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Decomposition of cyclohexanoic acid by the UV/H₂O₂ 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/H₂O₂ process). The effects of two pHs and common OSPW constituents, such as chloride (Cl[−]) and carbonate (CO₃^{2−}) were investigated in ultrapure water. The optimal molar ratio of H₂O₂ 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 CO₃^{2−} or Cl[−] significantly decreased the CHA degradation rate. The presence of 700 mg/L CO₃^{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/H₂O₂ 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 (H₂O₂) using ultraviolet (UV) light at 254 nm is one of the AOPs in which •OH are generated as shown in reaction (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

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than NAs) may affect the decomposition of NAs as they compete for the $\bullet\text{OH}$. 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 $\bullet\text{OH}$ in ultrapure water (Drzewicz et al., 2010). It was shown that the principal byproducts formed during $\bullet\text{OH}$ 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/H₂O₂ process under various conditions including the H₂O₂ 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 NaHCO₃ and NaCl (Fisher Scientific Co., Canada). An H₂O₂ 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 H₂O₂ 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 Ω × 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 $\mu\text{L}/\text{min}$, injected volume 20 μL .

Using these conditions, the detection limit of CHA was 20 $\mu\text{g}/\text{L}$ (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 H₂O₂ was measured using the iodine method (Klassen et al., 1994). In addition, the concentration of the H₂O₂ 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/H₂O₂ experiments

A UV collimated beam apparatus (Calgon Carbon Corporation, Pittsburgh, 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/cm². For the experiments on study of radical scavengers and real OSPW another UV lamp with slightly higher irradiance (0.20 mW/cm²) 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/H₂O₂ 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

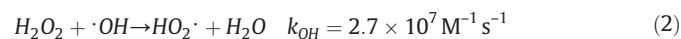
3.1. Effect of H₂O₂ concentration on CHA decomposition and byproduct formation

The degradation of CHA by the UV/H₂O₂ process was studied in ultrapure water at various H₂O₂ concentrations. The efficiency of the UV/H₂O₂ process in degradation of organic pollutants depends on the concentration of H₂O₂ 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 $\bullet\text{OH}$ (Drzewicz et al., 2010); therefore, optimizing the H₂O₂ 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 H₂O₂ concentrations of 0, 20, 40, 60, and 80 mg/L. In a control study it was determined that H₂O₂ alone (80 mg/L), without UV exposure, caused no CHA degradation. Similarly, in the absence of H₂O₂, 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).

Using the combined addition of H_2O_2 and UV exposure, significant removal of CHA was observed. Pseudo-first order degradation rate constants increased with increasing H_2O_2 concentrations, up to 60 mg/L (Table 1). In this H_2O_2 concentration range (i.e. 20–60 mg/L), the fraction of UV absorbed leading to the production of $\cdot\text{OH}$ must have increased, leading to a higher CHA degradation rate. At 80 mg/L H_2O_2 , the rate of degradation was slightly faster but was not statistically different from that at 60 mg/L H_2O_2 (based on the *t*-test analysis with 95% confidence interval that was carried out). The optimal concentration of H_2O_2 for the degradation of 10 mg/L of CHA appears to be 60 mg/L, consequently, the optimal molar ratio of H_2O_2 to CHA in the treatment was established to be 23. This ratio was verified for the CHA concentrations up to 80 mg/L.

Using the irradiance of the UV lamp at 253.7 nm, photon efficiency (mole of CHA degraded/mole of photon entering the solution) depending on H_2O_2 concentration was calculated (Table 1). These data indicate that increasing the H_2O_2 concentration, the degradation efficiency of the CHA increased, while maintaining the same amount of the photon entering the solution. The figures related to the rate of CHA degradation at different H_2O_2 concentrations and the formation and fate of the byproducts during the UV/ H_2O_2 of CHA using the optimum H_2O_2 concentration can be found in Supplementary material (Fig. SM-2 and Fig. SM-3).

The likely explanation for why, at high H_2O_2 concentrations (i.e. 80 mg/L), the reaction rate no longer increases proportionately is that H_2O_2 can also act as an $\cdot\text{OH}$ scavenger, producing the $\text{HO}_2\cdot$ radical and water (reaction (2)) (Buxton et al., 1988).



The $\text{HO}_2\cdot$ radical is much less reactive than $\cdot\text{OH}$, and it decays quickly to non-radical products (Bielski et al., 1985), often without reacting with organic compounds. Similar results were observed during decomposition by the UV/ H_2O_2 process for other organic compounds, such as parathion and anatoxin-a (Wu and Linden, 2008; Afzal et al., 2010).

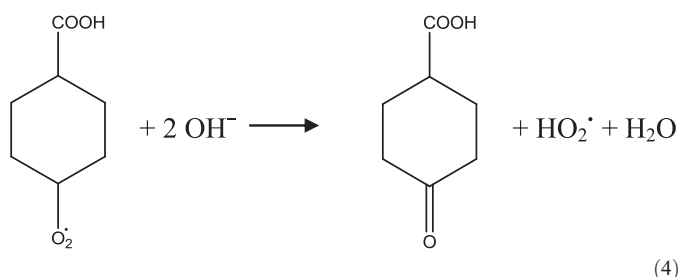
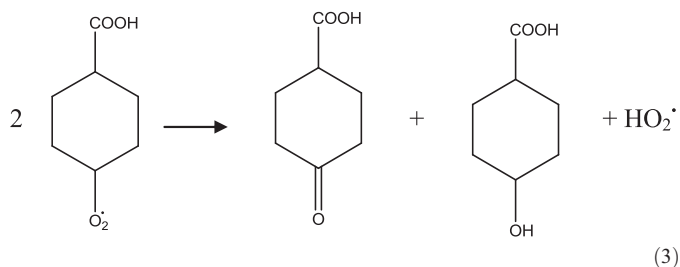
3.2. Effect of pH on the decomposition of CHA and byproduct formation

It has been shown in several studies that the pH has a significant effect on the reactivity of compounds, the formation of byproducts, and the overall effectiveness of AOPs (Bojanowska-Czajka et al., 2006; Homlok et al., 2010; Panades et al., 2000). The reactivity of hydrogen atoms at the α position of aliphatic acids, for example, can depend on whether or not the carboxylic acid group is protonated or dissociated (Hewgill and Proudfoot, 1976). However, the effect of pH on the decomposition of alicyclic carboxylic acids by the UV/ H_2O_2 process has not been investigated. Furthermore, decreasing the pH facilitates the removal of the solid particles from the OSPW (Zhu et al., 2011); therefore, a study of the effect of pH on the UV/ H_2O_2 treatment is very important.

The pKa of CHA is 4.9 (Serjeant and Dempsey, 1979). The initial pH of the CHA solution in two experiments was adjusted to 3.0 ± 0.1 and 9.0 ± 0.1 ; however no change in the pH (no more than 0.2) was

observed after the treatment. The results showed that at pH 3 (protonated CHA) and pH 9 (dissociated CHA) there was no significant difference in the pseudo-first order rate constant of CHA decomposition (Fig. 1). Thus, our observation at different pH, suggests that the hydrogen at the α position was not a significant source of overall reactivity.

In a previous study at pH 9, the degradation mechanism for CHA was described by reaction of $\cdot\text{OH}$ with CHA to produce an organic radical, which then reacted with dissolved molecular oxygen to form a peroxy radical (Drzewicz et al., 2010). The peroxy radical was then proposed to undergo a disproportionation reaction yielding oxo-CHA and hydroxy-CHA (reaction (3)), or a unimolecular decay, catalyzed by hydroxide anion, yielding only oxo-CHA (reaction (4)).



In this study, in order to confirm the proposed mechanism, we conducted the further investigations of byproduct formation under alkaline and acid conditions. If the reaction involving hydroxide ion was a significant process, then at pH 9 a relatively higher formation rate of the oxo-CHA should be observed, and a relatively lower formation rate of hydroxy-CHA should be observed, compared to pH 3. However, no experimental evidence for this was observed. In fact, there was less oxo-CHA at pH 9 than at pH 3 (Fig. 1). This suggests that the peroxy-CHA radical is relatively stable and does not undergo rapid unimolecular decay to oxo-CHA. As a result, the pH has no

Table 1

Pseudo-first-order degradation rate constant of CHA decomposition and estimated photon efficiency (mole of CHA degraded/mole of photon entering the solution) at different concentrations of H_2O_2 at pH 9 ($[\text{CHA}]_0 = 10 \text{ mg/L}$); UV lamp irradiance = 0.11 mW/cm^2 .

H_2O_2 concentration (mg/L)	Pseudo-first-order rate constant (min^{-1})	Photon efficiency
20	$5.65 \times 10^{-3} \pm 0.0009$	0.92
40	$1.30 \times 10^{-2} \pm 0.001$	1.58
60	$2.2 \times 10^{-2} \pm 0.003$	2.05
80	$2.5 \times 10^{-2} \pm 0.001$	2.15

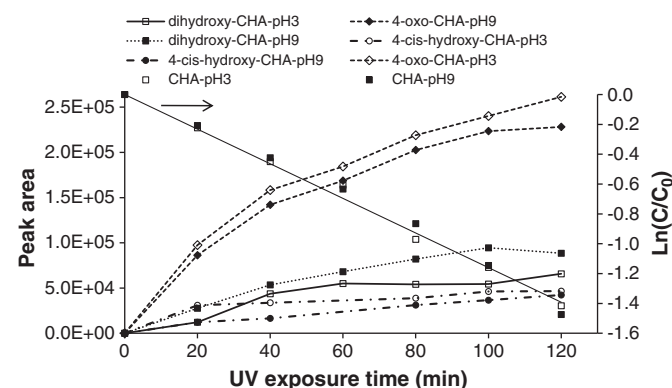
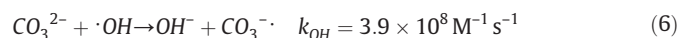
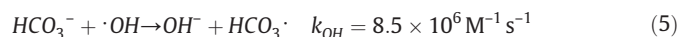


Fig. 1. Degradation and byproducts formation during UV/ H_2O_2 treatment of cyclohexanoic acid at pH 3 and pH 9 ($[\text{CHA}]_0 = 50 \text{ mg/L}$, $300 \text{ mg/L H}_2\text{O}_2$, UV lamp irradiance = 0.11 mW/cm^2); retention times: 4-oxo-CHA 12 min; dihydroxy-CHA 17 min; cis-4-hydroxy-CHA 13 min.

measurable effect on the type and relative yield of byproducts formed during the treatment of CHA in UV/H₂O₂ process in ultrapure water.

3.3. Effect of radical scavengers on the CHA treatment

Two of the most dominant anions in OSPW are carbonate and chloride, which are well-known radical scavengers. Carbonate and bicarbonate can react with •OH radicals (reactions (5) and (6)) to form carbonate and bicarbonate radicals (CO₃^{•-} and HCO₃^{•-}) (Buxton et al., 1988). However, at pH 7 to 9, the prevalent anion in OSPW is bicarbonate, which is less reactive toward •OH than the carbonate ion.



The carbonate radical is an electrophilic species that is very reactive toward electron-rich compounds, such as anilines (Larson and Zepp, 1988; Mazellier et al., 2003), phenols (Busset et al., 2007), sulfur containing compounds and carboxylic acids (Neta et al., 1988), albeit less reactive than •OH. Carbonate radicals last longer in solution than •OH and have high oxidation potential ($E_{\text{red}}^0 = 2.1 \text{ V}$). Carbonate may also react with H₂O₂ to form HO₂•, which is poorly reactive toward organic compounds (Draganic et al., 1991). Study of the influence of carbonate on the degradation rate of NAs is also important because addition of carbon dioxide may be used for densification of oil sand tailings (Zhu et al., 2011).

The other radical scavenger, chloride, also reacts with •OH with the second-order rate constant of $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988), which may have an additional negative effect on the AOP due to scavenging. Regardless, chlorine radicals (dichloride anion radical and chlorine atom) are formed during the UV/H₂O₂ treatment of solutions containing chloride (Jayson et al., 1973). Chlorine radicals are very reactive species toward organic compounds and are powerful oxidants (Martire et al., 2001). Furthermore, a final product of oxidation of chloride in the UV/H₂O₂ process is chlorine (Yu, 2004). Chlorine forms hypochlorous acid in water which is also a moderate oxidant and can be reactive toward organic compounds (Yu and Barker, 2003). An additional reaction that may occur during UV/H₂O₂ treatment is the reaction of hypochlorite with H₂O₂. Singlet oxygen is one of the products of this reaction which is well-known as an oxidant of organic species (Held et al., 1978).

Investigation of the scavenging effect of chloride and bicarbonate on the decomposition of CHA was performed in two separate solutions: the first contained 50 mg/L CHA and 500 mg/L Cl⁻, and the second contained 50 mg/L CHA and 700 mg/L CO₃²⁻ in ultrapure water. These concentrations of CHA, chloride and carbonate were chosen to approximate the average concentrations in the OSPW. The chloride anion rate constant for reaction with •OH is $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988), thus in OSPW the chloride anion may compete effectively for •OH with CHA for which the rate constant is only slightly higher, $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9 (Anbar et al., 1966). Comparatively, the bicarbonate hydroxyl-radical rate constant is $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; thus bicarbonate can effectively compete with CHA if the concentrations are about 1000 times higher than that of CHA.

Fig. 2 shows the results of the CHA treatment with UV/H₂O₂ in ultrapure water and in presence of chloride and bicarbonate ions at pH 9. The presence of 500 mg/L Cl⁻ in a 50 mg/L CHA solution decreased the pseudo first-order decomposition rate constant by 23%, whereas the presence of 700 mg/L bicarbonate decreased the rate by 55%. Even though the molar concentration of carbonate and chloride in the experiments were not the same and we cannot compare their scavenging effect to each other, the results indicated that carbonate at concentrations present in OSPW had a higher scavenging effect on the CHA degradation in UV/H₂O₂ process than did chloride, also at the same concentration as in OSPW.

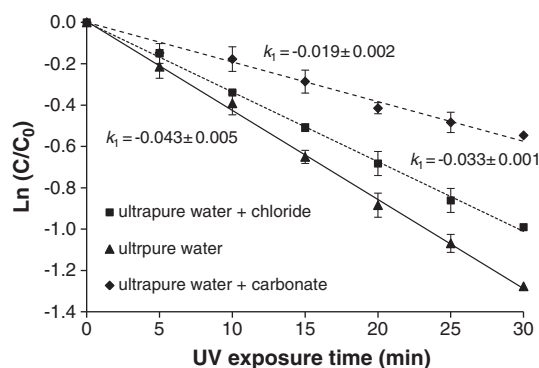


Fig. 2. Decomposition of CHA in ultrapure water and in presence of separate solutions one containing 500 mg/L chloride (Cl⁻) and the other one containing 700 mg/L carbonate (CO₃²⁻) ions at pH 9 ([CHA]₀ = 50 mg/L, 300 mg/L H₂O₂ in both solutions); k₁: pseudo-first-order rate constant (min⁻¹); UV lamp irradiance = 0.20 mW/cm².

Decreasing the scavenging effect of carbonate by acidification of the OSPW is not recommended because this would also increase the salinity of OSPW, and this may furthermore not be viable due to the additional treatment costs. Additionally, it has been shown that the •OH scavenging effect of chloride in UV/H₂O₂ systems increases at low pH (Liao et al., 2001).

Consumption of H₂O₂ during the UV/H₂O₂ process was also investigated in the UV/H₂O₂ process of CHA. It was observed that the H₂O₂ consumption increased from 2% in ultrapure water to 5% and 12% in presence of chloride and carbonate, respectively.

Despite the lower reactivity, the presence of chloride and carbonate ion did not change the type of byproducts formed, nor was there

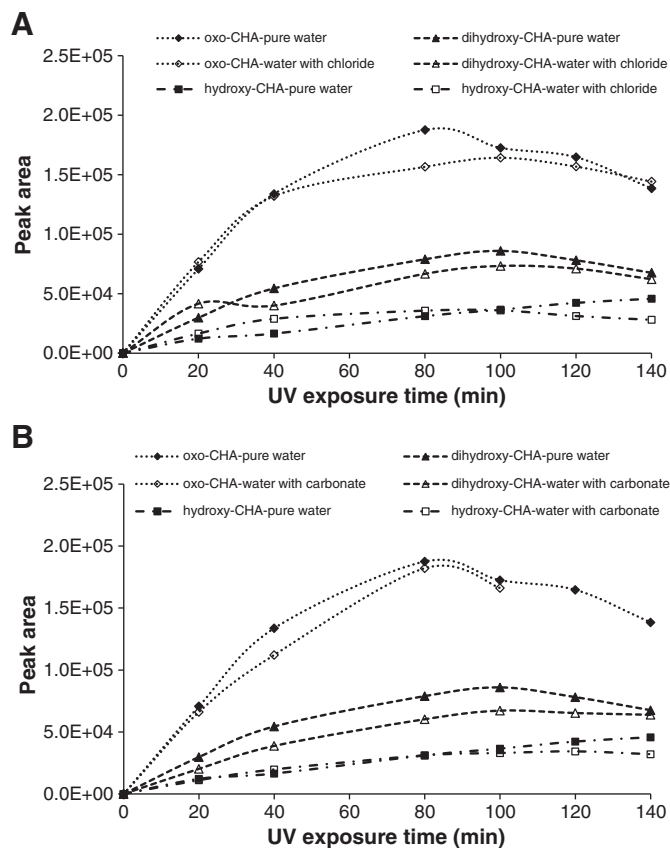


Fig. 3. Formation of three major byproducts during UV/H₂O₂ degradation of CHA at pH 9 ([CHA]₀ = 50 mg/L, 300 mg/L H₂O₂, UV lamp irradiance = 0.11 mW/cm²) in ultrapure water and A) in ultrapure water with chloride; B) in ultrapure water with carbonate; retention times: 4-oxo-CHA 12 min; dihydroxy-CHA 17 min; cis-4-hydroxy-CHA 13 min.

an effect on the relative proportion of byproducts. The formation and decay of the principal byproducts formed during the UV/H₂O₂ treatment of CHA in ultrapure water and in presence of chloride and carbonate are presented in Fig. 3.

3.4. The effect of real OSPW water matrix on decomposition of CHA

It is expected that dissolved organic matter in water can affect the decomposition rate of pollutants by the UV/H₂O₂ process. As with pollutants, organic compounds may react directly with H₂O₂, compete for •OH or absorb UV light. Organic compounds may also react with organic radical intermediates formed during the treatment, thus decreasing the decomposition rate of the target pollutants.

OSPW was treated with PAC in order to remove a portion of dissolved organic matter. After the PAC adsorption, the COD content, as well as the total extractable acid fraction concentration, were decreased significantly, while the alkalinity and Cl[−] ion concentration remained unchanged (Table 2). In real applications of AOPs in oil sand industry, sequential treatments will be applied and it is crucial to know how each step of the OSPW treatment can affect the following step.

As expected, the highest CHA degradation rate occurred in ultrapure water, followed by the OSPW after PAC adsorption, followed by the slowest rate in raw OSPW (Fig. 4). The pseudo-first order rate constant for CHA degradation in raw OSPW was 81% lower than that in ultrapure water. This may be explained by the fact that in the presence of COD, bicarbonate, NAs and organic compounds in the OSPW reduce the •OH concentration that is available to react with CHA, due to their combined scavenging effect (Afzal et al., 2010; Chelme-Ayala et al., 2010). Furthermore, some of the substances present in the OSPW absorb UV at 253.7 nm (the absorbance of OSPW at 253.7 nm is presented in Table 2); hence they may compete for photons, thus reducing the formation of •OH radicals and the subsequent degradation rate of CHA.

Compared with raw OSPW, the CHA degradation rate increased after PAC adsorption, but still remained significantly lower (62%) than its rate in ultrapure water. There are unknown constituents such as organic matter which are likely radical scavengers. The formation of byproducts during decomposition of CHA in OSPW was not investigated because of high interferences in chromatographic determination from water matrix.

3.5. Environmental significance and future work

This study demonstrates that UV/H₂O₂ is a promising process for the removal of CHA as a model NA compound in ultrapure water. This process can be applied to other NAs due to the similarity of the basic structure. However, the presence of radical scavengers needs to be carefully considered during the NA remediation in OSPW, because they may impose the adverse effect on the process efficiency. To compare different processes for management purposes, the treatment of model NA compounds using ozonation and the O₃/H₂O₂ process will be studied. Advanced oxidation technologies can be considered as great potential for OSPW remediation, especially if these processes are applied in combination with microbial degradations.

Table 2

OSPW quality parameters before and after PAC adsorption.

	COD ^a	Total extractable acid fraction ^b	Alkalinity ^c	[Cl [−]] ^d	UV absorbance ^e	pH
OSPW	225–258 mg/L	65–70 mg/L	672–708 mg/L	400–600 mg/L	0.605	8.4–8.8
OSPW after PAC adsorption	<10 mg/L	<5 mg/L	660–697 mg/L	400–600 mg/L	0.040	8.6–8.9

^a Chemical Oxygen demand (as mg O₂/L), measured according to Standard Method 5220 D.

^b Measured using FT-IR.

^c Measured based on Standard Method 2320 (mg/L as CaCO₃).

^d Measured by Dionex-ICS-2500 ion chromatography.

^e The average UV absorbance at 253.7 nm.

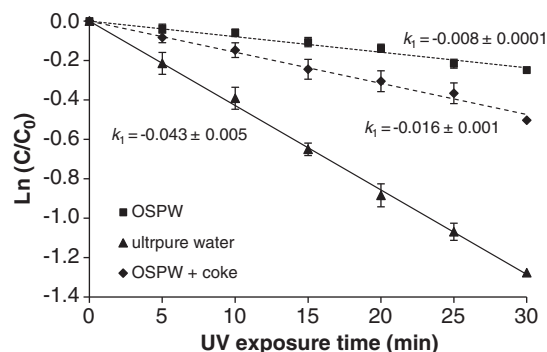


Fig. 4. Decomposition of CHA in raw OSPW and OSPW after PAC adsorption (both filtered through 0.45 µm) ([CHA]₀ = 50 mg/L, 300 mg/L H₂O₂); k_1 : pseudo-first-order rate constant (min^{−1}); UV lamp irradiance = 0.20 mW/cm².

4. Conclusions

The hydroxyl radical initiated degradation of a model OSPW alicyclic carboxylic acid, cyclohexanoic acid, in presence of carbonate and chloride ion, at two different pHs, and in OSPW matrix revealed new information about the feasibility of application of UV/H₂O₂ process for the removal of NAs from OSPW. Increasing the concentration of H₂O₂ increased the CHA degradation rate up to the optimal molar concentration ratio of 23. Changing the pH in ultrapure water had no significant effect on the CHA degradation rate and the formed byproducts. Carbonate and chloride ions, at concentrations similar to those in the OSPW, decreased the CHA degradation rate by 55% and 23%, respectively. It was also shown that the presence of the scavengers decreased the formation and further degradation of byproducts. Besides carbonate and chloride, other organic and inorganic compounds present in OSPW competed with CHA for reaction with •OH. PAC adsorption of OSPW may increase the efficiency of the UV/H₂O₂ process because of the removal of the some organic compounds. Acidification of OSPW, in order to decrease the concentration of the carbonate may improve the process efficiency. However, the higher scavenging effect of chloride at lower pH and increasing the ionic strength of the water because of the acidification may reduce the benefit of carbonate removal. As an overall conclusion, it was demonstrated that UV/H₂O₂ is an applicable method for CHA removal as a model NA in ultrapure water. However, the effect of radical scavengers on treatment efficiency should be considered in the real OSPW NA remediation.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at [doi:10.1016/j.scitotenv.2012.03.019](https://doi.org/10.1016/j.scitotenv.2012.03.019).

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