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Dechlorination and Decomposition of Dichloroacetic Acid by Glow Discharge Plasma in Aqueous Solution

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Abstract—Dichloroacetic acid (DCAA) is one of the most common, stable and carcinogenic byproducts in water and wastewater treatment. In this study, dechlorination and decomposition of DCAA by glow discharge plasma (GDP) in a sodium sulfate solution were investigated. Intermediate products were identified and determined by ionic chromatography. Different experimental conditions are discussed for the influence of the removal efficiency of DCAA, such as different pH, hydroxyl radical scavenger. Increasing pH was favorable for both removal and dechlorination of DCAA. Addition of organic addictives to the solution decreased both the removal and dechlorination of DCAA. Monochloroacetic, acetic acid, formic acid and oxalic acid were the major products. Final products were inorganic carbon and chloride ion. The possible dechlorination mechanism is proposed based on the distribution of intermediate products. Both radical and thermal reactions were involved in the dechlorination and decomposition of DCAA. Hydroxyl radicals may be the most likely active species responsible for the dechlorination and decomposition.

Keywords—Non-thermal Plasma; Dichloroacetic Acid;Dechlorination;Decomposition;Mechanism

I. INTRODUCTION

Dichloroacetic acid (DCAA) is one of the most common contaminants in wastewater[1]. DCAA can also be generated during the chlorination of drinking water[2], swimming pools[3]. DCAA has shown to be carcinogenic to animals after oral exposure, probable human carcinogen[4].

DCAA can be decomposed by ozonation oxidation[5], but the experimental installations are very expensive. Activated carbon adsorption may efficiently remove DCAA from aqueous solution[6], however, this is only a physical transfer process without eventually decomposing DCAA into harmless substances. Therefore, development of cost-effective and environmentally friendly approaches for DCAA dechlorination and decomposition are necessary.

Glow discharge plasma in aqueous solutions is an unconventional electrical process where plasma is sustained between a pointed electrode and an electrolysis solution surrounding it [7]. When normal electrolysis is carried out in an electrolytic solution with a point-to-plane electrode configuration, a sheath of vapor will be generated around the tip of the pointed electrode due to Ohmic heating [7]. In GDP, charged particles in the gaseous plasma are accelerated due to the steep potential gradient and rush into the solution leading to the formation of various active species such as hydroxyl radical (•OH), hydrogen atoms(•H) and hydrated electrons(e_{aq}^-)[8]. Due to its simple equipments, easy operation and no requirement of a special power source, GDP has received considerable investigations from environmental researchers in recent years [7]-[9].

It has been shown that not only •OH radicals but also reducing species were generated in GDP, a process which is very similar to what occurs in ionizing radiation of aqueous solutions[9]. Since chemical effects of GDP are very similar to that of ionizing radiation, an attempt was made to use GDP to dechlorinate and decompose the DCAA in the aqueous solution in the present study. To the best of our knowledge, there are only little mechanistic studies of using GDP for dechlorination and decomposition of DCAA.

II. EXPERIMENTAL

Experimental assembly consisted of a DC high-voltage power source and a cylindrical glass reactor. The reactor is showed in Fig .1. The anode was a pointed Pt wire sealed into a glass tube. The cathode was a stainless steel placed in another glass tube and separated from the anodic compartment by a sintered glass frit of medium porosity. The reaction vessel was surrounded by a water jacket, where the solution was maintained at 298 ±2K by running tap water. DCAA was dissolved in a sodium sulfate solution (with conductivity 5500μS/cm) and 150-ml portion was poured into the reaction for treatment. Initial pH was adjusted with dilute sulfuric acid or sodium hydroxide solution from 2 to 12. Prior to each run, the voltage was adjusted to 500V, the electrodes began discharging. In most cases, the current was kept 100 ±2mA.

During the discharge, the solution in the reactor was stirred persistently with a stirring hot plate and aliquots were periodically sampled out for analysis. Organic acids and chloride ion (Cl^{-}) were identified and determined by ionic chromatography (IC, DIONEX ICS-1100) combined with an Ion Pac AS-23 column. An aqueous solution of dilute KOH (10mmol/L) was used as the mobile phase. The flow rate was 1ml/min. The amount of total organic carbon (TOC) was measured by a TOC analyzer (SHIMADZU TOC-VCSH).

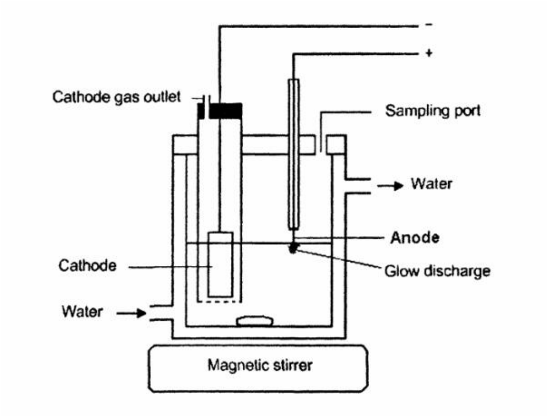

Figure 1. GDP reactor for dechlorination and decomposition of dichloroacetic acid

III. RESULITS AND DISCUSSION

A. *DCAA removal and chloride ion generation*

Decomposition and dechlorination of DCAA proceeded smoothly when the solution containing DCAA was subjected to GDP. Fig .2 shows the remaining TOC and DCAA and the generation of Cl^{-} during the 300min discharge.

It can be seen from Fig .2 that the remaining TOC and DCAA decreased while generated Cl^{-} increased with a rise of discharge time. After 300min of discharge, about 85% of DCAA was removed and 80% of TOC disappeared and 1.15mM Cl^{-} formed. It can be also observed that the disappearance of TOC was less than that of DCAA, suggesting that GDP leads to removals of DCAA and some organic intermediate products were formed during the discharge treatment. After six hours, the yield of Cl^{-} reached 100% (2mM) and the remaining TOC reached less than 5% of the initial value. It is apparent that most carbon atoms of DCAA were mineralized to Cl^{-} and inorganic carbon.

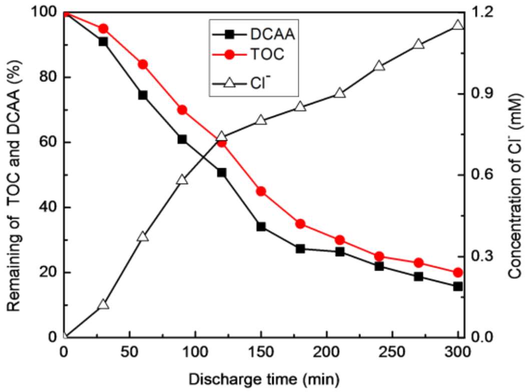

Figure 2. Removal of DCAA and generation of Cl^{-} during GDP treatment (voltage, 500 V; average current, 100 mA; [DCAA]0, 0.78 mM; pH0,7.0)

B. *Effect of initial pH on the dechlorination of DCAA*

A series of studies were carried out to investigate the effects of pH on DCAA removal and dechlorination. Fig .3 shows the removal of DCAA and the generation of Cl^{-}, with 120 min of discharge treatment, under different initial pH values.

As presented in Fig .3, the remaining of DCAA decreased while generated Cl^{-} increased with increasing initial pH. After 120 min discharge, with the pH value of 2, 43.25% of DCAA was removed and 0.65mM Cl^{-} formed. With the pH value of 12, 53.42mM of DCAA was removed and 0.82mM Cl^{-} formed. It further demonstrated that more DCAA was removed and more Cl^{-} was produced in alkaline solutions. Removal of DCAA increased with increasing pH values from 2 to 12.

The phenomena can be explained as follows.

In GDP of aqueous solutions, liquid water molecules were decomposed by the incoming positive ions ($H_2O_{gas}^{+}$) from the gaseous plasma into the following active species [7]:

$H_2O+H_2O_{gas}^{+}\rightarrow\bullet OH+H\bullet+H_3O^{+}(H^{+})$ (1)

And H• is the conjugate acid form of e_{aq}^{-}.

$H\bullet+H_2O\leftrightarrows e_{aq}^{-}+H^{+}$ pKa =9.6 (2)

When DCAA is present in the solution, the resulting active species react with DCAA via the following reactions [12].

$HCCl_2COOH + e_{aq}^{-}/H\bullet \rightarrow H_2CClCOOH + HCl$ (3)

$\bullet OH + HCCl_2COOH \rightarrow \bullet CCl_2COOH + H_2O$ (4)

As shown by reaction 2, e_{aq}^{-} was predominant at high pH (reaction 2). As a result, the removal of DCAA increased with increasing pH_0.

In basic media, •OH react with OH^{-}, thereby decreasing the recombination probability between •OH and e_{aq}^{-} [12].

$\bullet OH + HO^{-} \rightarrow \bullet O^{-} + H_2O$ $k_1 = 1.3\times10^{10}\ M^{-1}s^{-1}$ (5)

$\bullet OH + e_{aq}^{-} \rightarrow H_2O + OH^{-}$ $k_2 = 3.0\times10^{10}\ M^{-1}s^{-1}$ (6)

In basic media, the concentration of •OH decreased as a result of reaction 5, which indirectly increased the concentration of e_{aq}^- (reaction 6). Although •OH can also react with DCAA, the removal of DCAA increased. Therefore, the removal of DCAA and the generation of Cl^- increased with increasing pH_0 due to reactions 2, 5 and 6.

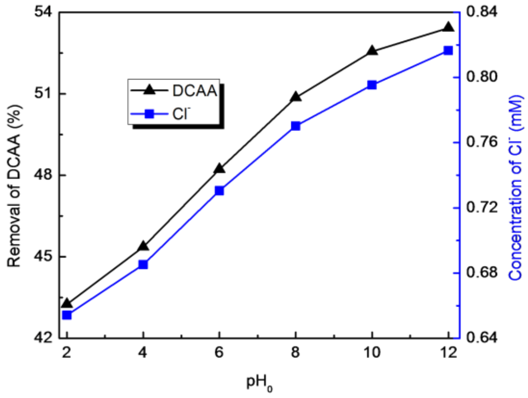

Figure 3. Effect of initial pH on the DCAA removal and Cl⁻ generation (voltage, 500 V; average current, 100 mA; [DCAA]0, 0.78mM)

C. Effect of organic additives on removal and dechlorination of DCAA

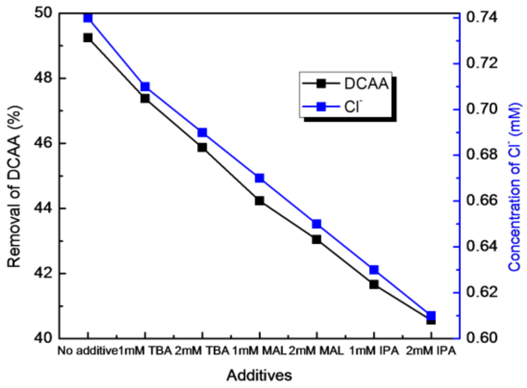

Figure 4. Effect of organic addictives on the dechlorination and decompositio of DCAA (voltage, 500 V; average current, 100 mA; [DCAA]0, 0.78 mM; pH0, 7.0)

In practice, wastewater often contains various other organics that consume the radicals [9]. Therefore, it is necessary to study the behavior of DCAA removal or dechlorination in the presence of them. In this experiment, tert-Butyl alcohol (TBA), methanol (MAL) and isopropanol (IPA) were chosen as the model compounds, as TBA, MAL and IPA were typical hydroxyl radical scavengers [10]-[12]:

$$\bullet OH+(CH_3)_2CHOH \rightarrow H_2O+\bullet(CH_3)_2COH$$

$$k_3 = 1.9\times 10^9\ M^{-1}s^{-1} \qquad (7)$$

$$\bullet OH + CH_3OH \rightarrow H_2O + \bullet CH_2OH$$

$$k_4 = 9.7\times 10^8\ M^{-1}s^{-1} \qquad (8)$$

$$\bullet OH+(CH_3)_3COH \rightarrow H_2O+ \bullet CH_2C(CH_3)_2H$$

$$k_5 = 6.0\times 10^8\ M^{-1}s^{-1} \qquad (9)$$

$$H\bullet + (CH_3)_2CHOH \rightarrow H_2 +\bullet(CH_3)_2COH$$

$$k_6 = 7.4\times 10^7\ M^{-1}s^{-1} \qquad (10)$$

$$H\bullet + CH_3OH \rightarrow H_2 + \bullet CH_2OH$$

$$k_7 = 2.6\times 10^6\ M^{-1}s^{-1} \qquad (11)$$

$$H\bullet + (CH_3)_3COH \rightarrow \bullet CH_2C(CH_3)_2OH + H_2$$

$$k_8 = 1.0\times 10^5\ M^{-1}s^{-1} \qquad (12)$$

The removal of DCAA and generation of Cl^- with 120 min discharge under different concentrations of TBA, MAL and IPA are given in Fig .4. Respectively, as indicated in Fig .4, both the removal of DCAA and generation of Cl^- decreased in the presence of •OH scavengers. This phenomenon can be explained by the fact that •OH radicals and H• atoms resulting from reaction can react mutually to form H_2O:

$$\bullet H +\bullet OH \rightarrow H_2O \qquad (13)$$

In the presence of TBA, MAL and IPA, •H atoms react with them, and the concentration of •H radicals decreased accordingly, which indirectly increased the concentration of •OH radicals by inhibiting the reaction. From the reaction rate($k_3 > k_4 > k_5$) above, we can see that IPA is more efficient than TBA and MAL in consuming •OH radicals. As a result, less DCAA was removed and less Cl^- was produced. It can also be observed that the reaction rate of the three additives with hydrogen atoms are all slow compared with hydroxyl radical($k_3 >> k_6$, $k_4 >> k_7$, $k_5 >> k_8$). The above experimental results further demonstrated that •OH radicals were the primary species for the removal or dechlorination of DCAA. It can also been demonstrated that the three organic additives can also involved in the reaction in the same way.

D. Intermediate products formation

To understand the decomposition mechanism of DCAA, an IC analyzer was used to monitor the intermediate products. Under the glow discharge electrolysis, DCAA was removed gradually to give the carboxylic acids with smaller molecular. The final products would be the inorganic ions carbon dioxide and water.

As indicated in Fig .5, monochloraacetic acid (MCAA), acetic acid (AA), formic acid (FA) and oxalic acid (OA) are the major intermediate products. At the beginning of the reaction, MCAA was appreciable and then its concentration decreased gradually with longer discharge time. In contrast, AA, FA and OA were minor in the whole process. MCAA and AA were formed as a result of further reduction of DCAA:

$HCCl_2COOH+e_{aq}/H\bullet \rightarrow H_2CClCOOH+HCl$ (14)

$H_2CClCOOH+e_{aq}^{-}/H\bullet \rightarrow H_2CCOOH+HCl$ (15)

FA and OA may be formed via the reaction:

$H_2CClCOOH+\bullet OH \rightarrow \bullet CCl_2COOH+H_2$ (16)

$\bullet CCl_2COOH \rightarrow :CCl_2+\bullet COOH$ (17)

$2\bullet COOH \rightarrow CO_2 + HCOOH$ (18)

$\bullet COOH + \bullet COOH \rightarrow H_2C_2O_4$ (19)

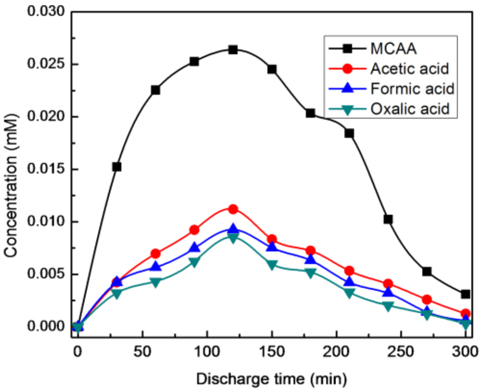

Figure 5. Intermediate byproducts formed during discharge treatment (voltage, 500V; average current, 100 mA; [DCAA]0, 0.78 mM; pH0, 7.0)

IV. CONCLUSIONS

DCAA can be efficiently dechlorinated by GDP, with longer times resulting in more Cl^- generation. Increasing pH can enhance its removal and dechlorination. Addition of organic additives can decrease its removal and dechlorination. Major products were monochloraacetic acid, acetic acid, formic acid and oxalic acid. Final products were inorganic carbon and chloride ions. Hydroxyl radicals may be the most likely ones for decomposition and dechlorination. In addition, some direct thermal reactions of DCAA maybe involved in the mineralization. Since our knowledge is rather limited, further research is needed to outline the mechanisms of DCAA removal and dechlorination.

ACKNOWLEDGEMENTS

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