Anodic Degradation of 2-Chlorophenol by Carbon Black Diamond and Activated Carbon Composite Electrodes

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A R T I C L E   I N F O

Article history:
Received 13 July 2015
Received in revised form 13 August 2015
Accepted 13 August 2015
Available online 21 August 2015

Keywords:
2-Chlorophenol
20CBD electrode
Activated carbon composite electrode
Electro-degradation

A B S T R A C T

A carbon black diamond composite electrode with 20% carbon black (20CBD) and activated carbon composite (ACC) electrode were prepared and used as anodes for 2-chlorophenol electro-oxidation. The electro-oxidation behaviors of 200 mg/L 2-chlorophenol on 20CBD and ACC anodes were investigated by cyclic voltammetry in aqueous solutions of 0.5 M H2SO4 (pH 0.55) and 0.25 M Na2SO4 (pH 7). Results indicated that the 20CBD and ACC electrodes are more active at low pH than at high pH and that no oxidation peak appears on the ACC electrode. The performance of the 20CBD and ACC electrodes during degradation of 200 mg/L 2-chlorophenol was investigated in an aqueous solution of pH 3 with 0.25 M Na2SO4 as the supporting electrolyte and applied current density of 30 mA/cm². Results showed that the 20CBD electrode produced the best degradation rate, COD removal efficiency, and current efficiency. The degradation efficiencies of the 20CBD and ACC electrodes after 6 h were 96% and 82.5%, respectively. The effects of solution pH, current density, and supporting electrolyte on the performance of the 20CBD were further investigated, and results showed that higher degradation rates are obtained at lower pH and with Na2SO4 as the supporting electrolyte. Removal efficiency also increased with increasing current density.

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1. Introduction

Chlorophenols are considered very toxic substrates with strong resistivity to biological degradation; thus, these compounds may cause serious environmental contamination [1]. 2-Chlorophenol has been classified as a priority pollutant by the Environmental Protection Agency [2]. Many uses for chlorophenols, such as in pesticides, herbicides, pharmaceuticals, dyes, and cellulose plants [1,3], have been reported. Given the strong toxicity nature and resistivity of these compounds to biodegradation, research efforts have been exerted to develop suitable techniques that can mineralize the chlorine and carbon atoms in chlorophenols. A number of techniques have been used to remove chlorophenols in wastewater, including advanced oxidation processes [4–6], adsorption [7,8], and photochemical degradation [9,10]. Among these technologies, electro-degradation of toxic and non-biodegradable chlorophenols has gained significant research attention because the technique features easy implementation, high efficiency, amenability to automation, and environmental compatibility (i.e., no requirement of chemical addition) [11]. One of the most important factors affecting the electro-degradation process is the nature of the electrode (anode) used in the process [12]. Many conventional anode materials, such as SnO2 and PbO2 [13], platinum [14], Sn–Sb–Ni [15], and BDD [16,17], have been tested for chlorophenol electro-degradation. Different materials, such as F-doped PbO2 [18], Ti-based oxide [19,20], Ti/RuO2/MnO2 [21], Erchitosan-PbO2 [22], and Pd/Ptfoam-Ni [23], have also been improved as anodes for electro-degradation of chlorophenol substrates. Most previous studies have attempted to propose an efficient electrode with suitable electrochemical properties, long service life, and cost. Electro-oxidation of phenol, chlorophenols, and many aromatic compounds produces hydroquinone, benzoquinone, and carboxylic acid substrates. Thus, chlorophenol must be electro-oxidized beyond the benzoquinone stage for adequate treatment because these intermediates are more toxic than chlorophenols themselves [24]. Chlorophenol oxidation occurs until the aromatic ring breaks, carboxylic acids form, and most acids are mineralized to CO2, which requires a suitable amount of quiz-free hydroxyl radicals electro-generated at the electrode surface. The amount of hydroxyl radicals generated depends on the electrochemical properties of the anode materials. Electrodes with a higher oxygen evolution potential can produce larger amounts of hydroxyl radicals and achieve suitable current efficiencies. A carbon black diamond (CBD) electrode was proposed for the first time by our laboratory for organic pollutant oxidation. This electrode had an inert surface and suitable oxygen evolution potential that depended on the CB percentage in the electrode. The potential window for a CBD electrode with 5% CB is

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http://dx.doi.org/10.1016/j.electacta.2015.08.062
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similar to that of a BDD electrode; however, decreases in potential window with increasing CB percentage, such as in 40% CB, were observed [25]. Benzoquinone electro-degradation on CBD electrodes has been investigated. Results reported for a 20% CBD electrode (20CBD) show a removal efficiency of 96.5% for 200 g/L benzoquinone after only 20 min of degradation [26]. Also, benzoquinone did not appear as an intermediate during phenol electro-degradation on the same electrode [25].

A 20CBD electrode is proposed in the present study for electrode-degradation of 2-chlorophenol, and its performance is compared with that of an activated carbon composite (ACC) electrode prepared as an anode for organic substrate oxidation using a novel method. The effects of mean parameters, such as pH, current density, and supporting electrolyte, are also investigated, and a pathway and mechanism of 2-chlorophenol degradation are proposed. To the best of our knowledge, anodic degradation of 2-chlorophenol is rarely studied in the open literature and this work is the first of its kind to compare the performance of CBD and ACC for this purpose.

2. Experimental

2.1. Electrode preparation

A disk of carbon black diamond composite electrode with 20% carbon black has been prepared with surface area 2.27 cm². Whereas, diamond powder (98.3% purity and average particle size 6 nanometer, Sigma-Aldrich) was mixed carefully with a precise percent of carbon black Super P (99% purity, average particle size of 13 nanometer and 550 m²/g specific surface area, Alfa Aesar). Powder mixture have been mixed with suspension (60 wt%) in water (Sigma-Aldrich) polytetrafluoroethylene as the binder and 1.3- propanediol (98% purity, Sigma-Aldrich) and then dried as described in previous work [25]. Activated carbon composite (ACC) electrodes with surface areas of 2.27 and 9.1 cm² were prepared by mixing 80% charcoal activated carbon (99.5% purity, average particle size 100 µm and 950m²/g specific surface area, Sigma-Aldrich) with 20% CB. The powder mixture was added to a liquid mixture of polytetrafluoroethylene and isopropyl alcohol with a 1:2 ratio. The electrode paste was kneaded neatly and then dried in an oven using drying sequence of 100 °C for 2 h, 180 °C for 1 h, 250 °C for 1 h, and at least 350 °C for 30 min to complete the sintering process and increase the electrode hardness.

2.2. Electrochemical oxidation behavior

Voltammetric experiments were conducted in one compartment of a 100 mL glass cell at 25°C to investigate the electrochemical oxidation behavior of 2-chlorophenol on the 20CBD and ACC electrodes. A solution of 0.5 M H₂SO₄ (97% Merck Pro Analysis) as a blank solution, and two aqueous solutions of 200 mg/L of 2-chlorophenol (99.5% Merck Pro Analysis) were prepared. One solution was composed of 0.5 M H₂SO₄ at pH 0.5, and another solution was composed of 0.25 M Na₂SO₄ at pH 7. Milli-Q water was used to prepare the solutions. A platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. Electrochemical active surface areas of the 20CBD and ACC electrodes were estimated by Chronoamperometry technique using an aqueous solution of 0.1 M K₂HPO₄ containing 5 mM K₃Fe(CN)₆. Effective area of the working electrodes were obtained by the Cottrell equation [27].

\[
I = \frac{nFAD^{1/2}C_0}{2RT^{1/2}}
\]

where \( I \) is the current (A), \( n \) is number of electrons, \( A \) is the active area of electrode (cm²), \( D \) and \( C_0 \) are the diffusion coefficient (6.20 × 10⁻⁶ cm²/s) and bulk concentration of K₃Fe(CN)₆ (mol/cm³). F is the Faraday constant (96.487 C/mol); while the remaining parameters have their usual meanings. The electrochemical experiments on 20CBD electrode and ACC electrode were performed by Autolab Metrohm potentiostat with NOVA 1.10 software.

2.3. Electro-degradation of 2-chlorophenol

An electrochemical cell with 100 mL of 200 mg/L 2-chlorophenol solution, 0.25 M Na₂SO₄, 3 mg/L (0.05 M) NaCl, and 0.1 M Na₂SO₄ + 3 mg/L NaCl as the supporting electrolyte was used for 2-chlorophenol degradation experiments on the 20CBD and ACC electrodes. The experiments were conducted at applied current densities of 8, 15, or 30 mA/cm² and pH 3, 7, or 11 at 25°C temperature. ISO-TECH programmable power supply IPS 3202 was used, whereas stainless steel cathode and C-MAG HS 7 magnetic stirrer were used for solution mixing.

2.4. Analysis method

The decomposition of 2-chlorophenol during electrolysis was examined by high performance liquid chromatography (HPLC) using an Agilent technology 1200 series. C18 column (4.6 mm × 250 mm × 5 µm) at 20°C was used as the separation column for 2-chlorophenol, hydroquinone, benzoquinone and other aromatic compounds. The eluent was used 60% acetonitrile/ 39.9% water + 0.1% H₃PO₄ (v/v), the injection volumes were 20 µL and eluent flow rate was 1 mL/min. The detection wavelength was set at 280 nm. Aliphatic acid intermediates were identified by using the mobile phase 25% methanol/10 mM NaH₂PO₄ solution (pH 2.7) and 0.7 mL/ min flow rate. The injection volume were 10 µL and the samples were filtered through a 0.25 µm membrane filter. Gas chromatography coupled with mass spectrometry (GC/MS) was used to identify the aliphatic acids that were generated by the 2-chlorophenol degradation. Samples were esterified and then extracted as describe by Li et al. [28]. The GC/MS (HP6890, Agilent) used a capillary column (HP-624, 25.0 mm × 0.25 mm × 1.0 mm, Agilent) followed by detection with an MS (Netwaik 5973,Agilent). The temperature program starts at 70°C and rises at a rate of 20°C/min until to 260°C. Holding time was 2 min for each increment. Helium was used as the carrier gas with constant flow rate of 54 mL/min and sample injection sample was 1 mL. The chemical oxygen demand (COD) was measured by the dichromate method. The suitable sample for measurement of COD was introduced into prepared solution of 0–1500 mg/L and 0–150 mg/L, including mercuric sulfate, H₂SO₄ and potassium dichromate and the mixture was then brooded for 2 h at 150°C in a HACH / DRB 200 thermo-reactor for COD and thermal digestions. COD concentration was measured color-metrically using an ORION A03700 spectrophotometer.

Current efficiency (CE) for electro-oxidation has been estimated by COD values, using the following relationship.

\[
CE(\%) = \frac{FV}{81.48 \Delta T(COD_2 – COD_1) \times 100}
\]

Where COD and COD₁ are the chemical oxygen demands at times t = 0 and t (in gO₂/L), respectively, and I is the current (A), F is the Faraday constant (96487 C/mol), V is the volume of the electrolyte (L) and 8 is the equivalent mass of oxygen (g equiv⁻¹).

3. Results and discussion

3.1. Anodic oxidation behavior of 2-chlorophenol on the 20CBD and ACC electrodes

Prior to the electro-degradation study, the electro-oxidation behavior of 2-chlorophenol was studied on 20CBD and ACC...
electrodes using a cyclic voltammeter in aqueous solutions of 0.5 M H$_2$SO$_4$ (pH 0.5) and 0.25 M Na$_2$SO$_4$ (pH 7) with and without 200 mg/L 2-chlorophenol and a sweep rate of 100 mV/s. Fig. 1(a) shows the cyclic voltammogram of the 20CBD electrode surface. Anodic peak potentials of 1.1 and 1.35 V were respectively obtained in aqueous solutions of 0.25 M Na$_2$SO$_4$ (pH 7) and 0.5 M H$_2$SO$_4$ (pH 0.5). Several studies have reported that anodic peak potentials shift toward lower potential values with increasing solution pH [29,30]. Anodic oxidation of 2-chlorophenol on 20CBD is clearly favored in acid medium. The anodic peak current in the 0.5 M H$_2$SO$_4$ (pH 0.5) solution was 10.5 mA, higher than that obtained in the 0.25 M Na$_2$SO$_4$ (pH 7; 6 mA). Fig. 1(b) shows the cyclic voltammogram of the ACC electrode surface. Oxidation peaks were absent in both aqueous solutions. This result may be attributed to two reasons: (1) The 2-chlorophenol oxidation peak potential and water discharge occur at the same region and cannot be separated [31]; and (2) direct electron transfer does not occur during oxidation and electro-degradation of 2-chlorophenol on the ACC electrode since it proceeds through indirect electro-oxidation [32]. Despite the absence of oxidation peaks on the ACC electrode, significant increases in anodic current were observed in both solutions containing 2-chlorophenol compared with the blank solution. The increase in anodic current in the low pH (pH 0.5) solution was also higher than that in the neutral solution (pH 7), which indicates that 2-chlorophenol electro-oxidation on the ACC electrode also favors the acid medium.

![Fig. 1. Cyclic voltammetry of 20CBD electrodes (a) and ACC electrode (b) in blank aqueous solution of 0.5 M H$_2$SO$_4$ and aqueous solutions of 0.5 M H$_2$SO$_4$ (pH 0.5) and 0.25 M Na$_2$SO$_4$ (pH 7) containing 200 mg/L 2-chlorophenol. Scan rate 0.1 V/s and 25 °C temperature.](image)

3.2. 2-Chlorophenol electro-degradation

Fig. 2 shows the electro-degradation trend of 200 mg/L 2-chlorophenol in 0.25 M Na$_2$SO$_4$ as the supporting electrolyte on the 20CBD and ACC electrodes at 30 mA/cm$^2$ and 25 °C. The ability of the 20CBD electrode to oxidize the 2-chlorophenol was clearly higher than that of the ACC electrode, and the degradation efficiencies of 2-chlorophenol on the 20CBD and ACC electrodes after 6 h of electrolysis were 96% and 82.5%, respectively. Furthermore, Fig. 3 shows the COD decay on the 20CBD and ACC electrodes after 8 h of reaction were 80% and 72%, respectively. Electro-oxidation of organic pollutants in electrochemical processes is related to the hydroxyl radicals generated by water decomposition on the electrode surface [33]. The stronger degradative ability of the 20CBD electrode compared with that of the ACC electrode may be attributed to the amount of electro-generated hydroxyl radicals on the surface of the former, which is greater than that on the latter.

Fig. 1 (blank solution runs) shows that the evolution of oxygen potential on the 20CBD electrode is 1.85 V versus Ag/AgCl; this value is higher than that on the ACC electrode (0.65 V vs. Ag/AgCl). This difference reveals the significance of generating larger amounts of hydroxyl radicals [34] on the 20CBD electrode compared with that on the ACC electrode. The electro-degradation results of 2-chlorophenol were subjected to kinetic equation analysis of different reaction orders. Suitable fittings were found for the pseudo-first order reaction, and the straight lines obtained for the 20CBD and ACC electrodes with an initial concentration of 200 mg/L are presented in the inset of Fig. 2. The pseudo-first order rate constants calculated for the 20CBD and ACC electrodes were 0.51873 and 0.26054, respectively, which confirms that 2-chlorophenol degradation occurs more extensively on the 20CBD electrode than on the ACC electrode. During the first hour of electrolysis on the 20CBD electrode, nearly 50% of the 2-chlorophenol according (Fig. 2) and 47.5% of COD according (Fig. 3) in the solution were decayed. However, incineration of the rest of the 2-chlorophenol and its intermediates required over 7 h of reaction. Electro-oxidation rates on the ACC electrode during electrolysis were fairly constant for the first 3 h of electrolysis. Such behaviors on the 20CBD and ACC electrodes demonstrate that the current efficiency decreases on the 20CBD electrode from 82% at the first hour of reaction time to 54% at the second hour as

![Fig. 2. The effect of the electrode materials on 2-chlorophenol anodic degradation with time (the pH: 3; the constant current density: 30 mA/cm$^2$; the initial concentration of 2-chlorophenol: 200 mg/L; volume: 100 mL; supporting electrolyte (Na$_2$SO$_4$) concentration: 0.25 M; temperature 25 °C). Inset fig. is corresponding kinetic analysis for different electrode.](image)
presented in the inset of Fig. 3, whereas that on the ACC electrode decreases from 43% to only 38% under the same conditions. The decrease in 2-chlorophenol and its intermediate concentration after the first hour of reaction on the 20CBD electrode subsequently decreases the reaction rate and current efficiency. When the ACC electrode surface area was increased (LACC) to fourfold that of the 20CBD electrode, electro-degradation rates and degradation performance similar to those achieved on the 20CBD electrode were obtained under the same operating conditions (i.e., current density, pH, supported electrolyte, and temperature). While the lower price of AC electrodes in comparison with diamond electrodes means that increasing the surface area of the ACC electrode costs less than producing a 20CBD electrode, the use of electrodes with larger surface areas will increase conduction in the electrochemical system as well as investment costs to obtain parallel systems. The active areas of 20CBD and ACC electrodes have been estimated by chronoamperometric technique and using Cottrell equation. The active areas of ACC and 20CBD electrodes were 34.7 cm² and 14.1 cm² respectively. The higher active area of ACC electrode compared to 20CBD electrode is due to the higher specific surface area of activated carbon particles used in preparation of the ACC electrode, which are responsible to provide more active sites. The active electrochemical areas of 20CBD and ACC electrodes are higher than the geometric area up to 6.2 and 15.28 times respectively. Although, the increase in electrochemical active area of ACC electrode was enhanced the anodic oxidation process. However, the removal rate of 2-chlorophenol and COD decay on 20CBD was the higher. This may be due to the amount of hydroxyl radicals produced on 20CBD electrode surface, which is higher than that of produced on ACC electrode surface.

3.2.1. pH effect

Electrolyte pH is an important variable to consider during electrochemical oxidation of organic pollutants. Several authors report that the pH does not exert significant effects on the oxidation process of organic pollutants [35,36]; other authors, however, indicate that pH exerts a significant influence [37–39] and suggest that the effect of pH largely depends on the nature of the pollutant and supporting electrolyte. Three pH values (i.e., 3, 7, and 11) were selected and applied to the electro-oxidation system with 0.25 M Na₂SO₄ and 30 mA/cm² to study the effect of pH on electro-degradation of 200 mg/L 2-chlorophenol. Fig. 4 shows that the electro-degradation efficiencies of 2-chlorophenol at pH 3, 7, and 11 after 8 h of reaction are 98.5%, 85%, and 50%, respectively. Electro-oxidation of 2-chlorophenol clearly favors the acid medium. This result is consistent with the results observed through cyclic voltammetry of 2-chlorophenol on the 20CBD electrode (Fig. 1(a)). Electro-oxidation of phenolic compounds has been investigated by many researchers using different electrode materials; most of these researchers report that the electrode is more active in low-pH electrolyte than in high-pH electrolyte [40–43]. This behavior may be attributed to many reasons. First, electrode fouling by deposition of a passive film on the electrode surface during phenolic compound oxidation occurs less extensively in low-pH electrolytes than in high-pH ones [44–46]. As well, the electrode current efficiency in acid medium is higher than that in basic medium [44], and the charge transfer process is faster at low pH than at high pH [43]. The oxidative potential of hydroxyl radicals also increases as pH decreases [47], thereby justifying the high reaction rate observed at acid pH.

3.2.2. Effect of applied current density

The electro-degradation trend of 200 mg/L 2-chlorophenol on the 20CBD electrode was examined as a function of electrolysis time with varying applied current densities (i.e., 8, 15, and 30 mA/cm²). Fig. 5 shows that the degradation rate of 2-chlorophenol and COD decay occur faster with increases in applied current density. For example, removal efficiencies of 54%, 60%, and 81% were obtained after 3 h of electrolysis, and COD decay rates of 37.5%, 48%, and 66.6% were observed at applied current densities of 8, 15, and 30 mA/cm², respectively. Therefore, electrochemical reaction with these parameters is not controlled by the mass transfer of 2-chlorophenol molecules toward the surface of the 20CBD anode. The increase in current density accelerates generation of hydroxyl radicals, which can maximize the incineration of organic pollutants. A competing reaction, the oxygen generation reaction, occurs on the anode surface in the electrochemical cell during electrolytic discharge of water as a secondary anodic reaction [33]. Thus, the increase in applied current density consistently causes increases in the rate of the secondary anodic reaction (oxygen generation reaction), which decreases the current efficiency [34,48]. The inset of Fig. 5(a) shows that the current efficiency at 8 mA/cm² is 96% for the first hour of electrolysis but decreases to only 88% and 82% when the applied current density is increased to 15 and 30 mA/cm², respectively.

Fig. 3. The effect of the electrode materials on COD decay with time (the pH: 3; the constant current density: 30 mA/cm²; the initial concentration of 2-chlorophenol: 200 mg/L; volume: 100 mL; supporting electrolyte (Na₂SO₄) concentration: 0.25 M; temperature 25°C). Inset fig. is the current efficiency of 20CBD and ACC electrodes.

Fig. 4. The effect of the pH on 2-chlorophenol degradation with time over 20CBD electrode (the constant current density: 30 mA/cm²; the initial concentration of 2-chlorophenol: 200 mg/L; volume: 100 mL; supporting electrolyte (Na₂SO₄) concentration: 0.25 M; temperature 25°C).
Effect of the supporting electrolyte

Supporting electrolyte materials, such as Na₂SO₄, KCl, Na₂NO₃, and NaCl, are used during electro-oxidation to increase electrolyte conductivity, decrease energy consumption, and organize mass transport by electrical migration and cell conductivity. Peroxodisulfate, Cl₂, hypochlorite, and hydrogen peroxide are distinct oxidants that can also be electro-generated on the electrode surface [50]. These generated radicals react with organic pollutants, leading to an increase in the global degradation of organic substrates. Using NaCl as the supporting electrolyte generates Cl• or ClO• ions on the anode surface; these ions are considered strong oxidants that can destroy organic pollutants when used at suitable concentrations in a neutral or high pH medium [51]. The major drawback of using NaCl as a supporting electrolyte is the possibility of producing chlorinated organic substrates during electrolysis [51–54]. Many reactions can also occur in parallel to electro-oxidation, thereby decreasing the efficiency of the electro-degradation process [51]. Using Na₂SO₄ as the supporting electrolyte forms peroxodisulfate, which is considered a strong oxidant that can enhance the electro-degradation process, on the anode surface [22,55].

The performance of the 20CBD electrode during electro-degradation of 200 mg/L 2-chlorophenol was investigated using different supporting electrolytes (i.e., NaCl, NaCl + Na₂SO₄, and NaCl + Na₂NO₃) in an aqueous solution of pH 3 and applied current density of 30 mA/cm². Fig. 6 shows that 0.25 M Na₂SO₄ is a more active supporting electrolyte than either 0.05 M NaCl + 0.1 M Na₂SO₄ or 0.05 M NaCl; in fact, the removal efficiencies of Na₂SO₄, NaCl + Na₂SO₄, and NaCl were 96%, 88%, and 78.5% respectively. Most previous studies report that the use of NaCl as a supporting electrolyte enhances the degradation efficiency of the electro-oxidation system. Conversely, other studies reveal that the organic electro-degradation process favors Na₂SO₄ rather than NaCl as the supporting electrolyte [56–58] and that the use of NaCl at concentrations of approximately 3 mg/L (0.05 M) decrease removal efficiency [52,59]. Degradation of chloro-organic substrates, such as chlorophenols, releases chloride ions into the electrolyte during electrolysis, thereby increasing the chloride ion concentration and decreasing degradation efficiency [57]. The likelihood that hydroxyl radicals, which are strong oxidants generated during oxidation, will react with Cl• ions and generate less reactive chloro-radical species is also high [60]. Such a reaction lowers the hydroxyl radical amount available [58,61] and decreases the efficiency of organic decomposition. All of these

15 mA/cm² and 30 mA/cm², respectively. The initial concentration of organic molecules and applied current density are notably related. The electrochemical reaction occurring at high initial concentrations decreases the effect of applied current density on the reaction rate and changes the reaction status from a charge transfer-controlled reaction to mass transfer-controlled one [49]. The first hour of electrolysis according to Fig. 5(a) shows that the increase in current density from 15 mA/cm² to 30 mA/cm² does not exert significant effects on the electro-degradation rate of 2-chlorophenol. The controlling step during this reaction period is clearly the mass transfer of organic molecules because the initial concentration can be considered fairly high. Electrolysis process with three different potentials like 1.4 vs. Ag/AgCl (oxidation potential), 1.9 V vs Ag/AgCl (oxygen evolution potential) and 4 V vs Ag/AgCl (high potential) have been applied to study the effect of electrode potential on the degradation of 200 g/L 2-chlorophenol in aqueous solution of 0.25 M Na₂SO₄ on 20CBD electrode. Low degradation rate of 2-chlorophenol was observed at 1.4 V vs. Ag/AgCl (oxidation potential) and 1.9 V vs. Ag/AgCl (oxygen evolution potential). However, on the other hand the degradation rate increased about more than 6 times using high potential, 4 V vs. Ag/AgCl compared to 1.4 V vs. Ag/AgCl and 1.9 V vs. Ag/AgCl. The higher degradation rate at high potential has been attributed to the higher oxygen evolution at high electrode potential, which led to higher mass transfer of 2-chlorophenol or enhanced the electrode surface ability against passivation [29].
reasons can justify the reduction in degradation efficiency observed when NaCl is used as the supporting electrolyte during 2-chlorophenol degradation on the 20CBD electrode.

3.3. Mean intermediates and proposed reaction pathway

The majority of the reaction products generated by electro-degradation were identified by comparing their retention times and mass spectra with those reported for pure standards through HPLC. GC/MS was also used to identify electrochemical reaction intermediates and confirm previous results. Hydroquinone, benzoquinone, and a mixture of carboxylic acid substrates, including maleic acid, fumaric acid, oxalic acid, and formic acid, were the main intermediate compounds identified during electrolysis. Fig. 7 shows the suggested mechanism of 2-chlorophenol electro-oxidation: The first step of the incineration process removes the chlorine atom from 2-chlorophenol, after which hydroxyl radicals attack the compound to generate hydroquinone. Hydroquinone molecules are subsequently dehydrogenated to benzoquinone. The availability of excess hydroxyl radicals breaks the benzoquinone ring to produce aliphatic carboxylic acids, such as maleic and fumaric acids. Further oxidation of maleic acid produces oxalic acid, the subsequent oxidation of which forms formic acid and, finally, carbon dioxide. This proposed pathway is similar to other chlorophenolic substrate decomposition reaction pathways [16,20,21,62].

4. Conclusion

The electro-oxidation behavior of 2-chlorophenol on 20CBD and ACC electrodes was investigated by cyclic voltammetry in acidic and neutral aqueous solutions. The anodic oxidation peak current of the 20CBD electrode in acid solution was higher than that in neutral solution, which reveals that 2-chlorophenol electro-oxidation is easier to achieve at low pH than at high pH. Conversely, no oxidation peak appeared on the ACC electrode in both aqueous solutions. 2-Chlorophenol electro-degradation rates were higher on the 20CBD electrode than on the ACC electrode; the 2-chlorophenol removal efficiencies of the 20CBD and ACC electrodes after 6 h of oxidation were 96% and 82.5%, respectively. The COD decay (80%) and current efficiency (82%) obtained on the 20CBD electrode were also higher than those obtained from the ACC electrode. Increasing the surface area of the ACC electrode by fourfold compared with that of the 20CBD electrode equalized the degradation rate of both electrodes. 2-Chlorophenol electro-degradation on the 20CBD electrode favored the acid medium, and removal efficiency of 98.5%, 85%, and 50% were observed at pH 3, 7, and 11, respectively, after 8 h of electrolysis. 2-Chlorophenol degradation rates increased with increasing current density. Na₂SO₄ as the supporting electrolyte promoted the electro-oxidation reaction more extensively than either NaCl alone or a mixture of Na₂SO₄ and NaCl.

Acknowledgement

This work was carried at the Center for Separation Science and Technology (CSST) and was financed through the High Impact Research Grant Project No.U.M.C/HIR/MOE/ENG/43.

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