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# Degradation of trichloroacetic acid with an efficient Fenton assisted $TiO_2$ photocatalytic hybrid process: Reaction kinetics, byproducts and mechanism

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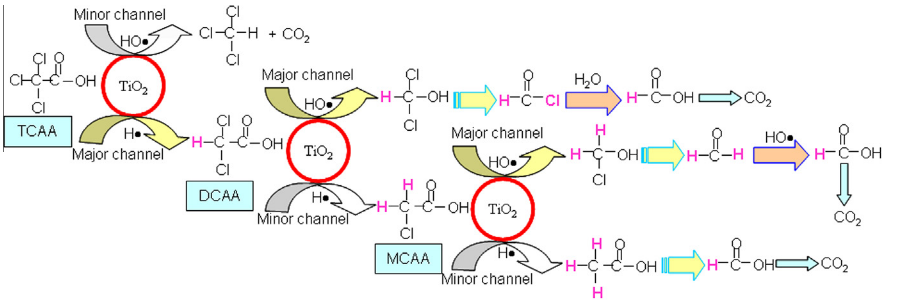
## HIGHLIGHTS

- Degradation kinetics is established and apparent rate constant is calculated.
- $CO_2$ and $Cl^-$ are the final byproducts in aqueous solution.
- Element mass balance for C and Cl is established.
- Degradation mechanism involves in dechlorination, decarboxylization and oxidation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Degradation kinetics, byproducts and mechanism for trichloroacetic acid were analyzed in an efficient $TiO_2$ photocatalytic process combined with Fenton reagent. Modified pseudo first-order kinetics was firstly established and it was more rigorous than the real first-order kinetics, and then the apparent rate constant was calculated and it mainly influenced by initial concentration of TCAA, aqueous solution pH and the dosages of $Fe^{2+}$ and $TiO_2$. Intermediated byproducts detected with ion chromatography, high performance liquid chromatography and gas chromatography methods were mainly $Cl^-$, dichloroacetic acid, monochloroacetic acid, acetic acid, formic acid and $CO_2$ in aqueous solution. To analyze the tracks of carbon and chlorine elements, main byproducts were quantified and the mass balance for carbon and chlorine elements was established. Mineralization of TCAA was 92% after 5 h and the final product is $CO_2$ and HCl. Degradation mechanism involving dechlorination, decarboxylization and oxidation was achieved, and the major degradation pathway was as follows: trichloroacetic acid → dichloroacetic acid → formic acid and monochloroacetic acid → formic acid and acetic acid → formic acid → $CO_2$.

## 1. Introduction

Chloroacetic acids, such as trichloroacetic acid (TCAA), dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA), have attracted researchers' attention because of their toxicity [1,2], persistence [3,4] and ubiquity in drinking water [5–9]. Many researchers have already proved that chloroacetic acids are the potential carcinogens [10,11], so it is urgent for us to develop laws and processes to control the application of chlorine disinfection and remove the chloroacetic acids from drinking water. Realizing the danger of chloroacetic acids, some researchers have devoted themselves to the treatments. Compared with biological or physical

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methods, safer and more efficient chemical methods have been widely adopted to degrade chloroacetic acids in recent years.

The breaking of C—Cl bond can result in the degradation of chloroacetic acids. TCAA and degradation byproducts can be reductively removed by zero-valent Fe [12,13], zinc [14] or bimetallic particles [15,16]; however, the potential release of metal ions affects water quality, leading to the secondary pollution in long term [17]. Electrochemical reductive dechlorination is efficient for TCAA [18,19], and the stepwise dechlorination from TCAA and DCAA to MCAA is achieved [20]. Because the degradation of TCAA or DCAA or MCAA strictly depends on current density, electrodes are easily corroded by high current in this electrochemical process. To increase the degradation efficiency of TCAA and simultaneously protect the electrodes, Esclapez et al. [21,22] have developed a hybrid sonoelectrochemical process at a low current density and obtained satisfying dechlorination efficiency. Summarily, the damage of C—Cl bond is an efficient degradation channel for TCAA in ultrasonic or electrochemical or special reductive reagents reaction, and $Cl^-$, DCAA, MCAA and $CO_2$ are the major byproducts in aqueous solution.

In addition, the fracture of C—C bond can also cause to destroy chloroacetic acids. Oxidative decarboxylization of TCAA has been investigated in advanced oxidation processes (AOPs) such as UV [23], $O_3$/UV [24], UV/$H_2O_2$ [25], $TiO_2$/UV, $H_2O_2$/catalyst and Fenton [26]; however, research has revealed that the ratios for degradation and dechlorination are both low. To increase degradation efficiency, Hu et al. [27] have developed an efficient sonophotocatalytic hybrid process combining with $TiO_2$/UV and ultrasonic, and found that degradation efficiency of this hybrid process is higher than that of the sum of individual sonolysis and photocatalysis reaction, suggesting that a synergetic effect happens between sonochemical and photocatalytic reactions. Ohsaka et al. [28] have investigated the photoelectrocatalytic degradation for chloroacetic acids and found that it is effective for DCAA while ineffective for TCAA in the presence of $O_2$, insisting that the degradation pathways for TCAA and DCAA are different. In other words, decarboxylization is feasible for DCAA or MCAA, while is unfeasible for TCAA. Czili et al. [29] also have observed that it is ineffective to remove TCAA in bare or silver-deposited $TiO_2$ photocatalytic reaction, although they have achieved promising results in the degradation of DCAA and MCAA. So, it seems that photocatalytic oxidation degradation is not an efficient method for TCAA, and probable reason is that TCAA owns more powerful molecular polarity ($K_a = 0.228$), compared with DCAA ($K_a = 0.05$) and MCAA ($K_a = 0.014$). Though it is hard to be destroyed via the decarboxylization, TCAA can be first degraded to DCAA via the reductive dechlorination and then produced DCAA is easily degraded through the decarboxylization.

In recent years, researchers have developed an efficient Fenton assisted $TiO_2$ photocatalytic hybrid process and made great progress in degrading dyes wastewater like Rhodamine B [30]. However, to the best of our knowledge, there is no research about TCAA degradation with this effective process. So it is valuable to investigate degradation kinetics, byproducts and mechanism. However, we have found that rule first-order kinetics ($\ln\frac{C_0}{C} = kt$) is always adopted to describe degradation reaction like photocatalytic or photoelectrocatalytic or Fenton reaction [31,32]. Actually, most degradation reactions deviate from first-order kinetics. Moreover, the effects of experimental conditions on $k$ are hardly studied in references. Fenton assisted $TiO_2$ photocatalytic reaction hybrid process for TCAA was investigated in previous paper [33], but apparent rate constant ($k_{ap}$), byproducts and mechanism were not analyzed. To deeply research the $k_{ap}$ and byproducts, degradation kinetics and the mechanism for TCAA are both investigated in this work.

## 2. Experimental

### 2.1. Reagents and chemicals

TCAA, DCAA, MCAA, $CH_3COOH$, HCOOH, Tert-butyl alcohol and 2,2,6,6-tetramethyl-1-piperidinyloxy were all analytical reagents and bought from China Chemical Reagent Company, and the Nano $TiO_2$ powder was purchased from Tianjin Chemical Reagent Company. $Fe(NO_3)_2$, $H_2O_2$, NaCl, $H_3PO_4$ and NaOH were all analytical reagents and bought from Qingdao Zhengye Chemical Reagent Company. High pure water (18.2 MΩ/cm) used in all experiments was prepared with a water purification instrument (Unique-R20, Research Scientific Instruments Company, China).

### 2.2. Hybrid process of $TiO_2$ photocatalytic reaction combined with Fenton

The hybrid process combined by $TiO_2$ photocatalytic reaction and Fenton reagent was carried out in a self-made cylindrical reactor equipped with a set of cool water recycling cloth and a UV light tube. The UV light ($\lambda_{max} = 254$ nm) was irradiated by a 50 W low-pressure mercury lamp which was placed in the center of the reactor and equipped with a protective quartz tube, and the irradiation intensity was about 35 mW/cm$^2$ measured with an ultraviolet intensity meter (ST-512). TCAA aqueous solution (150 ml) containing $TiO_2$ powder was transferred to the reactor under which $O_2$ was supplied with a stable flow rate of 40 ml/min. Started photocatalytic reaction when the adsorption for TCAA on $TiO_2$ surface and reactor interior had reached equilibrium in a dark environment, and then withdrew the samples from the middle of the reactor and measured their concentrations.

### 2.3. Analytical methods

The concentrations of TCAA, DCAA, MCAA, $CH_3COOH$ and HCOOH are analyzed with the high performance liquid chromatography (HPLC, LC-20AD, SHIMADZU) equipped with an automatic sampler (SIL-20A, SHIMADZU) and a chromatographic separator column (C18, 150 mm × 4.6 mm, 5 μm, SHIMADZU) which is maintained at 30 °C. Mobile phase consists of phase A (0.01 mol/L biphosphate-phosphoric acid buffer solution, pH = 3) and phase B (methanol), and flow rate of each phase is 0.5 ml/min. Automatic injection sample volume is 10 μl. The detection wavelength for MCAA, DCAA, TCAA, HCOOH and $CH_3COOH$ is 210 nm and retention time is 0.62, 0.87, 1.19, 3.84 and 5.78 min, respectively. And the standard deviation for them is 6.3%, 5.8%, 5.2%, 6.9% and 6.1% in triplicate experiments, respectively. Chloride ion is detected by an ion chromatography (ICS-2000, DIONEX) equipped with an automatic sampler (AS40) and an ion exchange column (IonPac AS19), and the mobile phase generated by an automatic eluent generator is composed by 0.012 mol/L $Na_2CO_3$ and 0.005 mol/L $NaHCO_3$, and flow rate is 1.2 ml/min and automatic injection sample volume is 25 μl. And the standard deviation for $Cl^-$ is 4.2% in triplicate experiments. Total organic carbon (TOC) is determined by a TOC analyzer (TOC-VCPN, SHIMADZU) equipped with an automatic sampler (ASI-L), and automatic injection sample volume is 2 ml. $CO_2$ is analyzed by a gas chromatography instrument (GC-9A, SHIMADZU) equipped with a chromatographic column (TDX-01, Length = 2 m) which is maintained at 100 °C. The temperatures of gasification chamber and thermal conductivity cell are both controlled at 120 °C. Hydrogen is selected as carrier gas and flow rate is 40 ml/min. Bridge current is 150 mA and injection amount is 1.0 μl.