Decomposition of aqueous chlorinated contaminants by UV irradiation with H$_2$O$_2$

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Abstract In the present study, the decomposition rates of carbon tetrachloride (CCl$_4$) and 2,4-dichlorophenol (2,4-DCP) in water by the ultraviolet (UV) light irradiation alone and H$_2$O$_2$/UV were experimentally investigated. The detailed experimental studies have been conducted for examining treatment capacities of the two different ultraviolet light sources (low and medium pressure Hg arc) in H$_2$O$_2$/UV processes. The low or medium UV lamp alone resulted in a 60$\%$–90$\%$ decomposition of 2,4-DCP while a slight addition of H$_2$O$_2$ resulted in a drastic enhancement of the 2,4-DCP decomposition rate. The decomposition rate of 2,4-DCP with the medium pressure UV lamp alone was about 3–6 times greater than the low pressure UV lamp alone. In the direct photolysis of aqueous CCl$_4$, the medium pressure UV lamp had advantage over the low pressure UV lamp because the molar extinction coefficient of CCl$_4$ at shorter wavelength (210–220 nm) is about 20 to 50 times higher than that at 254 nm. However, adding H$_2$O$_2$ to the medium pressure UV lamp system rendered a negative oxidation rate because H$_2$O$_2$ acted as a UV absorber being competitive with CCl$_4$ due to negligible reaction between CCl$_4$ and OH radicals. The results from the present study indicated significant influence of the photochemical properties of the target contaminants on the photochemical treatment characteristics for designing cost-effective UV-based degradation of toxic contaminants.

Keywords H$_2$O$_2$/ultraviolet (UV) light, advanced oxidation, UV light irradiation, chlorinated contaminants, photochemical treatment characteristics

1 Introduction

There have been increasing needs to develop cost-effective treatment technologies for degrading non-biodegradable or highly bio-refractory contaminants over the past decades. These contaminants include phenol, halogenated or chlorinated contaminants, pesticides, and explosives [1–6]. Due to the toxicity and low biodegradability of these contaminants, conventional wastewater and water treatment technologies have not shown cost-effective treatment efficiency [7]. Among the alternative treatment options, advanced oxidation has been widely used for treating toxic contaminants due to its strong oxidation capacity over a wide range of contaminants [8,9]. Advanced oxidation includes ozone, H$_2$O$_2$, ultraviolet lights, photocatalysts, and ultrasound [10–13]. H$_2$O$_2$/ultraviolet (UV) light, one of the advanced oxidation technologies, relies on oxidation by OH radicals, one of the most powerful oxidants, generated from photolysis of H$_2$O$_2$ and direct decomposition by ultraviolet lights (hv) [14–16]. The following equations represent the key mechanisms in H$_2$O$_2$/UV process [16].

$$\text{H}_2\text{O}_2 + \text{UV light} \rightarrow 2 \text{OH}^\cdot$$ \hspace{1cm} (1)

Toxic organic pollutants + OH$^\cdot$ → Less toxic products

$$\text{Toxic organic pollutants + UV light} \rightarrow \text{Less toxic products}$$ \hspace{1cm} (3)

For efficient oxidation of contaminants by H$_2$O$_2$/UV processes, UV irradiation is of prime importance because UV irradiation leads to direct photolysis of contaminants and initiation of OH radical generation for oxidation of contaminants [15,17]. Low pressure and medium pressure UV lamps have been used for H$_2$O$_2$/UV processes [18,19].
In general, low pressure UV lamps emitting UV light at 254 nm generate low energy irradiation which may not be suitable for treating high concentration of toxic contaminants. On the other hand, medium pressure UV lamps provide higher light intensity at wide range of wavelength (190–380 nm) which can be used for various water treatments. However, it requires high capital and operating costs.

In the present study, 2,4-dichlorophenol (2,4-DCP) and carbon tetrachloride (CCl₄) were selected as the target contaminants. 2,4-DCP is often found in the wastewater from various industries such as petrochemical, oil refinery, plastic, pesticides, pulp and paper [19]. CCl₄ has been widely used in fire extinguishers, as a precursor to refrigerants, and as a cleaning agent [1]. Due to their high toxicity, persistence in the environment and suspected carcinogenicity, both 2,4-DCP and CCl₄ cause serious ecological problem [19]. The treatment characteristics of 2,4-DCP and CCl₄ in water were investigated experimentally when the low and medium pressure UV lamps were utilized by H₂O₂/UV processes. Due to significant difference in the photochemical properties (i.e., molar extinction) of CCl₄ and 2,4-DCP, the oxidation efficiency of these contaminants by direct photolysis and hydroxyl radical-driven oxidation in the low and medium pressure UV systems were investigated for designing cost effective UV-based treatment processes.

2 Material and methods

2.1 Chemicals and photo-reactors used for the H₂O₂/UV processes

CCl₄ (Sigma Aldrich, MO, USA) and 2,4-DCP (Sigma Aldrich, MO, USA) were used as model compounds in the experiments, and each chemical was mixed with de-ionized (DI) water before being treated by the UV lamps and H₂O₂/UV systems.

The two photo-reactors were used to investigate treatment efficiency of CCl₄ and 2,4-DCP (Fig. 1). Reactor 1 was installed with the low pressure UV lamp (Voltarcs UV LUX, USA) while Reactor 2 was equipped with the medium pressure UV lamp (Voltarcs UV LUX, USA). The diagrams and specification of two photo-reactors are listed in Table 1.

2.2 Photochemical decomposition of 2,4-DCP and CCl₄

The oxidative degradation of 2,4-DCP by the UV lamp alone and the UV with 5–10 mmol·L⁻¹ H₂O₂ were investigated when the 50 mg·L⁻¹ of 2,4-DCP was treated