Dechlorination and decomposition of chloroform induced by glow discharge plasma in an aqueous solution

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HIGHLIGHTS

- Hydrated electrons played an important role for chloroform decomposition.
- Oxygen enhanced hydrolyses are critical for the chloroform mineralization.
- Energy efficiency of GDP is higher than those of the typical competitive processes.

ARTICLE INFO

ABSTRACT

In this study, efficient dechlorination and decomposition of chloroform (CF) induced by glow discharge plasma (GDP) in contact with a sodium sulfate solution was investigated. Intermediate byproducts were determined by ionic chromatography and headspace gas chromatography, respectively. Results showed that CF can be effectively dechlorinated and decomposed under the action of GDP. Both removal and dechlorination of CF increased with increasing pH and with addition of hydroxyl radical scavengers to the solution. Addition of H_2O_2 to the solution slightly decreased the CF removal. Formic acid, oxalic acid and dichloromethane were determined as the major intermediate byproducts. Final products were carbon dioxide and hydrochloric acid. Hydrated electrons were the most likely active species responsible for initiation of the dechlorination, and hydroxyl radicals may be the ones for the oxidation of the organic intermediate byproducts. Hydrolyses of the chloromethyl radicals contributed much in the mineralization of the organic chlorine. Reaction mechanism was proposed based on the dechlorination kinetics and the distribution of intermediate byproducts.

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1. Introduction

Chloroform ($HCCl_3$, CF) is widely used as solvents and as chemical intermediates [1]. During chlorination of water or wastewater (at the outlet of wastewater plant), CF is usually produced as a toxic byproduct [2,3]. CF is an omnipresent aqueous contaminant due to its carcinogenicity, environmental persistence and high solubility (8.22 g/l at 293 K) [1,4].

CF is toxic to microbes and is not susceptible to metabolic transformations [5]. Granular activated carbon (GAC) adsorption was often employed to remove CF from aqueous solutions [6]. However, the GAC adsorption is just a physical process without eventually decomposing it into harmless products. In addition, CF is hardly decomposed by advanced oxidation processes such as Fenton's reagent [7] because of its low reactivity toward the hydroxyl radicals (•OH) [8]. Sono-oxidation [9] and TiO_2 photo-catalysis [10,11] have been attempted for CF decomposition, but the two processes suffer either the process complexity or the low energy utilization efficiency. CF decomposition by electron beam (EB) irradiation has been investigated [12]. However, experimental and operating costs of EB radiation are usually prohibitively high. Therefore, development of alternative processes for CF mineralization is necessary.

Glow discharge plasma (GDP) in aqueous solution is also called contact glow discharge electrolysis (CGDE) [13,14]. It is an electrical process where plasma is sustained by glow discharges between a pointed electrode and the surface of an electrolytic solution contacting with it. 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

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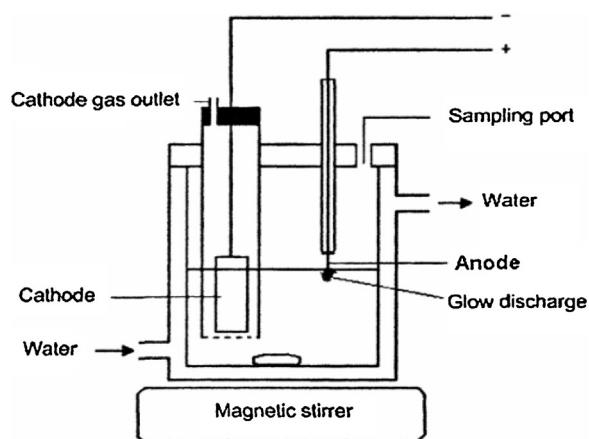*E-mail address:* lyjglow@sohu.com (Y. Liu).

Fig. 1. GDP reactor for dechlorination and decomposition of CF.

Fig. 2. Concentration variations of CF, TOC and Cl⁻ during GDP treatment (voltage, 500 V; average current, 100 mA; solution volume, 150 ml; [CF]₀, 0.84 mM; pH₀,7.0).

pointed electrode due to Ohmic heating. When the applied voltage is sufficiently high, the vapor breakdowns and GDP occurs. In GDP, charged particles in the gaseous plasma are accelerated due to the steep potential gradient and collide with liquid water molecules leading to the formation of various active species such as •OH radicals [15], hydrogen atoms (•H) [16] and hydrated electrons (e_{aq}^-) [17], a process being analogous to what occurring in ionizing radiation of water [13]. Due to its relatively low discharge voltage, easy operation and no requirement of special power source, GDP has received considerable investigations from environmental researchers in recent pasts [14,18–21].

Previous studies of GDP were mainly focused on the use of •OH radicals to oxidize the aromatic compounds. The roles of its reducing species played in the process of pollutant removal were rarely reported [22,23]. In this report, an attempt was made to use GDP to dechlorinate and decompose CF in aqueous solution, focused mainly on the optimizing the experimental conditions and the reaction mechanism. To the best of our knowledge, there is little information of using GDP for decomposing chlorinated methanes in aqueous media.

2. Experimental

Experimental assembly consisted of a DC high-voltage power source and a cylindrical glass reactor. The reactor is shown in Fig. 1.

The anode was a pointed Pt wire sealed into a glass tube. The cathode was a stainless steel plate placed in another glass tube and separated from the anodic compartment by a sintered glass frit of medium porosity. The reaction vessel was coated by a water jacket, where temperature of the solution in the reactor was maintained at 298 ± 2 K by running tap water. CF was dissolved in a sodium sulfate solution (with conductivity about 2.3 mS/cm) and 150-ml portion was poured into the reaction for treatment. Solution pH was adjusted with dilute sulfuric acid or sodium hydroxide to the expected value. Prior to each run, the point anode was dipped into the solution at ca. 2.0 mm. The applied voltage was adjusted to the desired value to commence the discharge. In most cases, the applied voltage was 500 V and the current was kept within 100 ± 2 mA.

During the discharge, solution in the reactor was stirred persistently with a stirring bar and aliquots were periodically sampled out for analyses. Organic acids and chloride ion (Cl⁻) were identified and determined by ionic chromatography (IC, DIONEX ICS-1100) combined with an IonPac AS-23 separation column. An aqueous solution of dilute KOH (10.0 mmol/l) was used as the mobile phase. The flow rate was 1.0 ml/min. CF and the volatile organic byproducts were identified and determined by a headspace gas chromatography coupled with an electron capture detector (GC,
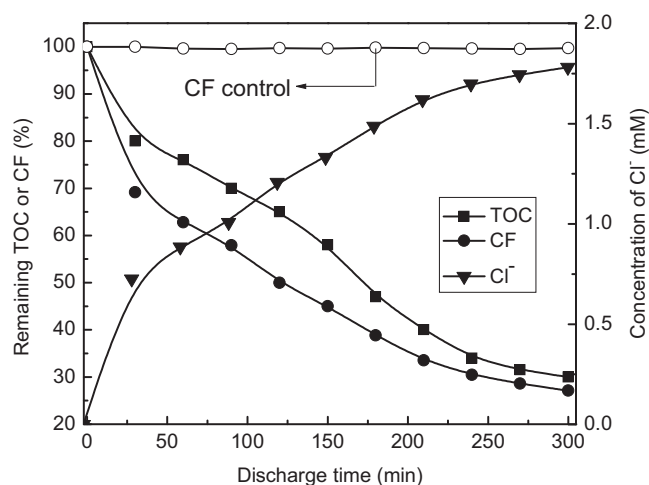
SHIMADZU GC-2010). Sampling solutions (10.0 ml) were transferred into the headspace bottles and sustained for 20 min under the stationary temperature of 323 K in a water bath. Then 1.0 ml portion of the gas above the solution was extracted with a headspace syringe (2.5 ml) after piercing the septa and was injected into the GC. Operation conditions of GC are: injection temperature, 473 K; detector temperature, 523 K; carrier gas flow rate, 3.0 ml/min; split ratio, 1:50; column gas flow rate, 1.0 ml/min; make-up gas flow rate, 30 ml/min; oven temperature was held isothermally at 313 K for 4 min and then ramped to 363 K at a rate of 293 K/min, further to 423 K at a rate of 303 K/min for 1.0 min. The amount of total organic carbon (TOC) was measured by a TOC analyzer (SHIMADZU TOC-VCSH). The organic intermediate byproducts were also identified by GC–MS (QP2010 Ultra).

3. Results and discussions

3.1. CF removal and Cl⁻ generation

Dechlorination and decomposition of CF proceeded smoothly when the solution containing CF was exposed to GDP. Typical curves for the concentration variations of CF, TOC and Cl⁻ during GDP treatment are shown in Fig. 2.

As indicated from Fig. 2, the amount of TOC and that of CF decreased monotonically while concentration of the generated Cl⁻ increased gradually with increasing discharge time. After 300 min of discharge, about 73% of CF was removed and 70% of TOC disappeared and 1.78 mM of Cl⁻ was generated. It can be also observed from Fig. 2 that the decay rate of TOC was less than that of CF, indicating that some organic intermediate byproducts formed during the discharge treatment. In order to clarify the chlorine balance, variation of [Cl⁻]/([CF]₀ − [CF]) with discharge time calculated from Fig. 2 are presented in Fig. 3.

As shown in Fig. 3, the ratio between the amount of the generated Cl⁻ and that of the CF eliminated was close to 3:1(2.8–2.9:1 in the figure) and increased with discharge time. This implies that very little chlorinated organic byproducts were formed during the discharge and that the formed chlorinated organic byproducts can also be dechlorinated by GDP. Detailed information concerning the mechanism of byproducts formation and dechlorination will be discussed in Section 3.5. After 400 min of discharge, CF was completely eliminated and dechlorinated with 98.5% of TOC removed, indicating that CF can be efficiently transformed to Cl⁻ and inorganic carbon under the action of GDP.