Mineralization of naphtenic acids with thermally-activated persulfate: The important role of oxygen

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HIGHLIGHTS

- Complete mineralization of NAs was achieved with substoichiometric persulfate.
- Dissolved oxygen played an important role as experimentally verified.
- The normalized rate constants of mineralization (k_n) are obtained.
- The radical mechanism is analyzed.
- The effect of chloride and bicarbonate as potential scavengers is investigated.

GRAPHICAL ABSTRACT
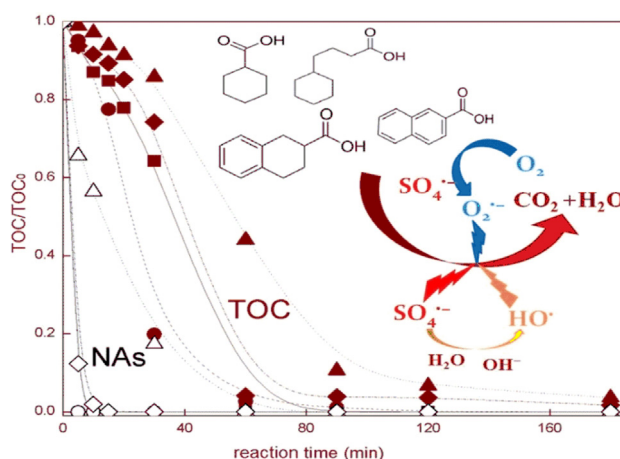
ABSTRACT

This study reports on the mineralization of model naphtenic acids (NAs) in aqueous solution by catalyst-free thermally-activated persulfate (PS) oxidation. These species are found to be pollutants in oil sands process-affected waters. The NAs tested include saturated-ring (cyclohexanecarboxylic and cyclohexanebutyric acids) and aromatic (2-naphthoic and 1,2,3,4-tetrahydro-2-naphthoic acids) structures, at $50\,mg\,L^{-1}$ starting concentration. The effect of PS dose within a wide range (10–100% of the theoretical stoichiometric) and working temperature (40–97 °C) was investigated. At 80 °C and intitial pH = 8 complete mineralization of the four NAs was achieved with 40–60% of the stoichiometric PS dose. This is explained because of the important contribution of oxygen, which was experimentally verified and was found to be more effective toward the NAs with a single cyclohexane ring than for the bicyclic aromatic-ring-bearing ones. The effect of chloride and bicarbonate was also checked. The former showed negative effect on the degradation rate of NAs whereas it was negligible or even positive for bicarbonate. The rate of mineralization was well described by simple pseudo-first order kinetics with values of the rate constants normalized to the PS dose within the range of 0.062–0.099 h^{-1}. Apparent activation energy values between 93.7–105.3 $kJ\,mol^{-1}$ were obtained.

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1. Introduction

Exploitation of non-conventional gas and oil resources has to deal with important challenges [1,2]. Increasing attention has been

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paid to the environmental impact of naphthenic acids (NAs) from oil sands process-affected water (OSPW). These species appear also in other industries such as wood preservatives and paint additives [3–5]. In general terms, NAs refer to carboxylic acids found in crude oil. The predominant species correspond to alkyl-substituted cycloaliphatic structures and also aromatic rings are present in some minor components but of significant environmental concern [5,6]. NAs have been reported as extremely persistent in the tailing ponds with in-situ degradation half-life higher than ten years [7]. Moreover, they have been observed to be of great hazard toward several testing organisms due to its acute toxicity associated to their complex structure and their transformation into oxy-NAs induced by oxygen-containing species upon long time retention in aquatic systems [8].

Some non-destructive methods, like adsorption, allow successful removal from the aqueous phase but transferring the NAs to the solid adsorbent which then has to be conveniently treated or disposed [9–11]. Biological treatments have proved to be cost-effective for partially reducing the toxicity of NAs [12], but complete decomposition of certain portion of recalcitrant NAs cannot be achieved by biodegradation [13]. Advanced oxidation processes (AOPs) have been widely investigated for the breakdown of many recalcitrant compounds due to their broad applicability [14–16]. AOPs are based on the action of the hydroxyl radical as main oxidizing species with a high redox potential ($E_0 = 2.8$). Meanwhile, sulfate radical-based AOPs exhibit competitive oxidation capacity ($E_0 = 2.5$–3.1) [17] for the degradation of different kinds of pollutants [18,19]. The generation of hydroxyl or sulfate radicals in advanced oxidation systems are commonly induced by metal catalysts [20], or energy sources, including thermal [21], light [22,23] and electrical [24]. Thermally-activated decomposition of persulfate (PS) gives rise to sulfate radicals according to Reaction (1):

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{\bullet-} \qquad (1)$$

Besides, mechanistic studies have shown that hydroxyl radicals, generated from the interaction of PS and hydroxide ions and/or water (Reactions (2) and (3)), could also participate in the breakdown of target pollutants [25].

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^\bullet \qquad (2)$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^\bullet + H^+ \qquad (3)$$
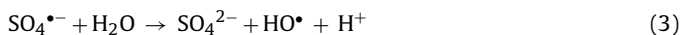
In recent years, several evidences have been reported that oxygen acts positively in PS-based oxidation systems at ambient conditions in the presence of various catalysts by transforming into reactive $O_2^{\bullet-}/HO_2^\bullet$ [26–28]. However, the stoichiometric contribution of oxygen as an oxidant in the PS-based systems for the mineralization of the target pollutants has not been documented in those literatures.

The mineralization ability of PS-based systems has been investigated with different organic contaminants. Complete [25] as well as partial [23,29] TOC removal has been reported. Kinetic studies of PS oxidation activated by different approaches confirm that several reactive species play a role in the mineralization process. As indicated before, those species include sulfate/hydroxyl radicals, but also PS ions and/or other intermediates. Models, such as those based on competitive reactions with steady-state approximation, have been used to describe the kinetics of PS oxidation [30–32]. In principle, the evolution of target pollutants can be described by a pseudo-first-order rate equation [33] and the values of the apparent rate constant and the corresponding normalized rate constants can be used to compare among different systems at a level of generality [34] so that they can provide information on the suitability of AOP methods toward given target pollutants. However, the apparent rate constants referred to specific compounds obviously serve only to describe the rate of disappearance of those species whereas

TOC-based kinetic studies are needed to learn on the rate of mineralization. So far, there is a lack of information on that respect in the literature.
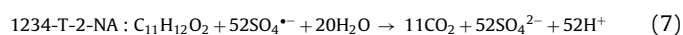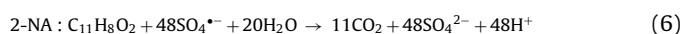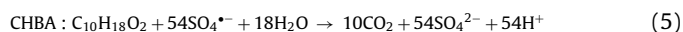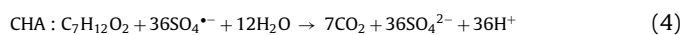
Because of the well-known stability of PS, remote/localized or even direct heating activation of PS could be used in several in situ thermal remediation (ISTR) technologies. Increasing the temperature will not only promote the decomposition of PS to sulfate radicals, but also would favor the activation of other related radicals [33]. Therefore, the application of ISTR with PS oxidation approach making use of the processing temperature of OSPWs, well above the ambient, is of promising potential for the abatement of NAs from those effluents [35].

A few hydroxyl or sulfate radical-based AOPs using different activation approaches have been checked for the degradation of NAs, such as UV/H_2O_2, $UV/S_2O_8^{2-}$ and Zero Valent Iron (ZVI) catalyze [6,22,36]. The generated hydroxyl radicals attack the 4 position of the hydrocarbon rings of cyclohexanoic acid and the α position of aliphatic chain [36], while the sulfate radicals provoke the decarboxylation of target pollutants [37]. Fenton, that is one of the main hydroxyl radical generating systems, has not been successfully used in NAs abatement, because of the basic pH (around 8) of the OSPW containing those species [38], whereas Fenton oxidation is strictly pH dependent (pH ≈ 3.5). Opposite to that, PS-based oxidation systems have proved to be effective for the degradation of pollutants within a wide pH range [25,39]. PS oxidation not relying on the action of radicals from PS has also been reported recently. Zhang et al. [23] investigated the degradation of 2,4-dichlorophenol with PS activated with CuO.

In the current work, the mineralization of four NAs (with and without aromatic rings) by catalyst-free thermally-activated PS oxidation is investigated and the corresponding constants are given. The NAs used as target pollutants include cyclohexanecarboxylic acid (CHA), cyclohexanebutyric acid (CHBA), 2-naphthoic acid (2-NA) and 1,2,3,4-tetrahydro-2-naphthoic acid (1234-T-2-NA). The two former are saturated-ring structures while the last are aromatic ring-bearing bicyclic ones. The role of oxygen is studied, as well as the effect of potential scavenging ions, like chloride and bicarbonate commonly found in OSPWs.

2. Material and methods

The NAs tested (CHA, CHBA, 2-NA and 1234-T-2-NA, see Fig. S1 in Supporting information) were purchased from Sigma-Aldrich (purity ≥98%). PS oxidation experiments were carried out in 100 mL glass batch reactors placed in a constant-temperature water bath with a shacking frequency equivalent to 200 rpm. Given amounts of PS and/or other reagents (scavengers or salts) were added into the reactors containing 50 mL of 50 mg L^{-1} NAs aqueous solution (0.39, 0.29, 0.29 and 0.28 mM of CHA, CHBA, 2-NA and 1234-T-2-NA respectively). Previous to the addition of PS, the reactors were preheated for 15–30 min to make sure that the reactions were initiated at the testing temperature (40–97 ± 1 °C). The degradation of the starting compounds during the preheating stage was always negligible in all the cases. Tests in inert atmosphere were also carried out, using an inert atmosphere chamber with the NAs samples and PS solutions previously bubbled by N$_2$ for 30 min. All the experiments were performed by duplicate and the differences were always lower than 5%. The theoretical stoichiometric dose of PS for complete oxidation of CHA, CHBA, 2-NA and 1234-T-2-NA was calculated from the reactions:

$$CHA : C_7H_{12}O_2 + 36SO_4^{\bullet-} + 12H_2O \rightarrow 7CO_2 + 36SO_4^{2-} + 36H^+ \qquad (4)$$

$$CHBA : C_{10}H_{18}O_2 + 54SO_4^{\bullet-} + 18H_2O \rightarrow 10CO_2 + 54SO_4^{2-} + 54H^+ \qquad (5)$$

$$2\text{-}NA : C_{11}H_8O_2 + 48SO_4^{\bullet-} + 20H_2O \rightarrow 11CO_2 + 48SO_4^{2-} + 48H^+ \qquad (6)$$

$$1234\text{-}T\text{-}2\text{-}NA : C_{11}H_{12}O_2 + 52SO_4^{\bullet-} + 20H_2O \rightarrow 11CO_2 + 52SO_4^{2-} + 52H^+ \qquad (7)$$