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A solar-driven UV/Chlorine advanced oxidation process

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ABSTRACT

An overlap of the absorption spectrum of the hypochlorite ion (OCl^-) and the ultraviolet (UV) end of the solar emission spectrum implies that solar photons can probably initiate the UV/chlorine advanced oxidation process (AOP). The application of this solar process to water and wastewater treatment has been investigated in this study. At the bench-scale, the OCl^- photolysis quantum yield at 303 nm (representative of the lower end of the solar UV region) and at concentrations from 0 to 4.23 mM was 0.87 ± 0.01. Also the hydroxyl radical yield factor (for an OCl^- concentration of 1.13 mM) was 0.70 ± 0.02. Application of this process, at the bench-scale and under actual sunlight, led to methylene blue (MB) photobleaching and cyclohexanoic acid (CHA) photodegradation. For MB photobleaching, the OCl^- concentration was the key factor causing an increase in the pseudo first-order rate constants. The MB photobleaching quantum yield was affected by the MB concentration, but not much by the OCl^- concentration. For CHA photodegradation, an optimal OCl^- concentration of 1.55 mM was obtained for a 0.23 mM CHA concentration, and a scavenger effect was observed when higher OCl^- concentrations were applied. Quantum yields of 0.09 ± 0.01 and 0.89 ± 0.06 were found for CHA photodegradation and OCl^- photolysis, respectively. In addition, based on the Air Mass 1.5 reference solar spectrum and experimental quantum yields, a theoretical calculation method was developed to estimate the initial rate for photoreactions under sunlight. The theoretical initial rates agreed well with the experimental rates for both MB photobleaching and CHA photodegradation.

1. Introduction

1.1. *Advanced oxidation processes in wastewater treatment*

Advanced Oxidation Processes (AOPs) have proven to be effective in degrading organic constituents in industrial wastewaters, including persistent organic pollutants (Ikehata et al., 2008). Most persistent organic pollutants are highly stable chemically and are not readily biodegradable; therefore, AOPs can serve as an alternative treatment to accelerate the biodegradability of these constituents (Gamal El-Din et al., 2011; Martin et al., 2010). In AOPs, a powerful oxidizing agent is generated [often this is the hydroxyl radical ($^•OH$)], which oxidizes persistent organic compounds to smaller molecules. The oxidizing ability of the hydroxyl radical arises from its high standard electrode potential of +2.7 V in acid solution, so it can react with most organic compounds through abstraction or addition reactions at almost diffusion-controlled rates (Andreozzi et al., 1999; Bolton, 2010).

The combination of AOPs with other treatment processes, such as pre-treatment or post-treatment, is widely used to improve the performance of AOPs and to increase the overall treatment efficiency (Gamal El-Din et al., 2011; Litter, 2005;

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Vogelpohl and Kim, 2004). The effectiveness of AOPs has been proven by various studies in the area of wastewater treatment (Oppenländer, 2003; Poyatos et al., 2010; Vogelpohl and Kim, 2004). Many of the developed AOPs involve the use of ultraviolet (UV) lamps. The principal drawbacks of UV-based AOP applications are the relatively high capital and operating costs for implementation and high use of energy to drive the UV lamps (Azbar et al., 2004). Thus, instead of using UV lamps, some studies have focused on using other alternative energy sources, such as sunlight, to initiate the existing UV-based AOPs (Galindo et al., 2001; Malato et al., 2002).

1.2. *The UV/chlorine AOP*

The photolysis of free chlorine has been observed under sunlight in outdoor swimming pools and reservoirs (Nowell and Hoigné, 1992a). Meanwhile, a significant rate of free-chlorine photolysis and formation of hydroxyl radicals during sunlight photolysis have been confirmed by Nowell and Hoigné (1992b). The potential of the UV/chlorine AOP has been explored by various studies of aqueous free-chlorine photolysis. Feng et al. (2007, 2010) and Watts and Linden (2007) investigated the photodegradation quantum yield of free chlorine, including the factors influencing the quantum yield and the photodegradation products in the photolysis process. Recently, the UV/chlorine AOP has been assessed and compared to the UV/H_2O_2 AOP (Jin et al., 2011; Watts et al., 2007) for treatment efficiency. The feasibility of UV/chlorine AOP for emerging contaminants removal in water and wastewater was examined by Sichel et al. (2011) at a technical scale with the consideration of energy consumption and cost reduction. The evidence of photolysis of free chlorine under sunlight and the development of UV/chlorine AOP suggests the potential for a solar-driven UV/chlorine AOP for applications in water and wastewater treatment.

The term 'free chlorine' is commonly used in disinfection processes and usually refers to the chlorine available to inactivate pathogens and terminate their reproduction activity. Since hypochlorous acid is a weak acid ($pK_a = 7.5$ at 25 °C), the ratio of HOCl to OCl^- is strongly pH dependent. For $pH < 5$, the dominant species is HOCl, whereas for $pH > 10$, OCl^- is dominant with a fraction >0.99. OCl^- is the target component in this study because its absorption is relatively strong in the UV region of the solar spectrum, therefore all experiments took place at pH 10. Oliver and Carey (1977) proposed the following photochemical reactions of OCl^-.

$$OCl^- + h\nu(\text{UV photons}) \rightarrow {}^{\bullet}O^- + {}^{\bullet}Cl \qquad (1)$$

$${}^{\bullet}O^- + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad (2)$$

The initial step involves the photolysis of OCl^- (reaction 1). The maximum of the OCl^- absorption spectrum is at 292 nm (Feng et al., 2007), but the high-wavelength tail significantly overlaps the UV end of the solar spectrum, as shown in Fig. 1. In this study, 303 nm was selected for bench-scale experiments because this wavelength is representative of the lower end of the solar UV emission.

According to the first law of photochemistry, absorption of photons is the first step for any photoreaction to occur. This principle is seen in the overlap of the absorption spectrum of the hypochlorite ion (OCl^-) and the UV end of the solar spectrum see Fig. 1. The overlap of these two spectra suggests that solar photons can probably initiate the UV/chlorine AOP as an alternative to conventional UV-driven AOPs.

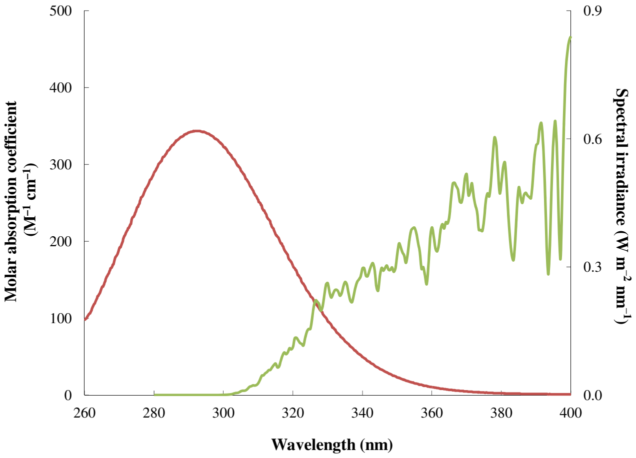

Fig. 1 – The OCl^- molar absorption coefficient absorption spectrum (solid line) and the solar spectral irradiance spectrum (dashed line) (obtained from the Air Mass 1.5 direct and circumsolar reference spectrum from the NREL (Renewable Resource Data Center, 2009)).

This study focuses on exploring the possibility of a solar-driven UV/chlorine AOP and its application in water and wastewater treatment. This process was first assessed at the bench scale using a narrow band interference filter (303 ± 8 nm) representative of the lower end of the solar UV region, where the quantum yields and hydroxyl radial yield factor were determined. The solar-driven AOP was first applied to the photobleaching of MB [a model compound for organic dyes] and then to the photodegradation of CHA [a simple model compound for the potentially toxic naphthenic acids present in typical oil sands process-affected water (Drzewicz et al., 2010; Gamal El-Din et al., 2011; Martin et al., 2010; Pérez-Estrada et al., 2011; Pourrezaei et al., 2011)] at the bench scale and under actual sunlight in Edmonton, Alberta, Canada, along with theoretical calculations.

2. Materials and methods

2.1. *Materials*

Analytical-grade reagents were used for all experiments. Water, from a Maxima Ultra Pure system with a resistivity of >18 MΩ cm, was used throughout the entire course of the experiments. Fresh sodium hypochlorite solution (10–15% by weight, Sigma–Aldrich Canada Ltd., Ontario, Canada) was used to prepare the active chlorine solutions. To achieve the maximum amount of the target OCl^- component in the samples, the pH was adjusted to 10 with a 3 mM sodium carbonate and sodium bicarbonate buffer solution for MB experiments and ~0.1% NaOH for the CHA experiments. DPD (N,N-diethyl-*p*-phenylenediamine) free-chlorine reagent (for