



# Reaction and diffusion of chlorine dioxide gas under dark and light conditions at different temperatures



YounSuk Lee<sup>b,\*</sup>, Gary Burgess<sup>a</sup>, Maria Rubino<sup>a</sup>, Rafael Auras<sup>a,\*</sup>

<sup>a</sup> School of Packaging, Michigan State University, East Lansing, MI 48824-1223, USA

<sup>b</sup> Department of Packaging, Yonsei University, Gangwon 220-710, Republic of Korea

## ARTICLE INFO

### Article history:

Received 2 May 2014

Received in revised form 8 July 2014

Accepted 13 July 2014

Available online 21 July 2014

### Keywords:

UV radiation

Fluorescent lamp

Activation energy

Degradation

Diffusion coefficient

## ABSTRACT

Chlorine dioxide (ClO<sub>2</sub>) gas is a powerful oxidizing agent in many industrial applications for food processing, drinking water and cleaning treatments. It is considered for use in an increasing number of fresh food applications over a wide range of temperature and pH conditions due to its sanitizing capability. During the disinfectant treatment in a closed chamber or packaging system, ClO<sub>2</sub> gas is typically exposed to environmental factors such as light, temperature, and humidity which influence its disinfectant efficiency. Determining ClO<sub>2</sub> gas reaction rates and mass transfer properties are extremely important for the design of proper sanitization treatments. The aim of this work was to determine the diffusion coefficient for ClO<sub>2</sub> gas in air and reaction rates under dark, UV-A and fluorescent lamp exposure. The effect of temperature on the diffusion of ClO<sub>2</sub> was also assessed. A system was designed to measure these properties. The diffusion coefficient was found to be 0.129, 0.145, 0.173 cm<sup>2</sup> s<sup>-1</sup> at 5, 23, and 40 °C, respectively. Degradation of ClO<sub>2</sub> gas under dark, UV-A and fluorescent lamp exposure was found to follow a first-order reaction. Degradation using a 40 W UV-A lamp was approximately four orders of magnitude larger than with a 34 W fluorescent lamp. A methodology is proposed for quantifying the amount of ClO<sub>2</sub> gas needed in a package and/or treatment chamber.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Chlorine dioxide (ClO<sub>2</sub>) is well known as a powerful oxidant in the presence of organic matter over a wide temperature and pH range (Rav-Acha et al., 1983). As an alternative antimicrobial to chlorine, ClO<sub>2</sub> has attracted significant commercial attention in the food industry because it can be used without altering the nutritive and organoleptic qualities of foods and does not produce appreciable levels of trihalomethanes, which pose potential health risks (Masschelein and Rice, 1979).

ClO<sub>2</sub> can generally be used either in gas or liquid form. In recent years, the application of gaseous ClO<sub>2</sub> has increased due to its higher antimicrobial efficacy when compared to equal levels of aqueous ClO<sub>2</sub>. The high penetration ability of ClO<sub>2</sub> gas can easily reach microorganisms that are protected from an aqueous phase by surface irregularities of the product or imbedded in the biofilm (Wu and Rioux, 2010). In addition, aqueous ClO<sub>2</sub> treatment may cause deterioration of the product due to the presence of residual water and unwanted condensation of ClO<sub>2</sub> on the surface. Many studies over the past decades have investigated gaseous ClO<sub>2</sub>

treatment of the surface of fresh produce (Lee et al., 2004; Han et al., 2004; Popa et al., 2007; Arango et al., Unpublished results), poultry (Ellis et al., 2006), and processed foods (Han et al., 1999). Most of the published research regarding food treatment applications evaluate the biocide efficiency of ClO<sub>2</sub> gas based on bacterial reduction at a given time.

ClO<sub>2</sub> could be used at different stages throughout the food chain process. It can be used in the processing line as a washing solution for fruits and vegetables, or can be applied inside a package in the gaseous form. There are two ways gaseous ClO<sub>2</sub> could be applied in the package, which are (i) sachets which contain chemicals that react to continuously generate and build up ClO<sub>2</sub> gas concentration in the headspace (Netramai et al., 2009), and (ii) direct injection of ClO<sub>2</sub> gas inside the package by means of a commercially available gas generator using a reaction with sodium chlorite and chlorine gas (Arango et al., Unpublished results, 2014). In the gaseous form, ClO<sub>2</sub> penetrates through irregularities and complex areas more efficiently than the aqueous form, making ClO<sub>2</sub> gas more effective than the aqueous form (Han et al., 2004).

To ensure microbial inactivation, gaseous ClO<sub>2</sub> must be uniformly distributed in a closed chamber or package and the concentration must be chosen to maintain antimicrobial efficacy. The diffusion of ClO<sub>2</sub> gas controls the distribution of the gas through

\* Corresponding authors.

E-mail addresses: [leeyouns@yonsei.ac.kr](mailto:leeyouns@yonsei.ac.kr) (Y. Lee), [aurasraf@msu.edu](mailto:aurasraf@msu.edu) (R. Auras).

the headspace air and is impacted by the sorption of ClO<sub>2</sub> gas by other surfaces such as the fresh produce and package material, the initial ClO<sub>2</sub> gas concentration, and the volume of air within the chamber or package (Jeng and Woodworth, 1990). Netramai et al. (2009) observed the mass transfer profiles of ClO<sub>2</sub> gas through different polymeric materials using an electrochemical detector. The results showed that BOPP, PET, PLA, nylon, and EVA/EVOH/EVA had greater barrier properties to ClO<sub>2</sub> gas compared to PE, PVC and PS. To the authors' knowledge, research on the diffusivity and stability of ClO<sub>2</sub> gas in a storage chamber or packaging system is nonexistent.

ClO<sub>2</sub> gas antimicrobial efficacy is also influenced by environmental factors such as temperature, relative humidity, and light (Busto-Ramos et al., 2008). Li et al. (2013) reported the self-decay behavior of ClO<sub>2</sub> in aqueous solution, but a detailed interpretation of these observations was not provided. They concluded that ClO<sub>2</sub> is more stable in acidic solutions at lower temperature than in alkaline solutions at higher temperature.

In the past decade, research on the photochemistry of ClO<sub>2</sub> gas has been conducted to evaluate the degradation of ClO<sub>2</sub> in the atmosphere due to its role in the depletion of the ozone layer (Dunn and Simon, 1992; Brusa et al., 1996). Vaida and Simon (1995) reported that ClO<sub>2</sub> undergoes electronically excited reactions in the presence of light and is vibrationally excited to chlorine oxide as a major photoproduct of the near-UV photolysis. It then decomposes rapidly to chlorite ions and oxygen atoms. Zika et al. (1984) reported that the primary photochemical reaction of ClO<sub>2</sub> in the gas phase corresponds to homolytic scission of one of the chlorine–oxygen bonds (ClO + O). The initial reaction of ClO<sub>2</sub> generates secondary products including doublet-state oxygen (O<sub>2</sub><sup>\*</sup>), chlorine (Cl<sub>2</sub>), and chlorine trioxide (Cl<sub>2</sub>O<sub>3</sub>).

The kinetics of the reaction of ClO<sub>2</sub> gas is consistent with simple electron-transfer theory (Huie and Neta, 1986). ClO<sub>2</sub> may form chlorite ions (ClO<sub>2</sub><sup>-</sup>) based on one electron-transfer reaction. A small amount may also decompose to chlorate ions (ClO<sub>3</sub><sup>-</sup>). Burton and Fisher (2001) reported that 60% of the ClO<sub>2</sub> added to a static system in the dark decayed to chlorite in 15 min at 25 °C and that the degradation of ClO<sub>2</sub> was more rapid than that of chlorine. Vogt et al. (1986) also mentioned that ClO<sub>2</sub> gas can be relatively stable at less than 15% in volume in dark condition.

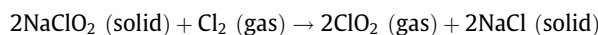
Cosson and Ernst (1994) showed that photodecomposition of ClO<sub>2</sub> in aqueous solution by irradiation with UV radiation leads to either photochemical bond breakage to form vibrationally excited ClO and atomic oxygen or isomerization to form the reactive ClOO molecule, respectively. So, ClO<sub>2</sub> is very sensitive to the exposure to UV radiation and degrades very rapidly to the fragmentation compounds. It could also be affected by the exposure to fluorescent lamp. General supermarkets in the food sale area are designed for lighting levels of around 1000 lx or even higher in order to highlight particular products and displays in many cases (Tassou et al., 2011). So, degradation of ClO<sub>2</sub> gas due to fluorescent lamp and UV radiation are important effect to understand for making sure that targeted concentration for microbial inactivation is achieved in the selected products. Degradation can reduce the effective concentration of ClO<sub>2</sub> gas that reaches the product.

The objectives of this study were to: (1) evaluate the stability and diffusion of gaseous ClO<sub>2</sub> at 0% RH in an unreactive closed container at 5, 23, and 40 °C; (2) quantify the effect of light on the degradation of ClO<sub>2</sub> gas at different UV-A and fluorescent lamp intensities; (3) use the results to predict the concentration of ClO<sub>2</sub> gas in packages and treatment chambers. This information should prove useful in the design of chamber and packaging systems for ClO<sub>2</sub> gas treatment and for further studies on application aspects of ClO<sub>2</sub> gas.

## 2. Materials and methods

### 2.1. Chlorine dioxide generation

A known amount of ClO<sub>2</sub> gas was generated by a Minidox-M unit (Cloridisy Solutions, Lebanon, NJ, USA), in which a mixture of 2% chlorine gas and 98% N<sub>2</sub> gas passes through a solid cartridge containing sodium chlorite. A UV–VIS photometric sensor in the ClO<sub>2</sub> gas allowed for the desired ClO<sub>2</sub> concentration to be delivered to a glass container, hereafter referred to as the reservoir (Fig. 1). The chemical reaction for the generation of ClO<sub>2</sub> gas is based on the following stoichiometry:



After reaching a predetermined concentration of ClO<sub>2</sub> gas, the reservoir was closed using gas-tight glass valves at the inlet and outlet ports. A detailed description of the equipment and ClO<sub>2</sub> measurement capabilities can be found elsewhere (see Arango et al., 2014).

### 2.2. Reaction experiments under no light, UV-A light and fluorescent lamp exposure

The closed reaction system consisted of the reservoir, a detector, and a gas flow pump, all connected together by PTFE tubing (Fig. 1). Treated glass was used (Pyrex 7740-Borosilicate glass, Corning Co., NY) for the reservoir to prevent any reactions with ClO<sub>2</sub> gas during the experiment. Initially, the 2200 mL reservoir containing a known concentration of ClO<sub>2</sub> gas was placed in the dark. A black blanket prevented the exposure to incident light. For each measured interval, the ClO<sub>2</sub> gas was pumped into the detector using a PTFE diaphragm pump (Model 07090-42, Cole-Parmer Instrument Co. Barrington, IL) until a steady concentration was observed. The level of ClO<sub>2</sub> gas in the reservoir was monitored using a UV/VIS spectrophotometer at 305 nm (Shimadzu UV-1800, Shimadzu Scientific Instruments, Columbia, MD). This experiment was repeated for various retention times. The reaction experiments under dark conditions were conducted at 5 ± 1, 23 ± 1, and 40 ± 1 °C.

The UV-A and fluorescent lamp exposure experiments were carried out with the same equipment. The ClO<sub>2</sub> gas was exposed to different intensities of UV-A (325–400 nm, 40 W, Q-Lab Co., Cleveland, OH) and visible light (fluorescent lamps 400–700 nm, 34 W, Philips Electronics Co., Somerset, NJ) at 23 ± 1 °C. Intensity was varied by using 1, 2, and 4 lamps for UV-A light (1.41, 2.34, and 5.73 mW cm<sup>-2</sup>, respectively), and 1 and 2 lamps for fluorescent light (354 and 667 lx, respectively). Light intensity was measured with a UV-AB light meter (Model UV-513AB, 280–400 nm, 0.01–40 mW cm<sup>-2</sup>, General Co., New York, NY) and a visible light meter (Model LM-120, Amprobe, Everett, WA) at the bottom of the glass container.

### 2.3. Diffusion experiments under dark conditions

Fig. 2 shows the experimental setup for measuring ClO<sub>2</sub> gas diffusion. It consists of three sections connected in series: (a) the ClO<sub>2</sub> gas generator that supplies a constant concentration of ClO<sub>2</sub> gas; (b) a UV/VIS spectrophotometer equipped with 100 mm cylindrical cuvette (Quartz spectrophotometer cell, Starna Cells, Atascadero, CA) for the determination of ClO<sub>2</sub> gas concentrations; (c) a 100 mm non-reactive PTFE tube (4.76 mm diameter) that connected the 2200 mL reservoir to the 400 mL collector (Pyrex 7740-Borosilicate glass, Corning Co., Corning, NY).

ClO<sub>2</sub> gas was delivered to the reservoir by the ClO<sub>2</sub> gas generator. When a predetermined concentration was reached, the inlet

Download English Version:

<https://daneshyari.com/en/article/223003>

Download Persian Version:

<https://daneshyari.com/article/223003>

[Daneshyari.com](https://daneshyari.com)