

Insights into ultrasound-promoted degradation of naphthenic acid compounds in oil sands process affected water. Part I: Accelerated H-abstraction and decarboxylation of aromatic and alicyclic compounds

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ABSTRACT

Propelled by enormous increase in demand for fuel sources, Canadian oil sands are becoming increasingly important as a fuel source due to their abundance and upgrading capability. However, extraction of bitumen, a high acid crude (HAC) oil, requires 2–3 units of water per unit of oil resulting in naphthenic acid (NA)-rich oil sands process affected water (OSPW) collected in effluent ponds. This study illustrates the role of sonochemistry in the accelerated degradation through H-abstraction and subsequent decarboxylation of aromatic and alicyclic naphthenic acid model compounds. Benzoic acid and 3-methylcyclohexane carboxylic acid were selected as model NA compounds to investigate the mechanism of hydroxyl radical (OH^*) initiated carboxylic acid degradation in 378 KHz sonochemical reactor. Established FTIR methods with low resolution LCMS spectroscopy confirmation were applied to determine the extent of carboxylic acid degradation and identify the formation of products. FTIR monitoring showed a non-linear degradation of carboxylic acids with formation of many intermediates highlighting the shift from cyclic carboxylic acids to cyclic alcohols during BA degradation. Subsequent decrease in carboxylic acid groups signifies scission of cyclic structures before complete mineralization. This is confirmed with the LCMS identification of products such as: 3-hydroxybenzoic acid and phenol. This study postulated new breakdown pathways for degradation of benzoic acid with complete mineralization at a sonochemical reaction time (SRT) of 4 h. A radical quenching process was also inferred through the formation of conglomerates during sonochemical degradation of BA. Extension of the study to 3-methylcyclohexane carboxylic acid (3mCHA) shows similar non-linearity with an increase in carboxylic acid groups indicating H-abstraction followed by ring-opened compounds. However, due to the complex nature of 3mCHA's ring-opened compounds, complete mineralization is not achieved. The putative role of sonochemistry is a promising and sustainable degradation method for mitigating NAs in OSPW, but sonication periods need to be considered carefully to ensure adequate mineralization of their constituents and combinatorial methods with other advanced oxidation methods may be needed to enhance industrial application.

In Part II, an *in silico* screening approach using first principles is reported to identify the breakdown of the organic compounds and determine molecular rates of reaction to confirm the mechanistic origins of the compounds formed.

1. Introduction

Georeferenced data on the spatial extent of oil sands deposits in Alberta recognized as the fourth largest crude oil reserve in the world, are estimated at 170 billion barrels and are a critical resource to meet the burgeoning demand for fuel production [1]. Heavy crude extraction processes for both hot water extraction in surface mining and pressurized steam transport in *in situ* mining require large quantities of water.

Recent estimates, using projected production trends, show that oil sands exploitation could result in 1.31 km³ yr⁻¹ of freshwater demand [2]. The by-product water produced after mining, commonly referred to as oil sands process affected water (OSPW), is currently subject to a 'zero discharge policy' and is collected and stored in tailings ponds or recycled into process operations [3,4]. OSPW consists of process contaminated water with unrecovered bitumen, petroleum based chemicals, sand, heavy metals, and other inorganic compounds [5–7]. The organic

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fraction in OSPW is comprised of a myriad of contaminants of which naphthenic acids (NA) are the primary recalcitrants causing serious environmental issues and exhibiting chronic and acute toxicity [5–7]. Due to their recalcitrant nature, NAs do not biodegrade easily and NA treatment has gained research interest as a treatment challenge to enhance recycling of OSPW [8]. Furthermore, recycling of OSPW is also limited in refining operations as the structure of NAs in recycled water enables them to act as surfactants [9] and cause the formation of stable emulsions, rendering oil–water separation challenges. To achieve sustainable expansion of oil sands, removing NAs is a primary target for treating OSPW and tailings ponds to make oil sands operations more sustainable. Naphthenic acids (NAs) are a resin group comprised predominantly of saturated aliphatic and alkyl substituted alicyclic and to a lesser extent, aromatic carboxylic acids. NAs contain several cyclopentane and cyclohexane (C5–C6) carboxylic acids originating from crude oil with residual OSPW concentrations estimated to range from 40 to 120 mg/L [10,11]. Early definition of classical NAs was obtained by chemically grouping of carboxylic acids represented by $C_nH_{2n-2}O_2$, (where n is the number of carbon atoms; Z is the hydrogen deficiency number due to ring formation or double bonds) and overlooked the inclusion of nitrogen and sulfur bearing compounds as well as other structures with multiple carboxylic acid groups and oxy-NAs.

Model NA compounds are typically carboxylic acids that cover two sub-classes of naphthenic acids: aromatic acids and alkyl substituted alicyclic carboxylic acids represented by the classical NA formula above. Although aromatic NAs are also minor components of NAs [11], they have received considerable attention as model compounds due to known degradation behavior. It is necessary to point out that the multiple carboxylic group and nitrogen and sulfur-containing NAs are not considered in the general formulation of NAs [12] and an extensive study of NA classes has been performed [13,14]. NAs are recalcitrant and their concentration in tailings ponds remains at ~19 mg/L even after several decades of storage [15]. A detailed review of NA structures shows that NAs possess both hydrophilic and hydrophobic groups, allowing them to act as surfactants owing to their polar carboxylic groups and nonpolar aliphatic ends. Spurred on by the need to better understand this complex group of emerging contaminants Headley *et al.* [16] have reported significant advances in the characterization, identification and quantification of NAs in environment samples. Multiple studies have examined the use of advanced oxidation treatment methods for OSPW using sonolytic methods and benchmarked them with the use of hydrogen peroxide treatment [17]. However, underlying principles of degradation were not addressed in the studies, as combination treatment approaches do not provide insight into individual process effects on degradation.

To date, ozonation is the most studied standalone chemical oxidation method for NA removal from OSPW and has been found to be suitable for low concentration NA (<50 mg/L) degradation under acidic conditions by 70–97% [18]. In alkaline conditions, ozone decomposes to hydroxyl radicals that react with NAs to lead to the bond scission of highly branched chains or cyclic fractions [19]. Hybridization of ozonation with peroxides and degradation of NAs by persulfate ($S_2O_8^{2-}$) and permanganate (MnO_4^-) as process intensification approaches showed mineralization of some NAs [20]. Fenton reagent and persulfate treatment showed the potential for complete mineralization [21]. Drzewicz *et al.* reported the closest investigation to 3mCHA on the degradation of cyclohexanoic acid (CHCA) under UV/ H_2O_2 [22,23] and concluded that some intermediates of CHCA also underwent radical oxidation. However, the degradation of 3mCHA depends on the amount of hydroxyl radicals. In addition, the hexane ring was degraded to an acyclic by-product. Hydroxyl radical scavengers and suspended particles also play a critical role in reducing the oxidative degradation of NAs [24,25]. These factors can lead to the partial or incomplete degradation of NAs collectively.

The purpose of this study is to investigate the effectiveness of sonochemistry in the degradation of NA model compounds from OSPW. This

comprehensive study to assess the sonochemical degradation of both aromatic and alicyclic NA model compounds. We hypothesize and validate the breakdown mechanisms for both model compounds to strengthen our confidence in the reproducibility of our findings and explain the hydrogen abstraction and decarboxylation process including ring opening through the reaction pathways. Benzoic acid has been studied by many research groups to model NA degradation due to its structural similarity to naphthenic acids [26,27,28]. Due to the alicyclic nature and predominance of C5–C6 structures of many naphthenic acids in OSPW, 3-methylcyclohexane carboxylic acid (3mCHA) was selected as a classical model compound in this study. The effect of sonochemistry on BA is extended further from earlier studies [29,30] to determine the degradation pathway of BA and confirm the products formed during sonication. The introduction of 3mCHA to extend the understanding of decarboxylation of alicyclic model NA compounds adds to the underlying sonochemical degradation of carboxylic acids.

2. Radical-initiated sono-degradation of NA compounds

Although the use of ultrasonic activation has long been applied into mainstream water treatment processes, challenges such as selective degradation, stereo-chemical degradation control, or interpretations of the underlying mechano-chemistry still represent unresolved issues. Overall, sonochemistry was deemed as a radical initiated degradation process but a lack of understanding of degradation pathways and has hampered its optimization and process intensification [31] when compared to other activation techniques, namely ozonation, photo-chemistry and electrochemistry.

2.1. Sonochemical degradation of BA and 3mCHA breakdown

In general during sono-degradation, organic compounds in water can be degraded through thermal decomposition or radical reaction in the interior of the cavitation bubbles and in the bubble–liquid interface region and undergo oxidation reaction with hydroxyl radicals and hydrogen peroxide in the bulk solution [32]. It was reported that due to the recalcitrance and complex composition of NAs, total degradation of NAs is not expected using ultrasound alone and a secondary oxidative process is often needed to result in mineralization [19]. To investigate this further, breakdown studies with BA and 3mCHA were performed.

2.1.1. Hypothesis of sonochemical BA breakdown

Singla *et al.* (2004) studied the mechanisms of the sonochemical degradation of benzoic acid (BA) in aqueous solution [29]. They determined that sonolytic degradation of BA was rather efficient and could undergo both pyrolysis and reaction with OH^\bullet radicals at $pH < pK_a$. However, when pH was higher than pK_a , BA was found to react with OH^\bullet in the bulk solution and can be inferred from the conversion of other radicals to hydroxyl radicals at higher pH . They inferred the production of mono-hydroxyl intermediates initially with ring opening of the intermediate products by continued sonication.

Further, Wu *et al.* also conducted a theoretical study on reaction pathways for BA [30]. Concomitant analysis of both studies shows that the initial degradation site for BA-hydroxyl radical (OH^\bullet) interaction, dictates the structures of the series of degradation products that follow before complete mineralization. There are 7 main paths benzoic acid can undergo upon initial radical attack: H-abstraction (H-abs), *ipso*-add, *para*-add, *m*-add, *m2*-add, *o*-add and *o2*-add [30]. Interpreted pathways, shown in Fig. 1, outline the differences between *m/o* versus *m2/o2* as being opposite and beneath the C = O in carboxyl group respectively. Of all the initial sites, *ipso*-add was the least likely due to the significant steric effect that occurs because of the carboxyl group. Pre-reactive complexes were formed as OH^\bullet approached benzoic acid through van der Waals and long range coulombic interactions. The relative energies and rate calculations in this study considered pre-reactive complexes as

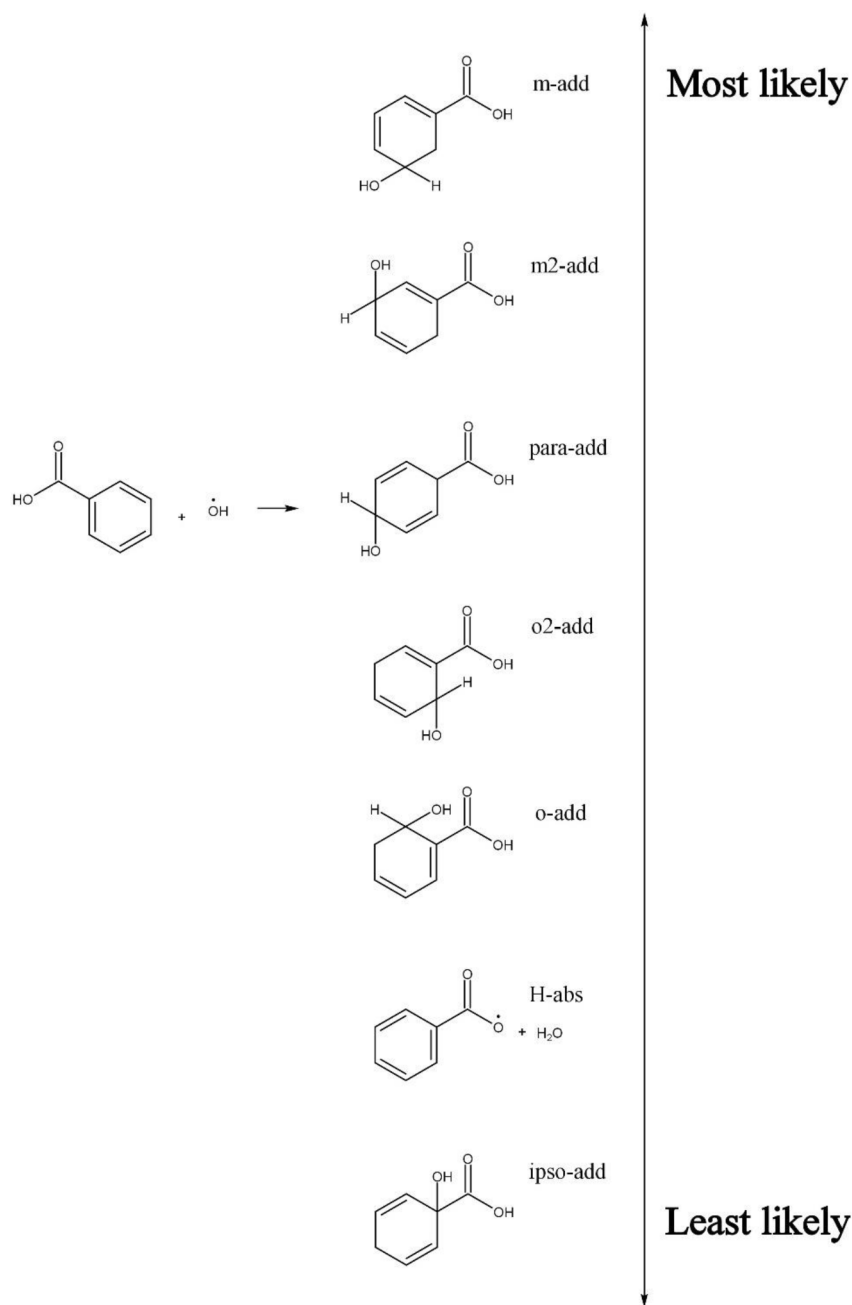


Fig. 1. Likelihood of initial sites of oxidation for benzoic acid in the aqueous phase (graphical interpretation from discussion in [30]).

it affected the relative stability of a reaction site. The energy barrier from the pre-reactive complex to the transition state was the least for o-add, m-add and m2-add [30]. However, o-add experiences steric hindrance, H-bond formation and the electron withdrawing effects of the carboxyl group (also seen in *para*-add) causing the meta additions the most likely site for OH^\bullet electrophilic attack. Additionally, the ortho additions occurred in the same plane as the benzene ring whereas the meta and para were above the ring. The accumulating effect of these factors explain the meta additions (particularly m-add) being ~ 1.3 times the rate of para addition, ~ 2 times the rate of the ortho additions and ~ 28 times the rate of H-abstraction [30]. Molecular reaction models in the presence of a water molecule greatly shifted the proportion to meta additions as the rate was ~ 3 times the rates of ortho and para and ~ 196 times the rate of H-abstraction due to loss of symmetry and H-bonding of water with the carboxyl group.

2.1.2. Degradation of 3-methylcyclohexane carboxylic acid

Degradation of 3-methylcyclohexane carboxylic acid, $z = 2$ naphthenic acid compound, is postulated via a generalized degradation as benzoic acid due to its structural similarity, with a few key differences. Like benzoic acid, there are two main routes of initial oxidation are H-abstraction and meta-addition. The meta additions are, as expected, the most likely sites. Due to the methyl group of 3mCHA located at one of the meta positions, the other meta position is primed for electrophilic attack. With benzoic acid, the aromatic ring provides stability to the chemical structure for shifts in electrons upon initial oxidation. This allows for the ring to be maintained through further degradation and formation of products such as 3-hydroxybenzoic acid, phenol and catechol. The lack of an aromatic ring in 3mCHA results in two routes of cleavage: symmetric and asymmetric. Asymmetric and symmetric cleavages are reaction mechanisms, primarily developed by Benson, Russell and Bennett, that describe possible reaction pathways taken by

radicalized non-aromatic compound in the presence of O_2 [33–35,54].

The asymmetric release of O_2 results in the addition of hydroxyl, ketone or hydroxyl ether, as postulated in Fig. 3. Alternatively, the symmetric release of O_2 will result in a ring opening mechanism akin to cyclohexane developed by M. Alam *et al.* [36]. The number of functional

groups on the cyclohexane backbone limits the number of H-shifts that take place (0–2 shifts). The methyl and carboxyl group in 3mCHA prevents H-shift from occurring resulting in a carbonyl or hydroxyl group added to the end of the open chain.

Due to the multiple products that result from ring opening of the

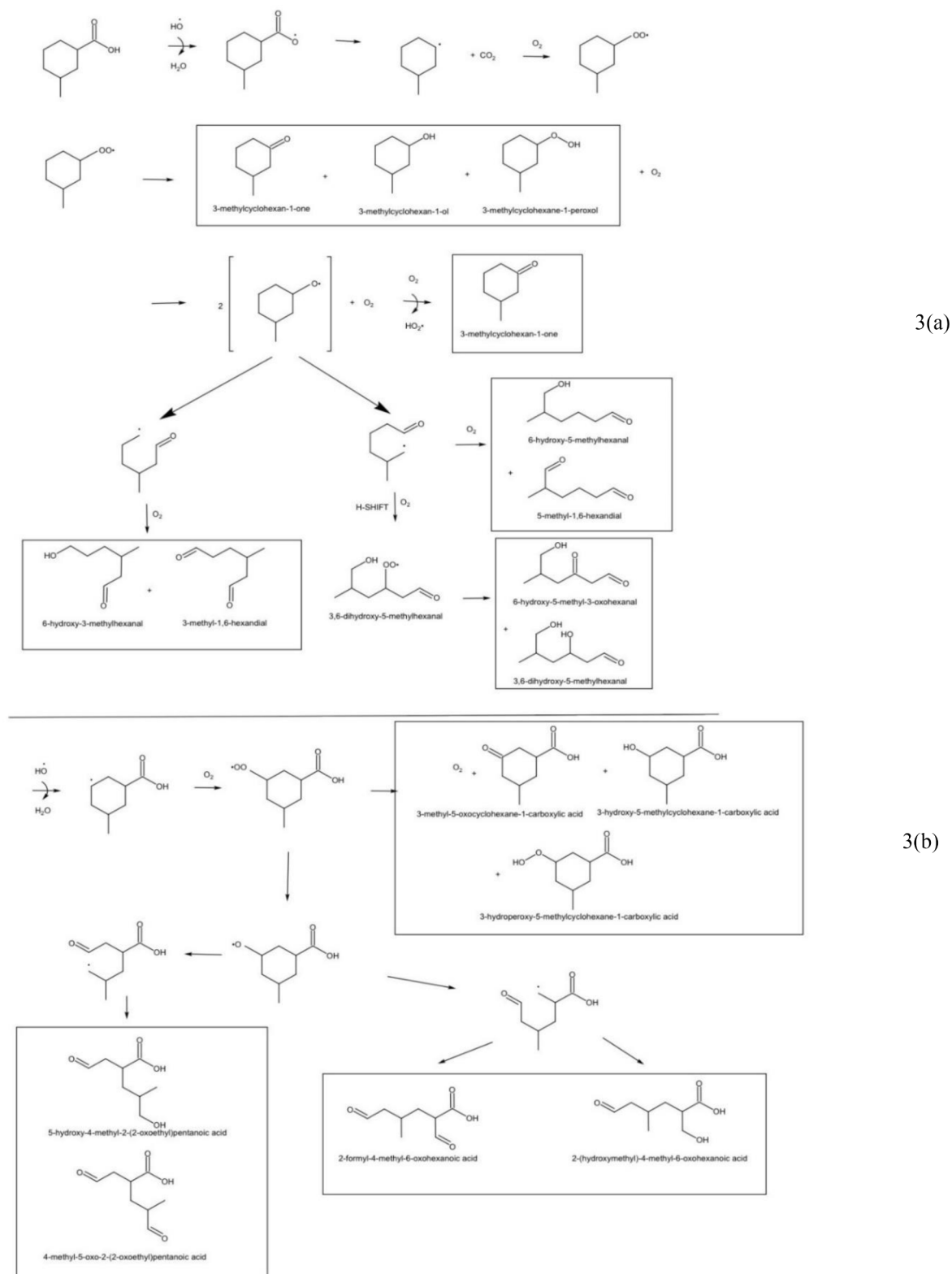


Fig. 2. New prediction of initial oxidation sites of 3-methylcyclohexane carboxylic acid. Proposed radical attack approach outlines two lines of electrophilic attack, 3 (a) H-abstraction and 3 (b) meta-addition (favoured).

cyclohexane, Fig. 2 shows the several hypothesized routes of degradation. Of the three initial meta additions (hydroxyl, carbonyl and hydroxyl ether) hydroxyl meta addition is the most likely to occur. The routes of ring opened structures have yet to be explored through kinetic modelling, but provide a basis of potential degradation structures and their pathways.

3. Experimental

3.1. Chemicals and reagents

Benzoic acid (BA, CAS 65–85-0) and 3-methyl-1-cyclohexanecarboxylic acid (3mCHA, CAS 13293–59) used in the sample preparation were from Sigma Aldrich Canada along with deionized water (Milli-Q/Milli-RO Millipore system, Milford, USA). Formic acid (CAS 64–18-6, Fisher Scientific Canada), methanol (Optima, CAS 67–56-1, Fisher Scientific Canada), and dichloromethane (DCM, CAS 75–09-2, Acros NJ, USA) were the solvents used for solid-phase extraction (SPE) and Fourier-transform infrared spectroscopy (FTIR). Oasis HLB (3 cc, 540 mg, P/N 186004134) cartridges were purchased from Waters (Milford, USA).

LCMS radical degradation product standards including; salicylic acid, phenol, catechol, p-benzoquinone, pyrogallol and mineralization product standards including oxalic and fumaric acid were obtained from Sigma Aldrich (Oakville, Ontario) to confirm the OH[•] degradation and pyrolysis products after sonication.

3.2. Sonochemical reactor setup and operation

Multiple studies have reported sonochemical degradation of BA and other carboxylic acids at low frequency ultrasound (20–40 kHz) and have reported partial breakdown of BA [29]. This study extends early reported findings to mid-frequency ultrasound and examines the extent of breakdown to develop new methods for NA removal. Benzoic acid and 3-methyl-1-cyclohexanecarboxylic acid stock solutions were prepared with Milli-Q water in a 500 mL beaker by stirring the carboxylic acid compounds in water for at least 1 h or until dissolution with a magnetic stirrer at 150 rpm.

Fig. 3 represents the experimental setup for performing the sonochemical experiments. The setup consists of a coolant-jacketed glass

cylindrical reactor with a diameter of 5 cm and 100 cm in height with a broadband transducer (Model: Meinhardt E/805/T/M) installed at the bottom in direct contact with the naphthenic acid compounds in water directly transferred after stirring into the sonochemical reactor. Ultrasound energy was supplied by a power amplifier (HM8001-2) through a wave function generator (HM 8032). The local temperature of the NA-water mixture was monitored with a K-type thermocouple. The O-ring grooved broadband transducer was clamped to the cylindrical reactor to ensure sealing of the sonochemical reactor (Ultraschalltechnik-Meinhardt GMBH, Germany). The coolant temperature was controlled at 25 °C using a thermostatic bath with a temperature shut-off for the transducer when the NA-water mixture local temperature exceeded 40 °C.

The sonochemical system was operated using at 378 kHz with an input power of 50 % or 304 W (amplitude) with previously reported high chemical cavitation yield of 4 μ mol/W/ml [37] and similar to empirical conditions described in Singla *et al.* [29,17]. Desired concentrations of 200 mL vol. of prepared naphthenic acid compounds in water were treated in the sonochemical reactor system for ascending durations (5 min to 4 hrs) as reported in Table 1.

4. Analytical

4.1. Solid-phase extraction (SPE)

Solid phase extraction of the naphthenic acids is essential to remove the broad –OH peak of water from FTIR spectra to interpret the organic acids and their fragmented compounds. The solid-phase extraction method was adapted from Gamal El Din *et al.* [38]. Aliquots of 50 mL were taken from the sonicated samples and acidified to pH ~ 1 using formic acid in preparation for extraction. In contrast to Gamal El Din's work, Oasis HLB SPE cartridges were used and were conditioned with 5 mL of optima water, 5 mL of methanol and with an additional 10 mL of optima water. The 50 mL acidic sample was loaded with the eluent released into the waste. A final rinse of 5 mL of optima water was performed before extracting the trapped analytes into the receiving tube with 6 mL of methanol. The methanol extracts were dried under a low velocity air stream in the fume hood. Mass of the receiving tube was recorded prior to extraction and with the dried sample to obtain the

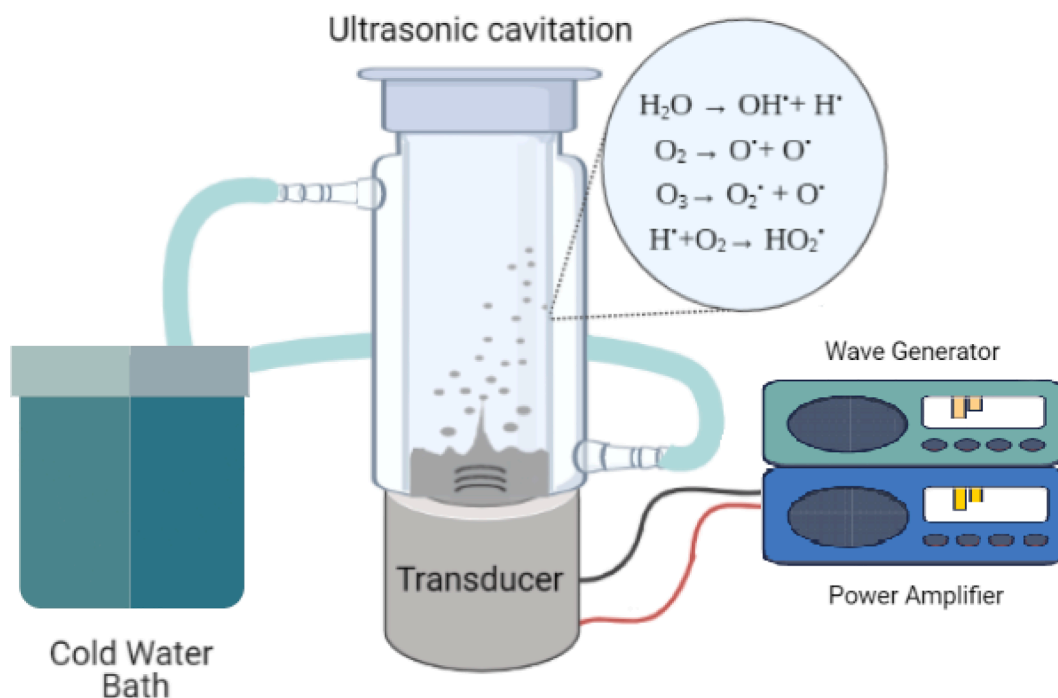


Fig. 3. Experimental apparatus used to conduct mid-frequency sonication at 378 kHz and 50% amplitude.

mass of the analyte from 50 mL sonicated solution.

4.2. Fourier transform infrared spectroscopy analysis (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a robust method for detecting NAs in tailings pond water adopted easily in the detection of oil-phase of NAs [39]. To prepare the dried analyte for FTIR, 0.5 mL of DCM was added and agitated using a vortex. The Thermo Scientific, model Nicolet 6700 infrared spectrometer was used in conjunction with ATR (attenuated total reflectance) multiple reflection (10) trough plate with zinc selenide crystal. The sample spectrums were recorded for 32 scans at a resolution of 4, from 4000 to 400 cm^{-1} in OMNIC software.

FTIR spectroscopy is a total quantification method and does not characterize or differentiate NAs and its fractionated compounds based on their type or source. FTIR detection optimized for carboxylic acid functionality was summarized by Ripmeester [40] and improved by Gamal El-Din and applies a fixed path length (3 mm) of KBr liquid cell and solid phase extraction (SPE) rather than liquid–liquid extraction (LLE) resulting in higher recoveries [38]. An ATR approach for C = O detection was applied in this study for increased resolution in the carboxylic functional group range without interference. This FTIR method measures these compounds directly using the C = O stretching vibrations of carboxylic acid functional groups at $\sim 1740 \text{ cm}^{-1}$ and their hydrogen-bonded dimers at $\sim 1700 \text{ cm}^{-1}$ [41]. The spectra were attained and processed by subtracting the DCM spectrum from the sample run. The peak heights were measured in OMNIC software, averaged and applied to calculate the concentrations of carboxylic acids for different sonication periods from the calibration curves. Dichloromethane (DCM), a high polarity solvent indicated by its higher dipole moment and dielectric constant, with low background absorbance in the carbonyl stretch region during FTIR detection, was chosen similar to many practitioners [42,40,38].

4.3. LCMS/MS analysis of Sono-degradation products

Characterization studies of naphthenic acids was reported performed using both high and low resolution mass spectrometry techniques including HPLC (high-performance liquid chromatography) coupled with molecular spectroscopy [43,16,44–46]. In this study, LCMS studies were applied to enhance the mechanisms of sono-degradation by identification of breakdown products of BA during degradation after confirmation of decarboxylation using FTIR by the method described in [43] to reduce the false positive identification of organic acids as LCMS methods do not require any pre-treatment. Chromatographic separation was conducted using a HPLC instrument (Agilent HPLC 1280; Sciex MS Model No. QTrap 4000 and Agilent UV detector Model 1100). The mobile phase consisted of 10 mM NH₄Ac in HPLC water (A) and methanol (B), and was pumped using a binary pump at a flow rate of 600 $\mu\text{L}/\text{min}$. Injections were made by auto sampler and volumes were typically 20 μL . Separation was performed on a reverse-phase column, Zorbax Eclipse Plus C8 (4.6 150 mm, 3.5 mm, Agilent). A gradient elution was utilized: 10% B 0–20 min, 95% B 20–30 min, and 10% B 30–40 min, allowing the system to equilibrate for 10 min before injection of the next sample. Detection was performed in the negative ion mode by enhanced MS scan mode ($m/z = 50\text{--}800$) at a rate of 4000 Da/s on a Quattro QQQ (triple quad), QTrap 4000 mass spectrometer. Typical mass spectroscopy parameters were set at source temperature of 400 °C and collision-activated dissociation (CAD) gas high. The complete HPLC-MS/MS system was controlled operated and analyzed by Analyst software (Applied Biosystems) v. 1.7.

5. FTIR results and interpretation

Fourier transform infrared spectroscopy (FTIR) has been previously established as a reliable method for naphthenic acid quantification in water samples [42,39,3,38]. This method was applied for single

naphthenic acids to allow for isolated tracking of degradation. Determination of unique naphthenic acids identity in environmental samples poses a challenge due to difficulty separating [39]. Isolated degradation tracking can be extrapolated to determine the level of degradation in an environmental sample. Although benzoic acid is not a naphthenic acid (according to the formula $\text{C}_n\text{H}_{2n-2}\text{O}_2$, $z = 2$), earlier studies use it as a model compound, which allows this study to compare aromatic vs aliphatic degradation with respect to 3mCHA.

Sonicated water samples were extracted with methanol, dried and dispersed in DCM to maintain consistent extraction expressed by reverse calibration with a detection limit of 10 mg/L [47]. The obtained spectra were analyzed using a method by Jivraj *et al.* by summing the peak heights at $\sim 1740 \text{ cm}^{-1}$ and $\sim 1700 \text{ cm}^{-1}$ for the C = O stretch of the carboxylic group monomers and dimers respectively [3,38,39,42,53]. In anhydrous conditions, hydrogen bonding between carboxylic groups is heavily encouraged allowing visual comparison of naphthenic acid degradation from the peak at 1700 cm^{-1} .

R. Singla *et al.* sonicated benzoic acid at 355 kHz and achieved mineralization at a rate of $< 40 \mu\text{M}/\text{h}$ [29]. Table 1 shows the degradation of carboxylic acid peaks for 50 mg/L after 4 h and 25 mg/L after 15 min confirming Singla's findings. Fig. 4 is adapted from Singla's work with modifications, particularly the production of 3-hydroxybenzoic acid instead of salicylic acid and the removal of 3, 5-cyclohexadiene-1, 2-diol and p-benzoquinone as possible degradation intermediates. 3-hydroxybenzoic acid is the primary degradation intermediate due to the preference of meta-addition as outlined by Wu *et al.* (2017) [18]. Ortho-addition experiences steric hindrance, H-bond formation and the electron withdrawing effects of the carboxyl group (also seen in *para*-addition) making the meta additions the most likely site for OH[•] electrophilic attack [48,29,49–52]. The FTIR spectra provides detailed insight into which path the degradation is likely to take. Fig. 5 shows the carboxylic acid peaks for 50 mg/L which decrease with time from 0 to 30 min, increase at 60 min and flatten altogether at 240 min. The aromatic stretching section clarifies that the right side pathway in Fig. 4 is predominant. For 0 and 15 min, the carboxylic acid peaks at 1732 cm^{-1} and 1694 cm^{-1} are strong along with the aromatic ring peaks at 1604 cm^{-1} and 1584 cm^{-1} indicating the presence of benzoic acid, 3-hydroxybenzoic acid and 3,4-dihydroxybenzoic acid. The 30 min spectrum shows a rapid degradation in carboxylic acids with a broader peak for aromatics indicating the formation of phenol, catechol and pyrogallol. At 1 h, the carboxylic acid peak rises with lower aromaticity, signifying ring-opening to small chain carboxylic acid such as muconic and fumaric acid. Four hours shows the depletion of carboxylic acids with a broad shift to C = C suggesting the complete degradation of benzoic acid. Four hours still has aromatic peaks present proposing a stabilized aromatic alcohol intermediate. In Fig. 6, the 25 mg/L series achieves total mineralization by 15 min of sonication as none of the above mentioned peaks are present in any of the spectra other than the control. This further confirms a slow and steady rate of degradation in higher concentrations where interference between intermediates may play a significant role.

The initial degradation for 3-methylcyclohexane carboxylic acid is predicted to be akin to benzoic acid. Enhanced by the methyl group at the other meta position, the likely site of addition is at the sole vacant

Table 1

Concentration of timed benzoic acid sonicated samples with starting concentrations of 50 mg/L and 25 mg/L. Samples were sonicated at 375 kHz at 50% amplitude.

Sonication Time (min)	Benzoic Acid 25 mg/L series (mg/L)	Benzoic Acid 50 mg/L series (mg/L)
0	21.3	41.0
15	3.10	40.0
30	3.71	11.4
60	3.76	17.8
240	2.90	2.56

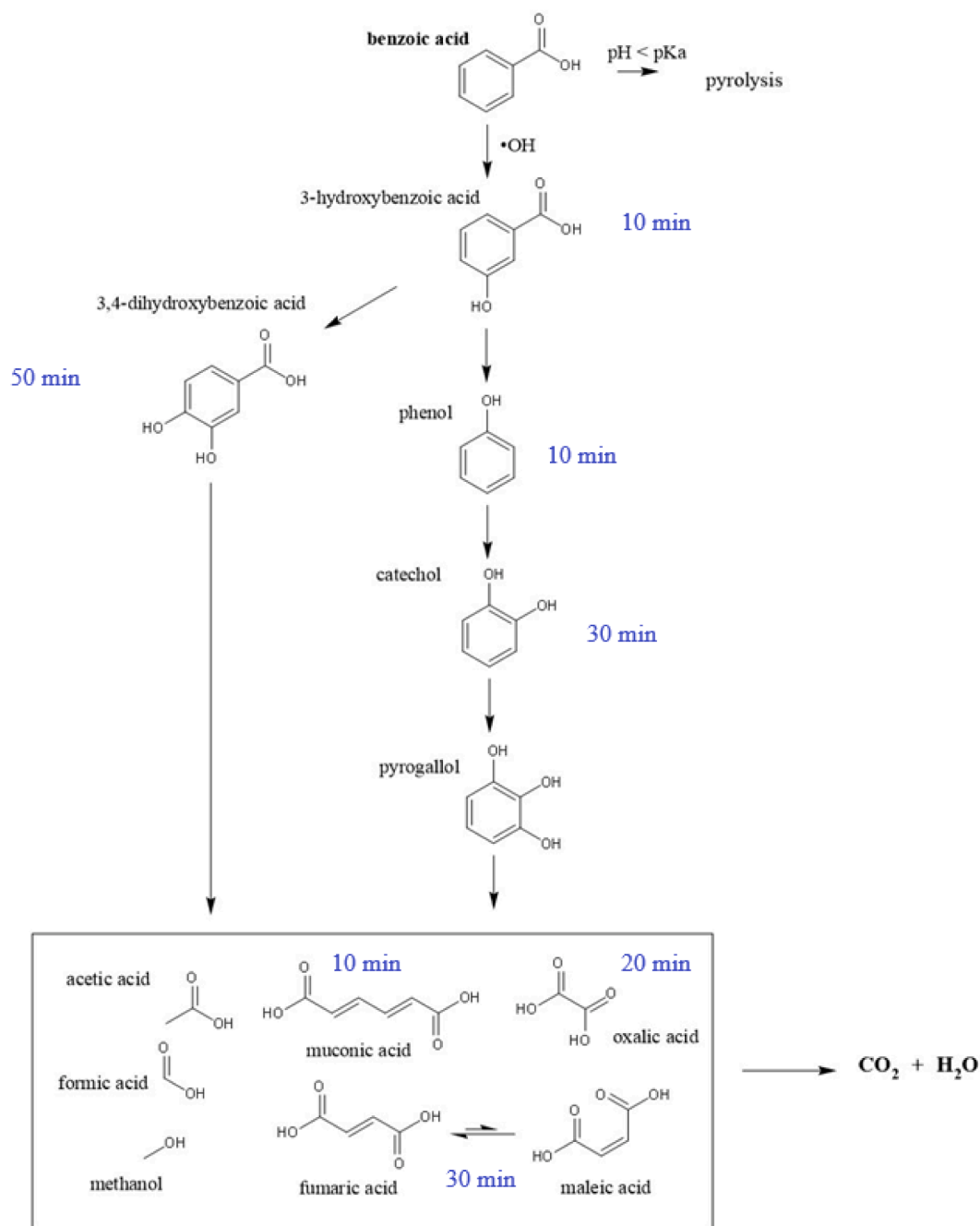


Fig. 4. New benzoic acid degradation pathway (modified from R. Singla *et al.* [29]). Sonication times indicate initial detection in LCMS analysis.

meta position. The major limitation in degradation is the lack of an aromatic ring, which not only facilitates abstraction but also stabilizes intermediates. The pathway of degradation shown in Fig. 3(b) is likely to occur (Table 2).

Fig. 7 shows a similar degradation for 50 mg/L with the peaks decreasing from 0->15->60->240->30 min. The decrease in carboxylic peaks from 0 to 30 indicates the H-abstraction pathway taking place proceeding to decarboxylation and ring opening. However due to the complex nature of the ring-opened products there is no sign of complete mineralization. The rise and subsequent fluctuation of the carboxylic acid peaks is due to the meta-addition of the OH radical and the proceeding intermediates all of which contain a carboxylic acid group. The horizontal shift in carboxylic peaks from 1703 cm^{-1} to 1712 cm^{-1} indicates the formation of complex potentially multi-carboxylated compounds which engage multiple dimers. This is further confirmed by the

C = C peak at 1636 cm^{-1} in 240 min signifying small chain unsaturated carboxylic acids.

The 25 mg/L series in Fig. 8 shows initial degradation of carboxylic acids and then peaks at 30 min and is interpreted by reaction site selectivity in relationship to concentration. Decarboxylation is favoured at high concentrations, while meta-addition is favoured at low concentrations. Although meta addition increases the complexity of the degradation products (Fig. 2), it enhances degradation though subsequent carboxylic acids reductions for a multitude of degradation routes towards mineralization. This complexity of products causes the broadening of the low concentration peaks with time in Fig. 8. Continued sonication is predicted to attain mineralization for 3mCHA.

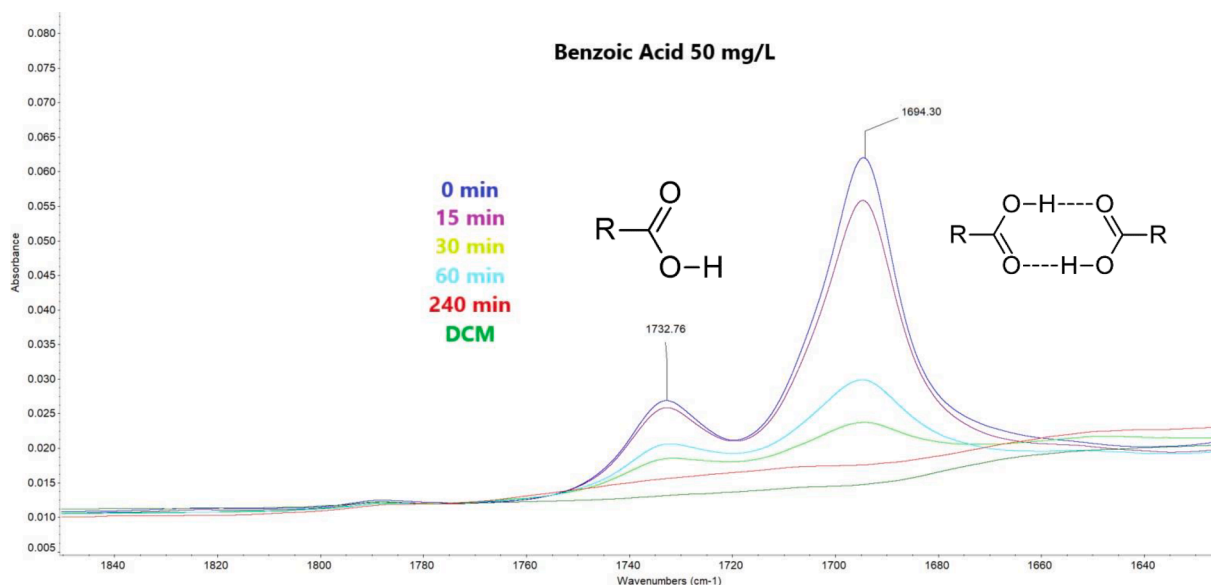


Fig. 5. The FTIR spectra of 50 mg/L benzoic acid at various sonication times. The peaks at 1732 cm^{-1} and 1694 cm^{-1} are the carboxylic acid peaks.

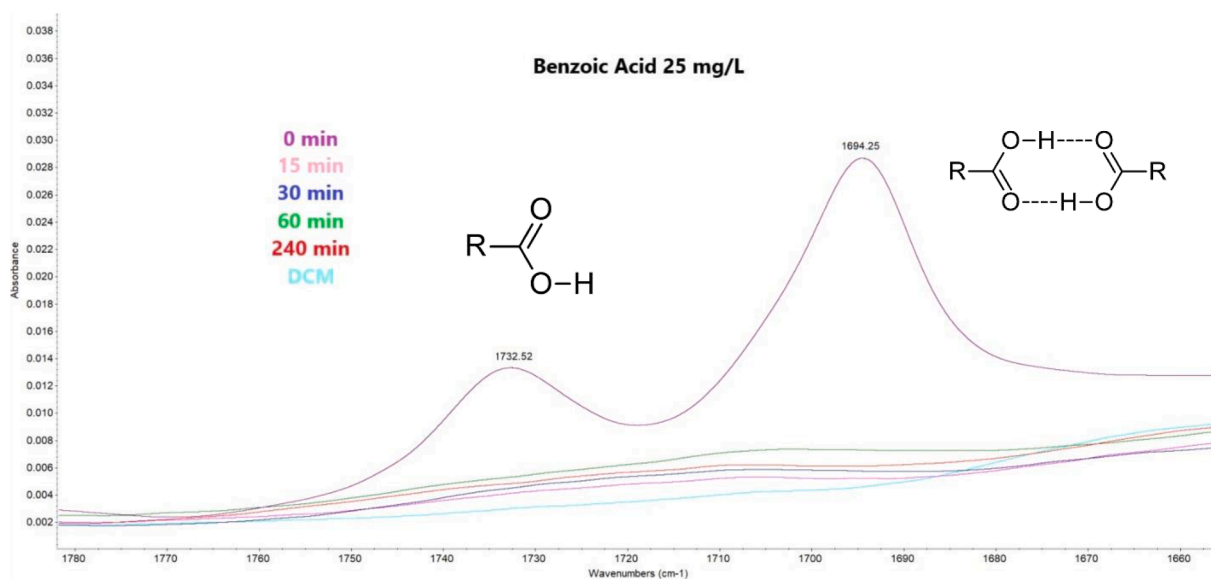


Fig. 6. Infrared monitoring of sonochemical degradation of benzoic acid (BA) spectra ($C_0 = 25\text{ mg/L}$). Carboxylic acids peaks are shown at 1732 cm^{-1} and 1694 cm^{-1} .

Table 2

Concentration of timed 3-methylcyclohexane carboxylic acid sonicated samples with starting concentrations of 50 mg/L and 25 mg/L. Samples were sonicated at 375 kHz at 50% amplitude.

Sonication Time (min)	3-methylcyclohexane carboxylic acid 25 mg/L series (mg/L)	3-methylcyclohexane carboxylic acid 50 mg/L series (mg/L)
0	28.4	40.2
15	19.3	30.0
30	34.3	13.7
60	20.4	26.4
240	21.5	23.4

6. Low resolution LCMS identification of benzoic acid breakdown products

FTIR analysis of sonicated benzoic acid confirmed mineralization

through the depletion of the carboxylic acid peak. In order to provide more details in the pathway of degradation for benzoic acid, liquid chromatography mass spectrometry (LCMS) was used to analyze the sonicated samples from 0 to 60 min. In Table 3, benzoic acid control and 1 min resulted in a single LC peak at 10.75 with a lone benzoic acid mass peak. At 5 min, the presence of the decarboxylated benzoic acid benzene ring is detected indicating the beginning of degradation. At 10 min, smaller LC peaks form at 5.9 min and 13.2 min. These smaller peaks begin to show the degraded pieces of benzoic acid such as the 3-hydroxybenzoic acid, phenol and muconic acid. Alongside decarboxylated benzoic acid benzene ring, several other combinations of segmented benzene rings are detected. Additionally peaks of compounded benzoic acid and 3-hydroxybenzoic acid radicals were detected indicating radical quenching. Unlike radical scavenging where the addition of a reagent stops the oxidation, radical quenching involves two radicals terminating by forming a conglomerate. These conglomerates are large structures, often formed between intermediate compounds, thereby

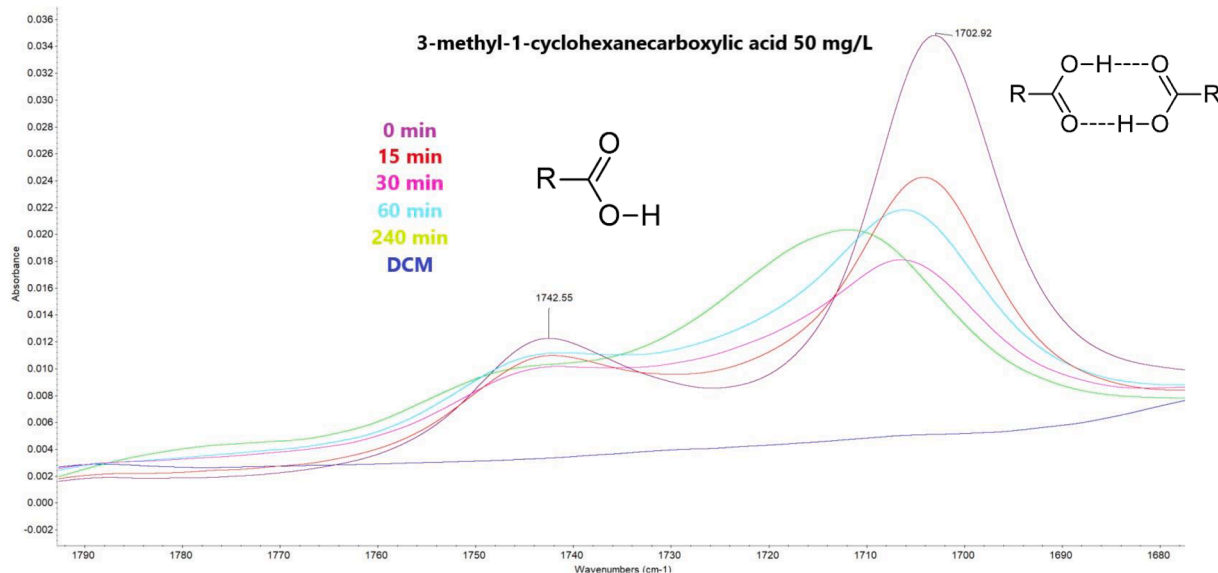


Fig. 7. Infrared monitoring of sonochemical degradation of 3-methyl-1-cyclohexanecarboxylic acid (3mCHA) spectra ($C_0 = 50 \text{ mg/L}$). Carboxylic acids peaks are shown at 1742 cm^{-1} and 1702 cm^{-1} .

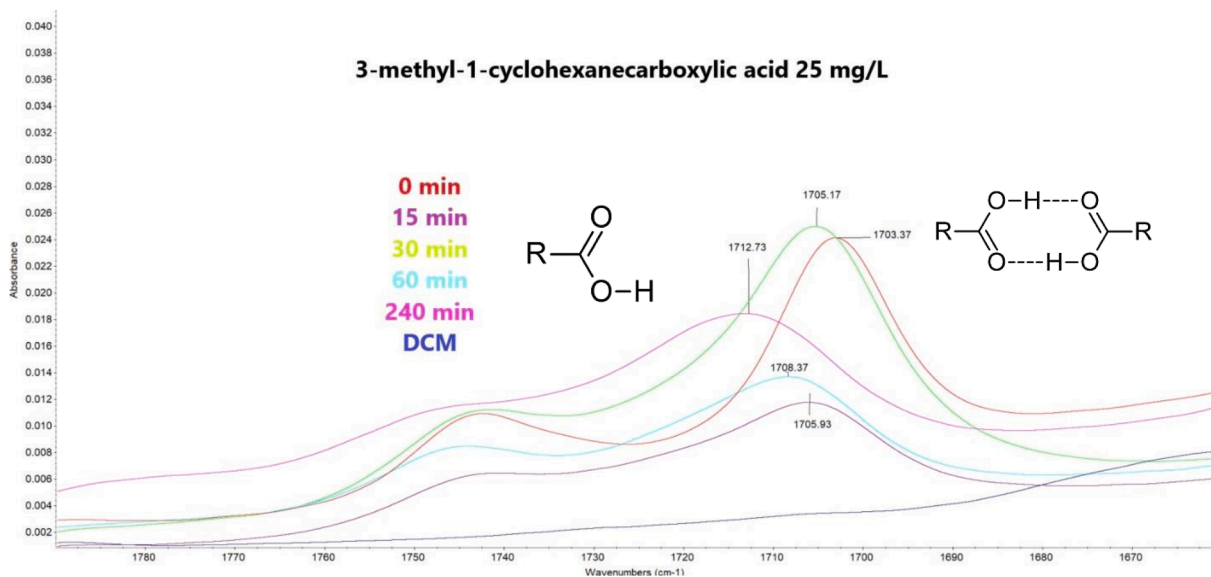


Fig. 8. Infrared monitoring of sonochemical degradation of 3-methyl-1-cyclohexanecarboxylic acid (3mCHA) spectra ($C_0 = 50 \text{ mg/L}$). Carboxylic acids peaks are shown at 1742 cm^{-1} and 1702 cm^{-1} .

making their multi-cyclic structures difficult to identify and pose additional challenges in mineralization.

At 20 min, formation of oxalic acid is detected. Degradation of benzoic acid for an excess of half an hour leads to a surge in conglomerates formed with common combinations including benzoic acid + catechol, + benzene ring, + 3-hydroxybenzoic acid, + oxalic acid and muonic + muonic acid. The number and dispersity of the conglomerates increases with time. This exemplifies radical quenching which is expected with a high volume of radicals existing within the same system. Fumaric acid also appears at 30 min confirming the FTIR results as when ring opening increases to achieve small chain carboxylic acids. The general benzoic acid pathway is upheld with the detection of all large compounds ($>60 \text{ m/z}$) except pyrogallol due to general instability. Catechol is not detected on its own rather only as a conglomerate with benzoic acid. Catechol, similar to pyrogallol, has more than one hydroxylated substitution making their structures highly susceptible to

ring-opening and radical quenching.

3, 4-dihydroxybenzoic acid was detected at 50 min concluding a heavy emphasis on the right side pathway of degradation for benzoic acid. The impeding effects of the mobile phase restricts the confirmation of mineralization and the concentration of naphthenic acids and their derivatives are impractical to determine with LCMS [43]. Therefore, the LCMS of benzoic acid sonochemical cavitation verifies the right side in Fig. 4 as the pathway of degradation with conglomerate production as a reaction inhibitor. The amendments from this study to Singla *et al.* is summarized in Table 4 with key intermediates and their routes of degradation displayed in Fig. 4.

7. Conclusions

Sonochemical degradation of naphthenic acid model compounds at higher frequencies of sonication elucidates the potential for radical

Table 3

Degradation compounds of benzoic acid detected by LCMS. Benzoic acid was sonicated at 375 kHz with 50% amplitude for ascending times to track degradation progress. *Benzene ring refers to decarboxylation and/or dehydroxylation of aromatic compounds in Fig. 4. Excess conglomerates are formed from radical intermediates.

BA Degradation Compounds	Sonication Time (min)										
	0	1	5	10	15	20	25	30	45	50	60
Benzoic acid (BA)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Benzene ring* (BR)			✓	✓	✓	✓	✓	✓	✓	✓	✓
3-hydroxybenzoic acid (3hBA)				✓	✓	✓	✓	✓	✓	✓	✓
3,4-dihydroxybenzoic acid (3,4-dhBA)											
Phenol				✓	✓	✓	✓	✓	✓	✓	✓
Muconic acid (MA)				✓	✓	✓	✓	✓	✓	✓	✓
Fumaric acid								✓	✓	✓	✓
Oxalic acid						✓	✓	✓	✓	✓	✓
BA + BA				✓	✓	✓	✓	✓	✓	✓	✓
BA + BR								✓	✓	✓	✓
BA + 3hBA				✓	✓	✓	✓	✓	✓	✓	✓
BA + Catechol								✓	✓	✓	✓
BA + Oxalic acid								✓	✓	✓	✓
MA + MA								✓	✓	✓	✓
Excess conglomerates								✓	✓	✓	✓

Table 4

Table compares benzoic acid degradation routes derived from Singla *et al.* [29], with new pathway identified in this study.

BA degradation reported R. Singla <i>et al.</i>	BA degradation reported in this study
1. Misidentification of initial to salicylic acid.	1. Accurate identification of 3-hydroxybenzoic acid during initial breakdown.
2. Formation of 2, 3-dihydroxybenzoic acid.	2. Formation of 3, 4-dihydroxybenzoic acid.
3. Degradation route including 3, 5-cyclohexadiene-1, 2-diol and p-benzoquinone.	3. Elimination of tertiary degradation route due to instability of products.
4. Fumaric/maleic acid, oxalic acid and acetic acid in small chain degradation products.	4. Addition of muconic acid, formic acid and methanol included in small chain degradation products.
5. Overall crosslinked degradation scheme.	5. Overall linear degradation route

based oxidation methods to mineralize NA compounds in water. Degradation pathway for BA was revised and reaction intermediates were summarized through the study. This approach was extended as a first study into the sonochemical degradation of alkaloid-aromatic acids in water that are more representative of NAs. It was inferred that mineralization can be achieved for BA. However, alkyl side chain addition and ring opening complexities limit sonolysis in 3mCHA. Coupled FTIR-LCMS analysis was applied to decipher both mineralization through carboxylic acid band reduction and identification with eventual removal of BA breakdown products from water and the use of a low resolution LCMS approach was applied for breakdown product identification. Radical quenching by NA compounds was appended to enhance the current understanding of partial mineralization by oxidation methods. We envision that the simplified analytical approach, albeit with two instrumentation methods, can simplify analysis of NA's from OSPW. The findings form the basis for developing rate kinetics and further investigation of first principle molecular models to provide insights into molecular level understanding of sonochemical effects; scalable to organic acids in Part II.

8. Supporting Information

Appended in the supplementary file of this manuscript are: ♣ Fig. S1 Calibration for benzoic acid at the carboxylic acid peaks (C = O 1732 and 1694 cm⁻¹) ♣ Fig. S2 Calibration for 3-methylcyclohexane carboxylic acid at the carboxylic acid peaks (C = O 1742 and 1702 cm⁻¹).

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

CRediT authorship contribution statement

Rija Ansari: . Deepak M. Kirpalani: Conceptualization, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ultsonch.2022.105929>.

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