Treatment of drinking water by UV/Cl_2: a study of β-cyclocitral, a cyanobacterial taste & odor compound.

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Abstract
Homogeneous photocatalytic processes are receiving increased interest with regards to drinking water treatment for emerging pollutants. Especially the UV/Cl_2 technique has a potential for real large-scale applications as it can combine disinfection with chemical oxidation using processes that are more familiar and widely applied by water supplies. However, more research is needed to understand the complex mechanisms involved, including formation of hydroxyl and chlorine radicals among others, as well as overall performance against various groups of emerging pollutants, such as the less-studied water taste and odor compounds (T&O). We present results on the UV/Cl_2 degradation of β-cyclocitral as a model of common cyanobacterial nor-carotenoid T&O in water. The study was conducted using a novel photoreactor set-up with custom-made UV-LED arrays, precise control of irradiance, continuous spectrophotometric – GC/MS monitoring and sensory evaluation of the process. Effects of key process parameters i.e. irradiance, concentration of Cl_2 and β-cyclocitral, water matrix (ultrapure and typical drinking water) on the kinetics as well as key degradation products and proposed pathways are presented. Effectiveness, efficiency and prospects of real applications of UV/Cl_2 for removal of hazardous T&O from drinking water are discussed.
Keywords: Advanced Oxidation Processes, UV/Cl_2, drinking water, Taste & Odor (T&O)

1. Introduction

Cyanobacteria can produce a wide range of (semi)volatile substances in water, including odorous ones that are called "taste and odour" compounds (T&O). Odorous cyanobacterial metabolites have negative impacts in drinking water systems, as they make water unacceptable by consumers. Cyanobacterial T&O include terpenoids, ionones, aldehydes, ketones, sulfurous compounds, amines and others (Watson, 2004). Among those, β-cyclocitral, a nor-carotenoid with a characteristic "woody –tobacco" odour can be produced at high concentrations in water from cyanobacteria genera such as *Microcystis* (Juttner, 1984). The chemical structure of β-cyclocitral is shown in Figure 1.

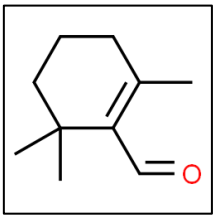

Figure 1. Structure of β-cyclocitral (source: Chemspider)

Removal of cyanobacterial T&O from drinking water is a challenge as some compounds (e.g. geosmin, 2-methylisoborneol - MIB) are resistant to common disinfectants and chemicals such as Cl_2, ClO_2, $KMnO_4$. On the other hand, adsorption by granular or particle activated carbon (GAC, PAC) can be costly as efficiency is reduced in the presence of natural organic matter (NOM) due to competitive adsorption (Newcombe et al., 2002). Various advanced oxidation processes (AOP) were oxidation of T&O proceeds via highly reactive oxygen species (ROS) have been proposed, however, large-scale applications are still limited due to large investment and operational costs (Antonopoulou et al. 2014; Fotiou et al. 2015). Recently, the homogeneous UV/Cl_2 process has gained interest in water treatment, as it is based on the synergistic effect between a commonly used disinfectant, chlorine, and UV, thus requiring only additional UV source operation (Remucal & Manley, 2016). The process has been found to be effective against common cyanobacterial T&O such as geosmin and MIB (Wang et al. 2015). The aim of this study was to explore the UV/Cl_2 degradation process of β-cyclocitral, as a model of common cyanobacterial nor-carotenoid T&O in water.

2. Methods

UV irradiation of solutions was carried out in photoreactors using F15W/T8 black light tubes (Sylvania GTE) and in-house built UVA LED arrays. The ferrioxalate system was used for actinometry (Kuhn et al., 2004). Analysis of β-cyclocitral and degradation products was carried out by high performance liquid chromatography (HPLC) with photo diode array detector (PDA) and by headspace solid-phase microextraction

(HS-SPME) coupled to gas chromatography – mass spectrometry (GC-MS). Spectrophotometric monitoring of the processes was also carried out in the UV spectral region. Chlorine concentrations were determined with a HACH chlorine photometer.

3. Results and Discussion

Degradation of β-cyclocitral by UV/Cl_2 is pH and irradiation wavelength dependent. At pH < 7.5 and λ < 400 nm chlorine photolysis produces mostly $OH^{\bullet}$ and $Cl^{\bullet}$ via hemolytic cleavage. At pH > 7.5 and λ < 320 nm, $O^{-\bullet}$ and excited single state oxygen atoms, $O(^1D)$, while at λ > 320 nm O_3 is formed via reaction of ground state oxygen atoms, $O(^3P)$ with oxygen in solution (Remucal & Manley, 2016). Typical absorption spectra of β-cyclocitral/chlorine in our study are shown in Figure 2.

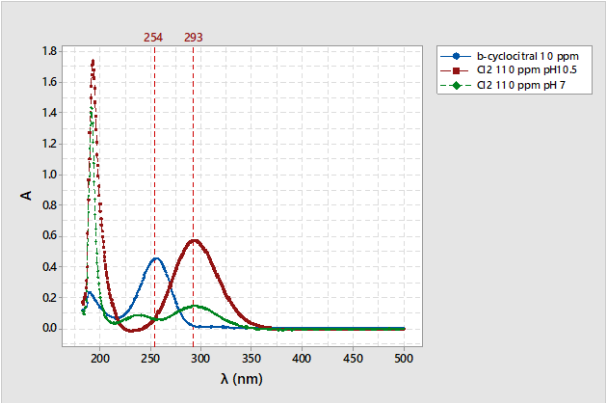

Figure 2. Examples of UV spectra of β-cyclocitral / Cl_2 in this study.

Results showed the synergistic effect of UV combined with chlorine on degradation of β-cyclocitral. Degradation pathways and rates depended on experimental conditions, i.e. UV source used, irradiance and pH. An example of photometric monitoring of the UV/Cl_2 degradation process of β-cyclocitral at various irradiances is shown in Figure 3.

It was concluded that the UV/Cl_2 water treatment process is effective in degrading nor-carotenoid cyanobacterial T&O from water. This process gains significant attention as it is proved that it is effective against a wide range of micropollutants in water. UV/Cl_2 has a higher potential for real large-scale applications than other AOP, as it combines with chlorination that is widely used in drinking water treatment plants.

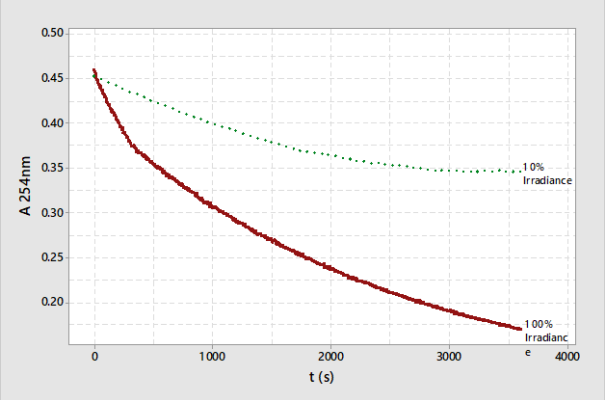

Figure 3. Example of spectrophotometric monitoring of the degradation process.

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