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Author: Yongjun Liu John C. Crittenden Lei Wang Panliang Liu



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

Yongjun Liu^{1,2*}, John C. Crittenden², Lei Wang³, Panliang Liu²

¹*College of Environmental Science & Engineering, Dalian Maritime University, Dalian 116026, P. R. China; E-mail: lyjglow@sohu.com; Tel. and Fax: 86-411-84727670*

²*Brook Byers Institute for Sustainable Systems, Georgia Institute of Technology, Atlanta 30332, United States*

³*College of Environmental Science & Engineering, Xiamen University of Technology, Xiamen 361024, P. R. China*

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.

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 H₂O₂ 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.

Keywords: non-thermal plasma; chloroform; dechlorination; reaction mechanism

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 293K) [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 towards the hydroxyl radicals ($\bullet\text{OH}$) [8]. Sono-oxidation [9] and

TiO₂ 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 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.

(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 $298 \pm 2\text{K}$ 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 500V and the current was kept within $100 \pm 2\text{mA}$.

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.

(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 $[\text{Cl}^-]/([\text{CF}]_0 - [\text{CF}])$ 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.

(Fig.3)

3.2 Effect of applied voltage on the removal and dechlorination of CF

Figure 4 shows the effect of applied voltage on the removal of CF and generation of Cl^- with 60 min of treatment.

(Fig.4)

It can be observed from Fig. 4 that both the removal of CF and the generation Cl^- increased slightly with increasing applied voltage in the range of 200-400V and sharply increased with increasing applied voltage from 400V to 550V. For example, at 200 V, only 2.1% of CF was removed and 0.03 mM Cl^- was generated, while approximately 37% of CF was removed and 0.9 mM Cl^- was generated in the case of 500 V. This is because the discharge is not fully developed when the applied voltage is below 450V, where the amount of the active species produced for CF dechlorination and decomposition was small, and the removal of CF and the generation of Cl^- were both trace [13, 16]. When the voltage was lower than 150V, no appreciable CF degradation was observed (not shown in the figure), indicating that direct CF reduction at the cathode was negligible. When the applied voltage was higher than 550 V, the platinum anode showed the signs of melting. Therefore, 500 V was chosen as the optimum applied voltage in the following experiments.

3.3 Effect of pH on the removal and dechlorination of CF

pH often played an important role in water and wastewater treatment. In order to better elucidate the role of pH in CF mineralization, pH variations under different initial pH values (pH_0) during the GDP treatment are presented in Fig.5.

(Fig.5)

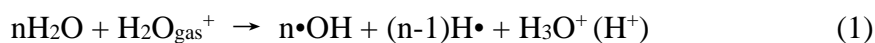
As shown in Fig.5, whenever the pH_0 was, the solution pH dropped with discharge time. When pH_0 was 11.0, the pH dropped gradually with discharge time. When pH_0 was 7.0, the pH decreased rapidly within 10 min and then fell slowly with discharge time. In the case of pH_0 4.0, the pH declined little in the whole process. The above

phenomena can be explained by the fact that hydrochloric acid (HCl), carbon dioxide (CO₂) and organic acids were generated during the discharge treatment (c.f. section 3.5). When pH₀ was high (11.0), HCl, CO₂ and organic acids dissolved in the solution and reacted with the hydroxide ion. With prolonging discharge time, carbonate/bicarbonate buffer formed in the solution, which inhibited the sharp decrease of pH. As a result, the pH dropped smoothly with discharge time in the whole process. When pH₀ was 7.0, HCl and organic acids dissolved and dissociated in the solution and a steep decrease of pH was observed. When dropped to 4.0, the pH varied slowly because the acid buffering of the solution, as in the case of pH₀ being 4.0. Fig.6 shows the removal of CF and the generation of Cl⁻ with 60 min of discharge treatment under different pH₀.

(Fig.6)

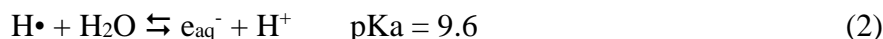
As presented in Fig.6, both the removal of CF and the yield of Cl⁻ increased with increasing pH₀. When pH₀ was 3.0, 25% of CF was removed and 0.58 mM Cl⁻ formed, whereas when the pH₀ was increased to 11.0, 42.5% of CF was removed and 1.02 mM Cl⁻ formed with the same discharge time. The phenomena can be explained as follows.

In GDP of aqueous solutions, liquid water molecules were decomposed by the incoming positive ions (H₂O_{gas}⁺) from the gaseous plasma into the following active species [13]:

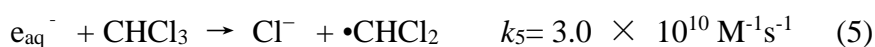


where “*n*” represents the non-Faraday value[13].

$H\bullet$ is the conjugate acid form of e_{aq}^- .



When CF is present in the solution, the resulting active species react with CF via the following reactions [8, 12].

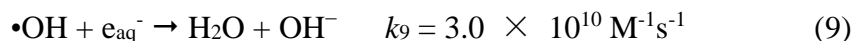
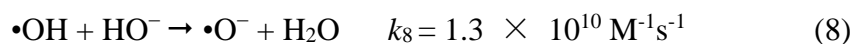


According to reactions 2-5, the decay of CF can be described by the following equation (eq.7):

$$-\frac{d[CF]}{dt} = (k_3 + k_4)[CF][\bullet H] + k_5[CF][e_{aq}^-] + k_6[CF][\bullet OH] \quad (7)$$

As shown by reaction 2, e_{aq}^- was predominant at high pH. As a result, the removal of CF increased with increasing pH₀, because the rate constant of reaction 5 is 3 orders of magnitude higher than those of reactions (3) and (4).

In basic conditions, $\bullet OH$ react with OH^- , thereby reducing the recombination between $\bullet OH$ and e_{aq}^- [24].

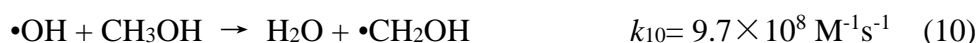


In basic media, the concentration of $\bullet OH$ decreased as a result of reaction 8, which indirectly increased the concentration of e_{aq}^- due to reaction 9. Although $\bullet OH$ can also react with CF, the removal of CF increased because the rate constant of reaction 5 is

much higher than that of reaction 6. Therefore, the removal of CF and the generation of Cl^- increased with increasing pH_0 due to reactions 2, 8 and 9. It can be observed from the control experiments of Fig.6 that the direct hydrolyses of CF were negligible under the present experimental conditions.

3.4 Effect of radical scavengers on CF removal and dechlorination

In this section, methanol and isopropanol were chosen as the typical $\bullet\text{OH}$ radical scavengers and H_2O_2 was selected as a typical e_{aq}^- scavenger to study the role of the active species played in the CF removal and dechlorination during the GDP treatment [24]:



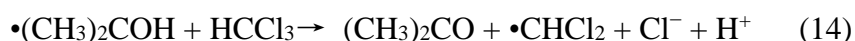
Removal of CF and generation of Cl^- , and $[\text{Cl}^-]/([\text{CF}]_0 - [\text{CF}])$ under different concentrations of methanol, isopropanol and H_2O_2 , with 60 min of GDP treatment are shown in Figs.7a and b, respectively.

(Fig.7)

As indicated in Fig.7a, both the removal of CF and the generation of Cl^- increased with the presence of $\bullet\text{OH}$ scavengers. This phenomenon can be explained by the fact that $\bullet\text{OH}$ radicals and $\text{H}\bullet$ atoms (or e_{aq}^-) resulting from GDP react mutually to form H_2O :



In the presence of methanol or isopropanol, $\bullet\text{OH}$ radicals reacted with them, and the concentration of $\bullet\text{OH}$ radicals decreased accordingly, which in turn increased the concentration of e_{aq}^- (or $\bullet\text{H}$) by inhibiting the reaction 13. From Fig.7, we can also see that isopropanol was more efficient than methanol in enhancing the CF removal and the Cl^- generation. Two reasons explain the phenomena. On the one hand, isopropanol is a more efficient $\bullet\text{OH}$ scavenger (reactions 10 and 11). On the other, the organic radicals resulting from reaction 11 can also react with CF via reaction 14 [25]:



Consequently, isopropanol is a more efficient accelerator than methanol in the CF removal and its dechlorination.

As also shown in Fig.7a, the removal of CF and the generation of Cl^- decreased with the presence of H_2O_2 . This is because the H_2O_2 competes with CF for the e_{aq}^- , and the removal of CF and the generation of Cl^- decreased accordingly. The present studies further demonstrated that e_{aq}^- played a dominant role in the removal of CF.

It can be observed from Fig. 7b that the values of the ratio between the amount of the generated Cl^- and that of the CF eliminated were ca. 2.4 in the cases of $\bullet\text{OH}$ radical scavengers, which were lower than that without organic additive (ca. 2.8). This means that the increase of the CF removal was more than that of its dechlorination in the presence of organic additives. As shown by reaction 12, the concentration of $\bullet\text{H}$ atoms increased in the presence of $\bullet\text{OH}$ radical scavengers, which would favor the

combination reaction between $\bullet\text{H}$ atoms and dichloromethyl radicals ($\bullet\text{CHCl}_2$) and the hydrolysis of the $\bullet\text{CHCl}_2$ radicals would be inhibited (reaction 21 in section 3.5). As a result, the ratio between the amount of the generated Cl^- and that of the CF eliminated decreased. In practice, real wastewater often contains various other organics that consume the $\bullet\text{OH}$ radicals. The present studies showed that GDP is very applicable in the removal of CF from real water. This further demonstrated that the reducing radicals other than the oxidative $\bullet\text{OH}$ radicals played important roles in the removal and the dechlorination of CF during GDP treatment.

3.5 Intermediate byproducts formation and possible reaction mechanism

In order to understand the mineralization mechanism of CF, GC and IC were used to monitor the intermediate byproducts. Fig.8 shows concentration variations of the major intermediate byproducts formed during GDP treatment at pH₀ 7.0.

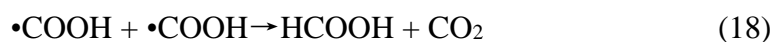
(Fig.8)

As shown in Fig.8, formic acid (FA), oxalic acid (OA) and dichloromethane (CH_2Cl_2 , DCM) are the major intermediate byproducts. The yields of both FA and OA increased to the maximums at 120 min and then decreased gradually. On the other hand, the yield of DCM increased smoothly within 30 min and then decreased gradually and finally disappeared. It is noted that tetrachloroethylene (C_2Cl_4) was also detected by GC at 30 min of the discharge. However, its concentration was too small to be quantitatively determined. FA may be formed by the hydrolysis and subsequent oxidation of $\bullet\text{CHCl}_2$ radicals [8]:

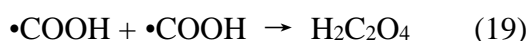




It should be noted that the direct hydrolysis of $\bullet\text{CCl}_3$ radicals from reaction 6 may also contribute to the formation of FA (via reactions 17 and 18) [8]:



OA was yielded by the combination of the $\bullet\text{COOH}$ radicals:



In practice, when FA was used as a starting material, OA was also yielded. This means that OA might result from FA via oxidation by $\bullet\text{OH}$ radicals:



DCM was formed as a result of combination reaction between $\bullet\text{CHCl}_2$ radicals and $\text{H}\bullet$ atoms:



Reaction 21 has been confirmed by the fact that the yield of DCM increased in the presence of $\bullet\text{OH}$ radical scavengers (not shown in the figure).

C_2Cl_4 was formed by the combination of dichlorocarbene ($:\text{CCl}_2$):



And $:\text{CCl}_2$ may be formed via the following reactions [26]:



By comparing Figs.2, 3 and 8, it can be found that the amount of organic byproducts is minor in comparison with that of CF removed, and the ratio between the

amount of the generated Cl^- and that of the CF eliminated was close to 3:1, which cannot be explained just by reactions 15-24 (if this is the case, much more intermediate byproducts than those shown in Fig. 8 would be formed). This may be due to the oxygen enhanced hydrolysis of the chloromethyl radicals such as [23, 28]:



The concentration of oxygen in air-saturated solutions is approximately 0.25 mM. In the presence of oxygen, the chloromethyl radicals react rapidly with it to form the corresponding peroxy radicals. The resulting peroxy radicals undergo rapid hydrolyses, leading to the formation of CO_2 and Cl^- . As reactions 26 and 28 are considerably faster than reactions 15, 16 and 17, less FA and OA were yielded.

It should be noted that hexachloroethane (C_2Cl_6) was not detected in the present investigation, possibly because the trichloromethyl radicals ($\bullet\text{CCl}_3$) produced in reactions 4 and 6 were trace and the resulting radicals were rapidly hydrolyzed into Cl^- and CO_2 in the presence of oxygen before combining into C_2Cl_6 [8].

No chloromethane (CH_3Cl) was detected in the present experiment, even when 1.0 mM DCM was subjected to GDP. However, CH_3Cl can be detected when 1.0 mM DCM and 1.0 mM isopropanol were both exposed to GDP. This means that H_3CCl might be formed in the mineralization processes of CF.

When DCM and C_2Cl_4 were used as the starting materials, Cl^- and CO_2 were

eventually and quantitatively generated. This demonstrated that the chlorinated byproducts can also be efficiently converted into Cl^- and CO_2 by GDP.

Based on the above observations, the probable reaction mechanism for CF dechlorination and decomposition by GDP is proposed in Scheme 1.

(Scheme 1)

It can be seen from Scheme 1 that the CF mineralization in GDP can be divided into three main steps: I) initiation of the reaction, II) hydrolysis of the chloromethyl radicals and III) oxidation of the organic acids. At the initial stage, CF preferentially react with hydrated electrons or $\bullet\text{H}$ atoms to form the corresponding dichloromethyl radicals with liberation of Cl^- (or HCl). In the second process, the resulting dichloromethyl radicals directly hydrolyzed to carboxyl radicals and HCl or subjected to oxygen enhanced hydrolyses to form CO_2 and HCl . The dichloromethyl radicals can also react with $\bullet\text{H}$ atoms or $\bullet\text{OH}$ radicals to form trace amount of chlorinated organic byproducts such as DCM and C_2Cl_4 . Subsequently, the resulting carboxyl radicals react with each other to form FA and OA. In the last step, the organic acids react with $\bullet\text{OH}$ radicals and are completely oxidized to CO_2 and H_2O . At the same time, the traces of the chlorinated organic intermediate byproducts are also mineralized to inorganic carbon and Cl^- (HCl) under the action of GDP.

3.6 Energy efficiency

Energy efficiency is an important indicator for comparing different techniques and for evaluating its potential industrial applications. In this study, the energy efficiency for CF removal (J_{CF}) is defined the quantity of CF removed per unit energy input,

which can be formulated as follows:

$$J_{\text{CF}} = \frac{\frac{1}{2} C_0 \text{Vol}}{U I t_{1/2}} \quad (29)$$

where C_0 is the initial CF concentration in mol/L, Vol is the liquid volume in L, U is the applied voltage in V, I is the current in A, and $t_{1/2}$ is the reaction time required for removing half of the initial CF molecules. Table 1 shows the energy efficiencies of the present work and some typical competitive methods.

(Table 1)

It can be seen that the energy efficiency of CF removal by GDP is in the same order of magnitude to that of ultrasonic oxidation and much higher than those of TiO_2 photocatalysis, especially in basic media and in the presence of hydroxyl radical scavengers. These demonstrated that GDP is a competitive process for CF removal.

4. Conclusions

CF can be efficiently dechlorinated and decomposed by GDP. The removal and the dechlorination of CF increased with increasing pH (from 2.0 to 11.0) and with addition of hydroxyl radical scavengers. Formic acid, oxalic acid and dichloromethane were the major intermediate byproducts. These byproducts can be fully mineralized to carbon dioxide and hydrochloric acid. Hydrated electrons were the main active species for initiation of the reaction, and $\bullet\text{OH}$ radicals were the ones for oxidation of the organic radicals and intermediate byproducts. Hydrolyses of the chloromethyl radicals and the chloromethylperoxyl radicals contributed much in the mineralization of the organic chlorine. Further studies on the mechanistic aspects are

underway.

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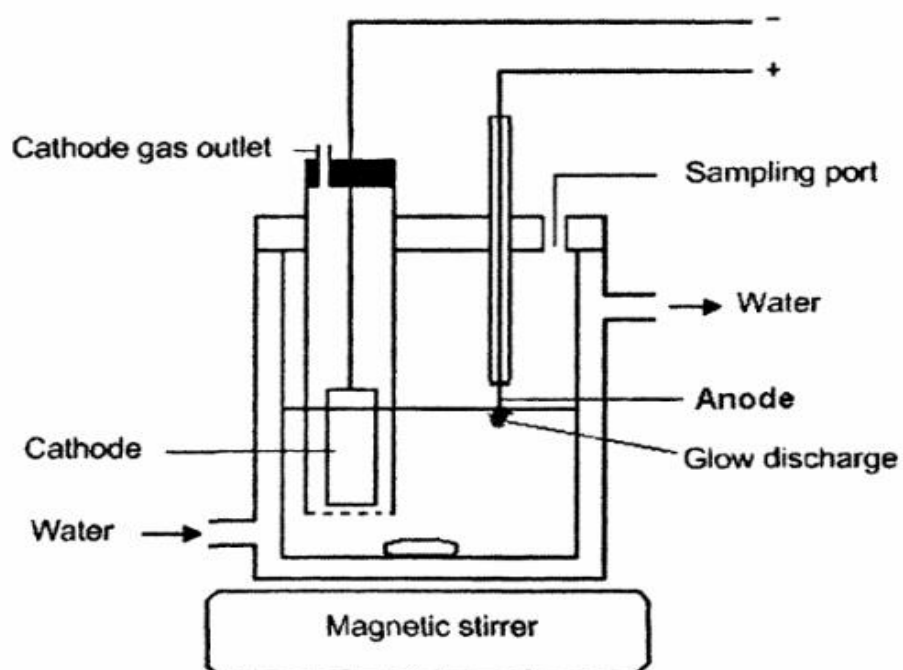


Fig.1. GDP reactor for dechlorination and decomposition of CF

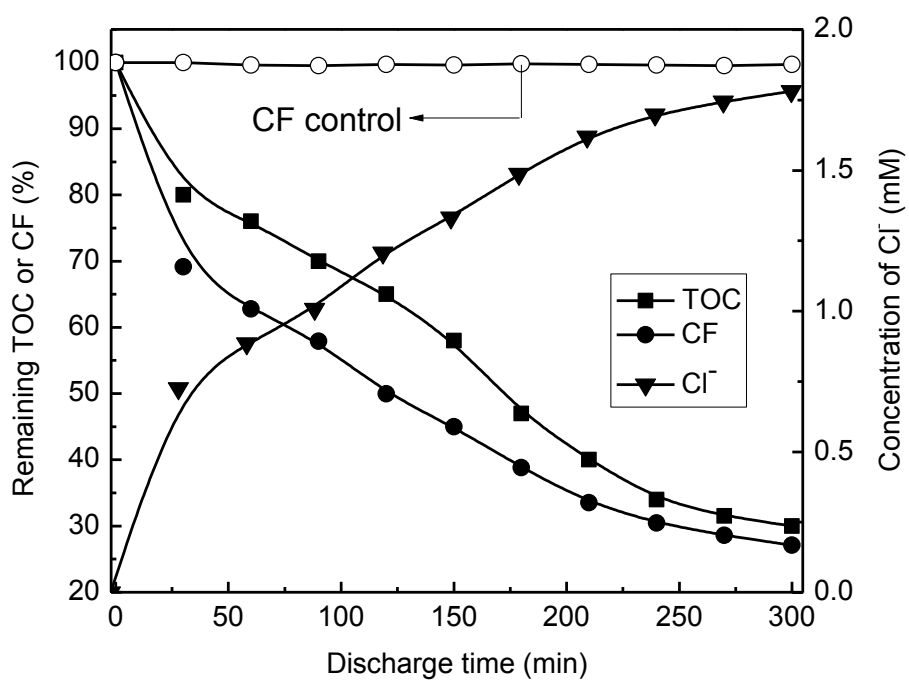


Fig.2. Concentration variations of CF, TOC and Cl^- during GDP treatment (voltage, 500 V; average current, 100 mA; solution volume, 150 ml; $[\text{CF}]_0$, 0.84 mM; pH_0 , 7.0)

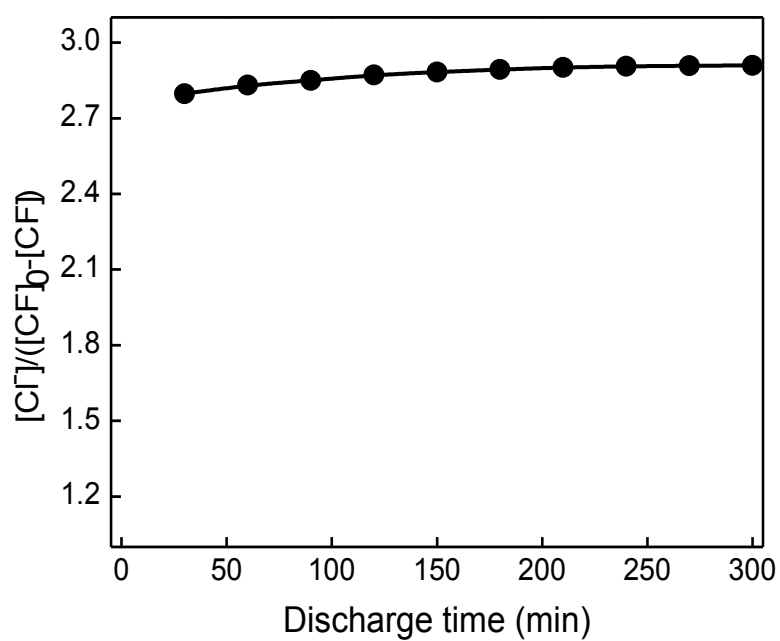


Fig.3. Variation of $[\text{Cl}^-]/([\text{CF}]_0 - [\text{CF}])$ during GDP treatment (voltage, 500 V; average current, 100 mA; solution volume, 150 ml; $[\text{CF}]_0$, 0.84 mM; pH_0 , 7.0)

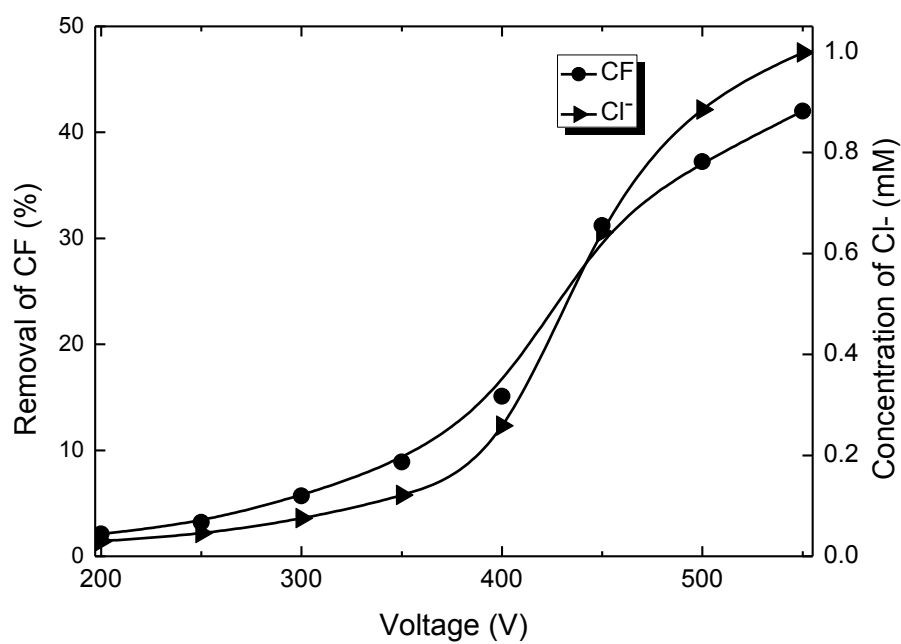


Fig.4. Effect of applied voltage on the removal of CF and the generation of Cl^- with 60 min of GDP treatment (current, 100 mA; solution volume, 150 ml; $[\text{CF}]_0$, 0.84 mM; pH_0 , 7.0)

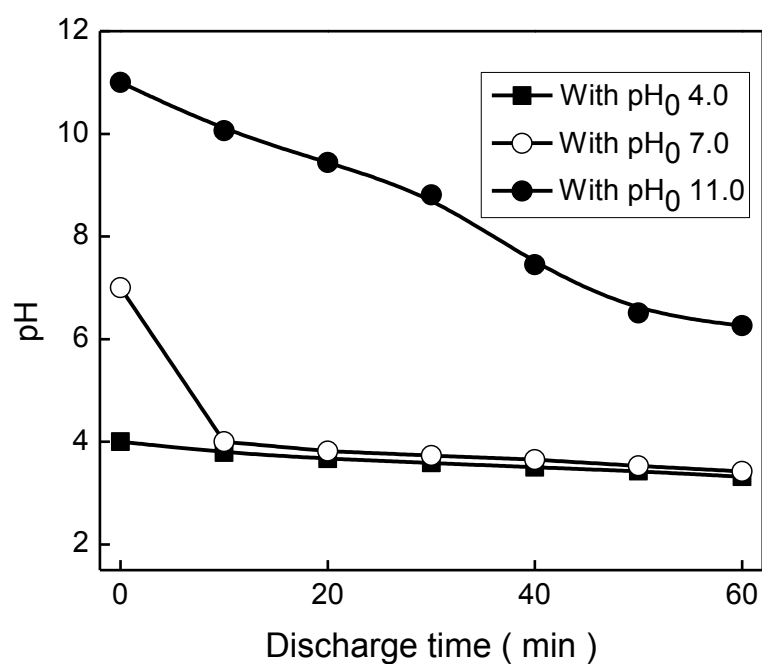


Fig.5. Variation of pH during GDP treatment under different pH₀ (voltage, 500 V; current, 100 mA; solution volume, 150 ml; [CF]₀, 0.84 mM)

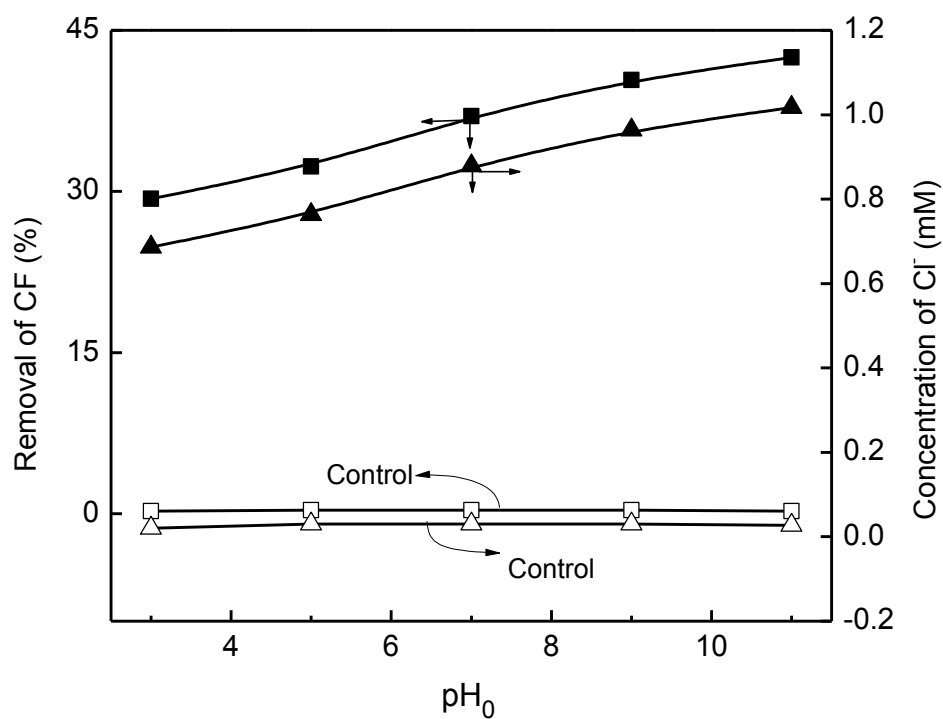


Fig.6. Effect of pH_0 on the removal of CF and the generation of Cl^- with 60 min of GDP treatment (voltage, 500 V; current, 100 mA; solution volume, 150 ml; $[\text{CF}]_0$, 0.84 mM)

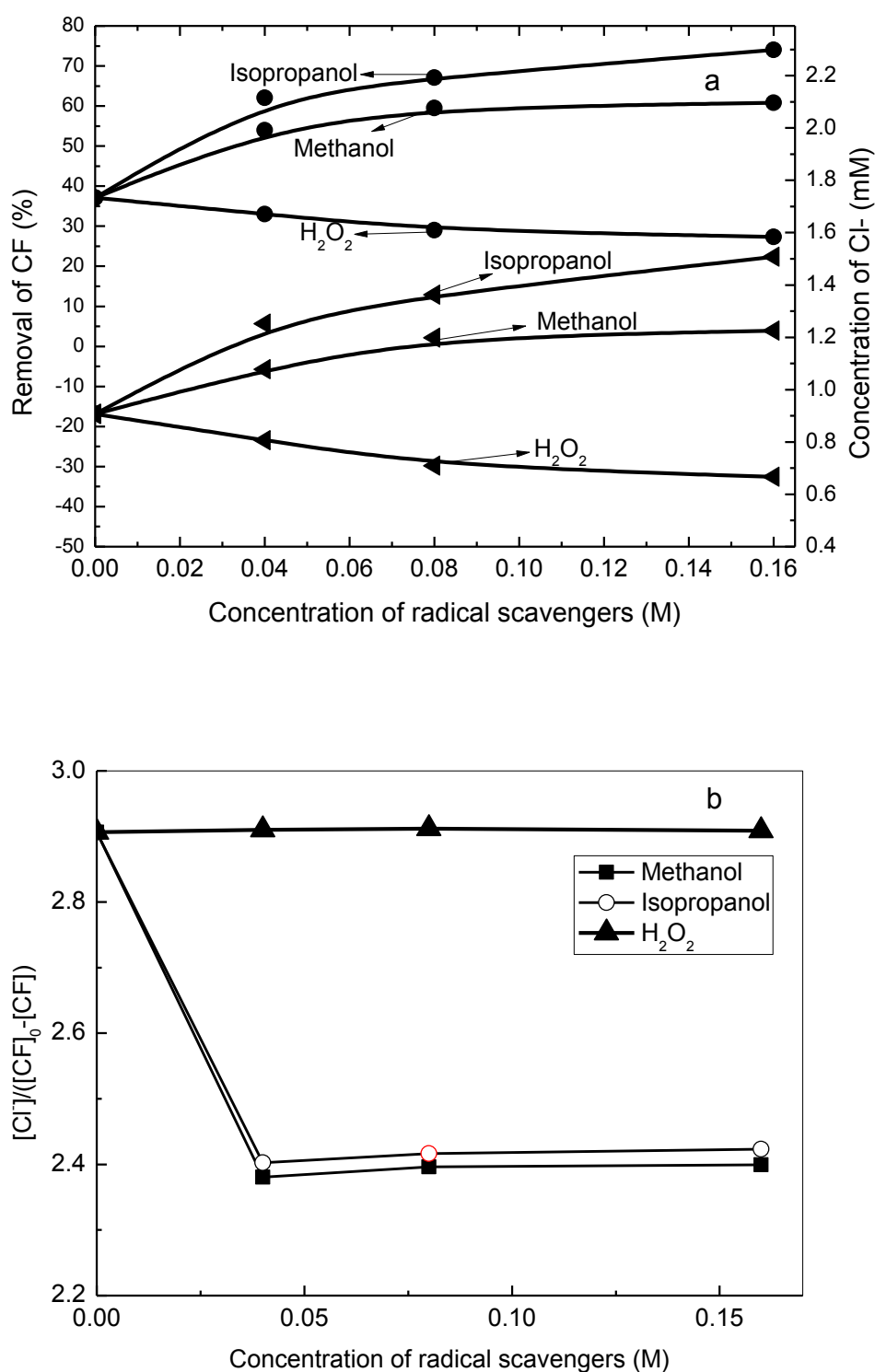


Fig.7. Effect of organic additives on the removal of CF and generation of Cl^- (a) and $[Cl^-]/([CF]_0-[CF])$ (b) (voltage, 500 V; current, 100 mA; solution volume, 150 ml; discharge time, 60 min; $[CF]_0$, 0.84 mM; pH_0 , 7.0)

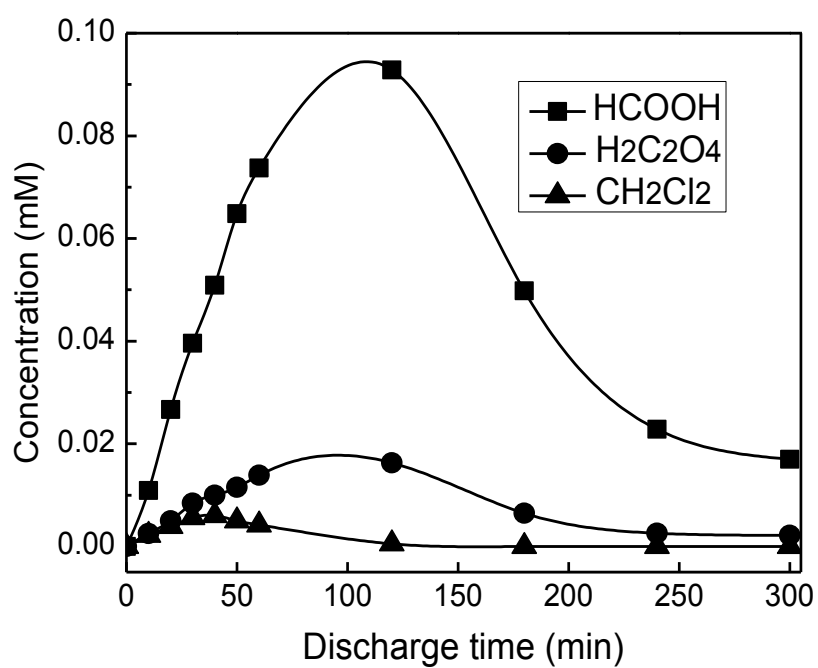
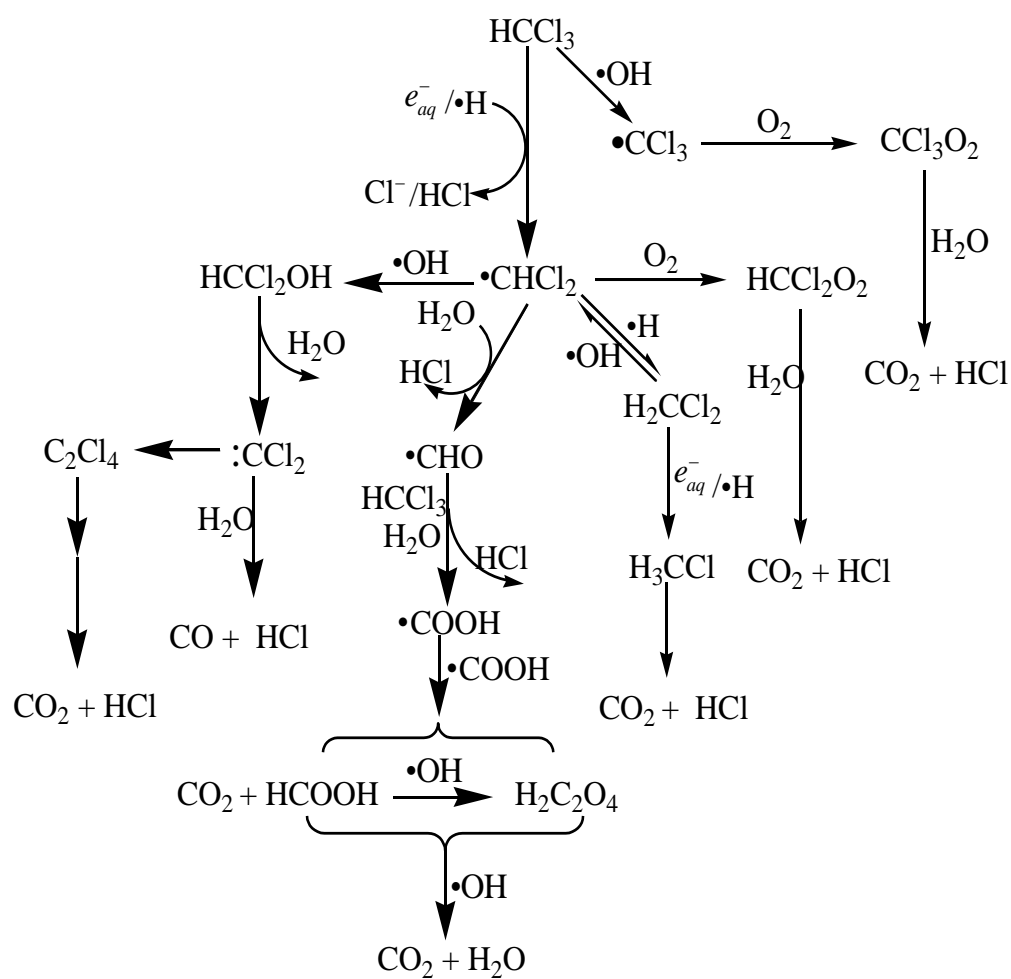


Fig.8. Intermediate byproducts formed during GDP treatment (voltage, 100 V; current, 100 mA; solution volume, 150 ml; $[CF]_0$, 0.84 mM; pH_0 , 7.0)



Scheme 1 Proposed reaction mechanism for CF mineralization in GDP

Table 1. Comparison of energy efficiency of GDP with those of other competitive technologies for CF removal

C_0 (mM)	Method and typical reaction conditions	J_{CF} (10^{-10} mol/J)	Removal efficiency at 60 min treatment (%)	References
0.84	GDP 50 W pH ₀ 7.0	2.1	37.1	This work
0.84	GDP 50 W pH ₀ 11.0	3.4	42.5	This work
0.84	GDP 50 W pH ₀ 11.0 0.16M isopropanol	8.5	88.2	This work
6.0	Photocatalysis 910 W pH ₀ 12.0, 0.5g/l TiO ₂	0.064	8.4	[11]
0.084	Sonolytic oxidation 18.4 W/l	1.26	13.2	[9]
0.2	Sonolytic oxidation 35 W	3.6	75.6	[29]