation. At higher initial concentrations, the phenoxy radical underwent a second
electron transfer leading to the formation of phenonium cation which also predominantly followed
the pathway B2-A2-A3-A4-A5 as in the case for acidic and basic initial pH. Conversely, at lower
initial phenol concentration, based on the data presented earlier, the pathway led to polymerization
rather than oxidation of phenol. Consequently, in this case, the phenoxy radical capable of reacting
with either the parent phenol molecule or another generated radical by C-C and/or C-O coupling
mediated the generation of dimers (+B4) which led to formation of more complex polymers by
further coupling reactions (+B5) (Tahar et al., 2009; Tahar and Savall, 2009; Wang et al., 1998).
Under these scenario, three possible pathways leading to total hindrance of phenol oxidation are
postulated as B1-B4-B5, B1-B2-A2-B3-B5 and B1-B2-A2-A3-B3-B5, with the later pathway
been the predominant as all the aromatic compounds were found in all the analyzed samples. The
possibility that this pathway occurs only in the range of pH greater than phenol pK_a is a subject
for further investigations.

CONCLUSIONS

In this present study, the influences of current density, initial pH, initial phenol concentration
and Na_2SO_4 electrolyte dosage on the electro-oxidation of phenol using Boron-doped Diamond
(BDD) and graphite cathode were investigated. Based on the results obtained, it was concluded that
within the investigated experimental conditions, the removals of phenol, TOC and COD were
mainly influenced by pH and initial phenol concentration with current density and Na_2SO_4.
Complete oxidation of aqueous phenol to CO_2 was achievable under initial acidic and neutral pH
conditions regardless of initial concentration of phenol; while at basic pH and low phenol
concentration, conversion of phenol to its aromatic and other polymerization byproducts hindered
phenol oxidation. Electro-oxidation of phenol was kinetically controlled process dominated by direct
oxidation process mediated by the electro-generated OH^- produced at the BDD anode surface.
Apparently, indirect oxidation in the bulk solution expected from in-situ generated oxidants
(such as peroxodisulfate, S_2O_8^{2-} and hydrogen peroxide, H_2O_2) didn't occur to improve the process
efficiency. The pathways for phenol oxidation were mainly initial pH and initial phenol
concentration dependent with effective phenol oxidation initiated by speciation of phenol molecules
and subsequent generation of aromatic intermediates which were further converted to aliphatic
acids. The final step in the pathway involved the destruction of the aliphatic acids to CO_2.

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