

MICROWAVE ASSISTED PHOTOCATALYTIC TREATMENT OF
NAPHTHENIC ACIDS IN WATER

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ABSTRACT

Naphthenic acids (NAs) are natural constituents of bitumen and crude oil, and predominantly obtained as the by-product of petroleum refining with variable composition and ingredients. Naphthenic acids are composed of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic acids. Naphthenic acids become a significant part of the tailings pond water (TPW) after separation from oil sands material. NAs are soluble in water and are concentrated in TPW as a result of caustic oil sands extraction processes. Tailings ponds near the Athabasca oil sands region near Fort McMurray, Alberta, Canada are contaminated with a variety of toxic organic compounds released in industrial effluent from the oil extraction processes. NAs are among the major water contaminants in those regions because of their toxicity and environmental recalcitrance. They may enter surface water systems due to erosion of riverbank oil sands deposits and through groundwater mixing. Significant environmental and regulatory attention has been focused on the naphthenic acids fraction of oil sands material to address these challenges and potential hazards. Biological, chemical, and photolytic treatments of water contaminated with NAs have been studied, but are either time consuming or involve significant capital investment. There is a growing need to develop more efficient and cost-effective treatment methods. Based on existing literature, microwave and photocatalysis for degradation of naphthenic acids in water may be one solution. A knowledge gap exists in determining the effect of microwave energy and/or photocatalysis on the rate and extent of NAs degradation in contaminated water.

Part of this work included evaluation of the physical and chemical properties of NAs. Dielectric properties, important for designing a microwave system, were investigated. Effects of temperature, concentration, and frequency of microwaves on the dielectric properties of NA-water mixtures were studied and were used in designing the treatment systems for NAs. Three laboratory scale systems, (1) photocatalysis, (2) microwave, and (3) microwave assisted photocatalysis systems were designed and developed. Experiments were conducted to determine the NA degradation efficiency of these systems for both commercially available Fluka NAs and those extracted from oil sand process water (OSPW). Effects of water source (deionised and river water) and use of TiO₂ catalyst in the degradation process, were also investigated. Degradation kinetics for total NAs as well as individual z-family were calculated.

Results show that the three developed treatment systems were able to degrade NAs at a faster rate than the methods reported to date. The concentration of higher molecular weight NAs ($z = -4$ to -12) decreased more significantly than the lower molecular weight NAs in all the three treatment systems. Toxicity assessments of the NAs samples before and after treatment indicated that photocatalysis and microwave assisted photocatalysis systems decreased the toxicity of Fluka and OSPW NAs completely (up to 5 min IC₅₀ v/v > 90%). The microwave system reduced the toxicity of water containing Fluka NAs from high (5 min IC₅₀ v/v = 15.85%) to moderate (5 min IC₅₀ v/v = 36.45%) toxicity. However, a slight increase in toxicity was noted post-treatment in OSPW NAs.

Microwave-assisted photocatalysis was the most rapid degradation system for OSPW NA extracts in water with a half-life of 0.56 h in the presence of TiO₂. The

microwave system degraded OSPW NAs in water at a more moderate half-life of 3.32 h. The photocatalysis system was the slowest with a half-life of 3.99 h under similar conditions.

High and ultra high resolution analysis of NA sample, estimations of cost and further efficiency related research of the developed systems to treat water with microbial load along with chemical contaminants are recommended for future work to further validate these treatment systems.

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I dedicate my research and this thesis to the loving memory of **Siddheswar Mishra** (1965-2008), my late uncle. I wish you were here to see me completing my Ph.D. thesis.

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LIST OF NOMENCLATURE

ACN – acetonitrile

ANOVA – analysis of variances

AOS- Athabasca oil sands

°C – degrees Celsius

C – Carbon

EC25 – effective concentration (25%)

EC50 – effective concentration (median, 50%)

ESI – Electrospray ionization

FT – Fine tailings

FTIR – Fourier transform infrared

IC – Ion chromatography

IC50- concentration that results in 50% metabolic inhibition in an organism

Ka – Weak acid dissociation constant

Kd – Dissociation constant

LC – liquid chromatography

LC₅₀ – concentration that results in 50% lethality in an organism

M – molar, mol L⁻¹

MAP – microwave assisted photocatalysis

MeOH – methanol

MeV – mega electron volt

MFT – mature fine tailings

Milli-Q – deionized and ultra-filtered water

m/z – mass to charge ratio

n – number of individuals in a sample (number of replicates)

n – a part of the molecular formula for naphthenic acids $C_nH_{2n+z}O_2$ a family classification indicating the CH_2 group in NA molecular structure

N – normal (or normality)

NA – naphthenic acid

NAA – naphthalene acetic acid

NaOH – sodium hydroxide

NH_4OH – ammonium hydroxide

OSPW – oil sands process water

P – p-value

PAH – polycyclic aromatic hydrocarbon

pH – the inverse logarithmic representation of the hydrogen proton $[H^+]$ concentration

pKa – the negative decimal logarithm of K_a

SE – standard error

SPE – solid phase extraction

TPW- tailings pond water

UV₂₅₄ – ultraviolet light at $\lambda = 254\text{nm}$

z – naphthenic acid family classification indicating hydrogen deficiency

ϵ' - dielectric constant

ϵ'' - dielectric loss factor

P_f - power factor

d_p - penetration depth

CHAPTER 1. INTRODUCTION

1.1 Background

Tailings ponds in the Athabasca Oil Sands (AOS) in Alberta, Canada are contaminated with various toxic organic compounds from caustic oil extraction processes (Clemente et al., 2005). Naphthenic acids (NAs) are among the most significant water contaminants in tailings pond water as a result. Significant environmental and regulatory attention is focused on the NAs fraction of oil sands material due to their persistence in the environment and aquatic toxicity in tailings pond water (TPW) (McMartin, 2003). NAs are natural constituents of bitumen and become concentrated as a by-product of petroleum refining. Naphthenic acids are a complex mixture of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic acids. They are soluble in water (0.06-4.52 mg/mL) and are concentrated in tailings pond water (up to 110 mg/ L); contribute greatly to the toxic characteristics of the water (Rogers et al., 2002a, b).

Occurrence, analyses, toxicity, and biodegradation of NAs were reported by Clemente et al. (2005) and Koike et al. (1992). The sodium salts of NAs are toxic to microorganisms with 30% (v/v) EC50 (Herman et al., 1994). NAs are toxic to fish with LC50 value between 4 and 78 mg/L (Wong et al., 1996). Lewis (2000) reported an oral LD50 between 3.0 and 5.2 g/kg for rats. The human lethal dose was reported as 1 L (Lee et al., 2000). They also reported that NAs stimulate cell proliferation at low doses (< 50 µg/mL) indicating that toxicity of NAs in TPW is a major concern.

The corrosivity of NAs is a major concern for the refinery industry as it limits the choice of materials used. Because of the corrosivity and environmental concerns, process-affected water requires treatment prior to disposal. There is an insufficient amount of information on separation and identification techniques for naphthenic acid mixtures. However, photolysis using ultraviolet and visible spectrum of light source has been reported by McMartin (2003) as one potential supplementary remediation method for NAs in natural surface water. Headley et al. (2009) reported photocatalysis using TiO_2 as one of the efficient NA remediation methods under natural sunlight. In this context, recent literature suggests that NAs could be separated from diesel fuel using microwave radiation (Chan et al., 2002; Kong et al., 2004, 2006). Similarly, removal of NAs from vacuum cut # 1 distillate oil of Daqing using microwave has also been reported (Huang et al., 2006). However, the uses of microwave and microwave assisted photocatalysis for degradation of NAs in water have not been reported. Therefore, a knowledge gap exists to quantify the effect of microwave energy and/or photocatalysis for this application.

1.2 Review of Literature

1.2.1 Physical and Chemical Properties of Naphthenic acids

NAs are predominantly mono-carboxylic acids obtained as a by-product of petroleum refining. They are composed of substituted cycloaliphatic carboxylic acids that include single rings and fused multiple rings. Frank et al. (2009) suggested that there is multiple carboxylic acid content within the higher molecular weight (MW) and cyclic structures of NAs. The carboxyl group in the structure is generally attached to a side

chain. Acid strength of naphthenic acid is lesser than low molecular weight carboxylic acids (Fan, 1991; Whelan et al., 1992; Brient et al., 1995; Headley et al., 2004; McMartin et al., 2004). Typical physical and chemical properties of NAs are given in Table 1.1.

Stoichiometrically, NAs are represented by the formula $C_nH_{2n+z}O_2$ where 'n' indicates the carbon number and z represents the hydrogen deficiency or the number of hydrogen atoms lost as the structures become more compact. Oil sands process water (OSPW) NA extract contains a higher percentage of higher molecular weight compounds along with some impurities, aromatic NA-like compounds of similar range of molecular weight (Qian et al., 2008 and Frank et al., 2009). Frank et al. (2009) suggested that OSPW NAs contain larger NA-like compounds with unsaturated rings within their structures. The $z = -4$ series of NAs predominates in Athabasca oil sands TPW (McMartin, 2003; Headley et al., 2004) and are more toxic than other NAs fractions. The physical, chemical, and toxicological properties of these compounds are directly related to the molecular weight and structure. Molecular weight affects polarity and non-volatility of naphthenic acids (Herman et al., 1993; Brient et al., 1995; McMartin et al., 2004; Headley et al., 2004). The solubility of NAs is related to media pH, with nearly complete solubility between 9-11 (Headley et al., 2002a, b & 2004). Typical NAs structures are given in Figure 1.1.

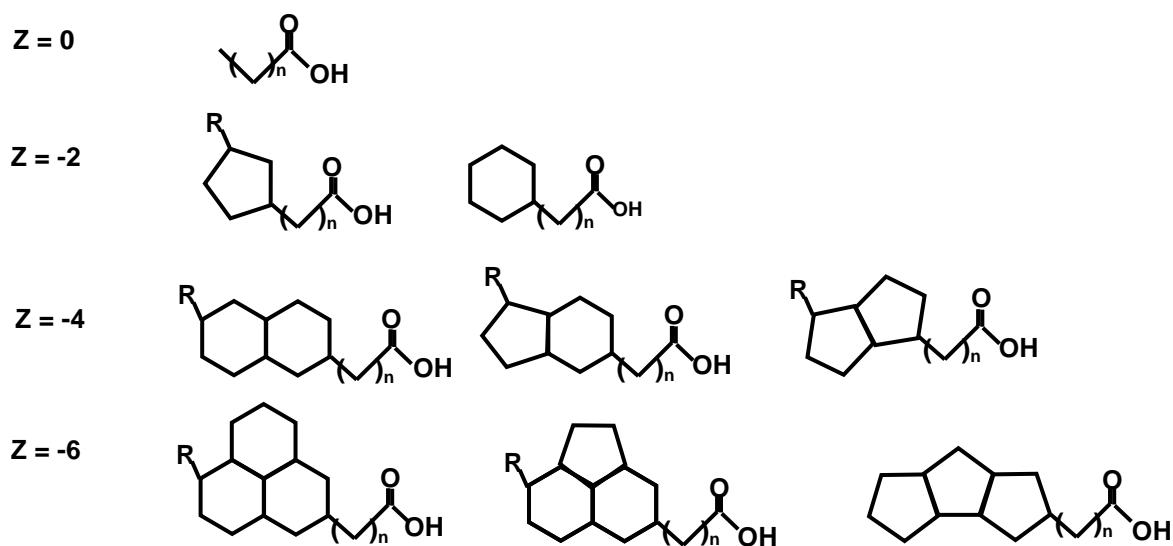


Figure 1.1 Typical naphthenic acid structures (McMartin, 2003).

Table 1.1 Physical and chemical properties of naphthenic acids (Brient et al., 1995; Herman et al., 1993; McMartin, 2003).

Property	Grade		
	Crude	Refined	Highly refined
Acid number, mg KOH/g	150-200	220-260	225-310
Acid number (oil-free)	170-230	225-270	230-315
Unsaponifiables, wt %	10-20	4-10	1-3
Phenolic compounds, wt %	2-15	0.1-0.4	0.05-0.4
Water, wt %	0.3-1.0	0.01-0.1	0.01-0.08
Specific gravity at 20°C	0.95-0.98	0.95-0.98	0.95-0.98
Viscosity at 40°C, cP	40-80	40-100	50-100
Refractive index, n_D^{20}	1.482	1.478	1.475
Avg. mol wt (oil-free)	240-330	210-250	180-250
Boiling point	250-350°C		

1.2.2 Source of Naphthenic Acids Contamination

NAs are a complex mixture of alkyl-substituted cycloaliphatic carboxylic acids (Young, 2006). Naphthenic acids are natural constituents of bitumen. They are oxidative products of petroleum hydrocarbons and may be the by-products of original plant transformation to oil (McMartin, 2003; Feinstein et al., 1991). The concentration of naphthenic acids in aquatic environments is usually low at 0.4 to 51 mg/ L (Clemente et al., 2005)

Holowenko et al. (2002) reported that 3 m³ water is used to process 1 m³ of oil sand and produces 4 m³ of tailings. Clemente et al. (2005) cited that Syncrude Canada Ltd., alone, processes 500 000 tonnes per day of oilsands containing, approximately, 10-12 % (wt) of bitumen. At an average, 200 mg of NAs are produced per kg of processed oilsands. Therefore, approximately 100 tonnes of NAs are released in oil sand process water (OSPW) per day by Syncrude Canada Ltd. The OSPW north of Fort McMurray, AB typically contains NAs in the range of 20-120 mg/L, which is considered toxic (Clemente et al., 2005). Due to the zero discharge policy of the Alberta government, OSPW and TPW are not released to the surface water sources, but are instead stored in large tailing ponds on site.

In general OSPW NAs have a dissociation constant (K_d) value between 1.3 and 17.8 mL/g (Janfada et al., 2006) and they undergo rapid sorption to soil. Thus, they do not significantly partition to water. Because of the moderately strong sorption to soils and relatively low solubility (0.06-4.52 mg/mL), oil sand NAs are less bioavailable in aqueous media.

1.2.3 Naphthenic Acids Toxicity

The toxic nature of naphthenic acids is mostly attributed to their surfactant characteristics due to the presence of a hydrophobic alkyl group and a hydrophilic carboxylic group in their salts (Rogers et al., 2002a, b; Clement et al., 2005; Frank et al., 2008, 2009). Naphthenic acids of low molecular weight are the most significant contaminants in the tailings pond water (Rogers et al., 2002b). The lower molecular weight (MW) NAs can more easily interact with biological tissue and, thus, have higher toxicity (Clemente et al., 2005). Toxicity of any given NA source is a function of both content and complexity. Toxicity decreases with the increase in carbon number content and structural complexity of the compound. There is structural difference between lower and higher MW NAs which contributes to the difference in their toxicity (Brient et al., 1995; Lai et al., 1996; Holowenko et al., 2002; McMartin, 2003; Frank et al., 2008, 2009). Holowenko et al. (2002) reported that fractions with carbon number, $n < 22$ are responsible for much of the toxicity of NAs. NAs with $z = -4$ and low carbon number (n) exhibit relatively higher toxicity (Lo et al., 2006). NA fractions with more rings (higher z values) and branches are relatively less toxic. Multiple rings with a higher number of carbon branches are relatively more resistant to microbial degradation. Lower molecular weights, less branched and lower carbon number (< 22) NAs are more bioavailable to microbe which degrades this NA fraction thus shifting the proportion of high molecular weight, higher carbon number (>22) NAs to higher side with aging. Thus, toxicity of oil sand process water decreases with aging (Holowenko et al., 2002; Frank et al., 2009). Frank et al. (2008, 2009) also suggested that there is greater carboxylic acid content

within the higher MW and cyclic structures of NAs. The presence of multiple carboxylic groups within their structure makes the higher molecular weight NAs more ionizable and less hydrophobic and accounts for the lower toxicity of higher molecular weight NAs than the lower MW NAs.

Toxicity of NAs also depends on the production and mining source. Commercially available NAs are more phyto-toxic than those from the AOS processes (Armstrong et al., 2008). This difference was attributed to the molecular weight distribution in NAs. Commercial mixtures have a higher concentration of lower molecular weight compounds and, thus, are more toxic than the OSPW NA extracts with a higher percentage of higher molecular weight compounds along with some impurities, aromatic NA-like compounds of similar range of molecular weight (Qian et al., 2008 and Frank et al., 2009). Frank et al. (2009) further suggested that OSPW NAs contain larger NA-like compounds with unsaturated rings within their structures.

Toxicity of NAs is also affected by the pH of the OSPW. The pKa value of NAs is in between pHs 5.2 and 6.0. If the pH of OSPW is higher than the pKa value, NAs exist in their ionized form as salts. In this form, NAs are highly polarized and cannot pass through biological membranes and, thus, are less toxic. When pH is below the pKa value, NAs are unionized in the neutral form. As such, they are more soluble in biological membranes and therefore more toxic. Salinity of the medium also affects toxicity as NA salts of naphthenic acid are known to be toxic to microorganisms with an EC50 of 30% (v/v) (Herman et al., 1994).

Toxicity Measurement of Naphthenic Acids

Different methods based on the use of different test organisms like bacteria, aspen, fish, zooplankton, and rat, have been used by researchers to measure the toxicity of NAs (Clemente and Fedorak, 2005). Microtox toxicity assay is one such method that uses *Vibrio fischeri*, a luminescent bacterium, as the test organism. A possibility exists for other organisms to respond differently than *V. fischeri*. MacKinnon and Boerger (1986) compared three test organisms (Rainbow trout, *Daphnia magna*, and *V. fischeri*) to measure the toxicity of oil sands tailings pond water. The tailings water was found to be more toxic to *D. magna* and R. trout compared to Microtox. However, they reported Microtox to be more reproducible compared to the trout and *D. magna* assays. Kaiser and Esterby (1991) reported Microtox method as quicker, easier and less expensive than other toxicity assays. Because of these observations, this assay has commonly been used to monitor toxicity of the oil sands tailing waters and naphthenic acids solutions (Clemente and Fedorak, 2005) and has thus been used for current research.

1.2.4 Corrosiveness of Naphthenic Acids

In addition to contributing to TPW toxicity, NAs cause corrosion in the oil sands refining processes. Most natural NAs occur in their sulfide form, mainly responsible for corrosivity. Clemente et al. (2005) reported that corrosivity of NAs depends on the total acid number (TAN) of the crude oil. Availability of a carboxylic group in the NA structure to react with metal ions determines the extent of corrosiveness.

Corrosiveness is also temperature dependent. Under favorable conditions, between 220 to 400°C, NA salts cause chelation of the metal ion leading to corrosion of

metal materials. At higher temperatures (>400°C), NAs and their salts decompose and the corrosivity decreases (Turnbull et al., 1998).

Wu et al. (2004), Slavcheva et al. (1999), and Turnbull et al. (1998) reported efforts made to limit corrosion caused by NAs. Three approaches are available including: (1) changing the refining process to reduce the acidity of crude oils; (2) controlling the flow characteristics such as velocity and flow; and (3) using materials and components that are more corrosion resistant.

Any treatment unit design must include appropriate choice of materials to avoid damage or structural compromise due to NAs corrosivity.

1.2.5 Techniques for Naphthenic Acid Analysis

Naphthenic acids are highly complex mixtures of compounds following the general formula $C_nH_{2n+z}O_2$. For each carbon number (n), there is more than one isomeric form of NA. Analytical methods to identify, separate, and quantify these vast forms have not yet been reported. However, methods to quantify the overall concentration of NAs by relating area to molecular mass to charge (m/z) distribution are available.

Analytical procedures such as high performance liquid chromatography (HPLC), electrospray ionization mass spectrometry (ESI/MS) and fast atom bombardment (FAB/MS), gas chromatography (GC/MS) with derivatization, Fourier Transform infrared (FT/IR), Fourier Transform ion cyclotron resonance (FTICR/MS), proton nuclear magnetic resonance (1H NMR) spectroscopy, and high performance liquid chromatography / high-resolution mass spectrometry (HPLC/HRMS) have been used for the characterization and quantification of NAs (Holowenko et al., 2001, 2002; Headley et

al., 2002a, 2009; Barrow et al., 2003; Clemente et al., 2003a,b; Lo et al., 2003; McMartin, 2003; Han et al., 2008; Martin et al., 2008 and Frank et al., 2009). A recent study by Martin et al. (2008) compared the low (ESI/MS) and high-resolution mass spectrometry (HPLC/HRMS) and suggested that ESI/MS is efficient for the characterization of commercial NAs, but it is prone to substantial false-positive detections and misclassifications in OSPW NA mixtures. Moreover, acidic compounds, hydrocarbons and PAHs do not show up in ESI/MS in -ve mode. Martin et al. (2008) also reported that there was three-fold lower response factor for total OSPW NAs in HRMS and it showed slight non-linearity in response for commercial NAs above 50 mg/L. Particularly for $z=0$, ESI/MS overestimates the concentration as compared to HRMS. ESI/MS cannot separate impurities and other NA-like compounds present in the sample. However, we can still be able to see the MS profile.

ESI/MS in negative mode is used by Water Science and Technology Directorate of Environment Canada (Saskatoon, SK) to quantify and characterize naphthenic acids concentrations following the standard procedure proposed by Headley et al. (2002a). This method allows a detection limit of 0.01 mg/L. The ESI/MS was used to quantify, analyze, and characterize NAs samples in this research because of its availability.

In electrospray ionization, the solution is bombarded to produce ions that can be mass separated and detected by m/z . The sample cone is kept at a different voltage (-ve 7 kV) than the surrounding walls (+ ve 100 V) of the system. Cone voltage creates negatively charged molecules in negative ion mode as a result of the difference in voltage between the cone and surrounding walls. These smaller charged particles move through a

capillary tube and past a drying gas (Nitrogen) to help reduce the size and increase the charge of the particles. The charge on the particles continues to increase as particle size decreases toward the Rayleigh limit, at which the repulsive Coulomb forces are equal to surface tension. Beyond the Rayleigh limit, the particle is broken into daughter particles that are also evaporated by the nitrogen drying gas. The process continues until the molecules are reduced to their quasi-molecular ionic form and are passed for mass analysis and production of mass spectra (McMartin, 2003; Headley et al., 2002a; Fenn et al. 1989).

Headley et al. (2002a) and Holowenko et al. (2002) reported that negative ion electrospray ionization MS is comparatively more useful for the quantitative analysis of naphthenic acids in aqueous solutions. Preparative solid phase extraction (SPE) methods can effectively concentrate aqueous NAs samples as well as reducing matrix interferences from salts during analysis. The ESI/MS and SPE method has been proven reproducible and quantitative for NAs analysis at relatively low concentrations (Jones et al., 2001; Headley et al., 2002a; McMartin, 2003).

1.2.6 Treatment Methods for Naphthenic Acids Contaminated Water

Many methods have been reported to date to reduce concentrations of organic and inorganic contaminants in water, including: chemical treatment, bio-remediation, photolysis/photocatalysis, and microwave treatment. All these methods have potential to be used for treating water contaminated with naphthenic acids. These methods are discussed in detail in the following subsections.

1.2.6.1 Chemical Treatment

Chemical treatment of water is a well established process by which organic and inorganic contaminants, and harmful microorganisms, are treated by the addition of a chemical agent to the water. Chemical treatment can promote pathogen removal, color, odor and taste removal, iron and manganese oxidation, and algal and biological growth prevention in water distribution (Sadiq et al., 2004).

The most common chemical treatment process used for drinking water is chlorination to eliminate bacteria, viruses, protozoan cysts, and other organic/inorganic contaminants (Koivunen et al., 2005). However, the accumulation of undesirable byproducts such as carcinogenic trihalomethanes, formed during the treatment process is reducing the attractiveness of chlorine use.

The chemical treatment method has been explored and proven effective for degradation of NAs in water. MacKinnon et al. (1986) explained two approaches including: (1) altering the pH of the solution to favor coagulation conditions and flocculation of NAs using anionic polyelectrolyte; or (2) allowing natural processes that degrade NAs to reduce concentration over one to two years during which tailings water is placed in shallow well aerated pits.

Scott et al. (2008) reported that ozonation of sediment-free OSPW can remove ~ 70% naphthenic acids and reduce toxicity after 50 minutes. The concentration of high molecular weight naphthenic acids (C_{22+}) is reduced more compared to the lower molecular weight NAs. Results indicate that ozonation is superior to biodegradation in terms of rate of degradation. The enormous volumes of oil sand process water and the

high cost of ozone production must be considered, however, when evaluating the practicality of large scale of ozonation.

These approaches demonstrate how the chemical treatment method of NAs appears to be either an overly complicated procedure or a long drawn out process. Also a small fraction of recalcitrant NAs remain after the chemical treatment (Scott et al., 2008). There is a definite need to find other solutions for the treatment of tailings pond waters that are more cost and time saving.

1.2.6.2 Bio-remediation

Bio-remediation occurs when plants and microbes remove metals and other contaminants from soils and water as part of their normal metabolic processes. Some plants and microbes are capable of taking up naphthenic acids from aqueous phase. Therefore, bioremediation may be a viable option for remediation of NAs contaminated TPW. The challenges with bio-remediation are that a significant residual concentration of approximately 19 mg/L remains and it is a considerably slower process (Scott et al., 2005). Results show that lower molecular weight NAs ($n < 22$) are more readily biodegraded than higher molecular weight NAs. Additionally, the commercial NA mixtures are more biodegradable than OSPW naphthenic acids. This is likely since the commercial mixtures tend to contain more low-molecular weight NAs than typical AOS NAs mixture.

The plants used in phytoremediation of contaminated waters selectively uptake naphthenic acid molecules; limiting the usefulness of this method. Therefore, plants alone are not capable of fully remediating TPW (Headley and McMartin, 2004). Arthur et al.

(2005) reported phytoremediation as one potential method for metabolizing organic compounds to a non-toxic form. Plants can also be genetically modified to metabolize toxic contaminants (Arthur et al. 2005). Toxicity reduction of NAs might be attributed to the biotransformation of NAs by the microbes in the root zone. Biryukova et al. (2007) determined the effectiveness of rhizosphere micro-organisms at breaking down naphthenic acids. Armstrong (2008) reported that different wetland plants significantly can reduce toxicity of NA.

Quagraine et al. (2005) reported the potential for bioaugmentation with selected bacteria to degrade the more refractory classes of NAs. Here, the use of attachment materials such as clays to concentrate both NAs and NA-degrading bacteria in surfaces and/or pores; synergistic association between algae and bacteria consortia to promote efficient aerobic degradation; and biostimulation with nutrients to promote the growth and activity of the microorganisms may further increase the degradation of naphthenic acids in oil sands process water. Indigenous aerobic microbial communities in oil sands tailings ponds biodegrade NAs (Herman et al., 1994; Clemente et al., 2005; Biryukova et al., 2007). Herman et al. (1994) reported that aerobic bacteria degrade NAs by oxidizing the carboxylated aliphatic side chain, which subsequently oxidizes the cycloaliphatic ring of NA. Several published research results show that various microorganisms are capable of breaking down the majority of the naphthenic acids within 20 days of being introduced to the system (MacKinnon et al., 1986; Lai et al., 1996; Quagraine et al., 2005). These results also show that microorganisms cannot readily break down the more complex structured naphthenic acids.

Han et al. (2008) used HPLC/HRMS for analysis of NAs and reported the influence of NA structure on biodegradation kinetics. They suggested that commercial NAs biodegrades faster than the OSPW NAs. The slower degradation rate of OSPW NAs was attributed to the recalcitrant fraction of NAs present predominantly in OSPW NAs and also to the high alkyl branching of these NAs. They also reported decreased biodegradation rate of both types of NAs (commercial and OSPW extract) with increased number of rings (more negative z value).

1.2.6.3 Photocatalysis

Photocatalysis is one of the most promising alternatives for water treatment (Doll et al. 2005; Linsebigler et al. 1995). Photocatalysis is a chemical process in which a catalyst accelerates a photoreaction primarily by generating high energy electrons and electron-hole pairs. Light sources, both visible and ultraviolet (UV) light, are used as the source of photons for most of the photocatalytic process. UV light is emitted in wavelengths in the range of 100 to 400 nm. According to Protosawicki et al. (2002) much of the water treatment value of UV light can be attributed to the UV-B (280 to 315 nm) and UV-C (200 to 280 nm) sub ranges. McMartin et al. (2004) and Dutta et al. (2000) reported that UV_{254} radiation has the most potential for reducing naphthenic acids and increasing their bioavailability.

A number of semiconductors are used as photocatalysts and are capable of providing electrons when they are activated at their band-gap energy levels by the incident UV-Vis radiations (Table 1.2) (Hoffmann et al., 1995). Titanium dioxide (TiO_2)

is the preferred photocatalyst because of its activity, non-toxicity, stability in aqueous solutions, and relatively low cost (Hsien et al., 2000).

TiO₂ is widely available in three crystalline structures, namely, *rutile*, *anatase*, and *brooklite*. Anatase exhibits better photocatalytic efficiency due to the lower recombination probability of electron-hole pairs (Doll et al., 2005; Hsien et al., 2000). This structure requires 3.2 eV for activation, requiring the use of UV light for actuation. The rutile structure, however, has a band gap value of 3 eV meaning it can be activated by solar radiation.

In heterogeneous catalysis, suspensions of TiO₂ are irradiated with UV wavelengths shorter than 390 nm, to produce photon energy greater than 3.0 eV, sufficient to initiate the photocatalytic reaction (Doll et al., 2005) (Figure 1.2).

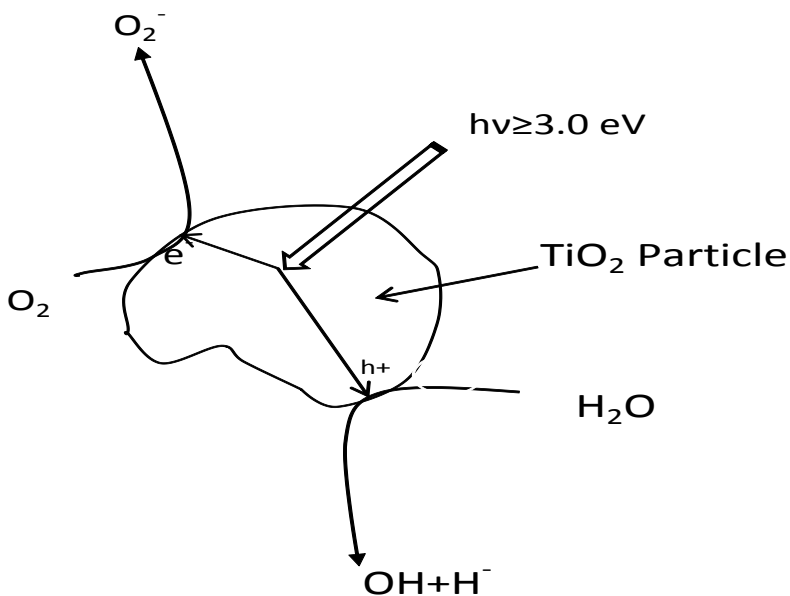


Figure 1.2 Effect of UV radiation on a TiO₂ particle dispersed in water (Hoffmann et al., 1995; Doll et al., 2005)

1.2.6.3.1 Mechanism of photocatalysis

Fujishima et al. (2008), Linsebigler et al. (1995), and Al-Rasheed (2005) elucidated the principle and mechanism of photocatalysis on TiO₂ surface. The incident photon causes the excitation of an electron from the valence band to the conduction band forming a positive hole in the valence band. Both the hole and the electron are highly energetic and hence highly reactive. The excited electron and the positive hole either recombine and release heat, or migrate to the surface, where they can react with the adsorbed molecule and cause either a reduction or oxidation of the adsorbate. The positive holes cause oxidation of the surface-adsorbed species while the electrons cause reduction. To maintain electro-neutrality, it is necessary for both the reactions to occur. Electrons are consumed in a reduction reaction such as absorption by oxygen molecules to form superoxide and the holes are available for oxidation. Doll et al. (2005) reported that if the photocatalysis is employed to carry out a reduction reaction such as the reduction and recovery of metals, then it is necessary to eliminate all other reducible species such as oxygen from the reaction.

Photocatalysis can be direct and indirect type (Fujishima et al., 2008; Linsebigler et al. 1995). Light-absorbing molecules (chromophores) absorb photons of ultraviolet and visible radiation and undergo chemical change. In direct photocatalysis, the target organic compound such as naphthenic acid acts as the chromophore. In the case of indirect photocatalysis, a catalyst like FeCl₃ or TiO₂ absorbs energy and then transfers it to the target compound for degradation via an intermediate such as a reactive oxygen species (Grzechulska et al., 2000; Mozumder, 1999; Suppan, 1994; Zafiriou et al., 1984).

Table 1.2 Band-gap energy and wavelength of common photocatalysts (Hoffmann et al. 1995).

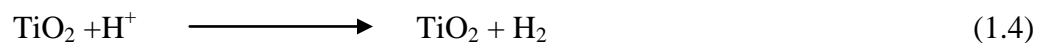
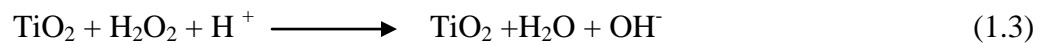
Catalyst	Band-gap energy (eV)	Wavelength (nm)
BaTiO ₃	3.3	375
CdSe	1.7	730
Fe ₂ O ₃	2.2	565
GaP	2.3	540
SnO ₂	3.9	318
SrTiO ₃	3.4	365
TiO ₂	3.0	390
WO ₃	2.8	443
ZnO	3.2	390
ZnS	3.7	336

Blake et al. (1999) and Al-Rasheed (2005) suggested the following equations showing the mechanism of oxidation and reduction reactions during photocatalysis.

Electron-hole pair formation:

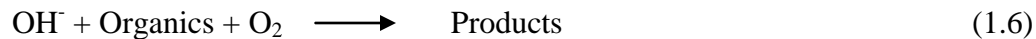


Electron removal from the conduction band:

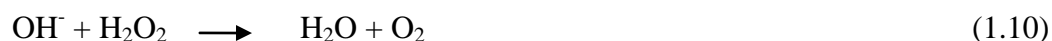
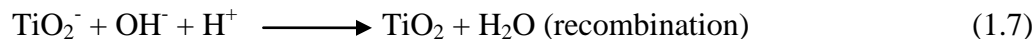


Oxidation of organic compounds:





Nonproductive radical reactions:



Fujishima et al. (2008) and Al-Rasheed (2005) reported the process of photocatalysis using titanium dioxide as the semi-conductor as follows:

1. An electron from the valence band of titanium dioxide is transferred to the conductance band. This creates an h⁺ hole in the valence band. Energy (usually from UV/ Vis) catalyzes this reaction.
2. Extremely reactive free radicals (such as OH[·]) form at the surface of the semi-conductor, and/or direct oxidation of the polluting substances.
3. The reaction is completed by reaction of the ejected electrons with electron acceptors.

The hydroxyl radical is ranked second among the known strong oxidizing agents (Al-Rasheed, 2005). The hydroxyl radical has a high potential for oxidizing pollutants that normally are hard to destroy, like halogenated organics, surfactants, herbicides and pesticides, to carbon dioxide.

1.2.6.3.2 Significance of photocatalysis in the water treatment system

The conventional water treatment processes have been found to be inadequate for removing new generation chemical pollutants and bacterial and fungal pathogens from water at affordable costs. These processes invariably use expensive chemicals, require long retention times, and have large annual operating costs. Photocatalysis, with all its variations and improvements, is considered to bring a revolutionary approach to addressing the current environmental problems. However, photocatalytic treatment has been undergoing critical evaluation in the last decade. Extensive work done in this area has shown the various advantages and disadvantages of photocatalysis for water and wastewater treatment.

Photocatalysis can be applied either as a homogeneous or a heterogeneous process. In homogeneous photocatalysis, the catalyst is dissolved in the water phase and needs to be separated after treatment. This may present some very tricky practical problems and may not be cost effective in large operations. In the heterogeneous process, the catalyst is used in a different phase and lends itself for eventual separation at the end of the treatment process (Doll et al., 2005).

Photocatalysis has been widely applied to remove a variety of pollutants from water (Al-Rasheed, 2005; Doll et al., 2005; Bhatkhande et al., 2001; Hsien et al., 2000; Hoffmann et al., 1995; Michael et al., 1995) as shown below.

Removal of trace metals

Trace metals such as mercury, chromium, lead, and others are considered to be health hazards. Therefore, removing these heavy metals from drinking water supplies is

critical for protecting human health. The environmental applications of heterogeneous catalysis include the processes for removing mercury, chromium, lead, cadmium, arsenic, nickel, and copper. The process has also been used to recover expensive metals such as silver, gold, and platinum from industrial effluents (Black, 2001; Ollis et al., 2001).

Removal of organic and inorganic compounds

Organic compounds such as alcohols, carboxylic acids, phenols and their derivatives, and chlorinated aromatics have been treated successfully using photocatalysis (Bhatkhande et al., 2001). A number of inorganic contaminants are sensitive to photochemical transformation at the catalyst surface. These include bromate, chlorate, azide, halide, nitric oxide, palladium and rhodium species, and sulphur species. Metal salts such as AgNO_3 , HgCl_2 , organometallic compounds (such as CH_3HgCl), cyanide, thiocyanate, ammonia, nitrites, and nitrates can also be removed from water (Bhatkhande et al., 2001; Michael et al., 1995).

McMartin (2003) has reported photolysis as one of the potential supplementary remediation methods for naphthenic acids. It is reported that photolysis increases the susceptibility of crude oil to biodegradation. Headley et al. (2009) reported that photodegradation of NAs on TiO_2 is feasible and is most efficient under sunlight. They have suggested selective photocatalysis of NAs under fluorescent light. Photolysis using ultraviolet radiation has been reported to be an effective method in selective removal of naphthenic acids and increasing their bioavailability for natural degradation (Dutta et al., 2000; Grzechulska et al., 2000; McMartin et al., 2004).

1.2.6.4 Microwave Treatment

Microwave disinfection and treatment of water is an innovative and complex system. Reactions performed under microwave irradiation occur at a faster rate and produce higher product yields. Microwaves are emitted in the electromagnetic spectrum between infrared and visible light, corresponding to frequencies of 0.3 to 30 GHz. According to Tian et al. (2005), the effects of microwave irradiation on reaction kinetics are a result of dielectric heating and non-thermal action. Microwave is a non-ionizing radiation that causes molecular motion by migration of ions and rotation of dipoles, but does not cause changes in molecular structure. Kong et al. (2006) explained the principle of microwave induced separation of molecules. At higher frequencies and varied electromagnetic fields, the dipole turning polarization cannot keep up with the rapid alternating electromagnetic field and an angle is lagged. This leads to microwave radicalization. The system dissipates and converts microwave energy to heat energy. The movement and interaction of the molecules blocks the directional change and rotation of the polar molecules, which lead to molecule vibration, mutual friction, and rise in the system temperature. Hong et al. (2004) explained that the non-thermal effect of microwaves occurs because microwaves cause polarized materials to line up with the magnetic field, resulting in the destruction of intra-molecular bonds and consequential denaturation or coagulation of molecules. As the technology is in its developmental stage, there is little documented work regarding its large scale application.

Lee et al. (2002) in their work on the purification of water using microwave energy have reported that microwaves are useful in the treatment of wastewater for a

number of reasons: microwaves destroy chemical and biological agents; microwaves decompose hydrocarbons when used in the presence of granulated activated carbon; microwaves decontaminate solids separated from the water; they oxidize gaseous components generated by organic decomposition; and they kill microorganisms found in water.

Another option for the use of microwaves in water disinfection is presented by Bergmann et al. (2002). They outlined a process by which traditional mercury lamps used in UV disinfection of drinking water were modified. The electrodes contained in traditional UV lamps were removed and the production of UV radiation was stimulated by microwaves. The system used in the experiments completed by Bergmann et al. (2002) included a glass reactor with contaminated water placed inside a microwave oven. It performed equally when compared against a traditional UV water disinfection process.

Horikoshi et al. (2004) reported the use of electrodeless microwave UV-Vis lamp to photo-degrade environmental pollutants in aqueous media. Zhang et al. (2006) have reported on microwave electrodeless lamp photolytic degradation of acid orange 7. Klán et al. (2002) have described the use and photochemistry of microwave electrodeless lamp (MWL). They have indicated that the coupled UV–vis/microwave irradiation from microwave electrodeless lamp could accelerate the degradation of organic pollutants.

The various advantages of using microwave electrodeless lamp for water treatment as reported by Klán et al. (2002) are:

1. a simultaneous UV and MW irradiation of the sample;
2. possibility to carry out photochemistry at high temperature;

3. higher photochemical efficiencies;
4. simplicity of the experimental setup using a wireless MW lamp;
5. the use of a commercially available microwave oven; and
6. the choice of the MWL material may modify its spectral output.

Klán et al. (2002) also reported technical difficulties with experiments at temperatures below the boiling point of the solvent. Most of the polar solvents absorb microwaves thus, hampering MWL operation. When overheated, MWL stops emitting UV light. Other disadvantage as reported may be that the microwave treatment system needs higher safety precautions.

Application of microwave can be a potential remediation method for naphthenic acids in water. But very few literatures are available on this. In this context, recent literatures suggest that NAs could be separated from diesel fuel using microwave radiation (Chan et al., 2002; Kong et al. 2004, 2006). Similarly, removal of naphthenic acid from vacuum cut # 1 distillate oil of Daqing using microwave has also been reported by Huang et al. (2006). Chan et al. (2002) suggested that the decrease of zeta-potential of electric double layer on the water in oil interface and the reduction of viscosity are responsible for the accelerated separation of naphthenic acids under microwave irradiation. The influences of dosage of alkali compound solvent, irradiation pressure, irradiation time, irradiation power, the settling time, and oil phase-to-solvent phase volume ratio has been investigated. The removal of naphthenic acids could be as high as 98.4% when the optimum conditions are as follows: Mp (Solvent Concentration) /MT(Theoretical Concentration)=1.5, 0.05 MPa, 6 min, 375W, 25 min, and an oil to

solvent phase volume ratio (O/S) = 10, respectively (Kong et al., 2006). Huang et al. (2006) reported the removal of naphthenic acid from the vacuum cut #1 distillate oil of Daqing using SH9402 type high performance microwave reaction system, a frequency of 2.45 GHz, a power of 375 W, and a resting time of 25 min. The acidity could be reduced from 0.63 mg KOH/g to 0.0478 mg KOH/g which is as per specification for lubricating oil. The scope of microwave assisted heterogeneous photocatalysis has also been reported by Kataoka et al. (2002). They have integrated a photolytic reactor system with a waveguide which allows concurrent application of microwave at 2.45 GHz and photocatalysis with higher conversion as compared to only photocatalysis for ethylene oxidation.

1.3 Critical Gaps in Knowledge

Many of the methods such as chemical and biological treatments as explained in the previous sections are already in use for treatment of different water contaminants including NAs. High cost and time involved in those methods and the possibility of formation of hazardous byproducts limit their effective use. The processes of photocatalysis and microwave treatment systems are still in developmental stages and have high potential for use in the treatment of contaminated water. Photolysis and some use of microwaves have already been reported to be effective in selective degradation of NAs as explained in the previous sections. However, photocatalysis and microwave assisted photocatalysis (MAP) of naphthenic acids in water in the presence of photocatalysts have not been reported so far. Kinetic and toxicological studies of these

treatment systems have not been done. There is a valid need to design, develop, and evaluate photocatalytic and microwave assisted treatment systems for NA remediation. In this regard, one of the most important design parameters, i.e. microwave properties or permittivity of NAs in water, has not been reported in literature. Study on these properties would contribute to the fundamental knowledge base. Since there is a dearth of published literature regarding applications of photocatalysis, microwave, and combined treatment systems for the removal and detoxification of specific target pollutants such as naphthenic acids, research is required to adequately assess the feasibility, potential benefits, and implications of these treatment systems. Critical gaps in knowledge exist with respect to the finding out the permittivity / dielectric properties of NAs in water, application and evaluation of photocatalysis, microwave and combined microwave assisted photocatalysis for the degradation and detoxification of naphthenic acids in water.

1.4 Research Objectives

The overall objective of this research was to design, develop, and evaluate a photocatalytic system, a microwave system, and a microwave assisted photocatalysis system to effectively degrade and detoxify NAs in water. *It was hypothesized that the developed systems would degrade the NAs in water at a faster rate and hence would reduce the toxicity of the NA water mixture to an acceptable level.*

To meet this overall objective, the following specific objectives were identified and are summarized in Table 1.3.

- i. to measure the dielectric properties of naphthenic acids in water;
- ii. to evaluate a laboratory scale photocatalysis system for the treatment of naphthenic acids in water;
- iii. to design and develop a laboratory scale microwave and microwave assisted photocatalysis systems for the treatment of Naphthenic acids in water; and
- iv. to conduct feasibility study, performance evaluation, and validation of the developed systems for degradation and detoxification of naphthenic acid mixtures.

Table 1.3 Research objectives by chapter.

Chapter	Objectives	Description of Chapter
1	Introduction, literature review, and objectives	<ul style="list-style-type: none"> • Information and review of available literature on NA chemistry, toxicity and analysis. • Information on available methods suitable for NA treatments. • Identification of critical gaps in knowledge, degradation systems and applications to remediation.
2	<p>To determine the permittivity or dielectric properties of NA in water.</p> <p>To investigate the effect of frequency of microwave and temperature and concentration of NA water mixture on the dielectric properties.</p>	<ul style="list-style-type: none"> • Permittivity/ Dielectric properties of NAs in water were determined. • Effect of temperature and concentration of NA water mixture on the permittivity were determined. • Effect of frequency of the microwave on the dielectric properties of NA in water was determined.
3	To design, develop, and evaluate a lab scale photocatalysis system for the treatment of Naphthenic acids in water.	<ul style="list-style-type: none"> • A laboratory scale photocatalytic treatment system was designed and developed and was evaluated for its feasibility to degrade and detoxify NAs in water
4	To design, develop, and evaluate a lab scale microwave system for the treatment of Naphthenic acids in water.	<ul style="list-style-type: none"> • A laboratory scale microwave treatment system was designed and developed and was evaluated for its feasibility to degrade and detoxify NAs in water
5	To design, develop, and evaluate a lab scale microwave assisted photocatalysis system for the treatment of Naphthenic acids in water.	<ul style="list-style-type: none"> • A laboratory scale microwave assisted photocatalytic treatment system was designed and developed and was evaluated for its feasibility to degrade and detoxify NAs in water
6	General discussion and conclusions.	<ul style="list-style-type: none"> • A summary of the conclusions obtained in each chapter. • A list of suggested future research directions.

1.5 Description of Chapters

The first chapter (Chapter 1) provided a general introduction to the thesis and outlines the background and the objectives of the research. Information and review of available literature on NA chemistry, toxicity, analysis, and available methods suitable for NA treatments were discussed. Critical gaps in knowledge, degradation systems, and applications to remediation were identified.

Chapter 2 describes the research to study the dielectric properties (permittivity) of naphthenic acids in water. This chapter addresses the first research objective. It covers the experimental set-up and the procedure adopted to determine the permittivity of naphthenic acids-water mixture. Effect of frequency of microwave and the temperature and concentration of the NA-water mixture on permittivity are reported. Dielectric properties, determined in this chapter, are used to select the material for the sample holder in the microwave (Chapter 4) and MAP systems (Chapter 5). Penetration depth of microwaves at 2.45 GHz is determined and accordingly the dimension of the sample holder and the position of the MW lamp in the sample holder are optimized to allow proper penetration of microwaves through the wall of the sample holder and the NA samples.

Chapter 3 addresses the second and fourth research objectives and describes the design, development, and evaluation of photocatalysis system for NA degradation and detoxification.

Chapters 4 addresses the third and fourth objectives of this research and describes the design, development, and evaluation of microwave treatment system for NA

degradation and detoxification. A laboratory scale microwave treatment system is designed and developed using the dielectric properties of NA-water mixture, determined in chapter 2, and is evaluated for its feasibility to degrade and detoxify NAs in water.

Chapter 5 addresses the third and fourth objectives of this research and covers the design, development, and evaluation of microwave assisted photocatalysis treatment system for NA degradation and detoxification. A laboratory scale microwave assisted photocatalytic treatment system was designed and developed using the dielectric properties of NA-water mixture, determined in chapter 2, and is evaluated for its feasibility to degrade and detoxify NAs in water. An electrodeless microwave lamp was incorporated to the microwave system, which emitted UV rays under microwave field. The synergetic effect of microwaves and UV rays on the degradation kinetics of NAs was determined.

Chapter 6 comprises of a general discussion of the results of the combined research and a summary of the conclusions obtained in each chapter, assessing the research approach and proposing directions for future research.

The final chapter (Chapter 7) is a compilation of all references for the previous chapters.

Each of Chapter 2 through 5 includes its own introduction, experimental section and subheadings.

CHAPTER 2. PERMITTIVITY OF NAPHTHENIC ACIDS – WATER MIXTURE*

This chapter addresses the first research objective. It covers the experimental set-up and the procedure adopted to determine the permittivity of naphthenic acids-water mixture. Effect of frequency of microwave and the temperature and concentration of the NA-water mixture on permittivity were investigated and are reported.

2.1 Introduction

Naphthenic Acids (NAs) are natural constituent of bitumen. These are the oxidative product of petroleum hydrocarbons, composed of substituted cycloaliphatic carboxylic acids. NAs include single and fused multiple rings in the structure. The carboxyl group is generally attached to a side chain. NAs are considered to be one of the major contaminants of TPW near oil sand processing sites and bitumen refineries. This contaminated water enters the surface water bodies during flooding or river bank erosion and the ground water by leeching. NA contaminated water, if consumed, may cause different health hazards to human and mammals. Reports suggest that NA contaminated water causes gastro-intestinal disturbances in humans. It also has notable effects on the formation of blood platelets, cell proliferation, and respiration. NAs are also of concern because of corrosive properties. It constrains the choice of material used in processing and refining unit. Thus water-containing NAs need treatment before its use. Chan et al.

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(2002) and Kong et al. (2004, 2006) suggested that NAs could be separated from diesel fuel using microwave radiation. Removal of naphthenic acid from vacuum cut # 1 distillate oil of Daqing using microwave radiation has also been reported by Huang et al. (2006). The use of microwave treatment for naphthenic acid in water has not been reported. Therefore, a microwave and a combined microwave assisted photocatalytic applicator for the treatment of NAs in water were designed and developed. Most useful quantities deemed necessary in the eventual design of a microwave applicator can be described in terms of the permittivity or dielectric properties. In this regard, the characterization and study of permittivity or dielectric properties is vital for understanding the response of NAs in water to microwaves. Permittivity properties play a critical role in determining the interaction effect between the electro-magnetic field and the material. In this research, a HP 8510 Network Analyzer and the coaxial probe reflection method were used to study the permittivity / dielectric properties of NA-water mixture. Effects of variables such as frequency, concentration, and temperature on the microwave properties of the naphthenic acid-water mixture were investigated. This work was extended to determine the effect of variables as mentioned earlier on the permittivity of Naphthenic acid-water mixture at different temperatures. The main objective of this research work is to measure the dielectric properties of naphthenic acids in water.

2.2 *Materials and Methods*

2.2.1 Sample preparation

Samples were prepared using commercially available naphthenic acids (Fluka, Sigma-Aldrich Inc., Saskatoon, SK) and Milli-Q water. A stock solution with a high

concentration of naphthenic acid (4000 ppm) was prepared using methanol. This was added to Milli-Q water for making the samples with desired concentration for experimentation. Keeping in mind the actual concentration of naphthenic acid in natural water resources in affected areas (up to 120 mg/L); samples were prepared with four different concentrations ranging between 40 to 100 ppm with an interval of 20 ppm.

2.2.2 Permittivity Measurement Setup

The HP permittivity measurement setup (Fig. 2.1) is a high performance microwave Vector Network Analyzer (VNA) system. It consists of a dielectric measurement kit (Agilent-HP 8510B, Agilent Tech, Mississauga, Ontario), a microwave signal source (Agilent-HP 8341B) and a test set (Agilent-HP8515A S-Parameter Test Set). The Agilent VEE (Vector network analyzer driver, Agilent Tech, Mississauga, Ontario) controls the Agilent-HP 8510 system as a whole. Commands issued through the Agilent-HP 8510 driver also control other units of the system. For coaxial probe measurements, the HP dielectric probe kit (Agilent-HP 8510B) is used, which consists of the probe, related software, and calibration standards. This open-ended coaxial probe (Fig. 2.2) connected to the Agilent-HP 8510B Network Analyzer is inserted into the sample. The vector network analyzer sends microwave signals and the coaxial probe conveys these signals to the sample. The sample reflects back a part of the signal which is received by the coaxial probe and conveyed back to the network analyzer for dielectric properties measurement. The magnitude and phase shift of the reflected signals depend upon the dielectric properties of the tested sample. The network analyzer system measures the reflection coefficients at the probe/material interface, based upon the

microwave signal transmitted to and received from the test material, and sends data to the computer where the coefficients are converted into dielectric properties of the test material. This coaxial probe method is convenient to use for the measurement of dielectric properties of liquids and semi-solids. It operates at a frequency range between 0.045 and 26.5 GHz. The Agilent-HP software program provides the permittivity based on the measured reflection coefficient. A block diagram of the Agilent-HP network analyzer and the coaxial probe measurement system is shown in Fig. 2.3 (Engelder et al., 1991; Agilent, 1986; Mishra et al., 2006a, b).

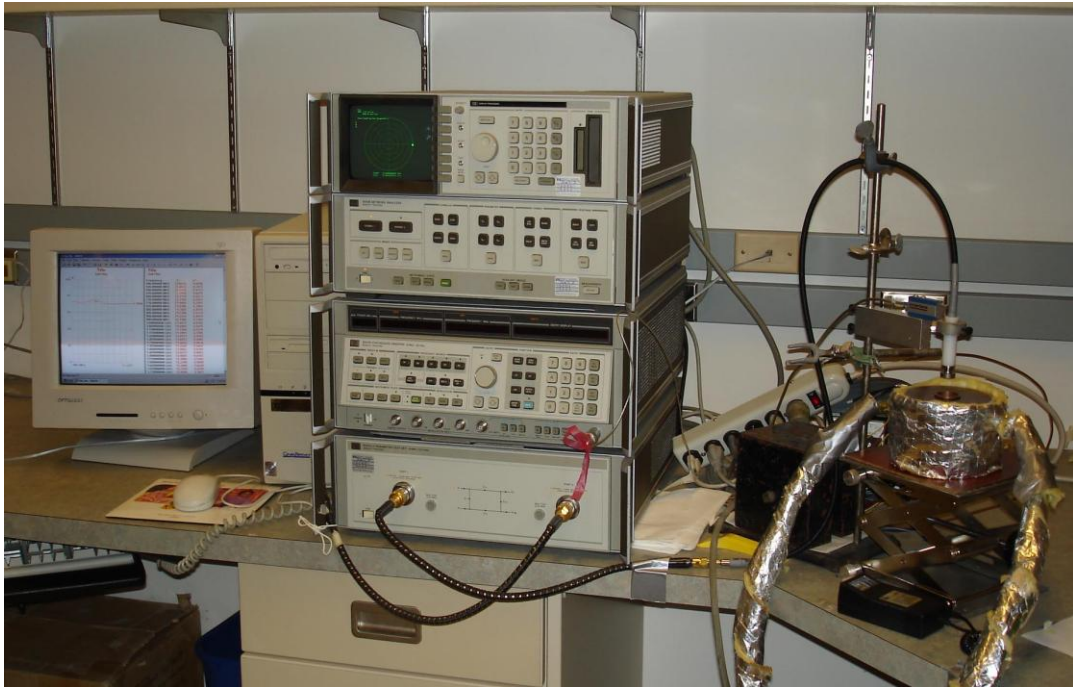


Figure 2.1 Permittivity measurement setup showing Agilent-HP 8510 system with coaxial probe.



Figure 2.2 Open-end coaxial probe with insulated sample holder.

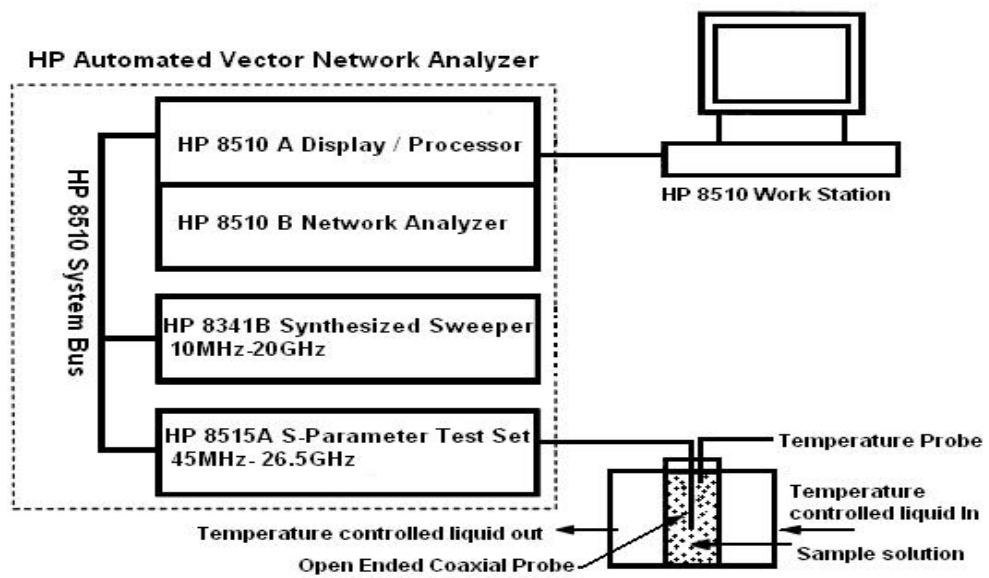


Figure 2.3 Schematic of Agilent-HP 8510 Network Analyzer and measurement system.

2.2.3 Measurement of Dielectric Properties of Naphthenic Acids in Water

The dielectric constant (ϵ') and the dielectric loss factor (ϵ'') were measured in the laboratory using the Agilent-HP 8510 measurement system. This system was used because of its availability and versatility to measure dielectric properties over a wide range of frequencies with adequate accuracy. Calibration of the system was performed each time before taking readings by following the user manual (Agilent, 1986) and measuring the properties of three known standards of air, short block, and distilled water at room temperature. Any systematic error during the measurement was removed during the calibration process. The system was tuned to the frequency range of 0.5 MHz to 5 GHz. The menu driven data acquisition software (V: 85070D, Agilent Tech, Mississauga, ON) installed in the attached computer was used for the measurement of dielectric values. NA-water samples each of 5 ml prepared in triplicate at different concentrations (40, 60, 80, and 100 ppm) were used for the measurement of dielectric properties of the sample at two different temperatures viz. 24 and 35°C. Out of these two temperatures, the former is the room temperature and the later is the target temperature of the sample during treatment. It is expected that while treating the water in the microwave field, the temperature of the sample would rise. This temperature is kept at a maximum level of 35°C. The temperature of the sample was maintained at the desired level using a constant temperature bath (Rose Scientific Ltd., Saskatoon, SK). Temperature of the sample was measured at regular intervals using external thermocouple and sensors (FISO Tech Ltd., Montreal, Quebec). Readings for the permittivity values were taken in triplicate using the Agilent-HP-VAN (Agilent Tech, Mississauga, ON) and the average

value was calculated. Dielectric constant and loss factor values were used to determine other parameters such as loss tangent or dissipation factor ($\tan \delta$), the power factor (P_f) and the penetration depth (d_p) at these temperatures. The first part of the experiment was to determine the effect of concentration on the dielectric properties at constant room temperature of 24°C, whereas the second part was to determine the effect of temperature on dielectric properties at constant concentration of the sample, viz. 100 ppm.

2.3 Results

The permittivity for the NA-water mixture was calculated from the experiments described in the previous section and further analyzed based on the theoretical analysis. The effects of various process parameters such as NA concentration, temperature, and frequency on the dielectric properties of the mixture are presented below.

The dielectric properties which are of interest in this study are the dielectric constant (ϵ'), the dielectric loss factor (ϵ''), loss tangent or dissipation factor ($\tan \delta$), the power factor (P_f) and the penetration depth (d_p). ϵ' is related to the ability of the material to store electrical energy, while ϵ'' indicates dissipation of electrical energy during the process. The dielectric properties of a material are given by $\epsilon = \epsilon' - j\epsilon'' = |\epsilon| e^{-j\delta}$, where ϵ = the complex relative dielectric constant; ϵ' = the relative dielectric constant; ϵ'' = relative dielectric loss factor; δ = dielectric loss angle and $j = \sqrt{-1}$. The loss tangent or dissipation factor is a measure of rate of loss of power and is defined as $\tan \delta = \epsilon'' / \epsilon'$. Lower value of loss tangent signifies lower loss in microwave power inside the material. The Power factor is the ratio of the real power to the apparent power and is a function of

the loss tangent. Power factor is defined as $P_f = \tan \delta / \sqrt{1 + \tan^2 \delta}$. Lower value of power factor signifies higher loss in the microwave power inside the material. The penetration depth is the distance from the surface of a dielectric material where the microwave field is reduced to 1/e of its value transmitted into the sample (Mishra et al., 2006a, b; Nelson, S.O., 1994; Tinga et al., 1973; Orsat et al., 2005; Venkatesh et al., 1998; 2004, 2005).

2.3.1 Dielectric Constant (ϵ')

Effects of concentration and temperature on the values of dielectric constant of NA-water mixture were determined and are discussed below.

2.3.1.1 Effect of Concentration

Dielectric constant for the NA-water mixture at 40, 60, and 80 ppm were measured. It is found that the values ranged between 72.8 to 78.2 at 40 ppm; 72.2 to 77.2 at 60 ppm; 71.7 to 76.4 at 80 ppm for the set frequency range between 0.5 to 5 GHz. At a particular concentration of 60 ppm the relative dielectric constant value decreases from 77.2 to 72.2 for the given set of frequencies. Similar decreasing trend was observed for other two concentrations viz. 40 and 80 ppm. At a particular frequency of 0.5 GHz, the relative dielectric constant values were found to be 78.2 for 40 ppm, 77.2 for 60 ppm and 76.4 for 80 ppm. This shows a decreasing trend in value of relative dielectric constant as the concentration of the sample increases (Fig. 2.4).

2.3.1.2 Effect of Temperature

The values for dielectric constant of NA-water mixture with constant concentration of 100 ppm were measured at two different temperatures viz. 24 and 35°C.

These values varied between 70.9 and 76.6 at 24°C and between 70.7 and 72.6 at 35°C for the same set of frequency range. Figure 2.5 shows that there is decrease in the value of dielectric constant for higher temperature at the same frequency.

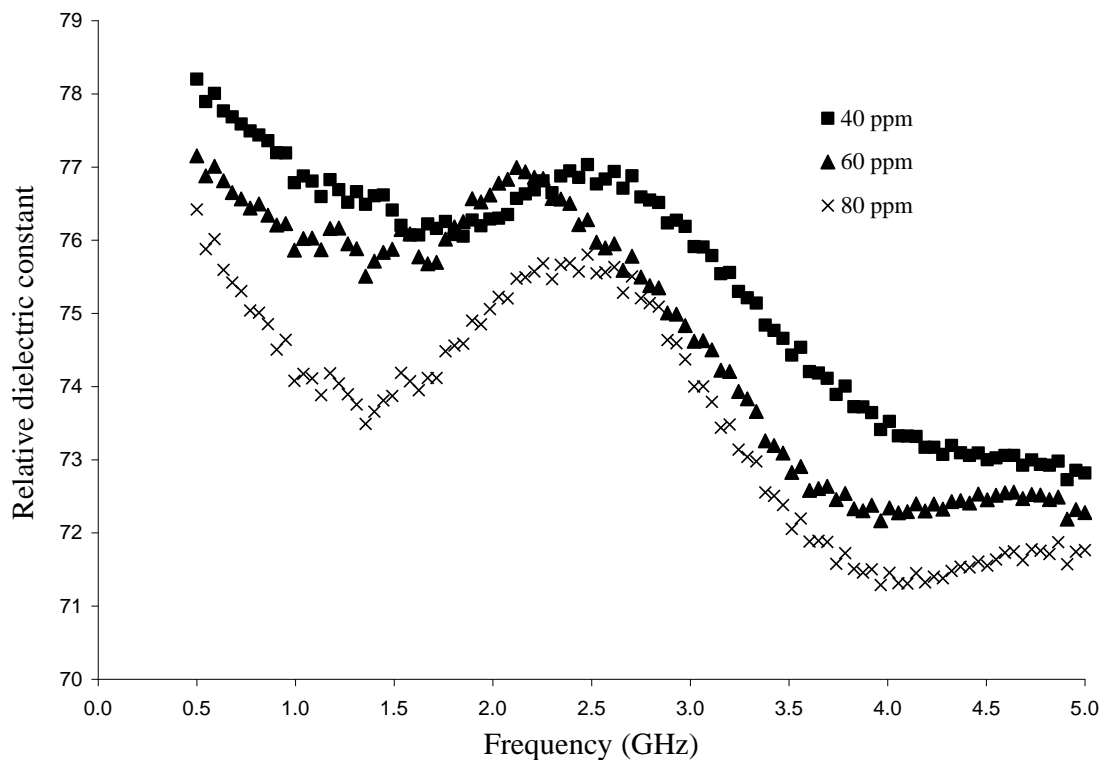


Figure 2.4 Variation of relative dielectric constant with frequency and concentration.

2.3.2 Loss factor (ϵ'')

Effects of concentration and temperature on the values of loss factor of the NA-water mixture were determined and are discussed below.

2.3.2.1 Effect of Concentration

The relative loss factor has an increasing trend with frequency. For 40 ppm sample, the value increased from 3.5 to 18.1; for 60 ppm it increased from 4.1 to 18.3 and

similarly for 80 ppm sample the relative loss factor increased from 5.7 to 17.8 when the frequency is increased from 0.5 to 5 GHz. The values show an initial jump between 0.5 to 1 GHz and then show a slight decrease until 2 GHz. Thereafter, it steadily increases till it reaches its maximum value for the set frequency range. For the lower frequency of 0.5 GHz, the relative loss factor increased from 3.5 at 40 ppm to 5.7 at 80 ppm. For higher frequency of 5 GHz, the value decreased from 18.1 at 40 ppm to 17.6 at 100 ppm. Experimental results suggest that the relative loss factor value decreases as the concentration of the sample increases at a higher frequency level, whereas it shows a decreasing trend at lower frequency range (Fig.2.6). It has the minimum value for 100ppm sample for the given set of frequency.

2.3.2.2 Effect of Temperature

The values for loss factor of NA-water mixture with constant concentration of 100 ppm were measured at two different temperatures viz. 24 and 35°C. It was found that the values ranged between 3.4 and 17.6 at 24°C whereas, the values ranged between 7.2 and 14.4 at 35°C at the same frequency range. Figure 2.7 shows that under lower frequency range, the values at 35°C are higher than those at 24°C. At frequencies higher than 1.6 GHz, the tendency changes and the values for loss factor are lower at 35°C than that at 24°C. There is decrease in the value of loss factor with increase in temperature at the same frequency.

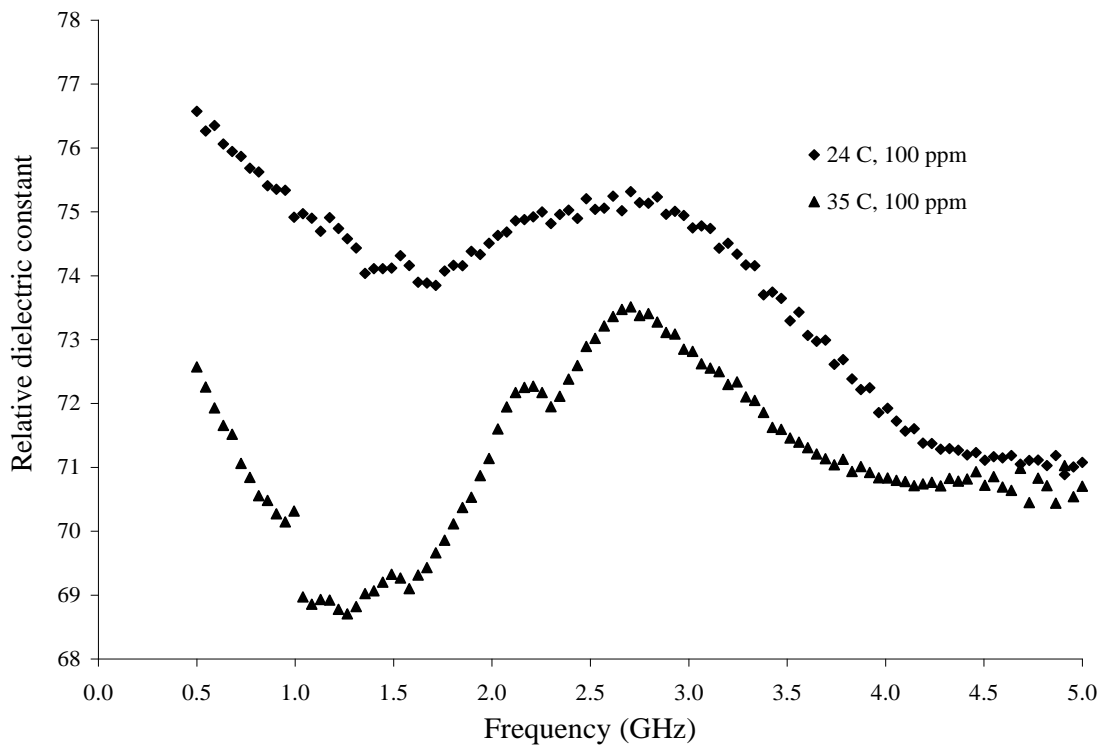


Figure 2.5 Variation of relative dielectric constant with frequency and temperature.

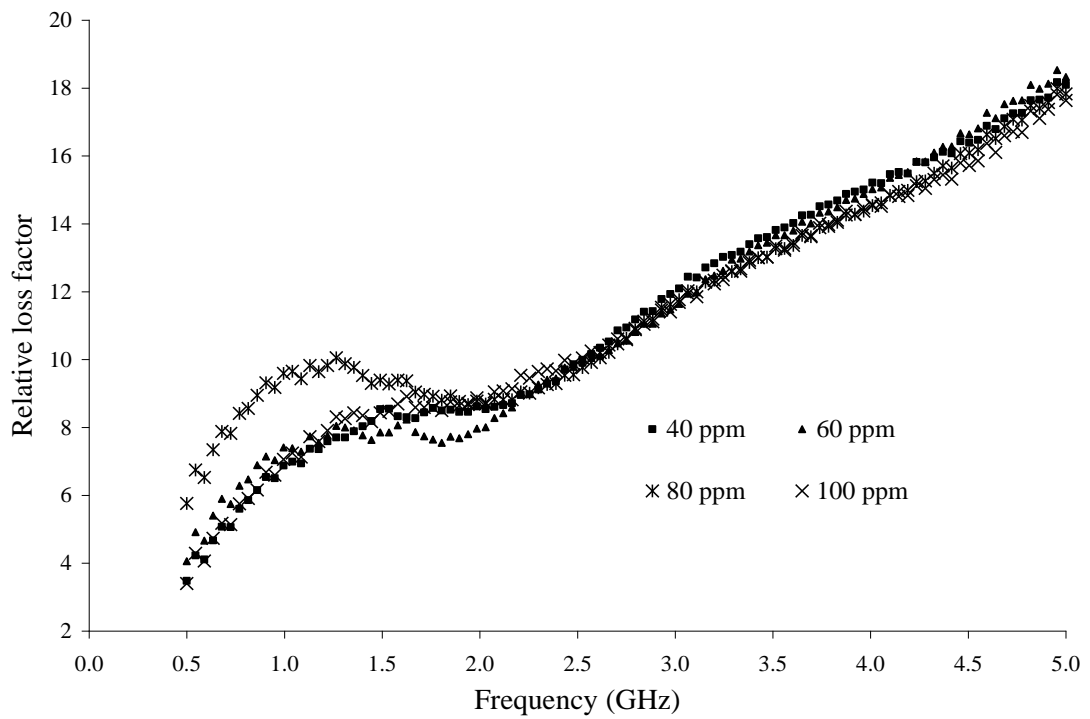


Figure 2.6 Variation of relative loss factor with frequency and concentration.

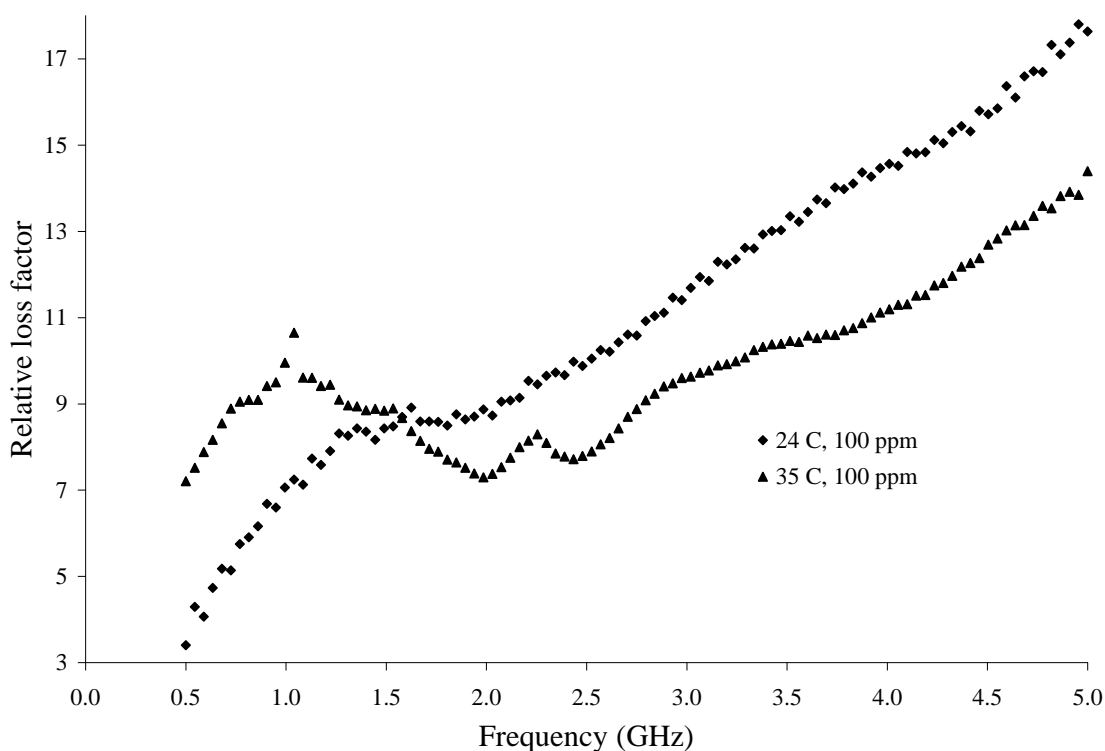


Figure 2.7 Variation of relative loss factor with frequency and temperature.

2.3.3 Loss tangent ($\tan \delta$)

Effects of concentration and temperature on the values of loss tangent of the NA-water mixture were determined and are discussed below.

2.3.3.1 Effect of Concentration

The loss tangent values initially increased, then showed a decrease as the frequency reached 2 GHz. Thereafter, they steadily increased with frequency until they reached a maximum at 5 GHz for the given set of frequencies. Loss tangent value increased from 0.044 at 40 ppm to 0.075 at 80 ppm at 0.5 GHz. It is found that the concentration does affect the value of loss tangent at lower frequency range. At higher

frequency range, concentration had no effect on the loss tangent value. Loss tangent as a function of frequency for different concentration is shown in the Figure 2.8.

2.3.3.2 Effect of Temperature

The values for loss tangent of NA-water mixture with constant concentration of 100ppm were measured at two different temperatures viz. 24 and 35°C. It was found that the value ranged between 0.04 and 0.25 at 24°C whereas, it ranged between 0.1 and 0.2 at 35°C for the same frequency range. In the lower frequency range, the values at 35°C were higher than those at 24°C (Figure 2.9). At frequencies higher than 1.6 GHz, there was decrease in the value of loss tangent with increase in temperature at the same frequency.

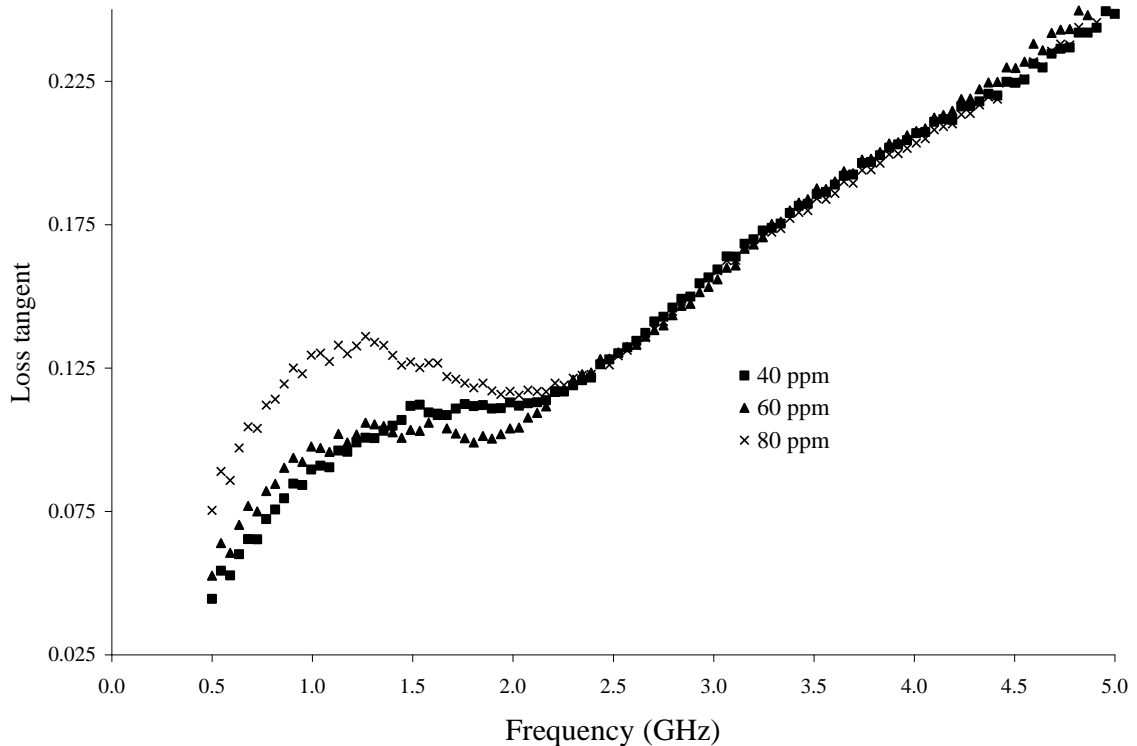


Figure 2.8 Variation of loss tangent value with frequency and concentration.

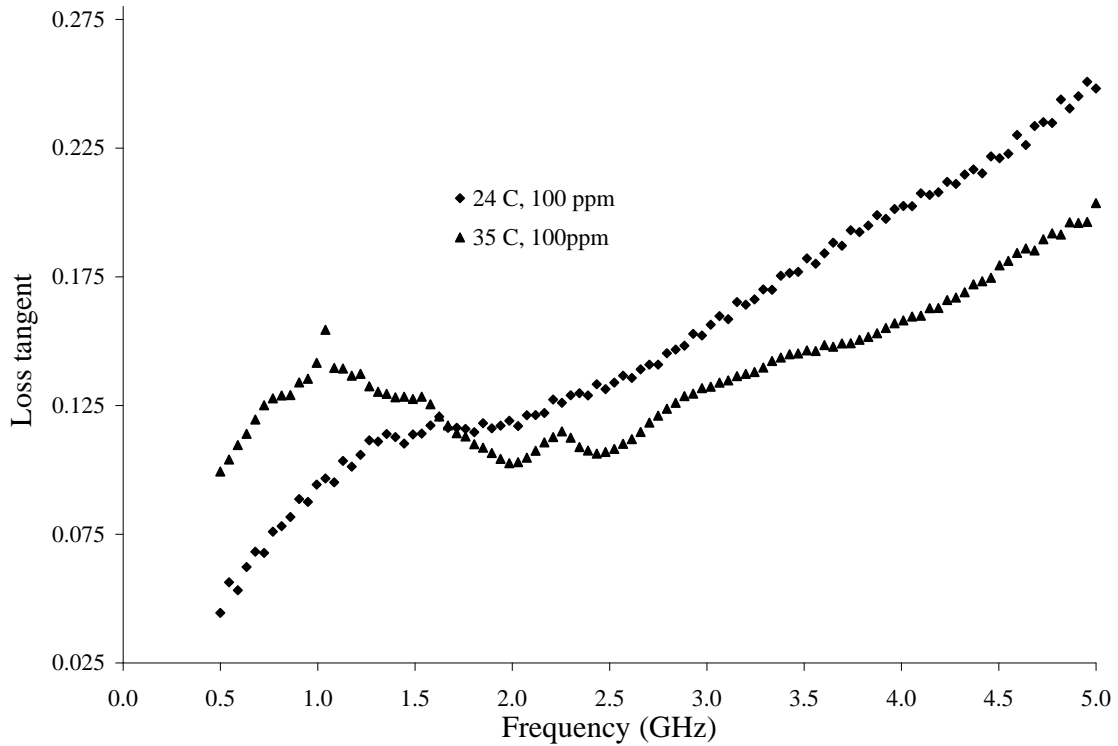


Figure 2.9 Variation of loss tangent value with frequency and temperature.

2.3.4 Power factor (P_f)

Effects of concentration and temperature on the values of power factor of NA-water mixture were determined and are discussed below.

2.3.4.1 Effect of Concentration

The power factor values followed the similar trend as that of loss tangent. For the initial phase up to 2 GHz, it showed sharp difference in value with change in concentration. Thereafter, it steadily increased with frequency until it reached a maximum at 5 GHz, for the given set of frequency. Power factor value increased from

0.044 at 40 ppm to 0.075 at 80 ppm at 0.5 GHz. Power factor as a function of frequency for different concentration is shown in the Figure 2.10.

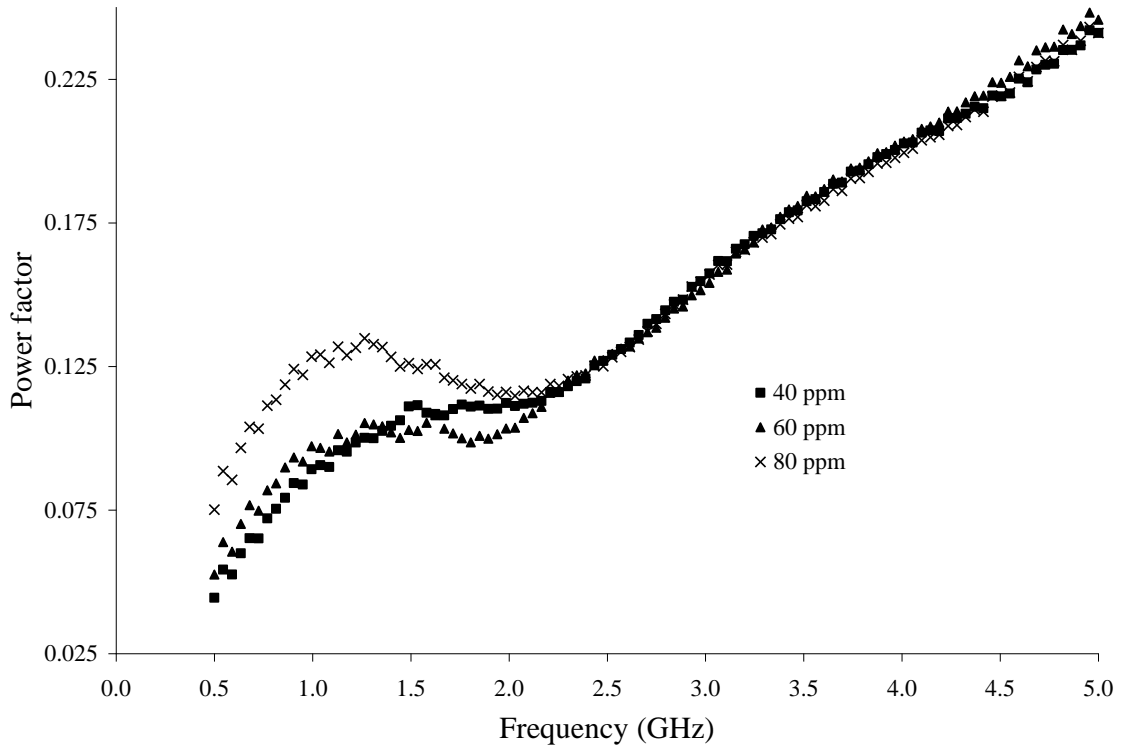


Figure 2.10 Variation of power factor value with frequency and concentration.

2.3.4.2 Effect of Temperature

The values for power factor of NA-water mixtures with constant concentration of 100 ppm were measured at two different temperatures, viz. 24 and 35°C. The power factor value ranged between 0.04 and 0.24 at 24°C, whereas it ranged between 0.1 and 0.2 at 35°C for the same frequency range. At lower frequency range, the power factor values at 35°C were higher than those at 24°C (Figure 2.11). At frequencies higher than 1.6 GHz, power factor decreased with increase in temperature at the same frequency.

2.3.5 Penetration depth (d_p)

Effects of concentration and temperature on the values of penetration depth of NA-water mixture were determined and are discussed below.

2.3.5.1 Effect of Concentration

Penetration depth for the NA-water mixture decreased with increase in frequency. The maximum value was at 0.5 GHz, whereas, the minimum was at 5 GHz. The values showed a sharp decrease between 0.5 to 1.5 GHz. Then it steadily decreased until 5 GHz. Figure 2.12 shows that the penetration depth had almost similar values at 40 and 100 ppm. At high frequencies, concentration does not affect penetration depth for the sample.

2.3.5.2 Effect of Temperature

Penetration depths for the NA-water mixture at concentration 100 ppm were measured at two different temperatures, viz. 24 and 35°C. The values ranged between 24.6 and 0.46 cm at 24°C whereas it ranged between 11.3 and 0.56 cm at 35°C for the same frequency range. Figure 2.13 shows that at lower frequencies, the values at 35°C were lower than those at 24°C. At frequencies higher than 1.6 GHz, temperature had no effect on the penetration depth for the sample.

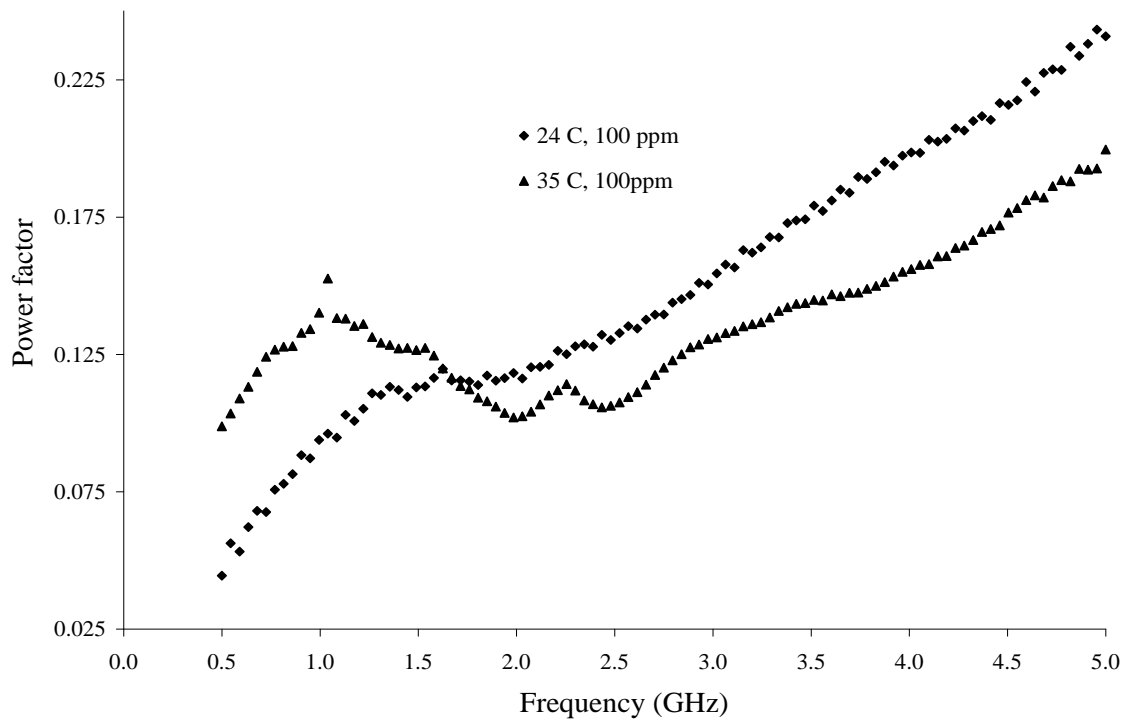


Figure 2.11 Variation of power factor with frequency and temperature.

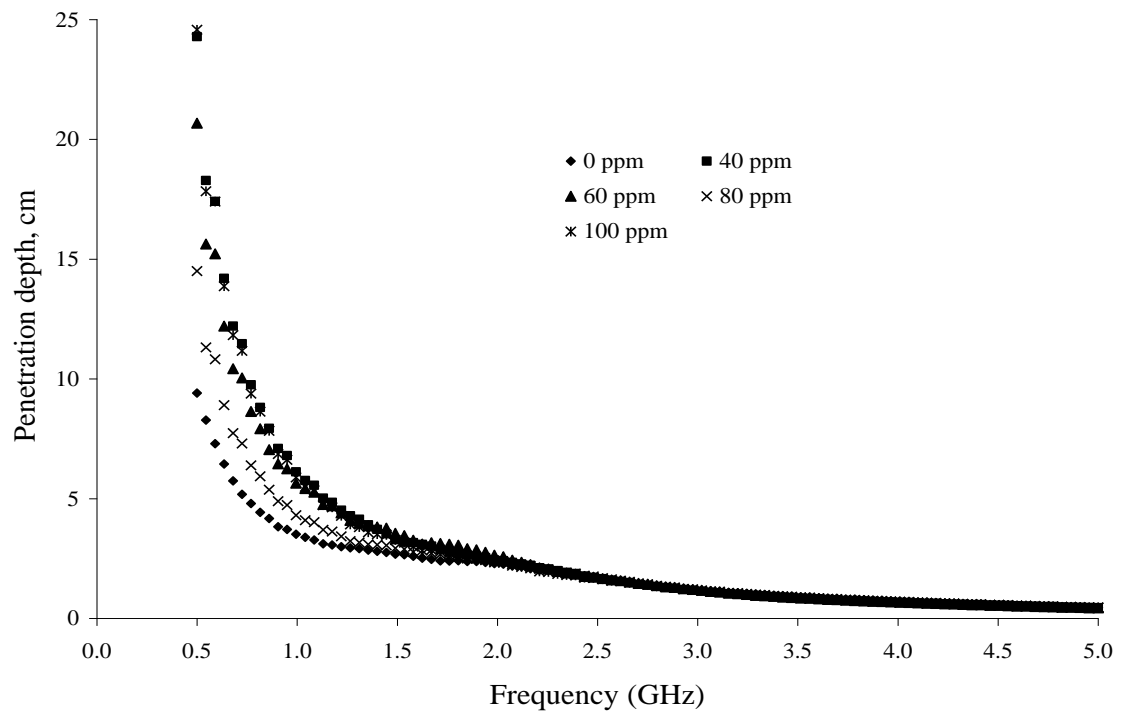


Figure 2.12 Variation of depth of penetration with frequency and concentration.

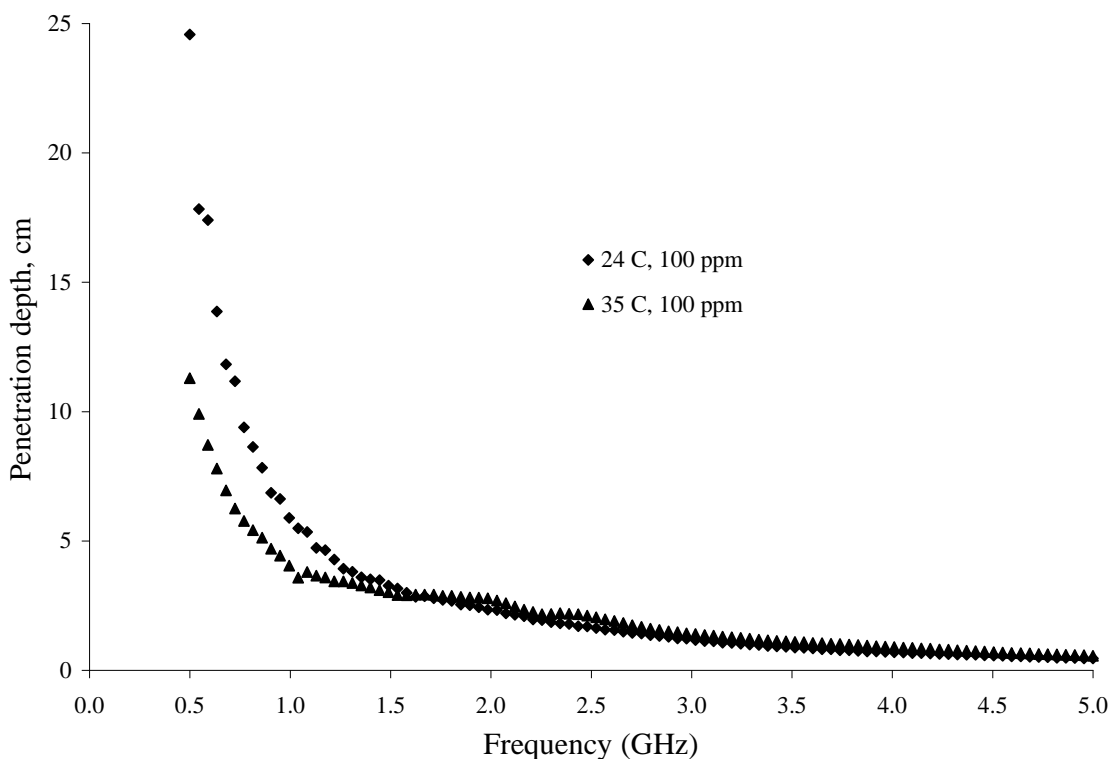


Figure 2.13 Variation of depth of penetration value with frequency and temperature.

2.4 Discussion

The experimental results show the variation of dielectric properties such as the dielectric constant, loss factor, loss tangent, power factor, and depth of penetration as a function of frequency, concentration, and temperature of naphthenic acid in water samples. It was found that the frequency and concentration have significant effect on the values of dielectric properties of NA-water mixture. This effect is much more significant in the lower range of frequency. Dielectric constant decreases as the concentration of the sample increases at a particular frequency. This may be because of the higher molecular weight and complex molecular structure of Naphthenic acids. This results in the longer relaxation time and decreased dielectric constant values. There is decrease in the value of

dielectric constant for higher temperature at the same frequency. Higher temperature of the sample results in the randomized agitation and Brownian movement of the individual molecule. This results in the decrease of the dielectric constant of the sample (Bottcher et al., 1973; Nelson, 2006). Loss factor decreases as the concentration of the sample increases at a particular frequency and there is decrease in the value of loss factor with increase in temperature at the same frequency for higher side of the set frequencies. Concentration of the sample does affect the value of loss tangent for the lower frequency range. After 2 GHz, it has least effect on loss tangent. At lower frequencies, the values of loss tangent at higher temperature are higher than those at lower temperature. At frequencies higher than 1.6 GHz, the tendency changes and there is decrease in the value of loss tangent with increase in temperature at the same frequency. With increase in temperature, relaxation time decreases and hence causes the dispersion peak to shift towards higher frequencies. This might be the cause for decrease in the value of loss tangent of Naphthenic acid at higher frequencies (Bottcher et al., 1973; Tang et al., 2002). At lower frequencies, the values of loss tangent at higher temperature are higher than those at lower temperature. At frequencies higher than 1.6 GHz, the tendency changes and there is decrease in the value of loss tangent with increase in temperature at the same frequency. At higher frequencies, concentration does not affect the penetration depth for the sample. At lower frequencies, the values of penetration depth at higher temperature are lower than those at lower temperature. At higher frequencies, temperature does not affect the penetration depth for Naphthenic acid. The temperature and concentration dependence of dielectric parameters of Naphthenic acid mixture is quite complex because of the nature of its molecular structure. Dielectric constant, loss

factor, power factor values obtained in this study show an inverse relationship with both concentration and temperature. Power factor and depth of penetration for the sample are not affected by both concentration and temperature. This might be attributed to the complex chemical and stoichiometric composition of Naphthenic acid mixture.

2.5 Conclusions

An attempt was made to determine and report permittivity as there was no information on the dielectric properties of NA and water mixture in literature. Effect of process parameters such as temperature, concentration and frequency of microwave on the permittivity value of NAs in water was found out. These data can add to the knowledge base and can be useful to scientific community and industry in designing and setting up a microwave applicator for the treatment of NA and water mixture.

CHAPTER 3. PHOTOCATALYSIS OF NAPHTHENIC ACIDS IN WATER

This chapter addresses the second and fourth research objectives including design, development, and evaluation of photocatalysis treatment system for NA degradation and detoxification.

3.1 *Introduction*

Naphthenic acids (NAs) are natural constituents of bitumen and the oxidative product of petroleum hydrocarbons. NAs are composed of substituted cycloaliphatic carboxylic acids. NAs are solubilized and concentrated in tailing pond water (TPW) during oil sands extraction and enter surface and subsequently ground water systems through mixing and/or erosion of riverbank adjacent to oil sands deposits. Clemente et al. (2005) reported that TPW in the Athabasca oil sands (AOS) north of Fort McMurray, AB may contain NAs as high as 110 mg/L. If consumed, NA contaminated water causes gastro-intestinal disturbances in human and also has notable effects on the formation of blood platelets, cell proliferation, and respiration (Lee et al., 2000).

Corrosion due to NAs is also a major concern for petroleum refineries, which limits the choice of materials used in equipment and supply chain. Thus, water containing NAs needs treatment prior to release or reuse.

McMartin (2003) reported that photolysis in presence of sunlight is effective for selective degradation of NAs. Application of UV radiation increased the NAs degradation rate. Photolysis not only degrades NAs, but can also increase their bioavailability.

Headley et al. (2009) reported that photodegradation of NAs on TiO₂ surface is efficient under natural sunlight. Photocatalysis in presence of UV light and a catalyst have not been reported for either degradation or increased bioavailability of NAs. To study this potential remediation method, a laboratory scale photocatalysis system was designed.

Commercially available Fluka NAs (Sigma-Aldrich, Oakville, ON) and an authentic OSPW NA extract were used in experiments to determine degradation kinetics of NAs in water with or without TiO₂ catalyst under UV₂₅₄. The ability of the system to degrade NAs and reduce toxicity was evaluated.

The main objectives of this research work were to evaluate a laboratory scale photocatalysis system for the treatment of naphthenic acids in water and to conduct feasibility study, performance evaluation, and validation of the developed system for degradation and detoxification of naphthenic acid mixtures in water.

3.2 *Materials and Methods*

3.2.1 Experimental Design

Experiments were designed to treat naphthenic acids in water using the photocatalytic treatment system. Three variables, NAs, water and TiO₂, were considered using 1 X 2 X 2 X 2 full factorial design (Table 3.1) with one treatment method, two types of NAs, two water sources, and two TiO₂ conditions.

Both Fluka and OSPW NAs were used; deionized and river water were tested; and particulate TiO₂ catalyst was either present (0.3g/L) or not. Therefore, eight treatment combinations for the treatment system were tested (Tables 3.2).

Table 3.1 Photocatalysis combinations with full factorial (1 X 2 X 2 X 2) experimental design.

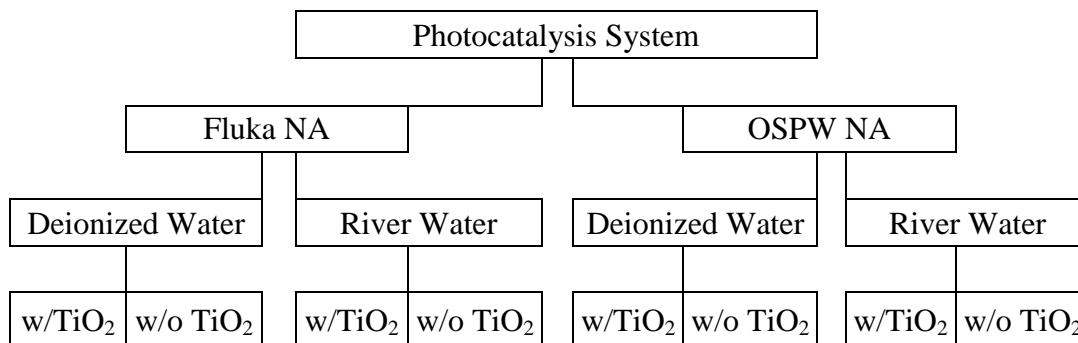


Table 3.2 Photocatalysis experiment combinations.

SI No.	Combinations	Explanation
1	Fluka-DI	Fluka NAs with deionized water
2	Fluka-DI-TiO ₂	Fluka NAs with deionized water and TiO ₂
3	Fluka-RW	Fluka NAs with river water
4	Fluka-RW-TiO ₂	Fluka NAs with river water and TiO ₂
5	OSPW-DI	OSPW extract NAs with deionized water
6	OSPW-DI-TiO ₂	OSPW extract NAs with deionized water and TiO ₂
7	OSPW-RW	OSPW extract NAs with river water
8	OSPW-RW-TiO ₂	OSPW extract NAs with river water and TiO ₂

In photocatalysis experiments, four initial concentrations (40, 60, 80, and 100 ppm) were evaluated in triplicate.

3.2.2 Sample Preparation for Photocatalysis System

Samples were prepared using both commercially available (Fluka) and OSPW naphthenic acids in deionized (Milli-Q) water and water from South Saskatchewan River at Saskatoon, SK.

A 4000 ppm stock solution of Fluka NAs was prepared in methanol to produce desired concentrations for experimentation (Table 3.3). For environmental relevance, samples were prepared at concentrations ranging between 40 and 100 ppm

Table 3.3 Sample preparation with Fluka naphthenic acids.

Concentration	Sample Size (mL)	NA (mg)	NA Stock (μ L)
40 ppm	100	4	1000
60 ppm	100	6	1500
80 ppm	100	8	2000
100 ppm	100	10	2500

3.2.3 Extraction of OSPW Naphthenic Acids

OSPW was collected from an oil sands extraction operation (Fort McMurray, AB, Canada) to produce the authentic NAs mixture. The NAs were extracted from OSPW using an adapted liquid-liquid extraction method described by Janfada et al. (2006). The final concentration of the NAs extract was determined by serial dilution and comparison to an aliquot of the oil sands NA extract produced by Rogers et al. (2002) and was found to be 6,800 mg/L. A five-point linear regression curve was created for quantification of the NA extract used herein and further verified by integrated area comparison of LC-MS

results for both the OSPW NAs extract and those for the commercially available Fluka NAs. The two methods were well correlated to confirm the OSPW NAs extract concentrations. OSPW NAs solutions were prepared as with the Fluka dilution method (Table 3.4).

Table 3.4 Sample preparation with OSPW NAs.

Sample Concentration	Sample Size (mL)	NA (mg)	NA Stock (μ L)
40 ppm	100	4	1500
60 ppm	100	6	2000
80 ppm	100	8	2500
100 ppm	100	10	3000

3.2.4 Experimental Setup

A photocatalysis system was designed using UV fluorescent tubes (Philips Ltd., Saskatoon, SK, 8W), concentric shell water jacketed quartz photo cells. This double-jacketed quartz reactor for photocatalysis was fabricated at the scientific glass blowing facility at the University of Victoria, BC, Canada (Figure 3.1). Cooling water was circulated through the outer shell to reduce heating load due to the UV source. Samples were collected every 30 minutes for 5 hours.



(a)



(b)

Figure 3.1 (a) Photocatalysis setup with UV lamps shown; (b) photocatalysis setup with insulation.

3.2.5 Analysis and Quantification of Naphthenic Acids in Water Sample

Electrospray ionization mass spectrometry (ESI-MS) in negative mode was used to quantify and characterize naphthenic acid concentration in the samples using method described by Headley et al. (2002). This method allowed for a detection limit of 0.01 mg/L (Headley et al. 2002).

In electrospray ionization, the solution is bombarded to produce ions that can be mass separated and detected by their mass to charge ratio (m/z). The sample cone is kept at a different voltage (-ve 7 kV) than the surrounding walls (+ ve 100 V) of the system. Cone voltage creates negatively charged molecules in negative ion mode as a result of the difference in voltage between the cone and surrounding walls. These smaller charged particles move through a capillary tube and past a drying gas (Nitrogen) to help reduce the size and increase the charge of the particles. The charge on the particles continues to increase as particle size decreases toward the Rayleigh limit, at which the repulsive Coulomb forces are equal to surface tension. Beyond the Rayleigh limit, the particle is broken into daughter particles that are also evaporated by the nitrogen drying gas. The process continues until the molecules are reduced to their quasi-molecular ionic form and are passed for mass analysis and production of mass spectra (McMartin, 2003; Headley et al., 2002a; Fenn et al. 1989).

3.2.6 Kinetic Analysis for Photocatalysis System

The degradation of NAs in water was considered a pseudo first order reaction (McMartin, 2003; McMartin et al., 2004), with the rate constant and the half-life period

calculated by Integrated Rate Law as summarized in Table 3.5 with ‘A’ being the total concentration of NAs.

Table 3.5 Integrated rate law for pseudo first-order degradation.

	Pseudo First-order Equations
Rate Law	$-\frac{d[A]}{dt} = k[A]$
Integrated Rate Law	$[A] = [A]_0 e^{-kt}$
Units of Rate Constant (k)	$\frac{1}{s}$
Linear Plot to determine k	$\ln([A])$ vs. t
Half-life	$t_{1/2} = \frac{\ln(2)}{k}$

3.2.7 Statistical Analysis

Standard deviation was calculated and error bars were plotted for each treatment using SPSS[®] 14.0 for Windows (SPSS Inc., Chicago, IL). SPSS was also used to perform univariate analysis of variance (ANOVA) and Tukey’s HSD test. Tukey’s HSD test examines all pair wise comparisons among means. ANOVA was performed to analyze treatment means and Tukey’s HSD test was done to compare the treatment means.

3.2.8 Toxicity Tests for Photocatalysis System

Microtox toxicity tests were completed before and after treatment by ALS Labs (Saskatoon, SK). Microtox Analyzer (Model #500, Strategic Diagnostics Inc., Newark, DE) with test organism *Vibrio fischeri* was used following the reference method proposed by Environment Canada (ERS1/RM/24). IC₅₀ value (max 100%) which is the half

maximal (50%) inhibitory concentration (IC) of a substance was measured at 5, 15 and 30 min residence time for each of the sample before and after treatment.

3.3 *Results and Discussion*

Commercially available (Fluka) and OSPW NAs standard were analyzed (Figure 3.2) at room temperature of 24°C. The x-axis shows m/z of individual NA species. The y-axis represents the percentage relative abundance of individual species of NAs. Comparison of carbon number and z-family distribution are given in Figure 3.3. The results indicate that commercial (Fluka) naphthenic acids and OSPW NAs have different composition and mass distribution. From the comparison it can be seen that Fluka NAs have higher density of components with lower mass to charge (m/z) ratio (157-297 m/z), whereas, this distribution in OSPW NAs shifts towards comparatively higher m/z ratios (195-325 m/z). This composition difference is proposed to affect the toxicity as explained in previous chapters.

Error bar plot ($R^2 = 0.944$) for rate constant values for each of the treatments can be seen in Figure 3.4. Results indicate that initial concentration of the sample has no affect on the reaction kinetics of the NA degradation. Keeping other variables, such as type of water and TiO₂, constant; the system took less time to degrade OSPW NAs than Fluka NAs. This could be because of the higher rate of degradation of NA-like compounds present in OSPW NAs. Frank et al. (2009) suggested that OSPW NAs extracts contain multi-carboxylic groups in their structures which are susceptible for photo-oxidation on TiO₂ surface. Thus, photocatalysis degraded OSPW NAs faster than the commercial NAs. The use of TiO₂ increased the reaction rate and made the

degradation process faster with shorter half-life period because of the catalytic effect of TiO_2 . Similarly, the type of water has significant effect on the degradation process of NAs. The use of river water made the degradation process slower as compared to deionized water for both Fluka and OSPW NAs extract. This can be attributed to the matrix effect of others salts and materials present in the river water.

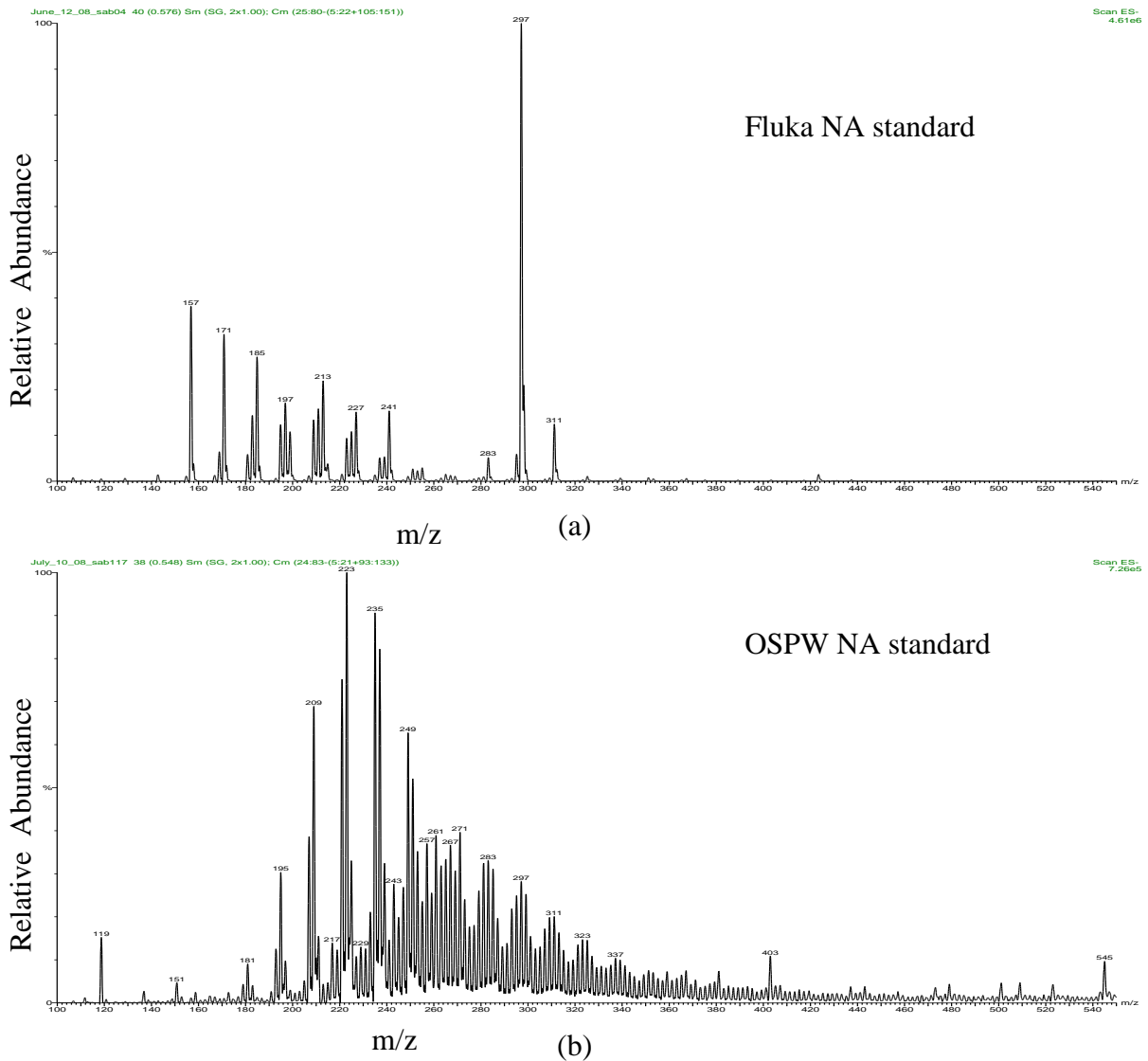
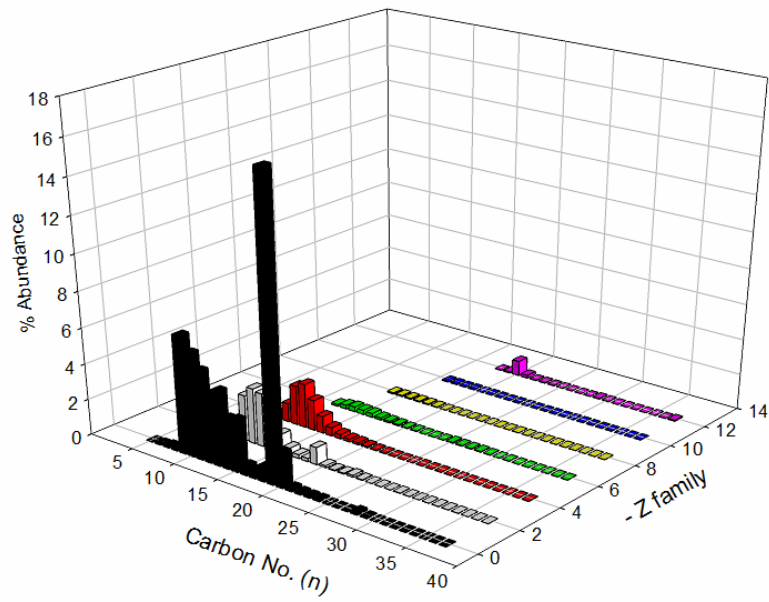
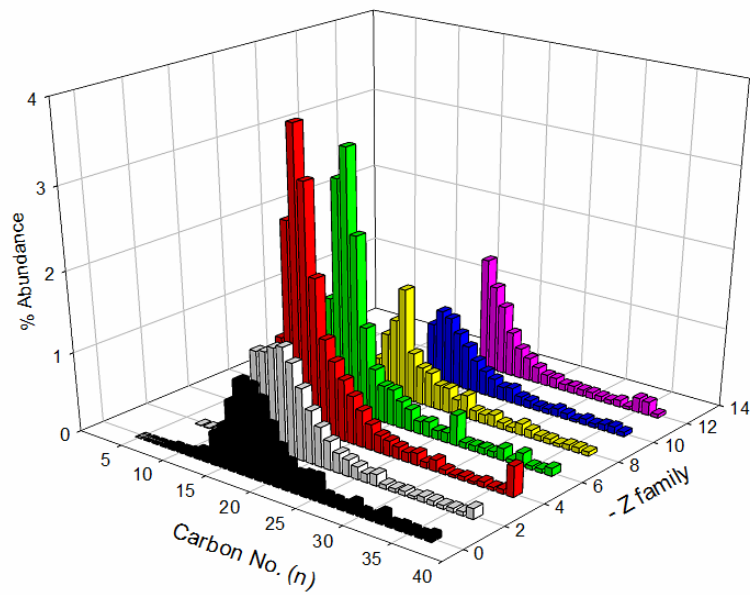


Figure 3.2 Mass spectra of (a) Fluka NAs and (b) OSPW NAs.



(a)



(b)

Figure 3.3 Comparison of carbon number and z-family distribution for (a) Fluka NAs (b) OSPW NAs.

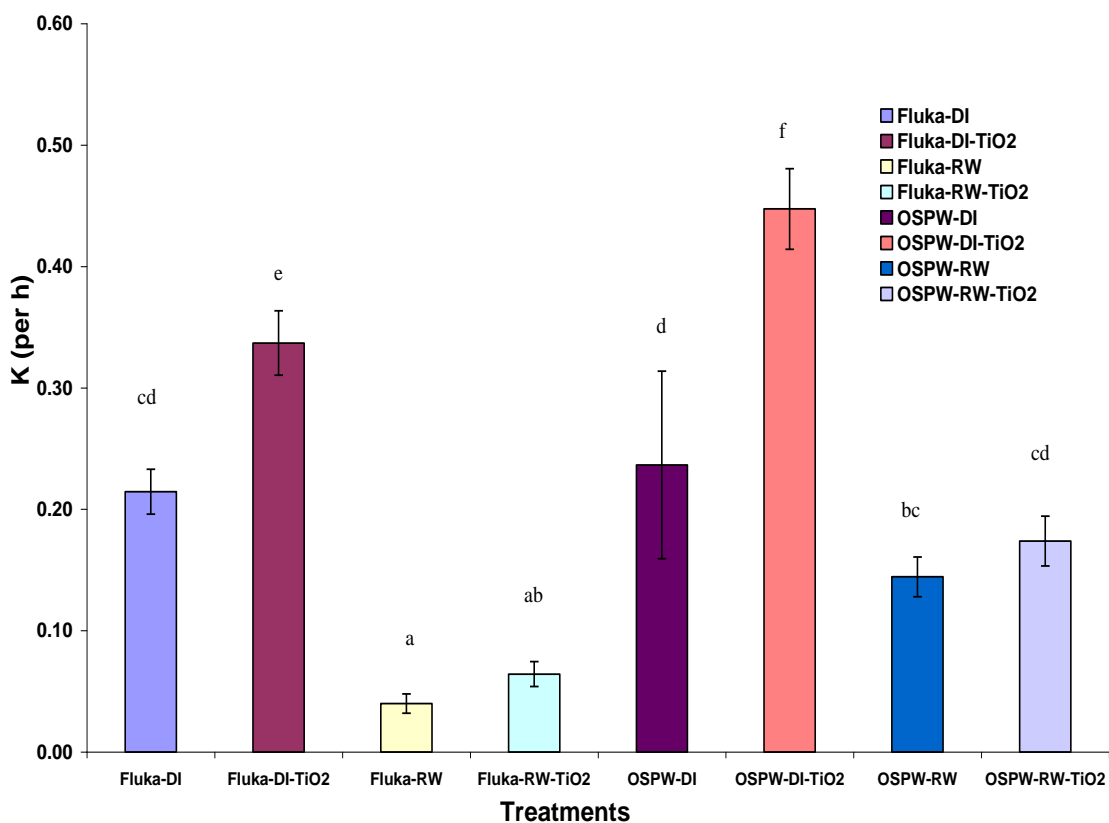


Figure 3.4 Values of rate constant (k) for different treatment combinations in photocatalysis system ($R^2=0.944$); means with the same letter designation are statistically not different ($P = 0.05$) by Tukey's HSD test.

For photocatalysis system, out of the eight different combinations as shown in Tables 3.1 and 3.2, degradation was faster for the combination of OSPW NAs in deionized water and with TiO_2 compared to river water. Comparison of chromatograms of this process combination before and after treatment of 5 hr is shown in Figure 3.5. This figure suggests that the lower molecular weight NAs are degraded more compared to higher molecular weight NAs. Carbon number and z-family distribution of the sample

before and after the treatment are shown in Figure 3.6. This figure shows that there is selective degradation of lower molecular weight NAs. NAs in the $z = -4$ and -6 (two and three -ring NAs) families with a carbon number ranging from 12 to 15 displayed the greatest loss of abundance after treatment. Similar result was observed for NAs with higher z values ($z = -12$, six ring NAs). This might be because of the presence of NA like compounds with multi-carboxylic groups in their structures, which degrades faster as compared to classical NAs, contributing to the higher overall degradation of NAs. Further investigation, using high and ultra high resolution MS, is necessary to study the influence of these NA co-extracts on the degradation kinetics. Rate constant (k) and half-life period for this treatment combination were $0.447 \text{ (h}^{-1}\text{)}$ and 1.55 h, respectively.

The data were statistically analyzed using univariate analysis of variance (Appendix A). It was found that for photocatalysis degradation process, the types of naphthenic acids, water, and use of TiO_2 have significant effect on the value of rate constant of the degradation process (at $P=0.05$). Also, the interaction between the type of water and use of TiO_2 has significant effect on the rate constant of the degradation process.

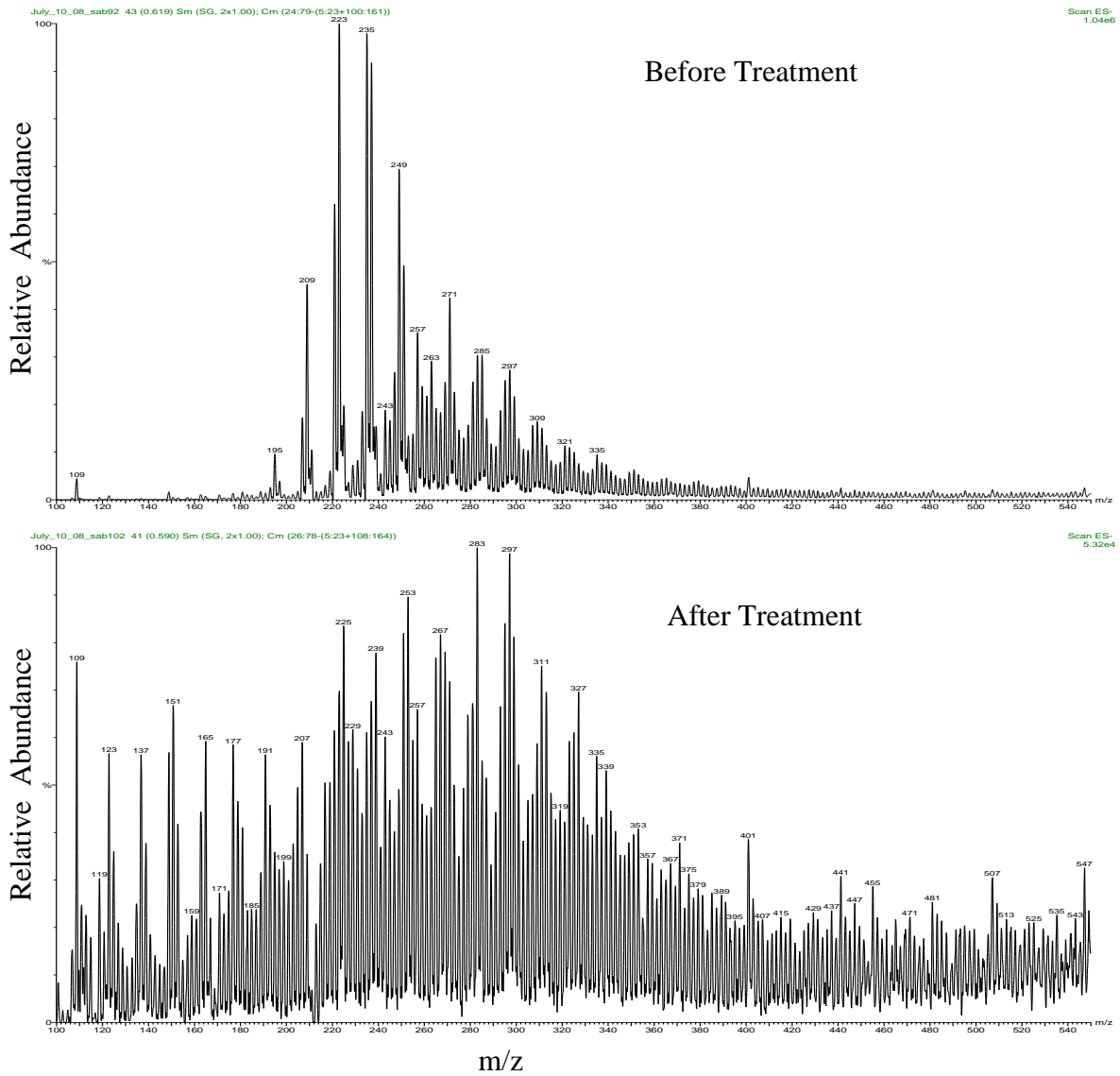
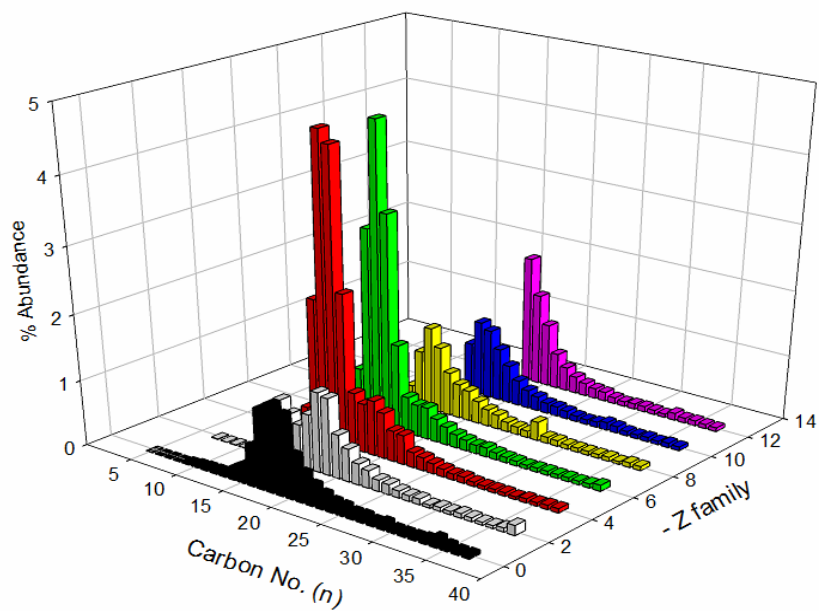
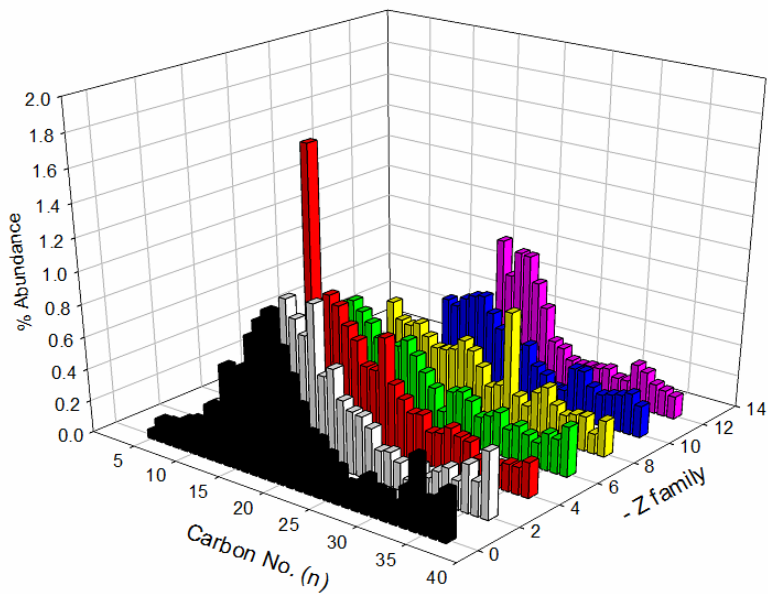


Figure 3.5 Mass spectral comparison of the oilsands process water NA extract before and after the photocatalytic treatment for 5 hr at 24°C.



(a)



(b)

Figure 3.6 Comparison of the oilsand process water NA extract (a) before and (b) after the photocatalytic treatment with respect to carbon number and z-family.

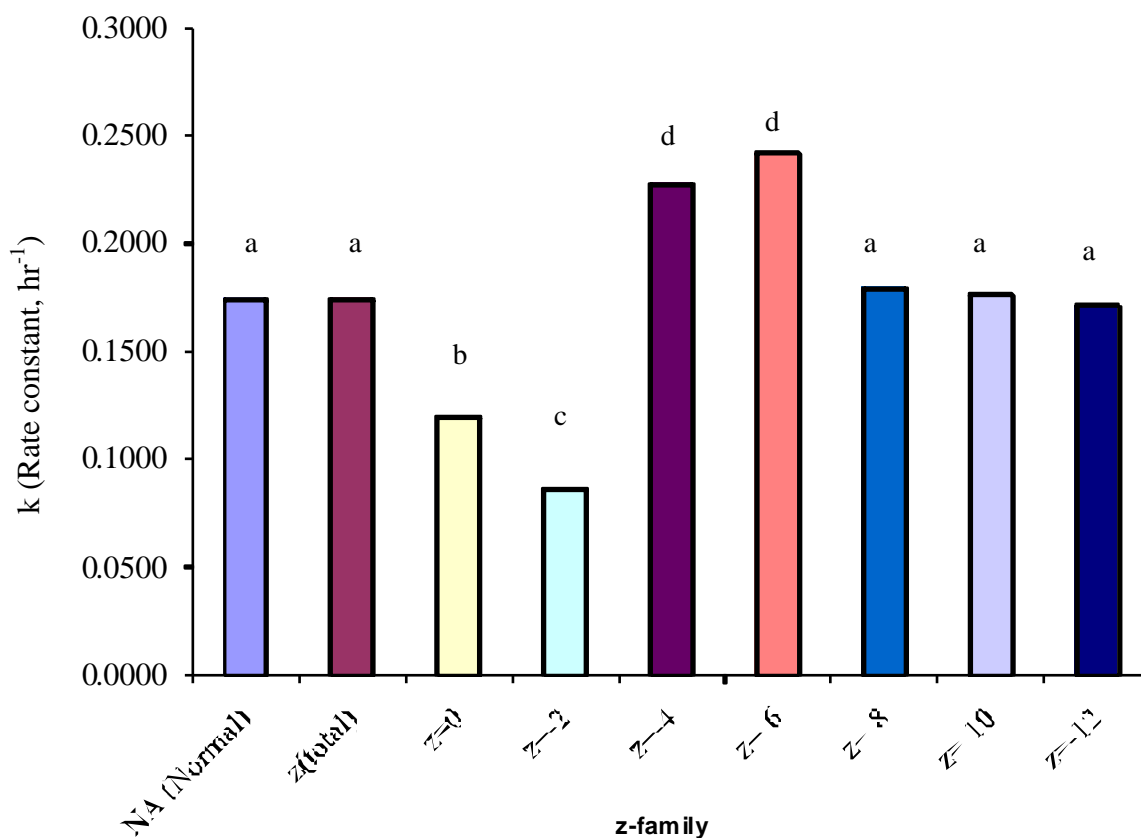


Figure 3.7 Variation of rate constant 'k' with z-family of OSPW NAs in river water due to photocatalysis for 5 hr at 24°C.

Further data reduction was done and the apparent distribution of concentrations of individual NAs according to its z value was determined. Kinetic analysis was performed and the corresponding rate constants for individual z series were found which can be seen in Figure 3.7. Rate constants of degradation of NAs with $z = -4$ and -6 were found to be higher than rest of the z-series. NAs with higher z values degraded faster than linear and single ring NAs. This may be because of the presence of unsaturated NA-like compounds (Frank et al., 2008, 2009) with higher cyclization, which degrades faster and contributes

to the faster degradation reaction kinetics of NAs with higher z . Also this result may be because of the use of low resolution ESI/MS for analysis of NAs, which is reported to do substantial false-positive detections and misclassification of OSPW NAs (Martin et al., 2008), thereby overestimating the NA concentration in the sample. There is a valid need of further data mining using high and ultra high resolution MS to support these findings.

Table 3.6 Microtox toxicity results for oilsands process water NA extract in deionised water with TiO₂ before and after photocatalytic treatment.

Photocatalysis System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC50 v/v (%)	25.92	>90%
95% Confidence Interval v/v (%)	23.54 to 28.54	N/A
15 min IC50 v/v (%)	18.34	>90%
95% Confidence Interval v/v (%)	16.92 to 19.88	N/A
30 min IC50 v/v (%)	15.65	>90%
95% Confidence Interval v/v (%)	14.20 to 17.24	N/A
Colour	None	None
Odour	Mild	Mild
Temperature (°C)	6.0	6.0
pH	9.67	7.66
Dissolved Oxygen (%)	81.8	83.5
Total Chlorine (mg/L)	N/A	N/A
Toxicity	High toxicity	No toxicity

Table 3.7 Microtox toxicity results for oilsand process water NA extract in river water with TiO₂ before and after photocatalytic treatment.

Photocatalysis System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC50 v/v (%)	30.84	>90%
95% Confidence Interval v/v (%)	28.61 to 33.24	N/A
15 min IC50 v/v (%)	22.92	>90%
95% Confidence Interval v/v (%)	21.75 to 24.15	N/A
30 min IC50 v/v (%)	20.11	>90%
95% Confidence Interval v/v (%)	19.05 to 21.22	N/A
Colour	Light yellow	None
Odour	None	Moderate
Temperature (°C)	15.0	15.0
pH	8.86	8.31
Dissolved Oxygen	80.8	78.7
Total Chlorine (mg/L)	N/A	N/A
Toxicity	Moderate toxicity	No toxicity

Microtox toxicity test results before and after treatment, for the sample with OSPW NAs in deionized water with TiO₂ which has the highest rate constant, are shown in Table 3.6. High toxicity of the sample with 30 min IC50 v/v (%) as 15.65 % could be treated and detoxified completely with final 30 min IC50 v/v (%) as more than 90 %. Similar results were found for the OSPW NAs in river water with TiO₂ which can be seen in Table 3.7. Moderate to high toxicity of the sample with 30 min IC50 v/v (%) as 20.11 % could be treated and detoxified completely with final 30 min IC50 v/v (%) value as

more than 90 %. This decrease in toxicity can be attributed to the selective degradation of lower molecular weight NAs (with $z = -4$ and -6) which are generally considered responsible for the toxicity of NAs.

3.4 Conclusions

A laboratory scale photocatalytic system was designed and developed. This system was evaluated for degradation and detoxification of NAs in water. It was found that the system is effective in degrading both commercial NAs and OSPW NA extracts at a faster rate with half life period ranging between 1.55 to 17.37 h for different combination of treatments. The apparent rate constants of degradation of NAs according to their z values were also found out. This system was also effective in completely removing toxicity of NAs which was confirmed by the Microtox tests. However these results must be interpreted in the context that the ESI/MS used in this research is not capable of distinguishing between classical NAs and other NA like compounds present in the sample. Further investigation using high and ultra high resolution MS is recommended as future work on the topic.

CHAPTER 4. MICROWAVE TREATMENT OF NAPHTHENIC ACIDS IN WATER

This chapter addresses the third and fourth objectives of this research and covers the design, development, and evaluation of microwave treatment system for NA degradation and detoxification.

4.1 Introduction

Naphthenic acids (NAs) are natural constituent of bitumen. These acids are the oxidative product of petroleum hydrocarbons, composed of substituted cycloaliphatic carboxylic acids. NAs get solubilized and concentrated in tailing pond water during the oil sands extraction process. Tailings pond water in the oil sands production facilities in north of Fort McMurray, AB, Canada generally contains NA as high as 110 mg/L (Clemente et al., 2005). The TPW enters surface and subsequently ground water systems through mixing and/or erosion of riverbank oil sands deposits. The NA contaminated water causes different health hazards in mammals. Reports suggest that NA contaminated water causes gastro-intestinal disturbances in humans. It also has notable effects on the formation of blood platelets, cell proliferation and respiration. Thus, water containing NAs needs treatment before it is used or allowed to natural water sources.

Chan et al. (2002) and Kong et al. (2004, 2006) suggested that NAs could be separated from diesel fuel using microwave radiation. According to Tian et al. (2005), the effects of microwave irradiation on reaction kinetics are a result of dielectric heating and non-thermal action. Microwave is a non-ionizing radiation that causes molecular motion

by migration of ions and rotation of dipoles, but does not cause changes in molecular structure. Kong et al. (2006) explained the principle of microwave-induced separation of molecules. At higher frequencies and varied electromagnetic fields, the dipole turning polarization cannot keep up with the rapid alternating electromagnetic field and an angle is lagged. This leads to microwave radicalization. The system dissipates and converts microwave energy to heat energy. The movement and interaction of the molecules blocks the directional change and rotation of the polar molecules, which lead to molecule vibration, mutual friction, and rise in the system temperature. Hong et al. (2004) explained that the non-thermal effect of microwaves occurs because microwaves cause polarized materials to line up with the magnetic field, resulting in the destruction of intramolecular bonds and consequential denaturation or coagulation of molecules.

Removal of naphthenic acid from vacuum cut # 1 distillate oil of Daqing using microwave has also been reported by Huang et al. (2006). Horikoshi et al. (2004) and Klán et al. (2002) have reported the use of microwave and electrodeless microwave UV-Vis lamp to photodegrade environmental pollutants in aqueous media. In order to understand the effect of microwave irradiation at 2.45 GHz, commercially available Fluka and natural OSPW NA extracts were used as the target pollutant. A laboratory scale microwave treatment system was designed and developed using the values of the dielectric properties determined in Chapter 2. Kinetics of degradation of NAs in water with or without a catalyst (TiO_2) under microwaves was investigated.

The objectives of this research work were to design and develop a laboratory scale microwave system for the treatment of Naphthenic acids in water and to conduct

feasibility study, performance evaluation, and validation of the developed systems for degradation and detoxification of naphthenic acid mixtures.

4.2 *Materials and Methods*

4.2.1 Experimental Design

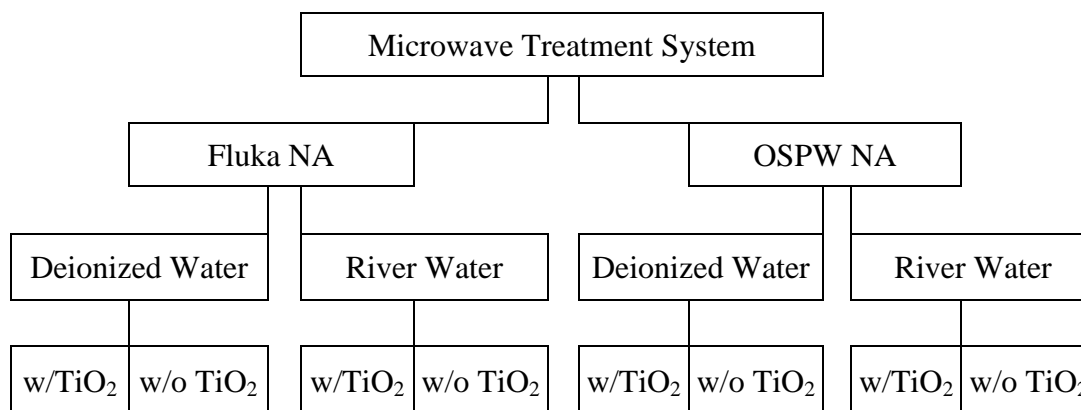
Experiments were designed to treat naphthenic acids in water using the proposed treatment method, i.e. microwave treatment. Details of the experimental setup and procedure are explained separately in the following sections. For this treatment method, there were three main factors (naphthenic acids, water, and TiO₂) each with two levels. All these variables were considered for 1 X 2 X 2 X 2 full factorial design with one type of treatment method, two levels of NAs, two levels water, and two levels of TiO₂.

Two types of Naphthenic acids (Fluka and OSPW Extracts) were used for sample preparation. Water was varied to two levels according to its source of origin (deionized and river). Similarly TiO₂ use was varied to two levels (with 0.3g/L in particulate form or without). This consideration gave us eight possible treatment combinations for each of the major treatment method as shown in Table 4.1 and 4.2. For microwave treatment system, experiments were designed for four initial concentrations (40, 60, 80, and 100 ppm). For each concentration, experiments were replicated three times to validate the results.

Table 4.1 Description for each of the treatment combination.

SI No.	Combinations	Description
1	Fluka-DI	Fluka NAs with deionized water
2	Fluka-DI-TiO ₂	Fluka NAs with deionized water and TiO ₂
3	Fluka-RW	Fluka NAs with river water
4	Fluka-RW-TiO ₂	Fluka NAs with river water and TiO ₂
5	OSPW-DI	OSPW extracted NAs with deionized water
6	OSPW-DI-TiO ₂	OSPW extracted NAs with deionized water and TiO ₂
7	OSPW-RW	OSPW extracted NAs with river water
8	OSPW-RW-TiO ₂	OSPW extracted NAs with river water and TiO ₂

Table 4.2 Different possible combinations in microwave treatment system with full factorial (1 X 2 X 2 X 2) experimental design.



4.2.2 Sample Preparation for Microwave Treatment System

Samples were prepared for the experiments using both commercially available (Fluka) naphthenic acids and naphthenic acid extracted from natural source, oil sand process water (OSPW) following the procedure proposed by Janfada et al. (2006)

described in the previous chapter. Both deionized (Milli-Q) water and water collected from Saskatchewan river at Saskatoon were used for the experiments.

Stock solutions with high concentration of Fluka (4000ppm) and OSPW naphthenic acid extract (6800 ppm) were prepared (Tables 3.3 and 3.4). These stock solutions were then added to water for making the actual samples with desired concentration for experimentation. Keeping in mind the actual concentration (upto 110 mg/L) of naphthenic acid in natural water resources in affected areas, samples were prepared with different concentrations ranging between 40 to 100 ppm with an interval of 20 ppm.

4.2.3 Experimental Setup for Microwave Treatment System

The microwave experiments were done using a household microwave (NNS615W, 1200 W, 2.45 GHz, Panasonic Canada Inc., Mississauga, ON) modified to accommodate the reaction chamber/ sample holder and tubing made of Teflon (Fig. 4.1). The sample holder was designed and fabricated in the Engineering Shop of the University of Saskatchewan (Saskatoon, SK). Dielectric properties (Chapter 2) were used to select the material for the sample holder. Penetration depth of microwaves at 2.45 GHz was determined as 2.18 cm for 100 ppm NAs in water mixture at 35°C and accordingly, the dimension of the sample holder was set (height = 15.24 cm and external diameter = 3.81 cm) to allow proper penetration of microwaves through the wall (thickness = 0.5 cm) of the sample holder and the NA samples. The system setup is shown in Figure 4.2.

Schematic of the system arrangement is shown in Figure 4.3. This is a batch type closed system. The sample water mixture inside the reaction chamber was circulated in

this closed system through a cooling coil made of stainless steel by an aquarium pump and brought back to the reactor/chamber. By allowing the sample to pass through the cooling system temperature of the sample could be reduced from about 78 to 35°C. So the degradation reactions could be achieved at room temperature. This also allowed the system to have sufficient residence time for the samples to stay inside the reaction chamber for maximum possible exposure to microwave radiation.

Experiments were done at 1200 W with four different initial concentrations (40, 60, 80, and 100 ppm) for both Fluka and OSPW NAs extract using deionized and river water. Use of TiO_2 was varied at 0.3 g/L as explained in previous sections of this report. Experimental design for this study is shown in Tables 4.1 and 4.2. Samples were collected every 5 minutes for 30 minutes. Experiments were replicated three times at each level.

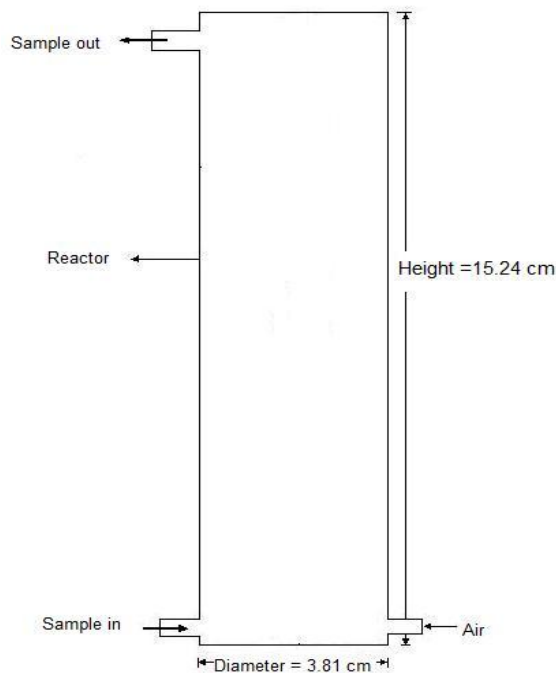


Figure 4.1 Schematic of reaction chamber/ sample holder used in microwave system.

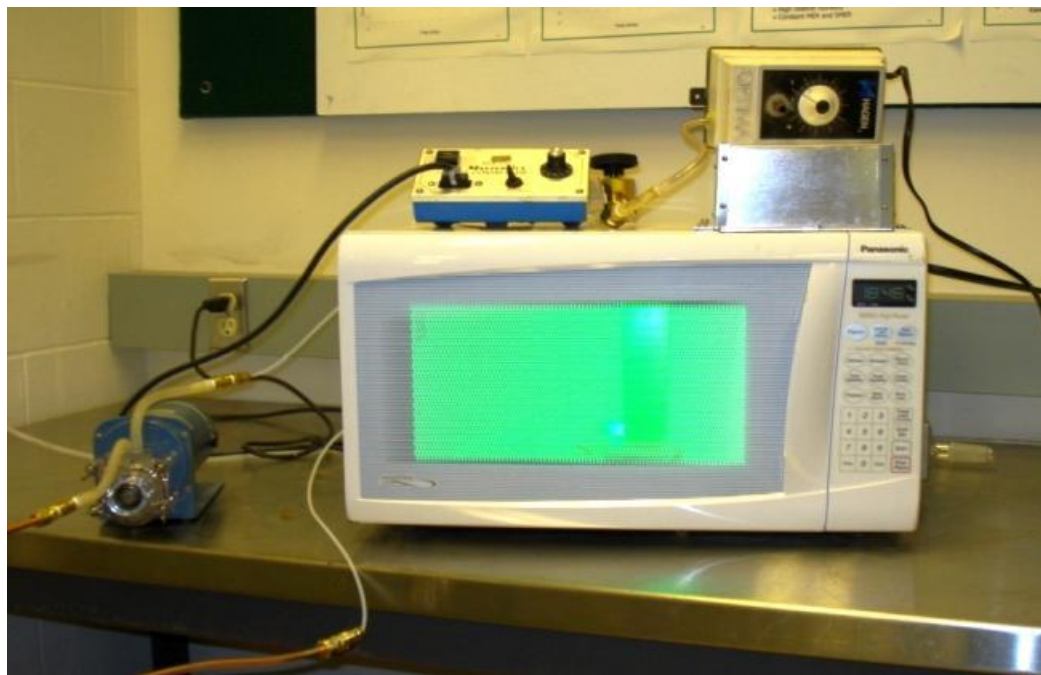


Figure 4.2 Microwave and Microwave assisted photocatalysis systems setup.

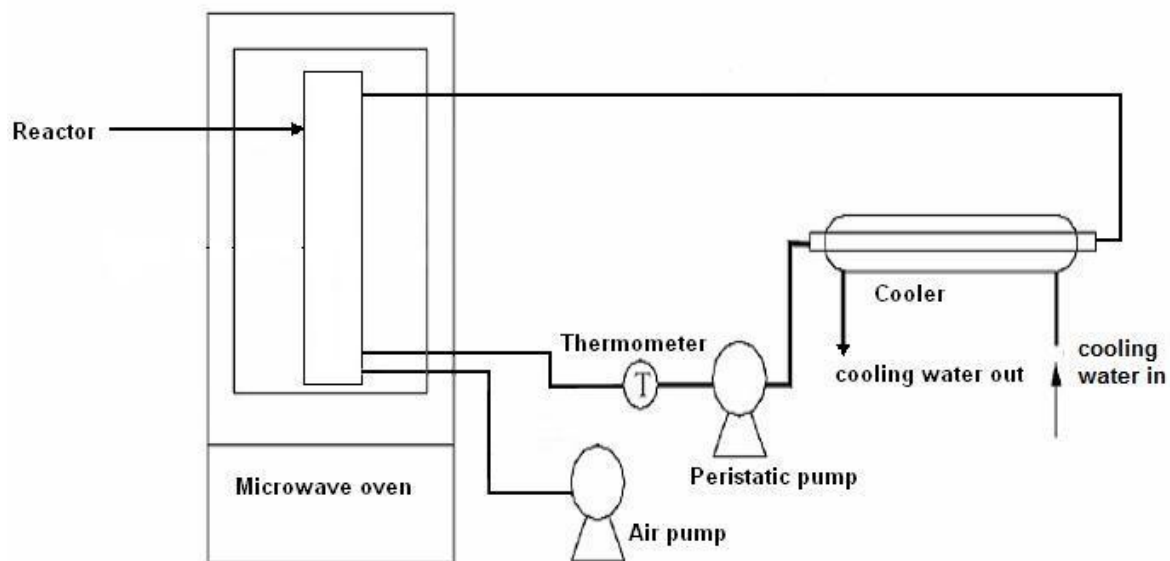


Figure 4.3 Schematic of microwave system setup.

4.2.4 Analysis and Quantification of Naphthenic Acids in Water Sample

Electrospray ionization mass spectrometry in negative mode was used at NWRI laboratory at Saskatoon, Canada to quantify and characterize naphthenic acid concentration in the samples following the standard procedure proposed by Headley et al. (2002). The detailed description is already given in Chapter 3 (section 3.2.5).

4.2.5 Kinetic Analysis for Microwave Treatment System

The degradation process of Naphthenic acids in water follows the pseudo first order reaction mechanism (McMartin, 2003). Rate constant and the corresponding half-life period for the degradation process were calculated following the ‘Integrated’ rate law as summarized in Table 3.5 in Chapter 3.

4.2.6 Statistical Analysis

Standard deviation was calculated and error bars were plotted for each of the treatment. SPSS[®] 14.0 for windows (SPSS Inc, Chicago, IL) was used to perform univariate analysis of variance (ANOVA) and Tukey’s HSD test. ANOVA was performed to analyze treatment means and Tukey’s HSD test was done to compare the treatment means.

4.2.7 Toxicity Tests for Microwave Treatment System

Microtox toxicity tests of the sample before and after treatment were done at ALS Lab, Saskatoon, SK. Microtox Analyzer (Model #500, Strategic Diagnostics Inc., Newark, DE) with test organism *Vibrio fischeri* was used. The reference method followed was *Environment Canada ERS1/RM/24*. IC₅₀ value (max 100%) which is the half

maximal (50%) inhibitory concentration (IC) of a substance was measured at 5, 15, and 30 min residence time for each of the sample before and after treatment.

4.3 Results and Discussion

Commercially available (Fluka) and OSPW NAs standard were analyzed. Mass chromatograms of these two types of NAs are compared in Figure 3.2. Comparison of carbon number and z-family distribution are shown in Figure 3.3. Results validate that commercial (Fluka) naphthenic acids and OSPW NAs have different composition and mass distribution. From the comparison, it can be seen that Fluka NAs have higher density of components with lower m/z ratio (157-297 m/z), whereas for OSPW NAs, this distribution shifts towards comparatively higher m/z ratios (195-325 m/z). This is why Fluka NAs behaved differently than OSPW NAs. This justifies the use of two types of NAs for this study.

Error bar plot ($R^2 = 0.948$) for rate constant values for each of the treatments can be seen in Figure 4.4. Most of the treatment combinations are statistically not different from one another except for the combination of Fluka NAs in river water. Presence of other organic contaminants in the river water and their misclassification as NAs by low resolutions ESI/MS, might be contributing to this result. With same type of water and TiO_2 used, the system took less time to degrade Fluka NAs than OSPW NAs extracts except for the case where river water was being used with TiO_2 . The use of TiO_2 reduced the reaction rate and made the degradation process slower with higher value of half-life period except for the OSPW NAs and deionized water combination. Similarly, type of water had significant effect on the degradation process of NAs. Use of river water made

the degradation process go faster, in absence of TiO₂, as compared to deionized water. With TiO₂, NAs in deionized water were degraded faster.

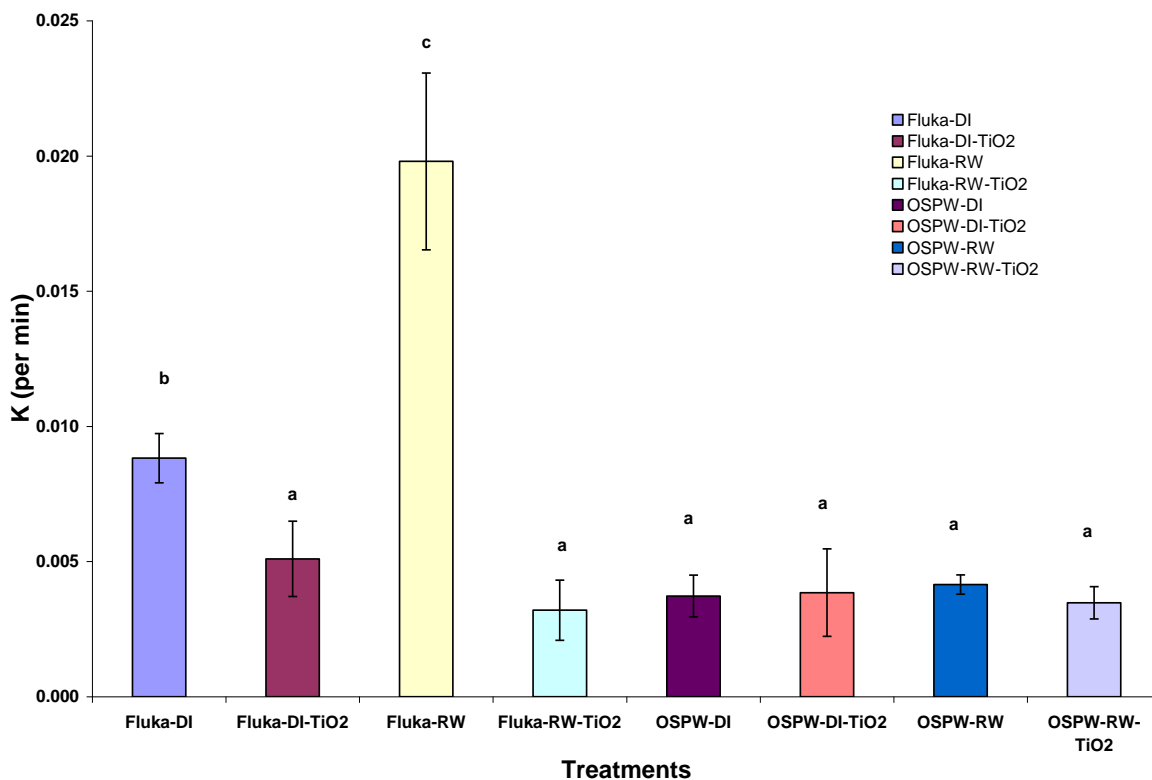


Figure 4.4 Values of rate constant (k) for different treatment combinations in microwave system ($R^2=0.948$); means with the same letter designation are not statistically different ($P = 0.05$) by Tukey's HSD test.

For microwave system, out of the eight different combinations as shown in Table 4.1, degradation was fastest for the combination of Fluka NAs in river water without TiO₂. Comparison of chromatograms of this process before and after treatment can be seen in Figure 4.5. Carbon number and z-family distribution of the sample before and after the treatment are shown in Figure 4.6. There is selective degradation of higher molecular weight NAs under microwave. The relative abundance distribution of NAs

shifts towards lower m/z ratio after the treatment. NAs in the $z = 0$ (linear or branched NAs) families with a carbon number ranging from 18 to 20 displayed the greatest loss of abundance after treatment. NAs in $z = 0, -2$ and -4 families with a carbon number ranging from 8 to 12 displayed greatest increase of abundance after treatment. Rate constant (k) and half-life period for this treatment combination were $0.0198 \text{ (min}^{-1}\text{)}$ and 35.01 min , respectively.

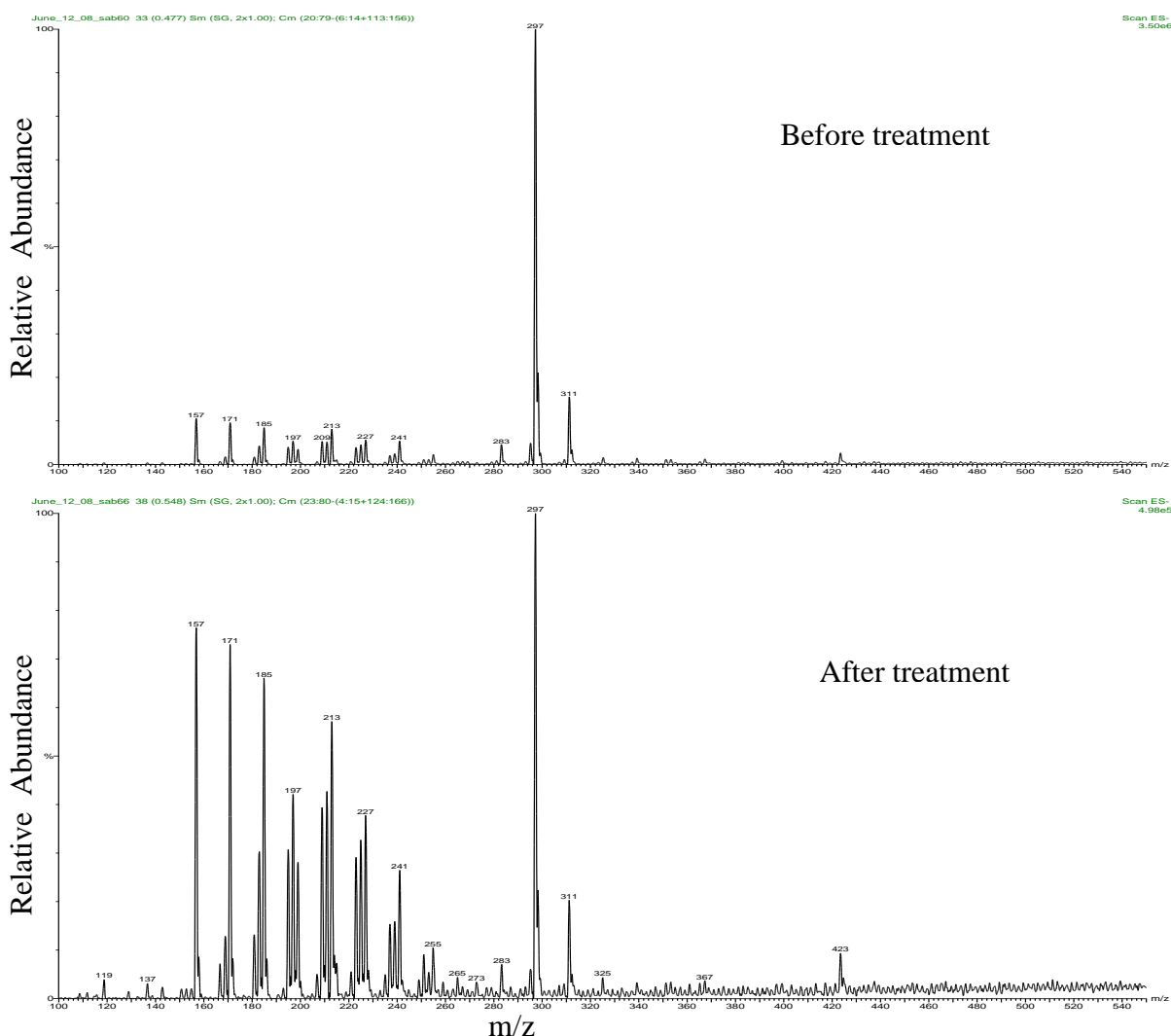


Figure 4.5 Mass spectral comparison of Fluka Naphthenic acids in river water before and after 30 min of microwave treatment.

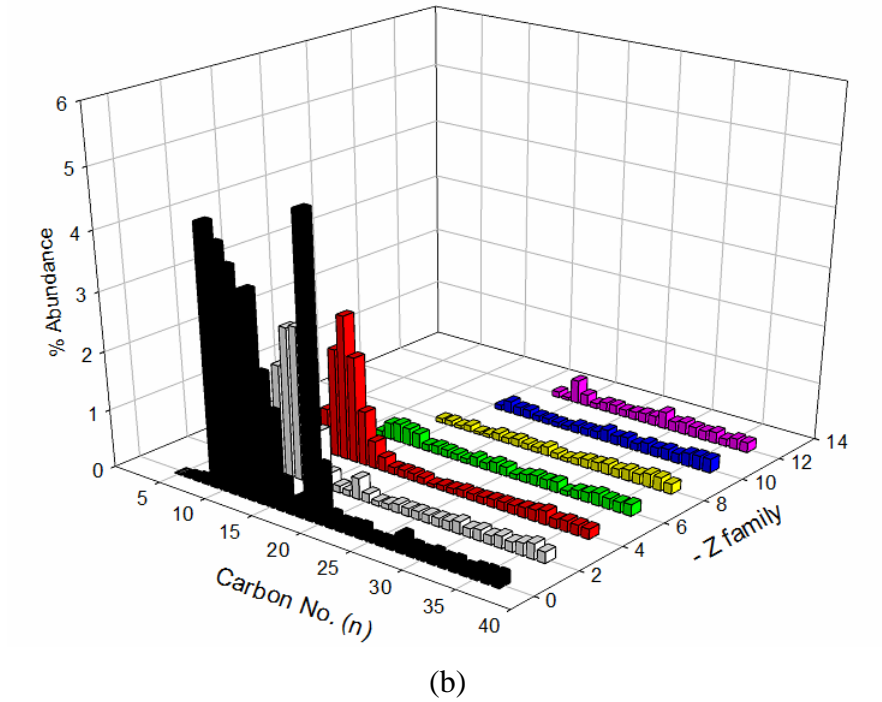
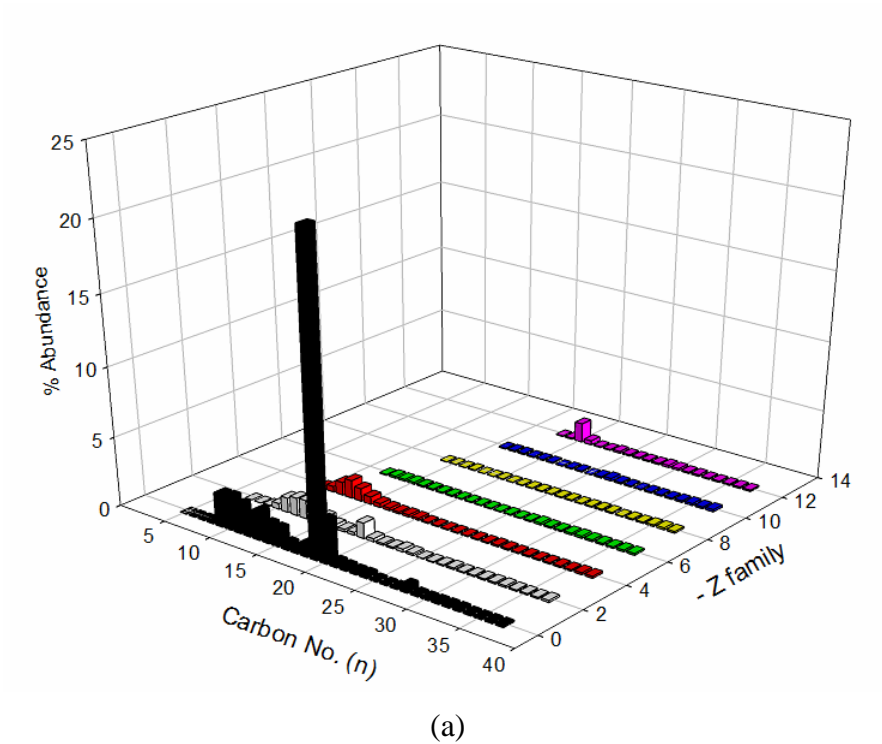


Figure 4.6 Carbon number and z-family distribution of the Fluka naphthenic acid in river water (a) before and (b) after microwave treatment.

The data were statistically analyzed using univariate analysis of variance (Appendix B). It was found that for microwave degradation process, the types of naphthenic acids and use of TiO_2 have significant effect on the value of rate constant of the degradation process (at $P=0.05$). Type of water did not have significant effect on the rate constant. Interaction among the type of naphthenic acids, water, and use of TiO_2 has significant effect on the rate constant of the degradation process.

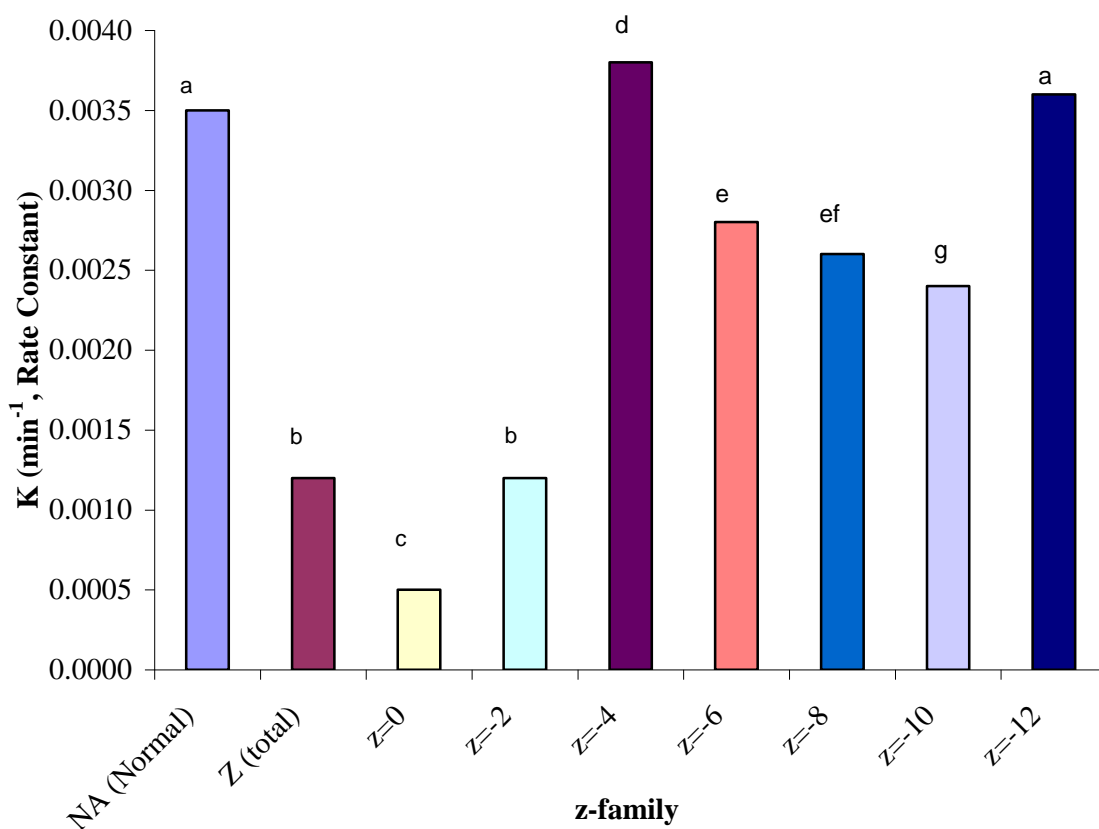


Figure 4.7 Variation of rate constant 'k' with z-family of oilsand process water naphthenic acid extract in river water in microwave treatment system.

Further data reduction was done and the apparent distribution of concentrations of individual NAs according to z value was determined. Kinetic analysis was performed and the corresponding rate constants for individual z series were found

out which can be seen in Fig. 4.7 and Appendix E. Rate constant of degradation of NAs with $z = -4$ was found to be the highest among the z -series. NAs with higher z values degraded faster than linear and single ring NAs. This may be because of the presence of unsaturated NA-like compounds with higher cyclization (Frank et al., 2008, 2009). These compounds might be degrading faster under microwaves and contributing to the faster degradation reaction kinetics of NAs with higher z . Also it is reported that longer chain and highly branched NAs are more prone for degradation. For this treatment system, rate constant of NA normal was more than that of NA total. This also supports the presence of NA-like molecules which are more microwave-degradable than the classical NAs. These results should be seen in the context that the low resolution ESI/MS used in this study for analysis of NAs, is reported to do substantial false-positive detections and misclassification of OSPW NAs (Martin et al., 2008), thereby overestimating the NA concentration. Therefore, further data reduction, using high and ultra high resolution analysis of the samples, is recommended as future work to validate these results.

Rate constant of NA-total was less than NA-normal. This suggests that the former degraded slower than the latter. This can be attributed to the presence of NA-like compounds with unsaturated rings and other non-classical NA constituents which might be competing with the classical NAs for the microwave energy and hence decreasing overall degradation.

Microtox toxicity test results before and after treatment, for the sample with Fluka NAs in river water which has the highest rate constant, are shown in Table 4.3. High toxicity of the sample with 30 min IC50 v/v (%) value as 9.4 could be treated and

detoxified partially with final 30 min IC₅₀ v/v (%) value as 22.85. Similar toxicity tests were done on samples taken before and after treatment for OSPW NAs in river water with TiO₂. The test result is given in Table 4.4. Though the overall concentration of NAs could be decreased significantly using microwaves, there was slight increase in toxicity level. The 30 min IC₅₀ v/v (%) value of the sample could be decreased from 20.11 to 17.65. This increase in toxicity can be attributed to the increase in relative abundance of lower molecular weight NAs as seen in the chromatograms which are generally considered responsible for the toxicity of NAs.

Table 4.3 Toxicological comparison of Fluka naphthenic acid in river water before and after microwave treatment.

Microwave Treatment System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC ₅₀ v/v (%)	15.85	36.45
95% Confidence Interval v/v (%)	13.95 to 18.01	34.25 to 38.79
15 min IC ₅₀ v/v (%)	11.85	25.81
95% Confidence Interval v/v (%)	10.39 to 13.52	24.23 to 27.49
30 min IC ₅₀ v/v (%)	9.4	22.85
95% Confidence Interval v/v (%)	8.20 to 10.78	21.38 to 24.42
Colour	None	None
Odour	Mild	Mild
Turbidity	Low	Low
Temperature (°C)	6.0	6.0
pH	8.47	8.51
Dissolved Oxygen (%)	71.8	74.6
Toxicity	High toxicity	Moderate toxicity

Table 4.4 Toxicological comparison of oilsand process water naphthenic acid extract in river water with TiO₂ before and after microwave treatment.

Microwave Treatment System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC50 v/v (%)	30.84	25.01
95% Confidence Interval v/v (%)	28.61 to 33.24	23.05 to 27.12
15 min IC50 v/v (%)	22.92	19.77
95% Confidence Interval v/v (%)	21.75 to 24.15	18.38 to 21.26
30 min IC50 v/v (%)	20.11	17.65
95% Confidence Interval v/v (%)	19.05 to 21.22	16.35 to 19.05
Colour	Light yellow	None
Odour	None	None
Turbidity	None	Moderate
Solids	None	None
Temperature (°C)	15.0	15.0
pH	8.86	8.11
Dissolved Oxygen (%)	80.8	77.8
Total Chlorine (mg/L)	N/A	N/A
Toxicity	Moderate toxicity	Moderate toxicity

It is proposed that the increased degradation and detoxification of NAs in microwave field might be because of the microwave-induced molecular separation (Kong et al., 2006) and non-thermal effect of microwaves (Hong et al., 2004). At higher frequencies and varied electromagnetic fields inside microwave cavity, the dipole turning polarization of NAs might not keep up with the rapid alternating electromagnetic field,

leading to molecule vibration, mutual friction, and radicalization. Microwaves also might be forcing the polarized NA molecules to line up with the magnetic field, resulting in the destruction of intra-molecular bonds and consequential denaturation or coagulation of molecules in the sample, thereby, exposing the NA molecules to high energy microwave radiation and hence degradation. Further investigation is necessary to validate this hypothesis.

4.4 Conclusions

A laboratory scale microwave treatment system was designed and developed. This system was evaluated for degradation and detoxification of NAs in water. It was found that the system is effective in degrading both commercial NAs and OSPW NA extracts in a faster rate as compared to the photocatalysis system, with half-life period ranging between 0.58 to 3.61 h for different combination of treatments. The apparent rate constants of degradation of NAs according to their z values were also found out. This system was effective in slightly removing toxicity of NAs which was confirmed by the Microtox tests.

CHAPTER 5. MICROWAVE ASSISTED PHOTOCATALYTIC (MAP) TREATMENT OF NAPHTHENIC ACIDS IN WATER

This chapter addresses the third and fourth objectives of this research and covers the design, development, and evaluation of microwave assisted photocatalysis treatment system for NA degradation and detoxification.

5.1 Introduction

Naphthenic acids (NA) are natural constituent of bitumen. These are the oxidative products of petroleum hydrocarbons, composed of substituted cycloaliphatic carboxylic acids. These acids include single and fused multiple rings in their structures. NAs are solubilized and concentrated in tailing pond water (TPW) during oil sands extraction and enter surface and subsequently ground water systems through mixing and/or erosion of riverbank adjacent to oil sands deposits. Clemente et al. (2005) reported that tailing pond water in the Athabasca oil sands (AOS) region may contain NAs up to 110 mg/L. If consumed, NA contaminated water causes gastro-intestinal disturbances in human and also has notable effects on the formation of blood platelets, cell proliferation, and respiration (Lee et al., 2000). Corrosion due to NAs is also a major concern for petroleum refineries, which limits the choice of materials used in equipment and supply chain. Thus, water containing NAs needs treatment prior to release or reuse.

Chan et al. (2002) and Kong et al. (2004, 2006) suggested that NAs could be separated from diesel fuel using microwave. Removal of naphthenic acid from vacuum cut # 1 distillate oil of Daqing using microwave has also been reported by Huang et al.

(2006). Similarly, photolysis of naphthenic acid in natural surface water using UV₂₅₄ source has been reported by McMartin et al. (2004). Headley et al. (2009) suggested that photocatalysis using TiO₂ can degrade NAs efficiently under natural sunlight.

Horikoshi et al. (2004) have reported the use of electrodeless microwave UV-Vis lamp to photodegrade environmental pollutants in aqueous media. Zhang et al. (2006) have reported on microwave electrodeless lamp photolytic degradation of acid orange 7. Klán et al. (2002) described the use and photochemistry of microwave electrodeless lamp. They have indicated that the coupled UV-vis/microwave irradiation from microwave electrodeless lamp could accelerate the degradation of organic pollutants. However, the possibility of combining photocatalytic degradation of naphthenic acids under microwave electrodeless lamp irradiation has not been investigated so far. In order to understand the synergetic effect of microwave irradiation and UV-vis irradiation commercially available Fluka and OSPW NAs were used as the target contaminants. The ability of the system was evaluated by the concentration of sample at particular interval.

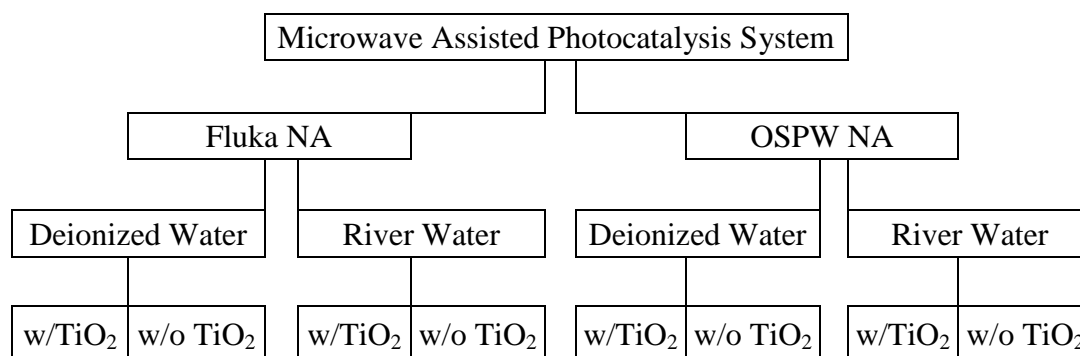
The objectives of this research work were to design and develop a laboratory scale microwave-assisted photocatalysis system for the treatment of Naphthenic acids in water and to conduct feasibility study, performance evaluation, and validation of the developed system for degradation and detoxification of naphthenic acid mixtures

5.2 Materials and Methods

5.2.1 Experimental Design for Microwave Assisted Photocatalysis System

Experiments were designed to treat naphthenic acids in water using the proposed treatment method, i.e. microwave-assisted photocatalysis (MAP). Details of the experimental setup and procedures are explained separately in following sections of this chapter. For this treatment method, there were three main factors (Naphthenic acids, water, and TiO₂) each with two levels. All these variables were considered for 1 X 2 X 2 X 2 full factorial design with one type of treatment method, two levels of NAs, two levels water and two levels of TiO₂.

Table 5.1 Different possible combinations in microwave assisted photocatalysis treatment system with full factorial (1 X 2 X 2 X 2) experimental design.



Two types of naphthenic acids (Fluka and OSPW extracts) were used for the sample preparation. Water was varied to two levels according to its source of origin (deionized and river). Similarly, TiO₂ was used in particulate form and its use was varied to two levels (with 0.3 g/L or without). This consideration gave eight possible treatment combinations for each of the major treatment method as shown in Table 5.1 and 5.2. For

this system, experiments were designed for three initial concentrations (40, 70, and 100 ppm). For each concentration, experiments were replicated three times to validate the results.

Table 5.2 Description for each of the treatment combination.

SI No.	Combinations	Description
1	Fluka-DI	Fluka NAs with deionized water
2	Fluka-DI-TiO ₂	Fluka NAs with deionized water and TiO ₂
3	Fluka-RW	Fluka NAs with river water
4	Fluka-RW-TiO ₂	Fluka NAs with river water and TiO ₂
5	OSPW-DI	OSPW extracted NAs with deionized water
6	OSPW-DI-TiO ₂	OSPW extracted NAs with deionized water and TiO ₂
7	OSPW-RW	OSPW extracted NAs with river water
8	OSPW-RW-TiO ₂	OSPW extracted NAs with river water and TiO ₂

5.2.2 Sample Preparation for Microwave Assisted Photocatalytic System

Samples were prepared for the experiments using both commercially available (Fluka) naphthenic acids and naphthenic acid extracted from the oil sand process water (OSPW) following the procedure proposed by Janfada et al. (2006) described in section 3.2.3. Both deionized (Milli-Q) water and water collected from Saskatchewan river in Saskatoon, SK were used for the experiments.

Stock solutions with high concentration of Fluka (4000 ppm) and OSPW naphthenic acid extract (6800 ppm) were prepared (Tables 3.3 and 3.4). These stock

solutions were then added to water for making the actual samples with desired concentration for experimentation. Keeping in mind the actual concentration (upto 110 mg/L) of naphthenic acid in natural water resources in affected areas, samples were prepared with different concentrations ranging between 40 to 100 ppm with an interval of 30 ppm.

5.2.3 Experimental Setup for Microwave-Assisted Photocatalytic System

The microwave assisted photocatalysis experiments were done in a household microwave (NNS615W, 1200 W, 2.45 GHz, Panasonic Canada Inc., Mississauga, ON) modified to accommodate the reaction chamber/ sample holder (Fig. 5.1) and tubing made of Teflon[®]. In addition to the microwave source, a microwave electrodeless lamp was used in this system. This lamp was custom built and procured from Primarc UV Tech. (Easton, PA). This electrodeless lamp, placed centrally inside the reaction chamber, was used as the source of ultraviolet rays. Microwave is absorbed by the electrodeless lamp which in turn emits the necessary UV rays (250-300 nm) for photocatalysis. Details on the principle of operation of this lamp are available in literature (Klan et al., 2002).

The system setup is shown in Figure 5.2. The sample holder was designed and fabricated in the Engineering Shop of the University of Saskatchewan (Saskatoon, SK). Dielectric properties (Chapter 2) were used to select the material for the sample holder. Penetration depth of microwaves was determined to be 2.18 cm for 100 ppm NAs in water mixture at 35°C and 2.45 GHz and accordingly, the external diameter of the sample holder was set at 3.81 cm and height was kept at 15.24 cm to allow proper penetration of microwaves through the wall (thickness = 0.5 cm) and the NA-water mixture. Schematic

of the system arrangement is shown in Figure 5.1. This is a batch type closed system. The sample water mixture inside the reaction chamber was circulated in this closed system through a cooling coil made of stainless steel by an aquarium pump and brought back to the reactor/chamber. Temperature of the sample could be reduced from about 78 to 35°C by passing it through the cooling system. Sufficient residence time was allowed for the samples by controlling the flow rate for maximum possible exposure to microwave and UV radiation.

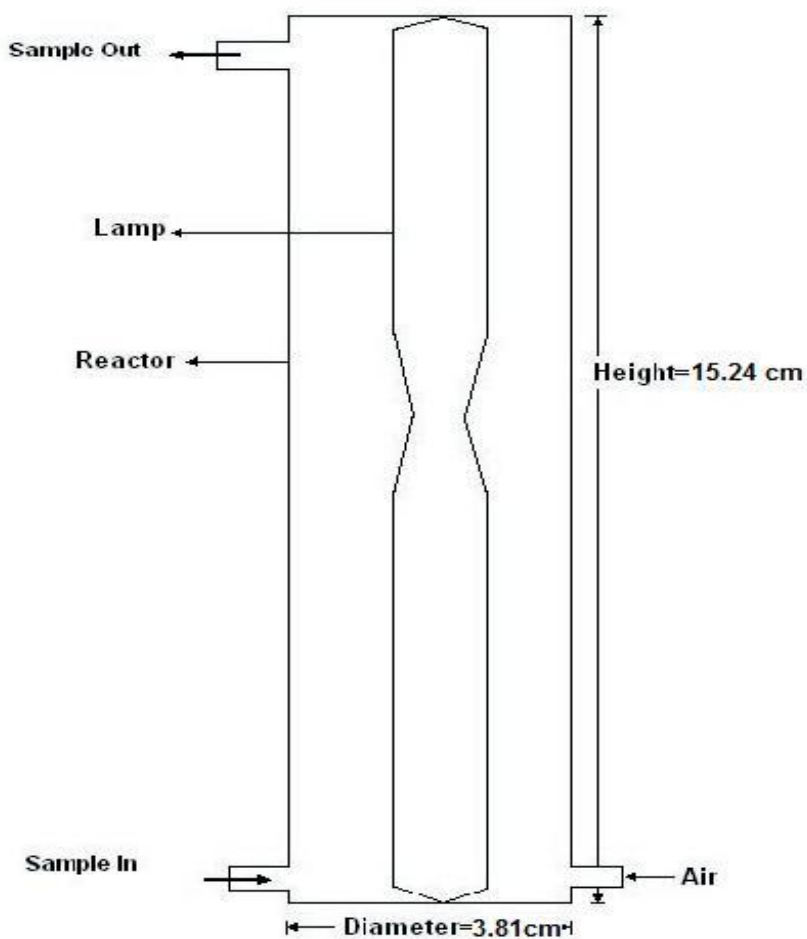


Figure 5.1 Schematic of reaction chamber (sample holder) used in microwave-assisted photocatalysis system with microwave electrodeless lamp.

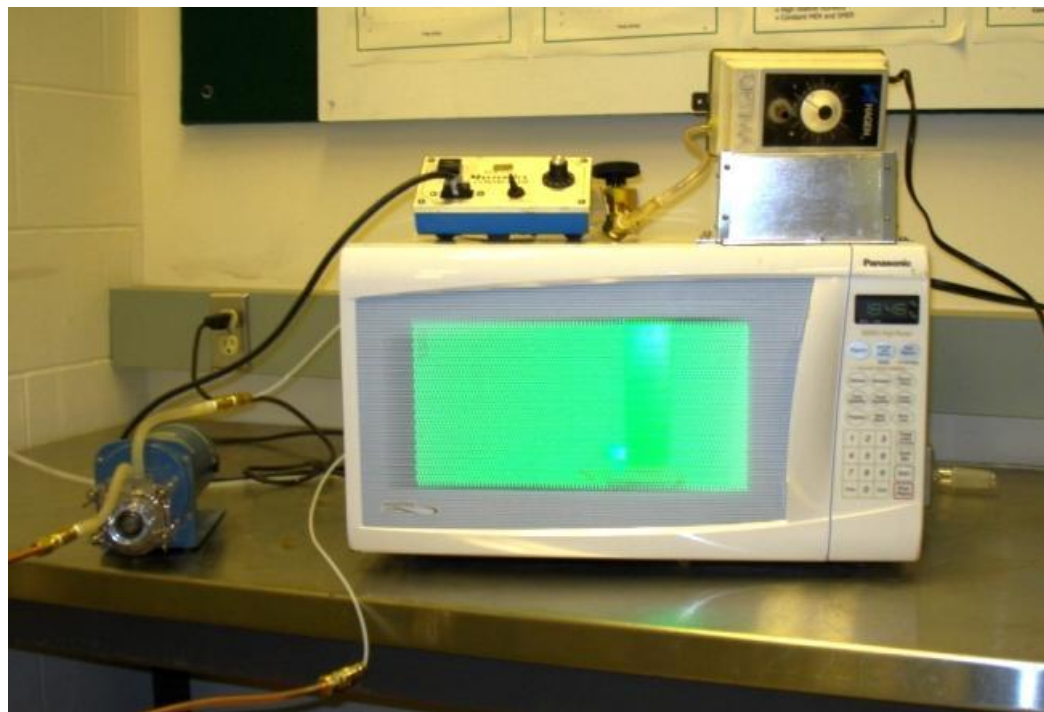


Figure 5.2 Microwave assisted photocatalysis systems setup.

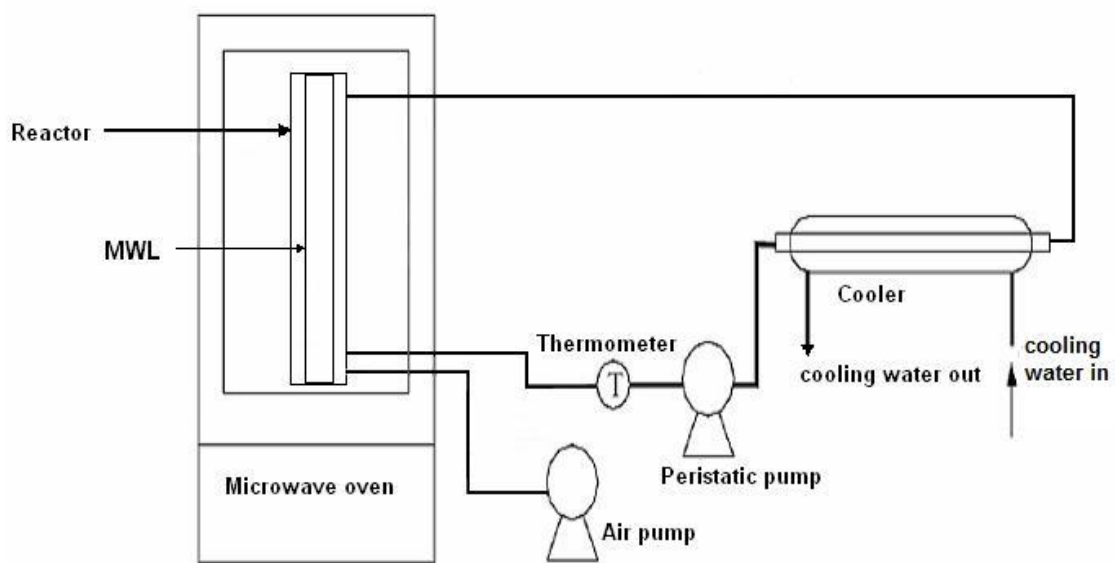


Figure 5.3 Schematic of microwave assisted photocatalysis system setup.

Experiments were done with three different initial concentrations (40, 70, and 100 ppm) for both Fluka and OSPW NAs extract using deionized and river water. Use of TiO_2 was varied at 0.3 g/L as explained in previous sections of this report. Experimental design for this study is shown in Tables 5.1 and 5.2. Samples were collected every 3 minutes for 15 minutes. Experiments were replicated three times.

5.2.4 Analysis and Quantification of Naphthenic Acids in Water Sample

Electrospray ionization mass spectrometry in negative mode was used at NWRI laboratory at Saskatoon, SK, Canada to quantify and characterize naphthenic acid concentration in the samples following the standard procedure proposed by Headley et al. (2002). The detailed description is already given in section 3.2.5 of this thesis.

5.2.5 Kinetic Analysis for Microwave-Assisted Photocatalytic System

Pseudo first-order reaction kinetic parameters such as the rate constant and the corresponding half-life period for the degradation process were calculated using the 'Integrated' rate law as summarized in Table 3.5.

5.2.6 Statistical Analysis

Statistical analysis of data was done using SPSS[®] 14.0 for Windows (SPSS Inc, Chicago, IL). Error bars were plotted for each of the treatment combinations. Univariate analysis of variance (ANOVA) and Tukey's HSD test were also performed. ANOVA of data analyzed the treatment means and Tukey's HSD test compared the treatment means.

5.2.7 Toxicity Tests for Microwave Assisted Photocatalytic System

Toxicity of the samples before and after treatment was analyzed at ALS Labs, Saskatoon using Microtox analyzer (Model #500, Strategic Diagnostics Inc., Newark, DE). *Vibrio fischeri* was used as the test organism. The reference method proposed by *Environment Canada* (ERS1/RM/24) was followed for the tests. Half maximal (50%) inhibitory concentration (IC₅₀) of the sample was measured at 5, 15 and 30 min residence time for both before and after treatment.

5.3 Results and Discussion

Mass chromatograms of both Fluka and OSPW NAs standard were compared (Figure 3.2 of chapter 3). Carbon number and z-family distribution of these two types of NAs are shown in Figure 3.3. Fluka NAs have higher density of components with lower m/z ratio (157-297 m/z) whereas for OSPW NAs this distribution shifts towards comparatively higher m/z ratios (195-325 m/z). Results validate the difference in composition and mass distribution of these NAs and explain why Fluka NAs behave differently than OSPW NAs. This justifies the use of two types of NAs for this study.

Error bar plot ($R^2=0.922$) for rate constant values for each of the treatments can be seen in Figure 5.4. Change in initial NA concentration did not affect the degradation kinetics, justifying the use of pseudo-first order analysis. At same level of water and TiO₂, the system took less time to degrade OSPW NAs than Fluka NAs. This can be attributed to the faster degradation of co-extracts/ NA-like compounds present in OSPW NAs which contributes to the overall degradation kinetics. The presence of multi-carboxylic groups, containing unsaturated double bonds in their structures, in higher

molecular weight fraction of OSPW NAs (Frank et al. 2009) makes them susceptible for photo-oxidation at a faster rate. The dielectric and non-thermal effect of microwave might add to the separation of molecules and hence, further degradation of unsaturated NA-like polar compounds present in OSPW NAs. Fluka NAs in deionized water degraded faster than OSPW NAs extract in absence TiO_2 . For Fluka NAs, addition of TiO_2 decreased the reaction rate and made the degradation process slower and for OSPW NAs addition of TiO_2 made the degradation process go faster, irrespective of the type of water used. Result also suggests that type of water has significant effect on the degradation process. Irrespective of the type, NAs in river water took more time to degrade than in deionized water except for the case where only OSPW NA was used without TiO_2 . This can be attributed to the matrix effect of others salts and materials present in the river water competing with NAs molecules for both microwave and UV radiation in the system.

For microwave-assisted photocatalysis system, out of the eight different combinations as shown in Table 5.1, degradation was fastest for the combination of Fluka NAs in deionized water without TiO_2 . Comparison of chromatograms of this process before and after treatment can be seen in Figure 5.5. Carbon number and z-family distribution of the sample before and after the treatment are shown in Figure 5.6.

Results suggest that there is selective degradation of lower molecular weight NAs under microwave assisted photocatalysis. The relative abundance distribution of NAs shifts towards higher m/z ratio after the treatment. NAs in the $z = 0$ (linear or branched NAs) families with carbon number ranging from 18 to 20 displayed the greatest increase

of abundance after treatment. NAs in $z = 0, -2$ and -4 families with carbon number ranging from 8 to 12 displayed significant decrease of abundance after treatment. Rate constant (k) and half-life period for this treatment combination were $0.039 \text{ (min}^{-1}\text{)}$ and 17.91 min respectively.

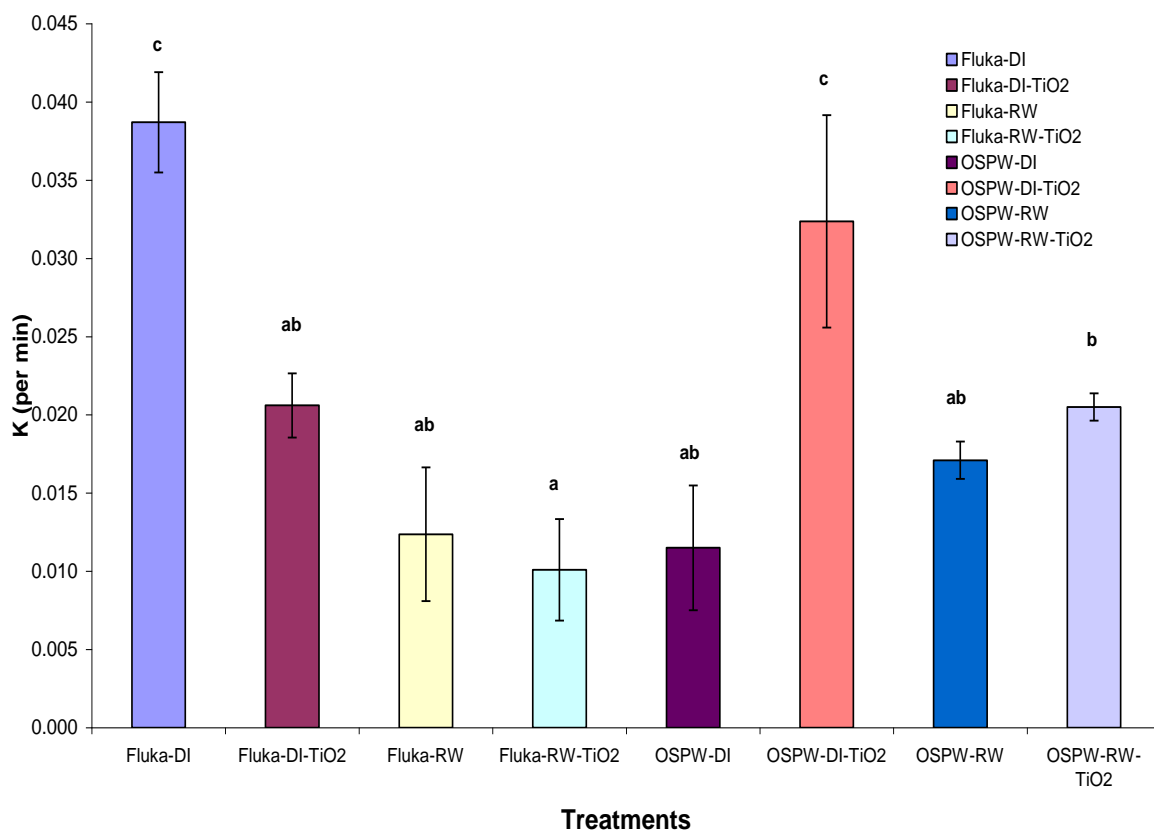


Figure 5.4 Values of rate constant (k) for different treatment combinations in microwave assisted photocatalysis system ($R^2=0.922$); means with the same letter designation are not statistically different ($P = 0.05$) by Tukey's HSD test.

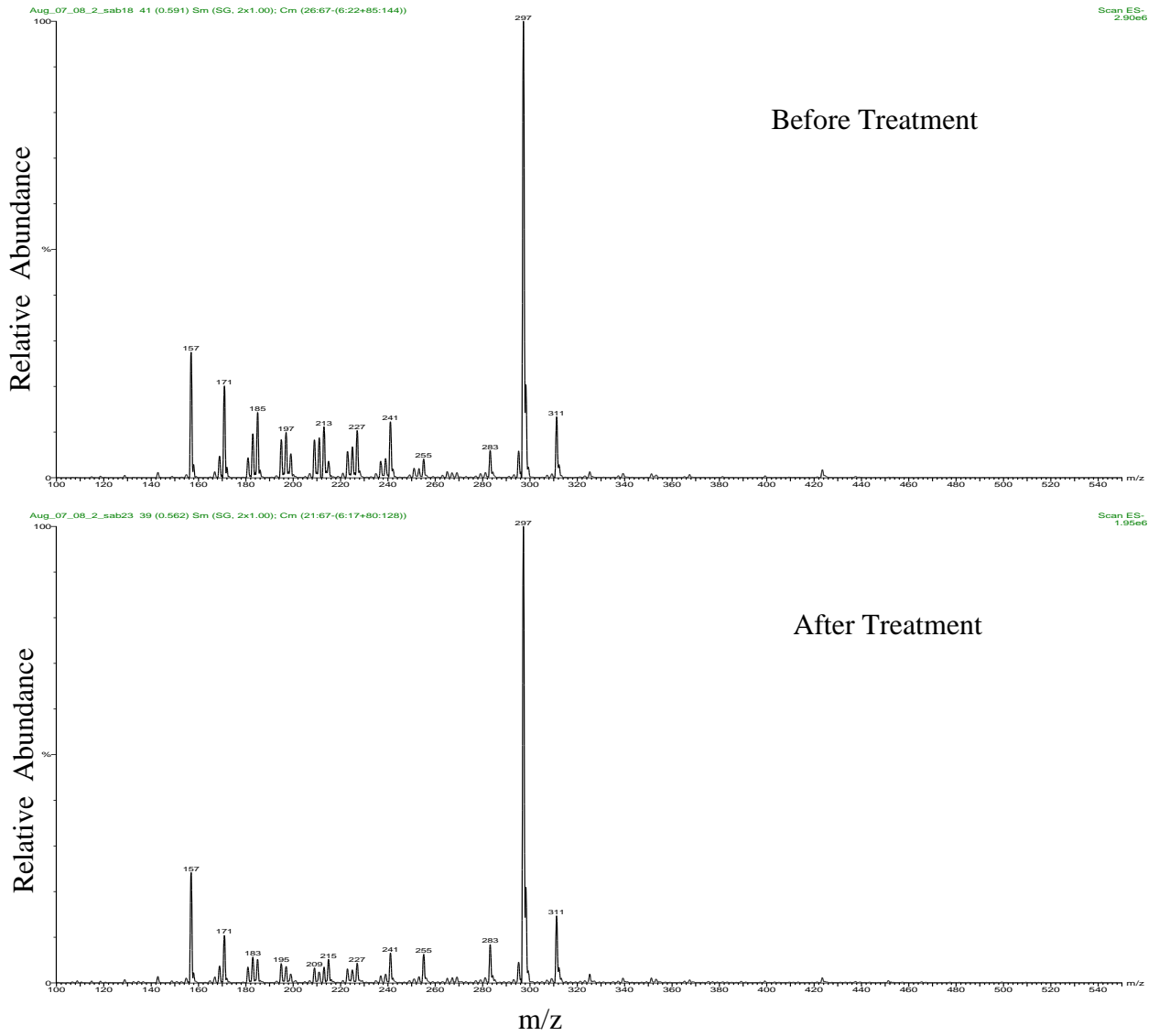
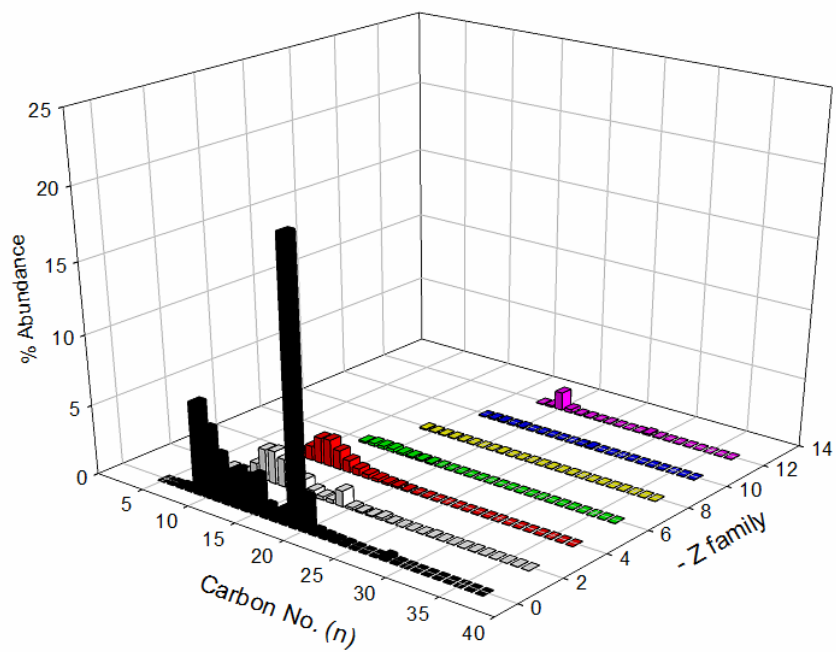
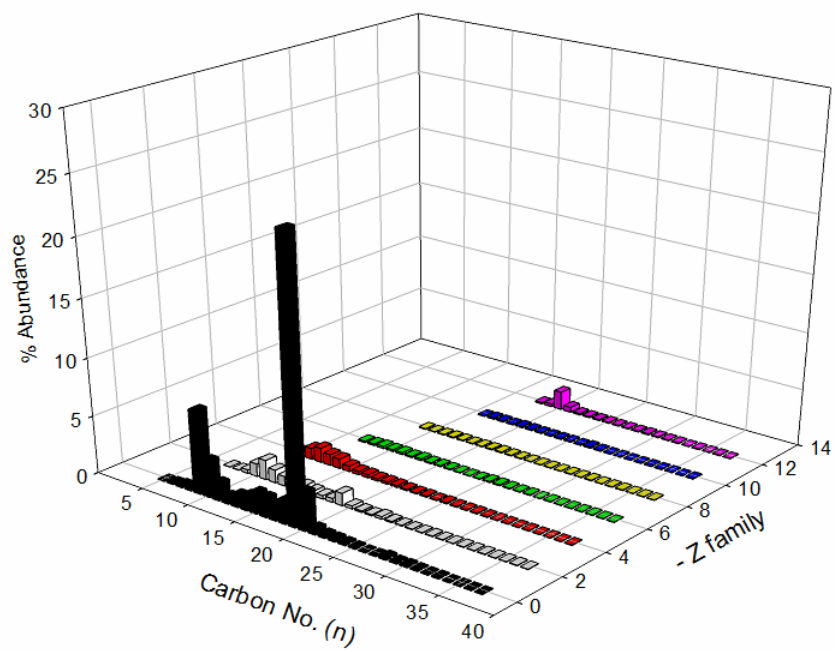


Figure 5.5 Mass spectral comparison of Fluka Naphthenic acids in deionized water before and after microwave assisted photocatalysis treatment.



(a)



(b)

Figure 5.6 Carbon number and z-family distribution of Fluka Naphthenic acids in deionized water (a) before and (b) after microwave assisted photocatalysis treatment.

Further data reduction was done and the apparent distribution of concentrations of individual NAs according to z value was found out. Kinetic analysis was performed and the corresponding rate constants for individual z series were found out which can be seen in Figure 5.7 and Appendix E. Rate constant of degradation of NAs with $z = -6$ was the highest among all the z-series. Statistical analysis of the results has supported this finding. NAs with $z = -4$ and -6 degraded faster than linear and single ring NAs and higher NAs ($z = -8, -10$ and -12).

Rate constant of NA-total was less than NA-normal. This suggests that former degraded slower than the later. This can be attributed to the presence of impurities and other non-classical NA-like constituents (Frank et al., 2008, 2009) which might be competing with the classical NAs for the light energy and hence decreasing overall degradation. Also this result may be because of the use of low resolution ESI/MS for analysis of NAs, which is reported to do misclassification and substantial false-positive detections of NAs (Martin et al., 2008). Also other acidic compounds, hydrocarbons and PAHs are reported to be transparent to ESI/MS in $-ve$ mode. Therefore, high and ultra high resolution analysis of NA samples is recommended as future work for further data mining.

The data were statistically analyzed using univariate ANOVA (Appendix C). It is found that for microwave-assisted photocatalytic degradation process, concentration of NAs in the sample had no significant effect on the degradation kinetics. Type of water used in the degradation process has significant effect on the value of rate constant of the degradation process. The types of naphthenic acids and use of TiO_2 in particulate form do

not have significant effect on rate constant of the degradation process (at $P=0.05$). Interaction between the type of naphthenic acids and TiO_2 has significant effect on the rate constant. Also the interaction among the types of naphthenic acids, water and use of TiO_2 has significant effect on the rate constant of the degradation process.

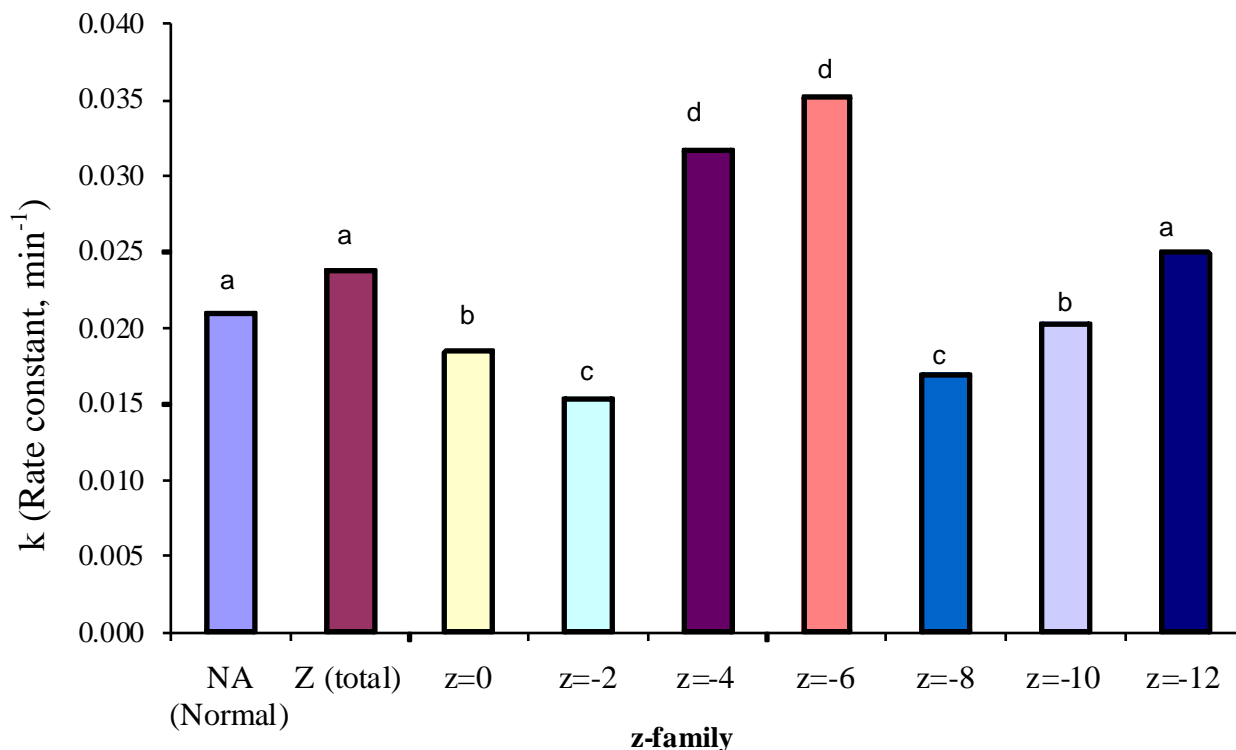


Figure 5.7 Variation of rate constant 'k' with z-family of OSPW NAs in river water in microwave assisted photocatalysis treatment system.

Microtox toxicity test result before and after treatment, for the sample with Fluka NAs in deionized water with the highest rate constant, is shown in Table 5.3. High toxicity of the sample with 30 min IC_{50} v/v (%) value as 11.13 % could be treated and detoxified partially with final 30 min IC_{50} v/v (%) value at 21 %. Similar tests were done before and after treatment for OSPW NAs in river water with TiO_2 . The test result is given in Table 5.4. With microwave assisted photocatalysis system the sample could be

degraded faster as compared to only photocatalysis or only microwave system and could be completely detoxified. Moderate to high toxicity of the sample with 30 min IC50 v/v (%) as 20.11% could be treated and detoxified completely with final 30 min IC50 v/v (%) value more than 90%. This decrease in toxicity can be attributed to the selective degradation of lower molecular weight NAs ($z = -4$ and -6) which are generally considered responsible for the toxicity of NAs.

Table 5.3 Toxicological comparison of Fluka NAs in deionised water before and after Microwave assisted photocatalysis treatment.

Microwave Assisted Photocatalysis System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC50 v/v (%)	18.54	38.74
95% Confidence Interval v/v (%)	15.67 to 21.93	35.16 to 42.66
15 min IC50 v/v (%)	12.49	25.96
95% Confidence Interval v/v (%)	10.78 to 14.46	23.24 to 29.02
30 min IC50 v/v (%)	11.13	21
95% Confidence Interval v/v (%)	9.45 to 13.12	18.68 to 23.60
Colour	White	None
Odour	Strong	Strong
Turbidity	High	Low
Solids	None	None
Temperature (°C)	6.0	6.0
pH	4.64	8.69
Dissolved Oxygen (%)	65.2	56.2
Total Chlorine (mg/L)	N/A	N/A
Toxicity	High toxicity	Moderate toxicity

Table 5.4 Toxicological comparison of oilsands process water NA extract in river water with TiO₂ before and after Microwave assisted photocatalysis treatment.

Microwave Assisted Photocatalysis System		
	<u>Before Treatment</u>	<u>After Treatment</u>
5 min IC50 v/v (%)	30.84	>90%
95% Confidence Interval v/v (%)	28.61 to 33.24	N/A
15 min IC50 v/v (%)	22.92	>90%
95% Confidence Interval v/v (%)	21.75 to 24.15	N/A
30 min IC50 v/v (%)	20.11	>90%
95% Confidence Interval v/v (%)	19.05 to 21.22	N/A
Colour	Light yellow	None
Odour	None	Mild
Turbidity	None	Moderate
Solids	None	None
Temperature (°C)	15.0	15.0
pH	8.86	7.70
Dissolved Oxygen (%)	80.8	79.4
Total Chlorine (mg/L)	N/A	N/A
Toxicity	Moderate toxicity	No toxicity

It is proposed that the increased degradation and detoxification of NAs in this system is due to the synergetic effect microwave and UV radiations. Microwave-induced molecular separation (Kong et al., 2006) and non-thermal effect of microwaves (Hong et al., 2004) might be causing the separation and coagulation of NA molecules in the sample. At higher frequencies and varied electromagnetic fields inside microwave cavity, the dipole turning polarization of NA molecules might not keep up with the rapid

alternating electromagnetic field, leading to molecule vibration, mutual friction, and radicalization. Also microwaves might be forcing the polarized NA molecules to line up with the magnetic field, resulting in the destruction of intra-molecular bonds and consequential denaturation or coagulation of molecules in the sample. Thereby, NA molecules become available in the solution and get exposed to high energy microwave radiation and further photo degradation by UV radiations. This synergetic exposure enhances the degradation of NAs as compared to either microwave or photocatalysis systems. Further investigation is necessary to validate this hypothesis.

5.4 Conclusions

A laboratory scale microwave-assisted photocatalytic treatment system was designed and developed. This system was evaluated for degradation and detoxification of NAs in water. It was found that the system is effective in degrading both commercial NAs and OSPW NA extracts in a faster rate as compared to the both photocatalysis and microwave system or any other method reported so far, with half life period ranging between 0.30 to 1.14 h for different combination of treatments. The apparent rate constants of degradation of NAs according to their z values were also found out. This system was also effective in completely removing toxicity of OSPW NA extracts which was confirmed by the Microtox tests. Considering the high volume of NAs produced each day during oil sand refining process and the environmental concerns associated with their disposal, this treatment system definitely has prospect in treating NAs in OSPW. However, further research on up-scaling of the laboratory setup for industrial use and the cost associated need to be done.

CHAPTER 6. GENERAL DISCUSSION AND CONCLUSIONS

Naphthenic acids (NAs) are natural constituents of bitumen and the oxidative product of petroleum hydrocarbons, composed of substituted cyclo-aliphatic carboxylic acids. NAs are solubilized and concentrated in tailing pond water (TPW) during oil sands extraction and enter at the surface followed by ground water systems through mixing and/or erosion of riverbank adjacent to oil sands deposits. TPW in the Athabasca oil sands (AOS) may contain NAs as high as 110 mg/L (Clemente et al., 2005). If consumed, NA contaminated water causes gastro-intestinal disturbances in human and also has notable effects on the formation of blood platelets, cell proliferation, and respiration (Lee et al., 2000). Corrosion due to NAs is also a major concern for petroleum refineries, which limits the choice of materials used in equipment and supply chain. Thus, water containing NAs needs treatment prior to release or reuse.

Significant environmental and regulatory attention has been focused on the NA fraction of oil sands material due to its persistence in the environment and aquatic toxicity at the levels found in the tailings pond water of petroleum and bitumen extraction facilities (McMartin, 2003). There is insufficient number of publications on separation and identification techniques for naphthenic acid mixtures.

Several methods including chemical and biological treatments as explained in the previous section (1.2.6) are already in use for treatment of different water contaminants including NAs. Time involved in those methods (namely, chemical, biological, and photolysis) and the possibility of formation of hazardous byproducts, limit their effective

use. The processes of photocatalysis and microwave treatment systems are still in developmental stages and have high potential for use in the treatment of contaminated water. Photolysis and some use of microwaves have already been reported to be effective in selective degradation of NAs as explained in the previous sections. However microwave and microwave assisted photocatalysis (MAP) of NAs in water in the presence of photocatalysts had not been reported. Kinetic and toxicological studies of these treatment systems had not been done. There is a valid need to design, develop and evaluate photocatalytic and microwave assisted treatment systems for NA remediation. In this regard, one of the most important design parameters, i.e. microwave properties or permittivity of NAs in water had not been reported in literature. There is a lack in knowledge base on these properties. Since there was a dearth of published literature regarding applications of photocatalysis, microwave and combined treatment systems for the removal and detoxification of specific target pollutants such as Naphthenic acids, research was required to adequately assess the feasibility, potential benefits, and implications of these treatment systems. There are critical gaps in knowledge with respect to the finding of the permittivity / dielectric properties of NAs in water, and application and evaluation of photocatalysis, microwave, and combined microwave assisted photocatalysis for the degradation and detoxification of Naphthenic acids in water.

The overall objective of this research was to design, develop, and evaluate a photocatalytic system, a microwave system and a microwave assisted photocatalysis system to degrade and detoxify NAs in water. To address these critical gaps in knowledge and the objectives of the research, several laboratory investigations were

carried out to study the permittivity of NAs in water. Appropriate systems focusing on the principles of photocatalysis, microwave and microwave assisted photocatalysis, were designed and developed. These systems were evaluated for degradation kinetics and detoxification of NAs in water to verify the hypothesis that *the developed systems would degrade the NAs in water at a faster rate and hence would reduce the toxicity of the NA water mixture to acceptable level.*

Conclusions from each of the chapters which address individual objectives of the proposed research have been presented in section 6.1 and specific recommendations for future research are listed in section 6.2.

6.1 Conclusions

6.1.1 Permittivity of Naphthenic Acids in Water

An attempt was made to determine and report permittivity or dielectric properties as there was no information on these properties of NA and water mixture in literature. The effect of process parameters such as temperature, concentration and frequency of microwave on the permittivity value of NAs in water was determined. Variation of dielectric properties such as the dielectric constant, loss factor, loss tangent, power factor, and depth of penetration as a function of frequency, concentration and temperature of naphthenic acid in water were studied. Dielectric constant decreased as the concentration of the sample increased at a particular frequency. The value of dielectric constant decreased at higher temperature at the same frequency. Loss factor decreased as the concentration of the sample increased at a particular frequency and there was decrease in the value of loss factor with increase in temperature at the same frequency for higher side

of the set frequencies. Concentration of the sample affected the value of loss tangent for the lower frequency range. After 2 GHz, it had least effect on loss tangent. At lower frequencies the values of loss tangent at higher temperature were higher than those at lower temperature. At frequencies higher than 1.6 GHz, the tendency changed and there was decrease in the value of loss tangent with increase in temperature at the same frequency. At higher frequencies, concentration did not affect the penetration depth for the sample. At lower frequencies, the values of penetration depth at higher temperature were lower than those at lower temperature. At higher frequencies temperature did not affect the penetration depth for Naphthenic acid. Dielectric constant, loss factor, power factor values obtained in this study has shown an inverse relationship with both concentration and temperature. Power factor and depth of penetration for the sample were not affected by both concentration and temperature. These data can add to the knowledge base and can be useful to the Scientific community and industry in designing and setting up a microwave applicator for the treatment of NA and water mixture.

Dielectric properties were used to select the material for the sample holder in the microwave and MAP systems. Penetration depth of microwaves at 2.45 GHz was determined and accordingly the dimension of the sample holder and the position of the MW lamp in the sample holder, were optimized to allow proper penetration of microwaves through the wall of the sample holder and the NA samples.

6.1.2 Photocatalysis of Naphthenic Acids in Water

A laboratory scale photocatalytic system was designed and developed as discussed in Chapter 3. This system was evaluated for degradation and detoxification of

NAs in water. The system is effective in degrading both commercial NAs and OSPW NA extracts with half-life period ranging between 1.55 h for the degradation of OSPW NA extract in deionized water to 17.37 h for the degradation of Fluka NAs in river water. Half-life for the degradation of OSPW NA extract in river water with TiO_2 was 3.99 h. This system was effective in completely removing toxicity of NAs (5 min IC 50 v/v >90%) which was confirmed by the Microtox tests. Use of TiO_2 increased the reaction rate.

6.1.3 Microwave Treatment of Naphthenic Acids in Water

A laboratory scale microwave treatment system was designed and developed as discussed in Chapter 4. This system was evaluated for degradation and detoxification of NAs in water. The system is effective in degrading both commercial NAs and OSPW NA extracts in a faster rate as compared to the photocatalysis system, with half-life period ranging between 0.58 h for the degradation of Fluka NAs in river water to 3.61 h for degrading same NAs in presence of TiO_2 . The use of TiO_2 reduced the degradation rate for possible combination of treatments for this system. Half-life for the degradation of OSPW NA extract in river water with TiO_2 was 3.32 h. The apparent rate constants of degradation of NAs according to their z-values were also determined. The microwave system was able to reduce the toxicity of water containing Fluka NAs from high (5 min IC₅₀ v/v = 15.85) to moderate (5 min IC₅₀ v/v = 36.45) toxicity level. But there was a slight increase in toxicity after treating the water with oil sands process water NA extract.

6.1.4 Microwave Assisted Photocatalytic Treatment of Naphthenic Acids in Water

A laboratory scale microwave assisted photocatalytic treatment system was designed and developed as discussed in Chapter 5. This system was evaluated for degradation and detoxification of NAs in water. The system was found to be most effective in degrading both commercial NAs and OSPW NA extracts in a faster rate as compared to the both photocatalysis and microwave system, with half life period ranging between 0.30 h for degradation of Fluka NAs in deionized water to 1.14 h for degradation of Fluka NAs in river water with TiO₂. Half-life of degradation of OSPW NA extract in river water in presence of TiO₂ was 0.56 h which was the least as compared to other two systems. Use of TiO₂ decreased the degradation of Fluka NAs whereas it enhanced the reaction kinetics for OSPW NAs. Microwave assisted photocatalysis system was also able to decrease the toxicity of Fluka NA and NA extracts from oil sands process water completely (upto 5 min IC₅₀ v/v > 90%). The apparent rate constants of degradation of NAs according to their z-values were also found out.

6.2 Recommendations for future research

Some of the important recommendations drawn from this study includes further understanding of the developed treatment systems as well as listed in this section:

1. Dielectric properties of oil sands NA extracts need to be studied at different frequencies, temperature and concentrations.
2. Further data mining by high and ultra high resolution mass spectrometry has to be done in future.

3. Toxicological study of the Naphthenic acid degradation process for each of the eight combinations has to be done to determine and compare the efficiency of the systems in decreasing toxicity level of NA-water sample.
4. Microbiological study needs to be done for the developed systems.
5. Energy and cost calculation of the systems needs to be done.
6. Scale-up of the reactor and commercial viability of the developed systems and techniques have to be determined.

CHAPTER 7. REFERENCES

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APPENDIX A. Univariate ANOVA for Photocatalysis Treatment System

Between-Subjects Factors

		N
Chem	F	16
	T	16
water	DI	16
	RW	16
TiO2	W	16
	WO	16

Tests of Between-Subjects Effects

Dependent Variable: Kavg

Source	Type III				
	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.517(a)	7	.074	58.107	.000
Intercept	1.332	1	1.332	1048.419	.000
Chem.	.069	1	.069	54.509	.000
Water	.310	1	.310	244.146	.000
TiO2	.085	1	.085	67.069	.000
chem * water	.002	1	.002	1.226	.279
chem * TiO2	.002	1	.002	1.812	.191
water * TiO2	.047	1	.047	36.683	.000
chem * water * TiO2	.002	1	.002	1.308	.264
Error	.030	24	.001		
Total	1.879	32			
Corrected Total	.547	31			

a R Squared = .944 (Adjusted R Squared = .928)

Post Hoc Analysis (Tukey HSD):

Between-Subjects Factors

	N	
factor	1	4
	2	4
	3	4
	4	4
	5	4
	6	4
	7	4
	8	4

Factor: Multiple Comparisons

Dependent Variable: Kavg

(I) factor	(J) factor	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.148125(*)	.0251997	.000	-.231584	-.064666
	3	.148925(*)	.0251997	.000	.065466	.232384
	4	.124600(*)	.0251997	.001	.041141	.208059
	5	-.047700	.0251997	.568	-.131159	.035759
	6	-.258575(*)	.0251997	.000	-.342034	-.175116
	7	.044500	.0251997	.647	-.038959	.127959
	8	.015075	.0251997	.999	-.068384	.098534
	2	.148125(*)	.0251997	.000	.064666	.231584
2	3	.297050(*)	.0251997	.000	.213591	.380509
	4	.272725(*)	.0251997	.000	.189266	.356184
	5	.100425(*)	.0251997	.011	.016966	.183884
	6	-.110450(*)	.0251997	.004	-.193909	-.026991
	7	.192625(*)	.0251997	.000	.109166	.276084
	8	.163200(*)	.0251997	.000	.079741	.246659

3	1	-.148925(*)	.0251997	.000	-.232384	-.065466
	2	-.297050(*)	.0251997	.000	-.380509	-.213591
	4	-.024325	.0251997	.975	-.107784	.059134
	5	-.196625(*)	.0251997	.000	-.280084	-.113166
	6	-.407500(*)	.0251997	.000	-.490959	-.324041
	7	-.104425(*)	.0251997	.007	-.187884	-.020966
	8	-.133850(*)	.0251997	.000	-.217309	-.050391
	4	1	-.124600(*)	.0251997	.001	-.208059
2		-.272725(*)	.0251997	.000	-.356184	-.189266
3		.024325	.0251997	.975	-.059134	.107784
5		-.172300(*)	.0251997	.000	-.255759	-.088841
6		-.383175(*)	.0251997	.000	-.466634	-.299716
7		-.080100	.0251997	.066	-.163559	.003359
8		-.109525(*)	.0251997	.005	-.192984	-.026066
5		1	.047700	.0251997	.568	-.035759
	2	-.100425(*)	.0251997	.011	-.183884	-.016966
	3	.196625(*)	.0251997	.000	.113166	.280084
	4	.172300(*)	.0251997	.000	.088841	.255759
	6	-.210875(*)	.0251997	.000	-.294334	-.127416
	7	.092200(*)	.0251997	.023	.008741	.175659
	8	.062775	.0251997	.246	-.020684	.146234
	6	1	.258575(*)	.0251997	.000	.175116
2		.110450(*)	.0251997	.004	.026991	.193909
3		.407500(*)	.0251997	.000	.324041	.490959
4		.383175(*)	.0251997	.000	.299716	.466634
5		.210875(*)	.0251997	.000	.127416	.294334
7		.303075(*)	.0251997	.000	.219616	.386534
8		.273650(*)	.0251997	.000	.190191	.357109
7		1	-.044500	.0251997	.647	-.127959
	2	-.192625(*)	.0251997	.000	-.276084	-.109166

	3	.104425(*)	.0251997	.007	.020966	.187884
	4	.080100	.0251997	.066	-.003359	.163559
	5	-.092200(*)	.0251997	.023	-.175659	-.008741
	6	-.303075(*)	.0251997	.000	-.386534	-.219616
	8	-.029425	.0251997	.934	-.112884	.054034
8	1	-.015075	.0251997	.999	-.098534	.068384
	2	-.163200(*)	.0251997	.000	-.246659	-.079741
	3	.133850(*)	.0251997	.000	.050391	.217309
	4	.109525(*)	.0251997	.005	.026066	.192984
	5	-.062775	.0251997	.246	-.146234	.020684
	6	-.273650(*)	.0251997	.000	-.357109	-.190191
	7	.029425	.0251997	.934	-.054034	.112884

Based on observed means.

* The mean difference is significant at the .05 level.

Homogeneous Subsets (Tukey HSD)

factor	N	Subset					
		1	2	3	4	5	6
3	4	.039900					
4	4	.064225	.064225				
7	4		.144325	.144325			
8	4			.173750	.173750		
1	4			.188825	.188825		
5	4				.236525		
2	4					.336950	
6	4						.447400
Sig.		0.975	0.066	0.647	0.246	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares

The error term is Mean Square(Error) = 0.001.

a Uses Harmonic Mean Sample Size = 4.000.

b Alpha = 0.05.

APPENDIX B. Univariate ANOVA for Microwave Treatment System

Between-Subjects Factors

N		
chem	F	16
	T	16
water	DI	16
	RW	16
TiO2	W	16
	WO	16

Tests of Between-Subjects Effects

Dependent Variable: Kavg

Source	Type III				
	Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	.001(a)	7	.000	62.757	.000
Intercept	.001	1	.001	566.734	.000
Chem.	.000	1	.000	145.738	.000
Water	1.44E-005	1	1.44E-005	6.289	.019
TiO2	.000	1	.000	83.410	.000
chem * water	4.73E-005	1	4.73E-005	20.587	.000
chem * TiO2	.000	1	.000	126.692	.000
water * TiO2	7.72E-005	1	7.72E-005	33.605	.000
chem * water * TiO2	5.28E-005	1	5.28E-005	22.981	.000
Error	5.51E-005	24	2.30E-006		
Total	.002	32			
Corrected Total	.001	31			

a R Squared = .948 (Adjusted R Squared = .933)

Post Hoc Analysis:

Between-Subjects Factors

	N	
factor	1	4
	2	4
	3	4
	4	4
	5	4
	6	4
	7	4
	8	4

Multiple Comparisons (Tukey HSD)

Dependent Variable: Kavg

(I) factor	(J) factor	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.005250(*)	.0010717	.001	.001701	.008799
	3	-.009450(*)	.0010717	.000	-.012999	-.005901
	4	.007150(*)	.0010717	.000	.003601	.010699
	5	.007500(*)	.0010717	.000	.003951	.011049
	6	.005825(*)	.0010717	.000	.002276	.009374
	7	.008050(*)	.0010717	.000	.004501	.011599
	8	.007450(*)	.0010717	.000	.003901	.010999
	2	1	-.005250(*)	.0010717	.001	-.008799
3		-.014700(*)	.0010717	.000	-.018249	-.011151
4		.001900	.0010717	.643	-.001649	.005449
5		.002250	.0010717	.443	-.001299	.005799
6		.000575	.0010717	.999	-.002974	.004124
7		.002800	.0010717	.200	-.000749	.006349

	8	.002200	.0010717	.470	-.001349	.005749
3	1	.009450(*)	.0010717	.000	.005901	.012999
	2	.014700(*)	.0010717	.000	.011151	.018249
	4	.016600(*)	.0010717	.000	.013051	.020149
	5	.016950(*)	.0010717	.000	.013401	.020499
	6	.015275(*)	.0010717	.000	.011726	.018824
	7	.017500(*)	.0010717	.000	.013951	.021049
	8	.016900(*)	.0010717	.000	.013351	.020449
4	1	-.007150(*)	.0010717	.000	-.010699	-.003601
	2	-.001900	.0010717	.643	-.005449	.001649
	3	-.016600(*)	.0010717	.000	-.020149	-.013051
	5	.000350	.0010717	1.000	-.003199	.003899
	6	-.001325	.0010717	.913	-.004874	.002224
	7	.000900	.0010717	.989	-.002649	.004449
	8	.000300	.0010717	1.000	-.003249	.003849
5	1	-.007500(*)	.0010717	.000	-.011049	-.003951
	2	-.002250	.0010717	.443	-.005799	.001299
	3	-.016950(*)	.0010717	.000	-.020499	-.013401
	4	-.000350	.0010717	1.000	-.003899	.003199
	6	-.001675	.0010717	.766	-.005224	.001874
	7	.000550	.0010717	.999	-.002999	.004099
	8	-.000050	.0010717	1.000	-.003599	.003499
6	1	-.005825(*)	.0010717	.000	-.009374	-.002276
	2	-.000575	.0010717	.999	-.004124	.002974
	3	-.015275(*)	.0010717	.000	-.018824	-.011726
	4	.001325	.0010717	.913	-.002224	.004874
	5	.001675	.0010717	.766	-.001874	.005224
	7	.002225	.0010717	.456	-.001324	.005774
	8	.001625	.0010717	.792	-.001924	.005174
7	1	-.008050(*)	.0010717	.000	-.011599	-.004501

	2	-.002800	.0010717	.200	-.006349	.000749
	3	-.017500(*)	.0010717	.000	-.021049	-.013951
	4	-.000900	.0010717	.989	-.004449	.002649
	5	-.000550	.0010717	.999	-.004099	.002999
	6	-.002225	.0010717	.456	-.005774	.001324
	8	-.000600	.0010717	.999	-.004149	.002949
8	1	-.007450(*)	.0010717	.000	-.010999	-.003901
	2	-.002200	.0010717	.470	-.005749	.001349
	3	-.016900(*)	.0010717	.000	-.020449	-.013351
	4	-.000300	.0010717	1.000	-.003849	.003249
	5	.000050	.0010717	1.000	-.003499	.003599
	6	-.001625	.0010717	.792	-.005174	.001924
	7	.000600	.0010717	.999	-.002949	.004149

Based on observed means.

* The mean difference is significant at the .05 level.

Homogeneous Subsets (Tukey HSD)

factor	N	Subset		
		1	2	3
7	4	.002300		
5	4	.002850		
8	4	.002900		
4	4	.003200		
6	4	.004525		
2	4	.005100		
1	4		.010350	
3	4			.019800
Sig.		0.200	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares.

The error term is Mean Square (Error) = 2.30E-006.

a Uses Harmonic Mean Sample Size = 4.000.

b Alpha = 0.05.

APPENDIX C. Univariate ANOVA for Microwave Assisted Photocatalysis

Treatment System

Between-Subjects Factors

N		
chem	F	12
	T	12
water	DI	12
	RW	12
TiO2	W	12
	WO	12

Tests of Between-Subjects Effects

Dependent Variable: Kavg

Source	Type III				
	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.003(a)	7	.000	27.036	.000
Intercept	.010	1	.010	764.475	.000
Chem.	1.44E-005	1	1.44E-005	1.074	.315
Water	.001	1	.001	41.063	.000
TiO2	2.82E-007	1	2.82E-007	.021	.887
chem * water	.000	1	.000	8.203	.011
chem * TiO2	.001	1	.001	94.221	.000
water * TiO2	5.42E-006	1	5.42E-006	.404	.534
chem * water * TiO2	.001	1	.001	44.265	.000
Error	.000	16	1.34E-005		
Total	.013	24			
Corrected Total	.003	23			

a R Squared = .922 (Adjusted R Squared = .888)

Post Hoc Tests (Tukey HSD)

Between-Subjects Factors

	N	
Factor 1	1	3
	2	3
	3	3
	4	3
	5	3
	6	3
	7	3
	8	3

Multiple Comparisons

Dependent Variable: Kavg

(I) factor	(J) factor	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.023733(*)	.0029911	.000	.013378	.034089
	3	.022867(*)	.0029911	.000	.012511	.033222
	4	.028600(*)	.0029911	.000	.018245	.038955
	5	.027200(*)	.0029911	.000	.016845	.037555
	6	.002000	.0029911	.997	-.008355	.012355
	7	.021600(*)	.0029911	.000	.011245	.031955
	8	.018200(*)	.0029911	.000	.007845	.028555
	2	1	-.023733(*)	.0029911	.000	-.034089
3		-.000867	.0029911	1.000	-.011222	.009489
4		.004867	.0029911	.729	-.005489	.015222
5		.003467	.0029911	.933	-.006889	.013822
6		-.021733(*)	.0029911	.000	-.032089	-.011378

	7	-.002133	.0029911	.995	-.012489	.008222
	8	-.005533	.0029911	.599	-.015889	.004822
3	1	-.022867(*)	.0029911	.000	-.033222	-.012511
	2	.000867	.0029911	1.000	-.009489	.011222
	4	.005733	.0029911	.559	-.004622	.016089
	5	.004333	.0029911	.822	-.006022	.014689
	6	-.020867(*)	.0029911	.000	-.031222	-.010511
	7	-.001267	.0029911	1.000	-.011622	.009089
	8	-.004667	.0029911	.766	-.015022	.005689
4	1	-.028600(*)	.0029911	.000	-.038955	-.018245
	2	-.004867	.0029911	.729	-.015222	.005489
	3	-.005733	.0029911	.559	-.016089	.004622
	5	-.001400	.0029911	1.000	-.011755	.008955
	6	-.026600(*)	.0029911	.000	-.036955	-.016245
	7	-.007000	.0029911	.331	-.017355	.003355
	8	-.010400(*)	.0029911	.049	-.020755	-.000045
5	1	-.027200(*)	.0029911	.000	-.037555	-.016845
	2	-.003467	.0029911	.933	-.013822	.006889
	3	-.004333	.0029911	.822	-.014689	.006022
	4	.001400	.0029911	1.000	-.008955	.011755
	6	-.025200(*)	.0029911	.000	-.035555	-.014845
	7	-.005600	.0029911	.586	-.015955	.004755
	8	-.009000	.0029911	.114	-.019355	.001355
6	1	-.002000	.0029911	.997	-.012355	.008355
	2	.021733(*)	.0029911	.000	.011378	.032089
	3	.020867(*)	.0029911	.000	.010511	.031222
	4	.026600(*)	.0029911	.000	.016245	.036955
	5	.025200(*)	.0029911	.000	.014845	.035555
	7	.019600(*)	.0029911	.000	.009245	.029955
	8	.016200(*)	.0029911	.001	.005845	.026555

7	1	-.021600(*)	.0029911	.000	-.031955	-.011245
	2	.002133	.0029911	.995	-.008222	.012489
	3	.001267	.0029911	1.000	-.009089	.011622
	4	.007000	.0029911	.331	-.003355	.017355
	5	.005600	.0029911	.586	-.004755	.015955
	6	-.019600(*)	.0029911	.000	-.029955	-.009245
	8	-.003400	.0029911	.939	-.013755	.006955
8	1	-.018200(*)	.0029911	.000	-.028555	-.007845
	2	.005533	.0029911	.599	-.004822	.015889
	3	.004667	.0029911	.766	-.005689	.015022
	4	.010400(*)	.0029911	.049	.000045	.020755
	5	.009000	.0029911	.114	-.001355	.019355
	6	-.016200(*)	.0029911	.001	-.026555	-.005845
	7	.003400	.0029911	.939	-.006955	.013755

Based on observed means.

* The mean difference is significant at the .05 level.

Homogeneous Subsets (Tukey HSD)

Factor	N	Subset		
		1	2	3
4	3	.010100		
5	3	.011500	.011500	
2	3	.014967	.014967	
3	3	.015833	.015833	
7	3	.017100	.017100	
8	3		.020500	
6	3			.036700
1	3			.038700
Sig.		.331	.114	.997

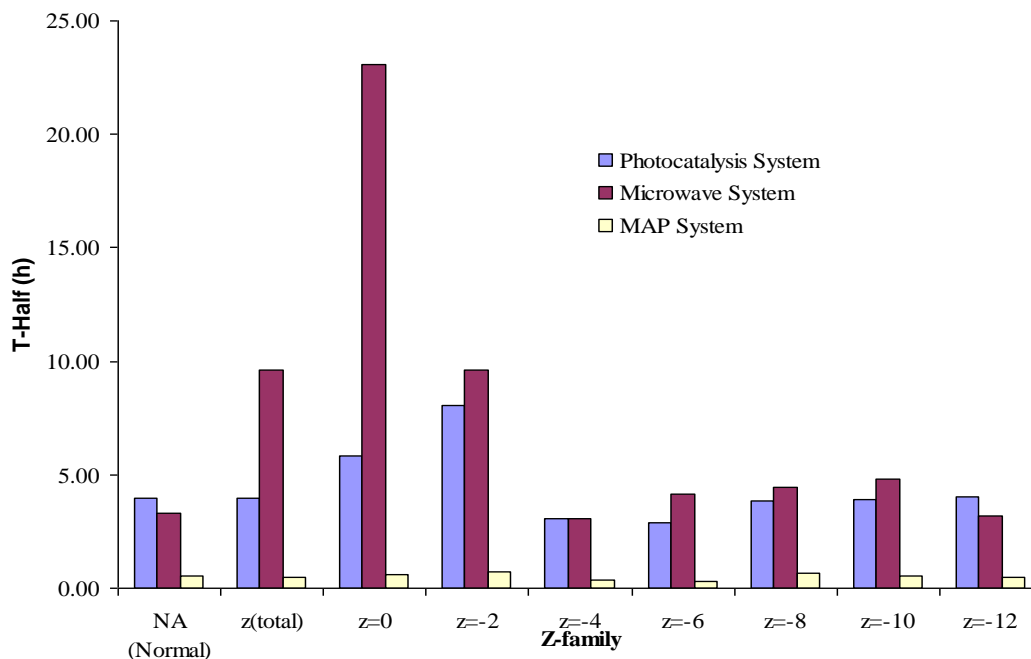
Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares. The error term is Mean Square(Error) = 1.34E-005.

APPENDIX D. Rate constant (k) and half-life periods for different treatment combinations

Sl No.	Combination	Photocatalysis System		Microwave System		Microwave Assisted Photocatalysis system	
		k (per h)	t _{1/2} (h)	k (per min)	t _{1/2} (h)	k (per min)	t _{1/2} (h)
1	Fluka-DI	0.215	3.23	0.0088	1.31	0.039	0.30
2	Fluka-DI-TiO ₂	0.337	2.06	0.0051	2.27	0.021	0.56
3	Fluka-RW	0.040	17.37	0.0198	0.58	0.012	0.93
4	Fluka-RW-TiO ₂	0.064	10.79	0.0032	3.61	0.010	1.14
5	OSPW NA-DI	0.237	2.93	0.0037	3.10	0.012	1.00
6	OSPW NA-DI-TiO ₂	0.447	1.55	0.0039	3.00	0.032	0.36
7	OSPW NA-RW	0.144	4.80	0.0042	2.78	0.017	0.68
8	OSPW NA-RW-TiO ₂	0.174	3.99	0.0035	3.32	0.021	0.56

APPENDIX E. Variation of half-lives with individual z-family of OSPW NAs in river water with TiO₂ for three treatment systems



The above figure compares the half-lives of individual z- families of OSPW NAs in river water with TiO₂ in three developed systems. It is observed that microwave assisted photocatalysis (MAP) system is the most efficient in degrading OSPW NAs, irrespective of their z-family classification, at a faster rate compared to only microwave and only photocatalysis systems. Microwave system took more time than photocatalysis system to degrade NAs of all z-family except for z=-12. There might be NA like molecules with multiple rings and multiple carboxylic groups in their structures which are misclassified by the ESI/MS as NAs with z=-12. For microwave system, half-life of NA normal was less than that of NA total. This supports the presence of NA like molecules in the sample which are more microwave degradable as compared to classical NAs and contributes to the lower half life of NAs in the microwave system.