Decomposition of cyclohexanoic acid by the UV/H$_2$O$_2$ process under various conditions

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ABSTRACT

Naphthenic acids (NAs) are a broad range of alicyclic and aliphatic compounds that are persistent and contribute to the toxicity of oil sands process affected water (OSPW). In this investigation, cyclohexanoic acid (CHA) was selected as a model naphthenic acid, and its oxidation was investigated using advanced oxidation employing a low-pressure ultraviolet light in the presence of hydrogen peroxide (UV/H$_2$O$_2$ process). The effects of two pHs and common OSPW constituents, such as chloride (Cl$^-$) and carbonate (CO$_3^{2-}$) were investigated in ultrapure water. The optimal molar ratio of H$_2$O$_2$ to CHA in the treatment process was also investigated. The pH had no significant effect on the degradation, nor on the formation and degradation of byproducts in ultrapure water. The presence of CO$_3^{2-}$ or Cl$^-$ significantly decreased the CHA degradation rate. The presence of 700 mg/L CO$_3^{2-}$ or 500 mg/L Cl$^-$, typical concentrations in OSPW, caused a 55% and 23% decrease in the pseudo-first order degradation rate constants for CHA, respectively. However, no change in byproducts or in the degradation trend of byproducts, in the presence of scavengers was observed. A real OSPW matrix also had a significant impact by decreasing the CHA degradation rate, such that by spiking CHA into the OSPW, the degradation rate decreased up to 82% relative to that in ultrapure water. The results of this study show that UV/H$_2$O$_2$ AOP is capable of degrading CHA as a model NA in ultrapure water. However, in the real applications, the effect of radical scavengers should be taken into consideration for the achievement of best performance of the process.

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1. Introduction

Naphthenic acids (NAs) are complex mixtures of alkyl-substituted aliphatic cyclic and non-cyclic carboxylic acids that are natural constituents of petroleum, including bitumen. In Northern Alberta, the surface mining oil sands industry extracts bitumen from the oil sands using hot process water (Masliyah et al., 2004). The soluble NA fraction of bitumen becomes concentrated in the resulting oil sands process affected water (OSPW), which is subsequently stored in large tailings ponds and continually recycled because of a zero discharge policy (Schramm et al., 2000). The concentration of NAs in tailing ponds depends on the specificity of the analytical method used (Martin et al., 2008), but the reported range is from 40 to 125 mg NA/L (Allen, 2008a) using Fourier transform infrared (FT-IR) spectroscopy.

The acute and chronic toxicity of fresh OSPW to aquatic organisms has been mainly attributed to NAs (Headley and McMartin, 2004;

Scott et al., 2005). Thus, the removal of NAs from OSPW has been one of the targets of remediation studies since the 1980s (Allen, 2008a). The existing technologies for the treatment of OSPW have mostly relied on natural microbial degradation, but this is too slow to keep up with the fast expansion of the industry. Thus, decontamination and detoxification of OSPW are still major challenges currently facing the oil sands industry (Allen, 2008b).

Advanced oxidation processes (AOPs) have been studied extensively in water and wastewater treatment and have been proven to be very effective for the removal of organic pollutants (Parsons, 2004). AOPs rely on the formation of reactive and short-lived oxidizing agents, such as hydroxyl radicals (•OH). Photolysis of hydrogen peroxide (H$_2$O$_2$) using ultraviolet (UV) light at 254 nm is one of the AOPs in which •OH are generated as shown in reaction (1).

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \tag{1}$$

The •OH is a very powerful oxidizing agent that reacts non-selectively with organic and inorganic substances. •OH can abstract hydrogen atoms from virtually any organic compound, although the rates of reaction change from compound to compound (Prousek, 1996). Therefore, other dissolved organic carbon in OSPW (i.e. other

than NAs) may affect the decomposition of NAs as they compete for the •OH. Furthermore, abundant inorganic anions in OSPW, such as chloride and carbonate/bicarbonate (Allen, 2008a), could act as significant hydroxyl radical scavengers in OSPW, further slowing the degradation of NAs.

To date, little investigation of the effect of AOPs on the treatment of OSPW has been carried out (Allen, 2008b). Recent studies showed that ozonation did not fully mineralize the parent NAs (Gamal El-Din et al., 2011; Scott et al., 2008b), but the subsequent microbial biodegradability and toxicity removal was increased (Martin et al., 2010; Scott et al., 2008a). It was also determined that the major intermediate byproducts of NA ozonation were oxidized NAs (Martin et al., 2010).

Cyclic structures are a prominent feature of NA structures in OSPW (Headley and McMartin, 2004), hence we previously selected cyclohexanoic acid (CHA) as a simple model compound to study the mechanism of NA decomposition induced by •OH in ultrapure water (Drzewicz et al., 2010). It was shown that the principal byproducts formed during •OH induced decomposition of CHA were hydroxy-CHA, dihydroxy-CHA, and oxo-CHA. Heptadioic acid and other simple carboxylic acids were also observed (Drzewicz et al., 2010).

The objective of this study was to assess the reactivity of CHA in the UV/H_2O_2 process under various conditions including the H_2O_2 concentration, pH of the solution, and the presence of carbonate and chloride as radical scavengers. The changes in byproducts formation in presence of these scavengers in ultrapure water were studied. In addition, the effect of OSPW matrix on the rate of CHA decomposition was investigated.

2. Material and methods

2.1. Chemicals and sample preparation

Cyclohexanoic acid (CHA, >99% purity) was purchased from TCI (Portland, OR, USA). A stock standard solution (2 mM) of CHA was prepared in ultrapure water and stored at 4 °C; working solutions were prepared daily from this stock solution. The pH of solutions was adjusted using 50% sodium hydroxide and 80% perchloric acid solutions (Fisher Scientific Co., Canada). Carbonate and chloride solutions were prepared using $NaHCO_3$ and NaCl (Fisher Scientific Co., Canada). An H_2O_2 stock solution (Fisher Scientific Co., Canada, 30% w/w) was used for the experiments, and catalase from bovine liver (Sigma-Aldrich, 2950 units/mg solid) was used to quench any H_2O_2 residuals in the sample vials as needed. Ammonium acetate, acetic acid, and methanol (LC-MS grade) were purchased from Fisher Scientific. All other chemicals and reagents were of analytical grade and were used as received.

Ultrapure water (resistivity $= 18 \, M\Omega \times cm$ and TOC<0.1 mg/L) was obtained from a Millipore and Elga system equipped with an Elix UV lamp. To investigate the effect of water matrices on CHA degradation, two other types of water were used: a sample of OSPW, supplied by Syncrude Canada Ltd., and the same OSPW sample after adsorption by commercial powder activated carbon (PAC) (5% PAC by mass for 3 h). The OSPW was filtered through a 0.45 μm filter and kept at 4 °C until use.

2.2. Analytical methods

A high performance liquid chromatograph (HPLC) coupled to an ion trap mass spectrometer (Varian 500-MS) was used for the analysis of CHA and its degradation byproducts. A Phenomenex, C8, 5 μm, 250 mm × 3 mm column was used for separations. The chromatographic conditions were: A, 100% methanol, and B, 4 mM aqueous ammonium acetate with 0.01% acetic acid, gradient elution from 30% to 70% A over 30 min, flow 200 μL/min, injected volume 20 μL.

Using these conditions, the detection limit of CHA was 20 μg/L (4 ng), and the retention time of CHA was around 40 min.

Fourier transform infrared (FT-IR) spectroscopy was used (Scott et al., 2008a) to determine the concentration of the total extractable acid fraction in the OSPW before and after PAC adsorption. Chemical oxygen demand (COD) and alkalinity were measured following standard methods (Clesceri et al., 2005). The H_2O_2 was measured using the iodine method (Klassen et al., 1994). In addition, the concentration of the H_2O_2 stock solution was controlled using UV–vis spectrometer before the preparation of the solutions. Chloride and carbonate were measured only for OSPW by ion chromatography and titrimetric method, respectively

2.3. UV/H_2O_2 experiments

A UV collimated beam apparatus (Calgon Carbon Corporation, Pittsburg, PA, USA) equipped with a 10 W low-pressure UV lamp (Calgon Carbon Corporation) was used. The light source had a monochromatic emission, predominantly at 253.7 (~254) nm, with irradiance at the sample position of 0.11 mW/cm^2. For the experiments on study of radical scavengers and real OSPW another UV lamp with slightly higher irradiance (0.20 mW/cm^2) was used. A control experiment was carried out and it was shown that with changing the UV lamp, no change in the system was observed except the change in decomposition rates (Fig. SM-1). A calibrated radiometer (International Light Inc. Model IL 1400A) equipped with a UV detector (International Light Inc. Model SED240) and a neutral density filter (Model QNDS2) was used to measure the irradiance at the sample surface.

For the treatment optimization and byproduct investigation, 10 mg/L of CHA was used in UV/H_2O_2 AOP. This optimization was verified for higher concentrations of CHA (up to 80 mg/L). However, for further studies, the CHA concentration was increased from 10 to 50 mg/L in order to be in the same range as the NAs concentration in OSPW.

The CHA solutions (15 mL) in glass Petri dishes (60 mm diameter) were exposed to UV light under a completely mixed condition without turbulence using a small magnetic stir bar, at room temperature (21 ± 2 °C). Hydrogen peroxide was added to the CHA solutions right before the UV exposure. Samples (200 μL) were taken at intervals of 10–20 min over 2 h for CHA and byproduct analyses. The experiments were performed in triplicate.

3. Results and discussion

3.1. Effect of H_2O_2 concentration on CHA decomposition and byproduct formation

The degradation of CHA by the UV/H_2O_2 process was studied in ultrapure water at various H_2O_2 concentrations. The efficiency of the UV/H_2O_2 process in degradation of organic pollutants depends on the concentration of H_2O_2 at the beginning of the process, such that sufficient hydroxyl radicals are produced over the entire process. Furthermore, the decomposition of CHA involves sequential reactions with •OH (Drzewicz et al., 2010); therefore, optimizing the H_2O_2 concentration was studied. The initial CHA concentration was 10 mg/L in all experiments, and the pseudo-first order degradation rate constant (k_1) was determined over 80 min of UV exposure with H_2O_2 concentrations of 0, 20, 40, 60, and 80 mg/L. In a control study it was determined that H_2O_2 alone (80 mg/L), without UV exposure, caused no CHA degradation. Similarly, in the absence of H_2O_2, CHA degradation was not observed, likely because CHA does not absorb UV at 253.7 nm. The fact that NAs do not undergo significant photolysis by direct UV at 254 nm had been previously confirmed (Headley et al., 2009; McMartin et al., 2004).