Electrochemical Degradation of Chloroform Using Ti/IrO₂ Anode and Cu/Zn Cathode

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Abstract: Electrochemical method is a promising technology for biorefractory organic wastewater treatment. In this study, commercial available electrode materials, Ti/IrO₂ and Cu/Zn, were used as anode and cathode, respectively, to treat CHCl₃-contaminated water. The performance was investigated through cyclic voltammetry and paired electrolysis in an undivided cell. The voltammetric data revealed that the Cu/Zn cathode exhibited good electrocatalytic activity toward CHCl₃ reduction. By contrast, no direct oxidation of CHCl₃ was observed at the Ti/IrO₂ anode. The reduction of CHCl₃ at the Cu/Zn cathode took place through a three-step consecutive hydrodechlorination mechanism. During the paired electrolysis with current density of 15 mA/cm², the chemical oxygen demand (COD) of CHCl₃ solution was decreased from 194 to 74 mg/L within 300 min with an energy consumption of 28.6 kWh · L⁻¹. A mild acidic environment (pH 4.6) was shown to be more favorable to CHCl₃ abatement. Decreasing the anode/cathode surface area ratio also had significant impact on CHCl₃ reduction, and the optimal ratio was 2.0. The results demonstrated that Cu/Zn cathode is a potential candidate for chlorinated organic compound removal. DOI: 10.1061/(ASCE)EE.1943-7870.00001035. © 2015 American Society of Civil Engineers.

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Introduction

Chlorinated organic compounds (COC) are frequently found in many surface and groundwater sources because of large scale utilization of chlorine-based chemicals in industry and household products (Huang et al. 2014). These substances are often associated with serious environmental and human health concerns. Chloroform (CHCl₃), one of the most dangerous and common COC, is often found in groundwater at industrial sites and tap water as a typical disinfection byproduct (Ali et al. 2014). Many evidences showed that CHCl₃ can cause depression of the central nervous system, mental confusion, and even cancer (Rossberg et al. 2002; Yang et al. 2014). Because of its serious impact on the environment and human health, CHCl₃ has been placed on the U.S. Environmental Protection Agency priority list of pollutants (U.S. EPA 2014).

Both destructive and nondestructive methods have been used to remove CHCl₃ and other COC from water. Nondestructive methods such as adsorption and extraction (Corsi and Card 1991) are less effective because the methods transfer pollutants from one phase to another. Therefore, destructive methods, such as aerobic/anaerobic degradation (Stucki et al. 1992; Perez-de-Mora et al. 2014), chemical oxidation (Reddy et al. 2007), photochemical oxidation (Mohseni 2005; Ohsaka et al. 2008), and chemical reduction (Harendra and Vipulanandan 2011), are more desirable. Although chemical methods are effective in degrading COC, expertise intensive chemicals such as H₂O₂ (Curtler et al. 1994), O₂ (Torun et al. 2011), and zero-valent iron (Janda et al. 2004; Fu et al. 2014) are often consumed. By contrast, biological processes often suffer from long reaction time and inhibitory effects because of the toxicity of COC or their partially dechlorinated intermediates (Stucki et al. 1992). Recent studies demonstrated that the electrochemical method is a promising alternative to conventional COC-contaminated wastewater treatment (Carter and Farrell 2009; Sonoyama et al. 2001; Niu et al. 2013). Carter and Farrell (2009) revealed that 1.7 mM trichloroethylene (TCE) could be completely removed in less than 10 min using boron-doped diamond (BDD) film electrodes at a current density of 20 mA/cm². Sonoyama et al. (2001) reported that trihalomethanes (THMs) in tap water could be decreased to concentrations below 1 parts per billion (ppb) using a Ag-impregnated activated carbon electrode. Moreover, the electrochemical process for COC treatment seldom involves the use of chemicals like H₂O₂ and O₂. By comparison, it is more economical and easier to operate than destructive chemical methods and has been widely investigated (Madsen et al. 2014; Isse et al. 2009, 2012; Sripriya et al. 2007; Sonoyama et al. 1997; Urtiaga et al. 2014; Hori et al. 2003). These studies were generally focused on the product distribution (Madsen et al. 2014), reaction mechanisms (Isse et al. 2009, 2012), and the effect of electrode materials on the electrochemical performance (Sripriya et al. 2007; Sonoyama et al. 1997; Urtiaga et al. 2014; Hori et al. 2003). BDD anode and Ag cathode were shown to be the most effective electrodes for the anodic oxidation and cathodic reduction, respectively (Madsen et al. 2014; Sonoyama et al. 1997; Urtiaga et al. 2014; Hori et al. 2003).
However, in the perspective of developing the electrochemical method into a feasible technology, the use of electrode materials of precious metal such as BDD and Ag is not very attractive for economic reasons. Thus, it is necessary to exploit some electrode materials with an affordable market price and a long working life to treat COC-contaminated wastewater.

In recent years, commercially available Ti/IrO$_2$ anode has been widely studied for organics removal from polluted waters owing to its good performance for chlorine evolution (Fan et al. 2014; Ikematsu et al. 2007; Barreto et al. 2014; Panizza and Cerisola 2009; Li et al. 2009b,a; Martinez et al. 2004; Motheo and Pinheiro 2000; Zaviska et al. 2013). Panizza and Cerisola (2009) demonstrated that a large variety of organic compounds could be effectively removed through electrochemical oxidation using Ti/IrO$_2$ anode with an effective Cl$^-$ concentration. Conversely, phenol could also be completely decomposed using Ti/IrO$_2$ based anodes (Li et al. 2009b). Meanwhile, the previous study on nitrate removal using the electrochemical method showed that the Cu/Zn electrode exhibited good performance in the cathodic reduction process (Li et al. 2009a). Nitrate could be selectively reduced to nitrogen at the Cu/Zn cathode. However, less attention has been paid to the Ti/IrO$_2$ anode and the Cu/Zn cathode for COC treatment. In addition, recent research revealed that an undivided cell is more effective for pollutant removal because of the possible synergetic effect between anodic oxidation and cathodic reduction (Scialdone et al. 2010; Li et al. 2009a). Scialdone et al. (2010) reported that a higher abatement of 1, 1, 2, 2-tetrachloroethane was obtained when the electrolysis was carried out in an undivided cell involving both oxidation at BDD and reduction at Ag, with respect to oxidation at BDD or reduction at Ag. Reduction intermediates resulting from the Ag cathode were oxidized on the BDD anode. Thus, overall abatement of 1, 1, 2, 2-tetrachloroethane was improved (Scialdone et al. 2010). This synergetic effect between anodic oxidation and cathodic reduction was also observed in nitrate removal using the Ti/IrO$_2$ anode and the Cu/Zn cathode in the previous study (Li et al. 2009a). The reduction intermediate resulting from the Cu/Zn cathode, such as ammonium, was oxidized to nitrogen by an oxidizing species generated at the Ti/IrO$_2$ anode, and hence, more nitrate was removed in a given electrolysis time (Li et al. 2009a).

In this study, Ti/IrO$_2$ and Cu/Zn were used as anode and cathode, respectively, to treat CHCl$_3$-contaminated water. The degradation mechanism and pathway of CHCl$_3$ were systematically investigated. A possible synergetic effect between Ti/IrO$_2$ oxidation and Cu/Zn reduction for CHCl$_3$ removal was explored. The influences of applied current densities, solution pH, and anode/cathode surface area ratios on the electrolysis were studied as well.

**Materials and Methods**

**Cyclic Voltammetric Experiments**

To verify the effectiveness of both direct oxidation and reduction for CHCl$_3$ abatement, cyclic voltammetric (CV) experiments were carried out in an undivided cell using a computer-controlled potentiotstat/galvanostat (CHI 660D, Shanghai Chenhua Instrument, Shanghai, China) at room temperature (25 ± 1°C). A three-electrode cell system with a saturated calomel electrode (SCE) as reference electrode was used. In the oxidation study, the working electrode was Ti/IrO$_2$ (TohoTech Company, Nagoya, Japan), and the counter electrode was a Cu/Zn (Cu: 62.2% by weight; Zn: 37.8% by weight) plate. For the reduction investigation, Cu/Zn was used as the working electrode, and Ti/IrO$_2$ was used as counter electrode. The supporting electrolyte was prepared with reagent grade NaH$_2$PO$_4$ and ultrapure water (resistivity-18.2 MΩ cm). Before use, the electrode’s surface was cleaned in an ultrasonic bath for 15 min. The working electrodes were cycled at a scan rate of 100 mV/s for at least three times. All of the solutions studied were deaerated by bubbling purified N$_2$ (99.99%) for 15 min prior to electrochemical measurements.

**Electrochemical Apparatus**

A cylindrical electrochemical cell with a net working volume of 700 mL was constructed with acryl plates. A constant reaction temperature was maintained by water cooling using an acryl jacket. The experimental apparatus is shown in Fig. 1. Ti/IrO$_2$ anode and Cu/Zn cathode have the same working area of 50 cm$^2$ (10 × 5 cm). Before use, the Cu/Zn electrode was polished with silicon-carbide papers and then carefully washed with ultrapure water for several times, whereas the Ti/IrO$_2$ anode was cleaned with ultrapure water. The distance between the anode and the cathode was 8 mm. A direct current (DC) power supply (HY-55, GuoDianYaGuang Power, Beijing, China) with a voltage range of 0–50 V and a current range of 0–5 A was used.

**Electrolysis Experiments**

Synthetic CHCl$_3$ solutions were prepared by introducing 1.5-mL reagent grade CHCl$_3$ into a 1,000 mL electrolyte (0.05 M NaH$_2$PO$_4$) using a syringe. The concentration of CHCl$_3$ was approximately 18 mM. The solution was stirred vigorously with a magnetic stirrer until CHCl$_3$ was completely dissolved. A 600-mL synthetic CHCl$_3$ solution was poured into the sealed electrochemical cell. The head-space was approximated to 100 mL. The electrolysis of CHCl$_3$ was performed in a sealed undivided cell under galvanostatic condition.

To investigate the possible synergetic effect between Ti/IrO$_2$ oxidation and Cu/Zn reduction, paired electrolysis was conducted with a current density of 30 mA/cm$^2$ for 300 min. Meanwhile, a blank experiment was performed in the absence of an electric field. Active chlorine formation was determined during the paired electrolysis. Its possible effect on the resulting intermediates was
investigated. Specifically, two samples (marked A and B) were withdrawn from the reactor at the end of the electrolysis. Then, an excess amount of Na$_2$S$_2$O$_7$ was added to Sample A to cease possible reactions between active chlorine and resulting intermediates of CHCl$_3$ immediately. Meanwhile, Sample B was placed in a sealed tube without the addition of Na$_2$S$_2$O$_7$ for 150 min. The resulting Cl$^-$ concentration in Sample A and B was compared.

The influencing factors tested in the experiments include the applied current densities (5, 15, 30, 45 mA/cm$^2$), initial solution pH (4.6, 7.0, 12.0), and surface area ratios of anode to cathode (1.0, 2.0, 3.0). The initial pH was adjusted to a desired value by adding 0.1 M H$_2$PO$_4$ or 0.1 M NaOH. Different anode/cathode surface area ratios of 1.0, 2.0, and 3.0 were achieved by changing the working surface of Cu/Zn electrode in between 50 cm$^2$ (10 × 5 cm), 25.0 cm$^2$ (10 × 2.5 cm), and 16.5 cm$^2$ (10 × 1.65 cm) while maintaining the Ti/IrO$_2$ anode to 50 cm$^2$ (10 × 5 cm). Throughout the electrolysis experiments in this study, a single Cu/Zn electrode was used, which showed to be always catalytically active regardless of the number of experiments or their durations. All the experiments were performed at 15 ± 1°C. Samples of 6.0 mL were periodically withdrawn from the electrochemical cell using a syringe for analysis. Variations of chemical-oxygen demand (COD) concentration and Cl$^-$ yield were determined.

The energy consumption (EC) for COD removal of CHCl$_3$ solution was estimated and expressed in kilowatt-hour per gram (kWh/g) COD. Average cell voltages at different current densities were taken for calculating EC, as follows (Santos et al. 2014):

$$\text{Energy consumption} = \frac{E \times I \times t}{3.600 \times (\text{COD}_0 - \text{COD}_t)}$$

where $t$ is the electrolysis time (s); $E$ (V) and $I$ (A) are the average cell voltage and the electrolysis current, respectively; COD$_0$ and COD$_t$ are COD concentration (mg/L) of CHCl$_3$ solution at time 0 and $t$, respectively.

**Analysis**

COD was determined by K$_2$Cr$_2$O$_7$ oxidation according to the standard method for water and wastewater measurement (Wei 2002). Cl$^-$ concentration was measured by means of an ion-chromatograph (ICS-900, Dionex, Massachusetts) equipped with an anion exchange column (Dionex IonPac AS 23, Massachusetts). The eluent was composed of Na$_2$CO$_3$ (1.8 × 10$^{-3}$ M) and NaHCO$_3$ (1.7 × 10$^{-3}$ M). The concentration of active chlorine was determined (as total mg Cl$_2$/L) by colorimetric method using a spectrophotometer (DR6000, HACH, Colorado). The solution pH was determined by a precision pH meter (ORION3, Thermo, Massachusetts). A GC-2014 gas chromatograph (SHIMAZU, Kyoto, Japan) equipped with a hydrogen flame ionization detector (FID) and RTX-5 column (SHIMAZU, Kyoto, Japan) was used to identify the electrolysis intermediates, such as dichloromethane (CH$_2$Cl$_2$) and monochloromethane (CH$_3$Cl). Minimum detection levels for both CHCl$_3$ and CH$_2$Cl$_2$ are 0.2 µg/L. The injector and detector temperatures were 230 and 250°C, respectively. The column was isothermal at 80°C for 4 min, ramped from 40 to 180°C, and then held for 10 min. The carrier gas, nitrogen, was set at a constant flow rate of 1 mL · min$^{-1}$.

**Results and Discussion**

**Cyclic Voltammetric Studies**

Fig. 2 shows the cyclic voltammograms recorded with the Ti/IrO$_2$ anode in the absence and presence of CHCl$_3$. It seems that CHCl$_3$ does not have a significant effect on the shape of the anodic part of the CV curve, suggesting the absence of a direct oxidation of CHCl$_3$ on the Ti/IrO$_2$ surface.

Cyclic voltammograms recorded with the Cu/Zn cathode in the absence and presence of CHCl$_3$ are depicted in Fig. 3. In the absence of CHCl$_3$, a peak appeared at around $E = -0.8$ V, which might be attributed to the reduction of Cu$_2$O to Cu species (Li et al. 2009c). Two irreversible reduction peaks were observed in the presence of CHCl$_3$, at $-1.34$ and $-2.15$ V versus SCE, respectively. This suggests that interactions between CHCl$_3$ and Cu/Zn surface existed. Similar reduction behaviors were observed by other researchers when CHCl$_3$ reduction was performed at Cu (Issa et al. 2012) and Ag cathodes (Issa et al. 2009; Durante et al. 2009). Reduction peaks presented at different potentials corresponded to reduction of starting CHCl$_3$ and its reduction intermediates dichloromethane (CH$_2$Cl$_2$). Potentials obtained at Cu/Zn ($-1.34$ and $-2.15$ V) are close to those at Ag for CH$_2$Cl$_2$ (−1.31 V) and CHCl$_3$
(-2.13 V) (Isse et al. 2009; Durante et al. 2009). Moreover, CH₂Cl₂ was detected as reduction intermediates during the paired electrolysis of CHCl₃ (paired electrolysis). Thus, it is reasonable to hypothesize that peaks presented at −1.34 and −2.15 V resulted from reduction of CHCl₃ and its reduction intermediates CH₂Cl₂, respectively. Therefore, similar to Ag and Cu electrodes, the Cu/Zn cathode used in the present study reduced CHCl₃ through a set of consecutive dechlorination steps. To be specific, a dissociative electron transferred to CHCl₃ first, resulting in the formation of trichloromethyl radical and a Cl⁻; then, the intermediate radical was immediately reduced to carbon, which was then protonated to be CH₂Cl₂ by H₂O (Isse et al. 2012; Durante et al. 2009). When the applied potential was negative enough, the same pattern was repeated until CH₃ was formed. The overall reduction pathway could be described as follows (Isse et al. 2012; Durante et al. 2009):

\[
\begin{align*}
\text{CHCl}_3 + e^- & \rightarrow \text{CHCl}_2 + \text{Cl}^- \quad (2) \\
\text{CHCl}_2 + e^- & \rightarrow \text{CHCl}^- \quad (3) \\
\text{CHCl}_2 + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{Cl}_2 + \text{OH}^- \quad (4) \\
\text{CH}_2\text{Cl}_2 + e^- & \rightarrow \text{CH}_2\text{Cl}^- + \text{Cl}^- \quad (5) \\
\text{CH}_2\text{Cl} + e^- & \rightarrow \text{CH}_2\text{Cl}^- \quad (6) \\
\text{CH}_2\text{Cl} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{Cl} + \text{OH}^- \quad (7) \\
\text{CH}_3\text{Cl} + e^- & \rightarrow \text{CH}_3 + \text{Cl}^- \quad (8) \\
\text{CH}_3 + e^- & \rightarrow \text{CH}_3^- \quad (9) \\
\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{CH}_4 + \text{OH}^- \quad (10)
\end{align*}
\]

Peaks at −1.34 and −2.15 V are attributed to the reduction of CHCl₃ to CHCl₂ [Eqs. (2) and (3)] and CH₂Cl₂ to CH₂Cl⁻ [Eqs. (5) and (6)], respectively (Isse et al. 2009; Durante et al. 2009). However, the peak corresponding to CH₂Cl⁻ reduction [Eqs. (8) and (9)] was not observed. The finding is consistent with previous studies at the Ag (Isse et al. 2009) and Cu cathode (Durante et al. 2009). This can be explained by the fact that the reduction potential of CH₂Cl⁻ at catalytic electrodes are slightly positive than that of CH₂Cl₂ at the same electrodes (Isse et al. 2009; Durante et al. 2009). Thus, the reduction peak of CH₂Cl⁻ at the Cu/Zn cathode was masked by that of CH₂Cl₂ in the present study.

Similar to Ag and Cu cathodes, the Cu/Zn cathode reduced CHCl₃ to CH₂Cl₂, CH₁Cl, and CH₃ sequentially. Furthermore, comparable reduction potentials indicate the electrocatalytic activity of Cu/Zn for CHCl₃, and CH₂Cl₂ reduction is comparable with that of Ag, which is the most active electrode material for organic halides dehalogenation so far. However, Cu/Zn is notably cheaper than Ag (10 times cheaper) and thus a potential candidate for COC-contaminated water treatment.

**Paired Electrolysis**

For the electrochemical degradation of pollutants performed in an undivided cell, cathodic reduction can be enhanced by coupling with anodic oxidation owing to the simultaneous oxidation of intermediates generated at cathodes (Li et al. 2009a, c; Scialdone et al. 2010). In the present experiment, the reduction of CHCl₃ at the Cu/Zn cathode resulted in the formation of intermediates CH₂Cl₂, CH₁Cl, and CH₃ sequentially. Furthermore, comparable reduction potentials indicate the electrocatalytic activity of Cu/Zn for CHCl₃, and CH₂Cl₂ reduction is comparable with that of Ag, which is the most active electrode material for organic halides dehalogenation so far. However, Cu/Zn is notably cheaper than Ag (10 times cheaper) and thus a potential candidate for COC-contaminated water treatment.

Thus, it is necessary to verify if there is a synergistic effect between Cu/Zn reduction and Ti/IrO₂ oxidation for CHCl₃ degradation.

The COD of CHCl₃ solution was reduced from 194 to 60 mg/L at a current density of 30 mA/cm² within 300 min. By contrast, no variation of COD and Cl⁻ concentration was observed in the blank experiment. Accumulation of CH₂Cl₂ as a reduction intermediate was observed during the electrolysis, whereas no CH₂Cl⁻ was detected. This is consistent with the CV analysis that CH₂Cl⁻ is easier to be reduced than CH₂Cl₂ at the Cu/Zn cathode, and thus, it cannot be accumulated. Active chlorine (as total mg Cl⁻/L) accumulation was detected as well because of the anodic oxidation of Cl⁻ generated at the Cu/Zn cathode [Eqs. (11) and (12)] (Bejankiwar et al. 2005)

\[
\begin{align*}
\text{Cl}^- & \rightleftharpoons \text{Cl}_{\text{ads}} + e^- \quad (11) \\
\text{Cl}^- + \text{Cl}_{\text{ads}} & \rightleftharpoons \text{Cl}_2 + e^- \quad (12)
\end{align*}
\]

The concentration of active chlorine was increased gradually as the electrolysis preceded and reached a maximum of 17 mg/L at the end of electrolysis. Additionally, Na₂S₂O₄ addition has negligible effect on the final Cl⁻ concentrations of Sample A (448.3 mg/L) and B (446.5 mg/L), suggesting that the active chlorine had negligible effect on CHCl₃ reduction intermediates. Meanwhile, a trace amount of CO₂ (data not shown) was detected at the end of the electrolysis. The corresponding carbon amount merely accounted for 1.85% (m/m) of the carbon in the starting CHCl₃, suggesting the mineralization of CHCl₃ and its reduction intermediates was insignificant. According to previous studies, combustion of organic compounds on oxide anodes took place as follows [Eqs. (13) and (14)] (Szpyrkowicz et al. 2001):

\[
\begin{align*}
\text{MO}_X + \text{H}_2\text{O} & \rightarrow \text{MO}_X^[·\text{OH}] + \text{H}^+ + e^- \quad (13) \\
\text{MO}_X^[·\text{OH}] + R & \rightarrow \text{MO}_X + \text{CO}_2 + \text{H}^+ + e^- \quad (14)
\end{align*}
\]

Hence, CO₂ probably resulted from the oxidation of CHCl₃, or its partially reduced intermediates mediated by a hydroxyl radical. However, Ti/IrO₂ anode has been reported to be an active electrode. The hydroxyl radical produced would react with its surface leading to the so-called higher oxide MOₓ⁺₁ [Eq. (15)] (Canizares et al. 2002)

\[
\text{MO}_X^[·\text{OH}] + R \rightarrow \text{MO}_X + \text{CO}_2 + \text{H}^+ + e^- \quad (15)
\]

The oxidizing capacity of MO is weaker than that of the hydroxyl radical (Comminellis 1994), and organic can only be partially oxidized [Eq. (16)] (Szpyrkowicz et al. 2001)

\[
\text{MO}_X + R \rightarrow \text{MO}_X + \text{product} \quad (16)
\]

In addition, Ti/IrO₂ anode has low oxygen evolution potential (Fig. 2) and will shorten the lifetime of produced hydroxyl radical, leading to a low chemical reactivity for organics oxidation. Therefore, little CHCl₃ or its reduction intermediates was oxidized to CO₂ during the electrolysis.

The insignificant mineralization caused by Ti/IrO₂ anode and negligible effect of electrogenerated active chlorine on CHCl₃ reduction intermediates indicate that the synergistic effect between cathodic reduction and anodic oxidation reported in previous studies (Li et al. 2009a, c; Scialdone et al. 2010) was not observed in the present study. CHCl₃ reduction was not enhanced by coupling the cathodic reduction at Cu/Zn with the anodic oxidation at Ti/IrO₂. COD removal of CHCl₃ solution was mainly due to the reduction of CHCl₃ at the Cu/Zn cathode.
**Influence of Applied Current Density on CHCl₃ Degradation**

The applied current density regulates the electron transfer capability in galvanostatic electrolysis and thus, may affect CHCl₃ reduction in this work. Considering the removal efficiency and energy consumption, the influence of current density on CHCl₃ degradation was investigated by setting the current densities between 5 and 45 mA/cm².

Fig. 4 shows the variations of COD concentration and Cl⁻ yield during the electrolysis at different current densities. It is shown that raising the applied current density from 5 to 30 mA/cm² led to a significant increase in COD removal and Cl⁻ production. The final COD removal efficiency and maximum Cl⁻ concentrations were increased from 20.4% and 299.3 mg/L at 5 mA/cm² to 68.9% and 407.8 mg/L at 30 mA/cm², respectively. As discussed above, COD removal was mainly attributed to CHCl₃ reduction at the Cu/Zn cathode. Raising applied current densities led to a greater charge passing into the electrochemical cell in a given period, resulting in a faster CHCl₃ reduction (Panizza and Cerisola 2006). However, when the current density was further increased from 30 mA/cm² to 45 mA/cm², insignificant improvement was observed for COD removal and Cl⁻ yield. Instead, the COD removal rate was slightly declined. This might be because of the increase of a side reaction of hydrogen evolution (Panizza and Cerisola 2004). Considering the anodic oxidation of Cl⁻ generated at the Cu/Zn cathode [Eqs. (11) and (12)], the dechlorination ratio (R) was estimated as follows:

\[
R = \frac{[\text{Cl}^-]_{\text{max}}}{[\text{Cl}^-]_0} \times 100\%
\]  

where \([\text{Cl}^-]_{\text{max}}\) is the maximum Cl⁻ concentration experimentally measured in the solution, including Cl⁻ resulting from the reduction of CHCl₃ to CH₄ and other partially dechlorinated intermediates. \([\text{Cl}^-]_0\) is the maximum release of Cl⁻ resulting from CHCl₃ reduction, assuming that all the starting CHCl₃ was transformed to CH₄. The estimated dechlorination efficiencies at 5, 15, 30, and 45 mA/cm² were 25.23, 34.43, 34.43, and 33.14%, respectively. It seems that increasing the current density from 15 to 30 and 45 mA/cm² has no significant effect on the estimated dechlorination efficiency. The weak effect may be attributed to the heavier hydrogen evolution at the Cu/Zn cathode at higher current (Radjenovic et al. 2012; Li and Farrell 2000). Nevertheless, the estimated efficiencies should be lower than real values because the Cl⁻ oxidized by the Ti/IrO₂ anode was not calculated in \([\text{Cl}^-]_{\text{max}}\).

According to Eq. (1), energy consumption of 5, 15, 30, and 45 mA/cm² for CHCl₃ solution treatment are 160.8, 239.9, 532.5, and 919.8 kWh · g⁻¹ COD, respectively, at the end of electrolysis. Considering CHCl₃ removal efficiency and energy demand, 15 mA/cm² is more favorable for scaled up or practical water treatment.

**Influence of Solution pH on CHCl₃ Degradation**

For wastewater treatment using the electrochemical method, solution pH usually affects the pollutant removal in both anodic oxidation (Hamidi and Amin 2014; Steven et al. 2013) and cathodic reduction processes (Dortsiou et al. 2013; Li et al. 2010; Ruotolo et al. 2006). In the present experiment, influence of solution pH on CHCl₃ degradation was investigated by comparing COD removal and Cl⁻ yield at pH 4.6, 7.0, and 12.0. Batch electrolysis with 18 mM CHCl₃ was carried out at 30 mA/cm² for 300 min.

As shown in Fig. 5, COD removal is similar at the three different pHs in the first 120 min. According to Li and Farrell (2000), solution pH had a small effect on COD reduction if the compounds undergo direct reduction at the cathodes. The minimal effect of pH on CHCl₃ removal here is consistent with the reduction mechanism involving direct electron transfer at the Cu/Zn cathode. During the electrolysis, however, the side reaction of hydrogen evolution would suppress the reduction of CHCl₃ and its partially dechlorinated intermediates. Hydrogen evolution is more favorable in acid condition during the electrolysis (Ludtke et al. 1998). Thus, the lowest Cl⁻ yield was obtained at pH 4.6. Li et al. (2010) reported a similar effect of hydrogen evolution on nitrate reduction at the Cu cathode.

After 180 min, different COD removal and Cl⁻ yield were observed at different pH values. The electrolysis performed at pH 4.6 was more effective, giving rise to a faster COD removal and the highest Cl⁻ yield. However, with the increase of electrolysis time, decline of Cl⁻ concentration was observed in all cases. Simultaneous oxidation of the generated Cl⁻ to hypochlorite (ClO⁻) at the Ti/IrO₂ anode [Eqs. (11) and (12)] may be responsible for the decline. Moreover, two Cl⁻ will be transformed to ClO⁻ if the electrolysis was carried out in an alkaline condition [Eq. (18)] (Scialdone et al. 2009).

\[
\text{Cl}_2 + 2\text{OH}^- \leftrightarrow 2\text{ClO}^- + \text{H}_2\text{O}
\]  

Fig. 4. Concentration of COD (solid line) and Cl⁻ (dashed line) during the electrolysis at different current densities; initial pH: 4.6

Fig. 5. Concentration of COD (solid line) and Cl⁻ (dashed line) during the electrolysis at different pH 4.6; applied current density: 30 mA/cm²
Thus, the Cl\textsuperscript{−} concentration at pH 12.0 was always lower than that in other conditions in this period, although its corresponding COD removal was not the lowest. In addition, Reyter et al. (2010) reported that Cl\textsuperscript{−} could be easily reduced to Cl\textsuperscript{−} at the Cu electrode at pH 12.0 [Eq. (19)]

\[
\text{ClO}^{-} + 2e + \text{H}_2\text{O} \rightarrow \text{Cl}^{-} + 2\text{OH}^{-} \quad (19)
\]

Cu/Zn electrodes usually show better electrocatalytic activity than Cu electrodes toward pollutants reduction (Máčová and Bouzek 2005). Thus, ClO\textsuperscript{−} reduction would occur with the reduction of CHCl\textsubscript{3} and its partially dechlorinated intermediates. Consequently, as shown in Fig. 5, CHCl\textsubscript{3} degradation was more efficient in acid condition in spite of the negative effect of the side reaction (hydrogen evolution). However, COD removal at pH 7.0 was less efficient than that at 12.0. This can be explained by considering the formation of passive layer [Fig. 6(b)] at pH 7.0 during the electrolysis. Before the electrolysis, the colour of Cu/Zn cathode is golden brown, as shown in Fig. 6(a). The black passive layer would reduce the active sites at the Cu/Zn cathode and inhibit the electron transfer.

**Influence of Anode/Cathode Surface Area Ratios on CHCl\textsubscript{3} Degradation**

During the electrochemical reduction of COC, product distribution depends greatly on the applied cathodic potential (Isse et al. 2009; Durante et al. 2009). For the electrolysis performed under galvanostatic condition, changing anode/cathode surface area ratio is a good way to independently control electrode potentials (Reyter et al. 2010) and thus optimize the product distribution. Electrolysis with ratios of 1.0, 2.0, and 3.0 was carried out at 5 mA/cm\textsuperscript{2} under mild acid condition (pH 4.6). Different area ratios were obtained by changing the cathode (Cu/Zn) surface in between 50 (S), 25 (S/2), and 16.5 (S/3) cm\textsuperscript{2}, respectively, while maintaining the anode (Ti/IrO\textsubscript{2}) surface at 50 (S) cm\textsuperscript{2}.

The resulting variations of COD concentration and Cl\textsuperscript{−} yield with respect to the electrolysis time are shown in Fig. 7. Apparently, the Cu/Zn cathode with S/2 surface area is the most efficient for CHCl\textsubscript{3} degradation. COD removal in the first 120 min was remarkably higher than those in other conditions. Moreover, the final Cl\textsuperscript{−} concentration (381 mg/L) is even comparable with that obtained in the electrolysis performed at 30 mA/cm\textsuperscript{2}. For paired electrolysis performed under galvanostatic condition, decreasing the cathode surface individually leads to a negative shift of the cathode potential (Reyter et al. 2010). In the present experiment, cathode potentials of Cu/Zn with a surface of S, S/2, and S/3 would be in the order of $E_S > E_{S/2} > E_{S/3}$. According to Li and Farrell (2000), the effect of cathode potential on the reduction rate ($k_r$) of chlorinated organic compounds can be described as follows:

\[
k_r = k_0 e^{-\alpha (E - E_{eq}) / RT}
\]

where $k_0$ is the standard rate constant, which is dependent on the chemical factors, $E_{eq}$ is the equilibrium potential for the redox reaction, $F$ is the Faraday constant, $R$ is the gas constant, $T$ is the temperature, and $\alpha$ is the transfer coefficient for the reduction reaction. According to Eq. (20), the ratio of reduction rates at three surface areas, S, S/2, and S/3, is then given by

\[
k_{S/2}/k_S = e^{\alpha (E_{S/2} - E_{S}) / RT} < 1
\]

\[
k_{S/3}/k_{S/2} = e^{\alpha (E_{S/3} - E_{S/2}) / RT} < 1
\]

Reduction rates were raised when the Cu/Zn surface was reduced from S to S/2 and S/3. Consequently, halving the Cu/Zn cathode surface area gave rise to a higher COD removal and Cl\textsuperscript{−}. The limited activity of the Cu/Zn cathode with the S/3 surface area can be explained by the depletion of active sites (Zhuo et al. 2011).

In addition, variation of COD concentration was merely observed in the first 120 min when Cu/Zn cathodes with S/2 and S/3 were applied. By contrast Cl\textsuperscript{−} concentrations were increased continually during the entire processes. The possible reason would be that high current densities led to polarization of Cu/Zn cathodes (Bard and Faulkner 2000), resulting in the negative shift of reduction potentials of CHCl\textsubscript{3} and the resulting intermediates. Consequently, complete reduction of these compounds was inhibited, whereas partial dechlorination of them was not suppressed.
Therefore, an increase of Cl<sup>-</sup> concentration without COD removal was observed between 120 and 180 min.

**Conclusions**

CHCl<sub>3</sub> can be degraded in an undivided electrochemical cell using Ti/IrO<sub>2</sub> anode and Cu/Zn cathode in aqueous solution. The removal of CHCl<sub>3</sub> was mainly attributed to the CHCl<sub>3</sub> reduction at the Cu/Zn cathode. Applied current densities, pH, and anode/cathode surface area ratio were found to influence the degradation of CHCl<sub>3</sub> to some extent. For CHCl<sub>3</sub> reduction, the Cu/Zn cathode exhibited comparable electrocatalytic activity with Ag, which is the most active electrode material for organic halide dehalogenation so far. Considering that Cu/Zn is notably cheaper than Ag, Cu/Zn cathode may be a good alternative for CHCl<sub>3</sub>-contaminated water treatment, especially in a scaled-up system. In addition, Cu/Zn cathode remains active during long lasting electrolyses, which demonstrates its good resistance to poisoning. The results provide important information for scaling up the electrochemical method and developing it into a feasible technology for halogen-contaminated water treatment.

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**References**


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