

## Electrochemical Degradation of Benzoquinone in a Flow through Cell with Carbon Fibers

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The anodic degradation of benzoquinone(BQ), a model compound for wastewater treatment was carried out using a home-made flow-through electrochemical cell with carbon fibers. To optimize the controlled current electrolysis condition of an aqueous BQ solution, the experimental variables affecting the degradation of BQ, such as the applying current, pH, reaction time, and flow rate of the BQ solution were examined. The degradation products of the oxidation reaction were identified by High Performance Liquid Chromatography and Inductively Coupled Plasma Atomic Emission Spectrometer. Low molecular weight aliphatic acids, and CO<sub>2</sub> were the major products in this experiment. The removal efficiency of BQ from the solution increased with the applying current and time. 99.23% of  $1.0 \times 10^{-2}$  M BQ was degraded to aliphatic acids and CO<sub>2</sub> when the applying current is 175 mA in a 12 hr electrolysis.

**Key Words** : Degradation of benzoquinone, Flow-through electrochemical cell, Carbon fibers electrode

### Introduction

The treatment of organic compounds as contaminants in wastewater is a subject of great interests, due to the ecological and health care issues. The industrial wastewater contains organic pollutants, especially, aromatic hydrocarbons that can be either toxic or resistant to the most aquatic microorganisms and mammals.<sup>1</sup> For example, aromatic amines, such as aniline and m-nitrosoaniline can react readily to convert hemoglobin to methamoglobin in the blood, thereby preventing the uptake of oxygen. These aromatic amines are commonly produced as by-products in the petroleum, paper, coal, and chemical industries.<sup>2</sup> Beside of this, phenols are found in the wastewater of the most processes that involve aromatic organic chemicals. The common contamination sources are pulp, paper mills, petrochemical refineries, herbicide, some plastics and glue manufacturing, and coke plants.<sup>3,4</sup> Many papers have reported on the treatment of these aromatic hydrocarbons contained in industrial and residential wastewater that are resistant to biological, ozone treatment and other chemical method.<sup>5-8</sup> Some studies have focused on determining the chemical or electrochemical oxidation conditions required to reach one of the following objectives: (a) to modify the chemical structure of an organic molecule making it more biodegradable; (b) to partially destroy the molecule to decrease its toxicity; (c) to completely oxidize the molecule to CO<sub>2</sub>, or other inorganic products.<sup>9-11</sup>

Electrochemical oxidation is currently accepted as the oxidative treatment of certain organic compounds<sup>12</sup> and has been utilized in the treatment of effluent streams in such a way that their Chemical Oxygen Demand (COD) was reduced or industrial toxic species were destroyed.<sup>13-15</sup> For the electrochemical treatment of phenols in water, the anodic oxidation of phenols with Ti/SnO<sub>2</sub> or Ti/IrO<sub>2</sub> electrodes have

been carried out in the presence of NaCl,<sup>16</sup> which catalyze an oxidation reaction by the participation of electrogenerated ClO<sub>4</sub><sup>-</sup> and it has been applied to wastewater treatment via the use of PbO<sub>2</sub> packed bed anodes.<sup>17</sup> In addition, the various anode materials such as noble-metal oxides and antimony-doped tin oxides have been employed for the oxidation of benzoquinone (BQ) and maleic acid at a high anodic potential. The efficiency of BQ oxidation was found to be depended on the properties of the anode materials.<sup>18</sup> Thus, the use of adequate anode materials for electrolysis is essential, because the efficiencies of degradation of organic materials depend on the nature of such materials. The most commonly used anode materials for the electrochemical treatment of organic pollutants are metal oxides such as, lead, modified lead oxide,<sup>19</sup> tin, and/or antimony because of economical requirements and the adsorption of products to the electrode surface are minimized. However, these materials would not be acceptable for wastewater treatment due to their inherent toxicity, the limited lifetime, and the price of anode materials.<sup>20</sup> The problem of mass-transfer limitations of a very dilute reactant can be solved by the use of an extended-surface and packed electrode.<sup>21</sup> Moreover, the anode materials showing a high current efficiency should be used for electrochemical treatments.

In the present study, a flow-through electrochemical cell (FTEC) packed with carbon fibers, was used to electrolyze BQ and optimize the parameters for its electrolysis, which is more stable than phenol.<sup>22</sup> Such electrodes are not only promoting for high mass-transfer rates, but also providing high surface areas within a compact volume without further contamination. However, it requires the separation between the electrolyte and the degradation solutions to achieve both high mass-transfer rate and high surface areas. Thus we designed the FTEC for the efficient treatment of BQ. The experimental parameters to affect the degradation efficiency

were optimized the applied input current, pH, reaction time, and flow rate. After the electrolysis of BQ, Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) and High Performance Liquid Chromatography (HPLC) were used to analyze the degradation products.

### Experimental

Fresh a  $1.0 \times 10^{-2}$  M of BQ (Aldrich, USA) solution was purified by sublimation. A 0.5 M sulfuric acid solution (MERCK, Germany) was used for electrolyte. For the working electrode, the carbon fibers (TOHO Rayon, Japan) were used after pre-treated in 6.0 M hydrochloric acid for 2 hr at 80 °C, rinsed with deionized water, and dried at 105 °C in an oven. A Vycor porous glass tube (pore size 4.0 nm, Corning, USA) was pre-treated in 1.2 M hydrochloric acid for 1 hr at 80 and rinsed with deionized water. For the adsorption of carbon dioxide,  $5.0 \times 10^{-2}$  M Ba(OH)<sub>2</sub> (Aldrich, USA) was used. Standard materials for HPLC, oxalic acid, succinic acid, maleic acid, and hydroquinone were purchased from Supelco Co. (USA). All aqueous solution were prepared with purified distilled water [Milli-Q system (18 MΩ · cm)].

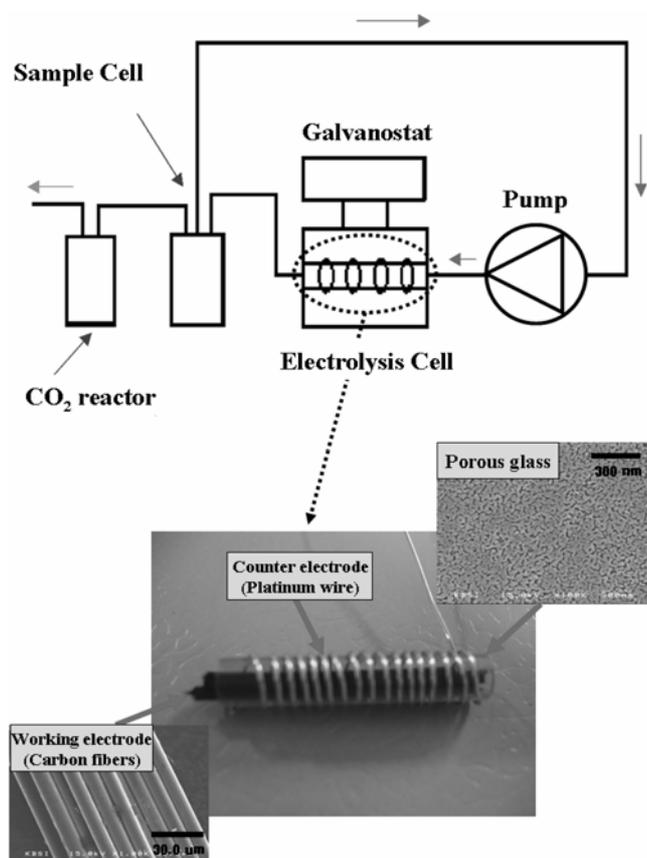
The electrochemical decomposition of BQ was conducted by a Potentiostat/Galvanostat (Model KST-P1, Kosentech Co. South Korea) using a home-made FTEC system. A peristaltic pump (Perkin Elmer, USA) was used to carry out the reactant solution. For a large electro-active surface area

per unit volume, a porous glass tube and carbon fibers was used to assemble a flow through cell. Figure 1 shows a detailed description of the FTEC used for the electrolysis of a BQ solution.<sup>23</sup> The similar type of flow cell was described previously.<sup>24</sup> Chromatographic analysis of the degradation products were carried out using an HPLC (Waters, Alliance, USA) with a C18 column at 25 °C and the UV detector was set at 210 nm. A  $5.0 \times 10^{-2}$  M of potassium phosphate monobasic solution was used as a mobile phase. The concentration of Ba<sup>2+</sup> ion was determined by ICP-AES (IRIS, Thermo Jarrell Ash, USA) with a CID detector at an emission line of 233.527 nm.

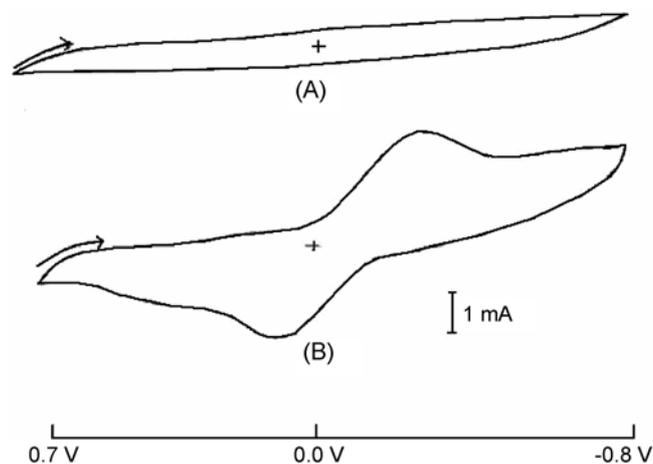
A  $1.0 \times 10^{-2}$  M of BQ solution was prepared by dissolving BQ in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The current was applied to the electrolytic cell shown in Figure 1. A separate exit was installed in the FTEC (Figure 1) to collect CO<sub>2</sub> that was bubbled through a basic solution of 0.05 M barium hydroxide during the electrolysis.<sup>8</sup> The efficiency of degradation was determined from the amount of CO<sub>2</sub> generated, which was calculated stoichiometrically from the concentration of residual Ba<sup>2+</sup> was determined by the ICP-AES. HPLC was used for the analysis of degraded intermediates and final products during the anodic oxidation process. The compounds were identified by comparing chromatograms of standards.

### Results and Discussion

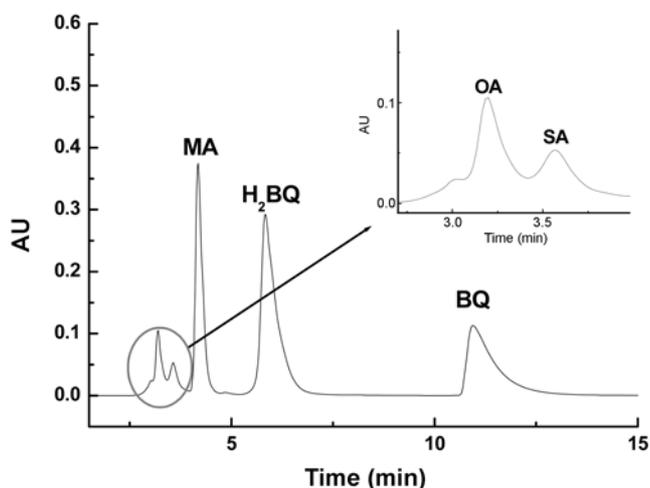
**Cyclic voltammetric behaviors of BQ.** Figure 2 shows recorded CVs for the carbon fiber electrode in a flow cell from +0.7 V to -0.8 V vs. Ag/AgCl at a scan rate of 50 mV/sec in (a) a  $5 \times 10^{-2}$  M of KCl solution and (b) a  $1.0 \times 10^{-2}$  M BQ solution containing  $5 \times 10^{-2}$  M of KCl solution, separately. The working electrode was carbon fibers. Platinum wire was used as a counter electrode and Ag/AgCl sat'd KCl was used as a reference electrode. As shown in Figure 2(b), a pair of redox peaks was observed at +0.05 V/-0.24 V vs. Ag/AgCl, which corresponds to the two-electron redox reaction



**Figure 1.** Flow-through electrochemical cell designed for controlled current electrolysis of aqueous solution of BQ.



**Figure 2.** Cyclic voltammograms recorded in (a)  $5.0 \times 10^{-2}$  M KCl, and (b)  $1.0 \times 10^{-2}$  M BQ aqueous solution with  $5.0 \times 10^{-2}$  M KCl using the carbon fibers electrode in the FTEC. Scan rate:  $50 \text{ mVs}^{-1}$ .



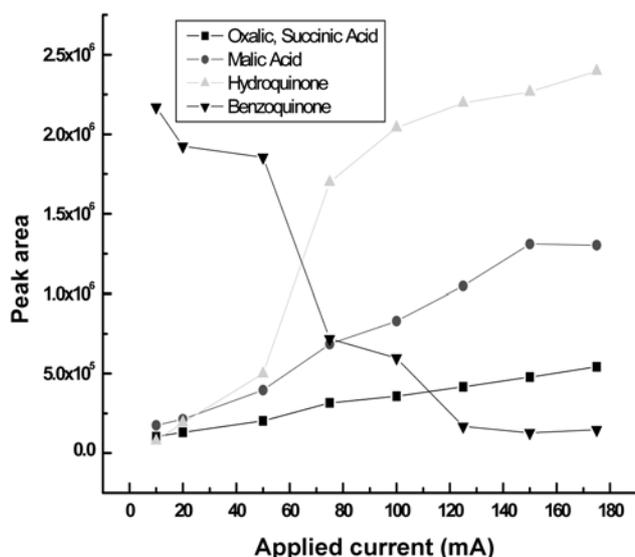
**Figure 3.** A chromatogram obtained for 25 mL of the degraded products of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ electrolyzed at 100 mA for 5 hr.

of BQ in an acidic solution as previously described<sup>25</sup>;



**The constant current electrolysis of BQ.** Galvanostatic electrolysis of BQ in aqueous solutions were performed with the home-made FTEC. The experimental variables for the electrochemical treatments of a BQ solution were optimized. A typical HPLC chromatogram obtained for the degradation products after the electrolysis of a  $1.0 \times 10^{-2}$  M BQ solution is shown in Figure 3. Five peaks with different retention times were revealed for the electrochemically treated BQ solution. The products identified by the authentic samples were oxalic acid ( $t_R = 3.19$  min), succinic acid ( $t_R = 3.57$  min), maleic acid ( $t_R = 5.85$  min), hydroquinone ( $t_R = 5.998$  min), and untreated BQ ( $t_R = 10.95$  min). The retention time of each product was confirmed using the standard aliphatic acid at same analyses conditions. In addition to these compounds, the chromatograms also showed very small peaks related to minor oxidation products, which were not identified. However, they may be the aliphatic acids because their retention times are very close to those of the identified acids.<sup>26</sup> The final product of the electrolytic degradation of BQ was  $\text{CO}_2$ , which was confirmed by the production of  $\text{BaCO}_3$  by precipitating from the produced  $\text{CO}_2$  and a  $\text{Ba}(\text{OH})_2$  solution.

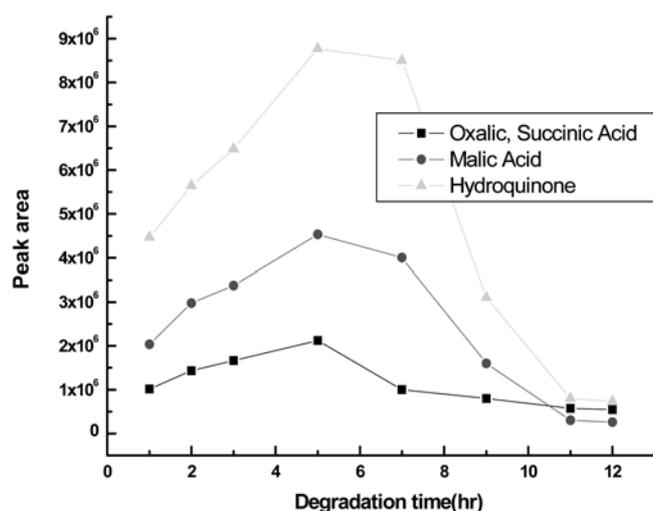
**Effect of applied current density and time on the degradation of BQ.** The effect of the applied current on the degradation of BQ was studied. The plot of the applied current vs. peak area is shown in Figure 4. Galvanostatic electrolyses for 25 mL of  $1.0 \times 10^{-2}$  M BQ aqueous solutions were carried out in a FTEC at a flow rate of 1.6 mL/min. The BQ solution was recycled through the FTEC and a reservoir bottle. Figure 4 shows the peak areas corresponding to the residual reactant and degradation products in solution as the function of applied current after the oxidation of BQ for an hour at the different applied



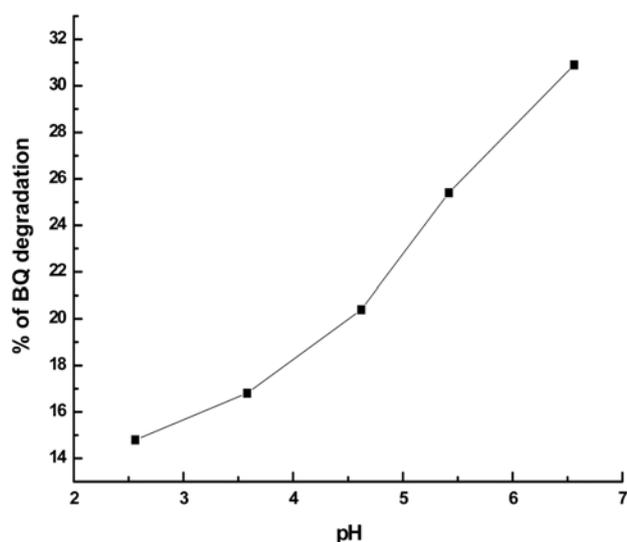
**Figure 4.** Product distribution as a function of the applied current for a controlled current electrolysis of 25 mL of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ on the carbon fibers electrode for 1 hr. Electrolyte: 0.5 M  $\text{H}_2\text{SO}_4$ .

current. The degradation products were identified as aliphatic acids, hydroquinone ( $\text{H}_2\text{BQ}$ ), and BQ, [similar to Figure 3]. The peaks of small aliphatic acids increased as the applied current increased to 175 mA indicating that the increase in the peaks of aliphatic acids observed at the current range between 10 and 175 mA might be due to the formation of further oxidation products of BQ.  $\text{H}_2\text{BQ}$  formed by the reaction between  $\text{OH}^\cdot$  produced in the strong acidic medium by the electrochemical oxidation of water, which was used as the solvent, and BQ present in solution. This reaction mechanism has been proposed by others for the electrochemical oxidation of aromatic compounds.<sup>27</sup> The amount of BQ decreased rapidly with increasing applied current up to 75 mA. For the electrolysis of BQ at an applied current higher than 75 mA, the rate of degradation increased slowly. This might be explained by the conversion of  $\text{H}_2\text{BQ}$  to aliphatic acids as the applied current was increased. The maleic acid content reached a maximum at an applied current of 150 mA and then decreased at currents higher than 150 mA, which was probably due to the further oxidation of maleic acid to  $\text{CO}_2$  at the higher applied current. The concentration of BQ decreased rapidly as the applied current was increased up to 100 mA, reaching a minimum value corresponding to about 50% of BQ, in the current range higher than 125 mA for an hour period of electrolysis. The optimum applied current was 125 mA for an hour period of electrolysis.

Figure 5 shows the effect of degradation time on the amount of BQ, which is converted to low molecular weight aliphatic acids and  $\text{CO}_2$ . The % produced aliphatic acids,  $\text{H}_2\text{BQ}$  and the unreacted BQ in a solution as a function of degradation time after at an applied current of 175 mA are shown in Figure 5. The amount of low molecular weight organic acids increased with increasing time, however, for



**Figure 5.** Product distribution as a function of reaction time for the controlled current electrolysis of 25 mL of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ on the carbon fibers electrode. Reaction current : 175 mA, Electrolyte: 0.5 M  $H_2SO_4$ .



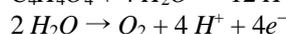
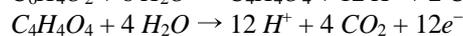
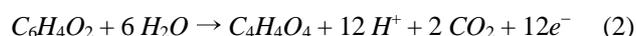
**Figure 6.** The percentage of BQ converted to  $CO_2$  as a function of pH for 25 mL of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ. Reaction time: 2 hr, Applied current: 175 mA. Electrolyte: 0.5 M  $H_2SO_4$ .

an the electrolysis time greater than 5 hr, the amounts of organic acids decreased, due to the formation of  $CO_2$ .

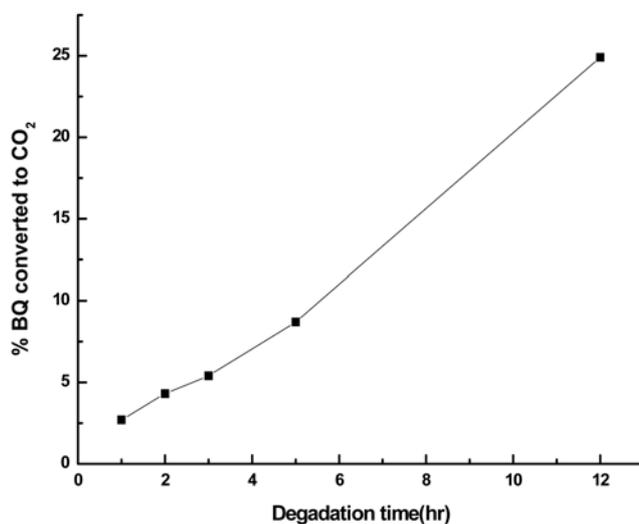
**Effect of pH on the degradation of BQ.** To investigate the efficiency of the degradation of BQ as a function of the pH of the medium, the pH of the solution was varied from pH 2.56 to 6.56 with an acetate buffer solution. Electrolyses were carried out at an applied current of 200 mA for 2 hr, when the complete oxidation of BQ occurs. Figure 6 shows the amount of BQ converted to  $CO_2$  at various pHs. As shown in Figure 6, the complete oxidation of BQ is favored at high initial pH values. The following mechanism, as shown in equation (2) is consistent with these observations since each step results in the production of hydrogen ions and an increase in initial pH would improve the driving force for each step.

**Table 1.** Percentage of BQ degradation as a function of applied current for a 12 hr period of electrolysis of 25 mL of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ. Amounts of  $H_2BQ$  and aliphatic acids produced.

Current (mA)	Products of degradation		Degradation of BQ (%)
	$H_2BQ$ and aliphatic acid (%)	$CO_2$ (%)	
50	29.01	18.83	54.70
75	23.64	22.34	55.43
100	28.81	26.26	62.97
150	40.89	35.39	85.61
175	47.03	41.65	99.23
200	49.10	42.45	99.62



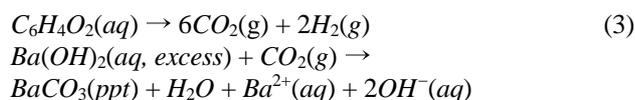
**The degradation of BQ to  $CO_2$ .** Table 1 summarizes the contents of products degraded as a function of applied current for 12 hrs oxidation of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ. The amounts of degradation products of BQ were determined from the ratio of the peak areas in the HPLC plot as shown in Figure 3. The results show that the complete oxidation of BQ to  $CO_2$  in an aqueous solution increased with higher the current density. At lower applied currents, the degradation products of BQ were mainly  $H_2BQ$  and aliphatic acids such as, oxalic acid and maleic acid. For 12 hrs electrolysis of BQ at an applied current of 50 mA, only 54.70% of the BQ was degraded to  $H_2BQ$ , aliphatic acids (29.01%) and  $CO_2$  (18.83%). However, 99.62% of the BQ was degraded to the  $H_2BQ$ , aliphatic acids (49.10%) and  $CO_2$  (42.45%) at an applied current of 200 mA. The degree of complete degradation was low at 50 mA reaction, however, the efficiency was rapidly increased at the applied



**Figure 7.** The percentage of BQ converted to  $CO_2$  as the function of time for 25 mL of a  $1.0 \times 10^{-2}$  M aqueous solution of BQ on the carbon fibers electrode under constant current electrolysis. Applied current: 100 mA, Electrolyte : 0.5 M  $H_2SO_4$ .

current over 150 mA and the ratio of aliphatic acid to CO<sub>2</sub> become constant. This means the complete decomposition of BQ needs longer reaction time.

Figure 7 shows the percentage of BQ converted completely to CO<sub>2</sub> as a function of degradation time for a 1.0 × 10<sup>-2</sup> M BQ solution at 100 mA. The efficiency of decomposition for the complete oxidation of BQ to CO<sub>2</sub> was determined by trapping the CO<sub>2</sub> produced with an excess amount of Ba(OH)<sub>2</sub> solution as described in the experimental section. The residual Ba<sup>2+</sup> ion in the solution was determined by ICP/AES. The efficiency of degradation of BQ as a function of the electrolysis time was calculated stoichiometrically using the following equation.<sup>3</sup>



As shown in Figure 7, the amount of CO<sub>2</sub> generated from the degradation of BQ increased with increasing electrolysis time and 26.0% of BQ was completely degraded to CO<sub>2</sub> in 12 hrs at an applied current of 100 mA. The degree of complete degradation would be increased as the applied current is increased. The complete degradation would be achieved as increasing the applied current and the reaction period.

### Conclusions

The anodic degradation of BQ was carried out and experimental conditions for the degradation of BQ were optimized. With 25 mL of a 1.0 × 10<sup>-2</sup> M aqueous solution of BQ, the efficiency increased with reaction time of up to 12 hrs. More than 99.0% of the BQ to H<sub>2</sub>BQ, aliphatic acids and CO<sub>2</sub> at currents higher than 175 mA for a 12 hr reaction. The degradation efficiency of BQ increased with an increase in the pH of the sample solution. The optimum efficiency was determined to be at a pH of 6.56. The final product of the oxidation of BQ was CO<sub>2</sub>. However, H<sub>2</sub>BQ and aliphatic acids such as oxalic, and maleic acid were produced as intermediates in the electrolysis of BQ. The optimized conditions for an electrochemical treatment of 25 mL of a 1.0 × 10<sup>-2</sup> M aqueous solution of BQ were as follows; an applied current of 175 mA, reaction time 12 hrs in a neutral solution.

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