



Trichloroacetic acid reduction by an advanced reduction process based on carboxyl anion radical

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HIGHLIGHTS

- CO_2^- radical reacted with TCAA at a rate constant of $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.
- Good degradation efficiency was shown in presence of dissolved oxygen.
- High dechlorination rate was obtained throughout the whole process.
- Both CO_2^- radical and e_{aq}^- were involved in the degradation mechanisms.

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ABSTRACT

UV₂₅₄ irradiation combined with TiO₂ in the presence of formate (FM) was used to develop a carboxyl anion radical (CO_2^-)-based process to degrade trichloroacetic acid (TCAA). The efficiency and mechanism of TCAA decontamination were examined, and its potential for practical use was then assessed by evaluating the effects of process variables (FM dosage, solution pH, temperature, HCO_3^- , dissolved organic matter, and NO_3^-), the treatability of residual FM, and the technical economy on TCAA. Results showed that even without O₂ stripping, the UV/TiO₂/FM process degraded TCAA more efficiently than the UV/TiO₂/O₂ aeration process. The kinetic and transformant investigation suggested that CO_2^- and hydrated electron (e_{aq}^-) were involved in TCAA degradation by attacking the C–Cl bond. The CO_2^- precursor (FM) had an optimum dosage. The redundancy analysis indicated that the effect of six variables on degradation efficiency followed the order of temperature > FM dosage > HCO_3^- > NO_3^- > pH. The remaining FM cannot be eliminated by the adsorption by activated carbon and magnetic ion exchange resin. The economic evaluation revealed that most of the expenses went to the production of primary radicals such as HO \cdot and e_{aq}^- (sources of secondary radical CO_2^-). Therefore, a simple, harmless, efficient, and low-energy-consuming process is desired to generate CO_2^- for halogenated pollutant removal.

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1. Introduction

The disinfection of drinking water, which dramatically decreases public health risk, has been considered an important technical advance in the last century. Among the currently available disinfectants, chlorine is the most frequently used disinfectant in drinking water because of its high inactivation efficiency, low cost, and residual disinfecting capacity [1]. However, the generation of harmful chlorinated disinfection byproducts (DBPs) accompanies the disinfection process [2]. Among these chlorinated DBPs, trihalomethanes and haloacetic acids (HAAs) have been the most

investigated; their occurrence and factors affecting their formation are relatively well-understood. Furthermore, great efforts have been made to develop proper technological solutions to control DBPs.

The best available technology that is recommended by the US Environmental Protection Agency for the control of DBPs is the removal of precursors, such as natural organic matter (NOM), by granular activated carbon (GAC) and/or membranes. Recently, magnetic ion exchange (MIEX) resin and UV-based advanced oxidation processes (AOPs) were reported to perform well in removing the precursors of DBPs [3–5]. Unfortunately, DBP formation also occurs in the water distribution system because of the reaction of chlorine with the organic precursor material associated with deposits on the pipe wall [6]. Therefore, tap water is unsafe

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until the secondary purification of DBPs is completed. Current high-pressure membrane processes, such as nanofiltration or reverse osmosis, are considered the most viable technologies for the removal of DBPs and other micropollutants from tap water [7]. However, membrane processes cannot really solve this environmental problem because membrane filtration only transfers DBPs from the feeding water to the membrane surface and concentrates the DBPs. Therefore, further treatment is still unavoidable.

The toxicity and persistence of chlorinated DBPs is associated with the carbon–halogen single bond (C–X; X = Cl, Br, I); therefore, a permanent solution to these issues should still involve the dechlorination of HAAs. Under oxidized conditions, HAAs are likely to have low reactivity because of the electron-withdrawing C–X groups in the molecular structure [8,9]. The oxidative cleavage of C–X needs a high oxidation potential (>2.0 V), whereas reductive cleavage can be achieved easily. Advanced reduction processes (ARPs) are characterized by the production of highly reactive reducing radicals, such as hydrated electron (e_{aq}^-), hydrogen atoms (H^\cdot), and carboxyl anion radicals ($CO_2^{\cdot-}$); these processes may be an alternative approach to dechlorination [10].

Several ARPs (such as ionizing radiation, vacuum-UV photolysis, UV combined with iodide or sulfite) have been reported to successfully achieve the dehalogenation of monochloroacetic acid (MCAA) [11], vinyl chloride [12], and perfluorochemicals [13]. Sulfite/UV ARP has attracted significant attention because of its mild operating conditions, high reductive e_{aq}^- (–2.3 V), and resistance to adverse effects of dissolved oxygen [14,15]. The challenge of sulfite/UV ARP is to control the formation of sulfur-containing organic intermediates [16]. Similar to e_{aq}^- , $CO_2^{\cdot-}$ (–2.0 V) is a strong reductant as the product of one-electron reactions between organic carboxylic acids (e.g., oxalate [17], formate (FM) [18], or citrate [19]) and e_{aq}^- , H^\cdot , and hydroxyl radicals (HO^\cdot). Despite its ionic and radical nature, $CO_2^{\cdot-}$ can be remarkably stable [20] and can be used to achieve high quasi-stationary concentration. The easy generation and relatively high stability make $CO_2^{\cdot-}$ -based processes attractive even though the reducibility of $CO_2^{\cdot-}$ is relatively weak compared to e_{aq}^- ; Cr(VI) and perfluorooctanoic acid were reported to realize effective depollution by $CO_2^{\cdot-}$ -based processes [19,21].

Photocatalytic remediation has been widely researched for the elimination of a wide variety of refractory organic contaminants. Photogenerated electron/hole pairs (e^-/h^+) are known to be formed once photocatalysts are irradiated. Electron traps (i.e. H_2O_2 , BrO_3^- , NO_3^- , persulfate, O_2) are usually employed to scavenge the photogenerated electrons and increase degradation efficiency [22]. Most organics are known to be destroyed by the HO^\cdot formed during the photocatalytic processes. Therefore, only h^+/HO^\cdot ($h^+ + OH^- \rightarrow HO^\cdot$) is utilized. If both e^- and h^+ can be used to degrade pollutants, the detoxification performance may be improved. FM was reported to react with e^- and h^+ to form strong reductant $CO_2^{\cdot-}$ [23]. Therefore, photocatalysis in the presence of FM was proposed to degrade chlorinated DBPs.

We have made a few attempts to understand the possibility of applying $CO_2^{\cdot-}$ -based-ARP to remove chlorinated DBPs. For this purpose, the typical UV/TiO₂ process combined with the addition of FM (UV/TiO₂/FM) was used to generate a $CO_2^{\cdot-}$ -based system; trichloroacetic acid (TCAA, one of the most frequently detected chlorinated DBPs) was chosen as the model compound. First, the efficiency and mechanism of TCAA decomposition by the UV/TiO₂/FM process were examined. The degree of the effects of common water quality variables and operational parameters was then investigated. The residual FM and further treatment were also discussed. Finally, technical economic analysis was performed.

2. Material and methods

2.1. Materials and reagents

TCAA, MCAA, chloronitromethane (CNM), dichloroacetic acid (DCAA), sodium FM, humic acid (HA), 3,4-dihydro-1-oxylato-2,2-dimethyl-2H-pyrrololium (DMPO), HPLC-grade methanol, and methyl tertiary-butyl ether were ordered from Sigma–Aldrich. Other reagents, such as $NaNO_3$ and H_2SO_4 , NaOH, HCl, $NaHCO_3$, and anhydrous Na_2SO_4 , were purchased from J&K Scientific. The 1 M FM stock solution was prepared with sodium FM weekly and placed at a 4 °C refrigerator. Commercial GAC (Taiyuan Xinhua Activated Carbon Company, China) with a specific surface area of 800 m²/g was washed repeatedly with 10% HCl and deionized water and then dehydrated. The virgin MIEX resin was obtained by Orica Watercare. Prior to use, MIEX was pretreated with tap water and deionized water successively. The TiO₂ solution was freshly prepared and needed constant stirring with a concentration of 5 g L^{–1} in deaerated Milli-Q water every day. Anhydrous Na_2SO_4 was calcined at 450 °C in a muffle furnace for 2 h before use. Approximately 18.2 MΩ cm ultra-pure water was used for solution preparation. Compressed N₂ and O₂ with high-purity were provided by Jingong Special Gas Co. Ltd.

2.2. Experimental procedures

A 0.5-L cylindrical glass reactor, as described in a previous work [24], was used to perform the experiments. A Heraeus ozone-free low-pressure UV lamp (GPH212T5L/4; 10 W, efficiency of approximately 35% at 253.7 nm, average equivalent fluence rate of approximately 26 μW cm^{–2}) was employed as a light source. 0.1 M HCl and NaOH was employed for pH adjustment. Subsequently, 2 mL reaction slurry were sampled at designed time intervals and filtered through a 0.22 μm membrane immediately. The oxygen-free water (final dissolved oxygen content was 0.27 ± 0.03 mg L^{–1}) was obtained by purging water with N₂ gas for 30 min. Experiments with 100 W UV input (10 GPH212T5L/4 lamps) were carried out in a Rayonet photoreactor using a similar experimental procedure above-mentioned.

The adsorption experiments of FM by GAC were operated in two parallel glass filter columns with 50 mm inner diameters. New activated carbon (effective size (ES) = 1.5 mm) was used at the beginning of the experiment. The filter depth was 600 mm (400 mm activated carbon and 200 mm sand; ES = 0.6 over gravel). The activated carbon columns were operated at a filtration velocity of 6.0 m h^{–1}. Backwashing was undertaken approximately twice per week. The residual FM in the effluent of both columns was monitored. The collected data were averaged for discussion. MIEX adsorption experiments were undertaken according to a method described by Bond et al. [3]. 20 mL L^{–1} resin was allowed to come in contact with 1000 mL of FM-containing water for 15 times in a 1 L beaker, which was equivalent to 1500 bed volumes of the resin service runs. Each contact period lasted for 15 min, followed by a 15 min settling period. Each MIEX adsorption experiment was performed three times. The FM concentration in the influent of the two filter columns was 1 mM. The feed water, prepared with dechlorinated tap water, was obtained by exposing tap water to air overnight.

2.3. Analysis methods

Inorganic anions (Cl^- and FM) were analyzed using ion chromatography (Dionex ICS-2000; California, USA). By using the USEPA method 552.3, MCAA, TCAA, and DCAA were measured using a Varian gas chromatograph (450-GC, Netherlands) equipped

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